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Trend Report : From biofuel to biorefinery – Renewables complement fossile resources

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Climate change and the finite nature of fossil resources will not only impact on future energy supplies. The industry is also looking for sustainable alternatives for resources which can be used as materials. This will be an important topic at this year's AchemAsia which opens on June 1st, 2010, at the China National Convention Center in Beijing.

The number of cars in China is growing steadily; it is expected to exceed 200 million in 2020. To meet the demand for fuel, the Chinese government has launched an ambitious program for the production of biofuels. China aims to produce 12 million tons of biofuels annually by 2020. The focus of the Chinese programs is on cellulosic fuels combined with a ban on 1st generation feedstocks like grain in order to avoid the competition with food production. About 700 million tons per year of agricultural waste are currently burned in China and could instead be used to produce biofuels.

But using biomass as a resource does not stop at filling car tanks. The chemical industry is also turning towards renewables in order to substitute fossil resources. The catchword in this context is "biorefinery".

There is no widely accepted definition of bio-refineries. The US Department of Energy offers a very wide definition: "A bio-refinery is an overall concept of a processing plant where biomass feedstocks are converted and extracted into a spectrum of valuable products." Analogously to petrochemical refineries, chemically "simple" raw materials are refined into higher-value materials and products. Here, the biofuels represent the main thrust of the products, while more complex chemicals and polymers play a significant role in terms of value creation. However, differences to oil refineries will probably always remain. For reasons of logistics alone, bio-refineries will probably not be able to match the plant size of oil refineries, as the raw materials required for bio-refineries are sourced from a wide area, while an oil refinery can be set up close to a point-like source.

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Widening the product range of first-generation biofuel plants

One obvious possibility for setting up a bio-refinery is to use the flow of materials in the production of first-generation biofuels for the production of chemicals. Biodiesel is produced from vegetable oil through a process of transesterification with methanol in the presence of a catalyst (usually alcoholates). Current trends in development focus on the use of heterogeneous catalysts and/or biocatalysts as well as uncatalysed transesterification at high pressures and temperatures. One entirely different concept involves the complete hydrogenation of the vegetable oil into propane and alkanes, which are then isomerised into hydrocarbon mixtures with high diesel qualities (cetane ratings of up to 90).

Another important aspect is the development of new sources of raw materials: oil plants which grow on land of very low agricultural quality or in arid regions, such as *Jatropha* and *Camelina*, the use of tall oil (a byproduct of cellulose manufacturing) or the use of microalgae. If a successful change could be made to these starting materials then it would be possible to avoid direct conflict with food production – an issue which has given rise to justified criticism of first-generation biofuels.

During the production of biodiesel, around 200 kg of glycerin is produced per ton of biodiesel. This glycerin used to contribute towards the creation of additional value in the oleochemistry industry, but due to the large-scale expansion of biodiesel production in recent years, it is now a waste product which has seen its value drop significantly. In addition to the traditional forms of use as anti-freeze, in the form of esters (glycerylmonoacetates, nitroglycerin etc.) or – after ethoxylation or etherification – as tensides and emulsifiers, there is a whole range of new lines of research into value-adding forms of use. Examples include hydrolysis to acrolein, hydrogenation into propanediol or the production of epichlorohydrin. Solvay has developed the so-called Epicerol process for this line of use, and the company DOW recently announced plans to build a plant in China with an output of 50,000 t/a.

However, in view of the heavy dependency of biodiesel production on fiscal incentives, many companies are hesitant to venture into production given that the long-term availability of this material has not yet been assured for the decades to come.

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Bioethanol as a platform chemical

Today, bioethanol is produced through fermentation of glucose with the aid of yeast. The glucose is sourced from sugar beet and sugar cane, rye, wheat and maize. If grain is used then an additional step is required beforehand to convert the starch into glucose with the aid of enzymes. The subsequent process steps of distillation, rectification and absolutization are necessary in order to produce ethanol with the required purity of above 99 %, which is a prerequisite for use as a fuel (admixture). A lot of energy is required to process the distillation residue into animal fodder; this has a significant negative impact on the CO_2 balance of current bioethanol plants. Consequently, new plants are aimed at improving the energy efficiency, e.g. through thermal integration with use of exhaust vapor compressors or through utilisation of the stillage in biogas production. In Brazil, the sugar cane trash has long been burned in boilers, adding to the cost-effectiveness and excellent CO_2 balance of the process.

Today, bioethanol (certainly on the basis of sugar cane) can compete in terms of cost with petrochemically produced ethanol. The production of ethyl tertiary butyl ether (ETBE) as a substitute for methyl tertiary butyl ether (MTBE) as a fuel admixture has also already been introduced at German production sites.

Ethanol is a typical platform chemical, for which there is a whole range of potential application lines. Examples include oxidation to acetic acid and subsequent conversion to ketene, the production of acetaldehyde on copper catalysts or the generation of butadiene on magnesium silicates using the Lebedew process. Another interesting technique is the production of ethylene on aluminum oxide catalysts with high selectivity (over 99 %) and high conversion rates (over 90 %). DOW recently launched a joint venture with the Brazilian sugar manufacturer Crystalsev for the production of "green polyethylene". A plant with an output of 350,000 t/a is due to be taken into operation in 2011. Other smaller plants already exist.

Second-generation biofuels

One of the special challenges in the use of renewable raw materials is not only to use specific plant ingredients which are concentrated in particular parts of the plant, but to take the entire body of the plant and make it accessible so that it can be used either to produce materials or generate energy. For example, in terms of the production of biofuels, this means that producers will not only want to use the starch contained in the maize or wheat grains to manufacture ethanol, but that they will also want to convert all of the leaves and stalks of the entire plant, which are primarily made of

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cellulose, to ethanol after saccharification. This is the type of approach people are talking about when they use the phrase ”second-generation biofuels“. With these biofuels, the ethanol yield per hectare of cultivated land could be significantly increased.

The ”lignocellulose-ethanol“ concept is based on exploitation of the hemicellulose and cellulose components of the plants as a source of sugar, which is then fermented in order to produce ethanol. In the biofuel production process, the lignin component remains unused. At present, there are two main lines of development:

In current cellulose production, part of the hemicelluloses go into solution. During the course of the process, these can be extracted from the so-called ”black liquor“, which also contains lignin. After the hydrolysis stage, the hexoses and pentoses which have been produced can be fermented; however, partially modified microorganisms or yeasts are required for this, as the latter in particular are not normally capable of taking up and metabolising pentoses.

In the second variant of the process, the complete lignocellulose biomass is solubilised, and the cellulose and hemicelluloses are hydrolised. This is done with the aid of mineral acids and uses expertise gained during the first half of the 20th century, when – particularly on the basis of research work carried out in Germany – wood was ”saccharified“ on an industrial scale in order to produce ethanol and food yeast. Problems associated with the process include the corrosion of plants and the continued, acid-catalysed reaction of the formed sugars, which results in the production of unwanted products which can obstruct subsequent fermentation. In addition, the waste water produced in the process is heavily polluted, as high salt loads are generated during neutralisation of the acids. By comparison, the alternative of recycling concentrated acids is very energy-intensive.

A lot of hope is also being placed in the development of enzymatic methods for saccharification of the cellulose constituents. All enzyme manufacturers of note around the world are currently active in this area. In many cases, companies have also opted for a cooperative approach, with the aim of delivering complete plants for cellulose saccharification rather than just the necessary enzymes. For example, DuPont and Danisco are working together to develop integrated solutions for the production of ethanol from biomass. In Germany, Südchemie and Linde have joined forces to realise joint plants for the production of ”cellulose ethanol“.

However, the methods known to date for enzymatic saccharification require highly complex pre-treatment of the biomass. In addition, the enzymes used so far are very

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expensive, although the price has gone down in recent years by more than one order of magnitude, as a result of which a number of larger pilot plants are set to be built in the near future.

On the basis of the hemicelluloses and the C5 and C6 sugars produced from them, a number of chemicals can – at least in principle – be manufactured with the aid of suitable microorganisms using techniques similar to the current "white biotechnology" techniques on the basis of glucose.

Another approach is to graft or cross-link the hemicelluloses, which do not have a very high degree of polymerisation. Bioplastics could then be derived from them ("Xylophan").

Biomass to Liquid: not just interesting for fuels

In contrast, the "Biomass to Liquid" concept is designed to produce synthesis gas (CO and H_2) from dry biomass. This can then be used to produce fuel either via the Fischer-Tropsch method or via the methanol route. For reasons of cost-effectiveness, large plants are required.

The most important concepts which are currently being explored at the Research Center in Karlsruhe and Choren GmbH have a preceding step of pyrolysis of the dry biomass at approximately 500 °C. Oil, gas and coke are generated in the process. The gas is used directly as an energy source for the pyrolysis stage, but the coke and oil are combined to a so-called "bioslurry", which is then gasified in a central plant.

Germany is currently at the forefront of technological developments in this area. Scandinavian companies like Chemrec lead the way in the gasification of "black liquor", the waste liquor produced in cellulose manufacturing.

In addition to synthetic fuels, syngas can also be used as the basis for the production of alcohols, aldehydes and short-chain alkenes using known methods. This means that polyolefins are also accessible on the basis of renewable raw materials.

The next step: integrated bio-refineries

The shift from fuel-based use to material-based use can be best realised in integrated bio-refineries. One possible starting material would be cereal or grain: starting from the processing of grain for the production of pure starch or sugar through enzymatic

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hydrolysis, a number of companies have now managed to integrate this with additional product streams which are based on these processes. One example of this is the production of lactic acid at the company Nature Works, which arose from a joint venture between DOW Chemicals and Cargill. This plant has an annual output of around 100,000 t of polylactic acid (PLA). Other companies which process grain have implemented forward integration by manufacturing e.g. citric acid or amino acids in fermentative processes (e.g. Arthur Daniels Midland, Decatur/USA).

Another concept allows use of the husks and straw which were previously treated as an organic waste stream. Analogously to second-generation bioethanol production, hemicelluloses and celluloses need to be solubilised and hydrolysed. Fermentative methods are used once again to manufacture the target products. In addition, it is also possible to manufacture products like Furfural.

Lignocellulose refineries avoid competition with food production

In order to get around the problems associated with competition with food production, many projects rely entirely on lignocellulose as the starting material. In integrated lignocellulose bio-refineries, a preferably large proportion of the natural synthesis output, i.e. the complex molecular structures in plants, is converted into products. Initially, the primary components cellulose, hemicellulose and lignin are isolated or extracted along with any additional extractives which may be contained like terpene. Usage of the lignin which is accumulated in the process is a significant factor in terms of commercial feasibility. This can be used either in synthetic resins as a substitute for phenols, or it can also be converted to low-molecular phenols. However, major development work is still required before this particular route will become available, as a very broad product diversity is produced on account of the complex structure of the lignin. The balance of the lignocellulose refinery is further improved by the fact that the accumulated waste streams can either be used thermally to generate electric energy or converted into synthesis gas.

In summary, we can therefore conclude that many roads lead to Rome! Whichever way, the challenge is to use the largest possible proportion of the biomass either for the production of materials or for energy generation, and to operate with maximum energy efficiency along the way. In the process, different ways of using these resources can be combined with each other for improved profit. For example, use of the hemicellulose fraction in cellulose processing could become an important factor in helping European cellulose plants to remain competitive in the face of the competition from Asia. In addition to the development of new solubilisation methods, suitably

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intelligent plant integration concepts which address the concerns of plants and operators are the key requirement for the commercial success of renewable resources.

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(This trend report was put together by a team of experts and international trade journalists on behalf of DECHEMA. DECHEMA does not accept any responsibility for incomplete or incorrect information.)

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