Perspective
Platform chemicals from crops

Mairi Black and Richard Miller*
Home-Grown Cereals Authority, Caledonia House, 223 Pentonville Road, London N1 9HY, UK

As industrialists and academics try to peer into the future of the chemical industry, many different scenarios are created and argued over. What many agree is that society will continue to need the products of the chemical industry to deliver the quality of life expected by the developed world and aspired to by the developing world and that, however the industry is structured, we will do things very differently. The reason is simple: we cannot continue to consume the resources of the planet at the rate we do today. If everyone enjoyed the lifestyle of North Americans we would need the resources of three planet earths.

CHALLENGE OF OIL

The key problem is our dependence on oil. The world consumes 84 million barrels of oil a day and that will increase by at least 40% over the next 20 years if patterns of consumption remain the same. We now consume two barrels of oil for every one barrel discovered and, increasingly, new oil and gas sources will prove more difficult and expensive to exploit (Chevron, www.willyoujoinus.com). We are currently burning through the fossil record at 20 million years a year (Tony Ryan, Department of Chemistry, University of Sheffield, personal communication). Those who study oil reserves talk about 'peak oil' or the 'Hubbert peak': the point at which exploitation of the reserves have reached a point whereafter production inevitably declines. Some experts put this point within the next five years, while others think that it could be thirty years away yet, but whoever is right, the peak is likely to be reached before those chemical plants currently under construction reach the end of their economic life. And after the peak it becomes very definitely a seller's market. Prices will remain high, and even increase, as competition grows for an ever depleting resource.

The chemical industry could go back to coal for its feedstock. It is, after all, where the industry originally developed, and the proven reserves of coal would, at current production rates, last around 170 years (data from www.worldcoal.org, 2005). However, using coal as a feedstock does not solve the problem of CO_2 emissions even with the development of CO_2 removal technologies. Right across the global economy we need to move from exploiting non-renewable to renewable resources wherever possible. Whatever else happens in the chemical industry of the future, we will increasingly use recycled and renewable feedstocks and renewable energy.

The obvious choice of new feedstocks for industrial chemistry is plants. All of the fossil carbon we are currently using originated as plant material. By switching from fossil hydrocarbons to plant-derived materials we shift from a long carbon cycle, in which the carbon we are using was last part of the atmosphere millions of years ago, to a short carbon cycle. Plants convert atmospheric carbon into biomass which we can convert into industrially useful products. CO_2 from products released back into the atmosphere during use, or at the end of life, is not increasing the atmospheric burden. It is not just a renewable carbon source we need for the chemical industry. We also need low-carbon emission energy sources. Only about 7% of world petroleum production goes into the chemical and materials industries; the rest is used for power generation, heating and transport. Some of that energy is used during the life cycle of products made from plant materials. So to gain the full CO_2 saving from using plants to generate renewable raw materials, we must also use renewable energy.

HYDROCARBONS TO CARBOHYDRATES

Switching to plants as a source of feedstocks is a dramatic shift. It means moving from a hydrocarbon-based economy to a carbohydrate-based economy. Many of our core chemical processes will need to change fundamentally. That is a big step, and it will be driven in the short term by the need for liquid fuels for road transport – a high-volume application that will encourage the development of new technologies, new markets and new industries.

Although it is a very significant shift in the emphasis of the chemical industry, we should not forget that plants have been a key source of commercial chemicals for a very long time. Figure 1 shows some of the key crops used for industrial purposes today. Crops are exploited for their oils, fibres, as a source of

* Correspondence to: Richard Miller, Home-Grown Cereals Authority, Caledonia House, 223 Pentonville Road, London N1 9HY, UK
E-mail: richard@miller-klein.com
(*Received 18 May 2006; accepted 30 May 2006*)
DOI: 10.1002/jctb.1613

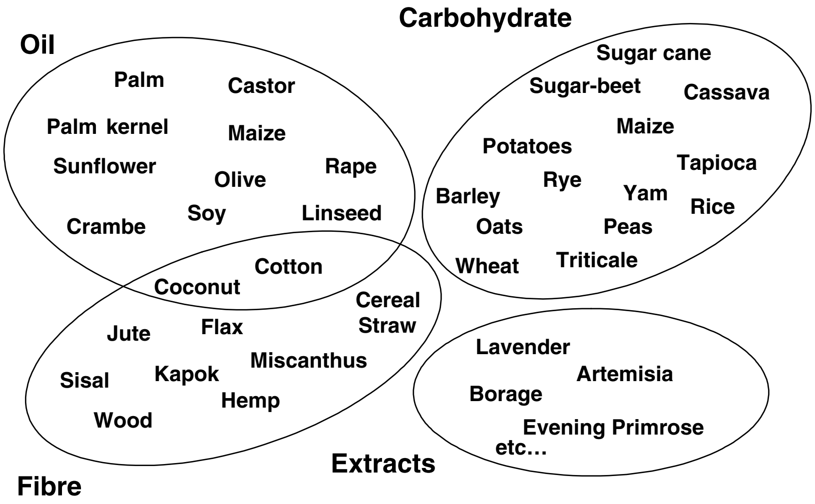

Figure 1. Crops used commercially for industrial applications.

carbohydrates and as a source of a wide range of complex chemicals extracted and used in medicine, cosmetics and many other high-value applications. Some of the numbers are very large. The European IENICA project estimated that globally 19.8 Mt of vegetable oils, 22.5 Mt of starch and 28.4 Mt of non-wood fibres are used industrially each year.[1] A further 42.5 Mt of wood fibres are used annually. These plant-based materials compete head to head on price and technical performance with petrochemical-based materials in applications from packaging, plastics and adhesives to cosmetics and lubricants. It is often assumed that plants can never compete on price with petrochemicals but, in the right application, they clearly can. One of the keys to their success in these applications is that they have developed over many years. As with their petrochemical competitors, they are very far along the technological learning curve, with very well-developed and integrated supply chains.

PLATFORM CHEMICALS

Encouraged by the historical success of plant-based materials in competing for commodity industrial markets, many groups have looked at the potential for further development of plant-derived chemicals. A study in the USA in 1999 recommended that industry should set itself the goal of increasing the percentage of chemical and material needs met from plant resources fivefold, to 10%, by 2020, with another fivefold increase, to 50%, by 2050.[2] More recently the BREW (Business Resource Efficiency and Waste Programme) project in Europe has estimated that approximately one-third of Europe's total need for organic chemicals in 2050 could be met using white biotechnology (biotechnology applied to industrial processes) to convert plant feedstocks.[3] Both of these studies assume that oil prices will remain sufficiently high to encourage the research and development needed to overcome the technical problems.

To reach this level of replacement of petrochemicals we need to go beyond both the existing plant-based commodities and high-value extracts, to high-volume commodity building blocks. Each of these small number of 'platform' chemicals stands at the apex of a cascade of transformations that produce hundreds of commercially important materials. A study in the USA published in 2004 described 12 key platform chemicals that can be produced from sugars through chemical processing or bioprocessing.[4] They are the 1,4-diacids succinic, fumaric and malic, 2,5-furan dicarboxylic acid, 3-hydroxypropionic acid, aspartic acid, glucaric and glutamic acids, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol, and xylitol or arabinitol. Each of these molecules has multiple functionalities and can be converted to a wide range of molecules using standard transformations. For example, 3-hydroxypropionic acid can easily be converted to acrylic acid, methyl acrylate, acrylamide, and 1,3-propanediol. Each of these latter compounds has current industrial applications and a current market. In 2004 Tate & Lyle and DuPont announced a joint venture to produce 1,3-propanediol from corn for use in DuPont's Sorona® poly(trimethylene terephthalate) textile fibre. This will be a direct replacement for the current petrochemical material, and is expected to be competitive on cost.

BIOREFINERIES

Other groups have produced different lists of priority platform chemicals based on which molecules and which transformation routes look the most cost effective. Ethanol was omitted from the US study[4] because it is mainly a fuel and has fewer options for conversion into other value-added molecules. However, it is likely to become a powerful driving force for the development of platform chemicals because of the use of ethanol as a liquid road fuel. Many governments are encouraging the use of

J Chem Technol Biotechnol **81**:1725–1728 (2006)
DOI: 10.1002/jctb

biofuels out of concerns for the environment and the future cost of oil and security of supply. In the UK, under an EU-wide initiative, the Renewable Transport Fuel Obligation has been introduced. This mandates that by 2010 5% of the UK supply of liquid road fuels will be bio-based. Some will be biodiesel from rapeseed or other plant oils, but a large proportion will be bioethanol. At 5% substitution, the UK annual market alone is about 1 Mt of bioethanol.

These initiatives are bringing significant investment into the market to build facilities capable of converting the fermentable carbohydrates from cereals into bioethanol. Beyond that people are looking at converting the structural biomass of plants – the cellulose and hemicelluloses – into fermentable sugars. This will make much more efficient use of the plant biomass produced by photosynthesis and increase the range of plant materials that can be used. In such a unit there is a need to make the maximum use of the starting biomass and to produce as little waste as possible. This leads to the idea of the biorefinery.

A biorefinery is analogous to a petroleum refinery. There are one or two key products in high demand that provide the basic economic justification for the plant – gasoline for petroleum refineries and ethanol for biorefineries – but once you have the basic process in place, adding additional processes will maximise the productive use of each tonne of feedstock and minimise the waste. We already know from the starch and oleochemical industries that everything that enters a plant as a raw material must leave as a product. Any waste that must be disposed of creates a cost that can erode the economics of a process. The chemical industry largely depends on achieving this with every barrel of oil, and the future chemical industry will need every tonne of plant biomass to be converted into as large a volume of commercially useful materials as possible. Biorefineries will initially be set up using starch or fermentable sugars as feedstocks, and using unfermentable materials and additional biomass from the fermentation process in combined heat and power units to produce the energy to run the plant. As technology develops, other plant materials such as cellulose and hemicellulose will be processed to sugars. This will provide C5 as well as C6 sugars and open up a pathway to platform chemicals. High-value materials may be extracted from the plants as a pre-processing step to increase the value of the product stream. Just as with the petroleum refinery, a whole complex of product streams and subsidiary processes will be grafted onto the bioethanol backbone, and a range of plant-derived platform chemicals will become commercially viable.

FUTURE NEEDS

Producing platform chemicals from crops in ways that are economically viable, and have lower environmental impact, poses many challenges. It creates a demanding research agenda, as well as a structural change agenda for both the chemical and agricultural industries. The specific technology challenges include:

- efficient extraction techniques that can be used with mixed and variable feedstocks;
- effective pre-treatment of biomass for fermentation and chemical processing;
- efficient processes for breaking down cellulose, hemicellulose and lignin;
- fermentation processes that can convert a variety of sugars into ethanol;
- low-impact transformations to target platform chemicals;
- new ways of integrating biotechnology and chemical transformation;
- processes that can tolerate highly variable feedstocks;
- converting established processes from existing plant-based materials processes to the new generation of biorefineries. For example, paper-pulp mills have for many years used the lignin-rich waste stream, 'black liquor', to generate heat, steam and power to operate the mill;
- developing flexible manufacturing plant that can be quickly reconfigured to take advantage of changing prices for products and feedstocks.

Technology is not the only challenge. The agricultural and chemical industries need to work together to create the new supply chain for crop-based industrial chemicals. If either group thinks that their new partners have exactly the same characteristics as the current supply chain there will be many dead-ends and false starts. Many in the chemical industry look at what is available from agriculture as a bulk commodity and assume that this is all that could be available. For example, when thinking about using wheat as a feedstock for a biorefinery, the protein content is a problem. It contributes little to the production of ethanol, and if burned to produce energy with the rest of the unconverted biomass it generates significant NO_x emissions. However, plant breeders have spent many years increasing the amount of protein in wheat to meet the needs of animal and human nutrition. Wheat varieties with a much lower protein content are quite feasible if there is a demand.

There is also a need for good economic modelling and life cycle analysis of the potential for biorefineries and plant-derived feedstocks. Although this approach could significantly reduce the environmental footprint of the chemical and chemical-using industries, these ideas need to be realised and demonstrated to be economically viable and environmentally acceptable.

Many different organisations across the globe are encouraging and funding research into delivering plant-derived platform chemicals to industry. In the UK, the Home Grown Cereals Authority (HGCA) is promoting research with a focus on cereals and oilseeds for biofuels. Recent and current projects include: development of a carbon accreditation scheme for bioethanol in the UK; assessment of the environmental impacts of growing cereals for biofuels; developing technical specifications and variety recommendations for the use of wheat for bioethanol; reduction of energy use and nitrogen emissions in the production of wheat for biofuels; and a study of potential designs for a wheat-based biorefinery.

Delivering the potential of plant-based platform chemicals will require extensive collaboration right across the supply chain and involving many different disciplines. There will be technical and economic challenges to satisfy the most demanding R&D teams, but the prize is well worth the journey.

REFERENCES

1 IENICA, [Online]. Report from the state of the United Kingdom forming part of the IENICA project (1999). Available: www.ienica.net [23 July 2006].

2 Renewables Vision 2020 Executive Steering Group, [Online]. *Technology Roadmap for Plant/Crop-Based Renewable Resources 2020: Research Priorities for Fulfilling a Vision to Enhance US Economic Security Through Renewable Plant/Crop-Based Resource Use* (1999). Available: www.eere.energy.gov [23 July 2006].

3 BREW, [Online]. *Medium and Long-Term Opportunities and Risks of the Biotechnological Production of Bulk Chemicals from Renewable Resources*. Available: www.chem.uu.nl/brew/ (http://www.chem.uu.nl/brew/BREWProjectProfile4.doc) [23 July 2006].

4 National Renewable Energy Laboratory, [Online]. *Top Value Added Chemicals from Biomass Volume I – Results of Screening for Potential Candidates from Sugars and Synthesis Gas* (2004). Available: www.eere.energy.gov [23 July 2006].

DOI: 10.1002/jctb