

## Second-generation pilot biofuel units worldwide

The production of biofuels from agricultural raw material is attracting great interest for many reasons, among them global warming, oil price hikes, the depletion of oil reserves and the development of new agricultural markets. However, the technologies currently under development are hindered by the fact that available land is limited and by a risk of competition with food crops. In the last few years, research and development efforts have sought to alleviate these limitations by exploring new pathways to convert little-used plant feedstocks to biofuels with better efficiencies. Large-scale research programs concentrating on these new technologies are underway in the U.S. and Europe, with industrial development expected between 2012 and 2020.

Production of the so-called "first generation" biofuels at industrial scale started on most continents nearly ten years ago in the case of VOME<sup>1</sup> (biodiesel), and more than twenty years ago for ethanol from agricultural feedstocks (biogazoline). The basic processes are well known, but renewed interest in these pathways since the beginning of the 21st century has led to significant progress in terms of product quality, utilities consumption and production costs. Yet these pathways continue to run up against limits. Eventually, large areas of farmland may be used to raise energy crops that are also used for food crops. Moreover, good sustainability practices must be implemented so that these pathways perform well in environmental terms.

Subsequent research programs focused on biomass-to-biofuel technologies, seeking to minimize environmental constraints and alleviate competition with food crops. The advantage of these so-called "second-generation" processes is that they use the lignocellulose in plants, i.e. the main component of the cell wall in any plant. This broadens the range of plants that can be converted to biofuels, including non-food crops that obtain significantly higher yields per hectare.

Today, major R&D efforts are focusing on two pathways for producing biofuels from lignocellulosic biomass:

- A biochemical pathway to ferment the sugars in lignocellulose and obtain ethanol the same product as existing bioethanol, a product that could be substituted for gasoline (Figure 1);
- A thermochemical pathway with two approaches to biomass conversion: gasification (an indirect method) and hydrothermal liquefaction (a direct method) (Figure 2).

Gasification involves producing a synthetic gas ( $H_2$ ,  $CO$ ,  $CH_4$ ,  $CO_2$ ,  $H_2O$ ) following a pretreatment that reduces biomass to particulate matter in dry or liquid form (slurry).

The gas can then be directed towards the production of various biofuels (Figure 3).

The biomass to liquid pathway (BtL) involves reacting the syngas using the Fischer-Tropsch process to yield synthetic diesel (FT diesel) that can be incorporated directly into diesel fuel, kerosene (potentially suitable for jet fuel) or naphtha (for petrochemicals or possibly gasoline).

The United States is also interested in exploring how this syngas can be used to produce ethanol.

[1] VOME: Vegetable oil methyl esters

## Second-generation pilot biofuel units worldwide

Fig. 1 - Lignocellulosic ethanol process

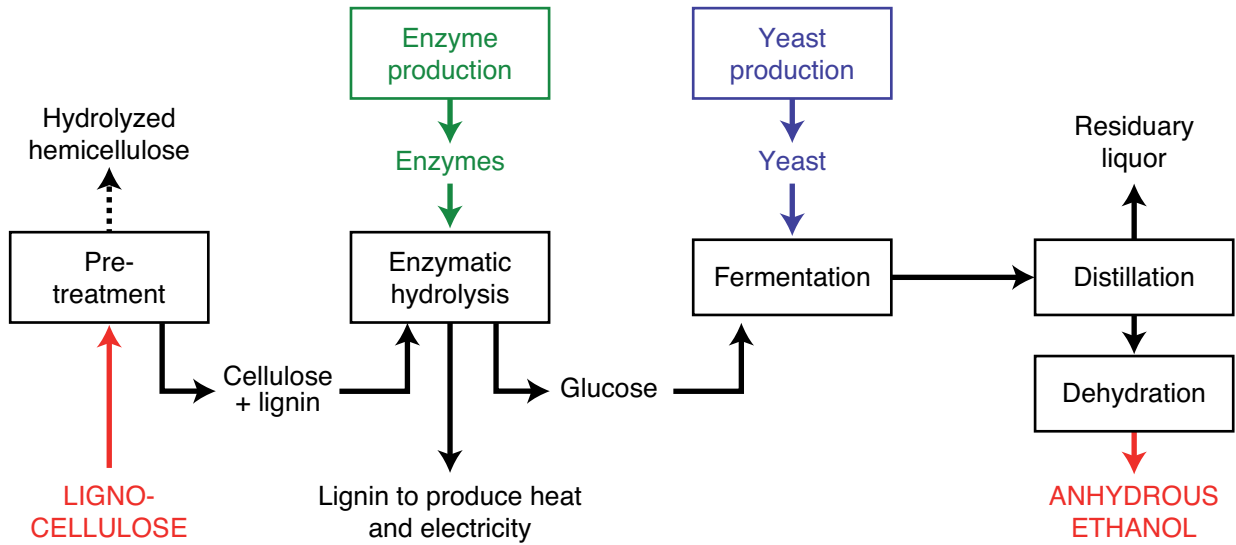
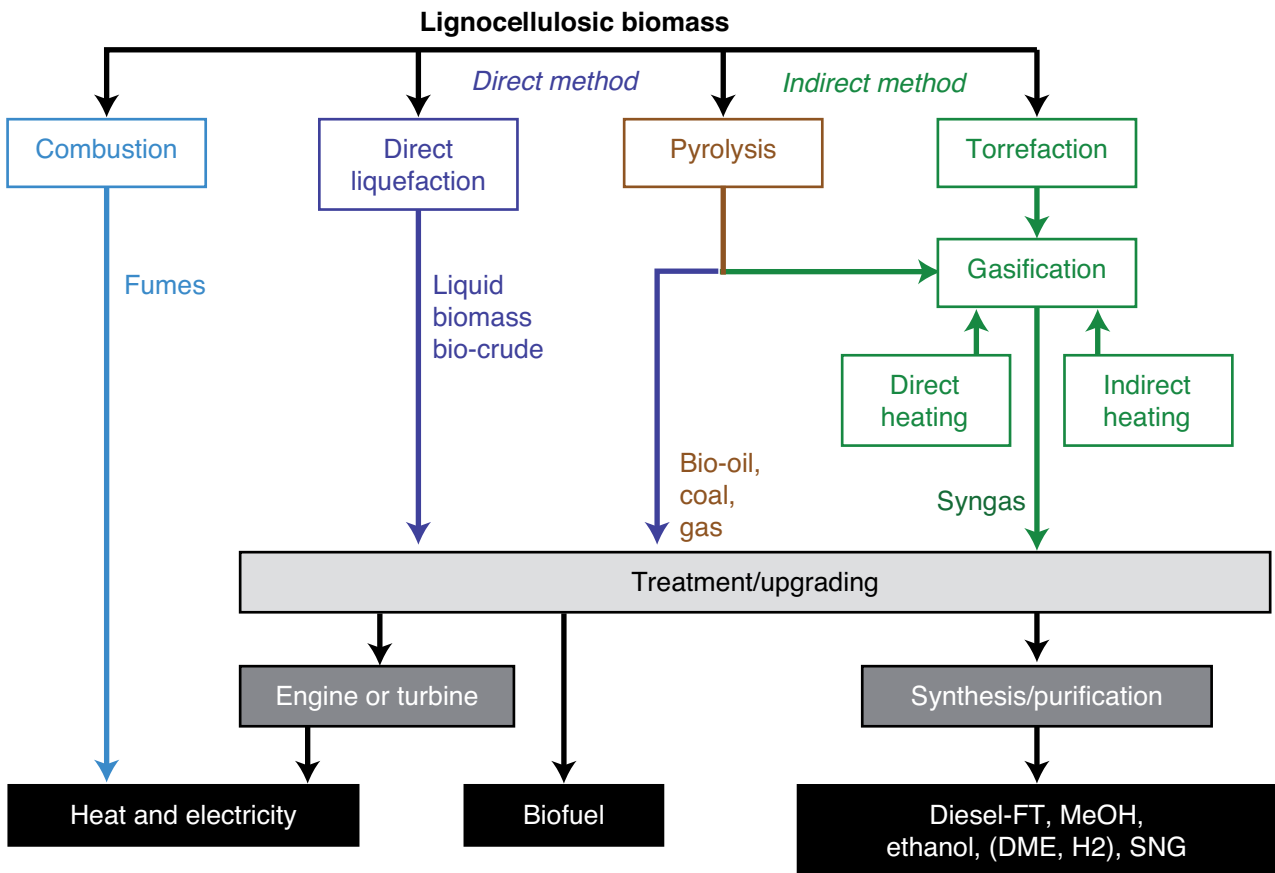
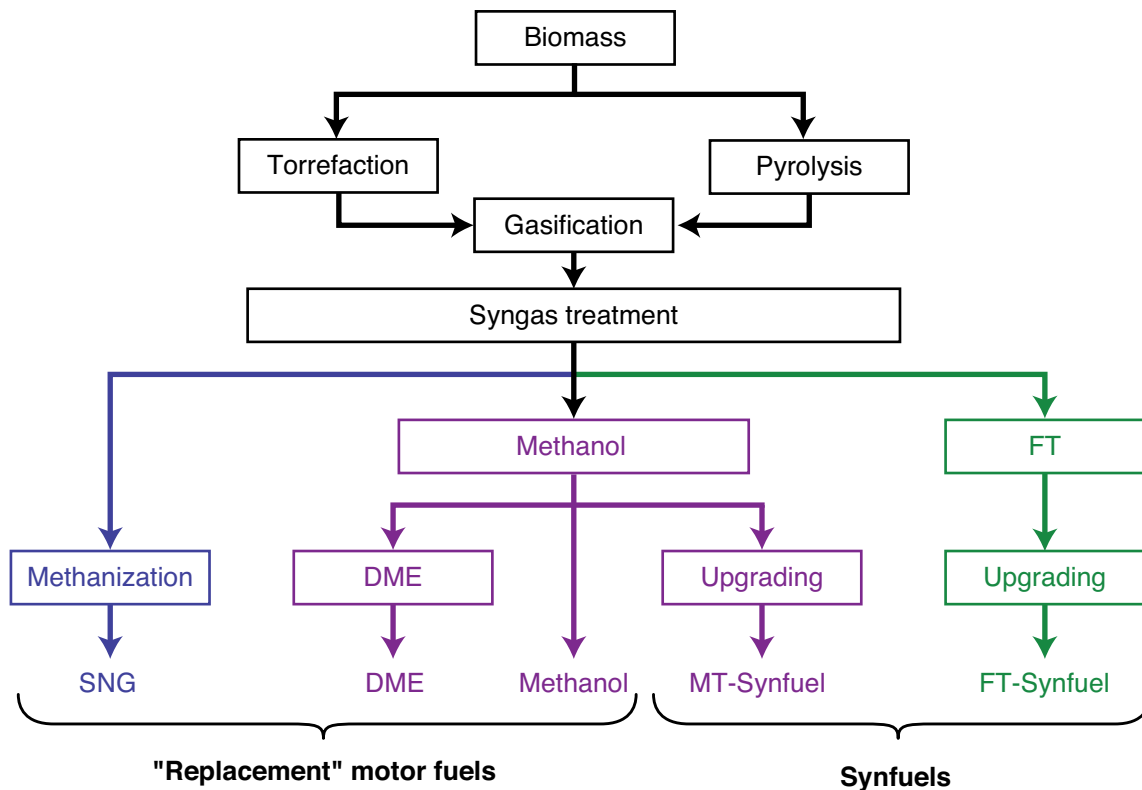


Fig. 2 - Energy pathways based on the thermochemical conversion of biomass



## Second-generation pilot biofuel units worldwide

Fig. 3 - Indirect thermochemical methods of transforming a synthetic gas into a biofuel



Other ex-syngas pathways can yield gaseous biofuels that represent fewer processing constraints, such as bioDME (dimethyl ether) or bio-SNG<sup>2</sup> (or biomethane). However, the use of these gases under atmospheric conditions implies major using constraints.

Hydrothermal liquefaction transforms biomass into biocrude from which a light fraction could be extracted to obtain a diesel following a hydrodeoxygenation reaction.

These thermochemical and biochemical processes offer ways to produce "clean" motor fuels (i.e. with substantially lower CO<sub>2</sub> emissions) from renewable materials. It is likely that they will become a permanent feature on the energy scene as the consumption of fossil fuel decreases. None of these techniques, which are all at different points in their development, has reached the industrial stage. After the laboratory study and experimental work are complete, a pilot unit is used to test all or part of a process on a smaller-than-industrial scale. For complex technological processes, the next step is a demonstration plant, which produces at near-industrial scale; however, its products are not marketed.

[2] SNG: Synthetic Natural Gas

### Current status of second-generation pathways and challenges to overcome

#### Biomass production

For all pathways producing biofuels from lignocellulosic biomass at industrial scale, there are challenges to overcome as far as the production of biomass is concerned. The so-called "dedicated" crops (e.g. miscanthus, switchgrass and short rotation coppice) are not currently an integral part of farm cultivation systems. Whether already underway or planned, large research projects are focusing on the adaptability of these crops to local conditions (e.g. geography, soil and farm economics), the technical routes to prefer for these crops (e.g. to control weeds, harvest and optimize logistics), the potential for genetic improvement of these plants and the social acceptability of growing these crops (particularly as regards the impact on the landscape).

It is also vital today to anticipate the socio-economic and environmental impacts that the development of these new pathways might have.

## Second-generation pilot biofuel units worldwide

### Biochemical conversion

Today, it is possible to produce ethanol experimentally from lignocellulose resources, so the question is not whether the basic research is feasible, but whether each stage can be optimized, especially from the economic perspective. Between now and 2015-2020, by which time industrial units should be coming onstream, technology leaps can be expected in this respect.

The pretreatment stage, which involves deconstructing the plant cell wall with, in some cases, the separation of cellulose, hemicellulose and lignin, can be carried out using different thermal, mechanical, chemical or even enzymatic methods. Researchers are investigating how to adapt these techniques to various plant species. The stage involving the hydrolysis of cellulose and possibly hemicellulose into sugars still needs to be optimized by improving the enzyme-producing strains. Finally, fermentation, of C5 sugars in particular, using new strains of microorganisms (yeasts and bacteria), is under study to boost the ethanol yield for this processing chain. Other methods of converting C5 sugars to ethanol are also under consideration.

### Thermochemical conversion

As a general rule, most thermochemical processes are well known from processing fossil feedstocks. The use of biomass as a raw material imposes new constraints which, depending on the technology concerned, can be more or less difficult to overcome.

The BtL production flowchart for the production of synthetic diesel (FT diesel) involves a complex sequence of technologies and has not yet reached the industrial demonstration stage. It is inspired by the coal-to-liquids (CtL) and gas-to-liquids (GtL) production chains, which exist at industrial scale but use different types of feedstock. Introducing biomass as the raw material means having to master elements that are new or more constraining.

Initially, biomass will inevitably have to undergo pretreatment as well as the necessary conditioning for shipment. Two solutions are currently under study: pyrolysis and torrefaction, both of which are being tested at pilot plants. For the production of synthetic diesel (Fischer Tropsch diesel), gasification requires advanced scrubbing (no tars, alkaline substances or HCN), an optimized molar  $H_2/CO$  ratio and a percentage of inerts ( $CO_2$ ,  $CH_4$ ,  $N_2$ ) that is as low as possible. Furthermore, given the fuel mass efficiency of the processing chain, large quantities of biomass (about one Mt/year) must be mobilized to make the installation profitable and produce a minimum quantity of product

(approximately 200,000 t). The logistics of supplying biomass to a BtL complex at a refinery may become a major limiting factor in deciding where to locate the installation. Efforts to improve mass efficiency are being made by using external (allothermal) energy inputs to produce a larger quantity of diesel per unit of biomass. Consideration is also being given to solutions – such as the addition of external hydrogen – that are technically simpler but cost more, in principle.

The processes used to produce DME, methanol, SNG or ethanol by gasification present the same uncertainties relative to the handling of biomass, shown previously, irrespective of the type of biofuel desired. Today, the constraints associated with these biofuels mainly arise from their use in fleets of passenger cars. Car manufacturers must specifically convert vehicles to use gaseous biofuels (DME and SNG) at atmospheric pressure. As in the case of LPG, the conventional diesel vehicle must be equipped with a new injection system to use these fuels, given their specific physical properties. These biofuels are also incompatible with polymer materials in certain respects.

As for BioSNG, it needs extra purification before it can be incorporated into an existing gas fuel distribution network, and the cost of compression is still high.

Depending on local fuel specifications, small concentrations of bioethanol and biomethanol can be added to gasoline, either pure or in their ether form, or used in FlexFuel vehicles adapted for that purpose.

The direct method of hydrothermal liquefaction draws primarily on two technologies. The first is hydrothermal conversion of biomass, whose technical feasibility has only been shown in the laboratory; this method still needs to be tested under operating conditions at a larger scale. The second is hydrodeoxygenation, well known when applied to petroleum products, but not yet demonstrated for a feedstock containing alkaline substances and large quantities of oxygen.

None of these processes are at the same stage in terms of knowledge and development. A biochemical process might be ready for industrial exploitation whereas a hydrothermal liquefaction method might still be at the lab stage. Often, researchers will use experimentation at pilot and demonstration plants to tackle the particular problems associated with a process.

Let's briefly look at existing and planned pilot plants, their location and their characteristics to get a general idea about where research is happening, which players are involved and what the development time frame might be.

## Second-generation pilot biofuel units worldwide

### Pilot plants producing lignocellulosic ethanol

#### In North America

The Canadians pioneered the construction of second-generation ethanol pilot plants. In 2006, Logen Corporation, a large manufacturer of enzymes for the textile, animal feed, and pulp and paper industries, built the first pilot plant in the United States. Since then, Woodland Biofuels and Sunopta/Greenfields Ethanol have each announced plans to build a unit. The purpose of all of these installations is to produce ethanol from agricultural and forest residues. This year, the Canadian government launched the NextGen Biofuels Fund, making USD 500 million available for the development of second-generation biofuels. Forty percent of this fund will serve to finance construction of the first demonstration plant at industrial scale.

In 2007, the United States Department of Energy made grants worth USD 385 million over four years to develop six industrial biorefinery projects to produce cellulosic ethanol along with co-products and electricity. Scheduled to start up no later than 2012, these units will have between 34,000 and 100,000 t/year of production capacities of cellulosic ethanol.

A grant of USD 200 million was also awarded to build pilot plants ranging from 80 to 15,000 tons in capacity. The first started operating in the autumn of 2007, owned by Abengoa Bioenergy, Europe's top ethanol producer and Number Five in the United States. The others are expected to come onstream in 2008 and 2009.

The government also earmarked USD 23.3 million to four industrial firms and one university to promote R&D programs on cellulosic ethanol.

In the United States, there are now four pilot and six commercial facilities planned, financed primarily by corporate ethanol, enzyme or agrifood producers. Some include installations to make ethanol from corn stover, but most use forest residues or dedicated crops (e.g. switchgrass).

#### In Brazil

This year, the foremost Brazilian oil company, Petrobras, will bring the country's first pilot plant for the production of cellulosic ethanol into service. The unit will be situated at its research center on Fundão Island in Guanabara Bay off Rio de Janeiro. Designed to convert sugarcane bagasse into ethanol with an improved yield, the pilot plant will also be equipped to use other by-products such as castor cake from Brazilian biodiesel units.

Petrobras also plans to have a semi-industrial demonstration unit up and running by 2010.

The Brazilian industrial conglomerate Vorantim—which also invested USD 60 million in research to improve the sugar yield of sugar cane—has put 20 million dollars into a pilot plant to make cellulosic ethanol from agricultural waste that should come onstream by 2009.

The Centro de Tecnologia Canavieira (Cane Technology Center), run by a Brazilian cooperative of sugar and alcohol producers, aims to build a pilot plant in the State of Sao Paulo (Piracicaba). The project is backed by growers that are financing sugar cane research.

In Brazil, first-generation ethanol is produced today from cane juice, while bagasse is used to generate heat and electricity for the distillery. The development of second-generation ethanol would make it possible to obtain a higher yield of ethanol per ton and per hectare of sugar cane, by adding a line to process the lignocellulose contained in bagasse. The cane leaves, which are currently left on the ground, as well as the lignin residues from the new extraction line, could then serve to fuel utilities production.

It costs very little more to make cellulosic ethanol from agricultural waste than to produce the ethanol currently on the market (less than USD 0.50 per liter, according to Dr. Bon at the Universidade Federal do Rio de Janeiro).

Ethanol producers do not yet favor adopting this new technology, which offers better efficiency per hectare but costs more. However, if ethanol demand and the value of farmland continue to rise – the price of the latter has doubled in the last three years – they may change their mind.

#### In Japan

Last January, Verenium Technology announced the start-up of a demo plant (capacity: 1,100 tons) using wood residue and agricultural waste.

In addition, the Japanese government plans to allocate USD 60 million for a second-generation initiative.

#### In Europe

The first pilot plant ever built in Europe – or anywhere in the world – is operated by Sekab in Örnsköldsvik, Sweden. Every year, it produces 100 tons of cellulosic ethanol. Since 2005, the company has been working at this site notably to validate technologies for a European research program (New Improvements for Ligno-Cellulosic Ethanol, NILE) coordinated by IFP.

## Second-generation pilot biofuel units worldwide

As 2007 drew to a close, Abengoa Bioenergy was about to open a pilot facility at its existing grain-to-ethanol plant in Babilafuente, Spain (capacity: 4,000 t of ethanol per year). The facility will use barley and wheat straw for the raw material; starch from the latter is used at the existing unit.

In France, a consortium of industrial, financial and research partners decided to launch the development of a lignocellulosic bioethanol production process that would include construction of a pilot plant (capacity: about 100 tons/yr) as well as a validation prototype.

Royal Nedalco recently announced that it was stepping up the pace of its cellulosic ethanol development program by building an industrial demonstration plant (capacity: 160,000 tons) in Sas Van Gent, Netherlands, in the next few years.

Danisco's enzymes division, Genecor, and energy provider Dong Energy have entered into collaboration to establish a pilot cereal-to-biofuel facility (capacity: 4,500 tons/year). It is slated to start up by 2009 near Kalundborg, Denmark.

Another Danish company, BioGasol, is working on a pilot plant at the Technical University of Denmark. In the spring of 2006, the Danish government made EUR27 million available to the cellulosic ethanol sector, mainly to create a demonstration plant in Denmark. BioGasol would like to take advantage of this opportunity to build a demonstration plant (8,000 t of ethanol a year) on Bornholm Island.

### Thermochemical pilot facilities

Biomass gasification can be considered for various fuel applications (FT diesel, DME, methane, ethanol, SNG) and energy applications (biofuels but also heat and electricity). Many players in the energy industry have developed pilot facilities and demonstration plants for gasification processes in Europe, the United States and Asia.

In the United States, the Department of Energy very recently made USD 7.7 million available to fund four research projects on thermochemical biomass-to-fuel processes using gasification. Most of these projects will concentrate their research efforts on the tar removal stage, that follows the gasification of biomass, and on the purification of syngas.

Biofuel production pilots that integrate all of the steps from biomass pretreatment to fuel synthesis are still few and far between; most of them are located in Europe.

### FT diesel

The first - and only existing - synthetic diesel pilot plant was built in 2005 in Frieberg, Germany. This project involved several stages and the  $\beta$  version (BtL capacity: 15,000 t/yr) is expected to start operating in the first quarter of 2008. Eventually, Choren Industries, working in cooperation with Shell, would like to establish a commercial facility (capacity: 200,000 t) near Lubmin.

This year, the Karlsruher Institut für Technologie, FZK, launched a pilot plant including decentralized pyrolysis pretreatment to evaluate the transportation of pretreated biomass. The pilot combines a gasifier to test ultimately synthetic diesel production.

Present capacity is 4,000 tons of product/year. Cereal straw accounts for the bulk of the raw material.

The Technische Universität Wien is working on different energy production pathways based on the gasification of biomass: cogeneration, BioSNG and BioFit (Fischer-Tropsch synthesis). The latter is under study at a small-scale pilot unit in Güssing, Austria that produces about 30 liters a day.

The pulp and paper industry is also interested in this production stream. The paper company Stora Enso is working with the Finnish oil company Neste to have a syndiesel pilot running by 2008 at the Varkaus pulp mill in Finland. The pilot unit would use forest residue and pulp/paper waste generated by the mill.

Newpage Corporation, a paper manufacturer based in the United States, has also formed a partnership with Chemrec, a Swedish company specialized in the gasification of a paper-making by-product: black liquor. They are planning to build a black liquor gasification plant to produce biofuels at the Newpage paper mill in Michigan (U.S.).

In France, the Commissariat à l'Énergie Atomique (CEA) is looking into the possibility of installing a pilot plant (capacity: 15,000 tons/year) in Bure (Lorraine), using the Fischer-Tropsch technology marketed by the company Axens.

### DME/Methanol

In Sweden, several bio-DME development programs are in progress. Chemrec and Volvo Transfer Technology have set up a pilot plant in Pitea to produce bio-DME from black liquor. A demonstration plant is planned by 2010.

The EU-sponsored Chrisgas project (2004-2009) aims to retrofit a cogeneration plant in Värnamo that closed in 2000 by installing a pilot platform to produce bio-DME and biomethanol.

## Second-generation pilot biofuel units worldwide

As part of the DME Vehicle project (EC), bio-DME is being used experimentally by a freight truck fleet in the city of Växjö.

Methanol fuel plants are more widespread today, especially in Sweden and Germany, but a large majority of the commercial units burn fossil natural gas. Nykomb Synergetics in Sweden as well as SVZ and the IEC (Institute for Energy Process, Engineering and Chemical Engineering) in Germany are backing large projects for biomethanol production units. The first two are in progress, the third is scheduled for 2009.

In the United States, the search is on for different ways to substitute ethanol directly for fossil gasoline. Range Fuels and Alico received DOE grants to develop two commercial units to produce ethanol by gasifying lignocellulosic material, one in Florida and the other in Georgia.

In the last few years, aware of its heavy oil dependency, China – particularly Shandong University and the national academy of sciences – has been investigating biomethanol as a replacement fuel for gasoline and bio-DME to replace diesel.

### SNG

The technology for producing synthetic natural gas from biomass seems well in hand. A company in the Netherlands, ECN, is soon to launch a pilot and the Technische Universität Wien plans to open a wood-to-SNG 1MW demo-plant by 2008 (the CHP gasifier is already in service) in Gussing, Austria.

The Catalytic Process Engineering Group at the Paul Scherrer Institut in Switzerland is working at the Gussing plant, hoping to apply this technology in Switzerland. The gas could be distributed via the existing natural gas network and used for various applications, such as gas heating, motor fuel for gas-powered vehicles or as a source of electricity and heat at gas-fired power plants.

If the term "second generation" covers the conversion of different biomass resources to biofuels using processes to be developed in the not-too-distant future, then other pathways may be viewed as third-generation. Among them is the use of families of algae that can fix CO<sub>2</sub> and convert it to intracellular lipid reserves. Given how fast algae grow, large quantities of oil could then be

extracted and converted to biofuels. Research programs have been undertaken, especially in the United States (by the NREL), Japan (which has USD 117 million allocated to this pathway), South Africa and Western Europe (France, Spain, the UK and Germany). Major technical and especially economic problems must be overcome to finish the laboratory phase and produce a biofuel whose quality is similar to that of the existing biodiesel.

Measured by the number of projects and their stage of development, the technology that has made the most progress is the biochemical method of producing ethanol. Very large sums have been spent on research in this area, especially in the United States, which sees it as the pathway that will best alleviate the constraints associated with the use of corn for food and feed.

Since Europe consumes more diesel and less gasoline, it is developing biochemical and thermochemical processes in parallel to cover the replacement of both. There are no plans to market these products on a large scale before 2015. Right now, Brazil produces the biofuel that is the world's cheapest replacement fuel for gasoline. Problems associated with land management will eventually push producers to adopt second-generation technology. Finally, Asia is gradually developing its first-generation pathways, but fossil fuels need to be replaced on such a tremendous scale that, in all likelihood, resource problems will soon emerge. Asia may then become a major target for American and European firms in this sector.

Let's recall that all of these prospective pathways will exploit biomass resources that are now only used to produce energy. The lignocellulosic residues of agriculture, forestry or the timber industry figure as the resources of choice. Although these resources are often widely dispersed and the costs of supply can be high, there is good reason to consider integrating high-productivity energy crops into agricultural and forestry systems. Energy crops not only achieve better per-hectare productivity, but are often less demanding than food crops with respect to soil quality. This would help make competition between different types of land occupancy less acute, although it would still be a factor to take into account.

*Daphné Lorne - daphne.lorne@ifp.fr  
Final draft submitted on December 10, 2007*