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REFINERY OF THE FUTURE: FEEDSTOCK, PROCESSES, PRODUCTS

Jean-Luc DUBOIS
ARKEMA

420 Rue d'Estienne d'Orves, 92705 Colombes, France
jean-luc.dubois@arkema.com

Jean-Luc DUBOIS is Scientific Director at Arkema a major International Chemical Company having its head office located in Colombes, France. He is in charge of Corporate R&D linked with Catalysis and Processes. He supervises the long-term projects in this area, and builds the relationships with academic partners and companies for collaborative research.
After being graduated from the Hautes Etudes Industrielles, he did a Voluntary Service Overseas in Saudi Arabia at the KFUPM/RI. He obtained is PhD from the Institut Français du Pétrole (French Institute of Petroleum) for his work on Catalysts for Oxidative Coupling of Methane. After a Post-Doctorate at the National Chemical Laboratory for Industry (Tsukuba, Japan), he found a Research Scientist position at the R&D Centre of the refining company elf-antar-france (now TOTAL), and stayed 2 years in the laboratories of Japan Energy in a collaborative research project on Hydrodesulphurisation catalysts. He moved to the chemical division of the group, elf-atochem (now in-part Arkema) in 1997, and successively stayed in the R&D Centres in Saint-Avold and Pierre-Bénite (France), where he worked on oxidation catalysts and started several research projects.
He has been member of the board of the Catalysis Division of the French Chemical Society. He has been member of the Comité National of the CNRS. He is the author of 80 publications and 80 patent applications.
Arkema is a member of the FP7 European Projects EuroBioRef and BioCore concerning Biorefineries. Arkema has 6 R&D centers in France, 2 in the USA, and 1 in Japan.

Abstract
This paper reviews the concept of Biorefineries, considering the available renewable resources. A particular focus will be given to the economy of biorefinery to stress the conditions in which a biorefinery can be made profitable. Several examples are used to illustrate the potential of these new technologies.

Introduction
In the Crude Oil (Petroleum) history, high prices are linked with a shortage of supply. This was the case with the early production, and again in the 70's, and more recently with the booming Asian economies. Finding alternative sources of carbon for fuels and chemicals is also stressed by the perspective of a peak oil, and taking into account impacts on global warming. New technologies are being developed using biomass to make low value products such as fuels, but also high value materials such as polymers.

There are efforts to classify biorefineries in standard types, based either on the biomass available (oilseeds, lignocellulosic crops, starch, sugar…), the platform chemicals (sugar, ethanol, oil…), the technologies (chemical process, thermochemical processes, fermentation…), or the final type of

products (fuels, chemicals or materials). Integrated Biorefineries combine several types of raw materials, technologies and products to generate the best value from the whole crops.
The development of biorefineries will need appropriate economic conditions. In the recent years, biomass prices are to some extent correlated to the crude oil prices. Some try to see in this the impact of the competition between food and fuels. The recent economic development of China, India, and Brazil for example, implies a higher demand for energy and higher revenues for workers. Obviously they expect a better living standard and expect higher quality food, thereby increasing the demand for edible oil and sugar.

High capital cost of biorefineries is one of the main reason why they are not more common today. A recent study listed 34 biorefineries in Europe, mainly located in western Europe. On top of the capital cost, labor cost and raw material cost are, of course, of primary importance. Biomass might seem to be available everywhere, but in fact the type of biomass which is grown depends of many factors, and especially of the climate. For example, for ethanol production, sugar cane (a tropical crop) is used in Brazil, corn is used in the US, and sugar beets and wheat are used in Europe. For biodiesel production, rapeseed oil is used in Europe, soybean oil is used in the US and palm oil in south east Asia. The biorefinery uses the available biomass, but at the corresponding cost.
The current paper addresses the various types of biorefineries schemes, and with examples of existing complexes analyses the economic variables which makes success stories.

Results and discussion

Among the different type of existing biorefineries, the most common ones are:

- Paper Mills
- Oleochemical plants
- Ethanol production units
- Biodiesel production units
- Sugar based complexes such as the Cargill (US) plant or the Pomacle (F) “Les Sohettes”
- Vegetable Oil Based plant

Arkema’s biorefinery in Marseille (F) belongs to the last family. It uses Castor Oil to produce the monomer of Polyamide-11 (sold as RILSAN-11), a highly technical polymer. This plant coproduces glycerine, heptanaldehyde-heptanol and heptanoic acid, and “Esterol” a solvent. This plant correspond to a type of biorefinery, in which a single type of raw material can be used. Here Castor oil is unique in the vegetable oil arena, since it is the only oil with a high content (85-90 %) of ricinoleic acid. Castor Oil is non-edible, as the castor meal. It is a tropical crop, with nowadays most of the production (about 80 %) being made in India.
The process in the Arkema plant, starts with a transesterification of castor oil with methanol, production the Castor Oil Methyl Ester (COME) and glycerine. The second step is a high temperature thermal cracking, in which only the Methylricinoleate will react, leading to methylundecylenate (a C11 unsaturated ester) and heptanaldehyde. After hydrolysis of the ester, the acid will be converted to 11-Bromoundecanoic acid, through an anti-Markovnikov mechanism. And finally, the Bromoacid is converted into the aminoundecanoic acid, and further purified to become a monomer of high value. In this process, the mixture of the esters which cannot be converted during the thermal cleavage, will be separated and sold as a solvent named “Esterol”. This solvent finds numerous applications, including demolding agent for concrete. Heptanaldehyde can be sold as such and finds applications in fragrances, and is hydrogenated to heptanaldehyde where it finds also a small market. Most of the heptanaldehyde is oxidized as heptanoic acid, and finds several applications such as aviation lubricant.
In this type of plant, with a single type of raw material, all the co-products are made with a constant ratio, and it is particularly important to find the best possible value for each of them. This also means that when the price of refined glycerine decreased from 1500 €/ton down to 400-500 €/t, the production cost of the other co-products increased. In this type of Biorefinery, it is important to identify the key product. There are 2 ways to calculate the production cost for all the products:

1. The production cost at each step is split between the products, which are then sold with a margin/profit (or not)

2. The co-products are assumed to be sold without any profit (meaning that as much production cost as possible are charged to the co-products), and the remaining production cost are allocated to the key product. This is a way to minimize the cost of the key product, but which will fluctuate with the value made on the co-product.

Both ways are acceptable, since it is impossible to make the product without the coproduct.

An other type of oil-based biorefinery, is the complex Elevance Renewable Sciences is building with Wilmar, based on ethenolysis of vegetable oils (metathesis with ethylene). In this case since the plant is being built in South East Asia, Palm Oil is a interesting raw material, but the technology itself will allow to use other vegetable oils such as soybean oil. This type of Biorefinery has a greater degree of flexibility, since by choosing the raw material mix, it is possible to tune the product slate. For example, if palm oil becomes expensive, and the demand for alpha-olefins is increasing, it is possible to switch to soybean oil, to some extent.

Conclusions

The paper discusses several practical examples of biorefineries, based on oil, wood and sugars, and brings data to evaluate the economical parameters such as production cost, and capital costs.

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