BIOREFINERY, THE BRIDGE BETWEEN AGRICULTURE AND CHEMISTRY

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The depletion in fossil feedstocks, increasing oil prices and the ecological problems associated with CO_2 emissions are forcing the development of alternative resources for energy (heat and electricity), transport fuels and chemicals: the replacement of fossil resources with CO_2 neutral biomass. When used in combination with environmentally sound production and processing techniques, the use of biomass can be seen as a sustainable alternative to conventional feedstocks. The production of chemicals utilises more effectively the intrinsic biomass (chemical) structure than the production of fuels or electricity from biomass does. The production of chemicals from biomass also saves more fossil energy than producing just energy. For example, some amino acids obtained from grass are very suitable starting materials for highly functionalized chemicals that are traditionally prepared from petrochemistry. Economical production routes of chemicals from biomass require large scale substitution of (bulk) chemicals which connects to current approaches and facilities (process integration) of the petrochemical industries to convert crude oil into chemical building blocks. Genetic modification of plants will increase the potential of biomass in the chemical industry because it allows an increase in the concentrations of the required (bio-)chemical pre-cursors e.g. amino acids, present. It will also be discussed how small scale (pre)processing of the biomass can be advantageous over large scale processing. This is because of lower transportation costs but also the opportunity to use process-integrations that can not be used on large scale. These integrations yield high efficiencies of energy utilization but require improvement on social or organisational levels.
Keywords: agriculture, bio-based products, bulk-chemicals

1 INTRODUCTION

The anticipated climate changes presumably caused by greenhouse gasses, the energy security and the high and fluctuating energy prices, urge us to look for alternative energy sources and for ways to increase the energy efficiency of processes for our heating, electricity, transportation and chemistry needs.

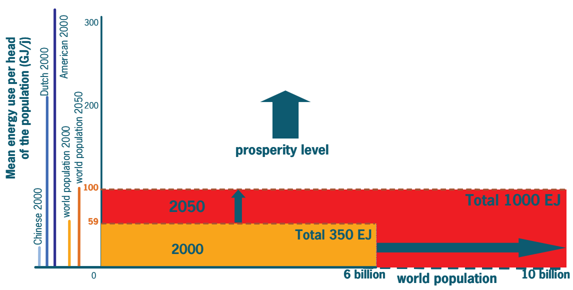

Figure 1: Energy consumption in 2050 three times larger than today

Global energy consumption is anticipated to triple in the next 50 years as judged by IPCC scenario B1. Figure 1 visualizes energy consumption by the surface that is obtain by multiplying the number of global population people (X-axis) and the average consumption pro caput (Y-axis). The population of Northern America consume more than the world average of 59 GJ per capita per year, while the Chinese population for example lie far below. In 45 five years the average is estimated to be 100 GJ capita per year for 10 billion people. By then the total consumption will be ca. 1000 EJ/year .

Several questions will be addressed in this paper: Can energy production, transport fuels and chemicals produced from plant material, compete with the same products when they are derived from petrochemical origin? Do we need to concentrate on specialty chemicals, bulk chemicals or just electricity? Should we direct our work towards one general starting material like Naphtha, or should we utilize the huge synthetic opportunities found in plant and microbial systems? Do we need to build large-scale processes or is it better to apply many small operations?

2 MARKET VALUE FOR DIFFERENT APPLICATIONS OF BIOMASS

If one wants to apply biomass to replace fossil raw materials, one can choose between the four major applications: heat, electricity, transport fuels and chemicals. Each of these groups represents about 20% of the total fossil consumption in the western world. If we compare the cost of these products at the wholesale level on an energy content basis, we see large differences. (table I first column).

Table I: Biomass can have different applications and contributions

	Integral cost prices (€/GJ end product)	Raw material cost *fossile* (€/GJ)	Potential Raw material cost *biomass* (€/GJ)	Netherlands energy is 3000PJ
Heat	4	3 (coal)	3 (wood)	20%
Electricity	22	6 (coal)	6 (wood)	20%
Transport fuel	10	8 (oil)	14 (sugar)	20%
Average bulk chemicals	75	30 (oil)	6 (biomass)	20%
Rest				20%

Also the contribution of the raw material costs expressed per GJ end product show large differences. Heat can be produced from coal for around 3 €/GJ. This is because one has almost 100% yield and cheap raw materials. The raw materials for electricity cost more than double. This is due to conversion yields <50%, raw material for transportation fuels cost about 8€/GJ (at oil prices of 50$/bbl) and finally the raw materials for the average (bulk) chemical cost 30 €/GJ of the end product. The latter is because expensive raw materials have to be used and yields are far below 100%.

3 VALUE PER HECTARE CULTIVATED INDUSTRIAL CROPS

Assuming that we want to make each of these product groups by agricultural processes, then the gross value per hectare as a heating raw material, would be around 640€ (at production levels of 10 tonnes dry weight per hectare per year). This will be too low for Dutch farmers to cover there costs and get some return. When the 10 tonnes is used as the raw material for the production of transport fuel, then 1360 €/ha would be the gross turnover. This could be just enough to cover costs and have some income for the farmer (this value compares well with the turnover of one hectare of wheat in The Netherlands). If all 10 tonnes were used as the raw material for chemicals, then 6400 €/ha could result. It is however not realistic to think that all 10 tonnes can be used in this way. Assume 20% of the dry weight of the harvest is represented by these precursor chemicals, 40% is used as a fuel and the last 40% as the raw material for electricity, then a value of 1940€ per hectare can be anticipated. With improved agricultural practices and the use of all the components of the plant, we expect that 20 tonnes per hectare could be obtained for several crops, which could bring the gross income per hectare to 3880€ per year.
In order to get a good net income, we need an effective bio-refinery system that is able to separate our harvested crop into at least the three fractions for our three purposes. These fractions can be used directly as the desired product or need a further conversion by chemical, enzymatic and/or microbial means.

4 VALUE OF THE PLANT COMPONENTS PER TON OF DRY WEIGHT

Biorefinery systems have been developed for various crops over the last 170 years in The Netherlands: Starch has been refined from potatoes on industrial scale since 1839 (Scholten), and sugar since the time of Napoleon. Starch is also fractionated from wheat. Soybeans are the raw materials for large bio-refineries to produce oil, proteins and valuable nutraceuticals. Each of these industrial bio-refineries produce one or more animal feed products. A well developed feed industry and infrastructure nowadays will be a valuable asset to start new bio-refineries. In the past 8 years Wageningen University and Research Center, together with the potato starch-company AVEBE and some other industrial partners have explored the development of a biorefinery for grass and other leaf materials like Alfalfa, beet leaf, etc. Because potatoes were only available for processing from August till March, the same factories could process grass using part of the equipment from April till August.

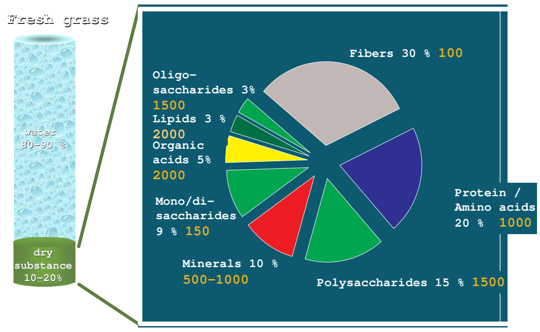

Figure 2: The separated components of grass value 700-800€/ton as compared to 50-70 €/ton raw materials

The most prominent components of grass are shown in figure 2. Fibers represent about 30% by weight and have a value of around 100€/ton fibers. The other components have much higher values. The average value of these components is about 800 €/tonnes grass (DW), while the grass input as such will cost between 50 and 80€ per ton dry weight. Grass therefore could become a very good crop for the production of bio-refinery products. However the market volume of the products indicated are not that large, so calculations should not be made on this basis if you want to have significant impact in the production of greenhouse gasses. Furthermore, the fractionation into 8 different fractions will need considerable technological development. Successful fractionation of grass into three fractions with the process line has been achieved (figure 3).

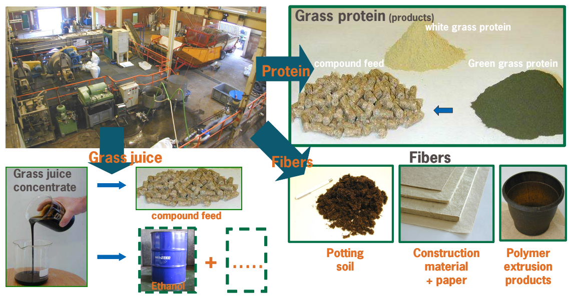

Figure 3: Pilot biorefinery line Foxhol (Groningen) (Prograss Consortium)

The central part of the process is a mechanical refiner as used in the pulp industry. In this unit operation, leaf material is broken allowing the fibers to be obtained in a rather pure form (<11 % of the protein remains). The protein is being recovered from the liquid fraction after heat coagulation and a separation step, while the rest of the juice is concentrated by evaporation. The process runs at 4 tonnes of fresh grass input per hour and gave the three fractions:

- proteins as a feed component for pigs and poultry
- fibers for building materials, filler materials for plastics and raw material to make a biofuel (see elsewhere in these Proceedings)
- soluble components such as amino acids,(polymeric) sugars, organic acids and minerals. These have been concentrated in the juice and can be used as a feed component, or as a fermentation raw material.

5 WHICH CHEMICALS HAVE THE BEST CHANCE TO BE RECOVERED FROM BIOMASS?

How can crop derived chemicals compete with (bulk) petrochemicals?

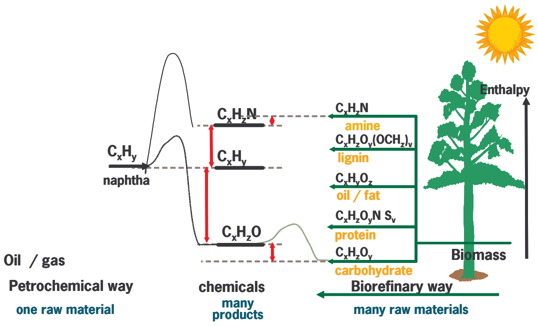

Figure 4: Functionalized chemicals can be made from biomass without major enthalpy differences, but not from naphta

Figure 4 shows products that are produced from oil. Naphtha is the general raw material for many chemicals. Olefins, like ethylene containing just carbon and hydrogen, can be produced very efficiently because no major enthalpy changes have to be overcome with consequently heat transfer. For the production of so-called "functionalized chemicals", like those that contain nitrogen and/or oxygen, major enthalpy changes have to be overcome and consequently heat has to be transferred. At the process conditions at which reactions are carried out, high temperatures and pressures and sometimes corrosive conditions are often required. As well as this, heat exchangers will contribute considerable costs to the overall investment costs for these products compared to the "non-functionalized products". The heat transfer will contribute to significant losses of energy unless one is able to have endothermic and exothermic reactions performed at similar temperatures. However, this is often unattractive because of reaction kinetics, but certainly not because heat transfer at small temperature differences need very large heat exchange surfaces and therefore high costs.
If one considers biomass as a mixture of various different components, which include components with a similar elementary composition as the nitrogen containing compound in the figure, hardly any heat has to be transferred if this component could be used as the building block for the production of the existing functionalized “petrochemical”. Also, if the structure is similar to the desired chemical, then probably only simple conversion steps are required to obtain the final product.. This approach is also possible for the production of oxygen containing chemicals and for olefins starting from carbohydrates and fatty acids respectively. In the latter, biomass routes have to compete with the strong position of the petrochemistry, while with the nitrogen and oxygen containing products, the petrochemical routes are not so strong as we will see below.

6 THE PRODUCTION OF ETHANDIAMINE AND BUTANDIAMINE FROM AMINOACIDS.

Ethandiamine is produced starting with ethylene by various routes: Oxydation to the epoxide followed by amination to ethanolamine and then to ethanediamine (a new route uses ethane that is oxidized directly to the epoxide). A number of producers use a route via the chlorination of ethylene followed by substitution of the chlorine with ammonia. Production of 1,4-butandiamine starts with propylene and uses ammonia and hydrocyanic acid. Starting from the amino acids serine and arginin respectively we can synthesize the diamine products using well described enzymatic and/or chemical conversion steps. Decarboxylation of serine forms ethanolamine, itself a petrochemical product, that is converted to the diamine by the addition of ammonia. Arginine is hydrolysed to ornithine and urea. Ornithin forms 1,4-butandiamine after decarboxylation. The global market for these products runs into millions of tonnes,. If we would have used the amino acids to make electricity by burning this biomass in a power plant, than we would have obtained the caloric value of these products, being around 20 GJ/tonne. The synthesis from oil and natural gas, to produce the ammonia and the electricity for the chlorine production, add up to ca.70 GJ/ ton of end product.

7 ECONOMICS OF THE BULK CHEMICALS

Comparing typical cost breakdown figures of non functionalized chemicals like ethylene and propylene, with those of functionalized chemicals such as those containing oxygen or nitrogen, described above, we can see major differences in raw materials cost and investment costs, table II.

Table II: Cost breakdown of (bulk)chemicals (€/ton) at 40$/bbl

	non-functionalised	functionalised
Raw materials	200	**650**
Capital	300-500	**400-650**
Operational	50	50
Recovery	50-100	50-100
Total	725	1300

The raw material costs are explained by the large amount of fossil raw materials needed (at oil prices of 40$/bbl). The differences in investment costs are explained by the additional costs for heat exchange at the process conditions and the investments for the production of chemicals like chlorine, ammonia, sulfuric acid and caustic soda.
The other operational and recovery costs being much the same for functionalized and non-functionalized chemicals. In specific cases the investment costs and raw material cost may differ significantly which will open up the production towards these chemicals. Although the global volumes of the products are large, they may be produced on much smaller scales and with

a simpler infrastructure compared to the petrochemical complexes around the world. This makes the competitiveness of this approach even more powerful, as more players than just a few petrochemical companies can enter these markets.

8 ONE SINGLE STARTING RAW MATERIAL OR MANY DIFFERENTIATED PRODUCTS TO OBTAIN FROM THE BIOREFINERY?

From the examples above it will be clear that we will not aim for one single starting point for the chemicals derived from biomass. On the other hand we also limit the chemicals to be accumulated in plants as final, or building blocks for fine chemicals, for the market. If the annual production volume is too low, fermentation processes starting from sugars, is the more preferred route. From an article in preparation one can derive that chemicals, with volumes above 25 000 tonnes/year have advantages to overcome the investment costs to be made for the production via plants, while products of lower annual volumes should be produced by fermentation. We believe that for competition with petrochemicals, this minimum also holds, and can be shifted towards larger volumes because one can benefit from the infrastructure and know how of the petrochemical industry. We expect that dozens of products, like the two amino acids previously mentioned, can be developed in this new approach. Typical volumes will be one million tonnes and higher.

9 MARKET EXPECTATIONS

The market for (bulk) chemicals is about one billion tonnes per year. About one quarter of this volume are functionalized and may be produced from plants in one way or the other. Currently functionalized materials utilize ca.10% of the total fossil raw materials in the west. Another 10% is used for the remaining (bulk) chemicals. If 20 % of the harvested plants components are used to obtain platform chemicals, the other 80% may be converted to transport fuel e.g. ethanol and what cannot be converted can be used to make biogas or burnt directly to electricity. A financial turnover is estimated at 200 G€ for the platform chemicals and about 150 G€ for the by-products. This total product value of 350 G€ can be obtained from about 125 million hectare assuming a yield of 10 tonnes/ha.year.

10 HOW CAN WE DEVELOP THE TECHNOLOGY TO MAKE THIS HAPPEN?

Several lines of improvement should contribute to the realization of the concept shown above: lower raw material price; better and cheaper refinery technology; genetic modification to allow accumulation of the desired chemicals; small scale (pre)processing and new material properties will allow higher prices in the marketplace.

- Once platform chemicals, from which traditional petrochemicals can be derived, can be produced at competitive prices, these platform chemicals might lead to novel chemicals that now would have been too expensive to produce with the 'petrochemical' toolbox. A total new chemistry might develop eventually.
- Today the price of crude sugar in Brazil is ca. 100$/tonne is similar in energy terms as oil at 40$/barrel. We will not be able to influence the oil price, but we will be able to further reduce the sugar prices by separating more valuable compounds from the crop and apply these as good platform chemicals at values of 700-800€/tonne. This will increase the margin or allow the supply sugar as a platform chemical in its own right at low prices. These low prices are not just the sole right for Brazil, also in Europe we will be able to benefit from this development because we have all the players closely available.

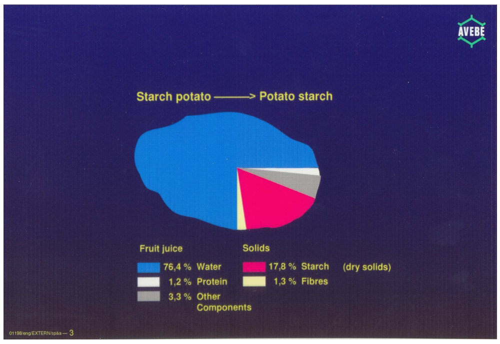

Figure 5: Using the potential components of Potato

- Figure 5 shows a typical potato used in industrial bio-refineries to obtain potato-starch, potato-protein and some side products. In comparison with wheat and corn that are competitive sources of starch, the large water content in potato is often regarded as a major drawback. This is because it increases the transportation costs and even more importantly, potatoes cannot be stored over the full year leading to a process that can only be operated for half the year, which naturally increases the capital costs per tonne of product. Assuming an accumulation limit of 5% of a certain product, due to biochemical feedback or compound toxicity at that concentration,.5 out of 25% of the potatoes dry weight components thus 20% of the overall dry weight contains the desired product, while in corn it would only 5% of 85%, thus 6% of the overall dry weight basis. If we reason that a seed is a lot more complex that the tuber as a storage organ, this 6% might well be an over estimation. Figure 6 shows results from AVEBE and Wageningen UR/PRI, in which the wild type concentration of the amino acid lysine is enhanced more than 15 fold in several mutant lines. The concentration being between 0.5 and 1.0% needs further enhancement to become competitive with the petrochemical sources.

With oil prices of 40$/bbl this will happen at 4-5% (fresh weight).

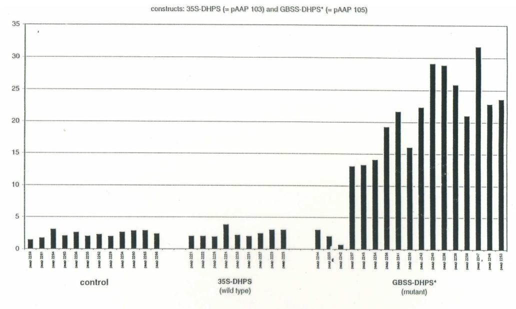

Figure 6: Lysine (%) in mature transgenic potato tubers

11 SMALL SCALE PROCESSING OF AGRICULTURAL PRODUCTS

Small scale pretreatment close harvest location, might have several benefits such as less transportation, short recycles of minerals and sand, new forms of integrations in energy utilization, organization and or labor. As well as this, it will also lead to a forward integration for the farmer who can get a greater part of the total added value in the chain. This will challenge many entrepreneurial farmers to optimize their part of the whole process. In many developing countries it is very difficult to get a good raw material supply, because of road infrastructure, or spoilage of the cassava root after harvesting or the bargaining power of the factories is too large, which decreases the incentives for the farmers to improve their yields. Wageningen UR has designed a mobile unit to process cassava roots. This can then be transported close to the production fields. The fruit juice, containing minerals, can be put back in to the soil, which will increase the yields of the subsequent crops. The starch is washed which removes soluble materials, while the fibers stay in the product that can be dried and shipped to e.g. potato starch factories that have spare capacity to purify the starch out of season. The first prototype has been tested in Africa and it is expected that many more will be built in the near future. Also in Europe e.g. sugar beet-production, preprocessing (of the beets) might be beneficial close to the field. This will decrease the transportation costs associated with water and sand content.

Figure 7: Mobile Cassava starch refinery in Africa

Also the minerals present in the beet can be recycled to the fields and do not need to be concentrated in the molasses that are shipped to fermentation industries. These industries need to concentrate these minerals for a second time, often with considerable costs. Finally the salts are recycled to the fields. Of course, preprocessing does not mean that the actual optimalized large scale process is scaled down. This would cause very high capital and labor costs. Only unit operations should be used on small scale that cannot easily be operated on large scale. This is amongst other, the reduction of the transportation costs but also the possibility to make an intermediate product that can be stored during the year, which will enable the large factory to run for the whole year. This leads to lower capital and labor costs, and better prices for by-products.

12 CONCLUSIONS

Biorefinery of crops into various fractions will increase the overall value of biomass. Platform chemicals can be derived from biomass under economical conditions. For the moment functionalized chemicals from biomass have the best chance to compete with those chemicals from petrochemical origin.
Small scale (pre)processing offers economic advantages and potential for forward integration to the farmer.