Petrochemicals and green chemistry

The petrochemical industry will experience structural and economic upheaval in the coming years, driven by the development of shale gas in the United States and increasing tensions surrounding the availability and price of certain intermediate products. A real opportunity exists to further develop a new chemical industry based on processing biomass; the basic framework is in place, but it will need several years to mature.

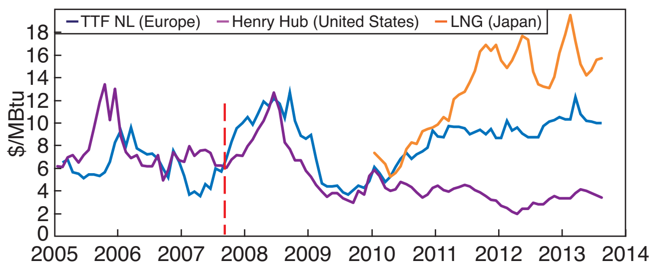
The huge influx of shale gas and oil into the US market has created new industrial momentum in the country. American petrochemicals, boosted by abundant and low-cost feedstocks, have regained its competitive edge and are shaking up the industry worldwide.

Impact of shale gas and oil production on hydrocarbon prices in the United States

Shale gas exploitation gained real momentum in 2007-2008 in the United States, first halting the decline of domestic production, then propelling it upward. Currently a net importer of natural gas, the United States should gain self-sufficiency by 2020 before becoming a net exporter. Shale gas production could make up nearly half of domestic production in about 20 years, totalling some 850 Gm^3/year.

This development has had a profound effect on global gas markets. Before 2007, American natural gas was statistically more expensive than European gas by \$2 to \$3/MBtu, but since 2010 these two markets have gone their separate ways. American gas has fluctuated between \$2 to \$5/MBtu while European gas, still largely indexed to oil, has stabilized at around \$10/MBtu — a gap of some \$6 with the United States that is likely to remain over the long term. Asia, meanwhile, imports gas at high cost — close to \$16/MBtu (Fig. 1).

Fig. 1 – Trend in natural gas prices worldwide



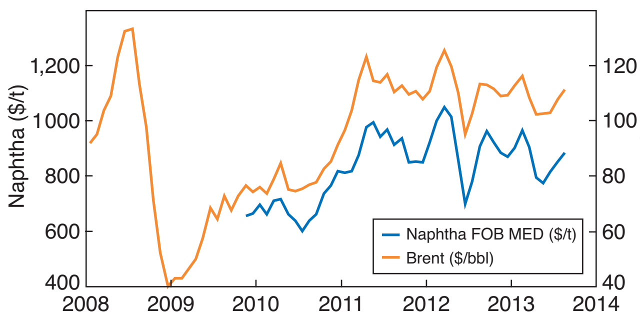
Source: Platts and Reuters

Petrochemical industry's resurgence in the United States

In Europe, petrochemical companies are penalized by a Brent price hovering above \$100 per barrel (bbl) (Fig. 2) and thus by a high price for naphtha (a cut derived from oil distillation), representing over 80% of steam cracker feedstocks.

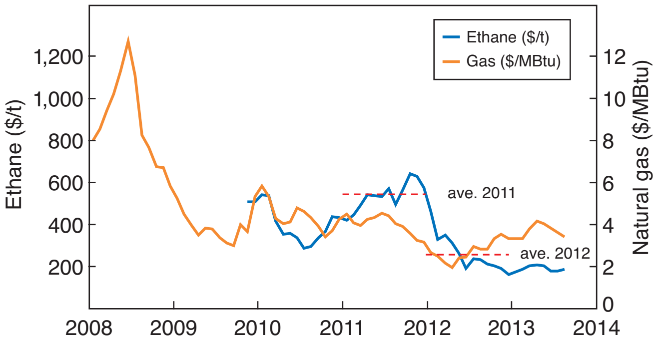
American steam crackers, however, benefit from current domestic shale gas developments, which are mainly geared toward deposits involving the production of Natural Gas Liquids (NGL). Because 70% of their feedstock are ethane and LPG, which are gas industry by-products,

Fig. 2 – Naphtha and oil prices in Europe



Source: Reuters

Fig. 3 – Ethane and natural gas prices in the United States



Source: Reuters

they also benefit from low market prices (Fig. 3) due to the abundance of American natural gas.

The value of the olefin mixture (Tab. 1) obtained from the steam cracker has little to do with the type of feedstock or region because the olefin market is largely globalized: $1,250 to $1,350/t from 2011 to 2012. The huge gap between the naphtha price in Europe and the ethane price in the United States thus has a direct impact on the steam cracker's margin.

Table 1

Olefin selection based on steam cracker feedstock

Charge	Ethane	Naphtha
Ethylene	94%	59%
Propylene	2%	26%
Butenes	4%	15%
Total	100%	100%

Source: IFPEN

From 2011 to 2012, ethane's gross margin in the United States fluctuated between $600 and $1,000/t of olefins produced, while Europe's gross margin for naphtha only reached $30 to $50/t. After deducting fixed costs, global olefin prices roughly equal their marginal production cost in Europe, which leaves little leeway for future investments and even raises the question of whether to shut down certain steam crackers, such as the Carling facility in France.

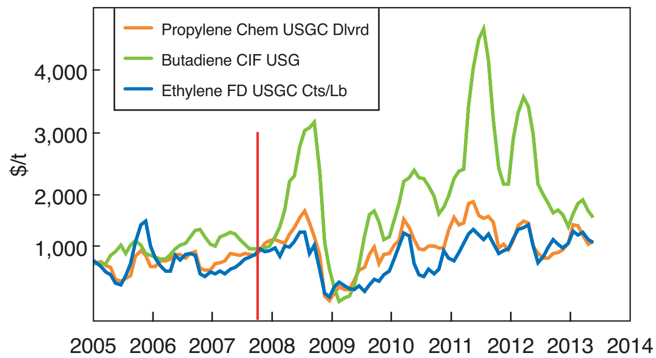
In the United States, however, the downward trend caused by economic forces in 2011 turned around in 2009 due to the influx of low-cost condensates from shale gas exploitation. Dormant capacities came back online by replacing part of the naphtha feedstock with ethane, allowing the industry to achieve roughly the same level of production as in 2000. The upswing in condensate production in the near future, justifies new steam cracker capacities — nearly 10 Mt of ethylene in four years.

Effects on the heavy olefins market

The influx of shale gas has also unsettled the global production of heavy olefins. For the iso-production of ethylene (the main product), completely replacing naphtha with ethane has reduced butadiene production by a factor of 6 and propylene production by a factor of 20. Alternative sources of propylene do exist: FCC process in refineries, propane dehydrogenation (eight five-year projects announced in the United States), and the use of other polymers as replacements for polypropylene. These solutions will undoubtedly not be enough to alleviate the tensions surrounding this olefin.

With regard to butadiene, which is suffering from both limited supply (the global production of butadiene is determined by the demand for ethylene) and growing demand (nearly 60% of butadiene demand meets the needs of the tyre industry, where it is hard to replace), it has experienced major fluctuations since 2009, with an overall upward trend. Since 2010, its price in the United States has swung between $1,500/t and $4,500/t, while ethylene has remained much more stable (Fig. 4). To limit availability-related risks for the tyre industry, a certain number of initiatives involving innovative processes have been launched, including the BioButterfly project (production of bio-based butadiene, a cooperative venture between Michelin, IFPEN and Axens).

Fig. 4 – Price trend for olefins in the United States



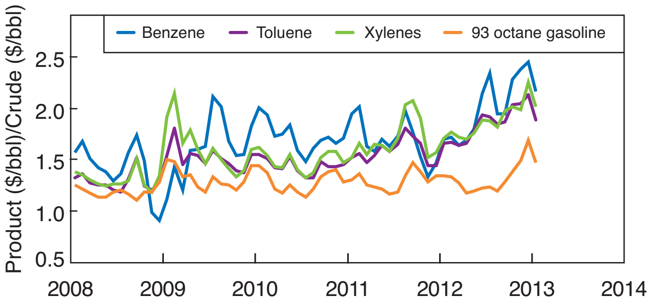
Source: Platts

Impact on the aromatics market

The aromatics market has been affected by the shale hydrocarbon revolution. Over the past two years, while gasoline prices in the United States have remained consistent with crude oil prices, benzene and xylenes have risen by nearly 50% compared to their 2008 benchmark value (Fig. 5). In the midst of strong Asian and North American demand, this tension seems to be related to the huge influx of shale gas and oil in the United States, for two reasons:

- the use of shale gas ethane to partially replace the naphtha used by American steam crackers has reduced pyrolysis gasoline production by nearly 40% and thus the production of benzene (half of which is derived from pygas) by some 550 kt/yr, representing 10% of total US production, a shortfall offset by imports ;
- with the development of light shale oil (nearly 2 Mbbl/d) with higher naphtha content and with naphtha surpluses caused by their replacement with ethane, a minority of refineries may have faced gasoline production bottlenecks (octane shortfalls and limited reforming capacities). It seems they resorted to temporarily adding aromatics (whose octane index is excellent), leading to market tensions and a doubling in the price of alkylate, another high-octane additive. However, because aromatics are much more highly valued in chemistry than as a base for gasoline and due to overcapacity in gasoline production at most American refiners, aromatics should find their way back to petrochemicals over the medium term and market tensions should ease.

Fig. 5 – Price trend for aromatics in the United States



Source: Platts

More generally, petrochemicals will experience upheaval in the availability and price of its major intermediate products in the coming years. These uncertainties will encourage downstream manufacturers to secure the raw materials they use by diversifying their supplies. Lastly, beyond the desire to free themselves from dependence on fossil fuel-based raw materials, the major decisive challenges facing manufacturers in terms of developing green chemistry are societal, environmental and technological in nature. These strategic incentives should foster the emergence of a new, non-fossil fuel-based chemistry supplied by biomass by 2020-2025.

Green chemistry boom: major challenges

While the UN estimates that the world population will exceed 9 billion by 2050, this demographic trend will be very unevenly distributed, with a slowdown in Europe and China and increases in Africa and India. Moreover, agricultural, energy and food challenges will be specific to each region. While farms might currently produce enough food to satisfy the needs of the overall population, the major producing regions are not the areas with the highest demand. Sufficient food will be produced as long as efforts are made to maintain regular production over time, to improve global food distribution and to limit the wasting of resources (the United Nations Food and Agriculture Organization estimates that some 50% of food produced worldwide is wasted).

These demographic trends will inevitably lead to increased demand for energy and consumer products (currently based on petrochemicals), and biomass is one of the solutions. While biomass is a renewable resource, it nevertheless remains limited, raising the issue of prioritizing its uses in order to reduce conflict.

The use of plant-based raw materials is also consistent with the industry's desire to be more environmentally-friendly, with the primary focus on reducing greenhouse gas emissions. Many climate policies are encouraging manufacturers to improve their energy efficiency by decreasing their business's overall carbon footprint, particularly by limiting their use of fossil fuel-based products. The increased use of biomass for food, energy and industrial purposes, however, could have an impact on the following areas: the greenhouse gas balance due to direct or indirect changes in the use of soils (cf. current discussions on Indirect Land Use Change – ILUC, especially concerning biofuels in Europe); water resources; and biodiversity, which must be preserved to ensure the resources' sustainability.

Finally, converting biomass to manufacture products that can directly replace petrochemical-based products requires a fairly extensive overhaul of traditional processes. Diversifying and optimizing white (industrial) biotechnology is a major concern and many companies specializing in metabolic engineering, molecular biology and even genetic engineering have emerged in recent years. It is essential to select and identify the right biocatalysts (microorganisms or enzymes), a task made all the more complex with manufacturers seeking to move toward flexible synthesis methods, i.e. a variety of raw materials and products. The medium-term development of bio-based processes (around 10 years) will require heavy investments and industrial partnerships between biomass, biotechnology and chemical specialists.

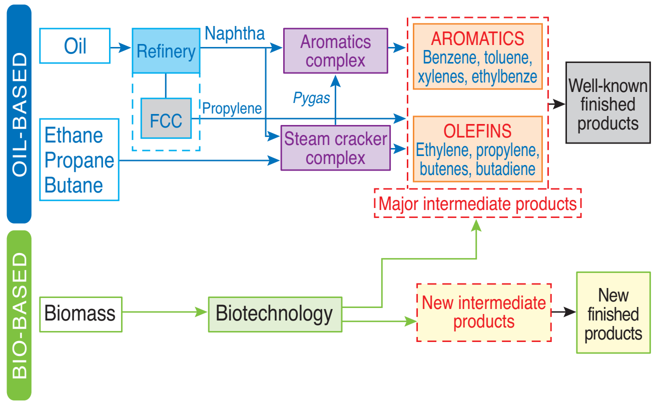
Implementation of new industrial processes

The transition from an industry strongly dependent on fossil fuel resources to a bio-based industry is occurring in the wake of the industrialization of second-generation biofuel production. Taking a page from traditional refineries, a new technological and industrial concept is emerging — the biorefinery. This new type of refinery simultaneously processes a variety of plant resources, converting them into a range of products and capturing higher value-added benefits (fuel, energy, chemicals, food, fertilizers, paper, etc.). But they also enable companies to reduce the environmental footprint of their conversion processes by optimizing mass and energy efficiencies.

To cite one example, the Pomacle-Bazancourt biorefinery near Reims, France, houses a white biotechnology research platform and an industrial complex that includes a sugar factory, glucose, starch and ethanol production units, and the Futurol project that produces second-generation pilot plant biofuels operated by the Procethol 2G consortium, of which IFPEN is a member.

Setting up such infrastructures is complicated, however, because it requires bringing together very different business sectors, including upstream biomass processors (starch, sugar, vegetable oil, wood) and downstream biochemical companies. The construction and operation of a biorefinery thus involves creating new industrial chains that support local economies, by optimizing the use of plant resources (resources not used by traditional food, paper and wood industries) and create more-cohesive regions by setting up short distribution channels.

Fig. 6 – Integration into traditional processes



Source: IFPEN

Intermediate chemicals produced by plant synthesis in biorefineries can then be integrated into traditional processing chains or processed in dedicated chains for the production of well-established or new finished products (Fig. 6). In the case of dedicated processing methods, a large number of conventional chemical processes are nonetheless used.

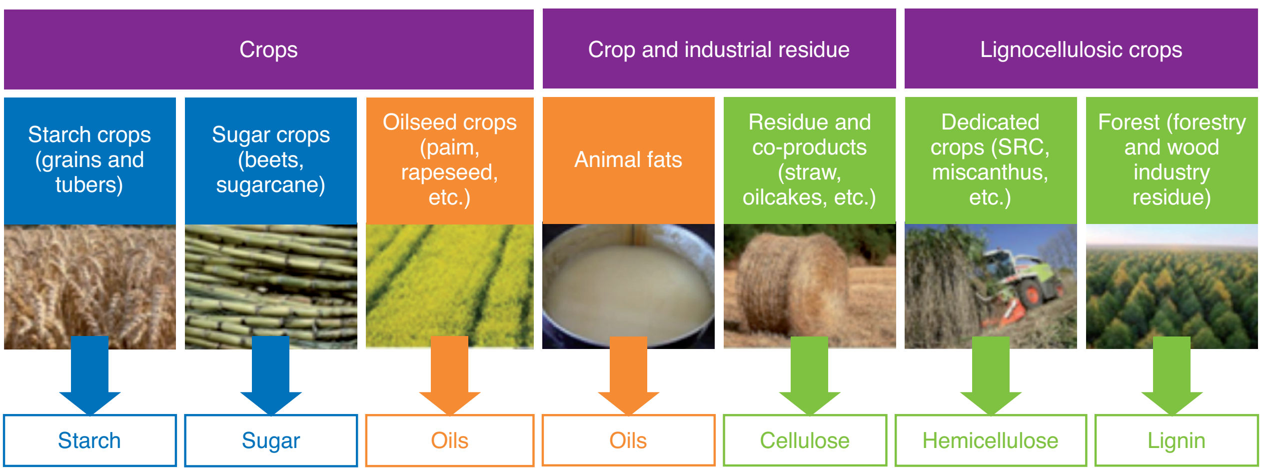
Biomass sectors and processing

Biomass can be divided into three categories and four sectors (Fig. 7): starch, sugar, oil and lignocellulose.

Algae could theoretically be a fourth biomass category but it is mainly used in food, pharmaceutical and cosmetic products due to the lipids and highly functionalized molecules that it contains.

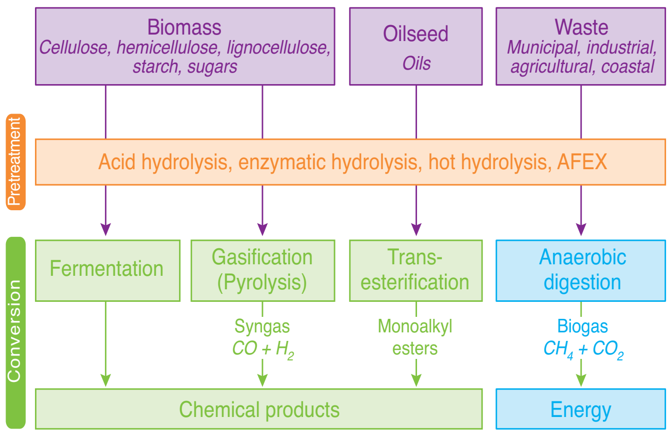
In order to recover the stored chemical energy and the organic compounds present in the biomass for industrial

Fig. 7 – Biomass categories and components



Source: IFPEN; BIPE

Fig. 8 – Biomass conversion options



Source: IFPEN; D. Sengupta & R.W. Pike, Chemicals from Biomass

purposes, biomass must undergo two processing stages (Fig. 8):

- mechanical and chemical pretreatment, which breaks down the plant matter's complex polymer structures into their constituent elements. At the present time, leavening agents, bacteria and other biocatalysts used in conversion processes are only capable of acting on monomers. The most common pretreatment processes are hydrolyses (simple, enzymatic or acid) and treatments with ammonia (Ammonia Fibre Explosion process – AFEX);
- conversion of molecules, depending on the desired type of conversion. Fermentation, pyrolysis or trans-esterification is used to produce intermediate chemicals or fuels, while methanation is performed to recover energy.

Growing interest in platform biomolecules

There are nearly an infinite number of molecules that can be synthesized from biomass at fairly advanced degrees of processing. A large number of studies have looked into the identification of these platform biomolecules (intermediates for synthesizing several by-products), with the aim of assessing their potential for future success in the chemical industry based on a number of criteria (see, for example, US Department of Energy, 2004 and 2009; European Commission, Brew 2006). These studies use similar assessment criteria, focusing on:

- the intensity of research on the biomolecule and its degree of development;
- its potential or the potential of its by-products for replacing its counterpart petrochemical molecules;
- the diversity of its by-products and their applications;
- the maturity level of potential markets;
- the level of complexity of production processes and by-products;
- the estimated production cost;
- the possibility of producing the biomolecule and its by-products in sufficient quantities for mass markets or high value-added markets;
- the applicability of production processes to an extensive range of molecules.

Even though these criteria play a decisive role in boosting the green chemistry sector, the polymer market (Fig. 9) acts as another incentive for manufacturers. Polymers have a wide variety of applications, encompassing in particular all elastomers and plastics, whose markets totalled nearly 30 and 300 Mt, respectively, in 2012 (American Chemical Society; Plastics Europe).

Fig. 9 – Platform molecules and polymers

ACIDS	
Acrylic acid →	Polyacrylates
Adipic acid →	Nylon 6,6
Succinic acid →	PBS, 1,4-Butanediol
FDCA →	PEF

OLEFINS	
Ethylene →	PE
Propylene →	PP
Isobutylene →	PIB, paraxylene
Ethylene Glycol →	PET

ALCOHOLS	
1,4-Butanediol →	PBS
Isobutanol →	PET
n-Butanols →	PB-1

AROMATICS	
BTX →	PET
Paraxylene →	PET

ISOPRENOIDS	
Isoprene →	PI
Farnesene →	Plastics

PP: Polypropylene, PIB: Polyisobutene, PBS: Polyisobutene succinate, PB-1: Polybutene-1, PI: Polyisoprenes

Source: IFPEN; Nexant

Polyethylene (PE) is the most widely used plastic, accounting for 30% of all plastics, and is thus of interest to manufacturers seeking to position themselves in the bio-based sector. Production units producing bioethylene from sugar cane bioethanol were already operating in Brazil in the 1980s and were producing 150 kt/yr of bioethylene for the production of PVC and PE. But with the drop in petroleum product prices in the early 1990s, production stopped and in 2010 Braskem was the first company to restart production of bioethanol for manufacturing PE (200 kt/yr). A new bioethanol-based bioethylene production process called Atol™, developed by Total Petrochemicals, IFPEN and Axens, has been on the market since 2013.

In addition to the sizable markets for replacing existing polymers with their bio-based versions, new types of biopolymers offer additional prospects due to their technical features, with the potential for a dramatic

Examples of bio-based products in the market

The Coca-Cola Company: a question of image

In 2010, Coca-Cola rolled out its bio-based PET PlantBottle® concept with a large-scale advertising and marketing campaign. According to the company, 2.5 billion PlantBottle® bottles were manufactured in 2010, resulting in savings of some 60,000 barrels of oil.

At present, the PET bottle is actually made with a maximum of 30% bio-based material (PET plastic combined with plant-based material made from sugar cane and the monomer paraxylene). The beverage giant is also partnering with three biotechnology companies, Gevo, Virent and Avantium, each working on a method for synthesizing paraxylene using bio-based materials. The consortium should enable Coca-Cola to achieve its goal of a 100% plant-based PET PlantBottle® by 2020.

Nike: a better-performing shoe

Nike recently unveiled one of its latest innovations: the GS Football Boot, whose sole is made of Pebax® Renu, a bioelastomer developed by Arkema, and Pearlthane®, a biopolyurethane developed by Merquinsa. According to Nike, the biopolymers in this shoe, which is exclusively designed for professional athletes, provide improved performance and lighten the shoe's weight by 15%, making it the lightest and best-performing shoe in the world.

Be.e®: an eco-friendly electric scooter

Introduced in July 2013, Be.e® boasts that it is the first electric scooter with a body completely made from natural resins. Designed by Waarmakers and manufactured by Van.Eko, two Dutch companies, the scooter consists of a monocoque made from Nabasco® bioresins; a composite material (hemp and flax fibres reinforced by polyesters and other additives) sold by NPSP Composieten; and an electric motor housed in the rear wheel. While the polyesters may still be fossil fuel-based, there is no doubt that the lively ferment in the polyesters field should eventually lead to the complete use of bio-based composite resins. Van.Eko highlights the little scooter's excellent performance in terms of its emissions and carbon footprint as well as the possibility of thermal recovery at the end of its life cycle.

Fig. 10 – Production of biomass commodities

WORLD

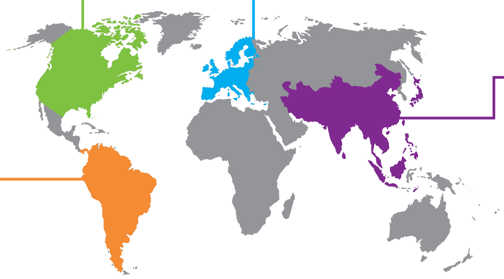
Capacities (ktpa)	2013	Addition*
Acids	50	+160
Alcohols	320	+50
Aromatics	0	+130
Isoprenoids	65	+60
Olefins	575	+1,240
Total	1 015	+1,640

NORTH AMERICA

Capacities (ktpa)	2013	Addition*
Acids	15	
Alcohols	180	
Total	195	

WESTERN EUROPE

Capacities (ktpa)	2013	Addition*
Acids	35	+25
Alcohols	10	
Isoprenoids	10	
Total	55	+25



SOUTH AMERICA

Capacities (ktpa)	2013	Addition*
Isoprenoids	25	+25
Olefins	230	+1,160
Total	255	+1,185

ASIA

Capacities (ktpa)	2013	Addition*
Acids	0	+35
Alcohols	135	+25
Olefins	345	
Total	480	+60

*Increases for the 2014-2015 period, 370 ktpa for location yet to be determined.
Source: IFPEN; Nexant

impact on these markets. One example is polyethylene furanoate (PEF). Completely derived from plant-based raw materials, this polymer poses serious competition to polyethylene terephtalate (PET), which currently represents some 20% of the plastics market. Developed by the Franco-German joint venture, Avantium/Alpla Werke Lehner, PEF should be commercially available in 2016.

A new industry under development

Bio-based versions of certain intermediate products are available (Fig. 10), such as ethylene glycol (MEG, a monomer used in the production of PET), a product derived from sugar cane by India Glycol for more than 20 years (120 kt/yr since 1989). This company also supplies Coca-Cola, which uses the product to produce its plant-based PET PlantBottle®.

Asia is currently the most productive region, followed by India (MEG) and especially China, which produces cellulosic sugars for synthesizing butanols (elastomers for the automotive industry and also paints, lubricants, plastics, fuels, etc.).

In South America, all current production units are located in Brazil, which is rich in plant resources and likely to be the site of most future facilities (mainly ethylene for producing PE).

It should be noted, however, that Figure 10 does not take into account existing or future biomethanol capacities even though biomethanol production is well established in Europe, particularly in Sweden and the Netherlands (450 kt/yr). Bioethanol also does not appear because it is often reported as a biofuel rather than a potential platform for chemicals, although production levels had already reached 17 Mtoe in 2006 (IAE). Furthermore, bioethanol produced for chemicals is directly used for manufacturing other products (for example, Braskem produces PE directly) and is not sold separately for the time being.

A number of other projects are also worth mentioning, including those conducted by companies in Europe and the United States (Dow, Solvay, Amyris, BioAmber, etc.) as well as Brazil, Asia and especially Thailand, which has an abundance of resources and fast-growing regional markets.

Conclusion

In addition to the need for the new, biomass-based chemical industry to mature and become established, the future development of green chemistry depends on two criteria essential for manufacturers:

- the availability of plant-based raw materials in sufficient quantities and at competitive prices;
- good market-growth prospects for these bio-based products.

Growth is especially critical given that the petrochemicals industry will experience structural and economical upheaval in the coming years driven by the development of shale gas in the United States. The industry is likely to experience increasing tensions surrounding the availability and price of certain key intermediate products, such as propylene, butadiene and benzene.

Fabio Alario – fabio.alario@ifpen.fr
Pierre Marion – pierre.marion@ifpen.fr
Mylène Tourigny
Final draft submitted in December 2013