

New Biofuel Technologies

New pathways are emerging in the wake of the boom in the biofuels market. Their development is driven by the search for improved product quality and a broader range of natural plant feedstock. Interested in these new pathways, the oil companies are seeking to differentiate themselves on a market that promises to be very competitive in future. This is a turning point in a sector that has historically been dominated by agrifood companies.

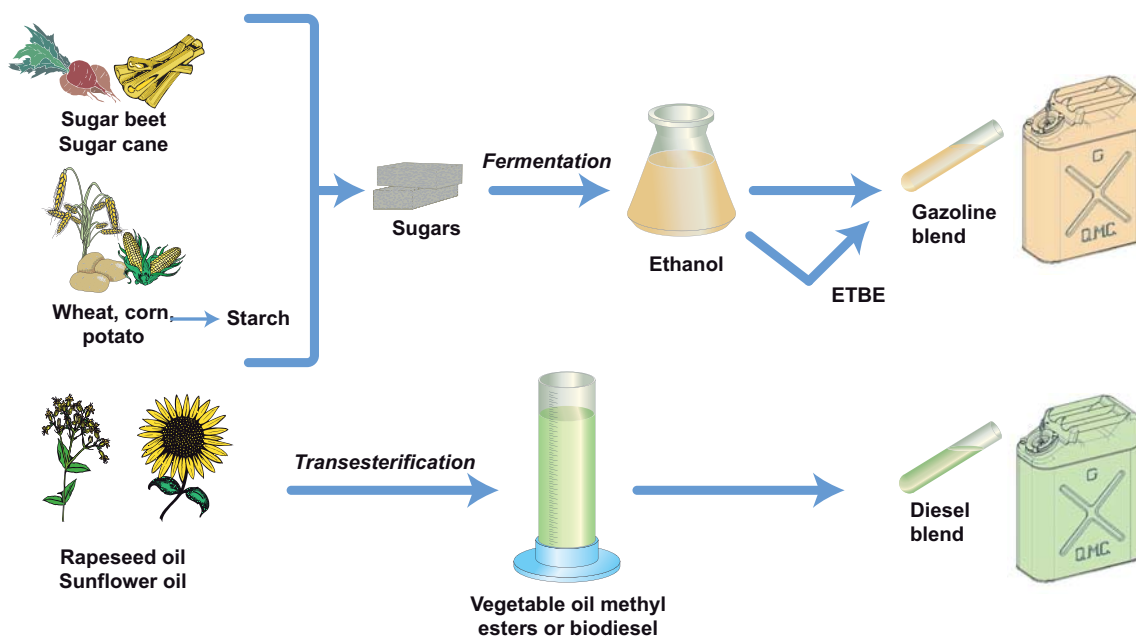
Today, there are two main types of biofuel (Figure 1): ethanol for use in “gasoline” type engines and vegetable oil methyl esters (VOMEs) for “diesel” type engines. Ethanol is the most commonly used biofuel in the world (cf. Panorama article “*Biofuels Worldwide*”). Its output is almost ten times that of biodiesel: 36 Mt in 2005, of which 80% was used for motor fuel, versus slightly less than 4 Mt for biodiesel.

Ethanol is currently made from two types of crop (Figure 1): sugar-producing plants (sugar cane, sugar beets) and plants yielding amylaceous material (wheat, corn). These different pathways all include a fermentation step to convert the sugars to ethanol and a distillation step, more or less advanced, to separate alcohol from water. This generates coproducts whose value often is key to project profitability. For instance, the ex-corn or ex-wheat pathway yields large quantities of grain residue (a little more than a ton of residue per ton of ethanol) that can be sold on the animal feed market.

Ethanol can be used pure, blended with motor fuels or in its ether form, ETBE, produced in reaction with refinery or petrochemical isobutene. It cannot be used pure or at very high concentrations (e.g. at 85% in E85) unless the vehicle has been modified for that purpose (injection systems, engine settings, compatibility of plastics and gaskets, special measures for cold starts when ethanol is used pure).

Ethanol is generally used at lower contents, between 5 and 10%. At these levels, the engine does not have to be adapted. On the other hand, certain technical difficulties can arise making it necessary to modify the logistics system. For instance, the gasoline and alcohol phases can separate in the presence of water at low ethanol concentrations, a phenomenon known as demixtion. Furthermore, adding ethanol to gasoline increases the vapor pressure, hence its propensity to evaporate. ETBE is used, mostly in Europe, to overcome these disadvantages.

Fig. 1 First-generation biofuel technologies



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VOMEs are produced from vegetable oils including rapeseed, sunflower, soybean or palm oils. When an oil is obtained by grinding oilseeds such as rapeseed, soybeans or sunflower seeds, a solid residue or "cake" is produced (1-1.5 ton per ton of oil) that is generally used for animal feed. Not suitable for direct use in existing passenger vehicle diesel engines, vegetable oils must be transformed by a reaction of transesterification with an alcohol—currently, methanol is used—to produce vegetable oil methyl esters and glycerin (0.1 ton per ton of VOME). A coproduct with numerous applications, glycerin contributes substantially to the ultimate profitability of this technology.

Like ethanol, VOMEs can be used pure or in blends. When used pure, the vehicle must be converted. Today, they are generally blended, with contents ranging from a few percentage points to 30% in captive fleets.

The new biofuel production pathways

In the wake of first-generation biofuels, other pathways are emerging based on other resources or other processing methods. The objective is to diversify available resources while improving product quality.

The pathways of intermediate generation

These new biofuel generations start with intermediate generation:

- **Animal oil** methyl esters. The use of waste animal fats broadens the range of suitable raw materials. While the potential of this type of conversion is limited, it could nevertheless prove useful in certain local situations.
- **Vegetable oil** ethyl esters (VOEEs). This variant of VOME fuel uses ethanol to synthesize the ester instead of methanol from natural gas. The final product possesses properties equivalent to those of VOMEs. Two regions of the world are interested in this technology: Brazil and Europe. In Brazil, this pathway is under development and can count on a plentiful supply of low-cost ethanol. In Europe, the main goal is to introduce ethanol into the pool of diesel fuel. The European automotive fuel market is characterized by high demand for diesel, which could become even more pronounced in future. Therefore, the development of biofuels in Europe necessarily involves heavy reliance on VOME technology. On the other hand, the need to optimize land areas used to produce biofuels militates in favor of developing ethanol (better yield per hectare). For this reason, the idea of adding ethanol to diesel fuel is very tempting. Since ethanol is not soluble in diesel and does not have physical properties compatible with direct use in a "diesel" engine, using VOEEs could be a good way to incorporate ethanol into diesel fuel.

However, the quantities of ethanol used are relatively low (15% by weight) and the final product is likely to be more expensive in Europe than VOMEs, due to technical constraints at the production stage and a large price difference between ethanol and methanol (a ratio of about 2 in 2006).

- **Syndiesel** obtained by **treating vegetable oils with hydrogen (hydrogenation)**. Two approaches are possible: coprocessing or the dedicated unit.

Coprocessing involves mixing a vegetable oil into an oil stream on its way to the hydrotreatment unit, then processing the mixture with hydrogen. The diesel leaving the unit contains some carbon of vegetable origin, which is impossible to distinguish from carbon of fossil origin. The advantage of this option is that biodiesel production can benefit from the effects of scale inherent to the oil industry. This avenue is being explored by the Brazilian state-owned company Petrobras via its H-bio product. Research in the United States has also explored other concepts based on the incorporation of streams of plant feedstock at refineries for coprocessing. In the next few years, these new options could herald the advent of new pathways, especially using fluidized catalytic cracking, for the production of biogasoline and other products.

The "dedicated unit" option has been developed by the Finnish company Neste Oil. The product obtained, NexBtL[®], is of 100% vegetable origin: no other oil besides vegetable oil enters the industrial unit. The properties of NexBtL[®] (e.g. a very high cetane number) make it very attractive as an addition to the pool of component streams used to make diesel fuel. This technology may develop further over the next few years. In Europe, at least four units (capacity: about 200,000 t/yr) are under construction or in the design phase. Finland is building one unit and has announced a second; both Austria and France each have one project in the design stage. This pathway not only yields diesel fuel of very high quality, but also allows some flexibility in the choice of vegetable oil used. Unlike the VOME pathway, which is constrained by the European standard to use rapeseed oil for the most part, NexBtL[®] biodiesel can be made from a wide variety of oils (palm, soybean or even animal fats).

Flexibility is a big asset, now that European rapeseed oil prices are so high (€605/t in October 2006), pushed up by strong demand for VOMEs. In comparison, the current prices of palm or soybean oil are significantly lower: about USD 500-520/t (€400-415/t) in October 2006. The companies investing in these new biofuel production units are integrated oil concerns. This is something new: until now, the biggest investors in biofuels have generally been from the agrifood sector.

It must be stressed that these units need substantial investment: this type of installation costs at least four times more

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than a VOME production unit of equivalent capacity¹. More research is needed to minimize costs. Because these technologies are so capital intensive, their profitability is very sensitive to the price of the raw material. Therefore, the development of this pathway is especially appropriate where cheap oil is available in sufficient quantity and the quality of the biofuel produced (cetane number > 80) will fetch a good price to help offset the heavy capital expenditure.

- **Butanol.** Here, the BP-Dupont project is an interesting example. The physical properties of butanol, a replacement fuel for gasoline, help overcome difficulties connected with the use of ethanol, e.g. problems of volatility or the fact that ethanol attacks some of the plastics used in the motor industry. Biobutanol can be blended with gasoline at contents as high as 10% volume without having to modify the engine. In future, it may be possible to boost this percentage to 16%². Biobutanol can also be used in blends with ethanol and gasoline or even diesel fuel.

The objective of the BP-Dupont project is to use biobutanol for the first time in Great Britain in 2007. Also involved in this venture, British Sugar aims eventually to convert a fermentation unit from ethanol to butanol. BP and Dupont are exploring the idea of producing biobutanol from a large number of raw materials: sugar cane, sugar beet, wheat, corn and lignocellulosic materials.

Second-generation biofuels

The so-called second-generation biofuels can be defined as those using lignocellulosic biomass as the raw material. The principal advantage is that they can be used to extract value from the most abundant carbon source on our planet (cf. Panorama article “Resources”).

Lignocellulosic biomass is composed mainly of three polymers from the cell wall of plants: cellulose, hemicellulose and lignin, present in varying proportions, depending on the plant (cf. Table 1).

Table 1
Composition of lignocellulosic biomass

Biomass	Lignin (%)	Cellulose (%)	Hemicellulose (%)
Softwood	27-30	35-42	20-30
Hardwood	20-25	40-50	20-25
Wheat straw	15-20	30-43	20-27

It also contains other elements (inorganic, silica, etc.) in proportions ranging from 5 to 15%.

(1) A NexBTL®-type unit costs €100 M versus €25 M for a VOME unit of equivalent capacity (i.e. about 160,000 t/yr).

(2) For all pathways that incorporate alcohol into motor fuels in Europe: existing regulations will have to be modified before any blend containing more than 5% can be developed.

These three polymers are closely interconnected in the layers of the cell wall, forming a rigid matrix that is hard to destructure.

Two pathways are under study today: one to **produce diesel motor fuel and kerosene (BTL)** and the other to produce **ethanol (Since ethanol is used to replace gasoline, it may be considered to be a biogasoline)**.

Biomass to Liquid technology

BTL technology is a “thermochemical” pathway whereby a liquid synfuel is obtained from biomass. It involves three important steps: biomass conditioning; gasification then processing of the syngas; synthesis of the motor fuel.

Some of these steps have been tested in industrial projects using natural gas (GTL) or coal (CTL) as the raw material. In the past, CTL technology has provided a solution to oil supply problems, for instance, in Germany during World War II and during the embargo on the apartheid regime in South Africa.

- *Biomass conditioning*

The first step is to transform the vegetable resource into a homogeneous material that can be injected into a gasifier. This usually involves thermal and mechanical transformations. Two methods can be used: **pyrolysis** and **torrefaction**.

Pyrolysis uses heat to break biomass down into three phases: solid (coal), liquid (bio-oil) and gas (mostly carbon dioxide, carbon monoxide, hydrogen and methane).

How these three phases are distributed depends on operating conditions (temperature, heating rate and residence time).

Slow pyrolysis, which is the better-known process, yields a solid (charcoal). Fast pyrolysis is the method envisaged for the BTL pathway. It involves maintaining a temperature of 500°C for a few seconds and produces mostly liquid (a bio-oil) with some coal in varying amounts.

Although these bio-oils look very much like petroleum, they are actually quite different. They contain several hundred chemical compounds (e.g. phenols, sugars, alcohols, organic acids and aromatic compounds) in proportions that vary greatly, and present the particularity of not being miscible with any petroleum product. These oils are then introduced directly into the gasifier.

Current research is seeking to convert these oils directly to motor fuels via hydrogen treatments. Although attractive, this direct pathway seems hard to implement, given the quantities of hydrogen needed and the fact that the chemical nature of the bio-oils produced is very different from that of conventional automotive fuels.

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The second method being considered for biomass pretreatment is **torrefaction**. Since the 1980s, a great deal of research has been done on the torrefaction of wood, which imparts very good resistance to attack by fungi and some types of insect. But it also lowers the mechanical strength of the wood, a characteristic exploited by BTL methods: torrefaction makes it easier to grind wood and thus obtain a finely divided solid suitable for certain gasification technologies.

Torrefaction is like a final drying operation (temperature: 240 to 300°C, residence time: up to one hour). Carried out at temperatures much lower than in pyrolysis, this process is much less energy intensive.

- *Gasification and syngas processing*

Unlike pyrolysis, which takes place in the absence of a reactive gas, gasification is a thermal operation that takes place in the presence of a gaseous reactive (water vapor, oxygen) and produces what is called a syngas that mostly contains hydrogen and carbon monoxide. It also contains impurities (carbon or inorganic) and other gases. In industrial use today, this mix is combusted in coal-fired or IGCC power plants (Integrated Gasification Combined Cycle). Blends like this were formerly used to power automobiles, e.g. the “Gazogène” wood gasifier used during World War II fuel shortages or water gas.

In a BTL process, which aims to produce a liquid motor fuel, the constraints imposed on syngas composition are more severe than for direct combustion. The idea is to maximize production of carbon monoxide (CO) and hydrogen (H₂) while achieving a H₂/CO ratio (about 2) compatible with motor fuel synthesis. It is also vital to eliminate impurities that would otherwise “poison” the catalyst used in Fischer-Tropsch synthesis. That's why biomass gasification generally takes place at a very high temperature (1,200°-1,300°C) and is followed by syngas purification steps.

These operations generate large quantities of CO₂, mostly as a result of combustion to supply process heat, and these emissions represent lost carbon that is not converted to motor fuel. This is the main explanation for the low fuel mass efficiency (< 20%). This efficiency could be increased by supplying additional external energy, electrical for instance, and/or additional hydrogen. In France, this solution has been proposed jointly by the French atomic energy agency (CEA) and IFP. For the two latter options, the overall energy efficiency of this technology is adversely affected (divided by two) in favor of the mass efficiency.

No specific biomass gasification technology has reached the industrial stage. Most of the solutions that have been put forward are derived from technologies for natural gas, coal or petroleum already in industrial use.

- *The synthesis of motor fuel*

Fischer-Tropsch synthesis, named for the two German chemists who invented it in the 1920s, is a reaction used to produce gasoline, diesel fuel and kerosene from syngas obtained by gasification.

This chemical reaction requires catalysts, of which two types are used: iron-based or nickel-based. In the presence of an iron-based catalyst, the Fischer-Tropsch reaction produces gasoline. In the presence of a cobalt-based catalyst, it yields bases for diesel fuel and kerosene. The products obtained are free of sulfur, nitrogen and aromatics.

The syndiesel has a cetane number of about 70, much higher than required under current standards (~50). Carmakers appreciate the fact that this motor fuel is of very high quality for vehicles. It emits fewer polluting emissions, especially particulates, than conventional diesel fuel.

Several Fischer-Tropsch technologies exist and some have reached the industrial or demonstration stage (Sasol, Shell, Statoil, Exxon, BP, Conoco, Rentech, IFP/ENI and Syntroleum).

Producing ethanol from lignocellulosic materials

The steps in the production of ethanol from lignocellulosic materials are much the same as those used in the ex-corn or ex-wheat process:

- the raw material is prepared;
- the cellulose is converted to glucose (sugar);
- the sugars are fermented to yield ethanol;
- the ethanol undergoes distillation and final purification.

We will only describe the first two steps. Unlike the other two, they are specific to the second-generation pathway.

- *Pretreatment of the raw material*

Two methods are currently used to pretreat the raw material once the straw has been shredded or the wood has been cut into chips. The structure of the lignocellulose is opened using the **steam explosion or heating in the presence of dilute acid methods**, offering access to the “sugars” (i.e. hemicellulose and cellulose); only cellulose can be converted to ethanol.

The dilute-acid pretreatment involves putting the plant material in the presence of an acid, preferably sulfuric acid, at a moderate temperature (about 150°C) for about 15 to 20 minutes. Processes that include a second step, carried out at a higher temperature (240°C for a few minutes), are also being investigated.

Steam explosion pretreatment. To destructure the lignocellulosic matrix, the raw material is briefly exposed to high pressure and temperature conditions (15 to 23 bar; 180 to 240°C) in the presence of steam then, suddenly, to low pressure. The development

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of this technology has been taken as far as the industrial stage (the Stake and Iogen processes).

Both of these pretreatments increase the cost of the process. In particular, they require investment in equipment that can withstand the pressure and corrosive acid conditions.

- *Converting cellulose to glucose*

The second stage consists of breaking down the cellulose molecules into glucose with the help of enzymes (enzymatic hydrolysis). From the economic standpoint, this operation is heavily penalized by the fact that enzyme consumption is between 10 and 100 times that of conventional methods (ex-corn or wheat). Many R&D projects aim to improve this method of conversion by optimizing the process directly and to work on increasing enzyme activity (molecular biology).

The glucose obtained is then converted in a very conventional manner, i.e. fermented, to produce ethanol. Some research studies are striving to combine the operations just described—enzymatic hydrolysis and fermentation—into a single step.

Using hemicellulose to produce ethanol is another avenue under investigation, the idea being to boost the competitiveness of this pathway. Today, glucose can only be obtained from cellulose, which represents 50% at most of lignocellulosic materials. Hemicellulose contains pentoses, which are sugars that cannot be converted to ethanol by the organisms usually used in fermentation. Obviously, this considerably inhibits profitability.

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First-generation biofuels are driving the development of new pathways, especially with a view to increasing “mobilizable” resources, including those that can be used as natural plant feedstock for refineries. This reflects the growing importance of biofuels in the oil-dependent transport sector. The avenues opened up by the Finnish firm Neste Oil and the Brazilian

national company Petrobras should see development in the next few years, because they allow biofuel technologies to benefit from economies of scale inherent to the oil industry. It also looks as if oil majors are moving into the biofuels market, historically dominated by agrifood conglomerates. Finally, oil companies have a competitive edge on this market owing to their knowledge of the transport sector (product quality) and to their technologies. Some majors are making a substantial move into the development of second-generation pathways.

A number of research projects now underway, especially in the United States and Europe, are focusing on second-generation technologies. IFP is a major player on the research scene both in France, where it is involved in the national bioenergy research plan, and in Europe, where it is leading the NILE³ Project bearing on the production of ethanol from lignocellulosic materials. A prime objective of these projects is to reduce production costs: today, it costs about €1/liter oil equivalent for both second-generation (ethanol and BTL) pathways. Ambitious targets have been set: €0.4/l for ethanol and €0.7/l for the BTL pathway by 2010-2015. Looking even farther in the future, some foresee a cost of €0.5/l oil equivalent for BTL. We might compare these figures with the current prices of gasoline and diesel fuel, which stand at €0.32/l and €0.37/l respectively, with the barrel of crude at USD 60.

Research on second-generation technologies is also seeking to find ways to market all coproducts. For instance, it is possible to produce ethanol and BTL motor fuels from lignocellulosic materials at the same industrial site, i.e. a biorefinery with a sugar platform as well as a thermochemical platform. Like existing refineries, it would produce a gasoline-type motor fuel (ethanol), diesel fuel, kerosene and bases of vegetable origin for the petrochemicals sector.

(3) *New Improvement for Ligno-cellulosic Ethanol.*

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