OVERVIEW AND POTENTIAL OF DEVELOPMENT OF BIOREFINERIES

- PANORAMA ET POTENTIEL DE DEVELOPPEMENT DES BIORAFFINERIES

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Study conducted for the ADEME by Hugues de Cherisey, Consultant

Technical coordination: Hilaire BEWA, Bioresources department
Production and Sustainable Energy Division – ADEME Angers
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EXECUTIVE SUMMARY

The development of biorefineries and plant chemistry has gathered pace since the first version of this study, conducted five years ago.

Cereal, beet and oilseed production sectors are very well structured. The same is true of the sectors which supply pulp factories. The other sectors for the supply of lignocellulosic biomass are however still at the development stage.

Although the sources of these different sectors are well identified, with each one retaining its particular characteristics, secondary processing produces identical platform chemicals which form the origin of the same derivatives.

White biotechnology is experiencing rapid growth, encouraged by the development of bioinformatics and high speed sorting tools. Changes in scale however, are still lengthy and expensive and the number of industrial implementations remains small, except in the field of first-generation bioethanol and biodiesel.

The development of a number of platform chemicals had been anticipated by experts. Certain forecasts have proved to be accurate (glycerol, sorbitol, succinic acid) but there have been delays in producing other chemicals by means of innovative processes (3-HPA, levulinic acid, furans). Conversely, we are witnessing “unexpected” developments in the manufacture of industrial projects using the fermentation of terpenes and butanol and by chemical conversion of bioethanol into ethylene and its derivatives.

The conclusion recommends support for the development of plant chemistry based on industrial implementations, including those related to first-generation biofuels. The French and European production chains have certain competitive benefits which should be taken advantage of in a small number of sufficiently ambitious projects.

RESUME

Le développement des bioraffineries et de la chimie du végétal s’est accéléré depuis la première version de cette étude, réalisée il y a cinq ans.

Les filières céréalières, betteravières et oléagineuses sont parfaitement structurées. Il en est de même de celles qui approvisionnent les usines de pâte à papier. Les autres filières d’approvisionnement en biomasse lignocellulosiques sont en revanche encore dans leur phase de développement.

Si l’amont de ces différentes filières reste bien identifié, chacune conservant toutes ses spécificités, les secondes transformations génèrent des molécules plateformes communes qui sont à l’origine des mêmes dérivés.

Les biotechnologies blanches connaissent un essor rapide, favorisé par le développement des outils de bioinformatique et de tri à haut débit. Les changements d’échelle restent cependant longs et coûteux et les réalisations industrielles sont encore en nombre limité, hormis dans le domaine du bioéthanol et du biodiesel de première génération.

Le développement de plusieurs molécules plateformes avait été anticipé par les experts. Certaines prévisions se sont révélées correctes (glycérol, sorbitol, acide succinique) mais d’autres molécules tardent à être produites avec des procédés innovants (3-HPA, acide levulinique, furanes). À l’inverse, on assiste à des développements “imprévus” de projets industriels de fabrication par fermentation de terpènes et de butanol ou de conversion chimique du bioéthanol en éthylène et dans ses dérivés.

Il est recommandé en conclusion de soutenir le développement de la chimie du végétal en s’appuyant sur les réalisations industrielles engagées, y compris celles associées aux biocarburants de première génération. Les filières françaises et européennes ont certains avantages concurrentiels qu’il convient de valoriser dans un petit nombre de projets d’ambition suffisante.
Abbreviations and logos

ACDV: Plant Chemistry Association [Association de la Chimie du Végétal] (France),
DNA: deoxyribonucleic acid (the chemical containing genetic code)
AGPM: General Association of Maize Growers [Association Générale des Producteurs de Maïs]
ASA: Alkenyl Succinic Anhydride
BDO: 1,4 Butanediol
TO: turnover (revenues),
EC: European Commission,
CEDUS: Study and Documentation Centre for Sugar [Centre d'Etudes et de Documentation du Sucre]
CEFIC: European Chemical Industry Council [Conseil Européen de l'Industrie Chimique]
CEPI: Confederation of European Paper Industries
CETIOM: Metropolitan France Oilseed Technical Study Centre [Centre d'Etudes Techniques des Oléagineux Métropolitains]
CGB: General Confederation of Beet planters [Confédération Générale des planteurs de Betterave]
DHA: dihydroxyacetone
€: euro(s),
FAO: Food and Agriculture Organisation
FCBA: Forestry Cellulose Wood Furnishing Technical Institute [Institut Technique Forêt Cellulose Bois Ameublement] (France)
FDCA: 2,5-Furandicarboxylic acid
FEDIOL: EU Oil and Proteinmeal Industry [Fédération européenne de l'industrie des huiles et tourteaux].
FOP: French Federation of oilseed and high protein seed producers [Fédération française des producteurs d'oléagineux et de protéagineux]
HMF:
3 HPA: 3-hydroxypropionic acid
IFP: French Institute of Petroleum [Institut Français du Pétrole]
INRA: French National Agronomic Research Institute [Institut National de la Recherche Agronomique]
ha: hectare(s),
hl: hectolitre(s)
k: “kilo” = x 1000, €k = x 1000 €, kha = 1000 hectares, etc.
m: million(s), mt = million tonnes, mha = million hectares, etc.
dm, d.m. = dry matter
MPG: mono propylene glycol (= 1,2-propanediol)
GMO: genetically modified organism
ONF: French National Forestry Office [Office National des Forêts]
ms: market share
PDO: 1,3 propanediol
PHA: Polyhydroxyalcanoates
PLA: Poly Lactic Acid
SME: Small and Medium-sized Enterprises
PNNL: Pacific Northwest National Laboratory (USA)

q, qs: quintal, quintals,

SNPAA: National Union of Agricultural Alcohol Producers [Syndicat National des Producteurs d’Alcool Agricole] (France)

t: tonne(s)

THF: tetrahydrofuran

UCFF: French Forestry Cooperation Union [Union de la Coopération Forestière Française]

$ US: United States of America dollars

EU: European Union

UIC: Chemicals Industries Union [Union des Industries Chimiques] (France).

USDA: United States Department of Agriculture

US DOE: United States Department of Energy

USIPA: French Federation of Starch and Starch Derivative Industry Unions [Union des Syndicats des Industries des Produits Amylacés et de leurs dérivés] (France)
I- INTRODUCTION AND PURPOSE OF THE STUDY

I.1 – GENERAL FRAMEWORK FOR THE STUDY

This report is an update to similar work carried out in 2005. The purpose was to form an overview of the biorefinery industry, analysing it in terms of an analysis of the plant production sectors which exist in France. These were identified as follows in 2005: wheat and maize, beet, rapeseed, sunflower and byproducts of the paper industry.

In 2010, the exercise was repeated, with a few changes. The sectors have now been now identified in terms of the key ingredient of interest. The sectors dealt with are therefore “starch”, “sugar”, “vegetable oils” and “lignocellulosic materials”.

As we shall see, this approach by plant raw material has the advantage of allowing the resource to be properly identified. However the different production chains are no longer completely separate: certain chemical synthetic intermediates can be obtained in their biosourced form from glucose derived from starch industries as well as from saccharose derived from sugar industries and, in the future, from cellulose derived from lignocellulosic production. In certain cases, glycerol from vegetable oils may be a precursor of chemicals which may also be obtained by glucose fermentation. It can thus be observed that the concept of the biorefinery is shifting. Having originally been positioned downstream from a single supply chain, biorefineries are gradually becoming industries which use various sources of biocarbon available locally at the best price (and which can be guaranteed to be renewable in origin).

Taking an upstream approach based on crop sector favours the point of view of producers and original biomass processors at the expense of that of the markets. As in 2005, we once again emphasise that the study model presented here should be completed with specific analysis of the needs of the various current and potential markets for bioproducts and their outlook for the future.

The territory for the study is primarily France for the detailed description of production sectors, the conclusions and the recommendations made. In terms of investigations into industrial projects in progress, a much wider view has been taken. Other European countries, the United States and Brazil have also been studied. The limited framework of such a study does not make it possible to seek very specific information on developments in Asia, where there are a good number of projects, some of which are at an advanced stage.

I.2 - BIOREFINERY, BIOREFINING AND PLANT CHEMISTRY

Much has been written about the word “biorefinery”, sparking investigation by a large number of specialists, before it became possible to offer widely accepted definitions. To put it simply, a biorefinery can be seen as an industrial plant, on a single site, which processes and refines biomass products, by analogy with oil refineries which process and refine petroleum-based products.

According to the French Plant Chemistry Association (ACDV), “plant chemistry” means “chemistry based on the use of plant resources”, meaning the recovery and processing of plant raw materials by the chemicals industry.

The term “biorefining” is used less often. It may be defined as the sequence of stages to produce chemicals or materials from raw biomass. It includes preprocessing and fragmentation operations on the biomass, as well as the successive conversion and processing operations, using biotechnological or chemical processes.
Although by nature the biorefinery is concentrated on a single site, biorefining may require the intervention of several facilities which may be geographically distant from one another and belong to different companies and industrial players.

A biorefinery, envisaged as a single industrial entity, becomes fully economically relevant if its range of products includes commodities and if economies of scale, such as the optimisation of logistics and investments made possible by its concentration, become key factors for its competitiveness. This economic optimisation may be accompanied by environmental optimisation including minimisation of final emissions, energy consumption and the consumption of other inputs. This is all the more important in that directly or indirectly, a number of existing biorefineries receive various public incentives and therefore have a duty to be exemplary as regards the environment, to justify their status as a model.

Biorefineries are in competition with oil refineries if they are capable of offering the market chemicals with similar properties and applications.

According to certain views of the concept of biorefineries, they should be capable of using a large number of different raw materials and producing many synthetic intermediates. It should also be able to optimise its supply and production according to the markets, upstream and downstream from its activities. This attractive flexibility is still more of a goal than a reality and involves potentially high investment costs for industrial plant and development, which in certain cases may not be profitable. It may be specified at this point that oil refineries generally process a specific quantity of crude oil. The animal feed industry is another possible model for comparison as it uses many different plant raw materials in a large number of animal feed formulas. The processes are however far more homogenous than those of a biorefinery, with only the feed formulas (= finished products) differing. It is interesting to note that the cattle feed industry has moved from a factory model used for all livestock markets to specialised sites for each animal species, calling into play the model in which the plant “processes all possible raw materials to make all possible products.”

Some of the various definitions of a biorefinery are supplied below:

- **Jens Borne**: “A biorefinery is an integrated system of interdependent processes, which converts a set of renewable feedstock most effectively into the actually most profitable portfolio of value-added products with a minimum of external energy needs and practically no wastes and emissions.”

  We will discuss later the stated objective of minimising external energy requirements, which sometimes appears to represent a simplistic viewpoint. With the current state of know-how, it seems appropriate to use cane sugar bagasses or black liquor from paper pulp plants to produce energy. Is it also necessary to burn beet pulp, rapeseed cake and dried wheat grain to avoid using “external” energy at all costs, or is it wiser to use these byproducts, which are all highly nutritional for animal feed?

- **J. Sanders’ definition**, which was adopted for the European Biopol project, actually relates to biorefining rather than a biorefinery: “Biorefinery is the sustainable processing of biomass into a spectrum of marketable products and energy.”
• W. Soetaert’s definition, which appears to us to be the most satisfactory, has been adopted by the European Euroview project: “Integrated bio-based industries, using a variety of different technologies to produce chemicals, biofuels, food and feed ingredients, biomaterials (including fibers) and power from biomass raw materials.”

From an examination of the other available definitions, we shall retain only a few additional concepts:

➢ That of “industrial cluster”, in other words bringing together on single site industries which may be different in nature, depending on the processes they use and products they manufacture. This is sometimes known as an industrial ecosystem, with the various companies on the site supplying each other with semi-processed products or energy and pooling resources for treating waste. A striking example in France is the Pomacle-Bazancourt site.

➢ The particular analysis by the petroleum group Shell in 2007, which at the time considered a biorefinery to be nothing more than the addition of a biomass processing facility to oil refineries!

The European projects Biopol, Biorefinery Euroview and, more recently, Star Colibri, have devoted themselves to listing, mapping and classifying European and North American biorefineries. We will not reproduce this very well-documented exercise here. A true taxonomy of biorefineries has been developed, classified according to the raw materials they use. A distinction is therefore drawn between the following:

➢ The cereal biorefinery, which uses cereal grains, principally their starch. It could possibly in the future use the entire plant, with some seeing it becoming a whole crop biorefinery.

➢ The oilseed biorefinery.

➢ The green biorefinery which uses raw materials with a high water content, from beet to potato and cassava, as well as some plants originally used for fodder. This “taxon” does not appear have garnered universal support. Although particular preprocessing is required for wet materials, potato and cassava are starchy crops and beet and cane sugar are sugar plants.

➢ The lignocellulosic feedstock biorefinery, specifying whether it uses only forest-based products or cereal straw and stalks, energy crops and lignocellulose rich waste too.

➢ The syngas biorefinery may relate to one of the previous taxons, according to the raw materials it uses. In addition to the Fischer-Tropsch process to produce hydrocarbons from synthetic gases, we shall see that some companies are developing the production of biofuels and chemical intermediates by microbial fermentation of the same gases.
I.3 – MAIN CONCLUSIONS OF THE STUDY CONDUCTED IN 2005

At the end of the previous study, conclusions were listed for each sector. A brief summary may be given here, along with a few commentaries as to their current status, at the risk of anticipating somewhat the study which follows:

- At that time, the major forward planning reference for plant chemistry was the 2004 study by the US DOE which listed 12 platform chemicals for the future.
  
  A particular chapter (IV.1) will be dedicated to commenting on this and successive forward planning approaches.

- At that time there were few plant chemistry industrial projects. Above all, reference was made to Cargill’s project (concerning PLA) and that of DuPont Tate and Lyle (on 1,3 propanediol), seen as bold adventures. First-generation biofuels were being developed. At that time there was unanimous acclaim for their virtues.
  
  Biosourced PLA and PDO have been developed and seem to offer genuine growth potential on their markets. Competition is becoming established. Strong first-generation biofuel production industry sectors have been formed and are the basis for future generations of biofuels.

- There were few links between the major French chemists and the food industry.
  
  Although a great deal of progress in dialogue has been made with the creation of the Plant Chemistry Association, there are still only a limited number of joint projects. Several partnerships have been formed between our food industry and chemical industrial players of other nationalities.

- Our cereal sectors were (and remain!) healthy, but they lacked industrial projects focusing on the production of chemicals such as lactic, succinic and levulinic acid.
  
  Although lactic acid is still produced outside France, our petroleum company, Total, has invested in its derivatives in Belgium. This year, two French companies are beginning the commercial production of succinic acid. Levulinic acid however is still a chemical “with its future before it”, with as yet nothing very significant either in France or elsewhere.

- At that time, sugar chemistry was seen as a young science, which deserved encouraging.
  
  The progress of biotechnology has changed the situation, with the emergence of new platform chemicals such as ethanol. Saccharose now appears to offer a substrate for the fermentation of a chemical by chemists.

- A large number of studies had been conducted on the use of beet pulps, which were used preferentially for animal feed.
  
  The situation is little changed today.

- Glycerol was the focus of attention, as France was about to become a major producer. It was appropriate to step up work on the creation of new outlets.
France has indeed become a major producer of glycerol. The emerging outlets in 2010 are not in all cases those envisaged in 2005, but the product is finding its markets and derivatives.

- The development of wholly plant-derived biodiesel, made from ethyl esters seemed conceptually attractive but was barely on the agenda in 2005.

  The technological challenge remains considerable but a project involving the entire sector has been engaged.

- The French paper industry provided major resources for industrial know-how but suffered from competition on other continents. The development of cellulose chemistry seemed promising for the future.

  Our paper industry is still suffering. It is owned in the main by foreign groups whose research is located for the most part outside France. Various projects have nonetheless been launched in our country for the use of lignocellulosic biomass. Terpene derivative markets are developing. France has insufficient resources which means they need to be supplemented.

I.4 – CHANGES IN THE GENERAL SITUATION SINCE 2005

During the past five years, a large number of events have disrupted the backdrop to the development of biorefineries and plant chemistry.

Public policies in favour of combating climate change are being strengthened, although as yet there is not a formal international consensus. The contribution to reducing greenhouse gas emissions has become a basis for promoting all industrial projects in plant chemistry.

The prices of all raw materials have been extremely volatile over the past years, including farm products.

The chaotic fluctuations in oil prices have once again sparked the never-ending debate on “peak oil” without having located it accurately as yet. Over and above the difficulty in producing accurate forecasts, the strong trend in increased prices continues.

Hunger riots have been caused by the sudden increase in the price of foodstuffs, especially where these are imported. The conclusions drawn are sometimes simplistic. It is argued that any farmland in the North sown with non-food crops is a further step towards starving the populations of the South, who need to be continually supplied with wheat and maize from Europe and North America and rice from Thailand. First-generation biofuels, which were previously wildly acclaimed, have now been accused of being responsible for the increased maize and wheat prices. Interest thus shifted to as yet non-existent products which could thus be assigned every virtue: second- and even third-generation biofuels!

Europe remains completely closed to the development of plant GMOs despite the fact that the total area sown with genetically-modified plants worldwide is more than 7 times greater than the surface area of farmland in France! White biotechnology is experiencing spectacular growth, without arousing any particular apprehension.

The current economic crisis is having many consequences: businesses are suffering, postponing or cancelling development projects, including in the field of plant chemistry. Conversely, massive public subsidies have so far been paid out to projects with a “green” connotation, including a large share for the development of next-generation biofuels. Huge support budgets have thus been mobilised in the United States.
The nature and sheer quantity of available information has greatly increased. The burgeoning of newsletters, blogs and documents placed online in the wake of conferences has led to a significant proliferation of documents accessible online, the quality and reliability of which is variable.

In 2005, most projects were still at the design stage. Companies were happy to speak about their overall vision of the avenues to be pursued. Today, investments have been committed, competition is alive and industrial players do not really like giving details about their work in progress. Interviews can therefore be frustrating, but are often followed up by the identification of several freely-available presentations by the same speakers at conferences, seminars or students' training sessions. Their content can prove to be richer and more detailed than what they had agreed to explain during face-to-face interviews or over the phone. This is not really surprising: it is easier to define the information one is willing to disseminate or withhold when you are preparing and rereading a PowerPoint presentation, than when you are replying off the cuff to questions which may become more probing.

While there are increasing quantities of qualitative information available on the Internet, reliable quantified information has become available systematically on a fee-paying basis, at prohibitive prices for the occasional needs of a study such as this one. This study therefore includes less quantitative data on markets and prices than the 2005 study. When the sources of information about prices and volumes are not supplied, the latter are the result of cross-checking and are presumed to be estimations by the author of this study.
II - ANALYSIS BY SECTOR

We shall study the following in turn:

- The starch sectors, in other words starch from wheat, maize and other starchy plants.
- The sugar sectors, i.e. beet and cane sugar.
- The vegetable oil sectors from oilseed plants.
- The lignocellulosic sectors, including the byproducts of the paper pulp industry.

II.1 - THE STARCH SECTORS

Starch is a glucose polymer. It is found in the reserve organs of many plants, either in their seeds (cereals and protein crops) or their below-ground organs, whether these are stems (potato tubers) or roots (cassava, taro, sweet potato, etc.).

The starch used by the starch industry comes principally from maize, wheat and potatoes in France and temperate regions. Rice and cassava are the major sources in tropical regions.

II.1.1 - BOTANICAL SPECIES, ORIGINS AND VARIETIES GROWN

The plant species concerned found in Europe are principally wheat, maize and potato. Peas are less common.

Soft wheat (*Triticum aestivum*) is a hexaploid graminaceous plant, with a C3 photosynthetic metabolism which was domesticated in the Near East. Wheat is an autogamous cereal; its varieties are generally pure lines. Hybrid wheats have been developed but their use is increasing slowly. It can be noted that hard wheat, used to produce pasta and semolina, is another species (*Triticum durum*) with a tetraploid genome.

There are winter varieties of wheat which are sown in the autumn and harvested the following summer, and spring varieties, sown in the spring and harvested a few months later. In France, there are very few spring varieties, these being far less productive, but they may take precedence in countries with harsh winters such as Canada as well as in certain subtropical regions, where the winter is not sufficiently marked.

In France, there are several hundreds of varieties listed in the catalogue. Of the 244 varieties of soft wheat being bred in France by 2009, around ten account for almost half of the crop area. In spite of effective selection enabling recent varieties to dominate the market, the lifetime of certain varieties may be very long. In 2009, the Apache variety, listed in 1998, was the most grown but Soissons, listed in 1988, still had a significant place. The leading seed producers on the French market include Limagrain, RAGT, CC. Benoist and Florimond Desprez. The seed renewal rate for soft wheat did not exceed 49% for the 2009-2010 campaign; 50% of sowing was therefore carried out using seeds bred on the farm (in the 2000s, the renewal rate was around 60%).

Maize or corn, *Zea mays*, is a diploid graminaceous plant with a C4 photosynthetic metabolism, domesticated in Mexico from teosinte. It is a monoecious species (meaning it has separate male and female flowers on the same plant), with anemophilous pollination. Maize is grown in the form of hybrid varieties. It is an annual plant, sown in spring and harvested in autumn. There are many different classes of earliness for maize, enabling them to be grown in a variety of climatic conditions.

The maize seed market is served in France by the Limagrain group (LG and Advanta brands), with a 19% market share in 2008-2009; Pioneer Semences (a DuPont subsidiary), 15.5% ms; Semences Dekalb (Monsanto group) 13.5% ms; RAGT, 10.4% ms, Caussade, 9.8% ms and a
dozen other companies. The offer is segmented and dynamic: 960 French and European varieties are listed in the catalogue in France, classified into 7 groups of earliness!

Several waxy varieties (with highly amylopectin-rich starch) are on offer for growing in France as well as varieties solely for industrial use (“VUIR”, variété à usage industriel réservé), not marketed but for contractual production only. Maize is a species which has undergone many genetic modifications (85% of the maize grown in the USA is GM!).

The potato, *Solanum tuberosum*, belongs to the solanaceae family, as do the tomato and aubergine. It was domesticated in the Andes in South America. It is a tetraploid plant with a C3 photosynthetic metabolism. Its tubers enable vegetative reproduction. The commercial varieties are clones.

The starchy varieties are used to produce starch. 17 of these varieties were marketed in France in 2009, grown mainly in northern and eastern France. Transgenesis has made it possible to develop disease and herbicide-resistant varieties, and modify the starch composition, which is more important for the purposes of this study (cf. II.1.2).

The pea, *Pisum sativum*, is an autogamous diploid plant in the fabaceae family. It was probably domesticated in the Near East and bred using seeds. The pea is a protein crop and its seeds have a high starch and protein content (23% dry matter). The varieties are lines.

The surface area of Pea crops in France reached 700,000 ha in 1993, as a result of an active support policy, as part of the CAP, to reduce dependency in Europe on imported soya meal for feedstock. This area has decreased significantly since then, due to a lack of incentives and also due to recurrent problems with a phytopathogenic fungus affecting the roots.

**C3 and C4 photosynthetic metabolism**

The photosynthetic metabolism is specified for each botanical species described in brief. The code C3 or C4 refers to the number of carbon molecules in the initial product of CO₂ fixing but, in addition to this biochemical detail, it indicates the photosynthetic performance and therefore particular growth.

Most flowering plants have a C3 photosynthetic metabolism. The atmospheric CO₂ molecule reacts with C5 sugar to form to C3 molecules (3-P-Glycerate) which will later be transformed into fructose (C6). The photosynthetic tissue and chloroplasts in C3 plants are homogenous.

In C4 plants, atmospheric CO₂ is fixed in the peripheral leaf cells and produces C4 oxaloacetate. This is transformed into malate, which migrates towards the innermost leaf cells where it is converted into pyruvate and CO₂ which then supplies the cycle with standard C3. The additional stage in the C4 metabolism enables better overall photosynthesis performance through the compartmentalisation of reactions and the concomitant reduction of the opposite reaction of photorespiration. In favourable conditions, C4 plants grow more quickly. C4 metabolism is not associated with a particular botanical group but is found in several crops (maize, sorghum, sugarcane, hemp, Miscanthus, etc.) or in particularly invasive weeds (foxtail grass, panicum, digitaria, amaranth, etc.).

It should also be noted that the carbon isotope C¹³ is not fixed in the same way in C3 and C4 plants, which must be taken into account when monitoring biosourced carbon in the products from corresponding crops. Cane sugar also contains more C¹³ than beet sugar.
The tropical species used for the production of starch—except for maize—are principally rice and cassava.

**Rice**, *Oryza sativa*, is a diploid graminaceous plant with a C3 photosynthetic metabolism, which was domesticated in the Far East. It is grown in all tropical regions and some temperate regions. Rice is autogamous. The varieties are generally pure lines but several seed producers have developed F1 hybrid varieties, obtained using a cytoplasmic male sterility system.

Genetic engineering has been operational on rice since the late 1980s but large-scale applications are still limited. Rice is a minor crop in France but Semences de Provence markets 8 varieties.

**Cassava**, *Manihot esculenta*, is a member of the Euphorbiaceae family which was domesticated in Brazil. The tuber roots are rich in starch. Cassava is reproduced vegetatively. It was brought to Africa as early as the 16th century. It has also become widespread in Asia and is a staple in traditional diets in many tropical regions. Cassava flour, which is rich in starch, is called tapioca.

### II.1.2 – CROP COMPOSITION

**For maize, wheat and rice**, the grain is the storage organ. The grain includes a very small germ which is rich in oil and enzyme activity, husks with very high levels of cellulose and protein and the albumen, which is reserve tissue, made mainly of starch.

The starch in traditional varieties of wheat or maize is composed of 75% amylopectin and 25% amyllose. “Waxy” wheats with 100% amylopectin have been developed by breeders but their use remains insignificant. Wheat albumin proteins, gliadins and glutenins, have elasticity properties allowing doughs made from soft wheat to rise.

There are waxy maizes grown in a regular fashion in France. Breeders have also developed amylose-rich maizes (60% amylose). There are also oil-rich maizes (8% dry matter) which have never experienced a genuine level of commercial success.

#### Wheat, maize and some byproduct compositions

<table>
<thead>
<tr>
<th>Content % of gross weight</th>
<th>Soft wheat</th>
<th>maize</th>
<th>Wheat bran</th>
<th>Distillers' dried wheat grains</th>
<th>“Corn gluten feed”</th>
<th>Corn gluten</th>
<th>Distillers’ dried maize grains and solubles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humidity</td>
<td>13.2</td>
<td>13.6</td>
<td>12.9</td>
<td>10</td>
<td>8.6</td>
<td>12.0</td>
<td>10.5 Humidity</td>
</tr>
<tr>
<td>Crude protein</td>
<td>10.5</td>
<td>8.1</td>
<td>14.8</td>
<td>33.8</td>
<td>28.9</td>
<td>19.3</td>
<td>60.6 Crude protein</td>
</tr>
<tr>
<td>Crude cellulose</td>
<td>2.2</td>
<td>2.2</td>
<td>9.2</td>
<td>9.2</td>
<td>5.6</td>
<td>7.5</td>
<td>1.1 Crude cellulose</td>
</tr>
<tr>
<td>NDF*</td>
<td>12.4</td>
<td>10.4</td>
<td>39.6</td>
<td>37.9</td>
<td>25.3</td>
<td>33.8</td>
<td>2.3 NDF*</td>
</tr>
<tr>
<td>Fats</td>
<td>1.5</td>
<td>3.7</td>
<td>3.4</td>
<td>6.5</td>
<td>5.1</td>
<td>2.7</td>
<td>2.5 Fats</td>
</tr>
<tr>
<td>Crude ash</td>
<td>1.6</td>
<td>1.2</td>
<td>3</td>
<td>3.6</td>
<td>4.7</td>
<td>6.1</td>
<td>1.8 Crude ash</td>
</tr>
<tr>
<td>Starch</td>
<td>60.5</td>
<td>64.1</td>
<td>19.8</td>
<td>18.2</td>
<td>12.6</td>
<td>18.0</td>
<td>17.2 Starch</td>
</tr>
</tbody>
</table>

Source: INRA tables for composition and nutritional value of raw materials

*: NDF (Neutral Detergent Fiber) is a common measure of fibre levels (lignin + cellulose + hemicelluloses + some pectins)
Potato tubers in starchy varieties contain 16 to 27% dry matter (75 to 80% of which is starch).

Cassava roots typically have the following composition: 70% water, 22% starch, 5% sugar, 1% protein, 1% fibre. There are however many variations according to varieties and growing conditions.

II.1.3 – AGRICULTURAL SIGNIFICANCE AND MAIN PRODUCING COUNTRIES

II.1.3.1 - RANKING OF PRODUCING COUNTRIES

Maize is a crop with a high yield, which may be grown in tropical or temperate regions; it is the cereal with the highest world production (820 mt in 2008). The United States produces over a third of the total crop, China one fifth, with the European Union and Brazil far behind. Wheat and rice are in second place, with roughly equivalent tonnages. The European Union is the leading wheat producer in the world, ahead of China and India. Rice is a crop which is grown for the most part in Asia, with China and India being the main producers.

### Production of wheat (soft and hard), grain maize and rice in 2005 and 2008 (million tonnes)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>EU 27</strong></td>
<td>135.4</td>
<td>150.3</td>
<td>63.2</td>
<td>62.5</td>
<td>2.7</td>
<td>2.6</td>
</tr>
<tr>
<td><strong>China</strong></td>
<td>97.4</td>
<td>112.5</td>
<td>139.4</td>
<td><strong>166.0</strong></td>
<td>180.6</td>
<td><strong>191.9</strong></td>
</tr>
<tr>
<td><strong>India</strong></td>
<td>68.6</td>
<td><strong>78.6</strong></td>
<td>14.7</td>
<td>19.3</td>
<td>137.7</td>
<td>148.3</td>
</tr>
<tr>
<td><strong>USA</strong></td>
<td>57.3</td>
<td>68.0</td>
<td>282.3</td>
<td><strong>307.4</strong></td>
<td>10.1</td>
<td>9.2</td>
</tr>
<tr>
<td><strong>Russia</strong></td>
<td>47.7</td>
<td>63.8</td>
<td>3.2</td>
<td>6.7</td>
<td>0.6</td>
<td>0.7</td>
</tr>
<tr>
<td><strong>Canada</strong></td>
<td>25.7</td>
<td>28.6</td>
<td>9.3</td>
<td>10.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Ukraine</strong></td>
<td>18.7</td>
<td>26.0</td>
<td>7.2</td>
<td>11.5</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Australia</strong></td>
<td>25.2</td>
<td>21.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td><strong>Pakistan</strong></td>
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<td>21.0</td>
<td>3.1</td>
<td>4.0</td>
<td>8.3</td>
<td>10.4</td>
</tr>
<tr>
<td><strong>Turkey</strong></td>
<td>21.5</td>
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<td>4.3</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>Kazakhstan</strong></td>
<td>11.2</td>
<td>12.5</td>
<td>0.4</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td><strong>Argentina</strong></td>
<td>12.7</td>
<td>8.3</td>
<td>20.5</td>
<td>22.0</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td><strong>Egypt</strong></td>
<td>8.1</td>
<td>8.0</td>
<td>7.1</td>
<td>6.5</td>
<td>6.1</td>
<td>7.3</td>
</tr>
<tr>
<td><strong>Brazil</strong></td>
<td>4.7</td>
<td>5.9</td>
<td>35.1</td>
<td>59.0</td>
<td>13.2</td>
<td>12.1</td>
</tr>
<tr>
<td><strong>Thailand</strong></td>
<td>0</td>
<td>39.0</td>
<td>3.9</td>
<td>3.8</td>
<td>30.3</td>
<td>30.5</td>
</tr>
<tr>
<td><strong>Indonesia</strong></td>
<td>-</td>
<td>-</td>
<td>12.5</td>
<td>16.3</td>
<td>54.2</td>
<td>60.3</td>
</tr>
<tr>
<td><strong>Bangladesh</strong></td>
<td>1.0</td>
<td>0.8</td>
<td>0.4</td>
<td>1.3</td>
<td>39.8</td>
<td>46.9</td>
</tr>
<tr>
<td><strong>Vietnam</strong></td>
<td>-</td>
<td>-</td>
<td>3.8</td>
<td>4.5</td>
<td>30.3</td>
<td>30.5</td>
</tr>
<tr>
<td><strong>Worldwide</strong></td>
<td>626.9</td>
<td>690.0</td>
<td>713.9</td>
<td>822.8</td>
<td>634.5</td>
<td>685.0</td>
</tr>
</tbody>
</table>

| **France** | 36.9       | 39.0       | 13.7       | 15.8       | 0.1       | 0.09      |
| **Germany**| 23.7       | 26.0       | 4.1        | 5.1        | -         | -         |
| **Italy**  | 7.7        | 8.9        | 10.4       | 9.5        | 1.4       | 1.4       |
| **UK**     | 14.9       | 17.2       | -          | -          | -         | -         |

Source: FAO – countries are ranked in decreasing order of their wheat production in 2008.
France is the leading wheat and maize producer in the European Union. It is followed by Germany for wheat and Italy for maize.
**Wheat, grain maize and rice in some major countries in 2008**

<table>
<thead>
<tr>
<th></th>
<th>Surface areas (million ha)</th>
<th>Production (million t)</th>
<th>Yield (qs/ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wheat</td>
<td>maize</td>
<td>rice</td>
</tr>
<tr>
<td>France</td>
<td>5.5</td>
<td>1.7</td>
<td>0</td>
</tr>
<tr>
<td>Italy</td>
<td>2.3</td>
<td>1.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Germany</td>
<td>3.2</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>UK</td>
<td>2.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Spain</td>
<td>0.4</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>Hungary</td>
<td>1.1</td>
<td>1.2</td>
<td>0</td>
</tr>
<tr>
<td>Poland</td>
<td>2.3</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>Romania</td>
<td>2.1</td>
<td>2.4</td>
<td>0</td>
</tr>
<tr>
<td>EU</td>
<td>26.5</td>
<td>8.9</td>
<td>0.4</td>
</tr>
<tr>
<td>China</td>
<td>23.6</td>
<td>29.9</td>
<td>29.5</td>
</tr>
<tr>
<td>India</td>
<td>28.0</td>
<td>8.3</td>
<td>44.0</td>
</tr>
<tr>
<td>USA</td>
<td>22.5</td>
<td>31.8</td>
<td>68.0</td>
</tr>
<tr>
<td>Russia</td>
<td>26.1</td>
<td>1.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Canada</td>
<td>10.0</td>
<td>1.2</td>
<td>-</td>
</tr>
<tr>
<td>Ukraine</td>
<td>7.1</td>
<td>2.4</td>
<td>0</td>
</tr>
<tr>
<td>Australia</td>
<td>13.6</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Pakistan</td>
<td>8.5</td>
<td>1.1</td>
<td>3.0</td>
</tr>
<tr>
<td>Turkey</td>
<td>7.6</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>12.9</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Argentina</td>
<td>4.3</td>
<td>3.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Egypt</td>
<td>1.2</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Brazil</td>
<td>2.4</td>
<td>14.4</td>
<td>2.9</td>
</tr>
<tr>
<td>Mexico</td>
<td>0.8</td>
<td>7.4</td>
<td>0</td>
</tr>
<tr>
<td>South Africa</td>
<td>0.8</td>
<td>2.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Thailand</td>
<td>-</td>
<td>1.0</td>
<td>10.2</td>
</tr>
<tr>
<td>Indonesia</td>
<td>-</td>
<td>4.0</td>
<td>12.3</td>
</tr>
<tr>
<td>Worldwide</td>
<td>223.6</td>
<td>161.0</td>
<td>159.0</td>
</tr>
</tbody>
</table>

Source: FAO. Outside the EU, countries are ranked in decreasing order of their wheat production. This data may differ from more accurate national statistics as it conflates different species and varieties of wheat (soft wheat, hard wheat, winter, spring).

**Potato**

The world potato harvest was **314 million tonnes** on 18 million hectares in 2008 (325 mt in 2005). The European Union is the largest producer (61.6 mt), followed by China (57 mt), India (34.5 mt), Russia (29 mt), Ukraine (19.5 mt) and the USA (18.7 mt). In Europe, Germany (11.4 mt) is ahead of Poland (10.5 mt), the Netherlands (6.9 mt) and France (6.6 mt).

The average world yield is 17.3 t/ha, 13 t/ha in China and 28.9 t/ha for the European Union, with higher values for countries such as Germany and France (44 t/ha).

*This production data should not be compared with the data for cereals presented above: the dry matter content in potatoes varies between 16 and 27% in France whereas it is around 86-87% for properly harvested cereals.*

The surface area for potato crops in France is around 150,000 ha and fairly stable. However, the area grown specifically with starchy varieties is falling (27,000 ha in 2005 and 22,000 ha in 2009). The yields for starchy varieties remain good, with an average of 44 t per ha. 251,000 tonnes of starch were manufactured in 2009. The crisis in the paper and glue industries, which use potato starch, as well as the competition between wheat and potato starches, have had a direct impact on the surface areas contracted for the production of starchy varieties.
Cassava
The main producing countries are Nigeria (45 mt), Thailand (28 mt), Brazil (27 mt), Indonesia (22 mt) and the Democratic Republic of Congo (15 mt), followed by Ghana, Vietnam, India, Angola, etc. In 2008 world production was approximately 230 million tonnes according to the FAO (with a total surface area of 18.7 million hectares). Average yields are 23.3 gross t/ha for Thailand, 17 t/ha for Vietnam, 14 t/ha for Brazil and only 11.8 t/ha for Nigeria and 8 t/ha for the DRC, with a world average of 12.5 t/ha. These figures are not very significant as they conflate the performance of secondary subsistence crops and that of farms organised to supply food-processing industries.

Few cassava producing countries have an effective starch production chain and industry. Outside of Nigeria and South Africa, the starch-extraction industry is virtually non-existent in Africa. In Latin America, starch extraction accounts for a very small part of total cassava production (although a lot of maize starch is produced). However, from 2006 onwards, Thailand used 50% of its annual cassava root production to extract some 2 million tonnes of starch, half of which was exported to Japan and Taiwan. The figures have since increased.

The harvests of the different crops presented have very different dry matter and starch contents. For a better appreciation of the potential sources of starch represented by each of the crops presented, a simple calculation may be performed as shown in the two tables below (which do not take into account extraction yields):

**Theoretical calculation of plant starch production by species**

<table>
<thead>
<tr>
<th></th>
<th>% Starch of gross weight</th>
<th>2008 world harvest mt</th>
<th>Starch equivalent mt</th>
<th>2008 France harvest mt</th>
<th>Starch equivalent mt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat</td>
<td>55-60</td>
<td>690</td>
<td>380-417</td>
<td>39</td>
<td>21.5-23.6</td>
</tr>
<tr>
<td>Maize</td>
<td>62-64</td>
<td>823</td>
<td>510-527</td>
<td>15.8</td>
<td>9.8-10.1</td>
</tr>
<tr>
<td>Rice</td>
<td>76</td>
<td>685</td>
<td>521</td>
<td>0.09</td>
<td>0.1</td>
</tr>
<tr>
<td>Potato</td>
<td>18</td>
<td>314</td>
<td>57</td>
<td>6.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Cassava</td>
<td>22</td>
<td>230</td>
<td>51</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Theoretical calculation of average starch production per species**

<table>
<thead>
<tr>
<th></th>
<th>% Starch of gross weight</th>
<th>Gross yield average t/ha – world</th>
<th>t starch / ha</th>
<th>Gross t yield/ha France*</th>
<th>t starch / ha</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat</td>
<td>55-60</td>
<td>3.1</td>
<td>1.7-1.9</td>
<td>7.5</td>
<td>4.1-4.5</td>
</tr>
<tr>
<td>Maize</td>
<td>62-64</td>
<td>5.1</td>
<td>3.2-3.3</td>
<td>9</td>
<td>5.6-5.8</td>
</tr>
<tr>
<td>Rice</td>
<td>76</td>
<td>4.3</td>
<td>3.3</td>
<td>6</td>
<td>4.6</td>
</tr>
<tr>
<td>Potato</td>
<td>18</td>
<td>17.3</td>
<td>3.1</td>
<td>4.4</td>
<td>7.9</td>
</tr>
<tr>
<td>Cassava</td>
<td>22</td>
<td>12.5</td>
<td>2.8</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*: data for France based on favourable yield hypotheses

These results are for informational purposes and hasty conclusions should not be drawn from them: they are averages from disparate data. They do however show that the overall supply is of the same order of magnitude for the three major cereals and much lower for cassava and potato.

With a yield of 20 t/ha, a cassava crop “contains” 4.4 tonnes of starch. Potato and cassava offer good potential per hectare, but the crop has a high water content, cannot travel and is difficult to conserve. It must therefore be processed in the immediate vicinity of growing areas. These results are for informational purposes and hasty conclusions should not be drawn from them: they are averages from disparate data. They do however show that the overall supply is of the same order of magnitude for the three major cereals and much lower for cassava and potato.
With a yield of 20 t/ha, a cassava crop “contains” 4.4 tonnes of starch. Potato and cassava offer good potential per hectare, but the crop has a high water content, cannot travel and is difficult to conserve. It must therefore be processed in the immediate vicinity of growing areas.

II.1.3.2 - CHANGES IN WHEAT AND MAIZE GROWING IN FRANCE

The surface areas of wheat and grain maize grown have not changed much over the past few years in France. For wheat they vary between 4.5 and 5 million hectares and for grain maize they are around 1.3 to 1.4 million hectares, with total areas for maize reaching between 2.85 and 3.2 million hectares when fodder maize surface areas are included.

Recent changes in surface areas of soft wheat and grain maize in France

Average maize yields vary between 85 and 95 quintals per hectare, in the absence of climatic incidents (2003). In 2009, the wheat yield was 77 quintals per hectare. There are still significant regional disparities (maximum quantities of 120 quintals per hectare were achieved in the Paris basin, whereas the harvest was disappointing in the South-West - between 45 and 70 quintals per hectare).

The yields of these two crops have not shown any recent marked change although they progressed regularly for many years. It was even considered that all major crops had a strong trend for linear progression in terms of yield in France.
Recent analysis of changes in yield for major crops in France (presentations at the academy of agriculture on May 5, 2010) offered the following conclusions:

- Medium-term progression for maize yields is advancing normally according to researchers, in spite of fluctuating annual results due to climatic conditions.
- The average yield of wheat however is growing more slowly than “predicted”. Current yields “should” be 14 q/ha higher than those observed. Genetic progress is advancing but a regular drop in control yields has been observed for the past 20 years. This appears to be linked in the main to two factors:
  - The change in production pathways, under the pressure of the CAP, with the reduction of inputs (nitrogen fertilisers, pesticides) and greater use of farm seeds.
  - Higher temperatures, which are unfavourable to winter crops but allowing improved yields for spring crops. Winter wheat is perhaps a “victim” therefore of global warming.
II.1.3.3 – FUTURE OUTLOOKS FOR CHANGES IN PRODUCTION AND YIELD OF WHEAT AND MAIZE

On a more global scale, it is worth examining changes in the production of wheat and maize.

Historic increase in world production of wheat due to increased demand

Source: Tereos – Talk by B. Chaud Panorama IFP Symposium 2010 – From Merrill Lynch USDA

World production of wheat is continuing to grow, with the surface areas sown remaining stable. Intensification of farming has enabled this significant growth in yield.

The forecasts for maize made by North Americans provide another view of the future. Apart from progress in farming practices and traditional seed selection, can technological breakthroughs, which would push still further the much-talked-about “agronomic potential” of a species, be expected?

Historic changes in maize yield in the USA (bushels per ha)

North Americans answer this question without hesitation: progress will continue and technological breakthroughs will emerge from plant genetic engineering. The first maize GMOs were herbicide-resistant. They do not allow any direct improvement in yield but make growing practices easier. Resistance to insects followed. It is now difficult to market a maize seed in the United States if it does not incorporate 2 or 3 transformation steps (one for herbicide resistance and one or two for insect resistance). This is but the tip of the iceberg of a technology which may gradually significantly remodel the metabolism of plants to improve their utilisation of water and nitrogen.

In France and part of Europe, we have not been involved in these technological developments, thus condemning the medium-term competitiveness of our agriculture with respect to that of other continents.

An ongoing outlook of growth forecast by the USDA with the development of biotechnology:

Our agriculture is at a stage at which its reasoning is based on both environmental and economic considerations. This is necessary but care must be taken to avoid extremes, such as demonising productivity (which is a goal in any sector of activity) and rebranding it “productivism”.

There is however a very high risk involved in not exploring the biotechnological avenues which will allow fresh growth in yields, most particularly in a context of climate change, to make increasingly rare farmland produce more (the surface area of farmland is decreasing very significantly year by year in France, to build buildings, roads and car parks).
II.1.4 – DESCRIPTION OF STARCH PRODUCTION CHAINS

II.1.4.1 - GENERAL PATTERN (see diagram in the appendices)

The general pattern, focusing on the wheat and maize sectors, is presented in appendix 1. The non-food wheat, maize and potato production chains are historically starch chains, from which glucose and all its derivatives can be obtained. The production of bioethanol from cereals is positioned separately but is most often developed by starch producers.

An extremely large number of different chemicals are produced or may be produced from starch. The pattern presented is therefore necessarily simplified and simplistic.

II.1.4.2 – STARCH EXTRACTION

Each crop species is treated using different processes, some elements of which may be detailed below:

- **Wheat** grains are first of all cleaned then ground into flour, as in milling processes. The byproducts of this first stage are bran and germs, which are separated in this dry process. The flour is moistened and the dough obtained is washed to extract the protein-rich gluten and wheat solubles.

- **Maize**, however, is treated using a wet process. The cleaned grains are left to soak in hot water containing sulphur dioxide to soften them. The soaking water, which is high in soluble substance content (up to 60 g/l) is recovered and used either for fermentation purposes (“corn steep”), or to enrich dried grains for animal feed.

  After soaking, the grains are coarsely ground a first time and degermed. They are then finely ground and sifted (to separate the dried grains) and centrifuged to produce the starch milk and proteins in the form of gluten.

  Wheat and maize germs are high in quality oils, used in the food industry. The oilcakes associated with oil extraction are used in animal feeds.

- **Potato starch.** After delivery and storage, the tubers are cleaned, rasped and crushed in water containing sulphur dioxide. Decantation allows the extraction of solubles and proteins. The starch puree is then sifted, to separate the pulps. Refining produces a starch milk from which native or modified starches are produced and dried.

II.1.4.3 – MAJOR PRODUCTS IN THE STARCH CHAIN

The main products may be ranked as follows:

- **Starch byproducts**, from the organs and tissue of the plant and from grain which does not contain any starch.

  For wheat, these are:
  - lignocellulose-rich wheat straw,
  - brans, with a high fibre and protein content,
  - protein-rich wheat glutens.
For maize, the co-products are:
- corn straw and stalks,
- corn gluten feed (a dehydrated co-product of wet starch extraction)
- corn gluten meal.

For potato, the co-products (80,000 t/year in France) are as follows:
- compressed or dehydrated wet pulp,
- potato protein concentrates, able to titrate 78% protein.

- **Bioethanol.** This is obtained by fermentation followed by distillation in specific industrial units. This sector is independent but often operated by starch producers. It supplies the fuel mass markets. Bioethanol co-products are distillers’ grains. For maize these are known as corn distillers, maize solubles or distillers’ grains. These are exhausted grains to which variable quantities of solubles are added.

- **Starches.** Starches may be native or chemically modified and have many different industrial applications.

- **Glucose derivatives** These may be obtained in one or more stages, depending on the chemical processes, or by fermentation. In this family of products, the origin of the starch hydrolised into glucose (wheat, maize or potato) is not important.

**Débouchés mondiaux des cultures amylacées**

![Diagram showing distribution of starch products]

**Source:** Syral

**II.1.4.4 – INDUSTRIES CONCERNED**

The processing of maize or wheat into chemicals of interest for the non-food industry is carried out by different industries:

**Starch producers** have a long-standing “biorefining” activity. They know how to extract the starch from wheat, maize or potato and recover its co-products. The vast majority of starch producers have glucose production alongside their starch production. Some industrial companies do not process the glucose, whereas others subject it to conversions by means of chemical or biological reactions, producing a range of chemicals to varying degrees of diversity.

In France, the following companies operate starch production plants:

- **Cargill** (Haubourdin, northern France – maize), a North American group and the leading starch producer in Europe.
• Chamtor (Bazancourt, Marne – wheat).
• Féculeria Haussimont (Haussimont, Marne - potato) in which the majority share is held by the French family packaging group, Sphère.
• Roquette Frères (Beinheim, Bas Rhin – wheat, maize; Lestrem, Pas de Calais -wheat, maize; Vécquemont, Somme – potato; Vic-sur-Aisne, Aisne - pea). Roquette is the second-largest starch producer in Europe, after Cargill.
• Syral - Tereos group (Marckolsheim, Bas-Rhin - wheat, maize; Nesle, Somme -wheat). Syral is the third-largest starch producer in Europe.

The major players in the sector worldwide include the following:

ADM = Archer-Daniels-Midland Company (USA and internationally), AVEBE (a Dutch group, specialising in potato starch), BENE0-Remy NV (Belgium – rice specialist and subsidiary of the German company, Südzucker), Chemstar Products Company (USA), China Essence Group Ltd. (China), China Sun Bio-Chem Technology Group Co Ltd (China), Grain Processing Corporation (USA, but a subsidiary of the Dutch chemicals group Akzo Nobel), Penford Corporation, Riddhi Siddhi Gluco Biols Ltd. = RSGB (Indian leader, with 25% of the national market – Roquette has acquired 15% of its capital) and Tate and Lyle PLC. (UK).

Ethanol producers. The development of biofuel ethanol has enabled growth in a specific industry, which is connected to both sugar manufacturers and starch producers. The following are wheat and maize alcohol or ethanol producers in France:

• Abengoa Bioenergy France, which brings together the Spanish firm Abengoa, dealer agencies and the maize production chain (Lacq site (Pyrénées-Atlantiques - 120,000 t fuel blends – producing 200,000 t ethanol including 160,000 tonnes from 500,000 t maize, the remaining 40,000 t is from wine production. Co-products: 150,000 t distillers dried grains).
• Brie Champagne Ethanol (Provins), a legacy unit which is still operating.
• Cristal Union, in a combined cereal/beet unit at Bazancourt, with a capacity of 280,000 t (167,500 t fuel blends).
• Roquette (Beinheim site – 95 kt fuel blends and production capacity of 160 kt).
• Tereos (Lillebonne site - 160,000 tonnes fuel blends in 2010, for a production capacity of 240 kt; Nesle site).

The main companies manufacturing fermentation products from the chemical processing of glucose are listed when the relevant chemicals are discussed. This will also be the case for companies manufacturing bioplastics using starch,

II.1.4.5 – THE ECONOMICS OF THE PRODUCTION CHAIN

II.1.4.5.1 – Standard conversion parameters

**Starch production:**

1 t wheat → 550 kg starch + 200-230 kg wheat offal + 100 kg solubles + 80 kg gluten
1 ha wheat → 75 qs grain → 4.125 t starch

1 t maize → 620-630 kg starch + 40-50 kg gluten meal + 60-70 kg germs + 190-200 kg corn gluten feed.
1 ha maize → 90 qs grain → 5.625 t starch
**Ethanol production:** 1 t = 12.65 hl  
1 hl = 79.05 kg

1 t wheat → 355 l = 280 kg ethanol

For the average French yield of 75 qs/ha:

**1 ha wheat = 26.5 hl = 2.1 t ethanol + 1.3 t corn gluten feed**

For a yield of 100 qs/ha: 1 ha wheat = 35.5 hl = 2.8 t ethanol + 1.7 t corn gluten feed

1 t de maize → 370 l = 290 kg ethanol

For the average French yield of 90 qs/ha:

**1 ha maize = 33 hl = 2.65 t ethanol + 2.75 t corn gluten feed**

For a yield of 100 qs/ha: 1 ha maize → 37 hl = 2.9 ethanol

II.1.4.5.2 – The cereals market

The future of French crops

France is a major exporter of wheat and maize, on markets with strong competition. Animal feed is the leading outlet for domestic consumption, particularly maize.

**Simplified assessment of the French soft wheat market 2008-2009 and 2009-2010 forecasts**

<table>
<thead>
<tr>
<th>Uses</th>
<th>2008-2009</th>
<th>2009-2010</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mt</td>
<td>%</td>
</tr>
<tr>
<td>Grain exports</td>
<td>16,5</td>
<td>44</td>
</tr>
<tr>
<td>grain exports to non-EU countries</td>
<td>9,6</td>
<td>26</td>
</tr>
<tr>
<td>exports within the EU</td>
<td>6,8</td>
<td>18</td>
</tr>
<tr>
<td>Flour exports</td>
<td>1,0</td>
<td>3</td>
</tr>
<tr>
<td>Animal feed</td>
<td>5,2</td>
<td>14</td>
</tr>
<tr>
<td>Breadmaking</td>
<td>3,0</td>
<td>8</td>
</tr>
<tr>
<td><strong>Starch production</strong></td>
<td><strong>2,6</strong></td>
<td><strong>7</strong></td>
</tr>
<tr>
<td>Biscuit manufacture</td>
<td>1,1</td>
<td>3</td>
</tr>
<tr>
<td><strong>Biofuel</strong></td>
<td><strong>0,8</strong></td>
<td><strong>2</strong></td>
</tr>
<tr>
<td>Malt production – pastries</td>
<td>0,9</td>
<td>2</td>
</tr>
<tr>
<td>Sundries and transfers</td>
<td>6,2</td>
<td>17</td>
</tr>
<tr>
<td><strong>Production total</strong></td>
<td><strong>37,1</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

*Source: FranceAgriMer, January 2010*

The share of starch and bioethanol in **outlets for French wheat** rose from 9% in 2008-2009 (3.4 million tonnes) to 11% (4 million tonnes) in 2009-2010.

Of the 13 - 16 million tonnes of **grain maize** harvested each year in France, around 2 million are used for starch production and 500,000 t for bioethanol production.

**World cereal trade**

Approximately 220 - 230 million tonnes of cereals are traded on international markets worldwide, including 110 - 140 million tonnes of wheat (of all types).
In 2008-2009, a total of 117.7 million tonnes of wheat were traded, with the USA remaining the leading exporter (24.5 mt), followed by Russia (19 mt), the European Union (18 mt), Canada (17.2 mt), Australia (13.5 mt) and Ukraine (8.2 mt). There is traditionally less maize trading, but this approached the level of wheat trading in 2007 (101 million tonnes) before slumping to 84 million tonnes in 2008. Between 85 and 90 million tonnes are expected this year. The main exporters are the USA (45 - 60 mt depending on the year), Argentina (12 - 15 mt) and Brazil (7 - 11 mt).

The prices of wheat and maize have undergone major fluctuations over the last few years, with a peak between the summers of 2007 and 2008. Since the end of 2008, there has been a return to more usual price variation intervals, between 100 and 140 €/t for crops arriving at French ports.

Changes in cereal prices in Europe
In spite of the sudden increases during the last few years, the price of wheat (without taking inflation into account) would appear to be continuing to fall on a structural basis, contrary to that of oil. This must be taken into account for plant raw materials chemical applications. Caution must however be maintained with respect to the future, since increased cereal consumption in large developing countries and the massive development of non-food uses may alter established balances.

II.1.4.5.3 – Specific data for the starch production sector

World starch or starch equivalent production (for products processed directly in starch production plants) amounted to 70 million tonnes in 2008, 75% of which was from maize. The US still dominates the market but the highest growth in supply and demand is in Asia.
Worldwide production of native starch equivalent (million tonnes)

<table>
<thead>
<tr>
<th></th>
<th>2000</th>
<th>2008</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>China</td>
<td>Included in “other”</td>
<td>14</td>
</tr>
<tr>
<td>European Union</td>
<td>8.2</td>
<td>9.5</td>
</tr>
<tr>
<td>Japan</td>
<td>Included in “other”</td>
<td>3</td>
</tr>
<tr>
<td>Other (Asia, Latin America, etc.)</td>
<td>15.5</td>
<td>18</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>48.5</strong></td>
<td><strong>70</strong></td>
</tr>
</tbody>
</table>

Source: USIPA

In the European Union, the share of maize starch is largest but the shares of wheat (especially in France) and potato (especially in Eastern Europe) are significant. Wheat starch production has grown considerably in France.

Native starch equivalent production in Europe and France in 2008

<table>
<thead>
<tr>
<th></th>
<th>Maize</th>
<th>Wheat</th>
<th>Potato</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production, kt</td>
<td>EU</td>
<td>4660</td>
<td>3670</td>
<td>1590</td>
</tr>
<tr>
<td></td>
<td>France</td>
<td>1155</td>
<td>1350</td>
<td>250</td>
</tr>
<tr>
<td>Dedicated farming surface x 1000 ha</td>
<td>EU</td>
<td>950 (42 %)</td>
<td>1050 (47 %)</td>
<td>250 (11 %)</td>
</tr>
<tr>
<td></td>
<td>France</td>
<td>210 (35 %)</td>
<td>360 (60 %)</td>
<td>30 (5 %)</td>
</tr>
</tbody>
</table>

Source: USIPA

Growth in starch tonnage produced in France by origin

Source: USIPA

**Potato starch market**

Potato starch production is organised with quotas set for the EU. The French quota is currently 265,000 tonnes, i.e. 13.6% of the total for the EU. 252,000 tonnes are expected to be produced this year from crops from some 1500 farmers, with 23,000 ha. French potato starch production will involve just over 1 million tonnes of potatoes. In France, there are 2 factories which process potatoes for starch: Vecquemont (Roquette Group) and Haussimont (Sphere Group).
II.1.5 – MAJOR PRODUCTS IN THE STARCH CHAIN

II.1.5.1 - PRODUCTS HIGHER UP THE CHAIN

Wheat straw, corn stalks and rice straw are lignocellulosic raw materials.

Cereal straw is traditionally used for cattle litter. A large share must be returned to the soil or in the form of manure, to preserve its humus and organic matter content.

Straw may be used as fuel, directly or in the form of agropellets, but they have the drawback of producing acid smoke and clinker. Recent technology, such as that developed in France by RAGT Energie (RAGT Group) enables these two drawbacks to be remedied with a straw pellet formula which includes mineral additives to neutralise the chemicals concerned. Other chemicals, such as downgraded grains, unfit for consumption, may be incorporated into the pellets.

Straw may be used in the building sector to make panels which provide excellent soundproofing and heat insulation. The French company Stramontec is active with these innovations.

Straw and stalks will be some of the raw materials for second-generation biorefineries: these will process them into biofuels and synthetic intermediates, using their cellulose and hemicelluloses and ultimately, their lignins.

Competition between uses is now foreseeable, since the straw resources which may be exported from farms are limited.

The entire maize plant, crushed and with added starch and glycerol, is used to produce “Vegemat”, a biodegradable composite biomaterial, by Vegeplast (Haute Garonne). Manufacture is based on a thermomechanical process. The applications for the product are very diversified (disposable cutlery, golf tees, vine hooks, nursery ties, dog chews, parachute rigging for the army and more recently, coffee doses).

Fibre and protein-rich wheat brans are traditionally intended for human food or animal feed. In second-generation processes, bran fibre fractions may be broken down into C6 and C5 sugars or directly fermented. The work done by Tereos and Deinove in the Deinol project consists of being able to incorporate brans into wheat ethanol production processes.

Wheat proteins may have various applications. They have been used for many years in cosmetics by Silab (Brive, Corrèze) for their tensile properties for skin care products. Wheat gluten is film-forming, thermoplastic and biodegradable. Syral (Tereos Group) is working on plastics which incorporate wheat proteins.
II.1.5.2 – STARCH

Starch is a D-glucose polymer, which is found in plants in two forms:
- Linear or lightly branched **amylose**, formed by chains of a few hundred α (1-4) glucose linkages.
- **Amylopectin**, a larger α-branched molecule comprising several thousand α (1-6) glucose linkages every 24 - 30 units. Phytoglycogen is analogous to amylopectin, branched every 10 - 15 glucose units.

Each plant species has its own specific size of starch grains: they are small in rice (2 μm) and much larger in potatoes (up to 100 μ). The starch grains arrange themselves in semi-crystalline granules: amylopectin is organised in crystalline leaflets, whereas amylose constitutes an amorphous area between the different leaflets.

Most plant starches are composed of 20-30% amylose and 70-80% amylopectin. Some species however have particular composition varieties, either of natural origin or produced by genetic engineering.

In industrial applications for starch, amylose or amylopectin may be preferable. As it is difficult to separate them, specialist varieties are appreciated.

**Typical composition of starches from different plant species**

<table>
<thead>
<tr>
<th>Species</th>
<th>Granule size</th>
<th>% amylose</th>
<th>% amylopectin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat</td>
<td>3-35</td>
<td>26-28</td>
<td>72-74</td>
</tr>
<tr>
<td>Full waxy wheat</td>
<td>?</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Cassava</td>
<td>3-30</td>
<td>17</td>
<td>83</td>
</tr>
<tr>
<td>Maize</td>
<td>5-25</td>
<td>25-28</td>
<td>72-75</td>
</tr>
<tr>
<td>Waxy maize</td>
<td>?</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Amylose-rich maize</td>
<td>4-20</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>Pea</td>
<td>?</td>
<td>17</td>
<td>83</td>
</tr>
<tr>
<td>Potato</td>
<td>10-100</td>
<td>20-22</td>
<td>78-80</td>
</tr>
<tr>
<td>Prevalent GM potato</td>
<td>?</td>
<td>0-2</td>
<td>98</td>
</tr>
<tr>
<td>Rice</td>
<td>2-15</td>
<td>17</td>
<td>83</td>
</tr>
<tr>
<td>Waxy rice</td>
<td>2-15</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

Starches produce 3 major categories of products: native starches, modified starches and derivatives. Globally, the modified starch segment is experiencing rapid growth.

**Break-down of French starch production by product families, 2008**

<table>
<thead>
<tr>
<th></th>
<th>Native starches</th>
<th>Modified starches</th>
<th>Sugars and other</th>
<th>Totals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native equivalent</td>
<td>635</td>
<td>580</td>
<td>1540</td>
<td>2755</td>
</tr>
<tr>
<td>kt</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%</td>
<td>23 %</td>
<td>21 %</td>
<td>56 %</td>
<td>100 %</td>
</tr>
</tbody>
</table>

*Source: USIPA*
The USA, the leading starch producer, was also the leading consumer of starch in 2009, totalling 51% of demand. Consumption (and production) is growing very rapidly in Asia (China, India).

There are many non-food applications for starch. These are found in the following fields:

- The paper and cardboard industry (56% of non-food uses in France).
- Pharmaceuticals.
- Textiles.
- Biodegradable plastics.

The general properties of starches are those of binders, thickeners / texturing agents, flocculating / retention agents, humidifiers, plasticizers, dispersants and film-forming agents.

Modified starches are starches which have undergone various processes, by heat treatment (which breaks the starch chains into shorter elements such as dextrins) or chemical treatment (etherification, esterification).

**The paper and corrugated cardboard sector** is the industry which consumes the most starch.

In paper manufacture, modified starch is usually used (cationic esters) for its binding, adhesive, plasticizing, flocculating and film-forming properties. It has two applications:

- It may be incorporated into bulk paper at between 2 and 4%. It strengthens it, ensuring internal cohesion by forming cellulose-starch-cellulose bonds. The increasing addition of recycled paper, which has degraded fibres, makes the use of increasing quantities of starch necessary.
- It is used at the gluing press to avoid the sheets of paper linting.
- It is used in layering products, as a paper “covering”.

**Biodegradable plastics** are produced directly with starch. This starch may be plasticized with a small quantity of water, using a plastifier which may be glycerol. The product obtained is cheap to produce and perfectly biodegradable, but it takes a long time to stabilise during the process, has limited mechanical strength and is sensitive to water. Producing mixes of biodegradable polyesters and starch enables the overall properties to be improved. Multilayer products are also manufactured using a more hydrophobic polyester to protect the starch core.

The following companies producing starch-based plastics may be noted:

- **Biotec** (Germany), now a subsidiary of the French packaging group SPHERE, produces Bioplast®, a starch-based biodegradable plastic.
- **Limagrain Cereal Ingredient** manufactures plastic films using wheat starch and a degradable polyester, marketed under the Biolice® brand.
- **Novamont**, an Italian company, is one of the pioneers in the sector. It manufactures biodegradable thermoplastics (Mater-Bi®) from maize starch.
- **Solanyl® / Rodenburg** (Netherlands and Canada), produced using potato starch.
- **Plantic** (Australia), with a range called Eco plast®.
The other applications for starches are in pharmaceuticals (tablet coatings, dissolving agents, toothpastes), cosmetics (in make-up and beauty creams), textiles (fabric finishes, dye stabilisers), glues (hot melt adhesives, stamps, bindings, envelopes, stickers), metalworks, construction (binders for concrete blocks), mining (ore flotation and sedimentation agents, dust binders) etc.

Cyclodextrins are cyclic polyglucoses with 6, 7 or 8 glucose patterns, produced by enzyme hydrolysis of starch. Cyclodextrins can form inclusion complexes with a very large number of chemical entities, “capturing” or “protecting” their chemicals. As a result they are used to protect aromas, pharmaceutical active materials, etc. or to trap foul-smelling volatile components. Cyclodextrins have attracted attention for many years but their markets remain small. Cargill, Roquette and Wacker should be noted as producers.

II.1.5.3 – GLUCOSE DERIVATIVES

Starch is broken down into glucose by enzyme hydrolysis and will be presented in detail in the chapter dedicated to white biotechnology (IV.4).

Glucose is a C6 sugar, which carries 5 alcohol functions and an aldehyde group, with linear repeats.

Glucose is one of the first products of photosynthetic metabolism.

Three representations of glucose, in linear or cyclic form

Fischer projection  
Chair form  
Haworth projection of β D glucopyranose

II.1.5.3.1 - GLUCOSE DERIVATIVES PRODUCED BY CHEMICIL CONVERSION

SORBITOL

Sorbitol is a polyol with 6 alcohol groups. It derives from glucose by catalytic hydrogenation, with excellent yields. It is manufactured by most major starch producers. Annual production from glucose probably amounts to 500,000 tonnes.

This chemical has important applications as a polyol where it may be in competition with petrochemical polyols and glycerol, from the oilseed and biofuel production chains. Sorbitol is however solid at room temperature, whereas glycerol is a liquid which creates a distinction between several of their applications.

Sorbitol has several uses as a pharmaceutical excipient, in cosmetics (toothpastes) and food processing industries.
Sorbitol is also used to produce polyol polyethers, which in turn are components in the manufacture of polyurethanes, and for the production of non-ionic tensioactive agents (sorbitan esters) and vitamin C.

The European liquid sorbitol market

Source: Syral

Sorbitol has constantly been considered to be an important platform chemical, since the US DOE-NREL study in 2004, until its recent update in late 2009.

Potential sorbitol derivatives, according to the 2004 US DOE study

Among the derivatives presented below, some may be obtained directly by glucose or sugar fermentation (lactic acid, propylene glycol). Glycerol has become a raw material which is widely available and there is no interest – at least in the current state of play - in producing it from sorbitol. It should be noted that glycerol may itself be converted into propylene glycol.
The dehydration of sorbitol into 1,4 sorbitan, followed by the esterification of the latter with fatty acids, enables the production of sorbitan esters which have many applications as non-ionic tensioactive agents in the cosmetics and pharmaceutical sectors (the market represents some 50,000 tonnes).

The production of ascorbic acid or vitamin C from sorbitol is developing. It actually involves a combination of chemical and biotechnological processes and a synthetic intermediate, 2-ketoglutaric acid. Worldwide ascorbic acid production is around 80,000 tonnes.

Sorbitol may be polymerised into polyol polyethers which can be used in the synthesis of polyurethanes.

ISOSORBIDE AND DERIVATIVES

These are undergoing particular development as part of the Biohub® programme, conducted by Roquette Frères and partners.

Isosorbide is obtained by dehydrating sorbitol. It is a cyclic chemical, which means that it has particular properties which are rarely found in major products from biomass, except lignin. Its derivative, isosorbide nitrate, is used in the pharmaceutical industry for its vasodilatory properties. In addition, isosorbide is a synthetic intermediate for Dimethyl isosorbide which is a “green” co-solvent and fluxing agent.

Isosorbide diesters and plant fatty acids have non-toxic lubrication and plasticizing properties which are similar to those of phthalates, used in the production of PVC.

Isosorbide has many potential applications in the production of polymers. Isosorbide could be used for example as a copolymer for PET, (polyethylene terephthalate) in order to increase its resistance to high temperatures. It would be in addition to or a substitute to ethylene glycol. A very pure isosorbide is necessary for such applications.
Several other polymers can be obtained from isosorbide:

**Polymer derivatives from isosorbide**

![Polymer derivatives from isosorbide diagram]

Source: Roquette

Other derivatives extracted chemically from glucose include:

- **2,5-furan-dicarboxylic-acid (FDCA) and hydroxy methyl furfural (HMF) which belong to the furan group.** Both these C6 molecules can be obtained by oxidative dehydration of hexoses (glucose for FCDA, fructose for HMF which may itself be converted into FCDA). FCDA derivatives may potentially be in competition with terephthalic acid, utilised in polyesters such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT). By reaction with diamines, FCDA may lead to new nylons. FDCA was on the list of the “top 10” in the 2004 DOE studies and has been “reconfirmed” in the 2009 update. **Avantium**, in the Netherlands, has a high-yield catalysis technology to produce furans from sugars. Avantium is working with **NatureWorks/Cargill** on the development of furan polyesters. Avantium is also exploring the potential of the derivative ethoxyethylfurfural (EMF) as an additive in diesel fuel.

![Hydroxymethylfurfural (HMF) and 2,5 FDCA]

**Hydroxymethylfurfural (HMF)**

**2,5 FDCA**

*FCDA and HMF, which are both C6, must not be confused with C5 furfural, which is also in the furan family but obtained by chemical conversion from xylose. Furfural will be dealt with in the chapter on lignocellulosic sectors.*

- **Levulinic acid.** This C5 molecule, now obtained by acid-catalyzed dehydration of glucose, is another “confirmed” platform among carbohydrates. Its potential derivatives represent considerable volumes:
  - **2-methyl tetrahydrofuran (MTHF),** an oxygen-bearing additive for fuels which can replace MTBE (Methyl tert-butyl ether).
- **delta-aminolevulinic acid (DALA)**, a biodegradable weedkiller,
  DALA and MTHF could enable the development of the levulinic acid market with values of around 100 - 250 kt/year.
- **tetrahydrofuran (THF)** which has many solvent applications and **1,4 butanediol (BDO)** which is also used as a solvent as well as in plastics and polyurethanes. The last two chemicals can also be obtained from succinic acid – described below – the commercial production of which by fermentation is in the start-up phase.

---

Levulinic acid is another “top 10” for which no innovative industrial productions with improved competitiveness have yet been seen. It could be one of the chemicals produced from lignocellulosic raw materials (cellulose and also hemicelluloses) in second-generation biorefineries. In the late 1990s, the North American company Biofine was promoting a cellulose-based production technology, which it claimed to have developed under licence from the Pacific Northwest National Laboratory. It is now worth keeping a close watch on developments by the North American company Segetis which manufactures levulinic acid derivatives (from China?) and is envisaging producing them from lignocellulosic biomass.

- **C6 glucaric (or saccharic) acid** is manufactured by oxydation of glucose or starch with nitric acid. Its derivatives are polymers (polyhydroxy polyamides) which may compete withnylons on their mass markets.
Glucaric acid was also in the 2004 US DOE “top 10” but was not included in later studies. The North American start up Rivertop Renewables says it has a high-yield production process for glucaric acid using glucose.

- **Alkylpolyglucosides (APG)** are a meeting-point between the starch and oilseed production chains. They are prepared from fatty alcohols (usually short chain, therefore not from metropolitan France) and short chains for glucose, and have tensioactive properties used in household detergents, shampoos and make-up removers. Cognis (bought out by BASF) is thought to be world leader for these products, with the world market totalling 200 kt. Seppic (a subsidiary of Air Liquide) and Uniqema-Croda also produce APG.

**Alkylpolyglucosides – General formula**

![Alkylpolyglucosides formula](image)

II.1.5.3.2 - GLUCOSE DERIVATIVES PRODUCED BY FERMENTATION

There is a long list of glucose derivatives obtained by fermentation. We will not examine here chemicals such as ethanol, lactic acid, 1,3 propanediol, butanol or isobutanol which will be the subject of separate chapters (cf. III), since they can come from several different production chains.

**SUCCINIC ACID AND 1,4 BUTANEDIOL**

Succinic acid is a chemical produced naturally by the basic metabolism of living organisms, in what is known as the Krebs cycle, which succeeds glycolysis in the glucose degradation pathways to produce the energy necessary for cell metabolism.

Succinic acid had been identified as a “top 10” potential platform chemical in the 2004 US DOE study and has been confirmed in this position in more recent studies.

The succinic acid molecule has 4 carbon atoms and can be compared to that of petrochemically produced maleic anhydride. “Petrochemical” synthesis of succinic acid takes place by catalytic hydrogenation of this chemical or maleic acid (both made from butane or sometimes from benzene). Its two symmetrical carboxylic functions give it specific properties. The present-day market is still limited (30 - 50,000 tonnes), at prices of approximately €2 - 2.5 per kg.

![Succinic acid, Maleic anhydride, Maleic acid](image)

*: not to be confused with malic acid.

The challenge of production by means of fermentation is not only to obtain a biosourced product but also to achieve an efficient process enabling the product cost price to be reduced significantly (below €2/kg) to open up a much wider field of applications for it. Specific strains of *Escherichia coli* are used in current processes.
There are many potential derivatives of succinic acid, for solvents and particularly thermoplastic polymers. They are in direct competition with petrochemically produced maleic anhydride derivatives (it should be noted that the price of maleic anhydride has ranged between $0.75 and $1.45/kg over the last two years). During production, succinic acid (like lactic acid) is first isolated in the form of salt, calcium or potassium. Succinic acid is interesting for its deicing applications at airports.

- Succinic acid may be used as a monomer of PBS polyester (polybutylene succinate), a biodegradable polymer which as yet has a limited market (less than 10,000 t); its application could however be greatly developed. The current producers of PBS are Showa, Mitsubishi and Ire chemical. The other PBS monomer is 1,4 butanediol (BDO), now produced from butane and which could itself eventually be made from biosourced succinic acid (subject to even lower process costs). There is a large BDO market (1.3 million tonnes). Its price over the last few years has ranged between €1.5 and €1.9/kg. BASF is a major producer of BDO. In mid-2010, the Californian company Genomatica, founded by researchers at the University of San Diego and a partner of several companies including DSM and Braskem, launched the trial production of BDO by sugar fermentation (glucose) and is thought to be working on producing BDO from cane sugar.

1,4 butanediol market and derivatives

- Polyisosorbide succinate (PIS) is another more recently invented polymer which uses two chemicals from the starch production chain: isosorbide and succinic acid. Roquette and its partner DSM are working on this development.

Polyisosorbide succinate
Succinic acid may also be converted into the following:

- **Tetrahydrofuran (THF)**, which has direct applications as a solvent,
- **Gamma butyrolactone (GBL)**, also used for its properties as a solvent.

THF, BDO and GBL are precursors of the polyester monomers Polybutylene terephthalate (PBT) and polytetramethylene ether glycol (PTEMG), currently produced from maleic anhydride.

2-Pyrrolidone is used as a solvent, plasticizer and coalescent agent for polymer emulsion coatings and as a precursor of **PVP (Polyvinylpyrrolidone)** for which there are many applications in the pharmaceuticals, perfume, paper, food processing industries and in detergents, as a binder or humidifier. Worldwide production is still limited.

Fumaric and malic acid can be obtained using very similar processes and are easily converted into each other. They have the same potential derivatives. Aspartic acid, an amino acid which is the basis of aspartame, is now produced by enzyme reaction from fumaric acid. Its derivatives have many potential applications in the field of solvents and polymers.

### Succinic acid is the subject of a number of fermentation production projects worldwide, two of which are in France (Bio Amber, a subsidiary of the American company DNP Green Technology and the French company ARD; Roquette, in partnership with the chemicals company DSM) and one in Spain (the Dutch company Purac, with the technological support of BASF). In the United States, Myriant technologies (a spinoff of BioEnergy International LLC) is working on its own project, using sorghum. Like lactic acid (cf. III.2), Succinic acid must be neutralised in the form of a salt during production to avoid it inhibiting the bacteria which synthesise it. This salt must then be retreated using an acid.

Bioamber, founded in March 2008, now has a first unit with an annual capacity of 2000 t, on the Champagne-Céréales’ Pomacle-Bazancourt biorefinery site, which can supply it with raw materials. The production technology uses a specific strain of *Escherichia coli* and elements of the process provided by DNP Green Technology. This North-American company, with mainly Japanese capital, uses know-how developed and patented by the US DOE (US Department of Energy). Bioamber will be the sole supplier of succinic acid to Sinoven Biopolymers, which already produces partially biosourced PBS on sites in China.
For succinic acid production, **Roquette** also uses technology developed in the United States, (Rice University) and has entered a partnership with the chemicals company **DSM**, providing it with a close connection with market needs. The manufacture of innovative polymers, such as polyisosorbide succinate, could enable Roquette to use several chemicals resulting from its biorefinery activities in the same product.

**In the autumn of 2009, Mitsubishi Chemical Corporation** (MCC-Japan) announced a plan to study the possibility of producing succinic acid and PBS with the Japanese public company PTT Public Company Limited (PTT-Thailand). A joint venture was to be set up during the course of 2010.

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**The different derivatives of succinic acid**

![Diagram of succinic acid derivatives](image)

*Source: Hong & Lee.*

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**GLYCOLIC ACID**

Glycolic acid (or hydroxyacetic acid) has exfoliating properties used in cosmetics.

Glycolic acid may be used to manufacture **PGA (polyglycolic acid or polyglycolide)**, a biodegradable thermoplastic polyester. It now has applications in surgery and has properties as a barrier against O₂ and CO₂. Wider potential uses may be envisaged with a competitive product, in the production of plastic bottles for sodas and fruit juices.
Glycolic acid is traditionally produced by the reaction of chloroacetic acid with soda.

PGA may be obtained from the polymerisation of glycolide, the cyclic diester of glycolic acid (the direct polymerisation of glycolic acid produces only oligomers). PGA may also be manufactured by polycondensation of halogenoacetates or from formaldehyde and carbon by catalysis in an acid medium.

As part of the BioHub® programme, Roquette is developing a competitive process for the production of biosourced glycolic acid, with the exclusive use of a microbe strain developed by Metabolic Explorer.

3-HYDROXYPROPIONIC ACID (3-HPA).

3-HPA is another (C3) chemical with confirmed “top 10” status which has not yet emerged industrially. No 3-HPA is produced from fossil resources. Cargill has been working for several years (since 2002?) on the production of this chemical by fermentation from glucose (illustrations in § IV-4.1.2) and has committed itself for this purpose to a partnership with Novozymes. A major reduction in costs is still necessary to ensure the competitiveness of acrylic derivatives (currently produced petrochemically). 3-HPA could also be produced from glycerol.

It may be noted that direct production processes for acrylic acid by fermentation are being developed (OPX technologies, in the USA). The direct commercial production of 1,3 propanediol from glucose is already being carried out by Du Pont –Tate & Lyle using Genencor technology. Metabolic Explorer has developed a bioprocess for the production of 1,3 PDO from glycerol (cf. III.3).

Potential derivatives of 3-hydroxypropionic acid

Source: Cargill – DC. Cameron
ITACONIC ACID

This C5 acid was in the top 10 list in 2004 before disappearing from the lists of important potential platform chemicals. Itaconic acid may be produced from glucose, succinic acid or xylose. It is used as an additive in polymer fibre mixes to make them resistant to abrasive substances. The markets remain limited, with excess supply compared to requirements.

![Itaconic acid molecule]

Polyitaconic acid is a super-absorbent and dissolving agent, with applications in detergents, water treatment, etc.

The potential derivatives of itaconic acid should be able to be positioned as competitors of those of maleic acid and maleic anhydride.

The North American company Itaconix produces itaconic acid and polyitaconic acid. It considers that major markets, replacing those for polyacrylic acid, may be developed if sufficiently low market prices can be achieved ($1.5/kg for itaconic acid and $3/kg for polyitaconic acid).

PHAs (POLYHYDROXYALKANOATES): PHBs (POLYHYDROXYBUTYRATES)

Polyhydroxyalkanoates are a group of biodegradable linear polyesters, produced naturally from sugars or fats and stored within the cells of certain bacteria. There are over 150 monomers which may be used to make highly varied thermoplastic and elastomer materials, with very different melting points, ranging from 40 to 180 °C. Certain products have good water resistance and heat stability properties, and are easy to use.

Two PHAs have been the subject of particular work: the homopolymer PHB (polyhydroxybutyrate) and the copolymer PHBV (poly-3-hydroxybutyrate-co-hydroxyvalerate) which have properties comparable with those of polypropylene for a large number of applications.

![Poly-hydroxybutyrate, PHV, Poly-4-hydroxybutyrate, PHBV molecules]

Several companies produce PHB/PHBV: the Brazilian company Biocycle Copersucar (from cane sugar?), the German company Biomer, the Italian Bio-On (Minerv-Pha™), the Chinese Ecomann, the Chinese Tianan Biologics (Enmat brand), the American Telles (Metabolix/ADM joint venture (Mirel) from maize glucose; Procter & Gamble began production of a wide range of PHB copolymers but sold the activity several years ago.

ADEME
Monsanto worked on the production of bacterial PHB from genetically modified plants before selling the technology (and the Biopol® brand) to Metabolix in 2001. In 2008, Metabolix succeeded in producing PHA from switchgrass, a graminaceous plant grown to produce cellulosic biomass. Metabolix already has tobaccos whose biomass contains 3 to 5% PHA and is already working on sugar canes and oilseeds. Its objective is to extract PHA from these plants, with the residues being used to produce energy or biofuels.
II.1.6 - FRENCH PRODUCTION CHAINS: STRENGTHS, WEAKNESSES AND PROSPECTS

The following table sums up the main conclusions about the French starch production chains

The following should be noted:

- **Ample quantities of the raw material are available in France.** Although the main purpose of our cereal crops is human food and animal feed, our production chains are confronted with tough competition on the corresponding world markets; there is a strategic need for other consolidated industrial outlets. In addition, the co-products of starch and ethanol, with high fibre and protein contents, are used extensively in cattle feed and contribute to reducing France’s protein dependency on America.

- **The French cereal and starch production chain brings together major players such as Champagne Céréales, Roquette and Tereos, each of which develops robust, original strategies in plant chemistry. Soufflet is perfecting a particular fermentation technology.** All these groups have international business, and are in a position to analyse and take part in the work in progress in other continents. Their industrial partnerships with French (Deinove, Metabolic Explorer) and North American (Amyris, DNP Green Technology) biotechnology companies allows them access to innovative processes. Their work upstream with chemicals industrial companies (DSM, etc.) ensure that they are firmly connected to the market.

- **The dividing line between the starch and sugar market is disappearing.** The production of chemicals by fermentation can often use either non-purified saccharose or non-purified glucose as a substrate. In the medium term, the development of second-generation biorefineries, capable of breaking down lignocellulose, extends the list of raw materials which may be used. These raw materials may come from forests as well as cellulosic crops or certain types of waste.

- **Unifying industrial development programmes, coordinated by businesses, have been undertaken.** They appear to be very successful, in terms of both results and models: BioHub®, conducted by Roquette, Osyris, with Soufflet. The development of R&D and teaching hubs developed by ARD with its partners on the industrial site at Pomacle Bazancourt should also be highlighted.

- **The links between these leaders in this cereal and starch sector and our major French chemicals companies are not yet close enough,** and they do not lead to significant joint development projects. It is however necessary to form strong production chains which create added value to offset the upstream costs of raw materials, which are structurally higher in Europe than in various tropical countries.

- **Our refusal of plant GMOs is not as yet a serious handicap in terms of competitiveness,** but will soon become one. Our wheat and maize yields remain at a good level but are not growing sufficiently. We are absent from active developments in plant biotechnology, which within a few years will ensure future gains in productivity for these species in America and Asia. In the long term, this will be very costly to our farming industry.
**SWOT analysis of the French production chain**

<table>
<thead>
<tr>
<th>Strengths</th>
<th>Weaknesses</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Wheat and maize are the two largest French crops. The production chains are fully structured.</td>
<td></td>
</tr>
<tr>
<td>- Large areas of farmland may be mobilised for non-food crops for industry.</td>
<td></td>
</tr>
<tr>
<td>- The French starch production chain includes recognised world leaders, committed to plant chemistry projects.</td>
<td></td>
</tr>
<tr>
<td>- Industrial development projects which have substantial public support are demonstrating their relevance and producing their first results.</td>
<td></td>
</tr>
<tr>
<td>- A few active and innovative white biotechnology companies.</td>
<td></td>
</tr>
<tr>
<td>- As yet limited partnerships between the French chemicals industry and cereal production chains.</td>
<td></td>
</tr>
<tr>
<td>- The mass production of materials polymers from cereal production chains is as yet a distant prospect in France, whereas in the USA it is already under way.</td>
<td></td>
</tr>
<tr>
<td>- The number of national innovations available for white biotechnology is still limited. It is still necessary to import North American know-how in a number of cases.</td>
<td></td>
</tr>
<tr>
<td>- No active development of plant biotechnology, which offers increased agricultural productivity for the future.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Opportunities</th>
<th>Threats</th>
</tr>
</thead>
<tbody>
<tr>
<td>- High, volatile oil prices leading to increased attractiveness of biomass products.</td>
<td></td>
</tr>
<tr>
<td>- Rich chemistry of glucose and its derivatives.</td>
<td></td>
</tr>
<tr>
<td>- First-generation biofuel support policy implemented (has allowed the emergence of industrial chains for new uses of cereals).</td>
<td></td>
</tr>
<tr>
<td>- The development of non-food outlets in Europe is called for (animal feed, a very large consumer of wheat and maize, is in structural crisis in France; French cereal exports are subject to a great deal of competition).</td>
<td></td>
</tr>
<tr>
<td>- Structural costs for agricultural raw materials remain higher in Europe than in many southern countries.</td>
<td></td>
</tr>
<tr>
<td>- Weak growth of local markets in the chemicals industry in Europe compared to those of Asia and other developing regions.</td>
<td></td>
</tr>
<tr>
<td>- Insufficient understanding in our country of the structural and precursor role played by first-generation biofuel production chains.</td>
<td></td>
</tr>
<tr>
<td>- Refusal of green biotechnology in France and part of Western Europe.</td>
<td></td>
</tr>
<tr>
<td>- Support policy for industrial research and development of biorefineries is far more active in the USA than in Europe.</td>
<td></td>
</tr>
</tbody>
</table>
II.1.7 - RECOMMENDATIONS

- **Pursuit of a significant support policy for short-term selection of outstanding industrial projects.**
  Detailed analysis, with stakeholders and Oseo, of the initial results and lessons to be learned from the BioHub and Osyris projects to determine how to replicate (and possibly improve) the project model in the medium term, conducted by industrial players with significant budgets.

- **Stimulation of our research into white biotechnology**, for starch and glucose derivatives, through stringent selection of a number of teams and promising projects, thus avoiding dilution of resources.

- **Stimulation of the definition of joint projects between the cereal and starch production chains and the French chemicals industry.** Which biosourced chemical(s) derived from glucose may be of interest to our large chemicals companies and which may be produced at an attractive cost in France? How can we form a shared vision for French production chains and implement projects in order to achieve processes and competitive products?

- **Pursuit of the support of first-generation biofuels by stimulating the improvement of processes and environmental balances.** Communication about their role in the development of sustainable agroindustrial production chains of fuels and intermediates for the chemicals industry.

- Implementing a coordinated, sustainable approach to education and the promotion of the current and future roles of **green biotechnology**. This will be a preliminary stage for active industrial and academic research in this strategic field for our medium-term agricultural competitiveness.
II.2 - SUGAR PRODUCTION CHAINS

Sugar or saccharose comes mainly from sugar beet in our temperate regions and sugar cane in tropical countries. Saccharose combines a glucose and a fructose molecule. When hydrolised, these two C6 monosaccharides are produced; these derivatives of the “sugar” production chain are thus equivalent here to those of starch and glucose.

II.2.1 - BOTANICAL SPECIES, ORIGINS AND VARIETIES GROWN

Here we will examine two species - beet, grown in our temperate regions, and sugar cane which is strictly tropical.

**Beet, Beta vulgaris** is a plant in the chenopodiaceae family (like spinach and Swiss chard) which was domesticated in the East of the Mediterranean basin. There are wild forms of beet (*maritima* sub-species) in the coastal regions of Europe. Sugar beet (*Beta vulgaris subsp. Vulgaris, cultivar Altissima*) has been grown for the production of sugar only since the late 18th century, following the embargo on sugar imports from the West Indies. It is a biannual species, with a C3 photosynthetic metabolism the root of which serves as a reserve organ which stores sugar (saccharose). Sugar beet is sown in the spring and harvested from the first autumn.

The French beet seed market is divided between a few players in a sector which has gone through various movements of concentration and alliances. Florimont Desprez dominated the market in 2009, with a market share of 45% and its brands SES Vanderhave and Florimond Desprez, followed by KWS (33% ms), under its own brand or that of its American subsidiary Betased. 6 of the 55 varieties marketed in France account for 54% of the seeds sold.

Although no genetically modified varieties are currently grown in France, 95% of beetroot seeds in the USA and Canada were GMOs in 2009 (glyphosate resistance).

**Sugarcane, Saccharum officinarum** is a perennial diploid, a reedy graminaceous plant which grows solely in warm regions. It is believed to have been domesticated in New Guinea. Its C4 photosynthetic metabolism gives it outstanding growth performance. Its flowers are hermaphrodites and its pollination anemophilous, but the varieties grown are not very suitable for flowering, reproduction taking place by stem cuttings. The varieties are clones.

The development of GMO varieties, which have a higher sugar content and are herbicide, drought and insect-resitant, is making good progress. Although as yet there is no commercial production of GMOs in Brazil, BASF, Bayer, Allelyx-Monsanto and the CTC (Brazilian canesugar technical centre) are carrying out developments and open-field tests. Other experiments with GM cane sugar are taking place in India and Australia. Major impacts of GMO technology on yields are expected in the future, which could further increase the competitiveness of this crop compared to that of beet.

II.2.2 – CROP COMPOSITION

Sugar beet roots naturally have a high water content. Modern varieties contain 15 to 18% of sugar. The cane stem, which serves as a reserve organ only at its base, contains 12 - 16% saccharose.
Typical sugar beet composition at harvest (g per 100g)

<table>
<thead>
<tr>
<th>Components</th>
<th>Gross %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pomace (pectins, cellulose, protein, minerals)</td>
<td>4.2 (4-5%)</td>
</tr>
<tr>
<td>Juice</td>
<td>95.8</td>
</tr>
<tr>
<td>Water</td>
<td>77.3</td>
</tr>
<tr>
<td>Saccharose</td>
<td>16.5 (15-18 %)</td>
</tr>
<tr>
<td>Other sugars</td>
<td>0.1</td>
</tr>
<tr>
<td>Mineral salts</td>
<td>0.5</td>
</tr>
<tr>
<td>Nitrogenous substances, (protein, amino acids, betaine)</td>
<td>0.9</td>
</tr>
<tr>
<td>Non-nitrogenous organic substances (pectins, organic acids)</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Source: IRIS (Sugar Industries Research Institute)

Typical sugarcane composition

<table>
<thead>
<tr>
<th>Components</th>
<th>Gross %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>70</td>
</tr>
<tr>
<td>Saccharose</td>
<td>14 (11-16 %)</td>
</tr>
<tr>
<td>Fibres</td>
<td>14</td>
</tr>
<tr>
<td>Miscellaneous, mineral salts, protein</td>
<td>2</td>
</tr>
</tbody>
</table>

II.2.3 – AGRICULTURAL SIGNIFICANCE AND MAIN PRODUCING COUNTRIES

II.2.3.1 - RANKING OF PRODUCING COUNTRIES

Sugar beet is a temperate crop, of relatively modest importance both in France and worldwide, compared to cereal and oilseed crops (in France, 350 - 370 000 ha, compared with 7.4 million ha for straw cereals and 7.6 million ha for oilseed and protein crops).

Main sugar beet producing countries

<table>
<thead>
<tr>
<th>Country</th>
<th>Production, mt</th>
<th>1000 / ha</th>
<th>Yield, t/ha</th>
</tr>
</thead>
<tbody>
<tr>
<td>France</td>
<td>29.4</td>
<td>30.3</td>
<td>400</td>
</tr>
<tr>
<td>Russia</td>
<td>19.4</td>
<td>29.0</td>
<td>853</td>
</tr>
<tr>
<td>USA</td>
<td>27.7</td>
<td>26.8</td>
<td>545</td>
</tr>
<tr>
<td>Germany</td>
<td>23.8</td>
<td>23.0</td>
<td>446</td>
</tr>
<tr>
<td>Turkey</td>
<td>12.6</td>
<td>15.5</td>
<td>315</td>
</tr>
<tr>
<td>Ukraine</td>
<td>13.4</td>
<td>13.4</td>
<td>666</td>
</tr>
<tr>
<td>China</td>
<td>6.2</td>
<td>10.0</td>
<td>248</td>
</tr>
<tr>
<td>Poland</td>
<td>11.8</td>
<td>8.7</td>
<td>286</td>
</tr>
<tr>
<td>UK</td>
<td>9.2</td>
<td>7.5</td>
<td>162</td>
</tr>
<tr>
<td>EU</td>
<td>122.1</td>
<td>101.5</td>
<td>2299</td>
</tr>
<tr>
<td>Worldwide</td>
<td>229.7</td>
<td>227.6</td>
<td>5691</td>
</tr>
</tbody>
</table>

Source: FAO. Yields are expressed gross rather than with reference to sugar levels as for all other French and European statistics.

In 2009, France produced 35 million tonnes of “in-quota” 16% sugar beet on 371,000 ha. It is the leading sugar beet producing country (and the leading producer in the world of beet sugar), with an intensive crop method and much better yields that countries such as Russia, which has a lower total harvest and twice the surface area seeded. World beet production is tending to fall in spite of an increase in average yields.
Main sugarcane producing countries

<table>
<thead>
<tr>
<th>Country</th>
<th>Production, mt</th>
<th>Surface areas, x million ha</th>
<th>Yield, t/ha</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brazil</td>
<td>396</td>
<td>649</td>
<td>5.4</td>
</tr>
<tr>
<td>India</td>
<td>287</td>
<td>348</td>
<td>4.5</td>
</tr>
<tr>
<td>China</td>
<td>90</td>
<td>124</td>
<td>1.4</td>
</tr>
<tr>
<td>Thailand</td>
<td>74</td>
<td>74</td>
<td>1.1</td>
</tr>
<tr>
<td>Pakistan</td>
<td>52</td>
<td>64</td>
<td>1.1</td>
</tr>
<tr>
<td>Mexico</td>
<td>47</td>
<td>51</td>
<td>0.64</td>
</tr>
<tr>
<td>Colombia</td>
<td>39</td>
<td>39</td>
<td>0.40</td>
</tr>
<tr>
<td>Australia</td>
<td>37</td>
<td>34</td>
<td>0.45</td>
</tr>
<tr>
<td>Worldwide</td>
<td>1376</td>
<td>1743</td>
<td>20.8</td>
</tr>
</tbody>
</table>

Sugarcane is a plant which is grown between latitudes 37 North and 30 South. Brazil is by far the leading producer, ahead of India and China. In 2008, gross worldwide sugarcane production was 7.7 times greater than beet. Tonnages, surface areas and yields of sugarcane are increasing in the main producing countries.

II.2.3.2 - CHANGES IN BEET GROWING IN FRANCE

Beet growing is located mainly in the northern half of France (12 départements centralise 90% of production with a total of 29 départements concerned). Beet growing is generally grouped around the supply area for a sugar production plant (within an average radius of 30 km) to which the growers are bound by contract.

The surface areas for beet growing have been falling steadily since the early 1980s, when they had reached 650,000 ha, almost twice as much as at the present time. These falls in surface area are offset by higher yields, which are also regular. From 50 t-55/ha with 16% sugar in the early 1980s, there are now an estimated 94.5 t/ha (16% sugar) in 2009-2010, a record production of 14.5 t of white sugar per hectare, compared to 8 t/ha in the late 1970s (the actual average harvest in 2009 was 74.8 t/ha but with an exceptional sugar level of 19.5%). The average growth of yields is 180 kg of sugar per hectare per year over the past 20 years. Although varietal improvement has made an essential contribution to this growth, the increase in average spring temperatures is also a significant factor in the growth in yields. In France, beet, contrary to wheat, is benefiting from global warming.

Changes in beet growing surface areas in France (x 1000 ha)

Source: Agreste - Semences et Progrès
II.2.3.3 – SUGARCANE IN BRAZIL

Sugarcane yield depends on the stage of the crop at the time of harvest. In Brazil, the yield is 90 t/ha for a cane aged 12 months and 110 t/ha for a crop aged 18 months. The sugar yield may be in excess of 10 t/ha, although this remains lower than recent French beet yields. According to their proponents, the current developments of genetically modified canes will eventually enable rapid acceleration in the increases in yields, which are already observed. The competition between the two crops in terms of sugar production per hectare will therefore continue.

Example of changes in sugarcane yields in Brazil: crops owned by the Guarani subsidiary of Tereos International (t/ha)

Source: Tereos - 2008-2009 annual report
II.2.4 – DESCRIPTION OF SUGAR PRODUCTION CHAINS

II.2.4.1 - GENERAL OUTLINE

The outline in the appendix is for beet. The particular features of the sugarcane production chain will be set out in the following paragraphs.

The beet production chain is defined around the production of saccharose, its derivatives and bioethanol. Its major upstream and downstream products are as follows:

- **beet pulp** which is consumed mainly for animal feed but which has potential for a number of other applications.

  *The analogous product of sugarcane is bagasse, which is high in cellulose. It is usually burned to produce the energy required to operate the sugar production plant. Use for animal feed (for ruminants) is rare. The bagasse, or whole cane, could eventually become the raw material for second-generation biorefineries.*

- **Saccharose** is a major food product and has many industrial applications in various production chains.

- **Bioethanol**, to be used for biofuel production, is close to the “alcohol” reserved for other food and industrial applications, but is produced using the same technology. It is produced by fermentation, from sugar, molasses, or beet juice.

- **Molasses** is a major co-product. It is used as a fermentation substrate for the production of various products (including bioethanol) and several different substances are extracted from it.

II.2.4.2 – STAKEHOLDERS

**Seed manufacturers for the beet production chain in France.** Florimond Desprez, mainly its subsidiary SES VanderHave, KWS, Deleplanque, Hillshög, Ringot Maribo, Betaseed and Momont.

In Brazil, the sugarcane breeding organisations include: the CTC Centro de Tecnologia Canavieirí, Canavialis, etc.

There are currently 26,000 **beet producers** in France.

**The sugar companies:** in 2009 there were 7 in Metropolitan France, with a total of 25 sugar production plants (30 in 2005), all in northern France:

- Groupe Tereos (9 sugar production plants)
- Saint Louis Sucre (4 sugar production plants)
- Cristal Union (5 sugar production plants)
- Groupe Vermandoise (4 sugar production plants)
- Other companies (3 sugar production plants)

5 sugar production plants produce cane sugar in French Overseas Départements (La Réunion, Guadeloupe, Martinique).

**The main sugar companies in Europe** are presented in the table on the following page. Mergers are continuing in the sector.
In Brazil, the main (cane) sugar producers are Cosan, the French family-owned group Dreyfus and the French cooperative group Tereos. Bajaj Hindusthan Ltd is the leading sugar and ethanol producer in India and Mitr Phol is the leading Thai sugar producer. In Australia, Sucrogen (formerly CSR sugar) dominates domestic production.

The top 10 sugar companies in the EU by 2009-2010 quota (% of total)

<table>
<thead>
<tr>
<th>Companies</th>
<th>Country</th>
<th>Quota</th>
</tr>
</thead>
<tbody>
<tr>
<td>Südzucker</td>
<td>Germany / Belgium / France / Poland / Austria / Czech Republic / Slovakia / Hungary and Romania</td>
<td>25.1</td>
</tr>
<tr>
<td>+ Raffinerie Tirlemontoise</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ Saint Louis Sucre + Agrana</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nordzucker + Danisco</td>
<td>Germany / Poland / Slovakia / Denmark / Finland / Sweden / Lithuania</td>
<td>15.6</td>
</tr>
<tr>
<td>British Sugar PLC</td>
<td>United Kingdom / Spain</td>
<td>11.1</td>
</tr>
<tr>
<td>Tereos</td>
<td>France / Czech Republic</td>
<td>10.9</td>
</tr>
<tr>
<td>Pfeifer &amp; Langen</td>
<td>Germany / Poland / Romania</td>
<td>8.0</td>
</tr>
<tr>
<td>Royal Cosun</td>
<td>Netherlands / Germany</td>
<td>7.1</td>
</tr>
<tr>
<td>Cristal Union</td>
<td>France</td>
<td>4.5</td>
</tr>
<tr>
<td>Polski Cukier</td>
<td>Poland</td>
<td>4.3</td>
</tr>
<tr>
<td>Groupe Vermandoise</td>
<td>France</td>
<td>3.2</td>
</tr>
<tr>
<td>Italia Zuccheri / Co.Pro.B</td>
<td>Italy</td>
<td>2.2</td>
</tr>
<tr>
<td><strong>Total top 10 groups</strong></td>
<td></td>
<td><strong>92.1</strong></td>
</tr>
<tr>
<td><strong>Other</strong></td>
<td></td>
<td><strong>7.9</strong></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

Main sugar producers worldwide in 2007-2008 according to the Brazilian group Cosan (production: million tonnes). Mergers have taken place since then.

The dotted sections on the graph show the sugar equivalents in bioethanol produced by certain companies. The “JV” bar corresponds to the capacities of the joint-venture formed by Shell and Cosan at the end of 2009. LDC + Santezlla has become a subsidiary of the French group Louis Dreyfus.

Source: Cosan
Main sugar producers in Brazil in 2008-2009

<table>
<thead>
<tr>
<th>Company</th>
<th>Number of sugar production plants</th>
<th>Cane treated, mt</th>
<th>Sugar production, mt</th>
<th>Ethanol production m hl</th>
<th>Comments</th>
<th>Later events</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cosan</td>
<td>22</td>
<td>44.2</td>
<td>3.3</td>
<td>17.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Santesila Vale</td>
<td>6</td>
<td>17.6</td>
<td>1.0</td>
<td>0.8</td>
<td>Bought out by L. Dreyfus.</td>
<td></td>
</tr>
<tr>
<td>Guarani (Tereos)</td>
<td>6</td>
<td>13.8</td>
<td>1.1</td>
<td>0.5</td>
<td>External growth.</td>
<td></td>
</tr>
<tr>
<td>Santa-Terezinha</td>
<td>8</td>
<td>13.8</td>
<td>1.1</td>
<td>0.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moema</td>
<td>7</td>
<td>12.7</td>
<td>0.7</td>
<td>0.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carlos Lyra</td>
<td>7</td>
<td>12.2</td>
<td>0.9</td>
<td>0.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sao Martinho</td>
<td>4</td>
<td>12.0</td>
<td>0.6</td>
<td>0.68</td>
<td>Partner of Amyris for its pilot site.</td>
<td></td>
</tr>
</tbody>
</table>

In terms of marketing beet pulps, a number of French market players have concentrated their efforts within Desialis, of which the major sugar and lucerne producers have a share of the capital.

Bioethanol production from beet

5 companies produce ethanol from beet in France.

- Cristal Union (Bazancourt: Cristanol, Arcy).
- Groupe Vermandoise (Toury)
- Saint Louis Sucre (Eppeville-Ham)
- Sica Vallée du Loin (Souppes)
- Tereos (Origny-Sainte-Benoite, Bucy, Lillers).

II.2.4.3 - THE ECONOMICS OF THE PRODUCTION CHAIN

II.2.4.3.1 - STANDARD CONVERSION PARAMETERS

These are as follows for beet, taking into account that approximately 30 kg of sugar per tonne of beet remains non-extractable.

In sugar production:

1 t beet “16% sugar standard” → 160 kg sugar + 500 kg damp pulp + 38 kg molasses 18 kg sugar.

1 ha of beet → 13 - 14.5 t (record yield) of sugar

In distilling:

1 t beet “with 16% sugar” → 90-100 l pure ethanol + 4-5 kg yeast + pulp (48-52 kg dry matter) + residual water (with 1 kg nitrogen and 1.6 kg pot ash per m³).

In other words: 1 ha of beet = 75 hl = 6 t ethanol = 3.84 toe

1t molasses with 48% sugar → 290 l pure ethanol + 420 kg vinasse
For ethanol: 1 t = 12.65 hl   1 hl = 79.3 kg

Sugarcane (typical data)

1 ha sugarcane → 80 t cane

1 t cane → 740 kg juice (135 kg sugar and 605 kg water) → 115 kg sugars and 35 kg molasses + 260 kg bagasse with 50% water.

1 ha cane → 8 - 11.5 t sugar → 4000 l - 5500 l ethanol

II.2.4.3.2 - SUGAR PRODUCTION IN FRANCE AND THE EUROPEAN UNION

The EU framework

Sugar beet production in the European Union is covered by a regulation stipulating the volumes and prices through to 2014. Quotas are allocated to sugar and isoglucose production companies via Member States. The quantities produced within the framework of the quota are intended for the domestic food sugar market. The quantities produced above the quota are for the chemicals and pharmaceutical industries and the fermentation industries (including the manufacture of alcohol). They may be exported as reserves up to the limit of EU commitments to the WTO, or carried over to the following campaign.

Historically, the Union had encouraged and protected its sugar production but has gradually been obliged to reform its "sugar regulations" due to international pressure. In 2001, it opened its market to the least developed countries (LDCs). In 2006, quota production was cut by 25% and the guaranteed price reduced by 30%. The EU moved from the position of net exporter of sugar to that of importer for 25% of its current consumption. It has become the second-largest importer of sugar in the world.

EU sugar import regulations are in fact complex. LDCs retain free access, without customs duties, to the EU market. ACP countries also have free access but with an overall safeguard agreement of 3.5 mt. The Balkan states and Moldova have a quota of 402 kt free of customs duties. The major producing countries (Brazil, India, Australia, etc.) have a total quota of 677 kt with reduced duties. The EU may also open additional sugar import quotas for non-food industrial use (400 kt in 2009-2010). EU imports were finally 2.9 mt in 2008-2009, for exports of 0.82 mt (4 - 6 mt prior to 2006).

Guaranteed minimum price for quota beet, euros per tonne

<table>
<thead>
<tr>
<th></th>
<th>Prior to the reform</th>
<th>2006-07</th>
<th>2007-08</th>
<th>2008-09</th>
<th>From 2009-10*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Price net of tax</td>
<td>43.63</td>
<td>32.86</td>
<td>28.76</td>
<td>26.95</td>
<td>25.41</td>
</tr>
</tbody>
</table>

*: until 2014-2015

Source: CGB

In 2008-2009, the average out-of-quota price in France amounted was €20/t (average sugar content of 16%) which proved not to be very attractive for producers. It was revised slightly upwards by industrial companies in 2009-2010. Any production outside quotas is the subject of a contract between the growers and a processing industrial company which may use the sugar for industry or export it, up to the quotas negotiated with the WTO.

In 2009-2010 the sugar production forecast in the EU was 17.3 million tonnes, including quotas of 13.4 mt of white sugar.
Sugar production in France

French production in the 2009-2010 campaign amounted to 4.7 million tonnes of beet sugar, broken down as follows:

- 2.96 mt sold in France or the EU (= quota for Metropolitan France).
- 300 kt for the chemicals and pharmaceutical industry.
- 600 kt sugar outside quotas, exported to non-member states.
- 650 kt of sugar equivalents, converted into ethanol/alcohol.

In 2008-2009, 3 million tonnes of sugar were consumed in France, 59.2% of which in the food and catering industries, 20.3% in the form of alcohol / ethanol, 13.3% in the form of refined sugar and 7.2% by the chemicals and pharmaceutical industry. Some 2 million tonnes of sugar were exported (to Spain, Italy, Germany, the United Kingdom, Switzerland, Algeria, Israel, etc.) and 430,000 t were imported.

II.2.4.3.3 - WORLD SUGAR PRODUCTION AND THE INTERNATIONAL MARKET

It is not easy to monitor world statistics, as some data is expressed in the form of raw sugar and other data as white sugar. A conversion coefficient of 0.92 is applied to calculate raw sugar as white sugar.

Production and consumption are growing steadily, with the growth in world population. Brazil is by far the leading producer, followed by the European Union, India and China. Brazil is the leading exporter, followed by Thailand and Australia. India is the leading importer, followed by the EU, Russia and the USA.

<table>
<thead>
<tr>
<th>Main sugar producing countries (millions of tonnes of raw sugar)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Country</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Brazil</td>
</tr>
<tr>
<td>EU*</td>
</tr>
<tr>
<td>India</td>
</tr>
<tr>
<td>China</td>
</tr>
<tr>
<td>Thailand</td>
</tr>
<tr>
<td>USA</td>
</tr>
<tr>
<td>Mexico</td>
</tr>
<tr>
<td>Australia</td>
</tr>
<tr>
<td>Pakistan</td>
</tr>
<tr>
<td>Russia</td>
</tr>
<tr>
<td><strong>Worldwide</strong></td>
</tr>
</tbody>
</table>


Source: CEDUS - Sugar statistical memo.
Changes in worldwide raw sugar production

The share of beet sugar is falling steadily, due to a drop in beet production in the European Union and the USA, but above all due to the increased tonnages of cane sugar.

However, the strong growth in sugarcane production in Brazil does not lead automatically to increased sugar production in this country, as the share of the cane harvest for direct manufacture of ethanol is growing very quickly.

In 2010, sugar production in Brazil should be up by 19.1% with a total of 34 million tonnes, compared with the 26.8 million tonnes of the previous year. The cane harvest has grown by 10%; 595 million tonnes of cane were processed compared to 541 mt the previous year. 43% will be transformed into sugar and 57% will be destined for bioethanol production.

The price of sugar is subject to cyclical variations, which are sometimes considerable, depending on world tensions between supply and demand. If price changes are considered over a long period, the extent of variations is smaller, with prices showing a distinct downward trend. On the contrary, the price of fossil resources is increasing structurally and has become
more volatile. In the future, prospective analysis must remain cautious; the growth in world sugar demand and the rapid development of new uses for biomass may cause market regulation models to change.

An examination of prices over a more recent period shows upward variations which are up to twice as large (see below). For specific analyses, the price of raw sugar must be distinguished from that of white sugar. The differential ranges from between $45 and $160/t, but mean values of $100/t are common.

Recent changes in raw sugar prices (US$/t), from July 2007 to June 2010

Source: France Agrimer
II.2.4.3.4 - ETHYL ALCOHOL PRODUCTION AND MARKET

In 2008-2009 France produced some 8.5 million hectolitres of alcohol from beet of which 8.5 mhl from sugar beet, including 6.8 of bioethanol, for incorporation in fuels.

The ethyl alcohol and bioethanol market will be dealt with in more detail in § III.1.

<table>
<thead>
<tr>
<th>Alcohol production in France (thousands of hectolitres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005-06</td>
</tr>
<tr>
<td>From sugar beet</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

*Source: CEDUS – Statistical memo, from CGB, SNPAA.*

In 2010, Ethanol production in Brazil should reach 274 million hectolitres, up 15% on the previous year (237 million hectolitres).

II.2.4.3.5 - BEET PULP PRODUCTION AND MARKET

On average, the treatment of one tonne of beets enables the production of 500 kg of wet pulp. The quantities of pulp available therefore depend directly on the size of the harvest. The pulp remains the property of the beet growers, which is grounds for their being involved in the way the co-product is used.

<table>
<thead>
<tr>
<th>Beet pulp production in France and the EU</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>France (2009-2010)</td>
</tr>
<tr>
<td>EU-27 (2007-2008)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>raw, kt</td>
</tr>
<tr>
<td>Wet pulp</td>
</tr>
<tr>
<td>Compressed pulp</td>
</tr>
<tr>
<td>Dehydrated pulp</td>
</tr>
</tbody>
</table>

*: with 10.2% dm; **: with 27.1% dm; ***: with 88% dm.

*Source: CEDUS*

The prices of pulp have varied greatly over the last few years. They correlate with those of other agricultural commodities (cereals) as well as with the health of consumer livestock breeding sectors and the behaviour of buyers, who may favour spot or forward purchases.

The average price for pulp paid to the producer was €0.5 /t of beet in 2003-2004. It increased to €1.89 /t in 2008 before falling again. The dairy crisis and the livestock crisis in general, as well as the plentiful last harvest of beets, will lead to market saturation and a fall in prices.

The market price for dehydrated pulp (the most transportable and storable presentation of the product) has varied between €110 and €240 /t over the last few years, peaking in early 2008. The average sales price in 2008 was almost €155 /t whereas that of compressed pulp was in the region of €78 /t.

II.2.4.3.6 - THE MOLASSES MARKET

328 kt of molasses were produced in France in 2007-2008 (664 kt in 2002-2003) and 2.546 kt in the 27-member EU. France imported 473 kt, including 350 kt from non-member states and 123 kt from the European Union.
II.2.5 – THE MAIN PRODUCTS IN SUGAR PRODUCTION CHAINS

II.2.5.1 - USE OF BEET PULP

It should be noted that 1 t of beet harvested produces approximately 500 kg of pulp with 10% dry matter.

Beet pulp and bagasse composition (% of dry matter)

<table>
<thead>
<tr>
<th>Components</th>
<th>Beet pulp</th>
<th>Bagasse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>18 – 36</td>
<td>45-55</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td>18 – 32</td>
<td>20-25</td>
</tr>
<tr>
<td>including arabinoses</td>
<td>~ 20</td>
<td></td>
</tr>
<tr>
<td>including galactoses</td>
<td>~ 7</td>
<td></td>
</tr>
<tr>
<td>Lignin</td>
<td>3 – 6</td>
<td>18-24</td>
</tr>
<tr>
<td>Pectin</td>
<td>15- 32</td>
<td></td>
</tr>
<tr>
<td>Protein</td>
<td>5 – 10</td>
<td></td>
</tr>
<tr>
<td>Minerals</td>
<td>3 – 12</td>
<td>1-4</td>
</tr>
<tr>
<td>Residual sugar</td>
<td>2 – 6</td>
<td></td>
</tr>
</tbody>
</table>

*Source: CEDUS

Pulp is a biomass resource which includes as much cellulose as hemicelluloses. It differs from straws and timber-based products due to its low lignin content and high pectin content, with the latter containing specific sugars such as ferulic acid.

As we shall see below, three major uses of many farming co-products may compete for beet pulp: animal feed, energy production and the production of derivatives processed to varying degrees for other industries.

**Uses in animal feed**

This is currently the traditional – and virtually the sole – outlet for beet pulp. The pulp is sold wet (close to sugar production plants) or dehydrated. It is considered to be an excellent source of fibre for the species which require it (sows and rabbits as well as for pets such as dogs). It is also a very good raw material for ruminant feed.

The marketing of wet pulp is decreasing steadily as it is difficult to conserve, even on farms. Furthermore, transport costs for such a raw material with a high water content quickly become prohibitive.

**Composition of beet co-products used in animal feed**

<table>
<thead>
<tr>
<th>Content % of whole</th>
<th>Dehydrated pulp</th>
<th>Dehydrated pulp with molasses</th>
<th>Compressed pulp</th>
<th>Molasses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humidity</td>
<td>10.9</td>
<td>11.7</td>
<td>75.9</td>
<td>75.7</td>
</tr>
<tr>
<td>Crude protein</td>
<td>8.1</td>
<td>8.8</td>
<td>2.1</td>
<td>11.0</td>
</tr>
<tr>
<td>Crude cellulose</td>
<td>17.3</td>
<td>17.1</td>
<td>5.0</td>
<td>0</td>
</tr>
<tr>
<td>NDF*</td>
<td>40.5</td>
<td>40.1</td>
<td>11.6</td>
<td>0</td>
</tr>
<tr>
<td>Fats</td>
<td>0.9</td>
<td>0.6</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Crude ash</td>
<td>6.8</td>
<td>6.3</td>
<td>1.6</td>
<td>9.8</td>
</tr>
<tr>
<td>Starch</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total sugars</td>
<td>6.6</td>
<td>8.9</td>
<td>1.2</td>
<td>46.6</td>
</tr>
</tbody>
</table>

*Source: INRA tables for composition and nutritional value of raw materials

*: NDF (Neutral Detergent Fiber) is a common measure of fibre levels (lignin + cellulose + hemicelluloses + some pectins)
Likewise, the production of compressed pulp is falling because the silage process required to preserve it remains delicate. For reasons of cost, it cannot travel more than 150 km from sugar production plants, and these have become fewer in number over the last couple of years. Furthermore, compressed pulp is increasingly in competition with cereal ethanol distillers' grains.

Dehydrated pulp is used most commonly in the major livestock breeding regions in western France, which are a long way from the sugar beet production areas.

Uses as sources of energy

Dehydration of beet pulp requires expensive energy. Once it is dry, however, the pulp may itself used as a fuel.

2.6 t dehydrated pulp can replace 1 t fuel. The LHV of dry pulp is 3700 kcal/kg.

In pulp dehydration technology, the efficiency of prior pressing has been gradually improved over the last 20 years, enabling considerable savings in the following phase, which requires heat energy. Two avenues are being explored:

- The first consists of burning part of the dry pulp obtained to dehydrate the rest at high temperature. The investment is moderate but 45% of the pulp produced appears to be necessary to achieve this. The implementation of such practices would reduce the pulp supply on the market by the same amount.
- Another industrial approach is to dry the pulp with superheated steam, using the sugar production plant's evaporation unit. This system definitely makes more energy savings, but the investment is a lot higher.

Other studies have shown that a sugar production plant may become fully self-sufficient for energy by burning ¾ of its pulp after steam drying it. The “pulp” co-product could then become the energy source for sugar production. Beet sugar production plants would change in this scenario, along the lines of the cane sugar production plant model or paper pulp plants where the combustion of co-products provides energy self-sufficiency.

Pulp may also be used to produce biogas by methanisation.

Other uses for pulp

Over the last few years the beet production chain and its partners (including ADEME) have been conducting a large number of studies aimed at exploring other uses for beet pulp. Few however have industrial applications. The products from beet are in competition with those from petrochemicals and from other plant chains.

The main properties of beet pulp which are of interest relate to their high polysaccharide content and in particular pectins, with texturing properties and reticulation capabilities, and which may be converted into polyols.

Pulp is also used in the following ways:

- Fermentation substrate. Lyven, which has become a part of the Soufflet group, uses beet pulp as a fermentation substrate in the solid phase to produce enzymes.
Sources of galacturonic acid derivatives. Mucic acid results from the oxidation of galacturonic acid, which is found in the pectins in beet pulp. It is a cosmetic additive Soliance, a subsidiary of ARD. Fatty alcohols may be grafted into galacturonic acid and the other sugars found in pectins to produce very high quality tensioactive molecules of the alkyl galacturonate type. Their applications are limited to highly specific niches, given their high cost (compared to products of cereal origin).

There are also older projects for use, such as the following:
- Paper pulp additive. White pulp, which is dried and micronized, could replace starch in its functions as a binder.
- Plant filler in composite cements, for applications in panels to be used for soundproofing and heat insulation. Beet pulp is in competition here with hemp, wood sawdust, cork and cereal straw.

Other research which has been conducted includes the following:
- Its capability for removing toxic ions in water treatment.
- The absorbent capabilities of reticulated beet pectins.
- Pulp-based polyurethanes. Without purification, by means of treatment with propylene oxide, pulp can be converted into viscous polyol, which can then be mixed with polyisocyanates to form polyurethanes.
- Pulp as a vanillin production substrate. The pulp pectins contain ferulic acid which is a precursor, by fermentation, of vanillic acid and vanillin. Beet pulp is in competition with other raw materials with a high ferulic acid content such as rice bran.

II.2.5.2 – SACCHAROSE USES AND DERIVATIVES

Saccharose, which is a combination of a fructose and a glucose, has specific properties. Its molecule has 8 hydroxyl groups, each of which has a particular reactivity. This is both a strength from the point of view of the range of possible reactions and a weakness in that it is difficult to produce one reaction at a time. Saccharose chemistry or sugar chemistry combines the transformations directly using the saccharose molecule as a whole. Whenever the molecule is hydrolysed into its two components, glucose or fructose chemistry comes into play, which is partially described in chapter II.1 on the starch production chains as well as in chapter III, devoted to certain chemicals which can be obtained from multiple plant resources (such as ethanol).

Direct (non-food) uses of sugar

Saccharose is used directly in the following:
- Cements and concretes, to delay setting,
- Casting, to facilitate demoulding,
• Tobacco (to maintain a sufficient level of humidity),
• Plant care products,
• Glues, as an additive,
• Leather tanning.

Sugar in polyurethanes
10,000 t of sugar is thought to be used in the EU in the production of rigid polyurethane foams.

Specific derivatives with high added value. The following can be listed:
• Fructooligosaccharides. These are short chains produced by enzymatic conversion of saccharose. They have bifidogenic properties, used in human and animal nutrition.
• Sucralose, which was discovered by Tate & Lyle in 1976 is an intense sweetener manufactured by grafting 3 chlorine atoms onto saccharose.
• Olestra is a fat substitute made from a saccharose polyester and fatty acids. It was developed by Procter & Gamble in the 1970s but was not approved by the FDA until 1996. It is used in crisps and snacking products. The market is growing rapidly (several hundred million dollars).
• Sucralfate is a complex of hydrogen sulphate, aluminium and sucrose used in the pharmaceutical industry, for the treatment of duodenal and stomach ulcers.
• Polysucrose is a copolymer of saccharose and epichlorhydrin used in biological laboratories to create density gradients.

Saccharose fatty esters: sugar esters and sugar glycerides
These have been produced for a long time in Japan and more recently in France. Sugar esters are produced by transesterification in which the reactive agents are saccharose plus short or longer-chain (including C18) plant fatty acid methyl esters. These are non-toxic biodegradable products.

Sugar glycerides are mixtures of sugar esters and partial glycerides, resulting from the reaction between saccharose and triglycerides.

Sugar esters and sugar glycerides have tensioactive properties and are used as wetting and dissolving agents. They have many food industry applications in breadmaking, biscuits, confectionery, dairy products, mayonnaises, margarines, beverages, etc. Their antibacterial and antifungal activities are also used in various food preparations and fruit coatings.

Sugar esters are used as detergents in applications for which their high price is not prohibitive. They are used for washing fruit and vegetables, sea food and poultry. Their low lathering properties lead to their use in washing products for delicate textiles.

In the pharmaceutical and cosmetics industries, their detergent, antiseptic and emulsifying properties are used in applications for which they are incorporated into creams and gels. Their ability to form microemulsions favours the absorption of active principles and is grounds for other uses. Sugar esters are part of the composition of tablets and capsules, either as a lubricating agent for their manufacture, or to improve the solubility, dispersion and absorption of active chemicals in the digestive tube.
The largest market for sugar esters is that of SAIB (Sucrose Acetate Isobutyrate) which is reported to reach 100 kt worldwide.

II.2.5.3 - USE OF MOLASSES

Beet and cane molasses are commonly used in animal feed and as a fermentation substrate. Various chemicals can also be extracted from it.

Source for the extraction of certain chemicals

- **Betaine** is a metabolic precursor of methionine. It is used as an additive in animal feed and in the pharmaceuticals industry. Betaine derivatives are also used in cosmetics (shampoos, bath foams, makeup removal milks) for their amphiphilic properties.

Fermentation substrate

- **Baker’s yeast**
  
  Yeast makers in the EU (Lessafre, CSM, etc.) consume 750,000 t of locally-produced molasses and 250,000 t of imported molasses (cane and beet), producing 900,000 t of yeast.
  
  1 tonne of molasses enables the production of approximately 1 t of yeast.

- **Production of organic and antibiotic acids**
  
  Beet molasses are used for the production by fermentation of many organic acids:
  
  - amino acids (L-lysine, L-tryptophan)
  - lactic, citric, itaconic and propionic acid, as well as antibiotics (β-lactams).
II.2.6 - THE FRENCH PRODUCTION CHAIN: STRENGTHS, WEAKNESSES AND PROSPECTS

Among intensively-farmed French crops, beet is a highly productive plant and its yields are growing regularly. The production chain is highly organised and is able to conduct effective lobbying in spite of being small. However, its sustainability depends largely on political decisions and international negotiations.

The industrial processing of beet is complicated because the harvest has high water content and must therefore be processed in units close to growing areas.

The beet production chain produces three major products: sugar, alcohol (or bioethanol) and pulp.

The importance of food uses for sugar tends to obscure its potential for industry. Sugar chemistry is still a recent science and yet already seems to be taking a back seat. Saccharose derivatives, by hydrolysis or direct fermentation, are now in direct competition with starch derivatives. In the future, they will be in competition with the products of cellulose breakdown.

In France, the development of alcohol production from biomass is a process which for the most part is directed towards the manufacture of biofuels, the development of which is defined by the authorities. In Brazil, where production costs are much lower and the resource far more plentiful, active sugarcane ethanol chemistry is being developed to serve markets with much stronger growth dynamics than in Europe.

An impressive variety of studies have been conducted on the potential uses of beet, but as yet most of these are for animal feed.

<table>
<thead>
<tr>
<th>Strengths</th>
<th>Weaknesses</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Very good productivity for sugar and bioethanol per hectare (compared to cereals and sugarcane alike)</td>
<td>- Small chain, with limited production capacities.</td>
</tr>
<tr>
<td></td>
<td>- High production costs.</td>
</tr>
<tr>
<td></td>
<td>- No significant project in France for the production of molecules for chemistry.</td>
</tr>
<tr>
<td></td>
<td>- Production chain highly dependent on international negotiations for sugar and national support for bioethanol.</td>
</tr>
<tr>
<td></td>
<td>- Specific chemistry (sugar chemistry) is as yet little developed.</td>
</tr>
<tr>
<td>- Growth in yields. Potential for genetic improvement of beet (traditional selection and GMO).</td>
<td></td>
</tr>
<tr>
<td>- Perfectly organised and structured production chain.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Opportunities</th>
<th>Threats</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Development of synthetic intermediate production technology using sugar fermentation.</td>
<td>- Very strong competition with sugarcane, in particular from Brazil, for the main beet products.</td>
</tr>
<tr>
<td>- Increased oil price, making production chains using biomass more competitive.</td>
<td>This competition is increasing in regions experiencing strong growth with respect to farming and the chemicals industry.</td>
</tr>
<tr>
<td></td>
<td>- Competition with cereals production chains (distillers’ grains/pulp bioethanol, saccharose/starch derivatives).</td>
</tr>
<tr>
<td></td>
<td>- National and EU refusal of GMOs limits the prospects of increased productivity.</td>
</tr>
</tbody>
</table>
II.2.7 - RECOMMENDATIONS

In the list of development prospects for plant chemistry and biorefineries which is the subject of this study, the beet production chain is something of a dilemma. It scarcely provides any specific products and remains small in size. Modern beet sugar and ethanol production plants are however models of efficiency for the processing of wet biomass. What proposal should be made? Unfortunately the following recommendations only defer the answer, due to a lack of sufficient information.

A fundamental question must be dealt with: what is the current and future competitive positioning of France’s beet production chain as a potential supplier for the chemicals industry compared to that of the following:

- cereals in France and the EU,
- sugarcane in tropical regions (particularly Brazil and Asia)?

Going beyond purely economic considerations, what strategic grounds are there for supporting the development of a chemicals production chain for beet derivatives in France and the EU?

One proposal might be to conduct a prospective analysis of the expected changes in the relative competitiveness of the beet, wheat and sugarcane production chains (expressed in terms of glucose or ethanol equivalents), available for chemical conversion or conversion by fermentation (cost per kg of glucose and litre of ethanol). The prospects for progress in farming practices and the genetic improvement of crops (either by traditional breeding or genetic engineering) should be taken into account. The changes to be expected in farming production costs and industrial processing costs must also be analysed (incorporating in particular a steady drop in labour cost differentials between Northern and Southern countries, as well as taking into account the levels of economies of scale and whether or not they are accessible, depending on the production chains and regions).

Stated in more direct terms, the questions which require an answer are the following:

- Could producing ethylene from beet make sense in France?
- Although production of succinic and lactic acid and other fermentation products in the EU takes place on a considerable scale in our region of the world, would the beet production chain be suitable for supplying the substrates?

Another way of seeing things should be put forward: sugar and ethanol production plants are biorefineries for wet biomass. By definition, wet biomass cannot be transported over long distances or stored for long periods of time. The development of second-generation technology will open up new possibilities for processing various plant species. What other crops, produced close to French sugar/ethanol production plants, could be processed there in the future, in order to make their business smoother?

**Work on developing applications for beet pulp** should be concentrated on a selection of two or three avenues which offer genuine promise for an industrial future. The quantitative development potential for fermentation technology in a solid medium appears to merit closer examination. What tonnages of pulp-based substrate could be consumed in the future?
II.3 - VEGETABLE OIL PRODUCTION CHAINS

So-called oilseed plants store most or part of their seeds' reserves in the form of oils, or in other words fats, which are characterised by their variable-length carbon chains and high energy density, due to their low level of oxidation.

II.3.1 - BOTANICAL SPECIES, ORIGINS AND VARIETIES GROWN

Many oilseed species are grown. In France and the EU, rapeseed and sunflower are in the leading positions. Mention will also be made here of crops which are important in other regions of the world or which are of particular interest for plant chemistry: soybean, oil palm, coconut tree and castor bean. Peanut, safflower, cotton, linseed, jatropha, jojoba and other more secondary species will not be described in detail here.

Rapeseed or canola, *Brassica napus var. oleifera*, is an annual plant of the Brassicaceae (cruciferous) family which is thought to have been domesticated in Europe. It has a mixed reproduction regime with a predominance of autogamous reproduction. Cross-fertilisation is carried out for the most part by insects. Its “amphidiploid” genome is an ancient combination of that of the cabbage (*B. oleracea*) and turnip mustard (*B. campestris*). No “wild rapeseed” is to be found. However, cultivated rapeseed can exchange low levels of genes with adventitious turnips.

There are winter rapeseed varieties, which are sown in autumn and harvested the following summer and spring, as well as rapeseeds which complete their cycle between early spring and summer. In France, winter rapeseed, which has a higher yield, is predominant. Spring rapeseeds are for use as “catch” crops. They are however predominant in cold countries (Canada) and subtropical countries.

There are different types of modern rapeseed varieties:
- Pure lines.
- Restored hybrids (between a female line, sterile male and a pollinating line)
- Composites of hybrids and lines or hybrids.

There is still a non-negligible amount of farm seed breeding (estimated at 26%). Some 150 winter rapeseed varieties are marketed in France. In 2009, 4 restored hybrids and 8 lines held the top 12 positions. Monsanto occupied 43% of the French rapeseed market, Advanta 14.5%, Momont 11.5%, Syngenta 8.5% and Euralis 7.5%.

Sunflower, *Helianthus annuus*, is an annual diploid, a composite flower whose capitula are like hermaphrodite flowers in the centre. It has a C3 photosynthetic metabolism. Sunflower was domesticated in the East of the United States and underwent initial active breeding as a staple crop in Russia in the 18th century.

The sunflower is an allogamous plant with entomophilous pollination. The sunflowers grown in France and many other countries are hybrid varieties, resulting from the pollination of lines with male cytoplasmic sterility and lines with a restorative function. In France, sunflower is sown in spring and harvested in autumn.

Over 230 varieties of sunflower of variable earliness are marketed in France, including over 45 “oil-bearing” varieties. 5 companies dominate the seed market: Syngenta seeds (NK and Dekalb sunflower breeding, taken over in 2009 from the Monsanto group) with total market share of 46% in 2009, Euralis-Semences 16%, Pioneer semences (DuPont Group) 15%, Limagrain 10.5%, etc.
The soybean *Glycine max* is a diploid plant in the Fabaceae family (= Papilionaceae) which originated in northern China. It is an autogamous plant and the varieties grown are pure lines. Most of the soybean grown worldwide is transgenic, the introduction of non-selective weedkiller resistance having enabled its growing area to be significantly extended in certain countries and providing crops which do not require ploughing on fragile soils. Varietal research on soybean remains highly concentrated in the United States and the EU’s own selection work is limited (45 soybean varieties are however marketed in France).

Oil palm, *Elaeis guineensis*, is a perennial plant in the Arecaceae family grown for its fruit, the pulp of which supplies palm oil and palm kernel oil, composed of various fatty acids (cf. II.3.2). It is a diploid, monoecious, allogamous species, which originated in western Africa, from Senegal down to Angola. It was not introduced into South-East Asia until the 19th century.

The coconut tree, *Cocos nucifera*, is another perennial plant in the Arecaceae family, which probably originated in South-East Asia and is grown in the entire wet tropical zone, especially in the coastlands. It is a monoecious and preferentially allogamous species.

The castor bean, *Ricinus communis*, is a plant in the Euphorbiaceae family (like cassava and the rubber tree). Its geographical origin is a subject of controversy; the species is found spontaneously in all the tropical regions in the world. The differences between wild and cultivated forms are minor. Maximum genetic diversity is seen however in Eastern Africa and India. A diploid and monoecious plant, the castor bean is preferentially allogamous and has annual and perennial forms.

II.3.2 – CROP COMPOSITION

Rapeseed

Rape seeds are small. They have a very hard shell which is difficult to crush and a kernel in which the cotyledons constitute the reserve organs, with a high protein and oil content.

The composition of the rape seed has been greatly modified by traditional breeding over the last 40 years. The oil of old rapeseed varieties was rich in erucic acid (C22), which is blamed for being a cause of vascular disorders. Furthermore, the oilcake contained a large number of sulphur compounds, glucosinolates, which cause growth disorders in monogastric animals (pigs and poultry). Varieties known as “single zero” varieties with very low erucic acid content were produced, followed by “double zero” or “00” varieties which contain only a very small quantity of glucosinolates. They became widespread on the market for many years. In Canada these 00 rapeseeds are known as “canola”.

At the same time as the selection of 00s, varieties with very high erucic acid content but very low glucosinolate content were developed for specific markets. More recently, the first rapeseeds with very high oleic acid content were developed. It can also be noted that genetically modified rapeseeds, with high lauric acid content were developed in the USA in the 1990s. They do not appear to have been grown on a large scale.

*There are 2 varieties of rapeseed with a high erucic acid content marketed on the French market (Obtenteur: Semences de France) and a variety with a high oleic acid content (Dekalb-Monsanto.*
Composition of rape seed and oilcakes

<table>
<thead>
<tr>
<th>Content</th>
<th>Rapeseed</th>
<th>Rapeseed oilcake</th>
<th>48% (high-protein) Soybean oilcake (by comparison)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of whole</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Humidity</td>
<td>7.8</td>
<td>11.3</td>
<td>12.2</td>
</tr>
<tr>
<td>Crude protein</td>
<td>19.1</td>
<td>33.7</td>
<td>45.3</td>
</tr>
<tr>
<td>Lysine</td>
<td>1.19</td>
<td>1.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Crude cellulose</td>
<td>8.2</td>
<td>12.4</td>
<td>6</td>
</tr>
<tr>
<td>NDF*</td>
<td>17.6</td>
<td>28.3</td>
<td>12.2</td>
</tr>
<tr>
<td>Fats</td>
<td>42.0</td>
<td>2.3</td>
<td>1.9</td>
</tr>
<tr>
<td>Crude ash</td>
<td>4</td>
<td>7.0</td>
<td>6.4</td>
</tr>
<tr>
<td>Starch</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Source: INRA tables for composition and nutritional value of raw materials

*: NDF (Neutral Detergent Fiber) is a common measure of fibre levels (lignin + cellulose + hemicelluloses + some pectins)

Double zero rapeseed oil (canola) is considered by the industry first and foremost as a source of oleic acid. This justifies the interest in high oleic rapeseeds, which contain a lot of in this fatty acid and have been appearing on the seed market since 2006.

However, in human food uses of rapeseed oil, its linolenic acid content is highly prized for the nutritional qualities it derives from the latter.

Fatty acid contents of rapeseed and other vegetable oils (%)

<table>
<thead>
<tr>
<th>Fatty acids</th>
<th>Type</th>
<th>Rapeseed</th>
<th>Sunflower</th>
<th>Soybean</th>
<th>Coconut</th>
<th>Palm</th>
<th>Castor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0:0</td>
<td>erucic</td>
<td>traditional</td>
<td>High-oleic</td>
<td></td>
<td>palm</td>
</tr>
<tr>
<td>caprylic</td>
<td>C8:0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>capric</td>
<td>C10:0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>lauric</td>
<td>C12:0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>myristic</td>
<td>C14:0</td>
<td>0–1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>traces</td>
<td>15–23</td>
</tr>
<tr>
<td>palmitic</td>
<td>C16:0</td>
<td>1–5</td>
<td>3</td>
<td>5–7</td>
<td>4</td>
<td>8–13</td>
<td>6–11</td>
</tr>
<tr>
<td>stearic</td>
<td>C18:0</td>
<td>0.5–2</td>
<td>1</td>
<td>4–6</td>
<td>5</td>
<td>2–5</td>
<td>1–4</td>
</tr>
<tr>
<td>ricinoleic</td>
<td>C18:1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>linoleic</td>
<td>C18:2</td>
<td>15–30</td>
<td>14</td>
<td>62–70</td>
<td>8 (&lt;10)</td>
<td>50–62</td>
<td>1–2</td>
</tr>
<tr>
<td>linolenic</td>
<td>C18:3</td>
<td>6–13</td>
<td>10</td>
<td>&lt;0.2</td>
<td>&lt;1</td>
<td>4–10</td>
<td>trace</td>
</tr>
<tr>
<td>eicosenoic</td>
<td>C20:1</td>
<td>1–3</td>
<td>6</td>
<td>&lt;0.5</td>
<td>&lt;0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>behenic</td>
<td>C22:0</td>
<td>0.5</td>
<td>-</td>
<td>&lt;1</td>
<td>&lt;0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>erucic</td>
<td>C22:1</td>
<td>0–5</td>
<td>&gt;45 (50)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>


**Sunflower**

Sunflower seeds have fibrous shells which are high in cellulose, and a kernel containing oil and protein (the cotyledons are the reserve tissue).

Sunflower oilcake produced in France is generally not dehusked. It is high in fibre, with lower concentrations of protein and lysine than soybean oilcake. Dehusked sunflower oilcake has a higher protein content. Only one processing plant in France produces it (in Lezoux, Auvergne). Imported oilcakes from Argentina or Eastern Europe are usually dehusked.
Composition of sunflower seed and oilcake

<table>
<thead>
<tr>
<th>Content % of whole</th>
<th>Sunflower seed</th>
<th>Sunflower oilcake</th>
<th>48% (high-protein) Soybean oilcake (by comparison)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>non-dehusked</td>
<td>dehusked</td>
<td></td>
</tr>
<tr>
<td>Humidity</td>
<td>7</td>
<td>11.3</td>
<td>10.3</td>
</tr>
<tr>
<td>Crude protein</td>
<td>16</td>
<td>27.7</td>
<td>33.4</td>
</tr>
<tr>
<td>Lysine</td>
<td>0.6</td>
<td>1</td>
<td>1.2</td>
</tr>
<tr>
<td>Crude cellulose</td>
<td>15.5</td>
<td>25.5</td>
<td>21.2</td>
</tr>
<tr>
<td>NDF*</td>
<td>28.8</td>
<td>41.1</td>
<td>35.9</td>
</tr>
<tr>
<td>Fats</td>
<td>44.6</td>
<td>2</td>
<td>1.7</td>
</tr>
<tr>
<td>Crude ash</td>
<td>3.4</td>
<td>6.2</td>
<td>6.7</td>
</tr>
<tr>
<td>Starch</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Source: INRA tables for composition and nutritional value of raw materials

*: NDF (Neutral Detergent Fiber) is a common measure of fibre levels (lignin + cellulose + hemicelluloses + some pectins)

The fatty acid content of sunflower varies according to the varieties:

- “Traditional” sunflower oil is above all high in double unsaturated linoleic acid (C18:2), with only 20% oleic acid and mere traces of linoleic acid (C18:3).

- The oil of high oleic sunflower varieties contains at least 75% oleic acid (C18:1). However, the content generally stipulated in production contracts is 82% or more, with bonus-malus systems. Certain recent varieties contain as much as 90% oleic acid. High oleic sunflower production has long existed but was practically non-existent in France before the turn of the millennium. Since 2007, high oleic varieties have accounted for 50 - 60% of surface areas. They are in demand for industrial applications of oil, in the food industry and for the production of biodiesel. Bonuses of €8 to €15/t make its production attractive.

- Linoleic sunflower oil contains over 72% linoleic acid.

Soybean is a plant which is grown above all for its high-protein oilcake, used for animal feed, with oil being a co-product. The soybean seed contains 35% crude protein and only 18% oil, while the oilcake may contain over 45% crude protein. Soybean oil has a similar composition to that of “traditional” sunflower oil. It is therefore high in linoleic and oleic acid.

Copra (coconut) oil, palm kernel oil and, to a lesser extent, palm oil are sources of “short-chain” fatty acids, which justifies imports of these raw materials from tropical regions for the applications concerned.

Castor bean seed has a high oil content. This may be as high as 55 - 60% or even more. It has a very particular composition, with ricinoleic acid accounting for around 90% of the fatty acids. It is a C18 molecule with particular properties and applications arising from its hydroxyl function at C12 and double bond. The other castor oil fatty acids are mainly C18 (linoleic and oleic acids). The castor bean seed contains highly toxic or allergenic proteins (ricin, ricinine) and particular precautions are required with regard to the use of its co-products (oilcakes).
II.3.3 – AGRICULTURAL SIGNIFICANCE AND MAIN PRODUCING COUNTRIES

The table on the following page presents the production, surface areas and yields for rapeseed, sunflower and soybean in the main producing countries in 2008.

II.3.1.1 - RANKING OF PRODUCING COUNTRIES

The leading rapeseed producers are the European Union, Canada and China. France is the second largest producer in the EU after Germany.

Russia is the leading producer of rapeseed, ahead of the European Union, Ukraine and Argentina. In Europe, France is ahead of Hungary, Bulgaria and Romania.

World soybean production (231 million tonnes) is much larger than that of rapeseed and sunflower (58 and 37 million tonnes respectively). It is concentrated in the United States, Brazil, Argentina and to a lesser extent in China. The European Union is a very minor producing region, dominated by Italy (346,000 t).

Main rapeseed, sunflower and soybean producing countries in 2008

<table>
<thead>
<tr>
<th></th>
<th>Production (million t)</th>
<th>Surface areas (million ha)</th>
<th>Yield (qs/ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>rape-seed</td>
<td>sunflower</td>
<td>soy-bean</td>
</tr>
<tr>
<td>Canada</td>
<td>12.6</td>
<td>0.11</td>
<td>3.3</td>
</tr>
<tr>
<td>China</td>
<td>12.1</td>
<td>1.85</td>
<td>15.5</td>
</tr>
<tr>
<td>India</td>
<td>5.83</td>
<td>1.11</td>
<td>9.0</td>
</tr>
<tr>
<td>Germany</td>
<td>5.15</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>France</td>
<td>4.72</td>
<td>1.61</td>
<td>0.06</td>
</tr>
<tr>
<td>Ukraine</td>
<td>2.87</td>
<td>6.53</td>
<td>0.8</td>
</tr>
<tr>
<td>Poland</td>
<td>2.1</td>
<td>-</td>
<td>0.77</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>1.73</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Australia</td>
<td>1.62</td>
<td>0.07</td>
<td>-</td>
</tr>
<tr>
<td>Russia</td>
<td>0.75</td>
<td>7.35</td>
<td>0.8</td>
</tr>
<tr>
<td>United States</td>
<td>0.66</td>
<td>1.55</td>
<td>80.5</td>
</tr>
<tr>
<td>Brazil</td>
<td>0.17</td>
<td>0.15</td>
<td>59.9</td>
</tr>
<tr>
<td>Romania</td>
<td>0.67</td>
<td>1.17</td>
<td>0.1</td>
</tr>
<tr>
<td>Hungary</td>
<td>0.65</td>
<td>1.47</td>
<td>0.07</td>
</tr>
<tr>
<td>Bulgaria</td>
<td>0.23</td>
<td>1.30</td>
<td>-</td>
</tr>
<tr>
<td>Paraguay</td>
<td>0.06</td>
<td>0.2</td>
<td>6.8</td>
</tr>
<tr>
<td>Argentina</td>
<td>0.02</td>
<td>4.65</td>
<td>46.2</td>
</tr>
<tr>
<td>Total EU</td>
<td>18.92</td>
<td>7.10</td>
<td>0.65</td>
</tr>
<tr>
<td>Total Worldwide</td>
<td>57.86</td>
<td>36.64</td>
<td>231</td>
</tr>
</tbody>
</table>

Source: FAO. The data has been sorted in decreasing order of rapeseed production for the different countries. The FAO data adds the results of winter and spring crops for rapeseed and may therefore differ from national data presented separately.

The main producers of palm oil are Indonesia (19.2 mt) and Malaysia (17.7 mt), with Nigeria, Thailand, Colombia, etc. far behind, for a worldwide total of 42.4 mt in 2008, much higher than in 2000 (21.8 mt). The majority - 34 mt - is exported, including 15.4 mt from Malaysia and 14.6 mt from Indonesia. The main importing countries are India (5.7 mt), China (5.6 mt) and the European Union (5.5 mt). By comparison, between 2000 and 2008, world palm kernel oil production rose from 2.7 mt to 4.9 mt, with exports reaching 2.7 mt from Indonesia (1.3 mt) and
Malaysia (1 mt), etc. to the European Union (0.7 mt), China (0.3 mt), the USA (0.3 mt), etc. (Source: Fediol – Oil World).

The leading coconut oil (copra oil) producers are the Philippines (1.2 mt), Indonesia (0.8 mt), India (0.4 mt) and Mexico (0.1 mt) for a worldwide total of 3.2 mt in 2008. This has been stable at between 3 and 3.5 million tonnes for the past 10 years. The leading exporters are the Philippines (0.8 mt) and Indonesia (0.6 mt) whereas the major importers are the European Union and the USA (0.5 mt). In 2008, the European Union consumed 677,000 t of coconut oil, with Germany (205 kt) and the Netherlands (152 kt) being the top users. (Source: Fediol – Oil World).

The main producing countries of castor bean seeds are India (1,120,000 t) China (220,000 t) and Brazil (120,000 t). World castor oil production is relatively stable, varying between 400,000 and 600,000 tonnes per year. In 2008 the European Union consumed 131,000 t of castor oil, France being the biggest user (46 kt), ahead of Germany (39 kt) and Italy (18 kt). (Source: Fediol – Oil World).

II.3.1.2 - CHANGES IN OILSEED CROPS IN FRANCE

The surface areas of winter rapeseed are growing, due in particular to the demand created by the development of biodiesel.

Areas for sunflower are flatlining, whereas the proportion of areas devoted to high oleic sunflower now varies between 50 and 60% of the total. As the yields are similar, high oleic sunflower is favoured by the purchasing bonuses offered by industrial users in their contracts.

Soybean surface areas had already exceeded 120,000 ha in 1990 and again in 2001, before dropping steadily to 26-29 000 hectares over the last few years, with this crop becoming a minor crop in France.

Changes in winter rapeseed and sunflower surface areas in France

![Graph showing changes in winter rapeseed and sunflower surface areas in France from 1998 to 2010](Source: Agreste – Semences et Progrès)
The average yield of winter rapeseed in France is following a general upward trend. It reached record levels in 2009: 37.7 quintals per hectare, taking national production to 5.6 million tonnes on 1.47 million ha. Yields of 40 - 45 q/ha have been obtained to the north of the river Seine. In 2010, 1.46 million hectares are expected to be harvested.

Changes in average winter rapeseed and sunflower yields in France

Sunflower yields have not experienced any marked change, varying between 20 and 25 qs/ha in French regions.

II.3.4 – DESCRIPTION OF VEGETABLE OIL PRODUCTION CHAINS

II.3.4.1 - GENERAL PATTERN (see diagram in the appendices for rapeseed and sunflower production chains)

Rapeseed and sunflower are oilseed crops. The main products in their production chain are oil and its derivatives, as well as oilcakes for animal feed. Biodiesel is the leading non-food outlet for the chain.

The diagram presented in the appendix shows the major product families which may be obtained from rapeseed and sunflower. These include:

(1) upstream, oil coproducts. These are:

- **Oilseed straw** (or stubble) usually remains in the field and is buried. Rapeseed straw is particularly difficult to crush and is not the subject of any particular programmes for its use (fuel, second-generation biofuels) like that of cereals.

- **Oilcake**, used for cattle feed and thus contributing to the protein autonomy of France and the EU; the latter is still a major importer of soybean oilcakes from America. Sunflower protein, extracted from the oilcake, may have other applications.
Oil refinery coproducts include various chemicals. Rapeseed oil marketed to industry is usually semi-refined (it is simply demucilaginated and neutralised). Refined oils, marketed after discoulouration and deodorisation, are for food uses.

(2) methyl esters are the main non-food products for the production chain. As well as being used as biodiesel, they are also used as they are in biolubricants and as solvents. When hydrogenated, these esters enable the production of fatty alcohols, the applications of which derive from their tensioactive properties. The massive production of rapeseed and sunflower oil methyl esters makes this family of chemicals a new oilseed chemistry platform.

(3) glycerol is a co-product from the manufacture of methyl esters. It has many long-standing applications and derivatives. Glycerol is a platform chemical and certain chemical intermediates derived from it are now beginning to be produced on an industrial scale (epichlorhydrin, monopropylene glycol). Other projects are currently being developed (1,3 propanediol, acrylic acid, etc.).

(4) other products from the transformation or direct use of oil such as alkyd resins, ethyl esters and various fatty acid derivatives offering new prospects. Unprocessed rapeseed and high oleic sunflower oils have their own applications as biolubricants.

II.3.4.2 - INDUSTRIES CONCERNED

Oil extractors are industrial companies which specialise in extracting oil from seeds. This sector is highly concentrated in France. Saipol, the main shareholder of which is Sofiprotéol, shares the market with the French subsidiary of the North-American company, Cargill.

Oilseed extraction, oil refining and biodiesel production sites in France (esterification).
Elsewhere in the world, excluding Cargill, major players in extraction include the American companies Bunge and ADM (Archer Daniels Midland).

**Specialist chemicals companies** process the oils.

**Diester Industrie**, a subsidiary in which Sofiprotéol has a 66% share, is the leading producer of biodiesel and methyl esters in Europe. Oleon (formerly Petrofina) and Novance are Sofiprotéol's two oilseed chemicals subsidiaries.

- The other oilseed chemicals players in the EU are the following:
  - The German company Cognis (formerly Henkel, bought out in June 2010 by BASF) with 4 sites in France. Based in Boussens (Haute Garonne), Cognis produces 60 kt of fatty alcohols, ethyl esters, CLA, sterols and 110 kt of methyl esters Cognis claims to be world market leader for APGs (alkyl polyglucosides), made from coconut and palm oil.
  - The British company Croda and its Dutch subsidiary Uniqema.
  - The ester producer Stéarinerie Dubois.
  - The Italian company Parodi.
  - The French company Seppic, a subsidiary of Air Liquide.

**Producers of plant-based lubricants** include companies of different sizes, most of them SMEs. CCL, Condat, Entreprise Charentaise de Lubrifiants, Fuchs Petrolub Ag, Igol, Motul, Novance, Panolin can be noted in particular. Major players such as Total and other petroleum companies (Shell, Exxon Mobil, etc.) also include biolubricants in their ranges.

**Solvent producers** include Oleon, Novance, Uniqema-Croda as well as Cargill, Halterman, etc. Printing ink manufacturers include companies such as Coates-Lorilleux, Sicpa, Spci, Sun Chemical, Trenal. The producers of plant protection adjuvant oils are Bayer, Novance, Surfagri etc.

**II.3.4.3 - THE ECONOMICS OF THE PRODUCTION CHAIN**

<table>
<thead>
<tr>
<th>Rapeseed and sunflower in France - Data in kt</th>
<th>Rapeseed</th>
<th>Sunflower</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seed production 2009</td>
<td>5546</td>
<td>1735</td>
</tr>
<tr>
<td>Seed production 2008</td>
<td>4718</td>
<td>1574</td>
</tr>
<tr>
<td>Seed imports 2008</td>
<td>589</td>
<td>67</td>
</tr>
<tr>
<td>Seed exports 2008</td>
<td>2107</td>
<td>279</td>
</tr>
<tr>
<td>Seed extraction 2008</td>
<td>3157</td>
<td>1062</td>
</tr>
<tr>
<td>Oil production 2008</td>
<td>1289</td>
<td>452</td>
</tr>
<tr>
<td>Oil imports 2008</td>
<td>393</td>
<td>281</td>
</tr>
<tr>
<td>Oil exports 2008</td>
<td>353</td>
<td>273</td>
</tr>
<tr>
<td>Apparent oil consumption 2008</td>
<td>1329</td>
<td>460</td>
</tr>
<tr>
<td>Oilcake production 2008</td>
<td>1766</td>
<td>513</td>
</tr>
<tr>
<td>Oilcake imports 2008</td>
<td>619</td>
<td>163</td>
</tr>
<tr>
<td>Apparent oilcake consumption 2008</td>
<td>2136</td>
<td>610</td>
</tr>
</tbody>
</table>

*Source: Prolea*
A few basic ratios:

**Rapeseed:**
- 1 ha rapeseed produces (approximately) 35 quintals of seeds.
- 1 t seeds enable the production of 420 oil and 560 kg oilcakes.
- 1 t oil + 0.1 t methanol → 1 t methyl esters + 0.1 t glycerol

1 ha rapeseed → 1.47 t oil + (1.96 t oilcake) → 1.47 t diester + 0.15 t glycerol
100 000 t diester = 68 000 ha rapeseed & 130 kt oilcakes & 10 kt glycerol

**Sunflower:**
- 1 ha sunflower → 24 quintals of seeds
- 1 t seeds → 430 kg oil + 550 kg oilcakes
- 1 ha sunflower → 1 t oil + 1.3 t oilcakes

100 000 t oil ↔ 100 000 ha sunflower
100 000 t diester = 100 000 ha high oleic sunflower (130 kt oilcake, 10 Kt glycerol)

Rape and sunflower seed prices have varied greatly over the last few years, as have all agricultural commodities: between 2001 and early 2008, the Rouen rape seed price varied between €190/t (early 2005) and €500/t in early 2008 with recent prices ranging between €205 and €350/t. Sunflower seed has followed a similar path, with minimum prices below €200/t in early 2006 and a maximum price of almost €640/t in early 2008. Soybean seed, which is the benchmark, meanwhile varied (CFR Rotterdam) between €190/t (January 2005) and €430/t (July 2008).

Oil prices have changed according to fairly similar trends, also with very high peaks in 2008.
II.3.5 – MAIN PRODUCTS IN VEGETABLE OIL PRODUCTION CHAINS

Vegetable oils are composed mainly of triglycerides, which are fatty acid and glycerol esters. The main derivatives of vegetable oils are linked on the one hand to those of fatty chains and on the other hand those of glycerol.

II.3.5.1 - COPRODUCTS HIGHER UP THE CHAIN

Rapeseed and sunflower oilcakes. These are high quality, protein-rich raw materials for animal feed (cf. composition tables in II.3.2). Rapeseed oilcake has the advantage of having a well-balanced Lysine content, a limiting amino acid in monogastric animal feed.

Rapeseed oilcake is used mainly in ruminant and pig feed. This is a good substitute for imported soybean oilcake, in rations which must however be less concentrated. The development of biodiesel has seen considerable growth in French rapeseed oilcake supply and much wider use in cattle feed formulas, thus reducing our protein dependence on countries in the Americas.

There are two categories of sunflower oilcake. When oil is extracted from the whole seed, the oil produced is said to be “non-dehusked”. It contains the entire husk, which is rich in cellulosic fibres. It is used in cattle feed (cattle are capable of digesting cellulose) and also in monogastric animal feed, which require fibres (sows, rabbits, laying hens). Dehusked sunflower oilcake has a higher protein content and is therefore suitable for more concentrated rations. It is produced on only one site in France, but large quantities are found in imported products.
Changes in rapeseed and sunflower oilcake production in France (x 1000 t)

Source: Prolea

**Phospholipids**, which are separated from oil during the initial stages of refining, are used as emulsifiers.

**Phytosterols**

100 g rapeseed oil contain 850 mg of sterols, accounting for 93.3% of its non-saponifiable fraction. These sterols are mainly beta-sitosterol (45-61% for rapeseed, 58-64% for sunflower), campesterol (28-40% for rapeseed, 8-11% for sunflower) and brassicasterol (13-17% for sunflower).

Traditionally, sterols are extracted from oils during refining (at the deodorisation stage).

Phytosterols have many properties. They have hypercholesterolemia-inducing activities, but also anti-cancer, anti-viral and anti-inflammatory activities among others. In cosmetics, sterols are emulsifying agents, the properties of which are reinforced in ethoxylated form. They favour the regeneration of irritated and burnt skin and are also used in treatment agents for their anti-ageing properties.

Phytosterols are used for their quality and purity in the following areas:

- the synthesis of steroids in the pharmaceutical industry,
- food,
- cosmetics.

There are phytosteroids which compete with those of rapeseed and sunflower in soybean oil and tall oil, a co-product from the manufacture of paper from soft wood.

**Tocopherols, including vitamin E**, are also isolated at the deodorisation stage, during the final stages of oil refining.
II.3.5.2 - SLIGHTLY PROCESSED OR UNPROCESSED PRODUCTS

High oleic sunflower, double-zero rapeseed and high erucic oils have direct applications as biolubricants. They are known as HETGs (Hydraulic Oil Environmental TriGlycerides). The performances of non-modified oils are limited but are suitable for certain lubrications which do not have stringent requirements in terms of temperature, for instance chainsaw chains. Such biolubricants are composed of refined oil and additives. They have the advantage of coming from renewable, biodegradable and non-ecotoxic resources.

High oleic sunflower oils are more resistant to temperature rise than rapeseed oils, the C18:3 linolenic acid content of which is relatively high. Rapeseed oil is however much cheaper and is preferred for all applications with less stringent requirements.

The development of biolubricants in France and the EU is highly dependent on incentives and environmental obligations imposed by the authorities, particularly for single-use lubricants or with regular accidental losses.

The EU lubricant market is worth around 5 million tonnes, including 1200 kt in Germany and 800 kt in France, between 100 and 200 kt of which is single-use lubrication. The EU market for biodegradable lubricants was no more than 125 kt in 2006 but has been growing steadily by 3-4% per year. Biolubricant market share is high in Germany (15%) and Scandinavia (11%), but remains low in France (1-2%?) and Spain. Petrochemical biodegradable lubricants should be distinguished from plant-based biodegradable lubricants. In 2005, the latter accounted for less than 1000 t in France compared to 3500 t of petroleum-based biodegradable lubricants.

In the United States, the plant-based biolubricant market remains very small (25kt in 2008 - source: United Soybean Board) but could grow with the development of high oleic soybean (standard soybean oil has to high linoleic acid content to perform well).

The oil used directly as fuel for diesel engines has undergone limited developments. The risk of damaging new engines is high, because they are not suited to fuel which is too viscous. Non-processed oil has a much more favourable carbon balance than biodiesel made from methyl esters, except in that its combustion produces aldehydes. Oil to be used for fuel must be refined or at least degummed, which vastly complicates processing it “on the farm”.

Rapeseed has minor applications in the field of plant care adjuvants and solvents but esters are the most successful in this area.

II.3.5.3 - OTHER RAPESEED AND SUNFLOWER OIL DERIVATIVES

Alkyd resins
Semi-siccative alkyd resins can be obtained from sunflower oil. These have applications in coverings (paints, lacquers, varnish) and inks. 5 - 10 kt of sunflower oil are thought to be used in this way each year.

Non-siccative alkyd resins can be obtained from rapeseed oil and terephthalic acid. The industrial applications are for minor markets for varnish or paints designed to dry other than by oxidation of carbon chain double bonds.
Polyols and polyurethanes
Rapeseed oil can be converted into hydroxylated oil with various alcohol functions. The resulting polyols have prospects in polyurethanes. Various research work has been published on this subject, but there has been no industrial development to date.

II.3.5.4 - METHYL ESTERS AND DERIVATIVES

Rapeseed and (high oleic) sunflower methyl esters are often known as VOMEs (vegetable oil methyl esters). They are produced by transesterification, in which the oil triglycerides react with methanol (which is of fossil origin). Glycerol is the coproduct of the reaction.

Transesterification

\[
\begin{align*}
\text{Transesterification} & \\
\text{H}_2\text{C} & \text{O} \quad \text{H}_2\text{C} \quad \text{H}_2\text{C} \\
\text{C} & \text{O} \quad \text{C} \quad \text{C} \\
\text{R} & \text{OH} \quad \text{OH} \quad \text{OH} \\
\text{H}_2\text{C} & \text{O} \quad \text{C} \quad \text{R} \\
\text{R} & \text{OH} \quad \text{OH} \quad \text{OH}
\end{align*}
\]

Progress in technology
Transesterification processes for the production of methyl esters have undergone major changes and significant improvements in their efficiency. The conventional process is homogenous catalysis in an alkaline medium. The continuous-flow heterogeneous catalytic process is more environmentally-friendly as its synthesis yields are higher. This facilitates purification and pollutant emissions are lower. It has been successfully implemented at the Diester biodiesel production plant in Sète. The glycerine obtained is very pure.

Biodiesel
This is the landmark application for rapeseed and high oleic sunflower methyl esters. “Traditional” sunflower oil methyl esters are not suitable for the production of biodiesel, due to their high linoleic acid content. VOMEs have properties which are very similar to those of diesel and are therefore suitable for mixing with diesel. The addition of high oleic sunflower VOME to rapeseed VOMEs enables the iodine value to be reduced, which is of interest for fuel formulators.

VOMEs may be included in traditional distribution circuits in this way. Rapeseed methyl esters also have the following advantages:
- better lubricating capabilities, enabling the sulphur content of diesel fuels to be reduced more easily, in keeping with the new standards.
- natural anti-wear properties, due to the ester function,
- odourless, non-toxic, over 98% biodegradable within 21 days,
- reducing the production of particles.

They have the drawback of lower heat stability, all the more so because the fatty acids used have double bonds.
## Comparison of diesel and rapeseed VOME properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Diesel</th>
<th>Rapeseed methyl esters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/m3, at 15 °C)</td>
<td>820-845</td>
<td>880-885</td>
</tr>
<tr>
<td>Viscosity at 40°C (mm²/s)</td>
<td>2-4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Flashpoint (°C) (lowest temperature at which the vapour emitted is inflammable)</td>
<td>&gt; 55 °C</td>
<td>188 °C</td>
</tr>
<tr>
<td>Cloud point (°C)</td>
<td>&lt; -5</td>
<td>-3</td>
</tr>
<tr>
<td>CFPP (°C) (Cold Filter Plugging Point, the temperature at which it clogs the filters)</td>
<td>&lt; -15 °C</td>
<td>-12 °C</td>
</tr>
<tr>
<td>LHV (kJ/kg) (quantity of heat released by combustion)</td>
<td>42,300</td>
<td>37,040</td>
</tr>
<tr>
<td>Cetane index (likelihood of spontaneous combustion)</td>
<td>51</td>
<td>49-51</td>
</tr>
<tr>
<td>Sulphur content (mg/kg)</td>
<td>350</td>
<td>10-2</td>
</tr>
</tbody>
</table>

*Source: Prolea*

In France, rapeseed and high oleic VOMEs are used mixed with diesel in variable proportions, ranging from a few percent to 7% in ordinary diesel and 30% for captive fleet fuel, the general objective being 5.75%. Pure use is possible but would require technical developments for engines.

Biodiesel production in France is regulated, with quotas allocated to industrial companies. Other incentive systems are in force in other countries. The map shown below includes industrial companies which produce biodiesel from raw materials other than vegetable oils.

**Biodiesel production in France: sites, players and capacities**

![Map of biodiesel production in France](image)

**Changes in biodiesel production in Europe**

![Map of changes in biodiesel production in Europe](image)
Biodiesel production is increasing rapidly worldwide. According to the international energy agency (IEA), in 2009, production had increased ten-fold during the previous eight years, reaching 10.9 billion litres (9.6 mt) in 2008, and could double again between 2009 and 2012. In 2010, forecasts were for production of over 15 mt. Europe is still dominating the scene as regards biodiesel made from rapeseed and sunflower oils. In the Americas, soybean oil is the most-used and palm oil – produced sustainably or otherwise – is used a raw material for biodiesel in South-East Asia.

In the USA, production has been stimulated by imports from the European Union until anti-dumping measures were taken, leading to purchases slumping. Production in the USA reached 2.7 billion litres (2.3 mt) in 2008 before dropping sharply in 2009, with a less than favourable trend for 2010. There are thought to be 180 biodiesel production plants in the USA, working at 15% of their capacity.

There are a dozen or so biodiesel manufacturing plants in Canada (using rapeseed) with production capacity which will reach 550 million litres (450,000 tonnes) on start-up of a new 225 million-litre unit currently being built in the west of the country.
Brazil now has 43 biodiesel production plants with a total capacity of 3.9 billion litres. Actual production of 2.4 billion litres (2.1 million tonnes) is expected from 2010 onwards. From 2008 onwards, the government has established a biodiesel incorporation rate: at the beginning of 2010, it decided to increase this from 4 to 5%.

Argentina has become a major producer of biodiesel with production capacity of 2.4 million tonnes, a very limited domestic market and therefore high export potential, both to its neighbouring countries (Brazil) and to Europe.

In Malaysia, and in other major palm oil producing countries in South-East Asia (Indonesia, the Philippines), many biodiesel production plants are planned, with capacity in excess of one million tonnes.

**Biodiesel eco-assessment**

Biodiesel's eco-assessments have been the subject of many studies and considerable controversy regarding methodological issues. The lifecycle analysis approach is already complex when a single parameter of a product is studied (energy balance or CO₂ balance) as the method for taking coproducts into account is disputed. Recent analysis models take a whole host of criteria into consideration. The desire to test the strengths and weaknesses of first-generation biofuels has meant that their fundamental role in the development of fossil fuel substitute production chains and reducing energy dependence on non-EU member states has been overlooked. The diversity in eco-assessments of the different fossil fuels depending on the nature and modes of operation of oil fields is not subject to the same scrutiny. It should also be noted that there are no oil spills from biofuels and that vegetable oil methyl esters are, on the contrary, outstanding biodegradable solvents which can help clean areas polluted by hydrocarbons on the coastline.

Following significant methodological work, a study on the lifecycle analysis of a large number of biofuels has been carried for the ADEME by BIO Intelligence Service. It also shows the good performance of vegetable oil methyl esters, including in intensive systems in Europe.

**Reduction in non-renewable energy consumption of various biofuels (as % of reduction compared to the fossil reference)**

<table>
<thead>
<tr>
<th>Biofuel</th>
<th>Reduction</th>
<th>Actual</th>
<th>Prospective</th>
</tr>
</thead>
<tbody>
<tr>
<td>EHMAU Used oil esters</td>
<td>65%</td>
<td>68%</td>
<td>69%</td>
</tr>
<tr>
<td>EMGA Animal fat esters</td>
<td>78%</td>
<td>81%</td>
<td>81%</td>
</tr>
<tr>
<td>HVP PVO Pure Vegetable Oil</td>
<td>81%</td>
<td>81%</td>
<td>82%</td>
</tr>
</tbody>
</table>

Source: ADEME / BIO Intelligence Service study - “LCA of first-generation biofuels in France”, February 2010.

EHMAU = Used oil esters, EMGA = Animal fat esters, HVP = PVO: Pure Vegetable Oil
In 2007, the French oilseed interprofessional body carried out a progress procedure to improve the energy balance and reduce greenhouse gas emissions for the entire biodiesel production chain. Many improvements are possible, mainly in agriculture, but also with respect to certain industrial operations. The procedure is ongoing.

Other rapeseed and sunflower methyl ester applications

Rapeseed and sunflower methyl esters are used as they are for the following:

- **Solvents for non-volatile and non-toxic printing inks.** The particular target for methyl esters relates to quickset offset inks, the drying of which is carried out both by means of infiltration in the medium and by oxido-polymerisation. The vehicle for these inks is traditionally composed of hard colophony resin and a mix of mineral oils, vegetable oils and alkyd resins. Rapeseed or soybean esters can replace mineral oils. They enable the resins to be solubilised whilst maintaining the necessary viscosity. They have the drawback of percolating the medium slowly, not allowing optimised fixing and drying, and of being expensive.

- **Plant care adjuvants or solvents** These replace petrochemical aromatic solvents. VOMEs have good properties and are biodegradable.

- **Surface-cleaning solvents.** These applications are at the technical development and commercial stage.

- **Biolubricants.** Rapeseed methyl esters can be used in cutting oils and for metalworking, to replace tallow methyl esters. This is a potential which is not yet exploited. Rapeseed methyl esters can be used in other lubrication applications, either as a lubricant base, or as an additive to lubricants made from petrochemical PAOs (poly-alpha-olefins).

- **Bitumen fluxes** Sunflower methyl esters can be used to replace oil-based fluxes. Sunflower methyl esters enable the viscosity of bitumens to be reduced without the high volatility of oil-based products. They are more biodegradable. The bitumen flux market is 54 kt in France.

Methyl ester derivatives

- **CLAs or Conjugated Linoleic acids** are produced industrially from sunflower methyl esters. CLAs exist in the form of many different isomers, including some which have well-established properties for human health (anti-cancer, antioxidant, cholesterol and fat reducing). **Cognis** produces two specific CLA isomers from high linoleic sunflower oil methyl esters (> 72%). These are for use in animal feed and enable the fat content of meats to be reduced. Presentations which are coated or come in the form of CLA calcium salts are necessary to avoid it breaking down in the cattle rumen.

- **Fatty alcohols** Rapeseed methyl esters can be hydrogenated to produce fatty alcohols.
Fatty alcohol applications can be broken down as follows:

- **Detergents:** 70% (mostly made from C12 or C14 chain alcohols, inevitably imported: copra, palm kernel)
- **Chemicals industry:** 18%
- **Lubricants:** 8%
- **Cosmetics:** 4%.

The last three sectors of application can use C18 chains, like those of rapeseed, sunflower and also soybean and palm.

C16-C18 fatty alcohols, like those from rapeseed, are used as anti-foaming agents and texturing agents for creams, pastes, polishes and lipsticks. There is a very high degree of competition with palm oil.

Rapeseed fatty alcohols are also converted into ethoxylated or sulfated alcohols, which are used on the cosmetics market for their tensioactive properties.

Fatty alcohols may also be used to produce APGs (Alkyl PolyGlycosides), surfactants of which the hydrophilic head is a sugar. Cognis is a major producer of these products. The fatty chains are generally short, from copra and palm kernel.

**Sulfo methyl esters** have applications as surfactants and foaming agents, in particular in cosmetics.

### Alkenyl Succinic Anhydrides (ASAs)
Produced by the reaction between maleic anhydride and an alkene, ASAs are a family of chemicals which are used in industry as paper gluing agents, detergents for oil products, additives for fuels, lubricants, and as wood processing products.

Petrochemical ASAs have been supplemented by MASAs (Methyl Alkenoate Succinic Anhydrides), chemicals produced by the maleinization of plant methyl esters (rapeseed or sunflower). Major work has been carried out on MASAs and their applications by the INP Toulouse Agro-Industrial Chemistry Laboratory.

[Molecular structure of ASA and MASA](https://example.com/structure)

MASAs are non-toxic wood protectors which can replace fungicides and toxic insecticides. They have major potential (10 million m³ timber in France). Developments are under way which show that such products can provide protection for risk class 3 (outdoor timber, subject to rapidly alternating damp and drying: windows, doors, external coverings) and 4 timber (outdoor timber, such as posts, fences, footbridges). Products are now at the pre-commercial stage, with companies such as Lapeyre carrying out the first industrial uses.

MASAs have other potential applications in the paper industry as gluing agents.
II.3.5.6 - OTHER FATTY ACID DERIVATIVES

Through biodiesel production, methyl esters produced directly by oil transesterification have taken a major place in the rapeseed and sunflower industrial production chain. More traditional oilseed chemistry often used fatty acids as raw materials (sometimes re-esterifying them with glycerol).

These products are purer, with a much better defined composition. They are also more expensive and used only for applications such as cosmetics. "Esterifiers" produce fatty acid esters with glycerol, ethanol or synthetic alcohols. Rapeseed fatty acids are still in competition with those of other vegetable oils.

- Today, vegetable oil ethyl esters are high added-value products, used as solvent adjuvants in plant care products and lubricants. They are produced by companies such as Cognis or Novance. Butyl esters have similar properties.

  The technology for the mass production of ethyl esters which could form a “100% plant-based” biofuel is currently being developed. A 10,000-tonne pilot system, using the Valagro process is in place at La Palice.

- Behenic alcohol is produced from high erucic rapeseed using specific technology. It is a cosmetic base, with a developing market.

  The other applications for erucic acid derivatives include erucamide, which has properties as an anti-blocking agent, for forming PVC or polyethylene.

- TMP trioleates (trimethylolpropane), used for high-performance lubrication are made from oleic acid, either from tallow (which remains inexpensive), or of plant origin, in particular rapeseed oil.

Prospects for new fatty acid derivatives

The uses for non-food long-chain fatty acids available in Europe remain for the most part limited to VOME applications in biodiesel. It is therefore strategically necessary to stimulate and develop active research which is able to open up other outlet opportunities for significant quantities. The avenues enabling the development of polymers and therefore biosourced materials are naturally among those to be investigated carefully.

The molecules available as oleic acid are long and monofunctional. However they have a double bond which is easy to break.

![Oleic acid](image)

Various research work is in progress, implementing biotechnological and chemical processes to create new synthetic intermediates from long-chain fatty acids. Certain yeasts can also convert fatty acids into diacids, which can then by polymerised or incorporated into polymers (polyesters, polyamides). Subject to hydrogenation of double bonds, chemicals with properties similar to those of polyethylene can be produced; these however remain biodegradable due to their ester bond every 18 carbon atoms.
Potential new oleic acid derivatives

The cracking of unsaturated fatty acids such as oleic acid enables odd C9 (or C11 for erucic acid) chains to be produced, which chemists are unable to produce other than by metathesis. This opens up avenues for applications of chemicals such as caprylic acids, pelargonic acids, etc.

9-Decenoic acid as a platform chemical

The particular feature of ricinoleic acid is the hydroxyl function on its carbon chain.

Castor bean ricinoleic acid derivatives.

Castor bean oil has many derivatives. We will list here those which are produced or consumed by French groups such as Arkema and Rhodia.
• **Polyamide 11.** Castor oil alcoholysis enables the production of methyl ricinoleate and glycerol. The C19 ester is cracked into heptanoic acid (C7) and a C12 methyl undecylenate. By hydrolysis of this methyl undecylenate, 10-undecylenic acid is produced which is converted by bromination and amination into 11-aminoundecanoic acid HOOC-(CH$_2$)$_{10}$-NH$_2$, the 11 polyamide monomer –[ (CH$_2$)$_{10}$-CO-NH$\_2$]–, marketed by Arkema under the Rilsan® brand. It is also used in an amide block polyether, Pebax®.

• **Sebacic acid.** This is produced by alkali fusion of oil. It has many applications in plastifiers, lubricants, hydraulic fluids, etc. It is a precursor of polyamide 6-10, produced by Rhodia.

![Undecylenic acid](image1) ![Heptanoic acid](image2) ![Sebacic acid](image3)

**II.3.5.7 - GLYCEROL AND DERIVATIVES**

**General information**

Fossil-based glycerol can be produced from propylene via epichlorhydrin.

Plant-based glycerol is a very long-standing coproduct of the manufacture of soaps and fatty acid derivatives.

For a few years now, most of this plant-based glycerol has been produced as a coproduct of the manufacture of biodiesel from rapeseed, sunflower, soybean and palm oil. **The production of 1 t rapeseed methyl ester yields 0.1 t glycerol. 200,000 t of glycerol are associated with the two million tonnes of biodiesel currently produced in France.** By comparison, the production of biodiesel in France in 2003 (357 kt) yielded only 36 kt of glycerol.

**Strictly speaking, glycerol** is the purified chemical from glycerine. When a high level of purity is required, successive distillations are carried out and the price of the finished product increases significantly (it varies by a factor of two between food and pharmaceutical grade - requiring 99.9% purity - and that intended for industrial processing). The possibility of using non-purified glycerol for the production of a derivative is a major factor in cutting cost prices.

**Worldwide glycerol production** was 800 kt in 2003, 100 kt of which was for the production of methyl esters. It is now around 1.8 to 2 million tonnes, with an average annual growth rate of about 50% over the last few years! 3 million tonnes are expected in 2012. With 300,000 t, Sofiprotéol is the leading producer in the world and plays a structural role in what is otherwise a very fragmented sector.

For many years, the **price of glycerol** has the reputation of being particularly difficult to predict. The development of biodiesel and consequently the supply of glycerol has brought down prices structurally but they remain highly volatile and the open market can come under stress very easily. The price of refined glycerol (which has a listed commodity price) was above $2/kg between 1995 and 1997. In 2002, it was below $1/kg. At the end of 2006, it was below $0.7/kg before doubling at the end of 2007, slumping and then picking up again recently.
The diversity of glycerol applications

50 years ago, glycerol already had 1500 known applications. Most of them correspond to small stabilised markets with no major development prospects.

- **Glycerol is used as is** in applications ranging from toothpastes to humectants and from preservatives to anti-freeze. A number of its derivatives have also been used in industry for a very long time.

- **Glycerol esters: traditional derivatives**
  - *Glycerol triacetate* is a well-known derivative, used in the tobacco industry (cigarette filters). It does not have any particular new prospects.
  - *Mono- and diglycerides* are also traditional derivatives, used as emulsifying agents in cosmetics and the food processing industry. The progress of their market depends on emulsifying agent formulation research.
  - Monoglyceride derivatives can be used as tensioactive agents, provided that the hydrophilic properties of the fatty acid are reinforced. Monoglyceride sulphates and ethoxylates have interesting properties. However, such products are generally produced from copra rather than rapeseed oil, in order to have C12 or C14 fatty acid chains.
  - *Nitroglycerin*, which is well-known as an explosive, is glyceryl trinitate, produced by reaction with a combination of nitric and sulphuric acids.

Glycerol as a platform chemical

In the study carried out in 2004 by the American National Renewable Energy Laboratory (NREL) for the US DOE, glycerol was classified among the top 10 potential platform chemicals for future biorefineries. It has since been confirmed in this position by other reference works (cf. § IV.1). Some consider glycerol to be the plant-based equivalent of propylene for petrochemicals.

**One American NREL view of glycerol derivatives in 2004**
Initial diagrams such as the two presented have been produced. Like C3 polyol, glycerol can be chemically or biotechnologically converted into a vast array of interesting chemicals.

The other NREL presentation of glycerol derivatives in 2004

![Diagram of glycerol derivatives]

And a more concentrated one by Sofiprotéol in 2010...

![Diagram of glycerol derivatives by Sofiprotéol]

The list of potential derivatives drawn up in 2004 omits what is now the most advanced project in terms of new, widespread use of glycerol: epichlorohydrin production. Historically, this chemical was considered to be the petrochemical precursor of glycerol rather than as one of its derivatives! This is a very clear illustration of the as-yet timid transition underway from petrochemistry to biomass chemistry.

The number of scientific articles on the new uses of glycerol doubled between 2000 and 2007, when it exceeded 7000. Still more have been written since then. The first specialist book, "The
The main existing or potential derivatives of glycerol as a platform chemical

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Main product</th>
<th>Applications</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reforming</td>
<td>Synthetic gas</td>
<td>Derivatives of a Fischer-Tropsch reaction</td>
<td>Good CO/H₂ ratio to produce methanol.</td>
</tr>
<tr>
<td></td>
<td>CO, H₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dehydration</td>
<td>Acrolein</td>
<td>A large number of polymer derivatives (paints and acrylic resins, textile fibres, ABS resins), detergents, etc.</td>
<td>Work by Arkema on acrylic acid production using acrolein.</td>
</tr>
<tr>
<td></td>
<td>Acrylic acid</td>
<td></td>
<td>Emerging processes for the direct production of acrylic acid and acrylonitrile from glycerol.</td>
</tr>
<tr>
<td></td>
<td>Acrylonitrile</td>
<td></td>
<td>Acrylic acid can also be produced by glucose fermentation (OPX in the USA). Cargill and Novozymes are conducting a project with 3-HPA as an intermediate</td>
</tr>
<tr>
<td>Selective oxidation or fermentation</td>
<td>Glyceric acid</td>
<td>Polymers, etc.</td>
<td>Still at the research stage.</td>
</tr>
<tr>
<td>Hydrogenolysis or fermentation</td>
<td>Propylene glycol, 1,2 propanediol</td>
<td>A food emulsifying agent, solvent and humidiifer. Anti-freeze, coolants, polyester fibres. Major markets.</td>
<td>Productions from glycerol by ADM (100 kt production unit), + projects by Cargill, Virent, Dow, Huntsman ?? Fermentation projects? Met Ex is developing a fermentation process. From glucose or glycerol?</td>
</tr>
<tr>
<td></td>
<td>1,3 propanediol (1,3 PDO)</td>
<td>A polyester component for fibres, films and coverings. Major market.</td>
<td>Met Ex has a process at the pilot stage for the production of 1,3 PDO from glycerol. DuPont / Tate &amp; Lyle produce 1,3 PDO from glucose.</td>
</tr>
<tr>
<td>Carboxylation</td>
<td>Glycerol carbonate</td>
<td>An emollient (cosmetics). Potential for producing polycarbonates.</td>
<td>Two processes have been developed but cost prices remain high. Stakeholders: Novance and Huntsman.</td>
</tr>
<tr>
<td></td>
<td>Glycidol</td>
<td>Polyglycidol, which can be used in epoxy resins or polyurethanes.</td>
<td>Glycidol can be produced from glycerol carbonate or epichlorohydrin.</td>
</tr>
<tr>
<td>Esterification, transesterification</td>
<td>Polyglycerols and their esters</td>
<td>Emulsifying agents for cosmetics and the food processing industry.</td>
<td>Many other potential applications: new polymers.</td>
</tr>
<tr>
<td>Etherification</td>
<td>Tert-butyl ether</td>
<td>Fuel additives competing with MTBE and ETBE.</td>
<td>No industrial development as yet.</td>
</tr>
<tr>
<td>Chlorination</td>
<td>Epichlorohydrid</td>
<td>Epoxy resins, etc.</td>
<td>Solvay 10,000 t production plant operational in France. Construction of a 100 kt plant in Thailand.</td>
</tr>
</tbody>
</table>
The table above shows that many transformations can be carried out by chemical synthesis and that biotechnological processes are operational or under development for a number of major derivatives (acrylic acid, Propylene glycol, 1,3 propanediol). Depending on developments, glycerol or sugars may be the raw materials for the same chemical intermediaries, resulting in increasing decompartmentalisation between plant production chains as regards the applications of their derivatives in the chemicals industry.

**Epichlorohydrin**

As stated, this application was not included in the NREL-US DOE study in 2004.

Epichlorohydrin production from glycerol can be summed up simply by the following reaction (*in fact, the process involves two successive reactions with dichloropropanol as an intermediate*). Approximately 1 t of glycerol is required to produce 1 t of epichlorohydrin.

\[
\text{HO-\(\text{O}-\text{OH} + \text{HCl} \rightarrow \text{CH}_2\text{Cl}\) + 2 H}_2\text{O}
\]

The annual demand for epichlorohydrin was 1250 kt in 2009, over half of which was in Asia (690 kt with an average growth of almost 6.7%/year) with a further quarter in Europe (300 kt with only 2.1% annual growth).

Epichlorohydrin has applications in the following areas:

- Epoxy resins (75-80% of uses) for rigid parts (cars, boat hulls, wind turbine parts, etc.), paints and adhesives.
- Paper reinforcement for the production of wet wipes.
- Flocculating agents.
- Other resins.

Epichlorohydrin is produced all over the world from propylene, vapocrackers and chlorine. Industrial users may have integrated production or purchase the product on the “free” market (around 700,000 t) from producers such as the Belgian group, Solvay, which has operators in different continents. The price of propylene quadrupled between 1999 and 2010, with a very short market and problems with local availability from 2005-2006 onwards, making it appropriate to seek alternatives.

**Recent relative changes in propylene and glycerol prices**

![Graph showing recent relative changes in propylene and glycerol prices]

Source: Solvay
Epichlorohydrin production from glycerol was developed by Solvay (Epicerol® process) with initial pilot trials in 2004-2006 in France, at its Tavaux site in the Jura (the project was backed by Agrice and the French Ministry of Industry). A glycerol conversion process has existed since 1931, which is described in the literature but inapplicable for industrial purposes. Development work was necessary and was formalised by the filing of 38 patents, many of which have already been granted in several countries in different parts of the world. A 10,000 t production plant has been built and has been up and running since 2007. It is on the site same as that consuming propylene.

The Epicerol® process enables not only the use of a biosourced raw material but also significant reduction of the environmental impact of epichlorohydrin production (water consumption divided by ten and chlorine and non-renewable energy consumption halved, the volume of chloride coproducts reduced by a factor of eight, 20% reduction in CO₂ emissions and 50% reduction in the consumption of non-renewable raw materials).

Solvay has undertaken the construction of another 100,000-tonne plant for the production of epichlorohydrin from glycerol at its Map Ta Phut site in Thailand, to serve the burgeoning regional markets.

**Acrylic acid**

Acrylic acid is usually produced from propylene. It has a large number of derivatives in paints, varnishes, thermoplastics and elastomers.

World demand for acrylic acid is 1.1 - 1.2 million tonnes, with prices having fluctuated in recent years between $1.1 and $2.5/kg at its highest levels.

The French chemical company Arkema is working on the pilot stage for the production of acrylic acid from glycerol, with acrolein as the synthetic intermediate. Arkema carries out this work on its Carling site in Moselle and works together with two laboratories in the region, which helps to fund this work.

Patents have been filed for various acrylic acid, acrolein and acrylonitrile production processes from glycerol. Recent progress in catalysis has provided improved yields and possibilities for working on different concentrations of glycerol solutions, without cosolvents and good regeneration of catalysts.

It should be noted that certain companies are working on the direct production of acrylic acid by fermentation from glucose. This is the case of the start-up OPX in the USA. Cargill and Novozymes are conducting a project in which 3-HPA will be an intermediate in the production of acrylic acid.

**Monopropylene glycol (MPG) or 1,2 propanediol**

This chemical has a very large number of applications in food processing and toiletries, anti-freeze liquids and defrosting products, and also as a component of unsaturated polyester resins.

MPG is usually produced from propylene oxide. Its worldwide market can be estimated at 1.8 mt. The price of the product has ranged between €800 and €1250/t over the last few years.

The toxicity of ethylene glycol (with a market of some 18 million tonnes!) and its derivatives favours the development of applications of propylene glycol.

The largest production of de propylene glycol from glycerol is that of Archer Daniel Midlands (ADM), in Decatur, Illinois, with a 100,000-tonne plant. It is not yet clear whether sorbitol could also be used as a raw material. Several other production projects were announced in 2007 (Dow, Huntsman, Cargill, Synergy) but these seem to have been delayed or cancelled.
There are projects for the production of MPG by fermentation, but from sugar. This is the case for Metabolic Explorer in France.

Glycerol carbonate $\text{C}_4\text{H}_6\text{O}_4$ has applications in solvents and potentially in polymers. It is a chemical which can be derived from petrochemicals (the North-American chemicals company Huntsman produces it) or from plant-based glycerol.

The ability of glycerol carbonate to be polymerised opens up prospects for it in competition with polyacrylates.

Two industrial processes enable glycerol to be converted into glycerol carbonate: that of Novance and Huntsman.

Novance has developed a continuous process which enables glycerol carbonate to be produced with a 90% yield from raw glycerine with the following reaction: 
\[\text{glycerol} + \text{urea} \rightarrow \text{glycerol carbonate} + \text{ammonia}.\]

The management of ammonia emissions increases implementation costs.

Glycerol carbonate can also be a precursor of glycidol and polyglycidol, which can be used in epoxy resins and polyurethanes. Glycidol is traditionally synthesised from epichlorohydrin.

In 2005, glycerol carbonate was presented as a potential platform chemical but, 5 years on, its production costs are still too high and the product has not been developed significantly.

**Polyglycerols and polyglycerol esters.** Polyglycerols are produced by oligomerisation in alkaline conditions. Their esterification with different fatty acids enables large families of products to be produced.

These compounds already have applications as emulsifying agents in cosmetics and in the food processing industry. They can be positioned as tensioactive agents and biodegradable lubricants, which may be able to replace polyoxyethylene at least partially. Applications can be expected in oil drilling and the decontamination of polluted soils.

Polyglycerols and polyglycerol methacrylates have interesting potential as wood treatment agents designed to keep its humidity level between 15 and 20%. For this application, they are in competition with polyethylene glycols. The performance of wood treated in this way makes it a rival for PVC.

**1,3 propanediol** (also known as 1,3 PDO), is a petrochemically produced chemical which can also be produced by glucose or glycerol fermentation. There is a specific paragraph about this chemical in III.3.

At the present time there is no industrial production of 1,3 PDO from glycerol. In France, Metabolic Explorer has developed a process which is still at the pilot stage.

**Polyurethanes.** These materials, which form a very diverse family, are produced from a polyol and a di-isocyanate. The presence of various gases enables their expansion. Novance has developed a process in which the expansion agent is water. The polyol used is glycerol-based, in which a –OH remains free, which makes it very hydrophilic.
Conclusions: glycerol

- Glycerol is indeed a platform chemical. With its three carbon atoms and three alcohol functions, it has a large number of potential derivatives.

- The glycerol offer has increased significantly and is continuing to grow. In our context it remains completely dependent on national policies with regard to support for VOME-type biodiesel production.

- There are currently two innovative projects using over a hundred thousand tonnes of glycerol for one application on one site: the Solvay project to produce epichlorohydrine and that of ADM to manufacture monopropylene glycol. Several projects similar to this one seem to have been cancelled or postponed.

- Glycerol derivatives are now produced mainly by chemical conversion, with regular progress being made as regards catalysis.

- To date, biotechnologies have not opened up tangible new avenues for glycerol.

- Glycerol carbonate has interesting properties but its production cost remains too high for mass uses to be developed.

II.3.6 – FRENCH PRODUCTION CHAIN: STRENGTHS, WEAKNESSES AND PROSPECTS

These can be summed up as follows:

<table>
<thead>
<tr>
<th>Strengths</th>
<th>Weaknesses</th>
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<tbody>
<tr>
<td>- The French production chain is highly organised and pro-active, emanating directly from farmers and with significant industrial plants.</td>
<td>- A chain with a virtual monopoly in France, with a lack of emulation on the part of competitors. Limited international dimension (Europe).</td>
</tr>
<tr>
<td>- The production chain’s environmental progress procedure.</td>
<td>- Biodiesel is not yet of 100% biomass origin (VOME methanol is produced from fossil resources).</td>
</tr>
<tr>
<td>- A good balance between the biorefinery outlets in the chain (food, animal feed, biofuels).</td>
<td>- EU oilseed production chains may not produce short-chain fatty acids (except for GMOs).</td>
</tr>
<tr>
<td>- Significant production of biodiesel enabling the development of VOMEs as a platform for chemicals.</td>
<td>- As yet, little use of the potential of white biotechnology in the sector.</td>
</tr>
<tr>
<td>- Active research into the uses of glycerol, the supply of which has increased significantly.</td>
<td>- Certain projects are taking a long time to reach the industrial stage (glycerol carbonate).</td>
</tr>
<tr>
<td>- Potential for development of odd-numbered fatty acid chain chemistry.</td>
<td>- There is as yet little cooperation on major projects between the food processing chain and the major chemicals companies in France.</td>
</tr>
</tbody>
</table>
A major asset of the French production chain is the quality of its organisation. France occupies a solid position in the production of long-chain fatty acid vegetable oils. The development of biodiesel has enabled an increase in the supply of glycerol and innovative applications.

II.3.7 – RECOMMENDATIONS

- **Strengthen biodiesel production** by providing stakeholders with visibility whilst encouraging them to increase their performance even further not only by improving the environmental performance of the production chain, but also by increasing their ability to drive and expand a modern oilseed chemistry sector in France and the EU.

- **C18 and C22 fatty acid chemistry, as well as that of their C9 and C11 derivatives must be developed by France’s public and industrial research teams.** A few promising projects, which highlight excellence in France and the EU, must be selected and given thorough support.

- **It is necessary to pursue the development of glycerol derivatives whilst concentrating efforts in this area** on a few projects capable of significant use by France’s national industry. The selection must be carried out with care, as glycerol has so many potential derivatives. The risk of developing technology in France and it being used subsequently in regions with a higher rate of growth must be taken into account. The interests of our national farming sector as well as those of our chemicals industries with operations in different continents must be taken into account. The case of **acrylic acid** deserves closer examination, since **Arkema** has large production sites in France.

- It would be appropriate to develop a project in France like the “Oilseed chemistry biohub” project (for fatty acid and glycerol chemistry), with ambitions and support of similar levels. This would involve drawing together the oilseed production chain, chemicals companies, SMEs and public research laboratories.
II.4. - LIGNOCELLULOSIC PRODUCTION CHAINS

Whilst the production chains above use reserve substances accumulated by plants in their seeds, roots or tubers, the so-called “lignocellulosic” chains are those which use plant walls which have a high cellulose, hemicellulose and lignin content. There is a very wide diversity of resources available, their nature and properties, if wood, agricultural straw and dedicated crops are taken into account as well as various types of plant waste.

II.4.1 - BOTANICAL SPECIES, ORIGINS AND VARIETIES GROWN

There is a very long list of species which supply or could supply such production chains. These include forest trees used traditionally by the pulp industry, textile crops (the fibres of which have traditional and more innovative uses) and lastly perennial or annual crops developed for the production of fuel biomass or second-generation biofuels.

FARMED TREES

Paper comes from the transformation of wood fibres. Softwood species have long fibres whereas hardwood species have short fibres. Pulp is the raw material used for paper. The major forest species used to manufacture paper include both softwood (pine, fir, spruce) and hardwood (eucalyptus, poplar, birch, aspen and various other species). The French paper industry consumes small size wood, formed trees being reserved for producing timber. It is also supplied by sawmill coproducts and recycled paper and cardboard.

Pine *Pinus sp.* Many pine species are used to produce cellulose pulp in temperate and tropical regions worldwide, with interesting coproducts (terpenes, tall oil). The example of maritime pine (*Pinus pinaster*) in France is interesting because it is the species found in the vast forests in the Landes (1 million hectares). Maritime pine was found naturally only on the coast. It has been grown in many other places since the nineteenth century. It is a monoecious and allogamous species with anemophilous pollination. Improved synthetic varieties have been developed by the INRA and are bred in seed orchards. The resulting improved woodlands cover approximately 10% of the Landes forest.

Eucalyptus. This genus, which originated in Australia and New Guinea, belongs to the Myrtaceae family which includes over 550 species. It is the most common hardwood species in the world. Eucalyptuses are preferentially allogamous, with hermaphrodite flowers displaying a marked protandry. Their pollination is entomophilous. The modern varieties are clones, which are bred by means of cuttings.

Poplars, *Populus sp.*, are trees which are grown for their rapid production of wood. Poplars are dioecious (each tree is male or female), with anemophilous pollination. Selected varieties are bred using cuttings. The poplar plantations, established for 15 - 25 years, are used to produce plywood, packaging, pallets, etc. or for oil extraction. Poplar is also suitable for high density crops (short rotation coppicing).
Although transgenesis on poplars has been mastered for a long time and clones with a low lignin content have been developed, commercial crops are not yet envisaged.

**Willow**, *Salix sp.*, are dioicous shrubs which are suitable for short or very short rotation coppicing (2-4 years).

**FARMED SPECIES**

**Wheat and other cereals** (maize, barley, oats, rye, etc.) can supply the lignocellulosic production chains with their straw, as well as the entire plant in the case of downgrading and certain coproducts with high fibre contents.

**Triticale**, *Triticosecale* is a farmed crop obtained by crossing wheat and rye. Active breeding began in the 1980s. Triticale, with its large volumes of straw, was originally developed as a cereal for animal feed as it has the characteristics of the productivity of wheat, the rustic nature of rye. It offers broader prospects for producing biomass for energy and other purposes. Like wheat, triticale is mainly autogamous and reproduces by self-fertilisation (the other member of its family, rye, is strictly allogamous).

The breeding of triticale is active, with almost one hundred varieties listed in the French catalogue (the seed manufacturers are Florimond Desprez, RAGT, Lemaire Desfontaines, etc).

**Linseed**, *Linum usitatissimum*, is a C3 plant in the Linaceae family, which has been grown by mankind since ancient times, having been domesticated in the Middle East. Linseed is an autogamous annual. Spring varieties dominate in Europe although winter forms also exist. Linseed is grown for the sclerenchyma fibre in its stems (textile linen) as well as for its oilseeds, the oil of which is high in linolenic acid (C18:3) as well as linoleic (C18:2) and oleic (C18:0) acid. High linoleic acid linseed varieties have been developed (called “Linola”).

Linseed is a species which is grown mainly in north-western France. The area cultivated in 2009 was less than 56,500 ha, compared with elsewhere in Europe: 11,500 ha in Belgium, 2100 ha in the Netherlands and a total of 1500 ha in Poland, the Baltic States and the Czech Republic. 85% of French production is purchased by China where the fibre is processed and resold on different markets, which are currently experiencing crisis. The price of scutched flax has dropped from €121 at the end of 2009 to €110/ql in September. To avoid unsold production, the profession wanted to limit crop areas in 2010 which nonetheless came to 50,000-53,000 ha in France (compared to the 2004-2005 campaign during which 81,500 ha were harvested).

**Hemp**, *Cannabis sativa* is dioecious (with separate male and female plants), with a C4 photosynthetic metabolism ensuring its very rapid growth. Hemp is another plant which was domesticated in ancient times in Central Asia, used both for the sclerenchyma fibre in its stems and the oil contained in its seeds.

12,000 hectares of hemp were grown in France in 2009, with the fibre being used increasingly in building materials. Due to the crisis in the construction sector, only 8000 hectares were sown in 2010. 7 varieties of hemp are bred in France.

**Cotton**, *Gossypium sp.* is a plant in the Malvaceae family with preferentially autogamous hermaphrodite flowers. Four species are grown: *G. arboreum* and *G. herbaceum* are the diploid species from the old word with short fibres; *G. hirsutum* and *G. barbadense* are allotetraploid species from the New World with long fibres. *G. hirsutum* largely dominates world production. Cottons are grown for their seed testa fibres. The less developed fibres of the down, formed by the epidermal hairs of the seed, are called linters and used to produce cotton wool, special papers and cellulose derivatives.
New crops dedicated to the production of lignocellulosic biomass:
These species are developed mainly for the production of fuel biomass or as a raw material for future second generation biofuels. Some of them are perennials and established for ten to fifteen years, with a quantity of harvestable biomass which increases gradually during the first few years. Others are annuals.

**Miscanthus, Miscanthus giganteus,** is a perennial graminaceous plant from Asia with a C4 photosynthetic metabolism. It is multiplied and planted in the form of rhizomes. Miscanthus reaches full production capacity after 2 - 3 years and has a lifespan of 15 years.

“**Switchgrass**, Panicum virgatum,” is another perennial C4 graminaceous plant which originated in North America. It is bred in the form of small seeds which are difficult to sow and reaches its maximum production after 3 years; it can be established for 10 years.

**Provence cane (Arundo donax)** is a fast-growing graminaceous plant, grown traditionally in southern France for the production of reeds for wind instruments (vibrating strips) and also to be planted as a windbreak. Provence cane forms large rhizomes which are used to multiply and transplant it. Its full biomass production capacity is reached after 2 - 3 years with a 15-year lifespan.

**Sorghum, Sorghum bicolor** is a diploid annual graminaceous plant with preferentially autogamous bisexual flowers. It is native to Africa and is grown in many different regions of the world, usually as a food cereal. It is a productive plant (with a C4 photosynthetic metabolism) but also hardy and requiring little water. 35,000 - 55,000 ha of grain sorghum are grown in France, where there is also active variety breeding. Certain sorghums have high plant development (“fibre” sorghum = paper sorghum) and they are used for the production of lignocellulosic biomass.

65 million tonnes of sorghum grain were produced worldwide in 2008, 517,000 t in Europe (source: FAO). French statistics state production of 322,000 t in France (58,000 ha, with a yield of 57.6 qs/ha) whereas the FAO states production of only 231,000 t for France on 37,000 ha!
II.4.2 – CROP COMPOSITION

II.4.2.1 - GENERAL INFORMATION

The composition of "lignocellulosic" biomass varies greatly according to species, age and nature of the organs harvested. The data available is heterogeneous, and the harvesting methods and analysis techniques are not always mentioned in the many references put forward.

The table presented below can therefore by used for informational purposes only; Apart from cotton linters, which are composed of almost pure cellulose, the raw materials usually available also have high proportions of hemicelluloses and lignin, which constitute excellent grounds for seeking to use these families of substances.

Typical mass composition of various lignocellulosic materials (% dry goods)

<table>
<thead>
<tr>
<th></th>
<th>Cellulose</th>
<th>Hemicelluloses</th>
<th>Lignin</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignocellulosic biomass</td>
<td>25-65</td>
<td>8-40</td>
<td>11-35</td>
<td></td>
</tr>
<tr>
<td>Softwood (Pine)</td>
<td>38-42 (45)</td>
<td>(7-15) 20-24</td>
<td>27-29 (34)</td>
<td></td>
</tr>
<tr>
<td>Hardwood (Poplar, etc.)</td>
<td>(38) 40-49 (50)</td>
<td>16-27</td>
<td>20-24 (30)</td>
<td></td>
</tr>
<tr>
<td>Wheat straw</td>
<td>30-43 (49-54)</td>
<td>22-35</td>
<td>15-23</td>
<td>4-9</td>
</tr>
<tr>
<td>Corn stalks</td>
<td>35-41</td>
<td>20-27</td>
<td>12-17</td>
<td></td>
</tr>
<tr>
<td>Bagasse</td>
<td>38-40 (44)</td>
<td>23-34</td>
<td>11-25</td>
<td>1.5-5</td>
</tr>
<tr>
<td>Cotton linters</td>
<td>80-85</td>
<td>1-3</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

REGIX programme median data (rounded up, excluding extreme data):

<table>
<thead>
<tr>
<th></th>
<th>Cellulose</th>
<th>Hemicelluloses</th>
<th>Lignin</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Immature whole plant cereals¹</td>
<td>23-32</td>
<td>15-21</td>
<td>8-11</td>
<td>5-6.5</td>
</tr>
<tr>
<td>Mature whole plant cereals</td>
<td>24-35</td>
<td>17-20</td>
<td>9-14</td>
<td>5-6.5</td>
</tr>
<tr>
<td>Perennials harvested green²</td>
<td>35-40</td>
<td>19-23</td>
<td>14-18</td>
<td>3.5-5</td>
</tr>
<tr>
<td>Perennials harvested dry²</td>
<td>35-50</td>
<td>23-25</td>
<td>17-21</td>
<td>2-3</td>
</tr>
<tr>
<td>Softwood chips³</td>
<td>36-41</td>
<td>19-22</td>
<td>27-28</td>
<td>0.8-2.1</td>
</tr>
<tr>
<td>Hardwood chips⁴</td>
<td>44-51</td>
<td>17-23</td>
<td>22-26</td>
<td>1.2-5</td>
</tr>
<tr>
<td>SRC⁵</td>
<td>52-63</td>
<td>13-19</td>
<td>18-22</td>
<td>1.6-2.4</td>
</tr>
<tr>
<td>VSRC⁶</td>
<td>48-54</td>
<td>15-17</td>
<td>18-21</td>
<td>1.4-4.4</td>
</tr>
</tbody>
</table>

1: maize, sugar, fibre and forage sorghums  2: Miscanthus, Switchgrass and Provence cane; 3: pine, spruce, fir; 4: hornbeam, oak, beech, poplar, linden; 5: Willow, eucalyptus, poplar, robinia short-rotation coppices (< 5 years); 6: Very short rotation coppices

Source: various including REGIX

The progress in France enabled by the REGIX programme

In many countries, major programmes for the use of lignocellulosic biomass have been initiated without any tangible homogenous data being really available (at least locally) about the agronomic potential, the composition of harvests and the considerations for the mobilisation of the different categories of raw materials under consideration.

The aim of the four-year REGIX programme was to begin to remedy this lack. It brought together partners from farming sectors (Arvalis Onidol) and forestry sectors (FCBA, ONF, Union de la Coopération Forestière Française) which had never had the opportunity to work together. The project was backed by the ADEME and ANR. An experimental network was formed nationwide in France in which the different crops were established, grown, harvested and analysed. Assessments of the constraints and overall cost of mobilisation have been carried out.
II.4.2.2 – THE MAIN COMPONENTS OF LIGNOCELLULOSIC BIOMASS

**Cellulose** is a glucose polymer with beta linkages (1-4). It is different from starch which has $\alpha$-(1-4) and $\alpha$-(1-6) linkages. Basic cellulose chains are connected together by hydrogenous bonds, thus forming microfibrils which are organised into sets, including a crystalline part and an amorphous part.

![Cellulose structure](image)

**Hemicelluloses** are a fairly large family of amorphous polymers with C5 monosaccharides (xylose, arabinose) and C6 monosaccharides (mannose, galactose, glucose) in the form of homo- or heteropolymers. The exact composition depends on the different plant species.

![Hemicellulose structures](image)

**Lignins** are reticulated amorphous polymers with a high molecular weight. They are composed mainly of phenyl propane type C9 units: coumaryl, coniferyl and sinapyl alcohols which in turn are assembled into different sub-units. Lignins are the only major components of plant biomass composed of aromatic molecules.

![Lignin structures](image)
In addition to these three basic components, wood also includes the following:

- tannins and coloured substances (in usable concentrations mainly in hardwood trees, such as oak and chestnut and in various species of exotic trees such as the Quebracho and certain true acacias),
- terpene compounds,
- proteins which remain in small quantities only in dead tissue.
- minor components (alkaloids, aldehydes, etc.).

Cereal straw and the vegetative parts of perennial graminaceous plants are also high in ash (2 - 7%) and may contain non-negligible quantities of chlorine and sulphur depending on the fertilisers and pesticides used on the crop. Cereal straws contain large quantities of potassium, the export of which must be offset by appropriate fertilisation.

The cereals for which the whole plant is harvested naturally contain large quantities of starch (4 - 29% in the REGIX experiments) and decreasing quantities of soluble sugars, as may be expected, with the stage of the harvest (from 9 - 16% to 2 – 8%). The protein content is around 6%.

The composition of the different lignocellulosic resources predisposes them or not to certain processes. Full-plant annual crops are more suited to the production of cellulosic ethanol, whilst perennial crops such as Miscanthus and switchgrass, whose composition is closer to that of wood, would be good candidates for BtL (Biomass to liquid) processes. Forage crops studied by REGIX have intermediate properties.
II.4.3 – SIGNIFICANCE OF THE RESOURCE AND HARVESTS

Forests - wood
Forests are highly heterogeneous because they include both monospecific eucalyptus or pine as well as unused or little-used ecosystems.

World forest surface areas cover 3.9 billion hectares including 830 million in South America, 810 million in ex-USSR countries, 780-734 million in Asia Pacific, 700 million in North America, 635 million in Africa and 192 million in Europe.

Forests in the EU
Forests in the 27-state EU cover 155 million hectares, unequally divided between the countries. France has the 4th largest surface area of forest in the EU, but is the 3rd largest behind Sweden and Germany for volumes of standing timber (expressed below in millions of cubic metres over bark).

<table>
<thead>
<tr>
<th>Country</th>
<th>Forest surface area (mha)</th>
<th>% surface area of the country</th>
<th>m³ over bark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweden</td>
<td>27.5</td>
<td>67</td>
<td>3155</td>
</tr>
<tr>
<td>Finland</td>
<td>22.5</td>
<td>74</td>
<td>2158</td>
</tr>
<tr>
<td>Spain</td>
<td>17.9</td>
<td>36</td>
<td>888</td>
</tr>
<tr>
<td>France</td>
<td>15.5</td>
<td>28</td>
<td>2465</td>
</tr>
<tr>
<td>Germany</td>
<td>11.1</td>
<td>32</td>
<td>2880</td>
</tr>
<tr>
<td>Italy</td>
<td>10.0</td>
<td>34</td>
<td>1447</td>
</tr>
<tr>
<td>Poland</td>
<td>9.2</td>
<td>30</td>
<td>1864</td>
</tr>
<tr>
<td>EU-27</td>
<td><strong>155.0</strong></td>
<td><strong>37</strong></td>
<td><strong>22580</strong></td>
</tr>
</tbody>
</table>

Forests in France cover 15 million hectares (woods and forests of over 0.5 hectares) to which 2 million hectares of non-forest woodlands can be added.

For the purposes of comparison, our crop surfaces occupy a total of 19 mha - 9.4 mha of which is for cereals (grain) and 2.2 mha for oilseed; built-up, covered and artificial surfaces cover 4.8 mha (growing regularly).

Three-quarters of forest areas in France are private and are subject to extremely variable intensities of use. The biological production of forests in France is 102 million m$^3$ of timber per year, 56 million m$^3$ of this is hardwood and 45 million m$^3$ is softwood. Average production per hectare per year is 19.7 m$^3$ for Douglas pine (7.5 t dry wood), 15.1 m$^3$ for fir or spruce (5 t), 11.8 m$^3$ for maritime pine (3.8 t) and 5.6 m$^3$ for oak (2.75 t).

Standing trees and sawlogs are evaluated for their volume of wood, over or under bark, whereas biomass is counted in tonnes and energy biomass in toes (tonnes of oil equivalent). Despite the existence of average conversion coefficients, it is not always easy to establish correspondences, as humidity levels vary considerably between standing timber and during storage before transformation.

Location of wooded areas in France

[Map of wooded areas in France]

Source: FCBA memo from IFN data.

Wood resources in France for second-generation biorefineries

A large proportion of the forest resources are at present unused. These include woods and forests which are not managed as well as forest slash (branches, tops, stumps, etc.) left on sites which are already managed. Certain first small-size cuts are sometimes not carried out and constitute non-negligible unused volumes. Several limits and constraints on the use of this entire potential must be taken into account:
• Many private forest owners remain reticent about use of their woods or forests, which they consider to be of a decorative nature or as part heritage. No forest policy in France has ever been determined enough to dare to penalise people for leaving their woodland uncared for. A major part of French forest resources remains unused in the long term.

• The mobilisation of new wood resources has proved to be difficult in practice. There is a lack of operators and access roads. The “easiest” thing to do is to collect slash in forests which are already managed.

Work by the CEMAGREF has enabled the quantities of slash which may be exported sustainably from forests without degrading soil fertility to be assessed. The situations are very variable. On certain sensitive soils, exporting slash must be avoided or its harvesting must be offset by adding mineral fertilisers. On the other hand, for soils which are not very sensitive, slash may be harvested twice during the life of softwood populations (during thinning and felling) without major restrictions in hardwood copses. It should be noted that the resource which can be mobilised sustainably is much smaller than that which is theoretically available. Best practice may be of major importance in limiting mineral exports (leaving slash to dry on site and thus returning leaves and needles to the ground).

According to experts, the resource available in France to produce forest chips is 10 million m$^3$, which is a considerable volume but nonetheless well below the previous estimate of 30 million m$^3$ in the study carried out by ADEME-SOLAGRO.

• There is increasing competition for their use. Various programmes have been implemented by ADEME and the public authorities over the past few years to promote wood-fired heating and cogeneration of heat and electricity from biomass (wood-energy schemes, CRE, Heat Fund, BCIA). Several have been very successful but the failure of certain major projects has shown that a mobilisation project on paper may prove to be difficult to implement. On a regional or national level, there is often insufficient consultation between stakeholders, and the different users of the resource are in fierce competition for it.

The change in use of sawmill coproducts may be given as an example. These include bark, sawdust, woodchips and various offcuts, which are often crushed into “sawmill chips”. Until about fifteen years ago, many sawmills were burdened with what was considered to be costly waste. Wood pulping industries developed their sawdust consumption to make chipboard and sawmill chip consumption for the production of pulp. Sawdust or chip truckloads – purchased cheaply – could be shipped from Brittany down to the Gascony heathlands, a region where the apparently plentiful resource is always limited given the local density of industries using it. The development of the drying of sawings from burning coproducts in sawmills and the rise of the fuel wood pellet production chain have led to a high level of competition for the use of most of these coproducts, considerably raising their price for all industries using them. The development of wood flour uses in composite materials will only increase the tension on prices. The use of the entire resource has not been the subject of a national consultation. The figures below show that there are already tensions, even before development of any new use.
Each year, softwood sawmills in France produce 5.3 mt of coproducts, or 1.6 mt of sawdust + 3.7 mt of wet sawdust chips. Hardwood sawmills produce around 1.1 mt of coproducts.

The total available subsequently is 6.4 mt.

In 2007 the French wood pulping industry consumed 6.6 mt of coproducts. France already had a deficit if the development of wood pellets is taken into account.

The tonnages of wood pellets are growing rapidly and in 2010 should consume 1 mt of wet wood.

In the meantime, the French wood pulping industry has reduced its activity due to the crisis. Its consumption is currently recovering. The tension on markets is therefore very significant and will remain unless a large wood pulping plant closes. The different players will therefore have to increase their use of logs from thinning. There is no resource available for new uses.

- The range of qualities of forest products which may be used in second-generation processes will depend on the processes used (thermochemical or biochemical). A raw material including needles, leaves, bark, or soil residues, cannot be treated in the same way as properly harvested straw or wood scraps.

Short rotation (SRC) and very short rotation coppicing (VSRC)

A non-irrigated willow VSRC is harvested once every 3 years, with (at the best) a yield of 36 t dm/ha (i.e. 12 t/dm/year). It will be left in place for a maximum of 24 years (8 3-year rotations). An irrigated SSRC can be harvested once every 2 years and produce up to 38 t of dm/ha (i.e. 19 t dm/ha/year).

“New” energy crops now represent very small areas and the interest of procedures such as that of the REGIX programme is to define their suitability and potential yields in the different climate and soil conditions in France.

<table>
<thead>
<tr>
<th>Yield</th>
<th>Median biological</th>
<th>Harvestable</th>
<th>Median biological</th>
<th>Harvestable</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Miscanthus</td>
<td>15.4</td>
<td>12</td>
<td>20 t from autumn harvests, 15 t from winter harvests</td>
<td>Loss of dry goods during drying out on the stalk but gains during drying</td>
</tr>
<tr>
<td>Switchgrass</td>
<td>13.2</td>
<td>10.5</td>
<td>18 t from autumn harvests, 14 t from winter harvests</td>
<td>Loss of dry goods during drying out on the stalk but gains during drying</td>
</tr>
<tr>
<td>H133 fibre sorghum</td>
<td>14.4</td>
<td>12.5</td>
<td>19 t</td>
<td>Best performance in southern France</td>
</tr>
<tr>
<td>Provence cane</td>
<td>13.9</td>
<td>11.1</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Full plant triticale</td>
<td>12.9</td>
<td>10.3</td>
<td>16-18</td>
<td>Best performance in northern France</td>
</tr>
</tbody>
</table>
Cereal straw

In France, cereal crops produce between 8 tonnes (barley) and 12 tonnes (triticale) of dry matter per hectare (10 t for wheat), half of which can be harvested. The yield of straws exportable from the plot is therefore 5 tonnes of dry matter for wheat. The humidity level is usually between 12 and 15%.

For the REGIX programme, the GIE Arvalis-Onidol assessed the straw resources which can be mobilised for new uses taking into account the needs for livestock farming as well as the necessary return of organic matter to the soils, to maintain suitable fertility and humus levels. The theoretical resource is over 28.5 million tonnes, but the part which can be mobilised does not exceed 3.3 million tonnes. It must supply the second-generation biofuel production chains as well as the heat production chains using straw-based materials, which are still limited but promising.
II.4.4 – DESCRIPTION OF LIGNO-CELLULOSIC PRODUCTION CHAINS

II.4.4.1 - GENERAL INFORMATION ABOUT PULP MANUFACTURE

There are two basic technologies for preparing paper fibres from wood:

- **Mechanical pulp manufacture** is carried out by pressing balls of debarked wood onto an abrasive surface (defibrators), using a rotational movement, or by crushing wood chips between two rotating grooved steel plates or between a stationary plate and a rotating plate (refiner). These types of pulp are called groundwood (GW) and refiner mechanical pulp (RMP) respectively. Mechanical pulps are used for the manufacture of products requiring little strength, such as newspaper, toilet paper, etc. In these pulps, the lignin is not removed (which explains why the papers in question turn yellow when exposed to light). Few coproducts are generated during pulp manufacture.

- **The purpose of chemical pulp** is to separate the cellulose fibres from the lignin by means of chemical agents, during cooking in boilers (digesters) using reagents and steam. The action of the heat and chemical products enables long wood fibres to be released without breaking them.

The main processes for the preparation of chemical pulps are the *alkaline kraft process using sulphate* and the *bisulphite process*.

Chemical pulps are used for the manufacture of products which call for a degree of strength, such as printing and writing papers, fine papers, wrapping papers, cardboards and special papers. They are also used to increase the resistance of certain products such as specialist papers.
The purpose of chemical pulp manufacturing technology is to isolate the cellulose. Most of the other components of wood are therefore to be found in its coproducts. Some can be used for specific applications but most are burned to generate the energy necessary to operate the plant.

Paper plants produce energy to supply the heating systems necessary for their processes as well as to drive electrical turbines. The basis of this energy is the combustion of wood coproducts, which cannot be used to produce pulp (bark, etc.) as well as coproducts with a high organic compound content (black liquors).

There is growing competition between the two functions: that of pulp production and that of energy production. Energy production is steadily gaining value, whereas that of pulp undergoes strong cyclical variations.

Paper co-products contain compounds which may be extracted directly from wood. The choice of source as “wood” or “paper coproduct” is mainly, but not exclusively, economic in nature. Coproducts, which are generally cheaper, may be contaminated by reagents used during the process.

**The Kraft process**

The Kraft process dominates the manufacture of chemical pulp. It consists of conducting controlled hot alkaline hydrolysis of the bonds between the cellulose and the other wood components (mainly hemicelluloses).

Wood shavings are pre-steamed at 70 °C. The volatile compounds are recovered at this stage (essence of turpentine). The wood is then placed in contact with white liquor containing caustic soda (NaOH) and sodium sulfide (Na₂S). Soda has a hydrolytic function. Sodium sulfide protects cellulose from oxidation due to its reductive properties and its specific delignification action by forming thiolignins from the lignin.

Cooking in the “digester” (at 160 °C, for 6 - 8 hours) enables a solid fraction to be separated, with a high concentration of cellulose, from the black liquor which contains mainly various lignin derivatives in the form of sulphurs and other compounds. The tall oil, which is high in fatty acids, resin acids and sterols is extracted by decantation of the black liquor. The black liquor residue is dried and burned. This operation enables not only the production of energy but also recycling of the vast majority of reagents. After combustion at 1200 °C, a green liquor composed of Na₂CO₃ and Na₂S is obtained. The soda is regenerated by adding lime:

\[
\text{Na}_2\text{CO}_3 + \text{CaO} + \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + \text{2 NaOH}
\]

The calcium carbonate precipitated is sent into a kiln to regenerate the lime.

Kraft paper retains a non-negligible proportion of lignin and also contains hemicelluloses.

The kraft process largely dominates the sector as it enables the production of high quality pulp for final products with high mechanical strength. It is energy-autonomous and enables excellent recycling of reagents.

A variant of the Kraft process (Prehydrolysis Kraft = PHK) entails prehydrolysis of the material by steaming at a high temperature. This allows separation of the hemicelluloses, thus producing very pure cellulose but with a low degree of polymerisation, making it suitable for particular applications. This process is not used in French plants.
The bisulfite process
This process has largely become insignificant in worldwide production (5%?) but it enables the production of purer cellulose, suitable for chemical processing. In France, only the Tartas plant belonging to the Tembec Group uses it. Here, wood is chemically treated using acid. The cooking agent is sodium bisulfite (NaHSO$_3$), calcium bisulfite, Ca(HSO$_3$)$_2$, magnesium bisulfite Mg(HSO$_3$)$_2$ or ammonium bisulfite NH$_4$HSO$_3$.

There are various coproducts. The components of tall oil (resins, fatty acids) cannot be separated and recovered. Most black liquors, containing sulfonated lignin, are burned, with sulphur dioxide recycling. They are a source of energy. These liquors can also be used for the production of lignosulfonates, the binding properties of which are used in various industrial applications. Certain volatile turpentine compounds (paracymene) are also recovered when the black liquor is discharged, at the end of cooking.

II.4.4.2 - GENERAL PATTERN OF THE PRODUCTION CHAIN

The diagram presented in the appendix positions the products and coproducts of the lignocellulosic production chains, setting out in particular the very specific products and coproducts associated with pulp production and pine resin tapping.

The function of lignocellulosic production chains is primarily energy production (firewood, charcoal) and materials. According to the FAO, 1.76 billion m$^3$ of firewood were produced in 2007 and 1.6 billion m$^3$ of roundwood. These production chains are often presented as requiring less inputs than farming production chains. If they are operated intensively, they are sustainably balanced only if a large part of the biomass is restored to the soil or if the soil is fertilised, all the more so if it is low in nutrients.

Material fibres
The direct uses of timber as a material are known, whether it is used in the form of solid wood or peeled wood (plywood, veneers) or in process or particle boards.

Wheat straw can be used directly for the production of insulation panels. This is the business of Stramontec (cf. II.1.5.1). Several plant fibres (wood, hemp, etc.) can also be incorporated into concrete-based composite materials.

Plant fibres can be used to reinforce thermoplastic polymers by slightly modifying their interface functions beforehand. Either the polymer or plant fibre may be predominant in the compounds obtained, depending on the desired properties.

Wood flour may be used as a composite with polyethylene (PE) as well as with PVC, with rates of incorporation as high as 20 - 30%. The potential market is considerable, with that of PVC reaching 2 - 3 mt in France. Wood flour can also be incorporated into polystyrene or polymethacrylate. Hemp fibres are used in polypropylene (PP) or acrylonitrile butadiene styrene (ABS) based composites whereas linen fibres are mixed with polyethylene. The association Fimalin brings together all the players in the linseed production chain in Normandy. Arkema is a stakeholder. Compounds comprising linen fibres as well as Rilsan® or PVC are being studied.
Cellulose. Its derivatives include both old products (viscose, rayon) and future products. Wood-based cellulose is in competition with that deriving from cotton linters, which is naturally purer and formed of longer fibres.

In second-generation processes using the biochemical route, cellulose becomes the direct precursor of glucose and in an industrial future to be defined, all derivatives of the latter should also be derived from lignocellulosic biomass.

_hemicelluloses and lignins are not yet products which are marketed as such but they are contained in products or co-products in the production chain and could eventually be the precursors of certain bioproducts which may be very specific. Hemicelluloses contain a high proportion of C5 sugars whereas lignins are the only sources of aromatic chemicals available in very large quantities in living matter._

The co-products of the paper industry derive essentially from the manufacture of chemical pulp from softwood using the kraft process. These include the following:

- **Lignosulfonates** or **sulfonated lignin**, derived from the concentration of acidic black liquor in the bisulfite process. They have binding and tensioactive properties. The volumes produced are considerable: a plant such as that belonging to Tembec in Tartas produces 150,000 t of pulp and 100,000 t of wet lignosulfonates = 50,000 t of dry lignosulfonates, the sales of which are vital for the economic balance of the unit. Twice these quantities are consumed in the plant to produce the energy necessary to operate it.

- Very pure ethanol can be obtained by fermentation from this acidic black liquor (12 million litres per year on the Tembec site in Tartas)

- **Turpentine** is the fraction of volatile wood compounds separated at the beginning of the wood cooking process, during pre-steaming. These compounds, which include a large number of turpentine chemicals, can be obtained directly by tapping the various species of pine. In this case, they offer the advantage of not having a high sulphur content, unlike the products deriving from the paper industry, which require meticulous refining. Although they are more costly, tapping products are sought after for applications in the perfume industry.

Tapping, which has a high labour cost, was discontinued in France in 1950. It continues in China, Brazil and Indonesia. The French profession had carried out development projects on optimised, semi-mechanised tapping techniques as part of “Eurogemme”, a European project, but they remain non-competitive at the present time.

- **Tall oil**, derived from the skimming of black liquor, contains a large number of chemicals, mainly fatty acid and resin acid soaps (rosin) as well as sterols.

The name “tall oil” comes from the Swedish “talolja” meaning “pine oil”.

*It should be noted that tapping provides access to turpentine and wood rosin but not to fatty acids and sterols which are not found in tall oil. The resin comprises approximately ¾ rosin and ¼ turpentine.*
To be more precise, the industrial companies in the sector refer to Gum rosin and Tall oil rosin, Gum Turpentine and Crude sulfate Turpentine.

- The other organic components of alkaline black liquor are lignin hydrolysates, which cannot be used for anything other than energy.

II.4.4.3 – THE ECONOMICS OF THE PAPER PRODUCTION CHAIN

 Worldwide pulp production is in the vicinity of 190 million tonnes and growing quite slowly, with occasional drops in crisis periods. In fact, major geographic redistributions of production are underway. Europe is stagnating, North America is falling whilst there is growth in Latin America (with production largely directed towards exports in countries such as Chile) and in Asia (to be used for regional consumption).

<table>
<thead>
<tr>
<th>Region</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
</tr>
</thead>
<tbody>
<tr>
<td>France</td>
<td>2547</td>
<td>2564</td>
<td>2466</td>
<td>2375</td>
<td>2340</td>
</tr>
<tr>
<td>European Union</td>
<td>37246</td>
<td>36205</td>
<td>41312</td>
<td>41392</td>
<td>39279</td>
</tr>
<tr>
<td>Total Europe</td>
<td>50556</td>
<td>49613</td>
<td>51432</td>
<td>51494</td>
<td>49111</td>
</tr>
<tr>
<td>North America</td>
<td>79991</td>
<td>78313</td>
<td>76892</td>
<td>75776</td>
<td>71778</td>
</tr>
<tr>
<td>Latin America</td>
<td>15001</td>
<td>15688</td>
<td>16682</td>
<td>18562</td>
<td>20394</td>
</tr>
<tr>
<td>Asia</td>
<td>37066</td>
<td>39398</td>
<td>41638</td>
<td>42525</td>
<td>45340</td>
</tr>
<tr>
<td>Other</td>
<td>5882</td>
<td>5967</td>
<td>5647</td>
<td>5853</td>
<td>5795</td>
</tr>
<tr>
<td><strong>Worldwide production</strong></td>
<td><strong>188234</strong></td>
<td><strong>188710</strong></td>
<td><strong>192169</strong></td>
<td><strong>194210</strong></td>
<td><strong>192418</strong></td>
</tr>
</tbody>
</table>

The countries in Northern Europe are the largest producers in this region. France is only in 5th position, on a par with Spain.

<table>
<thead>
<tr>
<th>Country</th>
<th>Production (kt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweden</td>
<td>11,467</td>
</tr>
<tr>
<td>Finland</td>
<td>8,735</td>
</tr>
<tr>
<td>Portugal</td>
<td>2,552</td>
</tr>
<tr>
<td>Germany</td>
<td>2,552</td>
</tr>
<tr>
<td>France</td>
<td>1,725</td>
</tr>
<tr>
<td>Spain</td>
<td>1,725</td>
</tr>
<tr>
<td>Norway</td>
<td>1,690</td>
</tr>
<tr>
<td>Austria</td>
<td>1,546</td>
</tr>
<tr>
<td>Other</td>
<td>3,990</td>
</tr>
</tbody>
</table>

**Source: CEPI**

French production suffers from competition from other regions where the production units are larger, offering better economies of scale. The number of pulp production plants fell from 19 in 1998 to 12 in 2010. Chemical pulp largely dominates French production but presents the largest falls in volumes.

**Recent changes in pulp production in France (kt)**
Wood consumption for wood pulp production was 8.3 million tonnes in 2008 and 6.3 mt in 2009.

### Recent changes in pulp production and trading in France

<table>
<thead>
<tr>
<th>Section</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of plants</td>
<td>17</td>
<td>17</td>
<td>16</td>
<td>15</td>
<td>14</td>
<td>12</td>
</tr>
<tr>
<td>Pulp production (kt)</td>
<td>2547</td>
<td>2564</td>
<td>2466</td>
<td>2375</td>
<td>2340</td>
<td>1724</td>
</tr>
<tr>
<td>Imports (kt)</td>
<td>2098</td>
<td>2048</td>
<td>1949</td>
<td>1863</td>
<td>1763</td>
<td>1745</td>
</tr>
<tr>
<td>Exports (kt)</td>
<td>595</td>
<td>517</td>
<td>519</td>
<td>527</td>
<td>469</td>
<td>407</td>
</tr>
<tr>
<td>Wood consumption for production (kt)</td>
<td>9036</td>
<td>9374</td>
<td>8820</td>
<td>8327</td>
<td>8310</td>
<td>6259</td>
</tr>
</tbody>
</table>

Since this map was published in 2007, the Tembec plants in Tarascon and Saint Gaudens joined the Fibre Excellence Group in 2010.

Source: FCBA
“Commercial” paper pulp, marketed as a commodity, has listed prices which are used as benchmarks. The NBSK “Northern Bleached Softwood Kraft”, a kraft chemical pulp using American softwood, with a price in dollars, is used most often to track market changes. Pulp prices are cyclical in nature, since production capacities and demand adjust according to one another with a time delay. In 2010, prices recovered considerably, exceeding $955/t in June. The worldwide pulp trade represents around 50 million tonnes.

Recent changes in the NBSK pulp price (US$ per tonne), before the strong recovery in 2010

![Pulp Price Chart]

**Worldwide pulp trade (million tonnes)**

<table>
<thead>
<tr>
<th>Region</th>
<th>2007</th>
<th>2008</th>
</tr>
</thead>
<tbody>
<tr>
<td>North America</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Western Europe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>China</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rest of the World</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: PricewaterhouseCoopers LLP from RISI-PPI

II.4.4.4 – INDUSTRIAL COMPANIES IN THE PAPER PRODUCTION AND CO-PRODUCT REFINING CHAIN

The paper industry is currently being restructured and in regular consultation on a worldwide scale. Some industrial companies market mainly processed products (papers, cardboards). This is the case of the North-American world leader **International Paper**, **Stora Enso** (Sweden) and **UPM-Kymmene** (Finland), etc. On the contrary, certain players are major sellers of pulp, such as **Fibria** (Brazil), **Weyerhaeuser** (USA), **Arauco** (Chile), **Tembec** (Canada), **Södra** (Sweden), etc.
Except for the **Gascogne** Group, the producers of cellulose pulp active in France have foreign groups as shareholders.

- **Mechanical and thermomechanical pulps**
  - **Cascades** (Cascades Group, Canada), in La Rochette (Savoie).
  - **UPM-Kymenene France** (UPM Group, Finland) in Stracel (Bas Rhin).
  - **Norske Skog** (Norske Skogindustrier Group, Norway) in Golbey (Vosges).
  - **Stora Enso** (a Finno-Swedish group) in Corbehem (Pas de Calais).

- **Chemical pulps**
  - **Fibre Excellence** (Paper Excellence BV (Netherlands), Asia Pulp and Paper - Sinar Mas Group, Indonesia). Two plants (bought in 2010 from Tembec): in Saint-Gaudens (Haute Garonne) using the kraft process on hardwood and Tarascon (Bouches du Rhône) using the kraft process on softwood. Saint Gaudens produces 207,000 t of pulp and Tarascon 250,000 t.
  - **Gascogne** Paper (kraft), Mimizan, (Landes).
  - **International Paper Celimo** (International Paper Group, USA) in Saillat (Haute Vienne) with a production of 250,000 tonnes of pulp.
  - **M-Real Alizay** (M-Real Group, Finland), kraft process, in Alizay (Eure).
  - **Smurfit Kappa Cellulose du Pin** (Smurfit Kappa Group, Ireland). Kraft process on softwood, Facture, (Gironde).
  - **Tembec** (a Canadian group), Tartas (Landes), using the bisulphite process on softwood; production: 150,000 t of pulp.

The manufacturers of softwood chemical pulp using the kraft process produce tall oil and turpentine.

- **Tembec** produces and markets lignosulfonates.

**There are few companies which refine pulp manufacturing co-products.** In France, **DRT** is active in this sector. It is the only company in the world which refines turpentine products from both turpentine and tall oil. Two other companies refine tall oil: the North American company **Arizona Chemicals** (which also has operations in Scandinavia) and the Finnish company **Forchem Oy**.

**In addition to DRT, the following companies market bark extracts:**

- **Berkem** (France), **Biolandes** (France), **Naturex** (France), **Blue California** (USA), **EPO** (Italy). For the purposes of this study it was not possible to verify whether or not all these companies perform the extraction themselves or market the products of third parties.

- The aim of the Bioextract project bringing together the Centre Technique du Papier, **Smurfit**, **Tembec** and **Biolandes** is to develop plant extracts from pulp production co-products to be used by Biolandes.

- Companies marketing plant tannins, such as **Omnichem** (Ajinomoto Group) in Belgium and **Silvachimica** in Italy.

**II.4.4.5 – LIGNOCELLULOSIC BIOMASS MOBILISATION COSTS**

The REGIX project, described briefly above, provides some preliminary answers to the question of the cost of mobilising farmed or forest biomass.

Farmed biomass costs €80 – €120/t packaged on site, plus loading and transport costs.
Farmed biomass production costs (€/t DG)

- Transport
- Stockage
- Rémunération Capitaux propres
- Charges diverses
- MSA
- Foncier
- Mecanisation + Main d’œuvre
- Intrants (dont amortissement plantation et manque gagner A1 / A2)

*NB: perennials are harvested at the end of the winter; yield is a 15-year average. Source: GIE Arvalis-Onidol*

Forest woodchips display an average cost of €72/t, ranging between €35 and €100/t.

Average price of forest woodchips produced within the framework of REGIX

Expressed in terms of energy content, costs are far more uniform, at around €22-23/mWh.
II.4.5 – MAIN PRODUCTS OF LIGNO-CELLULOSIC PRODUCTION CHAINS

II.4.5.1 - CELLULOSE AND DERIVATIVES

The bisulphite and prehydrolysis kraft (PHK) processes enable the production of cellulose without hemicelluloses. One tonne of wood is required to produce 350 kg of pure cellulose. Cellulose is characterised by its degree of polymerisation (DP), which can be modulated according to the bleaching parameters. Specialised cellulose types are now produced by certain pulp manufacturers and then processed into their derivatives by the chemicals industry (Akzo Nobel, Rhodia, Dow Chemicals, etc.). As the quality of cellulose is different depending on the different applications, pulp plants may specialise in order to serve primarily ether or acetate producers.

Cellulose ethers: carboxymethyl cellulose, ethylcellulose, hydroxyethylcellulose. These polymers are water-soluble enabling the viscosity of solutions to be adjusted. They are used as rheological agents (= texturising agents) in many different applications (including the Pharmaceuticals, Cosmetics, Food, Concrete - Building materials, Varnishes and paints, Paper, Adhesives, Detergents sectors). The Tembec plant in Tartas in particular produces cellulose pulp for the production of ethers.

There are two categories of cellulose ester:

- **Nitrocelluloses** have different applications depending on the level of nitration in the cellulose. They are used for their “energy” properties (in civilian and military explosives) as well as in lacquers, inks and varnishes for their film-forming properties (the “glossy” nature of cellulose varnishes). These applications are experiencing growth in Asia but are becoming less widespread in Europe since they produce volatile organic compounds.

- **Cellulose acetates or butyrates** are soluble in organic solvents such as acetone. They can be regenerated in the form of threads (with applications in textile fibres and cigarette filters) or films (book covers, overhead projector acetates, as well as polarising filters for LCD screens). Cellulose acetates are also used in the production of thermoplastics for various applications. Cigarette filters account for approximately 80% of the applications of cellulose acetates, produced by companies such as Rhodia.
Viscose. When treated with an alkaline solution then with carbon disulphide, cellulose can be converted into hydrosoluble cellulose xanthate. In acidic conditions, cellulose can be regenerated in the form of threads (Rayon, Viscose for non-woven applications, including cellulose sponges, textiles and tyres) or films (Cellophane). China is a major producer and consumer of viscose.

“Lyocell” cellulose is another form of regenerated cellulose which is dissolved directly, reprecipitated and forced through a die to produce high-quality fibres for textiles and non-woven fabrics. Lyocell is manufactured, for instance, by the Tembec Group and the Austrian company Lenzing.

Microcrystalline celluloses are used for their binding properties in pharmaceutical excipients and nutraceuticals.

The approximate breakdown of cellulose quantities by application is as follows:

<table>
<thead>
<tr>
<th>Applications</th>
<th>Approximate quantity, x 1000 tonnes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscose</td>
<td>+ / - 2,500</td>
</tr>
<tr>
<td>Cellulose acetates</td>
<td>700</td>
</tr>
<tr>
<td>Ethers</td>
<td>450 + / - 2 - 300 in China</td>
</tr>
<tr>
<td>Nitrocellulose</td>
<td>100</td>
</tr>
<tr>
<td>Microcrystalline cellulose</td>
<td>100</td>
</tr>
<tr>
<td>Total</td>
<td>+ / - 4,000</td>
</tr>
</tbody>
</table>

II.4.5.2 – TURPENTINE or PAPER ESSENCE

Turpentine, which is produced by the volatilisation of light softwood compounds during the presteaming stage of the kraft process, may also be produced by pine tapping in countries with low labour costs, where it is still practised.

Turpentine production in France may be estimated at between 7 and 8 kt.

Turpentine contains terpenes from 3 major groups, separated by distillation:
- Alpha-Pinene,
- Beta-Pinene,
- Other components including Delta-3-Carene.

Depending on the origin and species of wood, the respective proportions of these different components vary greatly.

Softwood terpenes have historically been used as solvents but their main outlets are now in the perfume industry. Terpenes are used in the form of alcohols, esters and hydrocarbons. Most of the chemicals obtained can also be produced petrochemically. There is therefore direct competition between plant and crude oil origins, with varying intensity depending on oil prices.

There are only two other integrated refiners worldwide, both in North America. Like DRT, they work on the entire production chain from full distillation to production by chemical conversion of terpene derivatives. The other industrial players are active on only a small part of distillation products.

The treatment of paper essences includes desulfurisation of the product. The distillations to be implemented are delicate operations, since the differences between the boiling points of the different chemicals to be separated are very small. All of the technology to be implemented, the
importance of the know-how and investments necessary greatly limit the number of industrial players active in this sector.

Some turpentine derivatives

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Product categories</th>
<th>Examples of chemicals</th>
<th>Markets</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-pinene</td>
<td>Hydrocarbons</td>
<td>α-pinene, Dipentene, Para-cymene</td>
<td>-</td>
</tr>
<tr>
<td>α-pinene</td>
<td>Terpene alcohols</td>
<td>Dihydromyrcenol, Menthol, Sanderol, Terpineol, Pinol.</td>
<td>Perfumes,</td>
</tr>
<tr>
<td>α-pinene</td>
<td>Camphor products</td>
<td>Camphor</td>
<td>(for camphor: uses in religious ceremonies, in India)</td>
</tr>
<tr>
<td>α-pinene</td>
<td>Esters</td>
<td>Menthanyl acetate, Terpinyl Acetate</td>
<td></td>
</tr>
<tr>
<td>β-pinene</td>
<td>Hydrocarbons</td>
<td>β-pinene, Myrcene</td>
<td></td>
</tr>
<tr>
<td>β-pinene</td>
<td>Terpene alcohols</td>
<td>Citronellol, Geraniol, Nerol, Nopol</td>
<td></td>
</tr>
<tr>
<td>β-pinene</td>
<td>Esters</td>
<td>Geranyl acetate, Nopyl acetate</td>
<td></td>
</tr>
<tr>
<td>β-pinene</td>
<td>Aldehydes/ketones</td>
<td>Derambrene (= Iso-E)</td>
<td></td>
</tr>
<tr>
<td>α-pinene and β-pinene</td>
<td>Polyterpene resins</td>
<td>Tackifying resins</td>
<td>Glues and adhesives, chewing gum, etc.</td>
</tr>
<tr>
<td>Δ-3-carene and α-pinene</td>
<td>Phenol-terpene resins</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Certain chemicals are low added-value commodities with a well-established market of several thousand tonnes. Geraniol thus represents a market of 15 kt, supplied by 4-5 players. Synthetic geraniol, obtained from isobutene and acetone by BASF (notably), is in competition with those extracted by DRT from paper essences or gum essences. Other chemicals are specialities, sometimes with very high added value, but for markets with small volumes.

Turpentine derivative prices have been increasing significantly for the past few years, with maintained growth in demand, in spite of the general economic climate with the resource being in limited supply. A few orders of magnitude for prices observed in mid-2010 can be noted:

- Turpentine: $4-4.5/gallon (≈ $1/l)
- α-pinene: $4/kg
- Pinol: $4.5/kg
- Dihydromyrcenol: $9/kg.

II.4.5.3 - TALL OIL AND DERIVATIVES

Tall oil is another co-product of Kraft paper production using softwood. It accounts for approximately 3% of the composition of the dry matter in pine wood. 30 – 50 kg of tall oil are produced for each tonne of pulp.

Annual tall oil production in North America is approximately 500 kt and around 400-500 kt in Scandinavia. In France, production may be estimated at between 20 and 30 kt.
Tall oil has the following overall composition:

### Composition of a typical tall oil from the USA

<table>
<thead>
<tr>
<th>Components</th>
<th>% weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin acids</td>
<td>42</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>48</td>
</tr>
<tr>
<td>Non-saponifiable materials</td>
<td>8.5</td>
</tr>
<tr>
<td>Water</td>
<td>0.8</td>
</tr>
<tr>
<td>Toluene insolubles</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*Source: Encyclopaedia of Chemical Technology*

The name “resins acids” (also known as rosin) covers a number of different chemicals which are close to abietic acid \( \text{C}_{19}\text{H}_{29}\text{COOH} \):

### Example of the composition of the “resin acids” fraction or Rosin in a tall oil

<table>
<thead>
<tr>
<th>Components</th>
<th>% weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abietic acid</td>
<td>35.4</td>
</tr>
<tr>
<td>Dehydroabietic acid</td>
<td>27.4</td>
</tr>
<tr>
<td>Palustrie/levopimaric acid</td>
<td>10.1</td>
</tr>
<tr>
<td>Isopimaric acid</td>
<td>5.6</td>
</tr>
<tr>
<td>Dihydroabietic acid</td>
<td>4.7</td>
</tr>
<tr>
<td>Pimaric acids</td>
<td>4.6</td>
</tr>
<tr>
<td>Other</td>
<td>12.2</td>
</tr>
</tbody>
</table>

*Source: Encyclopaedia of Chemical Technology*

The dominant fatty acids in tall oil are the same as those in many vegetable oils. However, their distribution varies according to forest species and therefore according to the regions of origin.

### Examples of fatty acid composition (% of total) in tall oil

<table>
<thead>
<tr>
<th>Components</th>
<th>&quot;Typical&quot; tall oil*</th>
<th>North American origin**</th>
<th>Scandinavian origin**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic acid C18:1</td>
<td>48.5</td>
<td>46</td>
<td>30</td>
</tr>
<tr>
<td>Linoleic acid C18:2</td>
<td>43.1</td>
<td>36</td>
<td>45</td>
</tr>
<tr>
<td>Pinolenic acid C18:3</td>
<td>3.5</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>Stearic and palmitic acids C18:0 and C16:0</td>
<td>2.1</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Eicosenoic acid</td>
<td>1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td>1.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Source: * Encyclopaedia of Chemical Technology, **: The chemistry of oils and fats. F. Gunstone.*

**Process**: Tall oil is found in black liquor in the form of soaps. The acidification of these soaps enables them to be separated from the black liquor and crude tall oil to be obtained. Refiners purchase acidified crude tall oil or sometimes black liquor, from which they extract the tall oil themselves, often on the same site as the paperworks.

**Crude tall oil** prices are closely correlated with those of crude oil. If the price of crude oil becomes too high, pulp producers burn their tall oil to avoid the purchase of expensive fuel and payment of the related carbon taxes.

The development of projects using tall oil for energy, such as SunPine in Sweden, is liable to cause considerable upset in a market with a limited supply of the resource. According to this project, 90,000 of the 450,000 tonnes of Scandinavian tall oil will eventually be used to produce
biodiesel, which will cause strong tensions on the tall oil market whilst having a negligible impact in terms of substitution for diesel fuels.

**Products extracted from tall oil and derivatives**

There are very few refiners who process tall oil in France: only DRT is active in this field.

Tall oil is broken down by distillation at high temperature into various components:
- Tall oil fatty acids
- Distilled tall oil
- Tall oil rosin
- Tall oil pitch, from which phytosterols (β-sitosterol) are extracted.

The applications of tall oil derivatives are set out in the table below.

<table>
<thead>
<tr>
<th>Original fraction</th>
<th>Product categories</th>
<th>Properties</th>
<th>Markets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acids</td>
<td>Oleic and linoleic acids</td>
<td>C18 chain fatty acids.</td>
<td>Industrial oils, cutting oils, lubricants</td>
</tr>
<tr>
<td></td>
<td>Fatty acid esters</td>
<td></td>
<td>Inks, lubricants</td>
</tr>
<tr>
<td>Distilled tall oil</td>
<td>Mix of fatty acids and resin acids</td>
<td></td>
<td>Industrial oils, soaps, industrial emulsifiers, inks, bitumens</td>
</tr>
<tr>
<td>Distilled tall oil and resin acids</td>
<td>Hydroxyl polyester resins</td>
<td>Tackifying resins for polyurethanes</td>
<td>Polyurethanes</td>
</tr>
<tr>
<td>Tall oil pitch</td>
<td>Tall oil pitch</td>
<td>Acid dopes for bitumens</td>
<td>Bitumens, road surfaces</td>
</tr>
<tr>
<td>Tall oil pitch</td>
<td>β-Sitosterol</td>
<td>Cholesterol inhibitors, Skin anti-inflammatory</td>
<td>Pharmaceuticals Dietetics - Nutraceuticals</td>
</tr>
<tr>
<td>Tall oil rosin</td>
<td>Acid rosins</td>
<td></td>
<td>Pigments</td>
</tr>
<tr>
<td></td>
<td>Rosin soaps</td>
<td></td>
<td>Rubbers</td>
</tr>
<tr>
<td></td>
<td>Rosin esters</td>
<td></td>
<td>Inks, glues and adhesives, cosmetics, road markings</td>
</tr>
<tr>
<td></td>
<td>Modified phenol resins</td>
<td></td>
<td>Varnishes, inks, paints.</td>
</tr>
<tr>
<td></td>
<td>Resinates</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydroxyl polyester resins</td>
<td>Tackifying resins</td>
<td>Polyurethanes</td>
</tr>
</tbody>
</table>
II.4.5.4 – OTHER PAPER INDUSTRY CO-PRODUCTS

Lignosulfonates are co-products of pulp production using the bisulphite process. They are marketed in liquid form, with 50% dry matter, or in powder. They have various uses in the following applications:

- concrete (dissolving, plastifying, setting delay agents)
- animal feed (cohesion of pellet feeds),
- leather and tanning industries (tanning agents),
- paper (in competition with starch, for its binding properties),
- wood panel industry (non-toxic binder),
- miscellaneous (fertiliser binding agent, dissolving agents, emulsifying and wetting agents for plant care products, etc.).

Lignosulfonate production

Sulfonated lignin may be a precursor of vanillin.

The sugars found in residual liquors may be fermented and converted into ethanol. Consequently, in some of its factories, Tembec produces very pure ethanol from the hexoses found in the liquors. This ethanol is used in applications in cosmetics, detergents, foodstuffs, etc.

Tannins. These cover a diverse family of polyphenols. Oak and chestnut wood are particularly rich in tannins. Their extraction during the course of paper making processes is the subject of R&D work but as yet there are no commercial applications. Specialist companies extract tannins from French and Italian oak and chestnut trees, and from exotic trees such as the South American Quebracho (Scinopsis sp.) and certain true tropical acacias (mimosaceae). Oak galls, leaves and pods of other plants are also sources of tannins. These chemicals maintain most of their applications in tanning (which overall still consumes several tens of thousands of tonnes per year) but have other uses in the production of beverages and wines, pharmaceuticals, cosmetics, (between a few dozen and a few hundred kg per year) and in the textile and metal processing sectors.
**Examples of water-soluble tannins**

![Acide ellagique](image1.png)  
![Acide gallique](image2.png)  

**Procyanidins extracted from pine bark** are polyphenols with a growing number of applications in nutraceuticals and cosmetics. These products are expensive in concentrated form (over €1000/kg). The geographical origins of extracts present on the market are mainly Landes pine and Chinese pines.

**Lignans** (Hydroxymatairesinol = HMR) and other flavonoids are found in high levels in softwood knots (where the branches are connected to the trunk). Wood knots account for 2 - 3% of the volumes of wood treated and cannot be transformed into pulp. Mechanical sorting of knots is possible before cooking. Use of their specific components is an interesting avenue, which is the subject of various research work.

### II.4.5.5 – SECOND-GENERATION BIOFUEL PRODUCTION

Second-generation biorefineries will process lignocellulosic raw materials to produce, as a priority, various kinds of biofuels. The chemicals obtained or co-products may be used as synthetic intermediates for the chemicals industry.

Here is an overview of the different avenues currently being explored:

**Those of the so-called thermochemical route.** These require a potentially large supply of heat energy and do not maintain the original structure of the biomass.

**Biomass gasification** consists of gradually raising the temperature of the matter with a limited and carefully controlled quantity of oxygen or air. This produces syngas, composed of carbon monoxide and carbon dioxide, hydrogen, water, methane, nitrogen and impurities including tars. There are a large number of processes and the composition of the gas obtained is variable. At a high temperature (800-1000 °C) and at atmospheric pressure, carbon monoxide and hydrogen are predominant. At a lower temperature (400-500 °C), the formation of methane is favoured.

The separation of carbon monoxide and hydrogen followed by a Fischer Tropsch reaction produces hydrocarbon chains of variable lengths (compatible with petrol or diesel) and water.

The many projects using this technology, include the following:

- **The French BioTfuel project**, backed by ADEME and the Picardy regional council, validated in 2009. This brings together the French Institute of Petroleum (IFP), the Atomic energy commission (CEA), Sofiproteol (Oil and Protein Production chain Funding Body), the petroleum group Total and the German industrial group Uhde. The aim of the project is to perfect a full process, from the preparation of biomass, roasting, gasification, purification of gases and Fischer Tropsch synthesis. The demonstrator remains at a modest scale and will produce 200,000 - 300,000 litres of biofuel annually.
• The Finnish paper manufacturing group UPM’s project, which involves studying the possibility of developing biofuel production by gasification of forest slash at its Stracelec site (near Strasbourg). UPM has developed the necessary technology in the USA with the Gas Technology Institute. Pilot studies have been conducted over the past few years, including on raw materials from Europe. The impact study.

• The project conducted by the CEA (Atomic Energy Commission), Air Liquide and the CNIM Group (Constructions Industrielles de la Méditerranée) in Bure-Saudron.

• The innovative developments of the North American company Coskata, which carries out microbial fermentation from syngas to produce ethanol. Biotechnology would therefore replace the Fischer Tropsch process, which is very energy-consuming. The French petroleum company Total became a shareholder in Coskata in 2010. Also in the USA, Ineos New Planet Bioenergy (a subsidiary of Ineos) has similar technology.

• The projects by Choren in Germany, the North American company ClearFuels Technologies, the Canadian company Enerkem and the Danish company Haldor Topsoe.

Biomass pyrolysis also consists of raising the temperature of the biomass, but without air. Historically this is the process used for manufacturing charcoal (at a temperature of approximately 350-400 °C at a low heating speed). At high temperatures, applied for a short period of time, large proportions of oils and tars are produced (pyrolisate), compatible with diesel fuel.

There are fewer projects. The example of Renewable Energy Institute in the USA can be noted.

The biochemical route favours the breakdown of the living matter polymers followed by their conversion by enzymes and the action of micro-organisms. Physical or physico-chemical preliminary treatments are necessary. Usually, cellulases and hemicellulases (cf. IV.4.1.1) are used, but a large number of developments are in progress in order to have microbial strains capable of using the cellulose and hemicelluloses directly as a substrate (cf. IV.4.1.1).

The many projects using the biological route include the following:

• The French project FUTUROL, which brings together a large number of partners on the Pomacle-Bazancourt site: Agro industrie Recherches et Développements (ARD), Confédération Générale des Planteurs de Betterave (CGB), Champagne Céréales, Crédit Agricole du Nord-Est, IFP, Institut National de la Recherche Agronomique (INRA), Lesaffre, Office National des Forêts (ONF), Tereos, Total and Unigrains. This 8 to 10-year project will consist of creating an industrial pilot from scratch, which will be operational by late 2010 or early 2011. Futurol includes the issue of the mobilisation and collection of all kinds of lignocellulosic biomass.

• The work implemented by the heavyweights in the enzyme sector such as Novozymes (work with companies of various nationalities such as Lignol, PRAJ, COFCO, SINOPEC, as well as several research centres) and Genencor (partnership with DuPont to produce cellulosic ethanol)).
• The many different projects implemented either by start-ups or by industrial companies already producing first-generation ethanol to develop cellulosic ethanol. The following can be listed: Abengoa (in the USA, from switchgrass and wood residues), Iogen in cooperation with Shell (Canada), Mascoma (USA), Poet (USA), Range fuel (USA), Verenium (USA), Zeachem (USA), etc.

• Tereos’ work with Deinove, which has already been mentioned, to produce ethanol directly from the lignocellulosic fractions of wheat, implementing certain deinococcus strains.

• The different projects for butanol and isobutanol production by fermentation (cf. III.5); some are deliberately directed towards the use of lignocellulosic biomass.
II.4.5.6 – XYLOSE AND ARABINOSE DERIVATIVES

Xylose and arabinose are constituents of hemicelluloses and can be produced by breaking down the hemicelluloses chemically (acid hydrolysis) and/or biochemically (hemicellulase action). Xylitol and arabinitol are produced by hydrogenation of xylose and arabinose. They were ranked in the "top 10" platform chemicals in the 2004 US DOE study. The 2009 update confirmed this position for them. They were selected by the European study BREW in 2006.

<table>
<thead>
<tr>
<th></th>
<th>xylose</th>
<th>xylitol</th>
<th>arabinose</th>
<th>arabinitol</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-Xylose</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-Xylose</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>xylose</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>xylitol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>arabinose</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>arabinitol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Many potential derivatives of this group of chemicals can be listed. The 2004 study included propylene glycol and ethylene glycol, as well as lactic acid and even glycerol!

To date, the most attractive xylose derivatives are hydroxylated furans such as furfural. Worldwide production is between 200,000 and 300,000 tonnes. It is obtained from biomass with a high pentosan content by companies such as the Belgian Transfuran Chemicals. Furfural has many derivatives including furfuryl alcohol (with applications as a solvent and synthetic intermediates for resins and plastics) as well as the other furan derivatives mentioned in § II.1.5.3.2, such as Tetrahydrofuran (THF).

![Furfural](image)

![Furfuryl alcohol](image)

Xylose can also be used for the production of non-ionic tensioactive agents.

II.4.5.7 – TOWARDS LIGNIN CHEMISTRY

Lignins remain the least known fraction of lignocellulosic matter. They are traditionally burned or used in the form of lignosulfonates by the paper industry and offer various potential applications, as well as the possibility of eventually producing a large array of aromatic derivatives.

A study by the Pacific Northwest National Laboratory (PNNL) for the US DOE was published in 2007 (Top Value-Added Chemicals from Biomass – Volume II – Results of screening for potential candidates from biorefinery lignin). It classifies the possible uses of lignin into three categories:

- The production of heat, fuels and syngas (short-term potentials).
- The use of lignin macromolecules (medium term).
- The production of aromatic derivatives and various monomers (long term).
The first category of use, which has already been dealt with, will not be discussed again in this section. Lignins have many advantages for their use in materials:

- their aptitude for reticulation and grafting to replace phenol in adhesives
- their capacity to make biodegradable materials “water repellent” by grafting aromatic compounds onto their sugars.
- their antioxidant properties to stabilise thermoplastics.

### Potential uses of lignins in materials

- Groupements fonctionnels : OH, COOH, C=O, CHO, OCH₃, SO₃
- Liaisons : C=C, C-O-C, C-C
  - Réticulation
  - Fonctionnalisation
  - Copolymérisation

The PNNL also envisages the use of lignins for the production of carbon fibres to replace polyacrylonitrile. Low-cost lignin purification must be mastered beforehand.

The PNNL study presents two possible alternatives for lignin derivatives in aroma chemistry:

1. The production – by technologies to be developed - of molecules maintaining the lignin structure. In this case the applications and markets will need to be developed.
The production of platform chemicals respecting the lignin structure

![Chemical Structures](image1)

(2) The conversion of lignins into benzene, toluene and xylene (BTX), according to technology still to be developed. This would provide access to the vast family of aromatic agents made petrochemically, the applications and markets of which are very well known.

**Conversion of lignins into well-known aromatic agents**

![Chemical Structures](image2)

**Information about BTX derivatives (Benzene, Toluene, Xylene)**

![Chemical Structures](image3)

Source: PNNL for US DOE, 2007
and those of phenol:

- bisphenol A
- cyclohexanol
- cyclohexanone
- nitrophenols
- aminophenols
- pigments, dyes, resol resins, antioxidants, urea resins, formaldehyde resins, alkyl phosphites and others

Source: PNNL for US DOE, 2007
II.4.6 - THE FRENCH PRODUCTION CHAIN: STRENGTHS, WEAKNESSES AND PROSPECTS

The paper production chain comes from a very old industry. The part which remains active in France is faced with competition from very large new units which benefit from strong economies of scale. They are located in Asia, Latin America and Eastern Europe. Maintaining a cellulose pulp industry in France therefore depends increasingly on the added value of its products. Consequently, these must constantly become more sophisticated, using the results of research and development which should be more active and better encouraged. One of the problems of the French paper sector is that most of it is owned by international groups whose decision-making centres and research units are located a long way away. Cellulose chemistry thus offers interesting prospects for added value with industrial know-how present in France, but there is not sufficient active research on this subject on a national level.

Traditional paper co-products (tall oil, turpentine, lignosulfonates) represent limited tonnages. Their use may grow, all the more so because their counterpart chemicals produced petrochemically will become more expensive, but national resources are insufficient. Upstream of the production chain, DRT can develop only by seeking new supplies on other continents.

Pulp plants have always produced energy. The risk that some might eventually be confined to the role of electrical thermal power stations working with “energy wood” should not be excluded. This would be regrettable for an industry which offers further potential for added value.

Paper wood and cellulose wood, timber, fuel wood, energy timber, etc. Are these various outlets for forests to be doomed to exclusion? How are they compatible, according to what vision and with which long-term objectives? Which activities have the best impact on the environment? Which create the most jobs? Which favour our external trade? The landscape remains ill-defined and there is acute strain between the different corporations concerned. Overall consultation is necessary but has not yet taken place. We believe the answer will take into account local situations, but strategic thinking must be done together on a national basis. The future of the different production chains cannot simply be abandoned to market forces when several of the sectors concerned benefit from direct or indirect public support.

The straw resource is both large and limited in France. France is a major cereal producing country but most of the straw produced already has a use. The fraction which is actually available, like wood, is already sought-after to produce fuels, materials, biofuels and maybe some intermediates for the chemicals industry. Here it will also be necessary to define the best balances between the different uses, nationally and locally, with all stakeholders.

New energy crops have sometimes been presented as miraculous by some of their promoters. While these plants enjoy rapid growth and exuberant vegetation, like all C4 plants, they require sufficient water and good land to express their potential. Work such as the REGIX programme provides the initial elements to enable their correct positioning to be defined in lignocellulosic biomass production in our various soil and climate conditions.

Various research and development projects have been undertaken in France on the production of second-generation biofuels. They remain few with modest resources, compared to the work undertaken in the United States. Too few biotechnology companies explore the possibilities for direct fermentation of cellulose and hemicelluloses in France. Our know-how about lignin chemistry is worth being assessed in detail.
## SWOT analysis of the French production chain

<table>
<thead>
<tr>
<th>Strengths</th>
<th>Weaknesses</th>
</tr>
</thead>
<tbody>
<tr>
<td>- France has major sustainably managed forest resources.</td>
<td>- A large part of our forest resources remain poorly used or not used at all.</td>
</tr>
<tr>
<td>- A large supply of farmed resources (co-products and dedicated crops).</td>
<td>- Poor competitiveness of our paper production industry. Its R&amp;D in France is becoming increasingly limited (groups with foreign shareholders concentrating their resources outside France).</td>
</tr>
<tr>
<td>- The French paper production industry is long-standing and has significant know-how and logistics.</td>
<td>- Strong competition for use which could be destructive between uses for heat, materials (including paper) and, in the future, fuels and chemicals. No organised consultation between all stakeholders.</td>
</tr>
<tr>
<td>- Know-how available for cellulose chemistry.</td>
<td>- Still very limited experience of new energy crops in France.</td>
</tr>
<tr>
<td>- Several projects explore the different second-generation technologies (thermochemical, biological) in France.</td>
<td>- Few biotechnology companies in France active for the fermentation of lignocellulose.</td>
</tr>
<tr>
<td>- Presence in France of one of the rare companies which biorefiners paper industry co-products (DRT).</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Opportunities</th>
<th>Threats</th>
</tr>
</thead>
<tbody>
<tr>
<td>- The political desire to develop second-generation biofuels.</td>
<td>- Increasing competition of very large foreign units in the paper production sector.</td>
</tr>
<tr>
<td>- Increased oil and petrochemical derivative costs favouring replacement products.</td>
<td>- The vital continuity between first and second-generation biofuels is as yet poorly understood by our political decision-makers.</td>
</tr>
<tr>
<td>- Progress of biotechnological tools enabling, in the long term, the direct fermentation of cellulose and hemicelluloses.</td>
<td>- Strong competition of North Americans massively developing technologies for the use of lignocellulosic biomass.</td>
</tr>
</tbody>
</table>
II.4.7 - RECOMMENDATIONS

- **Put into place an active consultation group consisting of all current and future stakeholders** concerning the production and use of lignocellulosic resources. Define the development prospects and breakdown desired of the different uses to protect the strategic interests of our country.

- **Pursue programmes following on from REGIX,** giving them a wider vocation (lignocellulosic raw materials for uses in fuels, composite materials and chemicals). Develop a realistic assessment of the national mobilisable resource.

- Communicate on the continuity between biofuels and first and second-generation biorefineries, demonstrating the major importance of the capacities for mobilisation and pre-processing of the forest and farmed biomass already available in France.

- Reinforce the pilot projects undertaken in the development of second-generation processes in order to be competitive in France and the EU, with what is being undertaken on the other side of the Atlantic.

- Provide targeted support for innovative biotechnological research projects on the fermentation of lignocellulosic materials.

- **Assess our know-how about lignin chemistry and provide support if necessary for drawing up a shortlist of promising projects.**
III – EXAMPLES OF BIOCHEMICALS WHICH ARE COMMON TO SEVERAL PRODUCTION CHAINS

Various chemicals which in 2005 could be associated with only one production chain, are now produced by at least two of the four previously described production chains. This type of development is set to continue. It should be noted that starch and cellulose are both glucose polymers. A large number of microorganisms can use glucose or saccharose as their carbon source. Certain C3 compounds can be produced from oilseed-based glycerol and from sugars from the previous production chains.

III.1 - ETHANOL (C2)

The terms ethyl alcohol ("pure alcohol") and ethanol (including bioethanol) are used, strictly speaking, to describe the same chemical but not the same product in terms of use, level of purification and regulatory and fiscal category. The term bioethanol is thus usually used in France only for approved productions for incorporation into biofuels (as they are or in the form of ETBE) whereas the term alcohol is used for other applications (farmed or synthetic alcohol). Here we will use the terms ethanol and bioethanol, distinguishing the products more precisely according to their status only when this is necessary.

The ethanol molecule

\[
\text{CH}_3\text{—CH}_2\text{—OH}
\]

Synthetic ethanol is produced by catalytic hydration of ethylene. Its production is declining with the rise of bioethanol.

III.1.1 – PRODUCTION OF BIOETHANOL

A large number of plants and plant wastes can be used to produce ethanol. Three major stages are found in all processes: pre-treatment and hydrolysis, fermentation and distillation. The yeast \textit{Saccharomyces cerevisiae} naturally converts C6 sugars or saccharose into ethanol. Beet or cane juices, molasses or sugar can thus be used as a substrate.

The production of ethanol from cereal grains can be carried out in two ways: either by fermenting the product of the hydrolysis of a starch milk (glucose), or by working directly on the ground grains which have undergone liquefaction and saccharification.

The challenge for second-generation biorefineries is to produce ethanol from lignocellulosic materials. The hydrolysis of cellulose by cellulases produces fermentable glucose. For increased productivity and to better use of biomass, microbial strains are being developed which can use glucose as well as C5 sugars, from the hydrolase of hemicelluloses by hemicellulases. The aim of other projects is to obtain strains which can hydrolyse cellulose and hemicelluloses themselves, making it possible to dispense with the use of enzymes.

After fermentation, ethanol is distilled and if necessary rectified (second purification distillation) and dehydrated in the case of a use such as fuel.

Ethanol can be directly mixed with petrol in varying proportions depending on the characteristics of the engine in the type of vehicles concerned. It can also be converted into ETBE (Ethyl Tert-Butyl Ether), by reaction with isobutene. ETBE found favour with French petroleum groups as it enables diluted crude oil to be used, does not pose specific problems for the storage and transport of ethanol (the rehydration of which had to be avoided) and can be easily incorporated into common petrol.
III.1.2 – WORLDWIDE BIOETHANOL PRODUCTION

Worldwide bioethanol production is dominated by that from the processing of maize starch in North America, followed by that obtained from cane sugar in Brazil. In France and the EU, bioethanol is produced from beet as well as wheat and maize. The aim of a large number of research and development projects is to produce ethanol from lignocellulosic biomass. In the future, ethanol may also be produced from a wide range of plant raw materials.

Bioethanol is now produced essentially for its applications in fuels. Significant projects for the production of C2 synthetic intermediates are being developed from cane ethanol in Brazil and will be described below.

Bioethanol production has grown considerably over the last few years, in direct relation with national programmes for the development of biofuels. In 2010 there will be almost 100 million m$^3$ (1000 million hl), the major part of which will be produced from maize in the United States (41 m m$^3$ in 2009, 45 m m$^3$ in 2010). Brazil manufactured some 27.4 million m$^3$ in 2009 and should produce 31.5 m m$^3$ in 2010 (+ 15%).

Changes in worldwide pure alcohol production (including bioethanol) x 1000 hl

![Changes in worldwide pure alcohol production](image)

*Source: CEDUS – Statistical memo - From F.O. Licht.*

Breakdown of worldwide production
The main bioethanol producing countries are listed in the table below.
Main ethanol producing countries (millions of hectolitres)

<table>
<thead>
<tr>
<th>Country</th>
<th>2006</th>
<th>2009</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>196.9</td>
<td>395</td>
</tr>
<tr>
<td>Brazil</td>
<td>178.3</td>
<td>278</td>
</tr>
<tr>
<td>EU</td>
<td>34.0</td>
<td>60.3</td>
</tr>
<tr>
<td>China</td>
<td>39.0</td>
<td>38.5</td>
</tr>
<tr>
<td>India</td>
<td>17.8</td>
<td>16.5</td>
</tr>
<tr>
<td>Canada</td>
<td>3.7</td>
<td>12</td>
</tr>
<tr>
<td>Thailand</td>
<td>3.9</td>
<td>7</td>
</tr>
<tr>
<td>Russia</td>
<td>6.1</td>
<td>5.3</td>
</tr>
<tr>
<td>Worldwide</td>
<td>517.7</td>
<td>860.4</td>
</tr>
</tbody>
</table>

Source: CEDUS – Statistical memo - From F.O. Licht.

In 2010 there are believed to be 201 ethanol production units in the US, with a capacity installed or under construction of 57 m $^3$. The federal objective is to achieve production of 136 m $^3$.

Although sugar cane (its sweet juice or, in the future, the whole plant) will remain the raw material for bioethanol in Brazil, the United States anticipates that the diversification of biomass resources used will be necessary. As the objectives for maize ethanol production have been practically met, dedicated crops and crop and forestry residues will have to take an important place, subject to second-generation technologies being mastered.

<table>
<thead>
<tr>
<th>Biofuel production (m $^3$) in 2022 in the United States: forecasts for the use of various raw materials</th>
<th>EPA forecasts*</th>
<th>USDA forecasts**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dedicated crops (sorghum and perennial graminaceous plants such as switchgrass)</td>
<td>29.9</td>
<td>50.7</td>
</tr>
<tr>
<td>Rapeseed, soybean and maize oil for biodiesel</td>
<td>5.1</td>
<td>1.9</td>
</tr>
<tr>
<td>Crop residues (corn stalks, straw, bagasse)</td>
<td>20.8</td>
<td>16.3</td>
</tr>
<tr>
<td>Forestry residues</td>
<td>0.4</td>
<td>10.6</td>
</tr>
<tr>
<td><strong>Maize ethanol</strong></td>
<td>57</td>
<td>57</td>
</tr>
<tr>
<td>Municipal solid waste and other</td>
<td>9.8</td>
<td>?</td>
</tr>
<tr>
<td>Animal fats</td>
<td>1.4</td>
<td>Not forecast</td>
</tr>
<tr>
<td>Seaweed</td>
<td>0.4</td>
<td>Not forecast</td>
</tr>
<tr>
<td>Imports</td>
<td>8.3</td>
<td>?</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>103.2</td>
<td>85.8</td>
</tr>
</tbody>
</table>

Source: from USDA – June 2010

* EPA = United States Environmental Protection Agency.
** USDA: United States Department of Agriculture.

The leading producer of bioethanol worldwide is the ADM Group (Archer Daniels Midland). In early 2010, the Brazilian company Cosan presented (see table below) its production ambitions for the joint venture it created with Shell. The data is changing rapidly as this year ADM is launching new units and increasing its production capacity from 20 to 60 mhl. The North American group Poet is also rapidly developing its production. In Brazil, Tereos, a shareholder in Açucar Guarani, is reinforcing its activities. The same is true of LDC-SEV (Louis Dreyfus Group), etc.
Ethanol producers, millions of gallons

NB: 1 million gallons = 38,000 hl  1000 million gallons = 38 mhl = 3.8 m m

In green, the capacities of the Cosan-Shell joint venture
The dotted sections correspond to the volumes of sugar produced by companies, expressed as ethanol equivalents.

Source: Cosan

The European Union is also experiencing strong growth in its production, in order to achieve the objectives for the rate of incorporation of biofuels into petrol. France is the leading producer, ahead of Germany and Spain.

The EU imported 2 million hectolitres of bioethanol in 2002 and 12.8 mhl in 2008, to which some 6 mhl appearing under other names should be added. Brazil is by far the leading supplier of the EU (according to the country’s own statistics, 14.7 mhl were exported to the EU in 2008).

Ethanol exports to non-member states are falling steadily (508,000 hl in 2008).

Use of farmed alcohol in Europe came to 53.5 million hectolitres (mhl) in 2008, broken down into fuel (29.1 mhl), food (11.9 mhl), industrial (8.5 mhl) and miscellaneous (4 mhl).

Recent changes in bioethanol alcohol production in Europe (x 1000 hl)

<table>
<thead>
<tr>
<th></th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
</tr>
</thead>
<tbody>
<tr>
<td>France</td>
<td>8,500</td>
<td>11,500</td>
<td>15,453</td>
<td>18,500</td>
</tr>
<tr>
<td>Germany</td>
<td>7,550</td>
<td>7,000</td>
<td>8150</td>
<td>10,500</td>
</tr>
<tr>
<td>Spain</td>
<td>4,782</td>
<td>5,733</td>
<td>5,439</td>
<td>5,900</td>
</tr>
<tr>
<td>UK</td>
<td>2,800</td>
<td>4,868</td>
<td>3,500</td>
<td>5,800</td>
</tr>
<tr>
<td>Poland</td>
<td>2,790</td>
<td>1,979</td>
<td>1,900</td>
<td>4,000</td>
</tr>
<tr>
<td>Other</td>
<td>7,598</td>
<td>8,147</td>
<td>10,933</td>
<td>15,620</td>
</tr>
<tr>
<td>Total EU</td>
<td>34,020</td>
<td>39,227</td>
<td>45,375</td>
<td>60,320</td>
</tr>
</tbody>
</table>

Source: CEDUS - From F.O. Licht and the European Commission.

In France, ethanol is produced mainly from beet, but the proportion from cereals is growing rapidly. In 2008, the volumes of bioethanol incorporated into petrol were 8.6 mhl (683 kt) including 2.8 mhl incorporated directly (219.4 kt) and 5.9 mhl (467 Kt) in ETBE, ensuring an effective rate of 5.55% (LHV), slightly below the objective of 5.75%.
Alcohol production in France (thousands of hectolitres)

<table>
<thead>
<tr>
<th></th>
<th>2005-06</th>
<th>2006-07</th>
<th>2007-08</th>
<th>2008-09</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beet</td>
<td>5,232</td>
<td>6,438</td>
<td>9,051</td>
<td>8,467</td>
</tr>
<tr>
<td>Cereals</td>
<td>1,433</td>
<td>1,509</td>
<td>2,885</td>
<td>6,571</td>
</tr>
<tr>
<td>Wine-related</td>
<td>857</td>
<td>1,138</td>
<td>709</td>
<td>700</td>
</tr>
<tr>
<td>Synthetic</td>
<td>1,030</td>
<td>1,151</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>Other</td>
<td>32</td>
<td>36</td>
<td>148</td>
<td>274</td>
</tr>
<tr>
<td>Total</td>
<td>8,594</td>
<td>10,272</td>
<td>12,796</td>
<td>16,012</td>
</tr>
<tr>
<td>Including bioethanol</td>
<td>5,400</td>
<td>7,900</td>
<td>10,300</td>
<td></td>
</tr>
</tbody>
</table>

Source: CEDUS -- Statistical memo, from CGB, SNPAA.

It should be noted that in France, biofuels are supported by two measures:

- Objectives for incorporation into fuels (6.25% of the total energy content of fuels in 2009, 7% in 2010), along with a general tax on polluting activities (TGAP) paid by fuel distributors in the event of the objectives not being honoured.
- Partial exemption from the domestic consumption tax (TIC) which is undergoing unfavourable changes. The TIC on petrol is €0.58/hl. That on bioethanol was €25.92/hl in 2006-2007. It was €37.92/hl in 2009 and will amount to €40.92/hl in 2010. No exemption is planned for 2012, even though petrol is favoured by its higher energy content by volume unit.

According to the CGB, in 2008 France imported over 10% of its ethanol consumption classified in a variety of low customs rate categories.

The main fuel bioethanol producers in France are listed in the table below.

Main fuel bioethanol producers in France

<table>
<thead>
<tr>
<th>Company</th>
<th>Sites</th>
<th>Commissioned</th>
<th>Raw material</th>
<th>Production capacity</th>
<th>2010 approvals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tereos</td>
<td>Origny (Aisne)</td>
<td>10/2006</td>
<td>Beet</td>
<td>240,000 t</td>
<td>70,000 t</td>
</tr>
<tr>
<td>Tereos</td>
<td>Lillebonne (Seine Maritime)</td>
<td>6/2007</td>
<td>Cereals</td>
<td>240,000 t</td>
<td>160,500 t</td>
</tr>
<tr>
<td>Cristal Union</td>
<td>Bazancourt (Marne)</td>
<td>1st phase 6/2007 Q2: 02 / 2009</td>
<td>Beet / glucose Cereals</td>
<td>120,000 t</td>
<td>167,500 t</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>160,000 t</td>
<td></td>
</tr>
<tr>
<td>Abengoa</td>
<td>Lacq (Pyrénées Atlantiques)</td>
<td>2007 09 / 2008</td>
<td>From wine Cereals</td>
<td>40,000 t</td>
<td>120,000 t</td>
</tr>
<tr>
<td>Roquette Frères</td>
<td>Beinheim (Bas Rhin)</td>
<td>04 / 2008</td>
<td>Cereals</td>
<td>160,000 t</td>
<td>95,000 t</td>
</tr>
</tbody>
</table>

Source: SNPAA
Productivity of different crops

It is difficult to compare farming models in very different climates and with different levels of intensification – and therefore cost prices. It is nonetheless interesting to examine the use of land required by the production of ethanol according to current models.

<table>
<thead>
<tr>
<th>Crop</th>
<th>l of ethanol / ha</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar cane</td>
<td>7500 (→ 9000?)</td>
<td>The promoters of GMO sugar cane are aiming for 12,000 l/ha!</td>
</tr>
<tr>
<td>Beet</td>
<td>6500-7500 (→ 8500?)</td>
<td>Regular growth in yields in France.</td>
</tr>
<tr>
<td>Maize</td>
<td>3500 -4500</td>
<td></td>
</tr>
<tr>
<td>Wheat</td>
<td>3000</td>
<td></td>
</tr>
<tr>
<td>Sweet sorghum</td>
<td>4500</td>
<td></td>
</tr>
<tr>
<td>Lignocellulosic plantation</td>
<td>-</td>
<td>Objective of 9000 l/ha</td>
</tr>
</tbody>
</table>

The price of ethanol in the European Union is aligned to a great extent with that ex Brazil, to which the freight costs and customs duties must be added.
III.1.3 – ETHANOL DERIVATIVES

In the 2004 US DOE study, ethanol was not considered to be a platform chemical. Before then, Brazil had however already envisaged the development of an industry using ethanol as a precursor for a large number of synthetic intermediates. In their update in 2009, Bozell and Petersen not only included ethanol in their “top 10” list but gave it the best score for all classification criteria (cf. IV.1).

Apart from its traditional use in food, pharmaceuticals and industrial solvents, the rise of the production of plant-based ethanol is ensured by biofuel support policies. Mass productions have been implemented with tried and tested logistics chains and processes, the cost prices of which are regularly being improved. In such a context, given the volatility and structural rise in oil prices, it is only natural that various industrial companies are undertaking projects for the production of chemical intermediates from bioethanol.

Synthetic intermediates which can be produced from bioethanol.

Ethanol as a precursor of ethylene
Ethylene can be produced with good yields (99%) by catalytic dehydration of ethanol at temperatures of around 300 °C.

\[ \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \]

Matter ratios clearly show the mass losses associated with the conversion of an oxidised molecule into a reduced molecule:

\[ 1.66 \text{ t ethanol} \rightarrow 1 \text{ t ethylene or } 1 \text{ t ethanol} \rightarrow 0.6 \text{ t ethylene} \]
Using biosourced ethylene, the production of all its C2 derivatives can be implemented using traditional petrochemical processes.

There are still a limited number of industrial projects being implemented. As yet they are all located in Brazil, close to the resource with the desire to meet well identified demands for biosourced products.

- **The Belgian group Solvay is going to manufacture PVC (polyvinyl chloride) from ethylene produced by the dehydration of sugar cane ethanol in its integrated plant** (Solvay Indupa) in Santo André, Brazil. The bioethylene production capacity will be 60,000 tonnes per year, enabling the production of 130,000 t of vinyl chloride monomer. The site has a total production capacity of 360 kt one third of which will be biosourced in the future. The Brazilian company **Copersucar** will manage the supply of ethanol to Solvay.

- The Brazilian petrochemicals company Braskem has been carrying out active work on the production of biosourced polyethylene since 2007. **Braskem is currently building a plant with a capacity of 200,000 t/year of ethylene, which will be manufactured using bioethanol**. The unit is located on the Triunfo site and should be operational within the next few months. It will produce both high and low density polyethylene.

- In 2007, **Dow** and the Brazilian sugar group **Crystalsev** announced the project to set up a joint company to produce polyethylene from sugar cane ethanol. Since then, the economic crisis has occurred. Dow appears to have other priorities. Crystalsev and its indebted shareholder Santelisa Vale have been bought out by the French group **Louis Dreyfus**.

For the planned Braskem plant with an annual production capacity of 200,000 tonnes, the hourly production data should be of the following order of magnitude:

\[
41.5 \text{ t ethanol} \rightarrow 25 \text{ t ethylene}
\]

333,000 t of ethanol will be required for the annual operation of the factory.

Worldwide ethylene production capacity is approximately 150 million tonnes. The product spot price has ranged between €1 and €1.4/kg over the last few years. Worldwide polyethylene production is approximately 70 mt, with a price which has fluctuated between €1.25 and €1.65 over the past few years. The price of PVC has ranged between €0.7 and €1.2/t over the past few years.

**Other projects using plant-based ethanol**

In late 2009, **Braskem** and **Novozymes** announced the launch of a development project for the production of **polypropylene** from sugar cane for at least a 5-year period.

The volume of the worldwide polypropylene market was 44 million tonnes in 2008, with a value of US$ 66 million. The price of the product has ranged between €1.1 and €1.25/kg over the last few years.
III.2 - LACTIC ACID (C3)

Lactic acid is produced by the fermentation of glucose or saccharose. This product is therefore common to the starch and sugar production chains, although the tonnages from maize glucose still dominate the market. Lactic acid may also ultimately be produced by fermentation of the products of cellulose break-down. Lactic acid production is largely dominated by the Dutch company Purac (200,000 tonnes/year). The North American company Cargill – Natureworks, manufactures lactic acid as an intermediate for the production of the polymer PLA (polylactic acid), with an industrial capacity of 140,000 t. The Belgian company Galactic is the third-largest operator, producing 70 kt. The worldwide market volume is believed to be 350,000 - 400,000 tonnes, with steady growth of around 7% per year; the development of PLA explains a major part of this.

Lactic acid exists in the form of two optical isomers L(+) and D(-) which are found in identical proportions in the productions obtained synthetically. The form of lactic acid found naturally in living beings is L(+).

Several microorganisms (bacteria - in particular lactic bacteria such as Lactobacilli - as well as filamentous fungi) produce lactic acid from glucose or saccharose. The processes and strains used are industrial secrets. Certain microbial strains may also be selected to produce the D isomer.

During the production of lactic acid by fermentation, it is necessary to render the medium obtained pH-neutral to avoid inhibiting the reaction. Calcium carbonate is usually used. The calcium lactate obtained is then treated with sulphuric acid to produce lactic acid, the co-product being calcium sulphate (gypsum). The introduction of sulphuric acid into the system degrades the results of the analysis of the lactic acid life cycle and alternative solutions are being sought.

Lactic acid is a C3 molecule, the properties of which are closely linked to its carboxylic and alcohol functions.

The main use of lactic acid is as a food preservative. The chemical is also converted into various derivatives:

- **Ethyl lactate**, a solvent used as a cleaning agent in electronics.
- **2-ethylhexyl lactate**, a heavier chemical which has fast-growing applications in agro-chemicals to replace certain solvents.
- Other products such as propyl and butyl lactates, which are used as new solvents.
- And of course **PLA**, which is described below.

Lactic acid may be a platform chemical for the production of the following:

- **acrylic acid** with a non-negligible market (1.2 mt with a price which has varied between $1.1/kg and $2.45/kg over the last few years).
- **1,2 propanediol** and **monopropylene glycol** (a commodity, used as a food emulsifier, pharmaceutical solvent, cosmetics humidifier, antifreeze, etc. Its price in Europe over the last few years has ranged between €0.8 and €1.3/kg). Projects for the direct production of 1,2 propanediol by glucose or glycerol fermentation are currently being developed (ADM, Metabolic Explorer).
- pyruvic acid.

The development of these derivatives from lactic acid will depend directly on the price of crude oil. At $100/barrel, the production of acrylic acid would become profitable and at $130/barrel, that of 1,2 propanediol could be attractive.

**PLA or polylactic acid** is a polymer composed of lactic acid which is produced by cycles converting two lactic acid molecules into lactides, followed by their polymerisation after the beginning of the cycles.

![Chemical structures of lactic acid, lactide, lactide, and PLA](image)

Cargill and its subsidiary Natureworks, which has a production capacity of 140,000 tonnes, began large-scale industrial production in 2003 selling its PLA under the Ingeo® brand. New players are appearing on the PLA market. Industrial property issues are complex for this product. In March 2010, CSM/Purac announced the beginning of construction of a 75,000 tonne, 45 million euro, L- and D-lactide plant in Rayong, Thailand. It should be operational mid-2011. The Futerro joint venture, between Galactic and Total, already has a production capacity of 2000 t. There are thought to be other significant industrial projects, mainly in Asia but also in Germany. Other companies produce small quantities of PLA, often for medical applications.

Various forecasts for the potential market for PLA by 2020 made during the last few years advance figures ranging from 1.5 to 30 million tonnes. The industrial challenge is of course to reduce production costs for lactic acid in order to obtain a PLA which is competitive with polyethylene. A price of $2.5/kg appears to be feasible. Competing uses with other biosourced plastics currently being developed are barely taken into account in the forecasts announced.

<table>
<thead>
<tr>
<th>Forecast year</th>
<th>2008</th>
<th>2015</th>
<th>2020</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lactic acid not including PLA</td>
<td>260</td>
<td>415</td>
<td>525</td>
</tr>
<tr>
<td>Lactic acid for PLA</td>
<td>108</td>
<td>540</td>
<td>1215</td>
</tr>
<tr>
<td>Total lactic acid</td>
<td>368</td>
<td>955</td>
<td>1740</td>
</tr>
<tr>
<td>PLA</td>
<td>80</td>
<td>400</td>
<td>640-900</td>
</tr>
</tbody>
</table>

*Source: Galactic*
PLA is a thermoplastic polyester which can be used in films, fibres, thermoformed packaging and coverings. It has good properties in terms of transparency. Natureworks/Cargill are touting the environmental and life cycle analysis performance of its product.

The properties of PLA depend however on its lactic acid L and D isomer composition. First-generation PLA, made with the L monomer, has a low melting point at 180 °C. The same is true for D-monomer polymers. A PLA made from a mixture of both isomers would have a melting point as low as 140 - 150 °C! However, an appropriate mix of L- and D-polymers – manufactured separately - enables the production of so-called second-generation PLA, with a melting point above 230 °C. Both polymers have opposing helixes which become interlocked, forming a more stable structure.

![Melting points of different polymers – Interest of second-generation PLAs](image)

PLA is biocompostable but only in industrial conditions (slow biodegradability). The industrial companies in the sector such as Galactic and Cargill are therefore developing recycling processes to enable new production of lactic acid from PLA at acceptable costs.

The cost prices and market values of lactic acid, lactides and PLA enable them to travel; the industrial strategy consists of producing them where the raw material and other cost considerations are most competitive.
III.3 - 1,3-PROPANEDIOL (C3)

The petrochemical version of 1,3-propanediol (or PDO) is produced from ethylene oxide by Shell in a plant with a capacity of 70,000 tonnes.

Biosourced PDO can be produced by glucose fermentation but also using glycerol.

\[
\text{1,3 propanediol}
\]

\[
\text{HO} \quad \text{-} \quad \text{OH}
\]

Genencor has long been working with DuPont to produce a strain of *E. coli*, comprising genes from two other microorganisms (yeast and *Klebsiella*), which ensures the bioconversion of glucose into 1,3-propanediol. To use the technology, DuPont has formed Dupont Tate & Lyle Bio Products LLC, a joint venture with the starch manufacturer Tate & Lyle, and built a 45,000 t industrial plant in Tennessee (USA). It carried out its first commercial productions in 2008. Its capacity increased by 35% in 2010. The raw material for PDO used by DuPont Tate and Lyle is maize glucose.

The synthetic route for 1,3-propanediol in *E. coli* modified by Genencor

The French company Metabolic Explorer is said to have effective technology to produce PDO from glycerol. This is not yet the subject of a partnership or industrial use.

Polytrimethylene terephthalate or PTT

1,3-propanediol can be polymerised with terephthalic acid to form a saturated polyester, Polytrimethylene terephthalate (PTT). PTT fibre is more elastic and resistant than polyester fibres obtained using other diols (Polyethylene terephlate (PET), from ethylene glycol or polybutylene terephthalate (PBT), from butyl glycol). In addition PTT competes with nylon in the upholstery sector, offering a softer feel.
The product has been marketed since 1998 by Shell. It has various applications in films, as a resin and as a textile fibre (particularly in rugs and carpets). Shell markets its petrochemical PTT under the Corterra® brand whilst DuPont sells its product made from renewable PDO under the Sorona® (fibres) and Biomax® PTT (application in packaging) brands.

Sales of the Sorona® polymer fibre made from PTT by Du Pont are growing rapidly and are expected to reach US$ 200 million in 2010.
III.4 – FERMENTATION-BASED ISOPRENOIDS

Terpenes (or isoprenoids) have already been dealt with once in this study, in the chapter on lignocellulosic production chains. These chemicals are found in softwood trees and used directly from pine tapping or as co-products of the pulp industry. Terpenes are actually produced from a large number of annual shrub or tree plant species, as well as from certain bacteria.

Isoprenoids have more or less complex structures, produced by the condensation of isoprene type molecules with 5 carbon atoms. From the molecules in the basic metabolism, there are two pathways designated by the name of certain intermediates, which enable the production of a common precursor for various terpenes, isopentenyl diphosphate (IDP).

- The so-called 6-step mevalonic or mevalonate (MVA) pathway, from acetyl-CoA.
- The so-called DXP (1-Deoxy-D-Xylulose-5-Phosphate) pathway and also the MEP (2-C-methyl-D-erythritol-4-phosphate) pathway, from pyruvic acid and glyceraldehyde-3-P (G3P).

\[
\text{IDP (isopentenyl diphosphate)}
\]

IDP can be converted into isoprene or be condensed several times to produce terpene molecules of different sizes, the basic structure of which contains a multiple of 5 carbon atoms.

Interesting innovations currently being developed include introducing the elements from the plant metabolic pathways concerned into well-understood bacterial microorganisms (such as Escherichia coli) or yeasts. This enables the production of terpenes from sugar and glucose by fermentation.

Terpenes are hydrocarbons which can have massive applications as biomaterials and biofuels.

III.4.1 - ISOPRENE PRODUCTION

Isoprene is a polyisoprene monomer, an elastomer which is similar to the natural rubber used to produce tyres:

\[
\text{CH}_2=\text{C}^{\text{CH}_3}\text{CH}^{\text{CH}_2}\text{CH}_3
\]

Natural Rubber (NR), from rubber tree latex, is mainly composed of chains of poly(cis-1,4-isoprene): the exact nature of its terminal groups is not fully known. Petrochemical polyisoprene or Isoprene Rubber (IR) is produced from the C5 co-products of ethylene production. The processes used enable the production of poly(cis-1,4-isoprene) to be maximised.
Genencor (Danisco Group) and the manufacturer of Goodyear tyres have formed a partnership to produce bioisoprene by fermentation.

The basis of Goodyear’s strategic analysis is as follows: the group’s requirements for synthetic and natural rubber are increasing rapidly and constitute one quarter of its raw materials consumption. The prices of fossil-based products are experiencing structural increase and the worldwide production of rubber tree rubber does not offer sufficient growth prospects.

Genencor wishes to develop its metabolic engineering activity and has taken this opportunity to advance its positioning in the bioproduct value chain by producing bioisoprene itself: both for Goodyear and other customers and applications. The isoprene is produced in the form of a gas, which facilitates its purification considerably.

Pilot manufacturing of Bio-Isoprene is thought to be already effective but commercial production is not expected before 2013. The target market, which is that of high quality isoprene (cis-polyisoprene), is thought to account for over 850,000 tonnes of product with a value of 1 - 1.5 billion euros. This is in the context of a larger market of some 5 million tonnes of potential applications for isoprene.

III.4.2 – BIOFUEL TERPENE PRODUCTION

The North American company Amyris Biotechnologies Inc. has gained major expertise in fuels and is developing production technology by fermentation (from sugars) for hundreds of terpene chemicals which can be used directly as diesel fuel, fuel for petrol engines or aviation fuel.

These are mainly C15 isoprenoids, like farnesene, to replace diesel directly after hydrogenation, and geranyl pyrophosphate (GPP) C10 derivatives: pinenes which can be hydrogenated into tetramethylcyclohexane, which can be used as a substitute for petrol or be incorporated into it.

C15 farnesene can be synthesised into a microorganism from IPP by the action of a farnesene synthase. It can then be hydrogenated into farnesane.
C10 geranyl pyrophosphate (GPP) can be produced in one metabolic step from IPP (the enzyme necessary is Geranyl diphosphate synthase).

\[ \text{\textalpha-pinene, which may be produced by modified Amyris yeasts.} \]
\[ \text{Limonene, another C10 terpene which can be produced from modified Amyris yeasts.} \]
\[ \text{One of the isomer forms of C10 tetramethylcyclohexane, which can be produced by hydrogenation of C10 terpenes.} \]

The Brazilian subsidiary of Amyris concluded several partnerships in late 2009 with major sugar producers active in the country, in order to use this technology: the international group Bunge, the Brazilian company Cosan, and Açúcar Guarani, the Brazilian subsidiary of the French cooperative group Tereos. During the same month, Amyris bought shares in the Boa Vista ethanol production plant belonging to the São Martinho group and is going to build its first farnesene manufacturing plant with an annual capacity of 100,000 m³ on the site.

In the United States, Amyris has been awarded a 25 million dollar subsidy by the US energy ministry to produce biodiesel from sweet sorghum. Amyris also has operations in Australia.

On 23 June 2010, the announcement that the French petroleum group Total had bought a 17% share in Amyris' capital once again demonstrates the interest aroused by the technologies developed by the North American company. Other announcements followed shortly afterwards, with the signature of partnerships with the Italian PET specialist, M&G – Mossi & Ghisolfi, which is working on second-generation fuel projects. More originally and further away from biofuels, an agreement has been concluded with Procter and Gamble to develop speciality products from among this group’s ranges.
III.5 - BUTANOL, ISOBUTANOL AND ISOBUTENE

These chemicals have the common feature of all being C4 and having possible applications in the field of fuels. Nevertheless they have different properties: butanol (n- or 1-butanol) and isobutanol are alcohols, one in the form of a linear chain, the other with branches, whereas isobutene is a hydrocarbon.

The emergence of production projects for these 3 chemicals is largely supported by public and industrial desire to develop second-generation biofuels, using, in the long term, a vast array of lignocellulosic raw materials. In 2005, these 3 chemicals were not very engaging as avenues whereas today there are a large number of companies actively working on the development of efficient production processes. Compared with ethanol, butanol and isobutanol have several advantages: stronger energy density; less hydrophilic; better compatibility both with fuel storage/transport infrastructures and with common automobile engines; lower vapour pressure; less corrosive. **Isobutanol is particularly compatible with diesel fuel, whereas butanol can be mixed with petrol.**

These three chemicals are now produced petrochemically and are also used in large quantities, for different uses, as are their derivatives, in solvents, varnishes, paints and polymers such as elastomer or thermoplastics.

**Butanol** is traditionally produced from propylene using the “oxo process”. The product has direct uses as a solvent in varnishes, paints and adhesives. Its derivatives (butyl acetate, butyl metacrylate, dibutyl phtalate [which now have limited uses]) have various applications (solvents for lacquers and varnishes and also as an “apple” food aroma in the case of butyl acetate, thermoplastics for polycrylates, plastifying agents for phtalates, etc.). Worldwide demand for butanol is estimated to be between 3.5 and 4 million tonnes for a value of some 4 billion euros. The price of the product has varied between €750 and €1200/t over the last few years. The main producers are BASF, Dow, Cel-Oxeno, Kyowa, etc. Butyl acetate has undergone fairly similar changes in price over the past few years, between €850 and €1170/t.

![Propylene, Butyraldehyde, Butanol](image)

N-butanol is naturally one of the so-called ABE fermentation products (acetone-butanol-ethanol) produced from *Clostridium acetobutylicum*. Large Chinese plants still produce butanol using this fermentation model. Recent project use selected mutant or GMO strains enabling specific production of butanol, one of the limiting factors being its toxicity for the microorganisms concerned. More tolerant strains and continuous or semi-continuous extraction processes are therefore necessary. The development of butanol production projects is often linked to that of second-generation biofuels, with lignocellulosic biomass as the target raw material in the medium term.

**Isobutanol** (2-méthylpropane-1-ol) is a branched butanol isomer which has slightly different properties. Isobutanol is also used as a solvent in varnishes, paints, etc. Its derivatives are similar to those of butanol (isobutyl acetate, used as a solvent for paints and lacquers as well as for its aromatic properties in the perfume industry, Diisobutyl Phtalate (DIBP) with plastifying properties).
Isobutanol is also a natural product of carbohydrate fermentation. Its biosynthesis pathways are however different from those of butanol.

**Comparative properties of isobutanol, butanol and ethanol for fuels**

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Isobutanol</th>
<th>n-butanol</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 20 °C</td>
<td>0.802</td>
<td>0.810</td>
<td>0.794</td>
</tr>
<tr>
<td>boiling point at room temperature, T °C</td>
<td>108</td>
<td>118</td>
<td>78</td>
</tr>
<tr>
<td>Water solubility at 20 °C (g/l)</td>
<td>85</td>
<td>77</td>
<td>miscible</td>
</tr>
<tr>
<td>Vapour pressure at 20 °C (hPa)</td>
<td>5.6</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>RON (Research Octane Number)</td>
<td>96</td>
<td>107</td>
<td></td>
</tr>
<tr>
<td>Compatibility</td>
<td>Diesel</td>
<td>Petrol</td>
<td>(Petrol)</td>
</tr>
</tbody>
</table>

A large number of biotechnology companies – some which have been set up very recently – are positioned on the production of butanol by fermentation. It is not always clear whether their target is solely n-butanol or if isobutanol is also part of their objectives. However the same metabolic pathways are not used.

The barriers to be overcome are however similar: the products of the reaction are inhibitors of the strains which produce them; the yields must be increased, with greater flexibility as to the fermentation raw materials; the strains must be made more hardy, and the separation and purification processes more effective to enable continuous fermentation in the long term.

**Main companies working on butanol or isobutanol**

<table>
<thead>
<tr>
<th>Company</th>
<th>Country</th>
<th>Chemical</th>
<th>Technological platform</th>
<th>State of progress</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arbor fuels</td>
<td>USA</td>
<td>butanol</td>
<td>Yeast. Use of cellulosic biomass.</td>
<td>?</td>
</tr>
<tr>
<td>Butamax*</td>
<td>UK</td>
<td>Isobutanol and butanol?</td>
<td>Modified Clostridium and E. coli.</td>
<td>2013: commercial</td>
</tr>
<tr>
<td>Butalco</td>
<td>Switzerland</td>
<td>butanol?</td>
<td>GMO yeast metabolising C6s and C5s – use of lignocellulosic biomass.</td>
<td>?</td>
</tr>
<tr>
<td>Butyl Fuel</td>
<td>USA</td>
<td>butanol</td>
<td>GMO and mutant Clostridium</td>
<td>?</td>
</tr>
<tr>
<td>Cobalt Biofuels</td>
<td>USA</td>
<td>butanol</td>
<td>Non-GMO strain of Clostridium</td>
<td>2010: pilot 2012: commercial</td>
</tr>
<tr>
<td>Green Biologics</td>
<td>UK</td>
<td>butanol</td>
<td>GMO Clostridium</td>
<td>Demonstration in India under construction</td>
</tr>
<tr>
<td>Met Ex</td>
<td>France</td>
<td>butanol</td>
<td>GMO Clostridium acetobutylicum</td>
<td>Preliminary industrial pilot 2009</td>
</tr>
<tr>
<td>Syngas Biofuels</td>
<td>USA</td>
<td>butanol</td>
<td>Fermentation of syngas produced by thermochemical catalysis</td>
<td>?</td>
</tr>
<tr>
<td>Tetra Vitae</td>
<td>USA</td>
<td>butanol</td>
<td>Non-GMO Clostridium beijerinckii strain</td>
<td>Pilot 10,000 l in 2010</td>
</tr>
<tr>
<td>Other projects</td>
<td>China</td>
<td>butanol</td>
<td>ABE fermentation of selected Clostridium → GMOs</td>
<td>Major ABE productions</td>
</tr>
</tbody>
</table>

*Butamax is a joint venture between DuPont and BP.*

*From Pomotum for NREL – USA - Mars 2010, adjusted.*
**Isobutene or isobutylene** could be produced directly by fermentation in gas form and is easy to purify, (technology developed by the French start-up **Global Bioenergies**). There are different possibilities of producing isobutene from cell metabolism chemicals in very few biological reaction steps Isobutene can also be manufactured by dehydration of isobutanol (the pathway chosen by the North American company **Gevo**).

Isobutene is a basis for the manufacture of oxygenated fuel additives such as MTBE (methyl-tert-butyl ester = \( \text{H}_3\text{C} – \text{O–C(CH}_3)_3 \), by reaction with methanol) and ETBE (ethyl-tert-butyl ester \( \text{H}_2\text{C–CH}_2–\text{O–C(CH}_3)_3 \)), by reaction with ethanol.

Isobutene is also the polyisobutylene monomer (polyisobutene, PIB), which has applications as a synthetic rubber (used notably as an inner lining for tyres, etc.) and also as a lubricant additive. The German company **Lanxess**, the world leader for synthetic rubber, revealed its interest in Gevo’s technology by becoming a shareholder in mid-2010.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Petrochemical production</th>
<th>Market</th>
<th>Applications</th>
<th>Fermentation production</th>
</tr>
</thead>
<tbody>
<tr>
<td>n–butanol = 1-butanol</td>
<td>( \text{C}<em>4\text{H}</em>{10}\text{O} )</td>
<td>Propylene (Oxo Process)</td>
<td>3.5-4 mt</td>
<td>Solvent, petrol additive. Derivatives: butyl acetate (solvent, aroma), butyl polyacrylate (thermoplastic), dibutyl phtalate.</td>
<td>Modified Clostridium acetobutylicum, Modified yeasts.</td>
</tr>
<tr>
<td>Isobutanol ( \text{C}<em>4\text{H}</em>{10}\text{O} )</td>
<td>( \text{C}<em>4\text{H}</em>{10}\text{O} )</td>
<td>Propylene carboxylation (via hydroformylation)</td>
<td>455 kt?</td>
<td>Solvent, diesel fuel additive Isobutyl acetate, (solvent, aroma), diisobutyl phtalate = DIBP (plastifying agents), paint additive.</td>
<td>Yeasts. Modified E. coli? Other?</td>
</tr>
<tr>
<td>Isobutene = isobutylene</td>
<td>( \text{C}<em>4\text{H}</em>{10}\text{O} )</td>
<td>Catalytic dehydrogenation of isobutane. Dehydration of isobutanol.</td>
<td>3 mt?</td>
<td>Precursor of ETBE and MTBE (oxygenating additives for fuels). PIB monomer (elastomer). Possible precursor of P-xylene, isoctene, etc.</td>
<td>Direct production in gas form. Dehydration of bio-isobutanol.</td>
</tr>
</tbody>
</table>

According to Gevo, the potential isobutanol market in the chemicals industry is broken down as follows: 455 kt (direct uses of the chemical), 3 mt for the production of isobutene and 33 mt for the production of P-xylene! For biofuels, the potential markets are highly attractive: some 500 million tonnes… Quantity will therefore not be a limiting factor for these markets!
Gevo has carried out a retrospective simulation of aviation fuel prices, for fuels made with corn starch isobutanol produced using its technology (diagram below). Comparison with actual kerosene prices shows once again the better stability of plant raw material prices but without including the changes to market regulations which would be caused by the development of their mass use as an energy source and the possible speculation arising from it.

**Retrospective simulation of price changes for Gevo isobutanol, made using maize starch compared to kerosene price changes**

*Source: EIA, OPIS, Gevo estimates*

*Standard Deviation (Month over Month % Change)*
- Gevo Jet Fuel: 18.8%
- Petroleum Jet Fuel: 68.1%

*Source: Gevo, 2010.*
IV - CROSSCUTTING ELEMENTS

This chapter presents various salient crosscutting elements with respect to the development of plant chemistry and biorefineries and the industrial operations they constitute.

IV.1 – THE FUTURE OF THE 2004 TOP 10 BUILDING BLOCK CHEMICALS

In 2004 the US Department of Energy (US DOE) had a study carried out which was entitled “Top Value Added Chemicals From Biomass - Volume I: Results of Screening for Potential Candidates from Sugars and Synthesis Gas”, the aim of which was to list the chemicals which could be derived from biomass with particular potential as platforms for the chemicals industry. Only chemicals produced from sugars and syngas were taken into consideration in this initial study.

300 chemicals were reviewed and were the subject of initial assessments. These did not make it possible to sufficiently reduce the number of “candidate” chemicals. By analogy with the petrochemical classifications for 8-9 platform chemicals, the biochemicals were classified as “building blocks”, according to their number of carbon atoms. These building blocks had been assessed iteratively according to a new set of criteria, including estimated raw material and production process costs, the technical complexity of the best available production processes, the number of functionalities and the abundance of derivatives, current uses in the present-day chemicals industry, sales prices and potential markets.

50 and then 30 (the “top 30”) chemicals were thus selected. They all have multiple functionalities which enable them to produce many different derivatives, as well as the potential to be produced from lignocellulose and starch. They are not aromatic chemicals derived from lignin and were not yet established commodities in 2004.

A second round enabled the list to be reduced to 14 chemicals appearing in a 12-line table, given the related nature of certain chemicals. The celebrated “top 10” list was drawn up in this way - but it has never strictly speaking been a list of 10!

The European project BREW was specifically devoted to the study of the impact of white biotechnology. Its final report in September 2006 presented a comparative analysis of different products, chosen according to the following criteria:

- Substances produced from biomass in large quantities, using biotechnology.
- Commodities now produced from fossil resources with the prospect of being produced from biomass, with processes involving the use of biotechnology.
- New biosourced chemicals offering functional analogies with petrochemically-produced chemicals.
- Potential biosourced platform chemicals which may be the source of a large number of derivatives with the prospect of being produced in large quantities.

27 “emerging biotechnologically produced” building-block chemicals were then selected according to an adjusted list of criteria:

- Potential for functional substitution for petrochemically produced substances and derivatives.
- Diversity of derivatives which can be obtained from the chemical, relating to its own functionalities.
• Strategic interest, relating to market prospects and other factors in the future development of the chemical.
• Technical complexity of synthesis pathways for the chemical from biomass and production of derivatives.

At the end of 2009, almost ten years after the first DOE report, two of its authors (Bozell and Petersen) re-examined the previous list, in the light of the following 9 criteria:

(1) Plentiful supply of literature (and therefore previous research) on the chemical.
(2) Chemicals whose production is associated with a technology which is applicable to a large number of products.
(3) Potential for direct substitution for petrochemicals.
(4) Manufacturing technology for the product applicable to large quantities.
(5) High potential as a platform (= with a large number of derivatives).
(6) Pilot or industrial productions currently being developed.
(7) Chemical already marketed.
(8) A product which can constitute a “building block” for biorefineries.
(9) Well-established commercial production from renewable carbon sources.

Comparison of three studies
A comparison of the 3 lists of chemicals obtained was carried out in the table on the following page. As Bozell and Petersen’s 9 criteria are expressed as “+”, “++” or “+++”, we have taken the liberty of counting the total “number of pluses” for each chemical, allocating a score out of 27 to each of the chemicals taken into account.

The table includes a total of 38 chemicals. Several comments can be made:

(1) Only 5 chemicals: glycerol, 3-hydroxypropionic acid (both C3), succinic acid (C4), levulinic (C5) and sorbitol (C6), were selected in all 3 studies.

(2) Ethanol, which has been produced from biomass since ancient times, does not appear in the 2004 DOE study. Bioethanol was then considered to be a biofuel rather than a platform for the production of major chemical intermediates. The implementation of projects for the production of polyethylene (Braskem) and PVC (Solvay), in Brazil, has encouraged the inclusion of ethanol and its derivatives – via ethylene chemistry – in the updated “top 10” list (which is now a list of 13!). Unknown in 2004, ethanol has become one of the top 3 chemicals in the 2009 study!

(3) Glycerol is one of the rare chemicals to appear in all 3 studies. It received the same maximum score as ethanol in 2009. It is true that the development of first-generation biodiesel enabled the quantities of glycerol to be increased by a similar amount, bringing down prices. There are a large number of current (epichlorhydrin) and potential (PDO, etc.) derivatives but it is difficult to predict the long-term availability as, unlike ethanol, glycerol will not be part of lignocellulosic production chains. In an even more hypothetical future, will it be a mass co-product of third-generation biofuels made from microalgae? Or a co-product of a broad oilseed chemistry, rejuvenated by the rising prices of fossil raw materials? Could glycerol, eventually at some future point in time to be defined, be produced from lignocellulosic biomass sugars?

(4) 3-HPA (3-hydroxypropionic acid) is another chemical whose interest was confirmed between one study and the next. The most visible project is that of Cargill and Novozymes, but this remains a long-term procedure (it was already made public in 2005).
<table>
<thead>
<tr>
<th>C</th>
<th>Nature</th>
<th>Chemical</th>
<th>DOE 04</th>
<th>BREW 06</th>
<th>Bozell 09</th>
<th>Biomass origin</th>
<th>State of development</th>
<th>Applications</th>
<th>Producers</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Carboxylic acid</td>
<td>Acetic acid</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>Sugar, starch (cellulose)</td>
<td>Commodity</td>
<td>Biofuel, (PE, PVC)</td>
<td>ADM, Cargill, Tereos, etc.</td>
</tr>
<tr>
<td>2</td>
<td>Alcohol</td>
<td>Ethanol</td>
<td>-</td>
<td>+</td>
<td>27</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Acrylic acid</td>
<td>Glycerol</td>
<td>Top 10</td>
<td>+</td>
<td>27</td>
<td>Oils, biofuel co-product</td>
<td>Commodity</td>
<td>Epichtordrin, (HPA, PDO)</td>
<td>Arkema, OPX, Sofiproto, ADM, Cargill</td>
</tr>
<tr>
<td>3</td>
<td>Carboxylic acid</td>
<td>3 HPA</td>
<td>Top 10</td>
<td>+</td>
<td>16</td>
<td>Starch, (glycerol)</td>
<td>Industrial R&amp;D</td>
<td>Acrylates, PDO</td>
<td>Cargill-Novozymes</td>
</tr>
<tr>
<td>3</td>
<td>Carboxylic acid</td>
<td>Lactic acid</td>
<td>Top 30</td>
<td>+</td>
<td>17</td>
<td>Starch, sugar</td>
<td>Commodity</td>
<td>Food, solvents, PLA</td>
<td>Purac, Cargill, Galactic, etc.</td>
</tr>
<tr>
<td>3</td>
<td>Carboxylic acid</td>
<td>Malonic acid</td>
<td>Top 30</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Alcohol</td>
<td>1,3 propanediol</td>
<td>Top 10</td>
<td>+</td>
<td>-</td>
<td>Starch maize (glycerol)</td>
<td>Commercial</td>
<td>Polymers and miscellaneous</td>
<td>DuPont (Met Ex)</td>
</tr>
<tr>
<td>3</td>
<td>Carboxylic acid</td>
<td>Propionic acid</td>
<td>Top 30</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td>BASF</td>
</tr>
<tr>
<td>3</td>
<td>Amino acid</td>
<td>Serine</td>
<td>Top 30</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Alcohol</td>
<td>1-butanol</td>
<td>Top 30</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Alcohol</td>
<td>1,4 - butanediol</td>
<td>Top 30</td>
<td>+</td>
<td>-</td>
<td>Glucose (xylose)</td>
<td>R&amp;D</td>
<td>Solvents, polymers, GBL</td>
<td>Genomatica</td>
</tr>
<tr>
<td>4</td>
<td>Carboxylic acid</td>
<td>Fumaric acid</td>
<td>Top 10</td>
<td>+</td>
<td>-</td>
<td>Starch, sugars</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Carboxylic acid</td>
<td>3-hydroxybutyrolactone</td>
<td>Top 30</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Malic acid</td>
<td>Top 30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Carboxylic acid</td>
<td>Succinic acid</td>
<td>Top 10</td>
<td>+</td>
<td>17</td>
<td>Starch</td>
<td>Pre-commercial</td>
<td>Bio Amber, Roquette, Purac</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Amino acid</td>
<td>Threonine</td>
<td>Top 30</td>
<td>-</td>
<td>-</td>
<td>Sugar, starch</td>
<td>Commodity</td>
<td>Feed</td>
<td>ADM, Ajinomoto</td>
</tr>
<tr>
<td>5</td>
<td>Alcohol</td>
<td>Arabinitol</td>
<td>Top 30</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Furan</td>
<td>Furfural</td>
<td>Top 30</td>
<td>+</td>
<td>18</td>
<td>Xylose (hemicellulose)</td>
<td>Commercial</td>
<td>Transfuran chemicals</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Amino acid</td>
<td>Glutamic acid</td>
<td>Top 10</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Isoprene</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>Sugar, starch</td>
<td>R&amp;D, pilot</td>
<td>Tyres, fuels</td>
<td>Genencor, Amyris</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Carboxylic acid</td>
<td>Itaconic acid</td>
<td>Top 10</td>
<td>+</td>
<td>-</td>
<td>Starch</td>
<td>Commercial</td>
<td>Itaconix</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Carboxylic acid</td>
<td>Levulinic acid</td>
<td>Top 10</td>
<td>+</td>
<td>21</td>
<td>Sugars, (lignocellulose)</td>
<td>Biofine/Biomelex technology</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Amino acid</td>
<td>Proline</td>
<td>Top 30</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Alcohol</td>
<td>Xylose, xylitol</td>
<td>Top 10</td>
<td>-</td>
<td>19</td>
<td>Hemicelluloses</td>
<td>Commercial</td>
<td>Furans</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Xyloonic acid</td>
<td>Top 30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Acronitic acid</td>
<td>Top 30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Adipic acid</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>Oils</td>
<td>R&amp;D</td>
<td>Polyamide 6.6 (= Nylon 6.6)</td>
<td>Verdezyne project</td>
</tr>
<tr>
<td>6</td>
<td>Citric acid</td>
<td>-</td>
<td>Top 30</td>
<td>-</td>
<td>-</td>
<td></td>
<td>Commercial</td>
<td>Food</td>
<td>ADM, Cargill</td>
</tr>
<tr>
<td>6</td>
<td>Furan</td>
<td>2,5 FDCA</td>
<td>Top 10</td>
<td>-</td>
<td>14</td>
<td>Fructose (starch)</td>
<td>R&amp;D</td>
<td>Polymers, fuels</td>
<td>Avantium</td>
</tr>
<tr>
<td>6</td>
<td>Carboxylic acid</td>
<td>Glucaric acid</td>
<td>Top 10</td>
<td>-</td>
<td>-</td>
<td>Glucose</td>
<td>R&amp;D</td>
<td>Rivertop Renewables</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Monosaccharide</td>
<td>Glucose</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>Starch, (sugar, cellulose)</td>
<td>Commodity</td>
<td>Glucose chemistry</td>
<td>Most starch producers</td>
</tr>
<tr>
<td>6</td>
<td>Furan</td>
<td>hMF</td>
<td>-</td>
<td>+</td>
<td>14</td>
<td>Glucose (starch)</td>
<td>Commercial</td>
<td>Plastics, fuels</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Levoglucosan</td>
<td>Top 30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Amino acid</td>
<td>Lysine</td>
<td>Top 30</td>
<td>-</td>
<td>-</td>
<td>Molasses</td>
<td>Commercial</td>
<td>Feed, pharmaceuticals</td>
<td>ADM, Ajinomoto</td>
</tr>
<tr>
<td>6</td>
<td>Sorbitol</td>
<td>Top 10</td>
<td>+</td>
<td>27</td>
<td>-</td>
<td>Starch</td>
<td>Commodity</td>
<td>Food, pharmaceuticals, isosorbide</td>
<td>A large number of starch producers</td>
</tr>
</tbody>
</table>
(1) **Lactic acid**, a long-standing product which is known for its many derivatives, was already identified as the precursor of PLA in 2004 but was not selected as part of the final “top 10”. PLA is a true innovation with potential for improvement of its characteristics: this has stimulated an interest for lactic acid.

(2) **Succinic acid** is found on all 3 lists and the growing number of industrial projects which are nearing completion demonstrates active industrial research. The development of major markets (and therefore good control of industrial costs) remains the future challenge.

(3) **Levulinic acid** also appears on all 3 successive lists. It is attractive due to its nature as a platform chemical but not yet the subject of major industrial development, thus remaining a chemical of the future, probably associated with the development of second-generation biorefineries.

(4) **Furfural** is a C5 furan. It is also a chemical whose mass future will depend on the success of lignocellulosic biomass processing technology. It is produced by the chemical conversion of xylose.

(5) **FCDA** is another furan but C6 and related to HMF. It is produced by the chemical conversion of fructose with growing yields, and has a large number of derivatives in polymers and additives.

(6) **Isoprene** only appears in the most recent study. The Genencor/Goodyear project was not announced until late 2008. This proves that prospective analyses by experts can be totally unaware of avenues with significant potential for impact.

(7) Having become cautious due to the example of Isoprene, Bozell and Petersen incorporated a thirteenth category of products in their new “top 10”, called “other hydrocarbons”, which is much less clearly defined than the other 12, and which we have not included in the table above. Projects such as that of Amyris, for the production of terpene biofuels, could be entered under the isoprene platform because IPP (isopentenyl diphosphate), a direct precursor of isoprene, forms the basis of the metabolic engineering involved.

(8) **C6 HMF** (hydroxymethylfurfural) has the same prospects as FCDA, to which it is similar. It is now produced from glucose by chemical conversion.

(9) **Sorbitol** is part of the group of chemicals which attract a constantly positive opinion. It has an important set of agrifood and pharmaceutical applications and its derivatives are actively developed for industry, particularly with isosorbide and its many derivatives in polymers.

(10) Several chemicals have disappeared in the 2009 “top 10” list, compared to that of 2004. This is the case notably of aspartic, glutamic, and itaconic acids, some of which have been commercially produced for a long time, but which the authors no longer considered to be sufficiently promising for the chemicals industry.

Going beyond these specific remarks, it can be concluded overall that the outlook is neither easy nor reliable, as it is prone to rapid changes. It can be satisfying to see the completion of projects relating to succinic acid, but worrying to realise that ethanol and isoprene were not taken into account six years ago. The studies concerned are still organised by researchers and experts, with the elements they have at their disposal, since industrial players are reluctant to communicate on subjects which are still at the exploratory stage. All of this is indicative of the current bustle of innovation as well as, in all probability, strategic risks which companies are obliged to take since they are convinced of the necessity for them to be positioned in this sector. Projects are completed only if major industrial players take over from researchers and start-ups and make the necessary investments.
IV.2 - SUBSTITUTES FOR FOSSIL PRODUCTS: SIMILARITIES AND ANALOGIES

In the development of biorefineries or major plant chemistry projects, **two complementary approaches** are taken, usually by different players:

- **The first consists of preferring existing markets and applications.** What is at stake in this case is to bio-source and make green chemicals identical to those produced petrochemically, in other words hydrocarbons and their derivatives. This is a technological and above all an economic challenge. The biosourced chemical must be competitive with its fossil-based counterpart. There do not appear to be any industrial companies basing their strategy on the hope of a sustainable premium on biosourced intermediate prices. However, the wager is that the structural increase in the price of petroleum-based raw materials will continue fast enough and will not affect the price of plant raw materials too greatly...

- **The second approach favours the development of a new form of chemistry,** based on unchanged biomass compounds, i.e. in highly oxygenated form. The issue at stake in the technological performance of production is a little less audacious as there is no longer any mass loss inherent in reduction reactions. It is however necessary to develop new applications and markets for products which are as yet poorly known by industrial companies at the end of the chain.

Production of ethylene and derivatives from ethanol (**Braskem and Solvay** projects), or epichlorhydrin from glycerol (**Solvay** project), are positioned clearly within the first approach. Although the chemicals produced are original, **Amyris’s technology as well as the Genencor / Goodyear project concerning isoprene also consist in reducing oxygenated biomass into terpene hydrocarbons.**

<table>
<thead>
<tr>
<th>Ethanol</th>
<th>Ethylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂-CH₂OH → CH₂=CH₂</td>
<td></td>
</tr>
<tr>
<td>C₂H₆O → C₂H₄</td>
<td></td>
</tr>
<tr>
<td>Molecular mass 46.07 → 28.05 (- 39%)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Glycerol</th>
<th>Epichlorhydrin</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOCH₂-CHOH-CH₂OH → CH₂-CH-CH₂Cl</td>
<td></td>
</tr>
<tr>
<td>\ / 0</td>
<td></td>
</tr>
<tr>
<td>C₃H₇O₃ → C₃H₇OCl</td>
<td></td>
</tr>
<tr>
<td>Molecular mass 92.09 → 92.5 (including 35 of Chlorine) (- 39% excluding Chlorine)</td>
<td></td>
</tr>
</tbody>
</table>

On the contrary, the production of isosorbide, succinic acid, lactic acid, 1,2 and 1,3 propanediol and their derivatives, etc. fall within the scope of the use of biomass maintaining its degree of oxygenation. Such chemicals can be the origin of derivatives which already have major applications (low market risk) or for which, on the contrary, development efforts are called for (high market risk).
Carbon and oxygen composition of certain platform chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Number of carbon atoms</th>
<th>% carbon mass</th>
<th>% oxygen mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>2</td>
<td>52</td>
<td>35</td>
</tr>
<tr>
<td>Ethylene</td>
<td>2</td>
<td>86</td>
<td>0</td>
</tr>
<tr>
<td>Glycerol</td>
<td>3</td>
<td>39</td>
<td>52</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>3</td>
<td>40</td>
<td>53</td>
</tr>
<tr>
<td>1,2 propanediol - MPG</td>
<td>3</td>
<td>47</td>
<td>42</td>
</tr>
<tr>
<td>1,3 propanediol</td>
<td>3</td>
<td>47</td>
<td>42</td>
</tr>
<tr>
<td>Propylene</td>
<td>3</td>
<td>86</td>
<td>0</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>4</td>
<td>41</td>
<td>54</td>
</tr>
<tr>
<td>n-butanol</td>
<td>4</td>
<td>65</td>
<td>22</td>
</tr>
<tr>
<td>Isoprene</td>
<td>5</td>
<td>88</td>
<td>0</td>
</tr>
<tr>
<td>Glucose</td>
<td>6</td>
<td>40</td>
<td>53</td>
</tr>
<tr>
<td>Isosorbide</td>
<td>6</td>
<td>49</td>
<td>44</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>18</td>
<td>77</td>
<td>11</td>
</tr>
</tbody>
</table>

It should be noted however that biomass sometimes contains a large amount of poorly- or non-oxygenated chemicals such as fatty acids in oilseed, or rubber latex.

Each of the approaches involves its own risks and uncertainties. Although it seems clear that optimum use of biomass must make the best use of its composition, it remains true that products such as fuels will remain, by nature, poorly- or non-oxygenated. It is particularly in the field of polymers that plant chemistry can innovate and develop chemicals which remain close to their raw material as regards their gross atomic composition and then offering better production mass yields.

IV.3 – THE IMPORTANCE OF INDUSTRIAL PARTNERSHIPS

There are fairly few innovative plant chemistry projects emerging on an industrial scale. Their implementation requires major investments and requires them to have been through all the scaling-up stages, which are particularly arduous with respect to biotechnological processes. Such projects generally call into play partnerships bringing together various players in the value chain.

The following scenarios may thus be found:

- **A player which has the know-how and logistical and industrial capacities necessary for the mobilisation and pre-processing of biomass.** This may be a starch producer, sugar or ethanol producer, oil producer or pulp producer.

- **A company specialising in biotechnology,** at least when it is at the heart of new conversion processes. A start-up, one of the two major enzyme companies (*Novozymes, Genencor-Danisco*) or a specialist division of a large group (*Cargill, Du Pont*) may be mobilised.

- **A chemicals company** which knows how to process and sell the chemical obtained on its own markets.

Practically speaking, three-way partnerships remain more difficult to manage than two-way partnerships; the partnerships observed are often formed around two players, before the progress of the project leads to the missing link being sought. When the conversion of the biochemical into a synthetic intermediate is carried out using a chemical process, the biotechnology partner obviously does not exist, but may be replaced by a chemical process specialist.
The following examples can be listed:

<table>
<thead>
<tr>
<th>Product</th>
<th>Biomass origin</th>
<th>Biomass mobiliser and pre-processor</th>
<th>Biotechnology company</th>
<th>Chemicals company or user</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycolic acid</td>
<td>Starch</td>
<td>Roquette</td>
<td>Met Ex</td>
<td>?</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>Starch</td>
<td>Roquette</td>
<td>Met Ex</td>
<td>DSM</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>Starch</td>
<td>Siclae</td>
<td>Bio Amber</td>
<td>?</td>
</tr>
<tr>
<td>Farnesene and derivatives</td>
<td>Sugar</td>
<td>São Martinho, Bunge, Cosan, Tereos,</td>
<td>Amyris</td>
<td>M&amp;G, Procter &amp; Gamble, Shell, Soliance, Total.</td>
</tr>
<tr>
<td>3-HPA</td>
<td>Starch</td>
<td>Cargill</td>
<td>Novozymes</td>
<td>To be defined</td>
</tr>
<tr>
<td>Isoprene</td>
<td>Sugar</td>
<td>To be defined</td>
<td>Genencor</td>
<td>Goodyear</td>
</tr>
<tr>
<td>L-Methionine</td>
<td>Starch</td>
<td>Roquette</td>
<td>Met Ex</td>
<td>Roquette?</td>
</tr>
<tr>
<td>PHA</td>
<td>Starch</td>
<td>ADM</td>
<td>Metabolix</td>
<td>?</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>Ethanol?</td>
<td>?</td>
<td>Novozymes</td>
<td>Braskem</td>
</tr>
<tr>
<td>1,3 Propanediol</td>
<td>Starch</td>
<td>Tate &amp; Lyle</td>
<td>Du Pont</td>
<td>Du Pont</td>
</tr>
<tr>
<td>PVC</td>
<td>Cane ethanol</td>
<td>Copersucar</td>
<td>Not applicable</td>
<td>Solvay</td>
</tr>
</tbody>
</table>

The oldest biorefineries were established at starch producers, sugar producers, ethanol producers, oil producers and pulp plants. They occupy large industrial sites, since raw material unloading and storage zones require significant volumes or surface areas. The pre-processing of raw materials uses major installations and equipment.

Food processing companies have developed chemical conversion workshops on their sites to process certain chemicals, broadening their range of products and positioning in the chemicals industry value chain.

Chemicals company rarely carry out the opposite approach, which would be to integrate part of their upstream supply in order to have better control of it. When the approach of producing biosourced chemicals is their own initiative, they seek credible partners, who are able to supply them, forming joint ventures with them as and when this is necessary.

The development of industrial biotechnology has led to new opportunities; certain biorefineries have been equipped with additional workshops. In some cases the development of processes has been completed on site. In such cases the biotechnology company acts only as a service provider, transferring the licence for a process, delivered at the pilot or preindustrial stage.

The history of biotechnology companies often begins in a university laboratory which has developed particular know-how on certain strains and certain metabolic pathways. Patents have been registered, generally relating to what is as yet purely intellectual property (strains, DNA sequences, metabolic pathways expressed in the laboratory, etc.) rather than industrial property.

The start-ups formed wish to demonstrate the potential of their technology, which is always lengthy and costly in spite of certain announcements. They therefore seek funding from investment companies and public grants. Strategies may therefore be differentiated. Some companies concentrate on core business upstream and get paid in royalties from licences they grant to industrial producers. Others on the contrary have the ambition of directly taking a larger share of the added value by carrying out the first step changes and supplying more elaborate processes, or by wishing to move from the status of technology supplier to that of chemical producer.
So, for instance, **Metabolic Explorer** is planning to produce 1,3 propanediol on a pilot scale. With ample capital and shareholders including major industrial players, **Amyris** is beginning pilot manufacturing of farnesene with the intention of becoming a producer of this chemical. **Genencor**, one of the two major industrial enzyme producers, is altering its strategy, with the objective of producing bioisoprene itself to be used by **Goodyear** as well as in other applications and by other customers. Danisco’s subsidiary also wishes to become a “biorefining” player in its own right rather than simply a service provider or biocatalyst supplier in the sector.

The plant chemistry value chain

![Plant Chemistry Value Chain Diagram](image)

*Source: Plant Chemistry Association*
IV.4 - BIOTECHNOLOGY AND BIOREFINERIES

IV.4.1 – WHITE BIOTECHNOLOGY TOOLS

The importance of white biotechnology in the development of biorefineries is evident at several levels:

- For *breaking down the macrochemicals* produced by biomass. Typically, hydrolase type *enzymes* are used.
- In the *production of platform chemicals by fermentation* (fermentation in liquid media).
- This is still marginal in the chemicals industry, in the production of pretreated substrates, by *fermentation in a solid medium*.

IV.4.1.1 - ENZYMES AND BIOCATALYSIS

Enzymes are proteins with a biocatalyst function; each is very specific to a substrate and a reaction. Enzymes are not destroyed by the reactions they help but are gradually degraded during the course of the industrial processes in which they are used; they are often lost at the end of a batch. In order to be active, an enzyme requires particular conditions (concentration in the substrate, temperature, pH) and, in certain cases, the presence of co-factors: organic biochemicals or mineral ions. Enzymes have long been used in various industrial sectors such as textiles (since the 1920s), detergents, starch production (since the 1950s-60s) and paper.

In the metabolism of living organisms, enzymes are catalysts for a wide variety of synthesis and degradation reactions. The industrial applications of enzymes, however, strongly favour the use of hydrolyases (amylases, proteases, cellulases, hemicellulases, lipases) which break down macrochemicals into smaller elements or monomers.

The industrial enzyme sector is highly concentrated, with a pronounced European leadership. Two Danish groups, Novozymes and Danisco, share two-thirds of the market between them (it should be noted however that Danisco’s subsidiary, Genencor, is of North-American origin).

The production of effective enzymes requires considerable know-how. The strains with enzymes having the desired properties must be identified (catalytic function, suitable pH and optimum temperature, stability in storage and process conditions for the application, reduced co-factor requirements, etc.) and companies then need to be in a position to produce them by fermentation, purify them and stabilise them. Genetic engineering technology now enables the expression and regulation of the enzymes sought in the most suitable microorganisms. Enzyme engineering technology enables the enzyme’s amino acid sequence to be reworked, for instance to improve its stability without altering its active site, etc.

**Starch enzymes and hydrolysis**

Starch hydrolysis has two stages:

- **Liquefaction and gelatinisation** of a concentrated starch suspension at 70-90 °C (but sometimes above 100 °C, in order to degrade the starch-fat complexes found in particular in corn grains). Various α-amylases then enable the amylpectin and amylose chains to be broken down into oligosaccharides (dextrins). α-amylases break down starch randomly, “in the middle” of the chains. Normally, α-amylases are active only in the presence of calcium.
• **Saccharification**, which consists of hydrolysing oligosaccharides into glucose monomers or maltose (= diglucose), in the presence of **glucoamylase** or **β-amylase** (which “attacks” attacks the chains at the end).

• If necessary, the conversion of glucose into fructose by an **isomerase glucose**.

**Lignocellulose hydrolysis enzymes**

Lignocellulose is a far more complex substrate than starch and it is more difficult to break it down at a later stage. It includes cellulose, hemicelluloses, pectins and, of course, lignin. Physico-chemical treatments always precede enzyme action.

**Cellulases** are a family of enzymes capable of breaking the beta-linked glucose chains which constitute cellulose at different points (1→4). They are classified into **endoglucanases**, which break the chains at the middle and are capable of attacking crystalline cellulose, **exoglucanases** which lyse the end of the chains and **β-glucosidases** which finalise the breakdown of the oligomers obtained into glucose molecules.

![Lyse sites in cellulose and cellulosolytic enzymes (simplified)](source)

Hemicelluloses bring together a more diversified group of enzymes, which are capable of breaking down more complex chains of hemicelluloses which can be composed of pentoses (xylose, arabinose), hexoses (glucose, galactose) and acid sugars. Certain hemicelluloses attack the centre of the chains, others the ends and others again the oligomers produced by the action of the former.

![Lyse sites of a hemicellulose high in xylose and the related hydrolases (simplified)](source)

Although pectin enzymes are produced and marketed, this is not yet the case of lignin enzymes, which are still hydrolysed mostly by thermochemical treatments.
Industrial producers have the capacity to manufacture purified enzymes but experience has shown that what are known as “cocktails” or enzyme compounds are most efficient in many different applications. This is particularly true for lignocellulose lysis which can only take place in the presence of many different enzyme activities.

Changes in the enzyme offer for biorefineries

This occurs in several directions. The following is observed particularly:

- Marketing of enzyme activities which are now traditional (hydrolases) but better suited to the conditions of more aggressive processes (high temperatures).
- A rapidly-growing offer of cellulase and hemicellulase cocktails at attractive prices, positioned as tools for the development of second-generation biorefineries. Genencor has thus announced that the cost of enzymes should not exceed US$0.50/gallon of lignocellulosic ethanol (i.e. 13 cents/l).

IV.4.1.2 - MICROBIAL FERMENTATION: FROM STRAIN SCREENING TO METABOLIC ENGINEERING AND SYNTHETIC BIOLOGY

Directed fermentations

For thousands of years mankind has been selecting microbial strains (“ferments”) for various food processing procedures. The most basic practice consists of using microbe populations found naturally in the environment and the substrate. Fermentations directed simply by controlling the conditions of the medium (nature of the substrate, any additives, aeration, etc.) are still used massively (water treatment, methanisation, silage of forage crops for animal feed, etc.).

The use of natural diversity

This was the foundation of recent developments and remains topical today. Particular strains can be sought to be used directly in fermentation processes, without using genetic engineering (Deinove strategy benefitting from the very broad diversity of deinococcus) or, on the contrary, only the genome fragments coding specific metabolic functions can sought in the microbial species studied. In both cases, particular attention is paid to microorganisms living in extreme media.

The constitution of “libraries” of varied microbial strains enables screening of them for their development on certain substrates and the production of certain chemicals, especially since robotised screening tools for the presence of substances (High-throughput screening - HTS) are being developed enabling the rapid, low-cost assessment of large numbers of strains.

Molecular biology and genetic engineering techniques enable high levels of expression of genes of the same microorganisms but above all the expression of genes from one species in another, thus transplanting a stage of a new metabolic pathway into bacteria or yeast of which the basic metabolism of which is fully known and understood.
Thus a small widely studied number of organisms are used as “technological platforms” or “microbial platforms”, with each company usually choosing one or two. These include the bacteria *Escherichia coli* and *Clostridium* and *Saccharomyces cerevisiae* yeasts. Patents which have been in place for a long time with a view to protecting these microbial species or certain of their strains themselves but some have now fallen into the public domain. DNA sequences, their expressions in these different microbial platforms and the applications for the strains obtained in the production of such or such a substance which are now subject to claims for intellectual or industrial property.

**Metabolic Explorer** has thus announced that it is working exclusively from *Escherichia coli* and *Clostridium acetobutylicum* bacteria. The production of 1,3 Propanediol for **Du Pont – Tate & Lyle** is carried out using an E. coli substantially modified by Genecor (cf. diagram below).

**Amyris**’s patents relate to the expression of metabolic pathways for the production of terpenes in various microorganisms but it appears to have a preference for *yeast* in industrial developments.

**Butalco** also uses *Saccharomyces cerevisiae* to produce ethanol from C6 and C5 sugars resulting from the breakdown of lignocellulose whereas Arbor fuels has butanol produced from this microorganism. **Butyl Fuel, Cobalt Biofuels, Green Biologics** and **Tetra Vitae** use various species and strains of *Clostridium* to produce butanol.

In the final analysis, **metabolic engineering** consists in using all the modern tools of biochemistry, molecular biology and microbiology to study metabolic pathways in various living organisms, identifying the corresponding enzymes and genes and having them expressed in the chosen strains. Metabolic engineering is defined as "the directed breeding of the formation of a product by the specific modification of metabolic pathways or the introduction of new pathways by the use of recombinant DNA technologies."

**A simplified representation of the metabolism of “reprogrammed” Escherichia coli for the production of 1,3 PDO by Genencor**

**Design and Built by Genencor**

**Source:** Genencor
For its implementation, metabolic engineering relies on genomics (knowledge of genomes), proteomics (knowledge of the proteins in an organism) and metabolic modelling which enables the natural metabolism of microbial strains to be described, and then have the metabolism of modified strains to be simulated “in silico” in order to make them produce a particular chemical.

According to Metabolic Explorer, it is appropriate to proceed with successive interactions, consisting in the following:

- Identifying the best biological pathways, using bioinformatics tools.
- Optimising the biological pathway from the raw material to the product
- Constructing the recombinant strain, using molecular biology tools
- Quantifying the modifications made
- Validating the effectiveness of the chosen metabolic pathway in silico.

The production or overproduction of a given chemical often implies upsetting the natural metabolism of the strain used, not only by incorporating new metabolic sequences into it but also by blocking certain reactions to avoid the chemical of interest being re-degraded by the microorganism.

The production of succinic acid is a good example as it is a chemical which is produced by all living organisms but which is not naturally accumulated or excreted. The creation of strains suited to the mass production of succinic acid will therefore consist of inhibiting or suppressing certain reactions of the basic bacterial metabolism which would tend to consume the succinic acid formed straightaway (cf. diagram on the following page).

In other cases, several parallel metabolic pathways may enable the desired substance to be obtained, by means of different synthetic intermediates. Metabolic engineering therefore consists of genuine flow management. The production of 3-hydroxypropionic acid (3-HPA) must respond to such an issue. Although it is simple on paper, its implementation appears in fact to be very complex, the work in progress by Cargill having been commenced many years ago (cf. diagrams on the following pages).
Modification of the Escherichia coli metabolism on a mutant of the K12 strain for the production of succinic acid

Production of 3-HPA: some elements for metabolic modelling

Design criteria:
- Energetics
- Maximum theoretical yield
- Availability of enzymes/genes
- Co-factor requirements of enzymes
- Intellectual property/FTO

Source: Bioamber
Source: DC Cameron, Cargill
The necessary metabolic engineering (inhibition of certain pathways)

Source: DC Cameron, Cargill

Synthesis biology, the most elaborate stage in metabolic engineering, consists in constructing – synthesising – all the parts of a microbial genome, according solely to the metabolic activities one wishes to see implemented by the microorganism thus constituted from scratch. The first laboratory results have been obtained very recently. The semantics may be more flexible and the construction of simple functional genomic fragments is sometimes considered to be synthesis biology already.

The long road to industrial development

The general concepts of metabolic engineering or synthesis biology appear simple, provided they are described in a vulgarised form. The rapid progress observed in the laboratory leads to the idea that “everything is possible”. Apparently, all that is needed is to programme a bacterium or yeast in the right direction, have a large fermenter impregnated with it and then recover the production after a few hours or a few days.

In fact, the changes in scale and industrial developments of biotechnological processes are particularly long, fastidious, risky and costly. A microorganism is a living being, the metabolism of which is an assembly of a very large number of synthetic and degradation pathways organised according to complex balances. A microorganism always produces a set of chemicals. The metabolites excreted in the medium are often inhibitors of the development of the microorganism itself as soon as they reach a certain level of concentration. Fermentation is therefore a complex operation, as are all the extraction and purification (downstreaming) operations which follow it.

The development of a production process by fermentation, from the selection of the chemical to the industrial pilot, is described by Metabolic Explorer in four stages, lasting a total of between 6.5 and 8 years. A full project, including the final industrialisation of the process, will therefore require at least ten years. These long lengths of time and the investments associated with them explain the requirements for capital in the sector and the as yet very modest number of projects reaching the industrial production stage. Many skills are required from bioinformatics, molecular biology, biochemistry and chemical engineering.
Development of strains, fermentation and purification processes: the Metabolic Explorer model:

With respect to the extraction and purification of the substances obtained, some of the previously quoted examples should be noted. During the production of succinic acid or lactic acid, the fermentation medium is neutralised, generally by calcium carbonate, otherwise the fall in pH would cause inhibition of the development of the strains used. In actual fact, calcium salts are isolated. These must be retreated with sulphuric acid to produce the corresponding acids, generating gypsum or another mineral co-product. Inversely, the purification of isoprene should be facilitated by the fact that the product will be obtained in gas form, separating it more easily from the liquid fermentation medium.
IV.4.1.3 - OUTLOOKS FOR SOLID SUBSTRATE FERMENTATION.

Solid substrate fermentation is a technology which is particularly suited to fungal microorganisms. Fungal microorganisms find it difficult to develop their mycelium in a liquid substrate because they gradually increase its viscosity, reducing oxygen circulation. Solid substrate fermentation is well-established, as it is used traditionally in Japan (koji fermentation) for the production of sake and “soy sauce”. Modern technologies consume particularly low amounts of water and energy.

Lyven, which has been a subsidiary of the Ingredients division of the Soufflet group since 2003, has developed a solid substrate fermentation technology in thick layers with a high yield.

In 2008, Soufflet initiated the Osyris programme, supported by the authorities (Industrial Innovation Agency), which aims to develop new solid substrate fermentation processes and new associated products.

Technology enables enzymes to be produced which may later be purified and — more originally — enabling the composition of a solid raw material to be modified. These may then be used in various applications. Some find their place in animal feed because the product obtained is enriched with vitamins and enzyme activities. The other applications which are more particularly of interest to this study concern the production of improved substrates for fermentations which will be implemented on more traditional models. These could be notably fermentations for the manufacture of intermediates for chemistry, which will become more effective through the use of these pretreated substrates.

IV.4.2 – THE ROLE OF BIOTECHNOLOGY IN THE PROJECTS IN PROGRESS

Biotechnology provides powerful tools opening up broad prospects, but as has already been mentioned, involving major constraints in terms of development. Although the range of chemicals which can be produced in the laboratory by culturing modified microorganisms (or soon, microorganisms created ex nihilo) is growing rapidly, there are still few industrial achievements. It is one thing to have a genetically and metabolically programmed strain, but another to use it in profitable industrial conditions. Biotechnology, and more particularly fermentation technology, offers two major advantages:

- The possibility of causing a whole set of reactions in a single step, which would need to be implemented successively using traditional chemical processes.
- Being able to work on non-purified raw materials, at low temperature and atmospheric pressure.

The development of biotechnology does not mean the disappearance of chemical processes – far from it. Once the platform chemicals have been produced from biomass, they must be converted or polymerised using more traditional processes.

The two examples presented on the following page offer a clearer understanding of the positioning of biotechnology in current industrial projects. The first brings together Cargill and Novozymes for the production of 3-HPA and acrylic acid from starch.

Biotechnology plays a role at two levels: in the use of enzymes to break down the biomass macrochemicals (in this case starch) and also in the implementation of fermentation processes to produce 3-HPA from glucose. Acrylic acid will be produced from this chemical using chemical processes.
Example of a partnership between starch-producing biomass user (Cargill) and an enzyme and metabolic engineering specialist (Novozymes).

Current petro-route for production of Acrylic Acid:

```
Propylene → Acrylic acid
```

New fermentation enabled route to Acrylic Acid

```
Starch, biomass → Glucose → 3-Hydroxypropionic acid → Bio-acrylic acid

Enzymatic process → Optimized pathway → Chemical downstream process
```

Source: Novozymes.

In the second example, the production of biosourced isoprene by Genencor/Danisco is a part of Goodyear’s polyisoprene production.

Positioning of biotechnology in biosourced polyisoprene production

Genencor will provide a biological “front-end” for the production of polyisoprene (synthetic rubber)

```
Current petroleum-derived method of producing polyisoprene

Crude oil → Refinery feeds an ethylene plant with multiple product/waste streams → C5 stream or “isoprene feedstock” → Purification capacity → Polymer-grade isoprene → Polymerisation capacity → Polyisoprene
```

Biological method for producing polymer-grade Biosoprene™ to be plugged into traditional polymerisation process to produce synthetic rubber

```
Feedstock (e.g. sucrose) → Fermentation process → Recovery and purification process → Polymer-grade Biosoprene™
```

Expected Goodyear footprint

Genencor footprint

Source: Genencor
IV.4.3 – GREEN BIOTECHNOLOGY

IV.4.3.1 - WORLDWIDE GROWTH OF GMOs

In 2009, 14 million farmers in 25 countries planted 134 million hectares of genetically modified crops. These figures are constantly growing. The USA has a total of 64 mha, Brazil 21.4 mha, Argentina 21.3 mha, India 8.4 mha, Canada 8.2 mha and China 3.7 mha. In Europe, Spain, Poland, Portugal, the Czech Republic, Romania and Slovakia grow GMOs. Paradoxically, France, Germany and few other countries have banned growing them but not imports.

Genetically modified seeds will be grown on 77% of soybean surfaces, 49% of cotton, 26% of corn and 21% of rapeseed surfaces worldwide. In the USA, 85% of the corn is GM which has usually undergone 3 modifications! It is impossible to want to be present on the American corn seed market without having herbicide- and insect-resistant varieties. Large-scale development is expected for rice and wheat, particularly in China.

Modifications currently included in commercial varieties relate essentially to agronomic characteristics (total herbicide resistance, with the advantage of not being very harmful to the environment; insect pest and virus resistance). The success of these GMOs is clearly linked to the elements of productivity they provide the farmer with, by limiting costly and sometimes toxic inputs and making yields regular. In different cases, the characteristics introduced are essential to the maintenance or local development of the crop, sometimes leading to the frequent errors of modern farming: only the most profitable crop and variety are grown, with all the inherent risks in the medium and long term, both in terms of plant protection (dissemination and concentration of fungal or bacterial pathogens) and the local economy (which depends on the price of a single crop).

Rapid growth in adoption of genetically engineered crops continues in the U.S.

Source: USDA
The position taken by France and certain other countries in the EU is surprising because it does not take into account the gains in productivity allowed by GMOs, nor the years of experience feedback as to the actual and supposed risks associated with the current GMO varieties. These countries import huge amounts of GMOs for cattle feed but ban growing them and thereby exclude themselves from the technological race which is underway. There is however considerable experience with GMOs (over 10 years' worth, and tens of millions of hectares) and few modern technologies have been tried and tested to the same degree. The weaknesses have been identified and relate mainly to the fact that the use of GMOs must not do away with observance of the basic rules of agronomy (crop rotation and diversity). The distorted competition between our producers and those on other continents is becoming worrying; “GMO phobia” has become insidiously cultural in the population of certain EU countries, leaving no possibility of political decisions making up for the lag in competitiveness of our farming industry.

Our own farming production chains communicate regularly on the non-GM nature of our wheat, beet and rapeseed in the name of consumer expectations. This is however due to the influence of lobby groups, fostered by the development of obscurantist fears. The reasoning which makes constant reference to the precautionary principle is disastrous as no human enterprise or technological development is ever risk-free. Risk must not be an obstacle when the experience gained is such that such risk is minimal and likely to be managed adequately. If the fears we allow ourselves with regard to GMOs were applied to other sectors of activity, we would not have at our disposal any of the products of the industrial revolution, or more recently, those of new communication technologies.

In the competition between sugar cane and beet, genetic engineering technology will soon weigh in the balance. The curve showing the growth in yields of non-GMO beet in France appears particularly convincing as it offers hope that the competitiveness differential with sugar cane will be gradually reduced. This is in fact a naive conclusion as there is very active work on development of genetic engineering applications for sugar cane, and Brazil is not a country to deprive itself of technology which favours the productivity of its crops.

IV.4.3.2 - DOES BIOREFINING START IN THE CROP?

Although EU citizens seem to accept that genomes can be reprogrammed or even that microorganisms can be created from scratch to produce drugs or other chemicals by fermenters, they remain concerned that crops should not be modified by modern DNA tools.

Going beyond the irrational arguments put forward “against GMO plants” as well as the real constraints relating to their reasoned use in sustainable farming, the question may be asked as to whether it is more effective to modify a plant so that is produces a particular chemical or whether it is better to expect the plant to produce as much biomass as possible with little differentiation.

Superior plants are organisms which are much more complex than bacteria and yeast. Their productivity depends on a very large number of factors, from the scope of their leaf surface, direction, and similar crops’ migration performance, including the efficiency of metabolic processes in the various organs. The plant is compartmentalised at many levels and cannot by any means be considered to be a box containing a sequence of enzyme activities. Any modification to an element of the metabolism must be part of the overall physiology of the plant.

It takes a lot longer to obtain a genetically modified plant variety than to reprogramme the metabolic pathways of a bacterium. The molecular biology tools are however the same or closely related. In vitro culture techniques now enable plants to be multiplied very quickly. Agronomical assessment cannot however be shortened: this involves several complete crop cycles of the variety obtained and therefore as many seasons, lasting several months.
Construction and pilot trials followed by industrial implementation of modified microbial strains would therefore appear to be far quicker on paper than the development of GMO crop varieties. In actual fact, some ten or so years of R&D are required in both cases, before the completion of commercial applications. To date, the metabolic engineering potential is larger for microorganisms than for higher plants. The investments to be made are not however of the same order of magnitude and the changes of scale do not represent the same degree of industrial endeavour. In one case the factory is the plant: its modification is complex because there are a lot of interacting parameters but it is easy to use it on a large scale: the new variety is sown, grown and harvested. In the other case, the living organism under consideration is simple and relatively easy to reprogramme but it is necessary to build factories to use its potential. Plant genetic engineering is therefore of major interest, all the more so because metabolic engineering will make progress on certain key crop species. In the short term however, green biotechnology will retain as its preferential objective the improvement of crop yields through pest and drought resistance, etc.

GMOs and improvement of crop composition for biorefineries

With respect to the specific production by plants of chemicals which are of interest for the chemicals industry (not including pharmaceuticals), the commercial applications of plant genetic engineering are still at the early stage. As was previously explained, there is a major challenge as plants must be made to produce particular chemicals which are competitive with respect to alternative routes (other crop species in regions with low labour costs and without any environmental constraints, fermentation of biomass or sugars, etc.). The following examples can be listed:

- **Syngenta** markets corn, the grains of which express microbial amylase activity, which facilitates their use and improves yields for ethanol production.

- Potatoes with a high Amflora amylopectin content by **BASF** are not a recent innovation, with the first application for permission dating back to 1996, but approval by the European Commission was granted only in March 2010. The amount of negative reactions to this authorisation is symptomatic as the benefits are simply not mentioned by detractors (better industrial yields, less water and energy consumption).

- **Metabolix** is developing switchgrasses to produce PHA which can be extracted from the harvest before the remaining biomass is converted using second-generation processes.

- **Calgene** (now **Monsanto**) rapeseeds which are high in lauric acid were developed in the late 1990s and are still not used on a wide scale. The production of short-chain fatty acids in temperate countries is theoretically attractive but must be competitive with coprah or palm kernel oil.
The positioning of green and white biotechnology: an attempted summary

Genetic engineering technology

- Application to crops
  - Improvement of the general productivity of the crop
  - Modification of the composition of the crop
  - Production of specific chemicals in the plant
  - Biomass with Improved composition
  - Short-term conflict?
  - Biomass at optimised cost and availability

- Application to microorganisms
  - Enzyme production
  - Construction of specialised strains
  - Breakdown of pre-treated biomass
  - Production of specific chemicals
  - Purification and use
### IV.4.4 – CONCLUSIONS: BIOTECHNOLOGIES AND BIOREFINERIES

Green and white biotechnology both constitute tools providing new development prospects for biorefineries. They will not replace chemical processes where these perform well and are implemented for specific conversion steps, from chemical to chemical. Biotechnology presents major development and implementation costs. Its introduction into industrial processes takes time but is becoming increasingly widespread. The main advantage of biotechnology is to enable sequences of reactions to be carried out in a single fermentation step, using microbial strains with a highly reprogrammed metabolism.

#### Simplified comparison of some technology which can be used in biorefineries

<table>
<thead>
<tr>
<th>Technology</th>
<th>Strengths</th>
<th>Weaknesses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green biotechnology</td>
<td>- Productivity and metabolic capacities of the plants grown.</td>
<td>- Complexity of metabolic engineering on higher plants.</td>
</tr>
<tr>
<td></td>
<td>- “Simplicity” of farm production.</td>
<td>- Agronomic assessment and seed multiplication times.</td>
</tr>
<tr>
<td></td>
<td>- Complexity of metabolic engineering</td>
<td>- Non-acceptance of these technologies in certain EU states.</td>
</tr>
<tr>
<td>Fermentations – Metabolic engineering</td>
<td>- Potential of microbial metabolic engineering and synthesis biology to produce a specific chemical from heterogeneous biomass (non-purified substrates). Possibilities of carrying out several successive chemical reactions in an industrial step. - Simple process conditions (Dilute aqueous suspension, temperature: 30-40 °C, atmospheric pressure).</td>
<td>- Complexity of changes in scale during developments. - Complexity of conducting fermentation and maintaining a strain. - Complexity of extraction and purification operations. - Management of confinement of GMO or recombinant strain.</td>
</tr>
<tr>
<td>Enzyme treatments</td>
<td>- Diversity of existing enzymes.</td>
<td>- Relatively high cost.</td>
</tr>
<tr>
<td></td>
<td>- Potential of enzyme engineering (improved performance)</td>
<td>- One enzyme = one step on one substrate.</td>
</tr>
<tr>
<td></td>
<td>- Reactions easy to implement.</td>
<td>- Does not self-multiply.</td>
</tr>
<tr>
<td>Chemical processes</td>
<td>- Well-controlled.</td>
<td>- Suited to a homogenous substrate.</td>
</tr>
<tr>
<td></td>
<td>- Regularly implemented.</td>
<td>- Often high energy (high temperatures and pressure) and water consumption.</td>
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<tr>
<td></td>
<td>- Purification often simplified.</td>
<td>- Catalysts sensitive to impurities.</td>
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<tr>
<td></td>
<td></td>
<td>- May be polluting.</td>
</tr>
</tbody>
</table>
IV.5 – BIOFUELS AND PLANT CHEMISTRY

Just as petrochemistry was born following the mass production of biofuels, the development of plant chemistry depends largely on the technological progress and industrial achievements associated with biofuels.

- **The manufacture of alcohol** is thus a very ancient human activity, but the production of first-generation bioethanol on a very large scale has enabled the fermentation processes necessary to be optimised and the production chains concerned for mobilising biomass to be organised. Without this, the current projects for the production of ethylene and derivatives from sugar cane ethanol in Brazil would not have emerged. Bioethanol, which was considered only as a biofuel, has now become a platform chemical for the chemicals industry.

- **The production of first-generation biodiesel has significantly stimulated the renewal of oilseed chemistry.** The development of new applications for plant methyl esters and glycerol derivatives is booming, thanks to the grants and incentives in favour of first-generation biodiesel. This biodiesel plays an important structural role in oilseed production chains, ensuring the emergence of dedicated biorefineries.

- Projects for the production of butanol, terpenes and other hydrocarbons from biomass using biotechnological processes have appeared more recently and are funded due to the potential they offer for applications in biofuels. They thus benefit from major public support and direct investments from oil giants.

- **Second-generation biofuels, from lignocellulosic biomass,** are still at the research or pilot stage but are backed by a huge wave of public financial support, leading to many technological developments which will be of benefit to plant chemistry. They will enable the creation of production chains for the mobilisation of original biomass or the renewal of the pulp production chains.

- **The third generation of biofuels – which will be produced from growing microalgae** – is the subject of prospects which sometimes reach into the realms of fantasy. The production chain does not yet exist and its overall outlook is very hazy. Requirements in terms of land, nutrients, extraction technology, the future of co-products and residues with a high nitrogen and mineral content are all issues to be tackled. Notwithstanding all of this, major public and private financial support is already enabling innovative companies to explore new potential. Will the future microalgae crops be destined to produce biofuels or synthetic intermediates with greater added value? Time will tell, but in any case, the projects will have been carried forward by the prospect of producing fuels.

- For the sake of completeness, a few notable exceptions can be listed. **The starch producing chains are pursuing their development of synthetic intermediates without the future of these intermediates being necessarily associated with that of fuels.** Like all vegetable oils, castor oil can be used for the production of biofuels, but the uses bringing most value to this minor production chain are in the field of biomaterials.

In the political choices for sustainable development and energy policy, fuels are therefore a key topic, which is more easily taken into account by decision-makers and investors than those relating to the strategic needs of our chemicals industry and farming production chains. The strong public impetus and massive financial investments will support, as a priority, the development of biofuels, with plant chemistry often having to follow in their wake.
All stakeholders and decision-makers must take on board and accept these realities and learn the lessons, the very first being that continuity is necessary. First-generation biofuels cannot be supported for a few years and then deemed to be imperfect and abandoned too soon due to the direct competition with fossil products. Second- and third-generation biofuels will only have a chance to be successful if they carry on from the first generation, which enabled the construction of high performance industrial plants, the organisation and continuous improvement of the performance of several production chains and significant technological developments. The issue of the use of land for food or non-food has been oversimplified. There is no biomass resource, the use of which will not have an effect on the overall balance of the needs of our human societies and the protection of the environment. We will be increasingly obliged to manage limited resources, recycle products and limit waste. Second-generation biofuels will inevitably be associated with fresh competition in terms of uses and – we can safely assume – those of third-generation biofuels too. We must beware of playing down recent developments in order to dream about the future. In the transition in progress, continuity is absolutely necessary, both in the field of biofuels itself and in collateral developments in plant chemistry.

IV.6 – RISKS AND REQUIREMENTS OF PUBLIC POLICIES

As has just been mentioned, the development of fuels, chemicals and materials from biomass finds its place in a transitional economy. Sustainably managed use of renewable resources, produced from biomass, must replace immoderate and often polluting use of fossil resources which appear to be inexhaustible.

Although there is as yet no consensus among experts as to the exact positioning of peak oil, it is nonetheless acknowledged that the price of fossil resources is increasing inexorably and becoming more volatile. The price of oil is becoming less and less predictable, even though it is a key reference for all business plans for plant chemistry projects. Fundamentally, the products from this sector are in competition with petrochemicals.

Going well beyond the related effects of the development of bioethanol, plant raw materials markets have also undergone and may once again undergo fresh disruption. The populations of developing countries are growing rapidly and they hope, once their standard of living increases, to consume richer foods and animal protein. We must not be naïve; uncontrolled demographics are the main culprit in the destruction of the environment and tension on the prices of our farming raw materials.

Contrary to what can be read sometimes, illegal deforestation in the Amazon is not carried out in order to plant biofuel-producing crops but to extend soybean crops in order to satisfy the new plant protein requirements for cattle feed in Asia and other growing continents. In spite of the progress mentioned in the previous chapters as regards farming production capacities on this planet, the balances are unstable. A period of growth which was too rapid for a local economy, a poor harvest in a major farming region are enough to send reassuring curves showing slowly decreasing prices for farming commodities into worrying spikes. Our world will not experience sustainable security for food, energy and other requirements until it manages its demographics – something which is far from being the case.
The development of non-food outlets may also contribute to reducing the volatility of farm product prices, not only because it diversifies their markets but also because it helps stimulate increased yields and broadens the offer of vegetable proteins, which are plentiful in the co-products obtained. On the other hand, the greater economic importance which farming commodities may take on could accentuate their attractiveness for speculation, so regulation mechanisms for excessive speculation must be developed.

Lignocellulosic resources which can be used directly for second-generation biorefineries are also limited, and competition between their uses is growing rapidly. Choices will be necessary but they will not be any easier to make than those which are now necessary for the use of land and farming raw materials. The world is hungry for food but also for fuels, materials and chemicals.

The volatile nature of the prices of benchmark fossil fuel commodities, the increasing needs of populations, the collective desire to protect the environment and the economic transition required will take a long time and will be difficult, because there is no way that it can consist in quickly replacing one resource with another. We are entering an era of complexity which must be managed with determination and sufficient humility and flexibility. There is no resource which can replace oil completely. Coal and gas will occupy an increasingly large position and clean uses must be learned for them. Biomass may become a major resource for the production of fuels, materials and chemicals, but it will not cover, either now or in the future, all the requirements which are now met by the oil industry. It must be managed in a particularly shrewd manner.

Concerted public policies have never been as necessary as they are today. They must be sustainable and have high ambitions for the development of production chains. In this respect, the EU offers greater continuity in terms of the vision than national policies which are too often affected by shifts in opinion. The citizens of rich EU states rarely perceive the movements occurring in the world and the vital efforts we must make to adapt ourselves. It is only too easy to refuse GMOs and any means of increasing farming productivity in a region of the world where there is no hunger and farming is a protected industry! Moreover, we are late in reducing our energy consumption in a country where there is a widening gap between our electricity and gas prices and those on the worldwide market. With the false guilty conscience of Northern countries, we do not want farmland to produce anything other than food, but we only slightly reduce our fuel consumption when the price goes up too much.

In the field of biofuels and plant chemistry, the USA has taken determined steps which they adhere to without any pangs of conscience. Their aim is quite simply to be energy-independent as a country, something which we would hardly dare aim for ourselves. The resources are mobilised and the risks accepted. Several projects have received massive support which will enable them to emerge on an industrial scale.

In these sectors of the use of biomass products, the consistency of farming, industrial and energy policies is vital. The development of biorefineries, enabling us to build a more sustainable chemicals industry, will be possible only if the farming and forestry production chains are consolidated, efficient new technologies are invented and used, major industrial investments are encouraged and supported and recycling of new products is planned at the design stage.
IV.7 – EUROPE, USA, BRAZIL, ASIA

In 2005, the territory for biorefineries appeared to be focused on North America and Europe, with a lack of sufficient visibility of what could be afoot in Asia.

By 2010, the landscape had changed. There were many more bioethanol and biodiesel plants in the countries which had implemented support policies for their production (USA, EU, Canada, Brazil, etc.). There are still only a small number of operational biorefineries producing synthetic intermediates for the chemicals industry. These generally result from extensions on the same sites as traditional industries (starch production plants, sugar plants, oil plants and pulp plants).

Although the most abundant upstream innovation still comes from the USA, the location of new industrial plants is chosen according to two criteria:

- The local cost of plant raw materials and the suitability of established production chains to mobilise large quantities of them.
- The regional prospects for growth of markets which could be served by these biorefineries.

Development of biofuel plants is thus continuing, significantly reinforced by public incentives, using local farming raw materials, in North America, the EU and Brazil as well as in various Asian countries, to produce fuels for national consumption and exports.

Plants designed to manufacture synthetic intermediates, entering into head-on competition with their oil-based counterparts, are being built more especially in Brazil and Thailand to serve regional markets, which are experiencing much stronger growth than those in the EU.

It is thus symptomatic to see Solvay developing the Epicerol® technology and initiating production in France but shortly afterwards beginning the construction of a plant with a capacity ten times greater than this, in Thailand. The first manufacturing plants for bioethylene and derivatives will be opened in Brazil (Braskem, Solvay). Companies such as Amyris also come to build their industrial pilots in this country. Sugar cane is still the most plentiful raw material and the least expensive for producing sugar. The territory of Brazil offers tremendous potential for expansion of this crop, outside of the Amazonian regions to be protected. Purac will be manufacturing lactides in Thailand. The volumes of raw materials necessary are of a lesser order of magnitude than those mentioned above and the Thai cassava production chain, which is well structured, may supply cheap raw materials to a factory which will be located close to the most dynamic markets in the world.

Other projects are positioned in China and India but are less easy to apprehend for the purposes of this study.

In the EU and the USA there are projects for innovative chemicals, which meet stringent criteria in terms of sustainability, for which the markets are yet to be created. The new plants are generally a part of pre-existing agroindustrial sites. Those allocated to the production of first-generation biofuels will play an increasingly important role.

What vision of the future can we develop and implement in the EU? We have an array of strengths and weaknesses. Our farming production chains are productive and well-structured. Our capacity for mobilising farming biomass has been proven. We know how to manage our farmland and forests sustainably. Our pre-processing industrial tools are high-performance. Our chemicals industry is the world leader and we have many leaders in biotechnologies. Our consumers are among the most sensitive to sustainable development issues and demand biosourced products. The cost of our farming or forest raw materials nevertheless remains high and our economies have prospects for only low levels of growth. Our biofuel support policies are hesitant. Our research and industrial innovation capacity is, as a whole, less than that of the USA.
Our development must take these situational elements into account. We must identify which farming production chains perform the best in terms of supplying our industry. Before other regions in the world, we must optimise our models and industrial profitability and concentrate on products with high added value.

IV.8 – DEVELOPMENT AND KEY FACTORS FOR THE SUCCESS OF BIOREFINERIES

Maturity of the sector

The idealised biorefinery, corresponding to one of the descriptions presented in the introduction to this study, is not yet a very widespread reality. There are industrial plants manufacturing a wide range of products (starch production plants, etc.) but they are usually supplied with plant raw materials. A large number of plant chemistry units are currently being built but their objective is to produce a single chemical, from – at least to begin with – a single source of biomass. The use of co-products is incorporated into the business plan but has only a secondary role.

Before setting out what may be the key factors for the success of biorefineries, it is appropriate to clarify a certain number of points:

• **The biorefinery as described at the beginning of this study corresponds to an industrial model in a mature sector.** There are therefore a limited number of players, who compete strongly in terms of costs, and all their parameters are optimised (supply, logistics technology, marketing offer, etc.). At this stage of development, the total amount of investment made is significant and constitutes a major barrier to the strong arrival of newcomers. This would be necessary for biorefineries to be able to ensure viable competition from now on with oil refineries, which have a fully mature model, following 150 years of history.

• **From another point of view, the (modern) plant chemistry industry is a sector which is only just beginning to develop.** There is a high degree of innovation, bringing technological breakthroughs, but industrial production is far from being optimised. Costs remain high. The markets are growing rapidly but they are still small and immature. There are a large number of competitors.

• Finally, there are plants positioned on specific markets which have been refining raw materials from plants for many years. The basic technologies have been stabilised but there are increasing numbers of applications for products and their development is being pursued. The example of DRT, which refines and transforms substances from pine, can be quoted, as can that of Arkema, whose Marseille factory has been producing undecylenic acid from castor oil for many years.

The reality of biomass uses for the production of fuels and synthetic intermediates is therefore a curious mix of industrial types, which is characteristic of a transitional situation. The key actors are both traditional industries, which are in control of their raw material mobilisation capacities, technologies and markets, and start-ups which have been created within the last 5 years! **The major strategic problem for the sector is that of the competition with the oil production chain; this can only be successfully achieved by combining breakthrough innovations with tried and tested industrial know-how.** It is easy to imagine that the biorefinery of the future must incorporate these two dimensions but such a prospect requires alliances; there is still a long way to go for such a stabilised model to be established. No sector can become mature nor optimise its model in just a few years, which means that there are major challenges under way and as has already been mentioned, continuity in public support policies is necessary.
State of play for the projects and chemicals of the future

The following diagram, taken from Roquette, shows the different levels of development of various production projects for biosourced synthetic intermediates.

Ethanol is shown here among the products at the most advanced commercial stage, for which production technologies have been optimised. Transformation into ethylene and its derivatives involves the construction of specific workshops but not the development of particular technologies, as these have already been achieved. Ethanol is produced in special plants, which may or may not be associated with sugar or cereal biorefineries with a wider vocation.

Little mention has been made of citric acid in this study, because its applications are above all in the food industry, pharmaceuticals and cosmetics.

Examples of products being developed in plant chemistry

The development of lactic acid, is, as been seen, linked to that of PLA. There are an increasing number of players, in spite of the barriers to entry constituted by patents.

Emerging competitive productions of succinic acid must find their markets, which should be developed as cost prices and prices come down. On the contrary, epichlorhydrin has well-established markets.
On the contrary, the production of certain chemicals with strong potential markets are still at the research stage. This is the case of adipic acid.

The diversity of products which may be manufactured by future biorefineries will thus continue to increase. It should be noted however that each plant will represent major investments and that once they have been built, their profitability will depend on the use coefficient. The image of totally flexible biorefineries adjusting their production to markets and raw materials available will probably be only a partial reality, simply because of the major investments to be made and their financial profitability. A plant must be operated at full capacity once it is available and past experience has often consisted of specialising a plant for one product and one supply chain. Present-day biorefineries which have diversified products are the fruit of long industrial developments.

**Another point of view on the different models of biorefineries in operation**

Let us examine the classification of biorefineries set out in the introduction, from another point of view. What is the main strategic issue for the different categories? The table below offers a simplified view, seen from France and directed towards “products”.

<table>
<thead>
<tr>
<th>Sectors served</th>
<th>Examples</th>
<th>Major issue</th>
</tr>
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<tbody>
<tr>
<td>Human food, animal feed, chemicals,</td>
<td>Starch production plants</td>
<td>- Reinforcing the value of the product mix and extending the position in the value chain.</td>
</tr>
<tr>
<td>pharmaceuticals.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Human food, animal feed, fuels,</td>
<td>Oil production plants with biodiesel production workshops</td>
<td>- Competitiveness of biodiesel with fossil fuels.</td>
</tr>
<tr>
<td>chemicals, .</td>
<td></td>
<td>- Current low share in outlets for the chemicals industry.</td>
</tr>
<tr>
<td>Fuels, animal feed</td>
<td>Ethanol production from cereals or beet.</td>
<td>- Competitiveness of the ethanol produced with that of sugar cane and petrol.</td>
</tr>
<tr>
<td>Fuels, energy</td>
<td>Cane sugar ethanol production</td>
<td>- Developing the upstream production chain</td>
</tr>
<tr>
<td>New biofuels</td>
<td>Production plants for butanol, terpenes and hydrocarbons from biomass.</td>
<td>- Validating processes on an industrial scale.</td>
</tr>
<tr>
<td>Materials, energy, chemicals</td>
<td>Cellulose pulp production plants</td>
<td>- Competitiveness with fossil fuels.</td>
</tr>
<tr>
<td>Fuels and other second-generation</td>
<td>Planned second-generation biorefineries.</td>
<td>- Competitiveness of small plants and added value of their products.</td>
</tr>
<tr>
<td>products</td>
<td></td>
<td>- Competing uses of the resource.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Validity of industrial processes.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Mobilisation of the resource and competing uses.</td>
</tr>
</tbody>
</table>

The major strategic problems which may be expressed for the different biorefinery models are closely linked to their level of maturity. Technology is limiting for new products whereas on the contrary traditional industries must find a better balance for their positions on diversified and complementary markets.

The different biofuels are presently dependent upon incentives enabling them to be competitive with their fossil counterparts, which enables States to regulate the development of the sector. In the medium term, subject to continued increases in oil prices, the strategic issue will change: the availability of raw materials which can be effectively mobilised will then become the limiting factor for the growth of the industrial plants concerned.
Present and future key factors for the success of biorefineries

The list which may be drawn up of the key factors of success therefore brings together criteria of very variable relative importance according to the stage of development of the technologies and products concerned. Simply put, biorefineries — like any other industrial sector — need markets, raw materials, high performance industrial plant and a robust financial structure enabling them to cope with the volatility of upstream and downstream prices, whilst innovating regularly in order to remain competitive. Bearing this rather evident statement in mind, the following appraisal may be made:

Working upstream to downstream.

- **Controlling the resource: capacity for sustainably and competitively mobilising sufficient quantities of biomass of adequate quality in spite of the multiplication of competing uses.** Here it is necessary to have the ability to structure profitable plant production chains. The biorefinery may be the key player in this structuring (the traditional French model) or this may be delegated to specialised partners locally or located in particular geographical regions (the Dutch model as well as several industrial players in various countries around the world).

- **Technological and industrial proficiency.** Increasingly, biorefineries bring together a new diversity of processes (mechanical, physico-chemical or biochemical pre-treatment; fermentation; chemical conversion; extraction, purification; effluent treatment; cogeneration; biomethanisation, etc.). This diversity of technologies must also include that of the skills and human resources to implement them. The mature biorefinery must be a fully integrated industrial complex, composed of several companies, (cf. the illustration on the previous page).

- **The ability to serve mature and emerging markets at the same time, demonstrating a prospective marketing vision.** Knowledge of the markets and their requirements is essential.

- **Innovation capacities** to develop and share technologies and differentiating products.

- **Management capabilities and strategic vision.** Biorefineries are called to become heavy industries with a requirement for a high degree of agility. The depth of vision of leaders, their ability to forge strong alliances at the right time (these are vital in this sector) and make winning wagers will be determining. It is not easy to manage complicated industrial complexes, regularly incorporating new technologies and serving markets ranging from food to fuels and chemicals, etc.

- **Financial capabilities: to develop the industrial resource and new technologies, as well as to resist the disruption caused by the volatility of commodity prices and markets.**
The incorporation of several biorefining players within a fully-fledged industrial ecosystem on a single site: the example of Bazancourt-Pomacle in Champagne-Ardenne
V – SUMMARY AND CONCLUSIONS

V.1 - GENERAL SUMMARY

In the introduction we emphasised the external events which have made their mark over the last five years. They have reduced the visibility we thought we had on oil prices, whilst these remain the benchmark for calculating the profitability of many plant chemistry projects.

However, at the same time, the demand for biosourced products and public encouragements in favour of their development have increased considerably. The support for first- and second-generation biofuels has enabled technological and industrial progress which is of benefit to the chemicals industry.

White biotechnology is booming. It is favoured by the development of capabilities for simulating a microbial metabolism by bioinformatics, then quickly carrying out a large number of sequencings, DNA summaries, screening and other operations enabling the creation of specialised strains, dedicated to the production of a particular chemical.

The number of actual industrial projects is growing rapidly but still remains limited, particularly with respect to the production of chemical intermediates. Changes of scale are difficult and take a long time when biotechnology is involved (the noticeable improvement of chemical catalysis performance also requires prolonged work). There are major industrial investments and risks remain on the markets. It can also be noted that projects begun 5 years ago have not yet been completed (production of 3-HPA and others, announced in 2007 (production of biosourced ethylene by Dow), seem to have been called off or postponed indefinitely. It can be noted at this point that although start-ups announce marketing of products within a short timeframe, whereas more “traditional” companies in the sector such as Novozymes and Genecor explain that a production project for new chemicals cannot be brought to fruition in less than 5 or 10 years as a minimum. The inconsistency seems to be in appearance only: certain young companies have in fact been undertaking development work for several years already, while others confuse the transfer from pilot to industrial production scale in their public communications.

Some of the emerging biosourced synthetic intermediates are those which were expected five years ago (glycerol, sorbitol, succinic acid), while others are chemicals whose importance had not been ascertained (ethanol, lactic acid). The true surprises are in terpenes (farnesene, isoprene) and other biosourced hydrocarbons. The future will show whether or not the wagers made have led to the hoped-for success. Other announced chemicals are however taking time to achieve industrial development.

There is a very high degree of pressure on all products from biomass (and the biorefineries manufacturing them) for them to be economically competitive and environmentally-friendly from the outset. The time required for petrochemicals to develop efficient procedures, become profitable and then slowly reduce their negative impact on the environment, sometimes seems to be forgotten. The political hesitation with regard to first-generation biofuels reveals the difficulty of understanding the time taken to develop plant and industrial production chains for optimised performance.

Plant chemistry still has a good reputation, as did first-generation biofuels to begin with. The word “biosourced” has not yet been attacked due to the nature of its prefix.

However, the chemicals industry remains too timid when it comes to asserting its vital role in our developed or developing societies. Chemicals companies sometimes give the impression of apologising for their existence, despite the products they make being an essential part of the basic daily life of the keenest green activists as well as that of poor populations in Southern countries.
While permanent progress can legitimately be expected from our chemicals industry (as for other sectors) with regard to the environment and safety, this must be done with the aim of making strategic industries for the EU and France more competitive.

The perception of biotechnology in the EU is disparate. White biotechnology is well accepted by our populations, even when it includes cutting-edge innovations. However green biotechnology is a source of concern for certain countries like France, although it is the subject of considerable ongoing development on other continents. Imbalanced competitiveness, which will become increasingly widespread, between farming models incorporating the use of genetically modified seeds and those which refuse it, is one cause for concern.

The debate as to whether or not farmland should be used to produce food focuses on a complex issue. Half of the world’s population are now city-dwellers, including in developing countries. Fuels are not an unnecessary luxury but vital for trucks to be able to deliver food to urban markets. In an energy transition model, the issue to be dealt with is not the relevance of biofuels but their rightful place. The same is true for organic chemistry, which must be innovative from now on when it comes to the raw materials it uses.

There are limited quantities of biomass, and highly limiting quantities of biomass available in the short and medium term.

It is very significant to note that Solvay, a chemicals group which is determinedly committed to the production of commodities from plants, forecasts that “25% of future growth in epichlorhydrin production could be biosourced”. We are therefore only at the stage where part of the growth rather than part of the total amount of certain commodities could come from origins other than oil. The growth curve for the plastics market presented below shows the scope of the challenges faced by the development of plant chemistry to lay claim to partial substitution of oil-based products.

The arrival of second-generation biorefineries will enable a significant increase in the resources available, but the biomass accessible in the short and medium term will remain limited and subject to ever-increasing numbers of competing uses. Particular attention should therefore be paid to the use of plant waste. It is not very wise to spend excessive amounts of time dreaming about the third generation in Europe, as it will inevitably take up a lot of land resources.

The development of biomass chemistry must be pursued and extended, but not naively. We must reduce our waste and considerably increase our recycling capacities and performance at the same time. The procedures in progress on the part of the promoters of PLA, a genuine “new polymer”, should be emphasised: they are already drawing up the recycling processes for their product.
The manufacture of 250 million tonnes of plastics, usually with a low oxygen content in their composition, would require the use of over 500 million tonnes of already pre-refined biomass. The largest current projects for biosourced plastics do not exceed 100,000 to 200,000 tonnes in capacity and can be counted on the fingers of one hand. The curve showing the growth and consumption of plastics has slowed down with the recent crisis but everything suggests that it will soon recover its previous rate of growth, bolstered by the demand in developing countries.
V.II - RECOMMENDATIONS

We are living in a period of transition, in terms of both energy and the resources used by the chemicals industry. This transition is neither spontaneous nor continuous, as shown by the events and crises of the last few years. The development of biorefineries and plant chemistry must be supported and assisted. Going beyond economic parameters, the meeting between the farming and forestry production chains and the chemicals production chain must be stimulated, as this brings together sectors which have poor knowledge of one another and which are not as yet on the same wavelength.

A sufficient diversity of production chains and projects must be supported, without falling into the common trap in France of spreading out the available resources to try and satisfy all those with demands and all the local entities which they are a part of. Biorefining is a heavy industry which must be concentrated in order to be competitive. It requires major R&D and equipment investments, with profitability outlooks which are still uncertain, linked for the most part to the respective changes in oil and farming commodities prices.

It is important to support what can be our field of excellence. France has strong advantages: plentiful resources, as well as the quality of organisation of its farming production chains and agro-food players. The EU is home to the largest chemicals companies in the world and world leaders in biotechnology. France has a responsibility to define its own policy for the development of plant chemistry, but should also integrate its efforts with those of neighbouring countries in order to create a sector which is competitive on a worldwide scale.

France is a major cereal producing country, with strong competition from other regions. Its crops are affected by climate change. We must offer our wheat and corn production chains new industrial outlets making the most of the excellence of our primary and secondary processing agro-food companies.

Our oilseed production chain is a model in terms of how it is structured. It must be supported in order to speed up its development into plant oil derivative chemistry.

France is a world leader in beet production. Beet also benefits from a perfectly structured sugar and ethanol production chain. We must define its specific positioning in the developments to be implemented, so as to enable it to highlight its specific advantages.

Traditionally, France reasons by plant production chain, whereas the same farmers produce cereals, oilseed and beet. Although processing industries will remain competitive, it is important to encourage an overall positioning of our farming industry as a new supplier to the chemicals industry. Our different farming production will increasingly be raw materials for the same chemicals. Farming also needs to be brought closer to forestry. New outlooks must be given to our pulp production chains and to the mobilisation of forest biomass. The REGIX programme very worthily got researchers and technicians from farming and forestry working together. This meeting of approaches and outlooks should be developed and brought to fruition, not only in terms of research but also in terms of industrial developments.

The mass production of oil-based fuels has enabled petrochemicals to boom. The boom of plant-based biofuels is a vital pillar of the development of biorefineries and plant chemistry. We should not now be demanding that our first-generation biofuels – nor even, in the future, second-generation biofuels! – offer a perfect profile, technically, economically or environmentally. However we should set the sectors concerned objectives in terms of dynamism, innovation and impetus for the industries which may grow in their wake. First-generation biorefineries act as a precursor, laying down essential structure, which must be recognised, highlighted and positioned as the springboard for future progress.
Biorefineries: overview and development

Biorefineries will not comply with a single model or predefined typologies. The support and assessment policies with regard to them should be taken into account. In particular, care must be taken not to fall into simplistic appraisals leading to certain models of life cycle analysis. The vocation of biorefineries is to produce a diversity of products offering the best use of resources rather than being energy self-sufficient. Uses of their co-products in animal feed will remain an essential element of their raison d’être.

We cannot be satisfied with the status quo in France as regards genetically modified crops. In spite of our country’s strong tradition for innovation, we are condemning our farming industry to gradual loss of its competitiveness. Mankind’s inventive capacity has led to the development of farming for 10,000 years: we must not let our country’s farming industry remain static. It is time to return to more rational and balanced analysis of the risks and benefits.

We therefore recommend the following:

- Pursuing a significant support policy for a shortlist of industrial projects in plant chemistry after having analysed in particular the initial feedback from the BioHub experience and the structuring capacity of models of industrial ecosystems incorporating research and training, such as the one in Pomacle-Bazancourt.

- Stimulating our research and development of white technology by identifying the project liable to favour the use of products from our farming and forest production chain. Work enabling the production of adipic acid must be examined carefully.

- Pursuing support for first-generation biofuels by positioning them in their role of creating new agro-industrial production chains. Farming production, supply logistics and transformation processes must gradually be optimised for their different technical, economic and environmental parameters. Collateral uses must be widely encouraged. Support for second-generation projects must be reinforced and follow on from the industrial reasoning already engaged.

- Developing sufficiently large projects in research and development on C18 and C20 adipic acid chemistry and C9 and C22 derivatives.

- Pursuing the developments of glycerol derivatives, with a preference for chemicals which can be widely used by our industry. Acrylic acid production is worthy of particular attention.

- Assessing our research and development capacities in the field of lignin chemistry and supporting a selection of projects offering prospects for industrial use in the medium term.

- Pursuing the REGIX programme broadening its field of action to other uses of lignocellulosic raw materials (composite materials, chemicals).

- Developing consultation groups with all stakeholders concerned by the competing uses of biomass resources (fuels, materials, chemicals).

- Relaunching active research and development into plant genetic engineering. Implementing a sustainable approach to teaching and promoting green biotechnology and its current and potential benefits.
APPENDICES

PRODUCTION CHAIN DIAGRAMS

Diagram of wheat and corn production chains (starch)
Diagram of beet production chain (sugar)
Diagram of rapeseed and sunflower production chains (vegetable oils)
Diagram of lignocellulosic production chains
Biorefineries: overview and development

Platform product

Future platforms

Polymers - biomaterials

BDO = 1,4-Butanediol (precursor of PBT and PTEMG monomers)
DALA = Delta-aminolevulinate (biodegradable herbicide)
FDCA = 2,5-furan-dicarboxylic-acid.
EMF = Ethoxymethylfurfural
GBL = gamma-butyrolactone (precursor of PBT and PTEMG monomers)
HMF = Hydroxymethylfuran
MPG = Monopropylene glycol
MTHF = 2-Methyl tetrahydrofuran (fuel additive – oxygenating agent)
PBT = Polybutylene terephthalate
PBS = 4,4 Bionolle Polyester
PEIT = Polyethylene isosorbide terephthalate
PGA = Polyglycolic acid
PIS = Polyisorbide succinate
PG = propylene glycol (anti-freeze, plastic monomer)
PHAs = Polyhydroxylcanoates (bacterial polymer usable as a bioplastic)
PHBs = Polyhydroxybutyrates (bacterial polymer usable as a bioplastic)
PLA = polylactic acid (biodegradable plastic)
PTMGE = Polytetramethylene glycol ether
PTT = Polytrimethylene terephthalate
PUs = Polyurethanes
PVP = Polyvinylpyrrolidone (many applications in pharmaceuticals, perfumes, paper, food processing, detergents, as a binder, humidifer, etc.).
THF = tetrahydrofuran (solvent, precursor of PBT and PTEMG monomers)
OILSEEDS (CANOLA, RAPESEED AND SUNFLOWER) PRODUCTION CHAINS

Seeds, water, fertiliser, plant care products, fuel.

- Canola, Rapeseed or Sunflower
  - Straw
  - Animal feed
  - Extraction
  - Oilcake
  - Animal feed

- Seeds
  - Extraction
  - Oilcake

- Animal feed (canola)

- Emulsifiers
  - Phospholipids
  - degumming neutralisation,
  - discoloration deodorisation
  - Soap stocks (phospholipids, soaps, triglycerides)

- Semi-refined oil
  - Refined oil
  - Transesterification
  - Transesterification
  - Distillation
  - Fatty acid derivatives (esters)
  - Biolubricants (canola, high erucic rapeseed or high oleic sunflower oils)

- Methyl esters
  - Glycerol esters
  - Sulfo methylesters
  - CLAs (sunflower)
  - Hydrogenation Distillation
  - Fatty alcohols

- Glycerol
  - Ac acid treatment
  - Raw glycerine
  - Distillation

- Surfactants, lubriacnts, wood
  - Surfactants
  - Distillation
  - Epoxy resins
  - Polyurethanes
  - Biodiesel
  - Fuel

- Animal feed

- Food uses
  - Pharmaceuticals
  - Cosmetics
  - Pharmaceuticals, Cosmetics
  - Food uses

- Polyols
  - Polyurethanes

- Paint

- Cosmetics, Lubricants

- Plant care adjuvants

- Hydrogenation Distillation
  - Ethoxylated or sulfated fatty alcohols

- ASA
  - Surfactants, (Cosmetics)

- Wood processing, paper gluing agents
LIGNOCELLULOSIC PRODUCTION CHAINS

Forest (Softwood or hardwood)

- Logs
- Bark
- Grasses
- Energy
- Forest chips
- Black liquor
- Procyanidins
- Bark extracts
- Green liquor
- Energy
- Energy
- White liquor
- HMR lignans and others, flavonoids, (E)-stilbene
- Extraction from chestnut or oak wood (by specialised companies)

Forest residues

- Compost
- Fuel hydrocarbons
- Enzyme hydrolysis
- C5, xylene
- C6, glucose
- Fermentation
- Ethanol, etc.

Grinding

- Wood chips
- Pre-steaming (kraft process only)
- Tannins (hardwood)
- Kraft alkaline process
- Black liquor ( lignin derivatives)
- Kraft lignin derivatives
- Energy
- Energy
- Acidic bisulfite process
- Cooking-defibration
- Black liquor

Bark

- Bark extracts
- Procyanidins
- Bark

Energy

Fuels, Energy

Cereal straw, power crops, SRC, VSRC

Pyrolysis or Gasification + Fischer-

Fuel hydrocarbons

Composite materials, polymer compounds

Enzyme hydrolysis

C5, xylene
C6, glucose

Furfural

Fermentation

Ethanol, etc.

Terpenes

Para-cymene

Industrial binders

Ethers: Carboxymethyl cellulose, Ethyl cellulose, Hydroxyethyl cellulose

Lignosulfonates

Energy

Industrial additives

Regenerated cellulose

Terpenes

Distillation

β-pinene
α-pinene
5,5-carrene

Nopol, Geraniol, Citronellol, Nerol, etc.

Polyterpenes

Adhesives

Pharma

Pharmaceuticals

Sitosterol
Sitostanol

Tall oil pitch

Tall oil

Hydroxy polyesters

Industrial oils, alkyd resins, soaps, industrial emulsifiers, bitumens, inks

Polyterpenes

Adhesives

Perfume industry

β-pinene
α-pinene
5,5-carrene

Nopol, Geraniol, Citronellol, Nerol, etc.

Polyterpenes

Adhesives

Pharma

Pharmaceuticals

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BRIEF DESCRIPTION OF COMPANIES

The list of players below makes no claim to be exhaustive. It lists companies which are particularly active in the mobilisation, processing and use of biomass products in the chemicals industry or biofuels.
COMPANIES UPSTREAM IN THE PRODUCTION CHAIN

SEEDS AND PLANT PRODUCTION

BASF PLANT SCIENCE is a division of BASF which is active in plant protection and plant biotechnology. It had revenues of 3.6 billion euros in 2009. Its main products are fungicides, herbicides and insecticides.

Since 1998, BASF Plant Science Biotech has brought together all the plant biotechnology activity for the BASF group.

In 2010, BASF was granted permission to produce its Amflora potato variety in Europe, in which the starch contains only amylopectin.

BASF Plant Science has been working with Monsanto since 2007 on the development of drought-resistant properties for corn, soybean, rapeseed, cotton and wheat seeds. A corn variety should be marketed in 2012 and the first wheat varieties are expected by 2020. BASF is working in partnership with the Brazilian Centro de Tecnologia Canaveria on the genetic improvement of sugar cane and with KWS Saat AG on the genetic improvement of beet.

BAYER

Bayer is a German chemicals and pharmaceuticals group which has operations on all continents, with a workforce of 108,000 and revenues of 31 billion euros in 2009. Its Bayer Crop Science division (formerly Aventis Crop Science, bought out in 2002) is active in plant protection and as a seed producer (soybean, hybrid rapeseeds, cotton, hybrid rices, vegetables) with major green technology activity. Bayer is working notably on drought-resistance improvement.

DOW AGRO SCIENCES

This division of the Dow Chemicals group had revenues of 4.5 billion dollars in 2009 and has 6000 employees, 400 of whom are in France. It was formed in 1989 by the merger of the farming divisions of The Dow Chemical Company and Elly Lily (Elanco). It became part of the Mycogen Seeds seed producing company in 1998 and, more recently the activities of Cargill Hybrid Seeds and the farming division of Rohm and Haas.

Dow Agro Sciences and its subsidiaries produce and market plant protection protects and corn, sunflower, rapeseed, soybean sorghum and alfalfa seeds.

Dow Agro Sciences, in partnership with Pionner Hi Bred, uses Bt protein insect-resistant genes on corn (Herculex technology – authorised events in imported products in the EU since August 2010).

Dow Agro Sciences and Monsanto have in partnership developed double herbicide-resistant Smartstax corn seeds which also have several forms of insect resistance including Herculex.

LIMAGRAIN

The cooperative group Limagrain has 600 farmer members in Limagne. Its subsidiary, Groupe Limagrain Holding, is a shareholder in Vilmorin et Cie, the fourth largest seed producer worldwide, with activities in major crops (corn, sunflower, wheat, barley, rapeseed, forage crops, etc.; LG, Advanta, Nickerson brands etc.) and vegetables and flowers (Clause, Tézier, Vilmorin brands, etc.). The holding company is also a shareholder in Limagrain Céréales Ingénieurs which produces functional flours.
In 2009 the Limagrain group had revenues of 1.2 billion euros and has some 6000 employees. It has operations in all continents.

MONSANTO

The North-American group Monsanto was historically a chemicals company before concentrating on seeds, plant biotechnology and crop protection. In 2009, Monsanto had revenues of 11.7 billion dollars, with just under 23,000 employees.

Monsanto created the systemic herbicide chemical Roundup (glyphosate) in the early 1970s. It is now in the public domain. Monsanto produced its first genetically-modified seeds in the 1980s. The group has very successfully developed Roundup-resistant soybeans and corns. Monsanto markets corn, soybean, cotton and rape seeds and is committed to the development of wheat and sugar cane varieties.

Monsanto is one of the favourite targets of “anti-GMO” organisations. The development of the company is continuing, whilst it is completely dependent upon the success of its products with farmers and the entire food processing industry. The soybean Roundup-resistance technology was so successful that it has been pirated in certain South American countries, without Monsanto receiving any royalties.

In 2010 Monsanto marketed Smartstax corn for the first time, which has undergone 8 modifications (several for insect resistance and two for herbicide resistance), developed in partnership with Dow AgroSciences. Various major seed manufacturers carry out Monsanto genetic constructions under licence for their own varieties, as it has become so indispensable on certain markets to offer seeds with certain properties. The innovations expected from research work in progress on corn relate to drought resistance and better use of nitrogen, enabling fertiliser requirements to be reduced. Monsanto is working with BASF Plant Science on these issues.

PIONEER HI BRED - DUPONT

Pioneer Hi Bred International had long been a major, independent, world-leading North American corn seed producer before it was bought out by DuPont in 1999. Pioneer Hi Bred is active worldwide producing and marketing corn, soybean, rapeseed, sunflower, sorghum, wheat, alfalfa and hybrid rice seeds, etc.

In 2006, Du Pont-Pioneer Hi Bred and Syngenta formed a joint venture to facilitate use of herbicide- and insect resistant genes, developed by either of the partners, in the varieties of the two companies.

DuPont Agriculture & Nutrition offers farmers a wide range of plant protection products.

RAGT

Having been set up in 1919 in the form of a farming cooperative, in 1944 RAGT became a limited company, with most of the shares owned by the founding farmers from the Averyron département. The RAGT is active in farming supplies and started working with seeds in 1951, before gradually becoming one of the leaders for major crop seeds in Europe. The RAGT group has revenues of 275 million and 1000 employees. It breeds 22 plant species and registers over 200 varieties each year.
Since January 2007, RAGT has been marketing a fuel pellet technology made from farmed resources (straws, downgraded cereals, etc.) incorporating mineral additives to avoid any emission of acid fumes and the formation of clinker.

SYNGENTA

The Swiss group Syngenta is a world leader in plant protection and seeds. It was formed in 2000 by the merger of the agrochemical activities of Novartis and AstraZeneca. It has operations in 90 countries with a workforce of over 25,000 and revenues of 11 billion dollars in 2009. The Sygenta group subsidiaries develop corn, soybean, beet, sunflower, wheat, vegetable and flower seeds. Syngenta is a major player in plant biotechnology, notably with developments in drought resistance, and marketed corn which has bacterial amylases in its grain, enabling vast improvement in ethanol production yields.

Since Syngenta has been allied with DuPont-Pioneer Hi Bred for the joint use of properties developed by both companies.

AGRO-INDUSTRY AND INITIAL BIOMASS PROCESSORS

ADM

Archer Daniels Midland Company is a powerful North American agroindustrial player which is particularly active in the processing of wheat, corn, oilseed, cocoa, etc. and in the production of food ingredients (lysine, threonine, citric acid, lactic acid, sorbitol, etc.). It has operations in 60 countries, operating over 230 factories and employing 28,000 people. In 2009 it had revenues of 69 billion dollars.

ADM is the world’s leading corn processor (50,000 t/day) and the group processes 91,000 t of oilseed daily. It is the world’s leading bioethanol producer (with capacities currently being expanded from 20 to 64 million hectolitres) and a major player in biodiesel (capacities of 17 million hectolitres).

ADM is developing a propylene glycol production project using corn starch and glycerol, a co-product of biodiesel. The plant, currently being built in Decatur, Illinois will have a production capacity of 100,000 t of finished product.

ADM is working with Metabolix on the development of PHA production, sold under the Mirel™ brand by their joint venture, Telles. At Clinton, Iowa, a 50,000-tonne plant began production in 2010. It represents an investment of 300 million dollars. The currently used raw material is glucose.

ADM is also a partner of PolyOne Corporation for the development of biosourced plastifying agents.

ADM is working with ConocoPhilipps for the production, by heat process, of second-generation biofuels which can be directly incorporated into petrol and diesel. It has also engaged a project aimed at the production of cellulosic ethanol by fermentation.

CARGILL- NATUREWORKS

Cargill is another major North American agro-industrial company which originally developed by trading grain. Its turnover in 2009 was 117 billion dollars (108 for the 2010 financial year). The company, which is family-owned, has operations in 68 countries, with some 160,000 employees.
Cargill is – amongst other things – the leading starch producer worldwide. In Europe, Cargill is also a major rapeseed processor, with operations in France in Saint-Nazaire, Montoir and Brest.

The Cargill group manufactures a wide range of biosourced chemicals including starches and derivatives (sorbitol, maltitol, erythritol, isosorbide), glycerol, biolubricants, polyols for the manufacture of polyurethanes, etc.

The wholly-owned subsidiary, Natureworks, was the first producer of PLA (polylactic acid) and is still by far its principal manufacturer, with a production capacity which recently reached 140,000 t. The product is sold under the brand name Ingeo™. Until mid-2009, Natureworks was jointly owned 50/50 by Cargill and the Japanese company Teijin. In March 2010, Cargill won an award for the development of a modified yeast capable of producing lactic acid in conditions enabling the purification of the product more easily (traditionally neutralised in the form of calcium salts and then retreated). Since mid-March 2010, Natureworks has also been marketing lactides.

Natureworks is working with Avantium on the development of furan polyesters which have properties similar to those of PETs.

Cargill has been working for many years with Novozymes for the production of 3-HPA as the precursor of acrylic acid. The group is also a partner of Gevo which develops isobutanol production technologies.

CHAMPAGNE-CEREALES – SICLAÉ– CHAMTOR- ARD – BIO AMBER - SOLIANCE

Champagne Céréales is a cooperative in north-eastern France with 8600 members and revenues of 830 million euros, collecting 2.2 million t of product.

Champagne Céréales is the majority shareholder in the Siclaé holding, a joint subsidiary formed with other cooperatives in 2005 (including Nouricia, EMC2, etc.), which brings together companies working in plant production processing. In 2008-2009, Siclaé had revenues of €1.5 billion. Since late 2009, Siclaé has been the sole shareholder of the starch and glucose producer Chamtor which processes 400,000 t of wheat per year, with revenues of €136 million in 2008-2009.

Siclaé also owns a 51% stake in ARD (Agro Industrie Recherches et Développements), a research centre dedicated to plant chemistry and described here with the biotechnology companies.

Champagne Céréales owns 26% of Bletanol, which itself owns 45% of the shares of the beet and wheat ethanol producer Cristanol, which is also a 55% subsidiary of the sugar producing group Cristal Union.

COPERSUCAR SA is the leading Brazilian sugar and ethanol producer and trader. Its shareholders are sugar cane producers, who have been working together in a cooperative since 1959, and set up the holding company Produpar which controls Copersucar. This year the group will market products resulting from the grinding of 114 million tonnes of sugar cane. It has 39 associated mills and processed 74 million tonnes in 2009-2010 (9% more than during the previous campaign), producing 18.7 mt of bagasse, most of which was used for cogeneration. During the same year, Copersucar produced 3.7 million tonnes of sugar (2% of worldwide production) and 3.4 billion litres of ethanol (34 million hectolitres, which is 4% of worldwide production). It marketed 5.2 million tonnes of sugar, of which 3.7 mt were exported, as well as 39 million hectolitres of ethanol, 6.3 mhl of which were exported. The 2009-2010 turnover was 7.9 billion reais (4.3 billion US dollars). In March 2010, Copersucar is believed to have signed agreements with Guarani, the subsidiary of Tereos International, for marketing the ethanol produced by the latter.
Copersucar is the partner of Solvay for supplying ethanol to its biosourced PVC production unit (the ethanol is transformed into ethylene then vinyl monochloride).

COSAN

The Cosan group is the second-largest sugar and ethanol producer in Brazil with revenues of 6.2 billion Brazilian reals in 2009. Cosan has an annual capacity for grinding 60 million tonnes of sugar cane (44.2 mt ground in 2009) in 23 industrial production units producing 2 billion litres of ethanol (20 million hectolitres). Cosan has 7 cogeneration plants with 5 more due to be built in the coming years.

In early 2010, Cosan signed an MOU establishing a joint venture with the petroleum group Shell for the production of ethanol, sugar and energy, as well as the supply and distribution of fuels.

CRISTAL UNION – CRISTANOL

The Cristal Union group was formed by the merger of the activities of four farming cooperatives. Cristal Union’s activities are the production and marketing of dehydrated sugar, ethanol, beet pulp and alfalfa. In 2009-2010 the group had revenues of 1.2 billion euros and a workforce of 1500. It produced 850,000 t of white sugar, 4.6 million hectolitres of ethanol (including production by Cristanol) and 159 000 t of dehydrated pulp and alfalfa. Cristal Union thus processes 20 - 25% of beet production in France.

Cristal Union controls 55% of the capital of Cristanol, a company dedicated to the production of ethanol from beet and cereals with production capacities of 3.5 million hectolitres per year, as well as 175,000 t of distillers’ grains and 75,000 t of pulp. 1 mt of beet and 500,000 t of wheat can be treated annually.

Cristal Union owns a stake of approximately 18% in ARD. There is a Cristanol distillery and a Cristal Union sugar production unit on the Pomacle-Bazancourt site, facilitating industrial synergies upstream from the plant chemistry industry.

CRYSTALSEV was a major ethanol and sugar producer in Brazil, and a subsidiary of the Santelisa Vale group which was bought out by the French group Louis Dreyfus in late 2009.

Crystalsev had been working with Amyris since 2008 on the production of biodiesel from sugar cane. Amyris has bought out the shares in the joint venture which had been set up to this end.

A collaboration project with Dow for the production of bioethylene from bioethanol had been announced in 2007 without being followed up on.

DREYFUS

Louis-Dreyfus is an international family-owned trading group (grains, maritime transport, energy, real estate, etc.), with over 10,000 employees in over 53 countries. Its revenues are estimated to be between 25 and over 30 billion euros. In autumn 2009, the Brazilian subsidiary of Louis Dreyfus Commodities (revenues of 21 billion euros), LD Commodities Bioenergia, bought out 60% of the shares in the Brazilian group Santelisa Vale. A new company formed by the merger of these two entities, called LDC-SEV, should have revenues of 8 billion euros. It controls thirteen sugar and bioethanol production units, with a grinding capacity of 40 million tonnes of sugar cane. It will produce 16 million hectolitres of ethanol per year.

With this takeover, LDC-SEV recovered the 73% stake held by Santelisa Vale in the Brazilian company, Crystalsev. The latter produced over 2 million tonnes of sugar and 10 million hectolitres of ethanol per year. With 17 production plants, Crystalsev processes approximately 40 million tonnes of sugar cane.
POET LLC is a North American company which specialises in bioethanol production and has become a major player in the sector (the group describes itself as the world’s leading producer). Poet has over 30 ethanol production plants across the country. Their raw material is currently corn. The group is believed to be working on the production of second-generation ethanol with aim of using the entire corn plant.

ROQUETTE FRERES

Roquette is a family-owned group, whose core business is starch production. It produces around 2.3 million tonnes of starch products and derivatives and is the 2nd largest company after Cargill in this activity. It is part of one of the four largest groups in the world.

Roquette is the world’s leading producer of polyols (sorbitol, mannitol, maltitol). The company manufactures over 650 products from 6 million tonnes of corn, wheat, peas and potatoes, thus using 500,000 hectares of crops. In 2008, it had revenues of 2.5 billion euros for 6000 employees. The group has 18 plants in Europe, North America and Asia. The group’s historic site is at Lestrem, in northern France. Its head office is located there, along with the largest cereal biorefinery in Europe.

Roquette has an R&D budget of around 50 million euros per year. The company is committed to a large number of partnerships and has developed ambitious plant chemistry programmes, particularly Biohub® with the backing of the French authorities.

Roquette produces isosorbide and is developing the production of its derivatives (isosorbide diesters, dimethyl isosorbide, isosorbide polymers). Roquette has initiated industrial production of succinic acid with the chemicals company DSM. The group is also well advanced on fermentation production projects for L-methionine and glycolic acid (using only microbial strains from Metabolic Explorer).

SOFIPROTEOL (SAIPOL – LESIEUR – GLON SANDERS – DIESTER INDUSTRIE – NOVANCE – OLEON)

Sofiproteol is the industrial and financial body of the French oilseed and protein crop production chain. With revenues of 5.5 billion euros and a workforce of 6000, Sofiproteol develops its activities in four main areas:

- The production of food oils (processing of oil seeds by its subsidiary Saipol, use of oils by its subsidiary Lesieur with revenues of some 800 million euros).
- Animal feed (with revenues of approximately 1.5 billion euros): the rapeseed and sunflower oilcakes produced by Saipol are used throughout the French cattle feed sector, in particular by the market leader and subsidiary of the group, Glon-Sanders.
- Biodiesel, produced by Diester Industrie, the European leader for biodiesel (revenues of 1.5 - 2 billion euros).
- Oil derivative chemistry (revenues of 450 million euros) with Novance, positioned in specialities and Oleón (formerly Fina Oleochemicals) in Belgium, active in commodities. Sofiproteol has stated the ambition of reinforcing this chemicals centre.
The Sofiproteol group has become one of the world’s leading producers of glycerol, on a market which is as yet very fragmented. It supports various research and development work on glycerol derivatives and fatty acids.

SOUFFLET
The French group Soufflet is a major European agro-industrial player for barley and wheat. With revenues of 3 billion euros (2008-2009), half of which was achieved in exports or outside France, the Soufflet group has over 3600 employees.

In 2003 Soufflet took over Lyven, which specialised in solid substrate fermentation. As part of the Osiris programme, Soufflet is developing this technology for the production of enriched substrates for use in animal feed and applications of the production of biosourced chemicals.

TATE & LYLE
Tate & Lyle is a British starch producer which had revenues of 3.5 billion pounds sterling in 2009-2010, with a workforce of 5700. The group has operations in Europe, North and South America and Asia. It produces starches, ethanol, sweeteners (in particular sucralose) citric acid, and so on.

In late June 2010, Tate & Lyle sold its refining activities and sugar brands to the leading US sugar producer, American Sugar Refining (ASR). In the coming months it is expected to sell off the rest of its sugar producing division in order to concentrate on starch derivatives.

Tate & Lyle and DuPont had formed a joint venture DuPont Tate & Lyle Bio Products, which produces 1,3 propanediol from glucose using fermentation processes developed with Genencor. 1,3 PDO is used by DuPont to manufacture PTT.

TEMBEC
The Canadian group Tembec Inc. is a producer of “forest products”, with operations in Canada, the USA and France. In France, Tembec has a plant in Tartas, Landes, which uses the bisulfite process to produce 150,000 t of high-quality cellulose pulp to be converted into cellulose ethers (75%) as well as nitrocellulose (25%). Tembec is active in research into cellulose chemistry and its derivatives.

In 2010, Tembec sold its other two French sites (Saint Gaudens and Tarascon) to Paper Excellence B.V., a company domiciled in the Netherlands but owned by the Indonesian group Asia Pulp and Paper.

TEREOS – SYRAL - GUARANI
The French cooperative group Tereos is a major player in the production of sugar, starch and bioethanol, with 33 industrial sites in Europe, Brazil and the Indian Ocean. In 2008-2009, Tereos had revenues of 3.4 billion euros and a workforce of 13,500. Tereos is the leading beet processor and the third-largest starch and glucose producer in Europe, as well as the 4th-largest sugar and ethanol producer in Brazil. The group processes some 4 million tonnes of cereals, essentially in France; Tereos France processed 15.5 tonnes of beet during its most recent financial year. Tereos produces a total of 7.6 mt of sugar equivalent from beet, cereals and cane.

Since late March 2010, the subsidiary Tereos International brings together the group’s food processing and bioenergy activities.

On April 30, 2010, Tereos International and the petroleum group Petrobras signed an agreement to allow the latter to have a 45.7% stake in Guarani, Tereos’ Brazilian subsidiary, which produces sugar and ethanol. Guarani is set to become the third-largest sugar and ethanol
producer in Brazil, after the takeover of the Mandu plant in Sao Paulo state, announced in early June 2010.

With production of 1.5 million tonnes of starch products, Tereos International's subsidiary Syral is the third-largest starch producer in Europe, behind Cargill and Roquette.

Tereos works with Amyris in Brazil for the production of diesel biofuel from cane molasses. In France, the group has formed a partnership with Deinove to explore the potential of deinococcus bacteria for improving the production of ethanol from wheat, using in particular the fibrous part of brans, opening the way for second-generation lignocellulosic ethanol. Tereos also takes part in Futurol and Biocore second-generation biofuel projects in France.

UNIGRAINS

Unigrains is the funding body for the French cereal production chain. It invests, as a minority shareholder, in food processing, agro-industry and biotechnology companies which use the products from this production chain, or contribute to its structure. In late 2007, it had investments worth 378 million euros in these companies. Unigrains is attentive to the development of plant chemistry and assists several innovative companies in this sector.

UPM is a Finnish company and one of the world leaders in the paper industry. In 2009, UPM had revenues of 7.7 billion euros and a workforce of 23,000. The group has 3 divisions: (1) paper (70% of the activity), (2) energy and pulp (UPM is the second-largest energy supplier in Finland, where it is associated with the EPR project) and (3) technical materials. UPM manufactures pulp in Finland and Uruguay (from eucalyptus). Its own production capacity is 3.2 mt. It has paper production operations across Europe, the USA and China.

At the Gas Technology Institute, near Chicago, UPM is conducting pilot work on the production of second-generation biofuels by Fischer-Tropsch gasification. The company is currently studying the possibility of implementing this technology on its French site in Stracel (near Strasbourg), which includes a chemical pulp manufacturing unit closed down in 1997.
AIR LIQUIDE - SEPPIC

Air Liquide is the world leader for gases for industry, healthcare and the environment, employing 42,000 people in 75 countries. It had revenues of €12 billion in 2009.

Air Liquide will intervene in the transformation of syngas derived from biomass for the production of second-generation biofuels in the project conducted by the CEA (Atomic Energy Commission) at Bure-Saudron with the CNIM group (Constructions Industrielles de la Méditerranée).

Seppic (Société d’Exploitation de Produits pour les Industries Chimiques) is a division of Air Liquide healthcare with 600 employees and 4 industrial sites. Historically it specialises in surfactants and manufactures high added value products for the healthcare, cosmetics and food processing markets, etc. 60% of the raw materials used by Seppic are of plant origin (fatty acid esters, glycerol, ethoxylated fatty alcohols, glucose, sorbitol, etc.). In particular, Seppic produces polymer excipients for cosmetics, sorbitan esters, etc.
**AKZO NOBEL**

This Dutch group has 57,000 employees and had revenues of some 14 billion euros in 2009. Akzo Nobel's activities are broken down into paints, coatings and varnishes, and speciality chemicals. Akzo Nobel is the parent company of starch manufacturers National Starch.

**ARIZONA CHEMICALS**

This North American company refines tall oil in the United States and Scandinavia and offers the market a wide range of derivatives. It has revenues of US$ 1 billion and 1000 employees.

**ARKEMA**

Arkema (formerly Atochem) was founded in 2004 by the Total group. The company has operations in 40 countries and had revenues of 4.4 billion euros in 2009 with a workforce of 13,800. It has 80 industrial sites. Arkema is organised into 3 business units: Vinyl products, the Chemicals Industry (acrylates, acrylic polymers, PMMA, etc.) and High Performance Products (technical polymers, specialty products made by the subsidiary CECA, functional ingredients).

Arkema uses castor oil to produce polyamide 11 and sebacic acid. Castor oil is imported from producing countries such as India, China and Brazil. In the 1980s, the French oilseed and protein plant production chain initiated a development programme for growing castor bean in France, but this did not arouse the interest of Altochem at that time. Polyamide 11 is marketed under the Rilsan® brand and is also used for the production of Pebax® (polyether block amide). Arkema's subsidiary CECA uses plant raw materials, notably in the production of bitumen additives.

Arkema is developing a project for the production of acrylic acid from glycerol on its Carling site, in Moselle, with regional university partners.

Arkema is a member of the Fimalin association, which brings together the players from the entire linseed production chain in Normandy to take part in the development of polymer compounds incorporating linen fibres (with PVC as well as Rilsan).

**AVANTIUM**

Based in Amsterdam, Avantium was founded in 2000 by a consortium of companies (Royal Dutch Shell, Eastman Chemical, Akzo-Nobel and Pfizer) to provide research and development services. Avantium has particular know-how in chemical catalysis, enabling it to work for oil companies such as Shell, Sasol, BP, Petrobras and Celanese as well as the IFP.

In 2005, Avantium initiated work on the conversion of biomass into chemical intermediates and fuels. Avantium has focused its efforts on furans and developed competitive technology for the catalytic conversion of various sugars into furans (hydroxymethylfurfural). This technology is known as YXY.

Avantium is working with Natureworks (Cargill group) on the development of YXY polyesters with properties similar to those of PETs.

Avantium is seeking other partners to develop applications for its technology in polyamides, polyurethanes and fuels (ethoxymethylfurfural = EMF). Avantium is building a pilot unit in 2010.
BASF

The German company BASF is the largest chemicals company in the world. In 2009 it had revenues of 50.7 billion euros (62.3 billion euros in 2008). BASF has operations in every continent and has a workforce of 105,000. The group’s activity is broken down into 6 segments: chemicals (inorganic chemicals and oil derivatives), plastics (including major traditional polymers as well as starch-based biodegradable plastics), high performance products, functional chemicals, farming products, oil and gas. Its product range is particularly diversified.

In terms of innovation, BASF concentrates its efforts in five areas: energy management, new raw materials, nanotechnology, plant biotechnology and white biotechnology.

A description of BASF’s subsidiary Plant Science, founded in 1998, which is active in plant protection and plant biotechnology, is to be found above.

BASF controls, implements and develops biocatalysis and fermentation technology. The group therefore markets enzymes (phytase) and products produced using white biotechnology (historically, vitamin B12).

In 2009, BASF took over the activities of Ciba which were mainly grouped together in the high performance products division.

In late June 2010, BASF bought out Cognis for 3.1 billion euros. Through this acquisition, BASF has become the world leader for chemical specialities for the cosmetics industry, having previously occupied 3rd place in the rankings. It remains the absolute leader for detergents and has moved up from 6th to 3rd position for additives for the food industry.

BRASKEM

The Brazilian petrochemicals company Braskem is experiencing robust development, through internal and external growth, with the stated ambition of becoming one of the leading players in the world. In 2009, its revenues were 19.5 billion reals (10 billion US dollars). Braskem is now in 8th position worldwide for the PE, PP and PVC family of products and in 3rd position in North and South America combined.

Since April 2009, Braskem has been building a 200,000-tonne plant to produce polyethylene from sugar cane ethanol which should be operational in the second half of 2010. This represents an investment of 500 million reals. It will consume 330,000 t of ethanol per year. Braskem is working on projects for the manufacture of polypropylene and EDPM (ethylene-propylene-diene monomer.). A few months ago, Braskem considered that world demand for biosourced polyethylene was 600,000 tonnes, with possibilities for substantial premiums on the price.

Braskem is a partner of Toyota Tsuho for the marketing of its biosourced polyethylene in Asia.

In 2009, Braskem signed a partnership agreement with Novozymes to develop the production of biosourced polypropylene from cane sugar. This project will last for at least 5 years.

With the North American start-up Genomatica, Braskem is studying the possibility of producing bioplastics from cane sugar (Genomatica has technology to produce butanediol from sugar).

CRODA – UNIQEMA

Croda is a British producer of chemical specialities with operations in 35 countries and a workforce of 3500. In 2009, Croda had revenues of 916 million pounds sterling.

Croda and its subsidiary Uniqema are active in oilseed chemistry. In particular, they manufacture various products from C36 fatty acid dimers (copolyesters, polyurethanes, epoxy resins).
DRT “Dérivés Résiniques et Terpéniques”:
DRT is a French family-owned group and the only refiner in France of pulp co-products and resin tapping products.

The DRT group has revenues of 220 million euros, 75% of which comes from exports, with 1200 employees, 700 of them in France. Its industrial sites are located in France (Castets, Vielle Saint Girons and Lespéron, in the Landes département), India (Roha) and China (Wuxi). It has a range of over 250 products. Every year, DRT consumes 120,000 - 130,000 tonnes of raw materials from France (pulp manufacture co-products) or abroad (tapping products, pulp co-products). DRT distills 35,000 t of paper essence and 5000 t of gum essence. The company has developed a forest platform in Madagascar which supplies it with pine essences and pine gum products.

DOW CHEMICAL COMPANY
The North American company Dow is one of the world’s leading chemicals groups; it produces specialities and commodities. In 2009 it had revenues of 45 billion dollars (67 billion in 2008) with 52,000 employees and 214 production sites in 37 countries. Dow bought out Rohm and Haas in 2009.

Dow is active on 8 market segments (electronics and speciality materials; coverings and building materials; healthcare and farming; performance products; basic plastics; basic chemicals; hydrocarbons and energy)

Dow gave information about various projects for the production of biosourced chemicals in 2007 (propylene glycol from glycerol, in the USA, ethylene from bioethanol, in Brazil), but the current crisis seems to have stopped or at least delayed these projects.

Dow’s performance products include epoxy resins. In 2007, press releases announced the group’s intention to produce biosourced epichlorohydrin from glycerol. Projects for the development of an industrial unit in China were announced in 2009.

Dow AgroSciences, described above, brings together the group’s seed and crop protection activities, with revenues of 4.5 billion dollars in 2009.

DSM
The Dutch company DSM (which stands for De Nederlandse Staatsmijnen = Dutch State Mines) was founded in 1902 and was originally active in coal mining. It is now an international chemicals group, with diversified activities in five areas: Nutrition, pharmaceutical products, performance materials (polyamides, polysterers, polycarbonates, adhesive resins), intermediates for polymers (caprolactam and acrylonitrile), chemicals and basic materials. As early as 1998, DSM bought out Gist-Brocades (enzymes and yeasts), positioning itself in biotechnology. DSM presents itself as controlling all of the value chain from pre-processing and conversion of biomass, right through to chemical derivatives and their applications.

DSM produces succinic acid chemically in Austria. The group is a partner of Roquette for the development of biosourced succinic acid production by fermentation.

DSM is active in the development of second-generation biofuels and takes part in EU and North American projects on this issue, working more particularly on producing yeast strains for use in biorefineries using wheat straw and other lignocellulosic materials.

In 2009, DSM launched a polyamide composed mainly of castor oil derivatives (EcoPaxx™).
DUPONT

DuPont is a North American group which is diversified into 5 types of activity: electronics and communication technologies, performance materials, coatings and colour technologies, safety and protection, agriculture and nutrition (including seeds and plant protection as stated above). DuPont is thus one of the rare companies in the world active upstream from agriculture (with expertise in variety selection and green biotechnology) through to commodity and speciality chemicals (including the production of biosourced materials and expertise in white biotechnology). DuPont had 60,000 employees and revenues of 26 billion dollars in 2009.

The Performance materials activity includes production and marketing of polymers including products made from PTT derived from biosourced 1,3 propanediol (marketed under the Sonora® and Biomax® brands). DuPont had worked with Genencor to develop technology for the manufacture of biosourced 1,3 PDO from glucose. Production is undertaken by the joint venture with starch producer Tate & Lyle, DuPont Tate & Lyle Bio Products. DuPont’s range of biosourced products also includes Cerenol™ polyols (made from PDO) and Hytrel® RS thermoplastic elastomers.

DuPont and BP have set up the joint venture Butamax™ Advanced Biofuels LLC to develop the manufacture of fuel butanol, aiming for a similar cost as that of ethanol. The pilot unit is being built in England and should be operational in 2010. The objective is to have commercial production by 2013.

DuPont has formed a 50/50 joint venture, “DuPont Danisco Cellulosic Ethanol LLC” with Danisco (Genencor) to develop integrated production technology for second-generation bioethanol.

FORCHEM

The independent Finnish company Forchem is one of the few tall oil refiners, in competition with DRT and Arizona Chemicals.

HUNTSMAN is a North American chemicals group which had revenues of 7.8 billion dollars in 2009 (10.2 billion in 2008).

Huntsman’s activities are divided into 5 segments: Polyurethanes, Advanced materials, Products for textiles, Performance products and Pigments.

Huntsman produces glycerol carbonate. In March 2009, Huntsman announced the launch of biosourced glycerol carbonate, a co-product of biodiesel. The group is a major propylene glycol producer. In 2007 it announced a project for the production of this chemical from plant-based glycerol, which does not yet appear to have been put into effect.

LANXESS is a German speciality chemicals company and world leader for synthetic rubber. In 2009, it had revenues of 5 billion euros.

In mid-2010, Lanxess was taken over by the North American company Gevo, which is developing technology for the production of butanol and isobutanol by fermentation. Isobutene (= isobutylene), a polyisobutene (PIB) synthetic rubber monomer may be derived from this.
M&G – MOSSI & GHISOLFI

M&G is an Italian family-owned company and world leader for the manufacture of PET (polyethylene terephthalate) for its applications in packaging. M&G has production capacities totalling 1.7 million tonnes of PET; in 2007 it had revenues of US$ 2.5 billion. The group is active in Italy, Brazil, Mexico and the USA.

Since 2005, M&G has been engaged in R&D activities relating to bioethanol and is conducting a project known as Pro.E.SA on second-generation biofuels.

M&G has initiated cooperation with Amyris, whose farnesene could become an ingredient for the manufacture of PET. M&G and Amyris intend to work together on the M&G’s Pro.E.SA project for second-generation biofuels.

PETROBRAS

Petrobras is the Brazilian petroleum company, in which the Brazilian state is the majority shareholder. The group has some 77,000 employees and had revenues of 92 billion dollars in 2009.

Petrobras has the ambition of becoming a major biodiesel producer (diesel fuels are required to contain 5% biodiesel by Brazilian law) and playing an active role in the development of the Brazilian ethanol production chain. At the end of April 2010, Petrobras and Terres International announced their partnership involving the gradual takeover by Petrobras of a 45.7% share in Accra Guarani S.A., a subsidiary of Terres. This alliance will enable Petrobras to secure its bioethanol supplies.

RHODIA

The French group Rhodia has operations in Europe, Asia, North America and Latin America. It had revenues of 4 billion euros in 2009, with a workforce of 13,600. Rhodia is organised into 6 business lines: “Polyamide” (polyamide 6.6 and technical plastic derivatives); “Nove care” (surfactants and speciality polymers; gauras and derivatives; phosphorus chemistry); “Sicle” (High performance silica, rare clays, diphenols for vanillin); “Acetol”: cellulose acetates, “Energy services” (CO₂ emission credits) and “Eco services”.

Rhodia consumes plant raw materials from various different production chains: purified pine, eucalyptus and spruce cellulose to produce cellulose acetates; fatty acids and glycerol from coconut, palm, soybean, rapeseed, peanut and castor bean to produce surfactants, solvents and technical polymers.

The biosourced products made by Rhodia include Tchany® extens PA 6 10, launched in 2009, for which the sebacic acid is produced from castor oil; vanillin, produced from ferulic acid from rice husks; surfactants manufactured from sorbitol and sorbitan; the green solvent has particular Augeo™ properties (glycerol cetal) produced from glycerol; Rhodapex® ESB-70 Nat, a surfactant made from ethylene oxide from sugar cane and palm lauryl alcohol, etc.

SOLVAY

Solvay is a family-owned Belgian multinational chemicals group. In 2009, it had revenues of 8.5 billion euros, with a workforce of 28,000. The group has two areas of business: chemicals and plastics (special polymers and vinyl polymers). Solvay has operations in 50 countries, with industrial units in Europe, Brazil, Korea, China, India, Russia, the USA, Thailand, etc.

Solvay is the world’s 4th largest epichlorohydrin producer after Dow, Hexion and Bohai.
Solvay pays great attention to sustainable development and has announced and begun two major projects in plant chemistry:

- **The production of epichlorohydrin from glycerol**, in France (Tavaux site, with an operational capacity of 10,000 tonnes) but above all in a plant being built in Thailand (with a capacity of 100,000 t, operational in 2012; the source will be palm glycerol, validated for its sustainable production) The “Epicerol®” technology is covered by a large number of patents and enables huge cuts in chlorine residues. Solvay serves the free market with epichlorohydrin for industrial companies which do not include its production in their chain. Solvay will thus balance its production of epichlorohydrin between that made from propylene (on its German site and part of its production in France) and that made from glycerol (on its site in Thailand and part of its production in France).

The Epicerol® technology enables significant reduction in the environmental impacts of the epichlorohydrin production.

- **The manufacture of PVC from ethylene produced by the dehydration of cane ethanol to sugar in an integrated unit** (Solvay Indupa) in Santo André, Brazil. The bioethylene production capacity will be 60,000 tonnes per year, enabling the production of 130,000 t of vinyl chloride monomer. One-third of the site’s production of 360 kt will thus be biosourced. The Brazilian company Copersucar will supply Solvay with ethanol.

Solvay participated in the French BioHub project.

**TOTAL and TOTAL PETROCHEMICALS**

The French petroleum group Total has 96,000 employees in 130 countries and had revenues of 131 billion euros in 2009.

Total has got involved in the development of first-generation biofuels by producing ETBE, which is compatible with petrol, from bioethanol and by incorporating fatty acid methyl esters from the oilseed production chain into its diesel fuel. Total is interested in second-generation fuels, as shown by its participation in two French projects, one using biochemistry (Futuroil) and the other using thermochemistry (BioTfuel). In 2009, Total bought shares in the North American companies Gevo (conversion of sugars into butanol and isobutanol) and Coskata (production of bioethanol from syngas produced by heat treating biomass). Total is also a stakeholder in the Bio-DME project initiated in Sweden in 2008 with the support of the EU for production and experimentation on DME for trucks, produced from paper black liquor. The Total group is also interested in the potential of microalgae.

In late June 2010, Total bought a 17% stake in the North American company Amyris Biotechnologies (production of terpene fuels from sugar), for 133 million dollars.

“The Group has chosen to actively build up its skill in the field of biotechnology, by means of partnerships with university laboratories or start-ups”. This is the direction for Research and Development in the “Gas and new energies” department which runs the corresponding activities.

In 2007, the subsidiary Total Petrochemicals formed the joint-venture Futerro with the Belgian company Galactic for the production of PLA from sugar.

**TRANSFURAN CHEMICALS** is a Belgian company specialising in the production of furfural and derivatives from hemicelluloses from lignocellulosic waste.
BIOREFINERIES: OVERVIEW AND DEVELOPMENT

The list of biotechnology companies presented is very incomplete because a large number of start-ups have come into being over the last few years and are in competition with the companies who have been active in the sector over a longer period. Differing positioning can be observed, with some companies remaining dedicated to research and others aiming to produce biochemicals or biofuels for which they have developed the manufacturing technology.

AMYRIS

Amyris Biotechnologies Inc. is a North American company which was founded in 2003. It develops production technology by fermentation (from sugars) for terpene chemicals (farnesene, tetramethylcyclohexane, etc.) able to be incorporated directly into diesel, petrol or kerosene. Amyris developed its know-how by making strains capable of producing Artemisinin, a pharmaceutical terpene chemical used to treat malaria. Amyris then acquired strong competences in the field of fuel chemistry.

Amyris Brasil, the group’s Brazilian subsidiary, formed several partnerships in late 2009 with major sugar and bioethanol producers, with operations in that country: the multinational group Bunge, Cosan, and the Brazilian subsidiary of the French cooperative group Tereos, Açúcar Guarani. The aim is to use Amyris’ technology to produce biofuels and other chemicals from cane sugar. The products obtained will be marketed by Amyris. Amyris will produce biodiesel from Açúcar Guarani molasses.

During the same month, Amyris announced that it was forming joint venture SMA Indústria Quimica S.A with another Brazilian sugar and ethanol producer, the São Martinho group. The agreement was revised in April 2010 but it is indeed on one of this partner’s sites that Amyris will be building its first farnesene production unit, with an annual capacity of 100,000 litres, which should be operational in 2010.

Since late 2009, Amyris has had support worth 25 million dollars from the US energy department for the development and production of biodiesel from sweet sorghum.

In Australia, Amyris is working with other companies on the production of aviation fuels

At the end of June 2010, there were a large number of announcements regarding Amyris. The French petroleum group Total bought a 17% stake in its capital for US$ 133 million. Amyris also signed an agreement with Soliance (a subsidiary of ARD) which is beginning to develop chemicals for cosmetics using Amyris technology. During the same month the company also signed a partnership with M&G Finanziara (for the introduction of farnesene as an ingredient in PETs), another with Procter & Gamble (for the development of speciality chemicals) and another again with Shell (supplier to the oil company of diesel fuel made from farnesene). At the end of July 2010, Amyris Brasil announced it was commencing 6 months of tests on its renewable diesel fuel on a captive fleet of vehicles with SPtrans (the public transport system in the city of São Paulo, Mercedes-Benz, Petrobras and the transport company Viação Santa Brígida).

ARBOR FUEL INC.

ARBOR FUEL INC. is a North American biotechnology company, positioned on the development of second-generation biofuels produced by fermentation. Arbor Fuel is believed to have yeast strains enabling the production of butanol and ethanol, from C6 and C5 sugars as well as strains being developed to directly metabolise cellulose and hemicellulose.
ARD (Agro Industrie Recherches et Développements)

ARD is a research organisation owned by Sicla (43%), Cristal Union (18%), Chamito (8%), the Caisse Régionale du Crédit Agricole du Nord Est and alfalfa cooperatives. Located on the Comacle-Betancourt biorefinery site, ARD was founded in 1989 to develop new uses for the agro-supplies of its shareholders (cereals, beet, alfalfa, etc.). ARD has skills in white technology (positioned as a benchmark platform), green chemicals (biofuels, solvents, surfactants) and agri-materials.

ARD’s subsidiary, Soliance, specialises in ingredients for cosmetics and produces notably DHA. Soliance has annual revenues of 15 million euros. In June 2010, Soliance signed an agreement with the North American company Amyris to use is terpene chemical production technology in its product ranges.

ARD has formed a joint venture known as Bio Amber with DNP Green Biologics. Its industrial demonstration unit Biodémo is producing its first batches of succinic acid on the Pomacle-Bazancourt site. The unit has a capacity of 2000 tonnes. ARD and Soliance have a total of around 140 employees.

ARD has created an innovation platform, Bioraffinerie Recherches et Innovations (BRI), to be the international benchmark centre for biorefineries. The project has been approved by the Industries and Agro-Resources competitiveness cluster and mobilises investments worth 21 million euros. BRI will also host a chair in white biotechnology and a research unit for the Paris Ecole Centrale, AgroParisTech and further education establishments in Reims.

BIOMETODES

Biométhodes is a French company, present at the Evry Genopole specialising in enzyme engineering. BioMéthodes successfully develops technology for applications in healthcare but has also engaged in the development of processes to convert lignocellulosic biomass into ethanol and sugars into biohydrogen. With this in view, Biométhodes signed a partnership agreement in 2008 with Virginia Tech Intellectual Properties Inc. (VTIP).

BUTALCO GmbH is a Swiss company, founded in 2007, which develops processes for the production of ethanol and butanol by yeast fermentation (Saccharomyces cerevisiae) metabolising C5 and C6 sugars produced by the breakdown of lignocellulose. A pilot project is to be implemented and operated on the site of Hohenheim University in Germany as of summer 2010.

BUTAMAX Advanced Biofuels is a joint venture, formed in 2009 between DuPont and BP, to develop biobutanol from various plant raw materials.

COBALT BIOFUELS

Cobalt biofuels was founded in 2006 to develop technologies for the production of butanol, using particular non-GMO strains of Clostridium, capable of metabolising C5 and C6 sugars and using starch, cellulose, hemicelluloses and pectins as raw materials. Cobalt Biofuels plans to have an operational unit by the end of 2011.

COSKATA

Coskata is a North American company which develops original technology for the production of ethanol by gasification of biomass followed by biofermentation of the syngas obtained. The microbial strains used convert carbon monoxide and the hydrogen from the syngas into ethanol. They are not very sensitive to the impurities found in the syngas.
Coskata claims that it can produce 380 litres (100 gallons) of ethanol per tonne of carbon dry matter. It promises flexible technology in terms of dry matter, which does not require the use of enzymes and uses very little water. A specific ethanol purification process has been developed in which it is obtained in smaller concentrations than following tradition sugar fermentation. A pilot plant has been running in Pennsylvania since late 2009.

The French petroleum company Total became a shareholder in Coskata in 2010.

DEINOVE

Deinove is a start-up which was set up in 2006 specifically to use the potential of the group’s deinococcus bacteria, which have particular self-reconstruction properties in their DNA in the case of radiation damage. These bacteria are found naturally in particular environments. They have a particularly large genetic and metabolic diversity.

Deinove has announced two areas of development: one in the production of second-generation ethanol, by developing thermophilic deinococcus strains, which are capable of using cellulose and hemicelluloses directly as a substrate; the other aims at developing deinococcus applications in the field of green chemicals, in particular the production of organic acids (succinic, lactic, fumaric and butyric acids).

Deinove is working with Tereos to develop new avenues with better performance for the production of bioethanol, including in particular the fibrous part of wheat grains, found in the bran. Both partners are the main players in the Deinol project, costing 21 million euros with 9 million euros’ worth of support from Oséo. It also involves the CNRS, Montpellier University and the LISBP in Toulouse. Deinol is aiming to increase the yield of ethanol and co-products in an existing bioethanol plant, with the prospect of developing innovative second-generation processes. On July 1st, 2010, a press release announced the signature of a research partnership between Deinove and the Finnish technical research centre VTT, which has vast knowledge of the enzyme degradation of lignocellulose. The VTT will take part in the Deinol project.

DNP GREEN TECHNOLOGY

DNP is a North American company with Japanese and North American shareholders which uses US DOE patents for the production of succinic acid by fermentation using specific strains of E. coli.

DNP has set up a joint subsidiary with ARD (in the Champagne Céréales group) known as Bio Amber to develop the production of biosourced succinic acid. In 2010, the pilot unit on the Pomacle site will produce 2000 t of product.

GALACTIC

Galactic is a subsidiary of the Belgian multinational sugar producing group Finasucré, founded in 1994. Galactic is the second largest producer of lactic acid and lactates after Purac (the 3rd largest after Cargill if the lactic acid production by Cargill-Natureworks, dedicated to the production of PLA, is taken into account). Its total production capacities are 100,000 tonnes, in Belgium, the USA and China. In 2007, Galactic set up a joint venture, Futerro, with Total Petrochemicals for the production of PLA (Poly Lactic Acid) and more particularly the production of second-generation PLA. Galactic currently produces 2000t of PLA.
GENENCOR, DANISCO group

Danisco is a Danish group in the sugar producing world which produces and markets bio-ingredients for food-processing and other industries. Danisco has a workforce of 7000 with revenues of 13 billion Danish crowns in 2009-2009. Its Genencor division (4 billion Danish crowns in revenues) is the second largest in the world, after Novozymes, on the enzyme market.

- Genencor worked with DuPont to develop the production of biosourced 1,3 propanediol (PDO).
- Danisco has formed a 50/50 joint venture “DuPont Danisco Cellulosic Ethanol LLC” with DuPont to develop integrated production technology for second-generation bioethanol. Genencor presents a large range of enzymes and enzyme cocktails with cellulosic activity.
- Danisco works with the tyre manufacturer Goodyear Tire & Rubber Company to develop biosourced isoprene “Bioisoprene®” from biomass (sugar?, other?) to manufacture synthetic rubber. Pilot productions were carried out in 2009 and commercial production is planned for 2013.

GENOMATICA

Genomatica is an American start-up which has a technological platform enabling it to produce a large number of biochemicals from plant raw materials. Genomatica is interested only in products with very large markets and highlights its capacities for the production of 1,4 Butanediol (BDO) from sugars (glucose, xylose), with a modified E. coli strain, as well as butanone (or ethyl methyl ketone - MEK).

In late 2009 the announcement was made that Genomatica is studying the possibility of working with the Brazilian petrochemicals company Braskem to produce biosourced polymers (from cane sugar converted into BDO).

In mid 2010, Genomatica announced the successful pilot production of 3000 litres of BDO from glucose.

Genomatica is a partner of several companies including Cargill/Natureworks, Dow, DSM (which produces succinic acid with Roquette), Kyowa Hakko, Unilever and Verenium.

GEVO

Gevo is a North American biotechnology company, which specialises in the production of isobutanol, also with projects for the production of isobutene (= isobutylene).

Gevo offers an integrated technological solution, GIFT®, for the manufacture of isobutanol on sites which are currently dedicated to the production of bioethanol.

Gevo has formed strategic partnerships with Cargill, using its patented strains of yeasts, and the engineering company ICM, which is an expert in bioethanol production processes.

The French petroleum group Total became a shareholder in Gevo in 2009 through its subsidiary Total Energy Ventures. The German speciality chemicals company Lanxess, a leader for synthetic rubbers, also became a shareholder in Gevo in mid 2010, with a stated interest in its bioisobutene production technology.

GLOBAL BIOENERGIES

This French start-up, created in 2008, is based in the Evry Genopole and is developing a project for the production of isobutene (= isobutylene) by fermentation, from sugars. In February 2010, Global Bioenergies received funding worth €760,000 from Oseo to accelerate the development of its process. The product is obtained in gaseous form, which greatly facilitates its extraction and purification.
ITACONIX
This North-American company manufactures itaconic acid and linear or branched polyitaconic acid polymers by fermentation from sugars (corn glucose, etc.) for use in detergents, water treatment and other applications using the superabsorbent properties of these polymers. Itaconix is also working with public backing on the production of itaconic acid from wood.

LS9 is a North American start-up based in San Francisco, with a pilot plant in Florida. Its technology enables the production of alkanes and alkenes from modified Escherichia coli strains into which a sequence of blue microalgae genes have been introduced. LS9 is developing production processes for diesel fuels and surfactants from cane sugar juice. It is a partner of Procter & Gamble for the work on this family of products.

METABOLIC EXPLORER (Met Ex) is a French “biological chemistry” start-up, founded in 1999 and based in Clermont-Ferrand. It has about one hundred employees.

Met Ex is positioned in commodity chemistry developing solutions for substitutes for fossil raw materials. The company has two bacterial platforms: *E. coli* and *Clostridium acetobutylicum*.

Metabolic Explorer has projects which have reached different stages for the production of five substances by fermentation:

- **L-méthionine**, an amino acid which is important for animal feed, which was still produced synthetically, from propylene.
- **Glycolic acid**.

  The production licences for these two products have been granted to Roquette.

- **1,3 propanediol** (PDO), from glycerol, using a process which is believed to be more economically viable than that of Genencor / Du Pont – Tate & Lyle.
- **Monopropylene glycol (MPG) or 1,2 propanediol**.
- **n-butanol** for its applications in the chemicals industry (solvents, paints, adhesives).
- As part of the Bio Hub project, Met Ex has been developing technology for the production of glycolic acid by fermentation, with Roquette, since 2006. An effective bacterial strain was discovered mid 2008.
- Métabolic Explorer wants to improve its position on the value chain by becoming a producer of some of the molecules it is working on. A pilot plant has been built on the company’s site.

METABOLIX
Founded in 1992, the US biotechnology company Metabolix Inc is dedicated to the production of polyhydroxyalkanoates (PHAs), using metabolic engineering tools. Metabolix has formed the joint venture Telles with ADM which produces marketed PHAs for its own account by corn glucose fermentation using modified microorganisms. A new 50,000-tonne unit, marketed under the Mirel brand, has been operational since April 2010. It was built by ADM for a cost of US$300,000. In 2010, Papermate adopted Mirel’s product for the casing of biodegradable pens.

Metabolix is also developing genetically modified plant which are capable of producing PHAs, using technology purchased from Monsanto in 2001. The company has produced modified varieties of switchgrass (*Panicum virgatum*) producing PHAs which can be extracted before using the rest of the plant to produce energy. Work on sugar cane and oilseed plants is in progress.
Metabolix also plans to implement a project for the production by fermentation of a C4 platform chemical, which may have derivatives with broad applications in resins, polyurethans, solvents and beauty care products. Watch this space!

**MYRIANT TECHNOLOGIES**
This North American start-up, created in 2004, originally used know-how from the University of Florida. Myriant has developed technology for the production of **D-lactic acid**, for which **Purac** has been granted the exclusive licence.

Myriant is finalising technology for the production of **succinic acid** by fermentation and has received commitment for 50 million dollars’ worth of support from the US energy department to build a production unit, using sorghum, in Louisiana. Myriant is also working on the production by fermentation of fumaric and malic acids.

**NOVOZYMES** is a subsidiary of the Danish pharmaceutical group **NOVO NORDISK**.
Novozymes is the world leader on the industrial enzymes market (47% market share, ahead of **Danisco**). The company also produces and markets strains of microorganisms for industrial use and pharmaceutical ingredients. In 2009 its revenue was 8.5 billion Danish crowns.

Novozymes is a partner of **Cargill** in a project for the production of **3-HPA** (3-hydroxypropionic acid, a potential precursor of acrylic acid from corn glucose).

Novozymes is also a partner of **Braskem** in a project for the production of polypropylene from cane sugar.

Novozymes is actively developing new enzymes and technologies enabling the improvement of the breakdown and lignocellulosic raw materials, as well as the production of second-generation biofuels. In Brazil, Novozymes is a partner of the sugar cane technical centre (Centro de Tecnologica Canaviera) on a project using bagasse. In China, Novozymes is working with the China National Cereals, Oil and Foodstuff Corporation (COFCO) and Sinopec (using corn stalks).

**OPX BIOTECHNOLOGIES** is a North American synthesis biology and metabolic engineering company, which has the support of various investment funds. OPX is developing technology for the production of **acrylic acid** by fermentation from sugars, on an **E. coli** platform. OPX is also working on biofuel production.

**PURAC**

Purac is a subsidiary of the food-processing group **CSM**, a leader in ingredients for bakeries, which had revenues of 2.6 billion euros in 2009 and has over 8400 employees in 25 countries. Purac specialises in fermentation technologies, with revenues of €355 million in 2009 and a workforce of 1000.

**PURAC** is the world-leading producer of **lactic acid**, producing a total of 200,000 t on 3 sites: in Thailand (from cassava starch), in Brazil (from sugar) and in the United States (from corn glucose). The main derivatives of lactic acid are produced in the Netherlands whereas lactides and D-lactic acid are produced in Spain.

A 75,000-tonne lactide plant, representing an investment of 45 million euros, is currently being built on the Rayong site in Thailand. This unit will produce **L- and D-lactides** from lactic acid produced by the different Purac plants. The company is therefore intending to develop second-generation **PLAs**, with a high melting point.

The technology for the production of D-lactic acid comes from the biotechnology company **Myriant technologies**.
With the Dutch company **Symbra Technologies**, which specialises in expanded polystyrene, and the Swiss engineering company **Sulzer Chemtec Ltd**, Purac is building a production plant for PLA foam.

Purac and the Japanese company **Totobo** have begun working together on the production of PLAs for particular applications which will be sold under the Vyloeco® brand.

With the technological support of a **BASF** subsidiary, Purac is developing the production of biosourced succinic acid on its Spanish site.

**PROTEUS**

Protéus is a French biotechnology company specialising in proteins and protein engineering, and developing innovative biocatalysis processes.

In 2006, with **PCAS**, Protéus set up a joint subsidiary, **PCAS Bio solution**, to develop manufacturing processes for chemicals of pharmaceutical interest.

More recently in 2009, Protéus entered into a partnership with **ARD**. During the same year, the company formed a partnership with the **Singent** group to develop enzymes for manufacturing biofuels.

**SYNTHETIC GENOMICS Inc. (SGI)**

SGI is a North American company which is engaged in the development of synthesis biology technology.

SGI is working with Exxon Mobil on the production of biofuels from microalgae. The company is also a partner of the BP group.

**TETRAVITAE Biosciences Inc.** is a North American company which is developing technology for the production of **butanol** by fermentation using a particular strain of *Clostridium beijerinckii*.

**VERDEZYNE – CODAGENOMICS**

This North American company, which is supported by investment funds, is active in metabolic engineering and synthesis biology. It is developing two specific projects on a yeast platform, one for more efficient production of **ethanol** from C6 and C5 and the other for the production of **adipic acid** from vegetable oils or alkanes. It works with companies such as **Lallemand** on improving GMO yeast strains which produce ethanol, and with **Novozymes** and **Genencor** to modify the properties of industrial enzymes. Verdezyne is also a partner of **Syngenta**.

**VERENIUM**

The North American company Verenium develops enzymes and technology for the production of second-generation ethanol from cellulosic biomass.

For the development of enzymes, Verenium works with or for large groups such as **BASF**, **Bunge, Cargill, Danisco** and **Syngenta**.

As regards the production of cellulosic ethanol, its pilot plant in Louisiana, which is currently being optimised, has capacity of 5300 m³ per year. Another pilot plant with a capacity of 1400 m³ is operational in Japan. It uses timber waste. In Thailand, a third pilot plant with a capacity of 3000 m³/year uses sugar cane co-products in Thailand. In 2008, Verenium also began work with **BP** on the development of technology for the production of cellulosic ethanol.
ZEACHEM is a North American company which develops technology combining biochemical and thermochemical processes to manufacture ethanol, acetic acid and ethyl acetate from cellulosic biomass. The biomass used comes from wood, switchgrass and corn stalks. It is broken down using a chemical process into C5 and C6 sugars, then undergoes acetogenic fermentation. A pilot plant with a capacity of 250,000 gallons (9500 hl) per year will commence operations in Oregon. Zeachem also plans to develop a set of C3 chemicals (propionic acid, propanol and propylene).