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Second generation biofuels: a new milestone reached

The commissioning of several commercial lignocellulosic ethanol production units worldwide marks a new stage in the development of second generation biofuels. Certainly many obstacles, both technological and economic, still remain to be overcome, and considerable investment amounts will have to be mobilized to develop and sustain these sectors. Favourable evolution of the regulatory environment in the markets remains the key to their future.

Current position of biofuels in the energy mix

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In 2012, the biofuels sector represented approximately 3.4% (62 Mtoe) of global energy consumption of all fuels combined in the road transport sector, which accounted for a total volume in the order of 1.89 Gtoe. In Europe, the consumption of first generation (1G) biofuels - produced from food crops (sugar cane, corn, wheat, rapeseed, soya, palm, etc.), grew significantly in the past decade, promoted by a favourable regulatory environment: directive 2009/28/EC (RED) promoting the use of renewable energies, set a specific target of inclusion of a 10% share of renewable energies in the total consumption of motor fuels for 2020. For instance, according to EurObserv'ER, the share of biofuels in road transport consumption in the EU rose from 0.2% in 2000 to 4.7% (13.6 Mtoe) in 2013. Germany and France are the biggest consumers of fuel ethanol and biodiesel in the EU.

Widely decried in recent years due to their controversial impact, the maximum share of 1G biofuels in the target defined by the RED is subject to final negotiations within the EU around the value of 6%. In order to stay on track for the 2020 target of 10% incorporation of renewable energies, this capping will entail a contribution from other types of renewable fuels, such as advanced or second generation (2G) biofuels (produced from residue or other lignocellulosic matter), and renewable electricity, mainly *via* electric vehicles.

The major economic and technological challenges of the 2G biofuels sector

Many economic and technological challenges still remain to be taken up for 2G biofuels to play a significant part in the energy mix.

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Although 2G ethanol production has now entered the industrialization phase, major economic challenges nonetheless remain the keys to success in ongoing deployment of units and the sustainability of the sector.

This mainly involves further reducing the cost of the biomass, which accounts for around 25% of the total production cost. In addition to the necessity to ensure supplies at low prices, there is also a need for control of and guaranteed access to significant and sustainable volumes.

As an example, in the Liberty project recently implemented in Iowa in the United States by the POET/DSM partnership, biomass supplies were the subject of many upstream studies. A research partnership was set up between Iowa University and the US Department of Agriculture (USDA) which provided the finance, and biomass supply contracts were then signed with some 600 farmers. Corn crop residue (cobs, stalks, leaves, husks) were selected as raw material for this unit which, at full capacity, will use 285,000 t/yr of biomass.

The unit operated by POET/DSM uses bales of residue (EZ bales) whose composition has been specially developed for the exclusive use of the project. Several criteria, including their composition, impact on soil renewal, and their drying and storage conditions have been analyzed (Fig. 1).



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Fig. 1 – Comparison between the composition of bales used in the Liberty project and that of traditional bales



Source: LIBERTY project data

In addition to the resource, which remains a key obstacle in terms of cost reduction, other items are concerned when considering how to improve sector profitability:

- optimization of the pre-processing stage;
- enzymatic hydrolysis, whose cost currently accounts for approximately 25% of the total production cost;
- optimized use of lignin, a co-product of the process of converting biomass to 2G ethanol: either use in manufacture of materials (glues, resins, etc.), which could represent a high added value output, or energy valorization for biorefinery requirements.

In addition, the development and increased use of lignocellulosic resources will call for a set of incentive measures from government to ensure future supplies for all the projects expected, both in the energy sectors, especially for 2G biofuels, and in respect of all other known and potential uses (bio-based chemistry, materials).

In terms of technology, the improvement of biomass pretreatment processes, especially in association with breakdown of the lignocellulosic matrix in order to convert it into simple sugars, remains a major challenge. This highly energy-intensive stage still involves obstacles to be surmounted (deterioration of sugars, formation of toxic compounds, etc.). More generally speaking, the challenges related to "genetic engineering" will have to be mastered in order to ensure long term maintenance of performance and secure the development of biomass materials in their environment.

Lastly, upscaling from the pilot project to the commercial production unit entails process adaptation. At present, only a handful of promoters of 2G ethanol production units have taken up this challenge.

What do we mean by lignocellulosic biomass?

Current estimates are that at least 5% of the world's total production of biomass could be used for energy production, making a total 13.5 billion tonnes of available raw materials (*i.e.* 6 Gtoe of primary energy).

According to Directive 2009/28/EC, biomass is defined as "the biodegradable fraction of products, wastes and residue from biological origin from agriculture (including vegetable and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste".

2G biofuels are produced from lignocellulosic biomass, a non-food resource, available in large quantities and in different forms:

- farm residue: cereal crop straw, stalks, sugar cane bagasse;
- forestry residue (branches, twigs, damaged trucks left in the forest);
- timber industry waste (sawdust, scraps) and paper waste (used paper, black liquor);
- high yield crops: annual plants (triticale, alfalfa, etc.), short rotation perennial crops (miscanthus, giant reed, poplar, willow, etc.);
- household waste (organic fraction) and industrial waste (pallets, etc.).

Lignocellulose is made up of three polymers: cellulose, hemicellulose and lignin. These three components combine to form a three-dimensional rigid, complex and very resistant structure.

The composition of the lignocellulosic biomass that can be used in 2G biofuels production is shown in the table below.

	Table 1		
Lignocellulosic	biomass	composition	

Lignocellulosic biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Wheat straw	33	23	17
Corn cobs and stalks	45	35	15
Newspapers	40-55	25-40	18-30
Hardwood	40-55	24-40	18-25
Softwood	45-50	25-35	25-35
Miscanthus	45	30	21
Sugar cane bagasse	42	25	20

Source: Advances in Valorization of Lignocellulosic Materials by Biotechnology: an overview. BioResources, 2013, 8, 3157-3176.





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Lignocellulosic biomass valorization processes

The choice of lignocellulosic biomass valorization process depends on the characteristics of the input biomass, its availability and the type of output fuel required. Two main types of process are used to convert the lignocellulosic biomass into biofuel: biochemical and thermochemical processes. A third, hybrid process combines these two processes (Fig. 2).

Fig. 2 - Main processes for conversion of lignocellulosic biomass



Source: IFPEN from Advanced Biofuels

Biochemical valorization

The aim of the biochemical process is to hydrolyze the lignocellulosic biomass in order to extract sugars which will then be fermented. The main product produced by this type of process is known as "cellulosic" ethanol, made in four stages (Fig. 3).

Fig. 3 – Biochemical valorization of biomass



Source: IFPEN

Pretreatment

Before being converted into fuel, the lignocellulosic biomass must be broken down in a pretreatment stage, by thermal and/or chemical action. This is a key stage in the technologies developed by industry. This stage extracts the lignin, which is non-fermentable. In addition to lime treatment, which appears to be the most



economical, there are alternative solutions giving access to the "sweet" part of the biomass, the only part that can be turned into ethanol: these include cooking in the presence of dilute acid (chemical process) and steam explosion (physico-chemical process).

The main stakeholders owning pretreatment technologies are the Austrian company Andritz and the Finnish company Valmet. Unit promoters have their own technology (POET, Abengoa, etc.).

Cellulose hydrolysis

An acid or micro-organisms (specific enzymes) act as a catalyst in this stage, which consists of splitting the polysaccharides that make up the cellulose and hemicellulose into simple, fermentable sugars (glucose, pentose, saccharose, etc.). Enzyme fermentation is by far the most common method. The Danish company Novozymes appears to be the best known enzyme supplier. IFPEN is also highly committed in this respect with the Futurol project. Other players such as DSM and Dupont Danisco license their enzymatic hydrolysis process.

Ethanol fermentation and distillation

Alcoholic fermentation of the C5 and C6 sugars released by yeasts is similar to that for production of 1G biofuels. In France, Lesaffre has established itself as a supplier of yeasts for production of 2G biofuel (partner in the Futurol project).

Launched in 2008, the Futurol project aims to develop and commercialize a complete solution for production of cellulosic ethanol, from the field to the end-product. The project has developed a process that is particularly well optimized in terms of industrial integration and performance. Thanks to its pilot plant and the involvement of its partners, the project has made breakthroughs in terms of the three key elements - pretreatment, enzymes and yeasts. The project will use a cocktail of enzymes which can be produced in situ in the process from co-products, giving performance equivalent to the industrial cocktails available. The yeasts are used to ferment all the sugars likely to produce ethanol. Industrialization of the project technology is expected from 2016 and the process will be marketed by Axens. Led by the company PROCETHOL 2G, the Futurol project has 11 partners. The project is supported by Bpifrance and approved by the IAR (Industries and AgroResources) competitive cluster (Fig. 4).



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- a Commercial unit under construction, production start up planned in early 2015
- b Brazilian installation in partnership with GranBio

c - Unit in partnership with Raizen

Source: IFPEN

The centuries-old process of enzymatic hydrolysis has paved the way for large scale development of 2G ethanol production units. In the past two years, there have been many announcements of unit commissioning: Beta Renewables in Crescentino (Italy), POET/DSM and Abengoa in the United States, GranBio in Brazil and more recently Raizen (Shell-Cosan joint venture) in Brazil. In 2015 Dupont-Danisco will commission its commercial unit in Nevada.

Thermochemical valorization

Thermochemical processes (thermal treatment) break down the lignocellulosic matrix and convert the solid and heterogeneous biomass into fuel, in the form of either gas (synthesis methane backed by the Gaya project coordinated by GDF Suez in France) or liquid. R&D works are ongoing on three processes for the production of liquids biofuels (mainly biodiesel and biojet):

fast pyrolysis followed by upgrading aimed at maximizing the liquid phase obtained. In this process, the liquefaction stage takes place in the absence of any hydrogen or catalyst (flash pyrolysis). The product obtained is pyrolysis oil, or bio-oil, which can be used directly to produce electricity or steam. This mixture cannot however be used as it is, in a conventional combustion engine, and must therefore undergo an additional conversion or upgrading phase (catalytic hydrotreatment) to turn it into a compatible liquid biofuel. While flash pyrolysis has already been industrialized (FORTUM unit), the conversion of pyrolysis oil into fuel is still at the R&D stage. IFPEN, BTG and VTT are working on this subject;

- direct liquefaction of biomass whose end product, called biocrude, is more stable than bio-oil and convertible to a diesel substitute. Research works undertaken by the Dutch research centre TNO-MEP have led to development of the Hydrothermal Upgrading process;
- catalytic pyrolysis aims to combine flash pyrolysis and conversion in a one and the same unit. The company Kior built an industrial demonstration unit in the United States, but recently filed for bankruptcy;
- the Biomass to Liquids or BtL process: this process uses gasification (thermal treatment) to produce a synthesis gas (syngas) which, after purification, is converted using synthesis processes, in particular Fischer-Tropsch catalytic synthesis into liquid diesel or kerosene type products. The end-products are very high quality (absence of sulphur, high cetane number). Axens is already marketing the Fischer-Tropsch Gasel® technology for BtL.

However, to minimize thermal losses and benefit from economies of scale, the envisaged production capacity of projects is over 100,000 tonnes of fuels. Taking into account the mass yield of the entire chain of processes (18% for operation at 100% from lignocellulosic biomass), the mobilization of a very large quantity of biomass, in the order of a million tonnes per year, will be required. Supply chain logistics may therefore become a major limiting factor in the choice of biorefinery location. After a relatively dynamic period, several European projects, including those led by Choren, Linde-Forest BtL and NSE Biofuels, are currently stopped due to their promoters' financial difficulties.

As regards the French project BioTfueL, led by a group of six partners (Avril, Axens, CEA, IFP Energies nouvelles, Thyssenkrupp Industrial Solutions and Total), it is making progress towards construction of two demonstrators. In November 2014, Bionext, which associates all the partners in this programme, announced that the detailed project design phase had been completed and that the project could enter its demonstration phase. To achieve this, two pre-industrial units will be built for a total project investment of €180 million. The Avril site in Venette (Picardy) will house a €12 million biomass preparation installation using the torrefaction process. The Total site in Dunkirk (Flanders establishment) will house the gasification unit at the heart of the process, together with the Fischer-Tropsch synthesis





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process developed by IFPEN. It entails an investment of almost €110 million. In September 2014, the construction contracts for the main works packages at the Total site in Dunkirk were signed by Bionext with Prosernat (for synthesis gas treatment) and the SME RBL-REI (for load preparation), as well as with ThyssenKrupp Industrial Solutions (for the gasification unit and overall integration of the facility) with onsite works start up planned in the first quarter of 2015.

In addition, in October 2014 the CEA inaugurated the platform for biomass pretreatment by crushing at Bure-Saudron for its Syndièse project.

These thermochemical processes do not entail any selectivity in their processing methods (less complex pretreatment), which is an advantage compared with biochemical process. Nevertheless, these biomass conversion methods are still coming up against major technical obstacles (product quality in particular, presence of impurities, etc.) and economic difficulties (high costs), and no production unit is yet operational on an industrial scale.

Hybrid valorization

The hybrid process combines thermochemical and biochemical methods. Obtained *via* a biomass gasification stage, the synthetic gas is then fermented into mainly alcohol. The American firm IneosBio and the New Zealand start-up LanzaTech operate this process. IneosBio has started up a unit of this type in Florida. LanzaTech plans to start up its unit in the United States in 2016.

Existing and planned 2G biofuel capacities

The number of commercial units producing lignocellulosic ethanol has risen sharply in the last two years. Their total capacity reached 350,000 t/yr at the end of 2014 (Fig. 5).

Several other units are under development and represent an additional capacity of 137,000 t/yr in the short term.

Sharp rise in investment

2G biofuels (mainly biodiesel and bioethanol), together with new technologies such as the production of synthetic diesel by Hydrogenation of Vegetable Oils (HVO) are booming. The number of commercial-scale ethanol production units has increased very significantly, particularly in 2013 and 2014 (start up of two units in the United States, one in Europe and one in Latin America). In Brazil, the need to increase biofuel production due to the new obligations concerning integration of biodiesel and ethanol contributed to this growth in investment.

Fig. 5 – Commercial 2G biofuel units under construction or in production (capacity >10,000 t/yr)





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While new investors are still cautious in the short term, several projects are already under way with existing stakeholders (2G ethanol) and major developments are also expected in biodiesel with the commissioning of pilot projects (Fig. 6).





Generally speaking a more favourable and stable regulatory environment will be needed to support investment in the biofuel field.

In the United States, uncertainty about the next Renewable Fuel Standard proposal led by the Environmental Protection Agency (EPA) on compatibility of biofuel mandates, and the end of credits for "blenders" since the end of 2013, are two factors which could limit biodiesel consumption in the coming years and therefore the volume of investments allocated to development of this biofuel.

In Europe, procrastination in respect of the new targets for incorporation of biofuels in the RED, and the current absence of quantitative targets beyond 2020, do not favour the development of new sectors.

Lastly, the profitability of 2G biofuel production projects will depend both on an oil price rise and on increased recognition of the problems caused by CO_2 in transport.

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