

Biorefineries for the chemical industry – A Dutch point of view

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1. Introduction

As a major policy goal for 2020, the Dutch government has defined that 10% of the energy use should be provided by renewable sources to meet its Kyoto objectives. Biomass is expected to be a major contributor with an anticipated share of more than 50% of the policy goal mentioned. Further, the Ministry of Economic Affairs has defined some very ambitious policy targets for biomass in the longer term (2040), namely 30% fossil fuel substitution in the power and transportation sector and 20-45% fossil-based raw material substitution in the industrial sector. It has been calculated that the energy substitution policy goal corresponds with a long-term required biomass substitution volume of about 600 – 1000 PJ_{th}/a, in a scenario in which severe energy savings have also been taken into account (Ministry of Economic Affairs 2003). Adding the very ambitious raw material policy goal an additional biomass substitution volume of several hundreds PJ_{th}/a will be required.

Presently, biomass in the Netherlands that is not used for food applications is mainly utilized as animal feed and fuel for power (and heat) production. Biomass is converted mainly by means of direct/indirect cofiring in conventional coal-fired power plants and also by stand-alone combustion plants (Cuijk, Lelystad). To meet the longer term policy ambitions biomass has to be applied in additional market sectors of the Dutch economy, using new thermo-chemical and (bio)chemical conversion/production processes, such as advanced gasification and fermentation technologies. A current disadvantage of these processes is that final products will be produced that are more expensive than their concurring fossil-based alternatives. Prolonged financial governmental support (e.g. investment subsidies, fiscal measures), necessary to support successful market implementation, is lacking at the moment in the Netherlands. Further, to meet the longer term policy ambitions, the use of potentially available relatively cheap organic side- and waste streams will not be sufficient. The use of dedicated, relatively expensive “energy” crops, grown both in and outside the Netherlands (import), is therefore inescapable.

Within this framework biorefineries are believed to play a major role in the transition to a more sustainable Dutch economy. Realization of high-efficient biorefining processes at places where biomass can be gathered, grown and/or imported and where the “green” products can be sold to a cluster of chemical and material industries, are believed to be key technologies to meet the longer term policy goals.

The chemical and material industries are founded upon innovation. Due to the emerging interaction between chemistry, biology and process engineering the industries of 2020 will be significantly different from the industry of today. However, not only technological development encourages a change in the design of processes and products but also pressure from consumers and the general public fuel a transition to a more sustainable industry. This strengthens the discussion on if and how the use of renewable resources can add to a future scenario of an continuing innovative chemical industry taking into account the wishes and constraints of all current and future stakeholders.

This paper firstly provides the societal and institutional context for the transition to sustainability in evolving the chemical industry. Secondly, it reviews various perspectives on the future of a modified chemical industry, partly resulting from emerging technological opportunities. Thirdly, taking into account these emerging technological opportunities this paper discusses the potential of the use of biomass in the chemical industry of today and tomorrow. Special emphasis will be given towards the potential that “biorefineries” offer the chemical industry.

2. Historical Outline – The Chemical Industry: Current Situation and Perspectives

This paragraph has the objective to present an overview of the chemical products that the current industry produces. It also gives an overview of the technological pathways that are involved in the production of these chemical products. This overview provides the scope of chemical products and chemical intermediates that need to be produced from biomass. This paragraph also provides an overview of currently produced biomass based chemical products.

2.1 Overview of products and markets

The oil industry may be divided into several important refinery sectors and products including: gas for commercial energy supply, heavy gasoline for car fuels, naphtha for the petrochemical industry, kerosene for aviation fuel and oil residues used in bitumen and lubrication oils. This review is focused on the naphtha fraction in the petrochemical industry and the gamut of chemicals, products, applications and markets that can be derived thereof.

The current chemical industry’s most important feedstock is naphtha which may be cracked to obtain a range of olefins such as ethylene, butanes and other small (un)saturated hydrocarbons as well as aromatic compounds such as benzene and alkyl benzenes. These simple hydrocarbons form the backbone of the possible products that are generated in the chemical industry today. The scope of different chemicals (and transformations) that can be achieved from naphtha for the chemical industry is illustrated schematically in Figure 1.

In principal they can be transformed to the bulk of chemicals produced by two initial key pathways:

- They may be directly isolated, used and transformed by various chemical techniques to a range of compounds or
- Undergo a gasification process to form synthesis gas (CO and H₂), which upon recombination allows access to another branch of alternative chemicals and technologies.

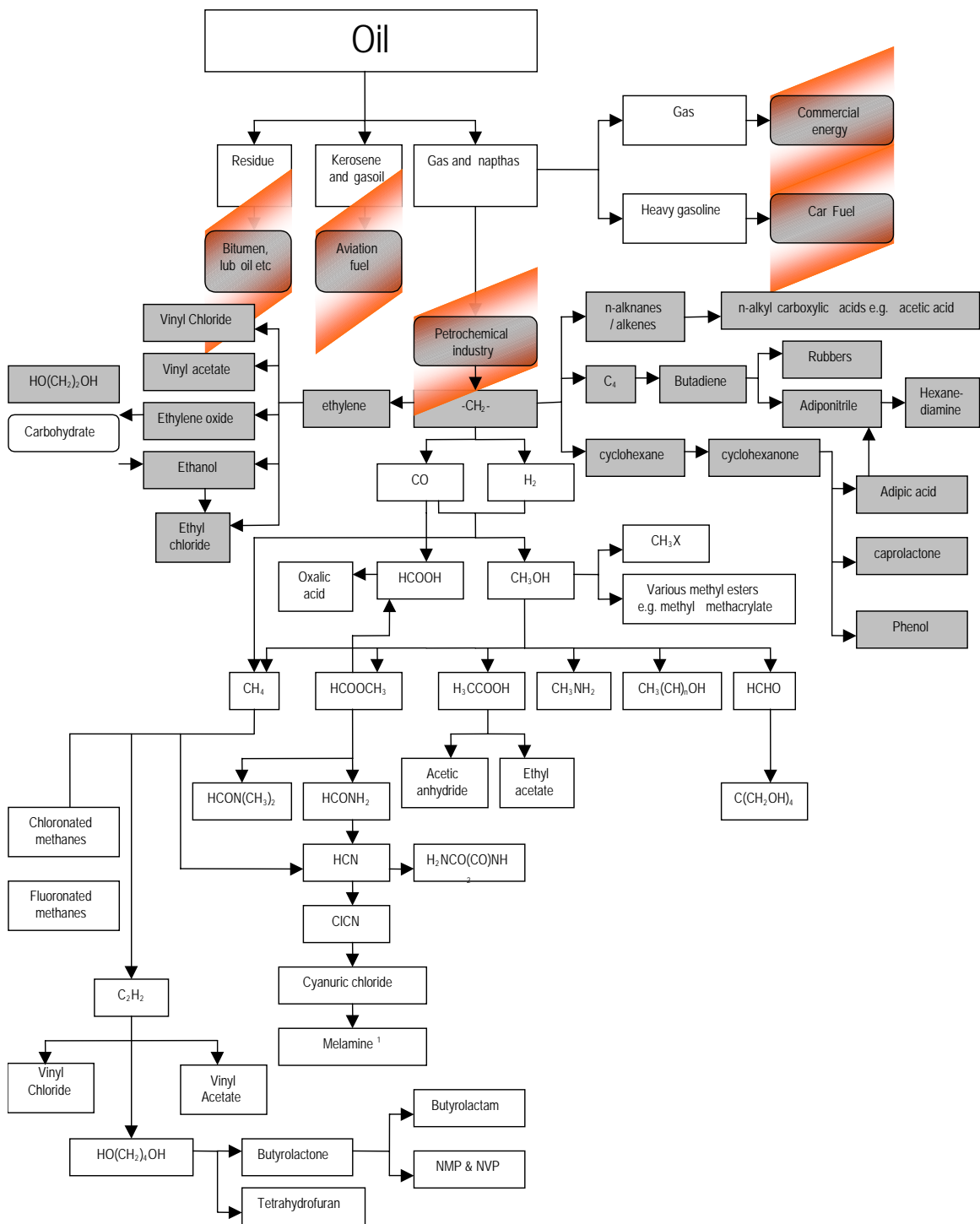


Fig. 1 Schematic representation of chemical transformation steps in the (petro)chemical industry

The chemicals described in Figure 1, derived from the small (un)saturated hydrocarbons and synthesis gas, allows for an array of chemicals of technological and economically important products, applications and markets to be obtained. For example:

- Vinyl monomers for plastics used in pipe, packaging and rubber applications
- Monomers for polyester and amide synthesis utilised in fibres (for textiles), engineering materials and some container materials
- Solvents for a.o. the paint industry
- Chemicals for the pharmaceutical industry
- Chemicals for the insecticide and herbicide industry

2.2 Technological pathways

A closer examination of the chemical transformation steps (Fig. 1), involved in converting one substance into another, reveals some generic approaches in the type of chemistry and technology used in the chemical industry:

- Oxidative and reductive techniques are most prolific
- Introduction of nitrogen into chemical structures is most frequently achieved by initial amination or amidation reactions with ammonia
- Carbonylation reactions are frequently used to make small incremental changes in chain length and for the introduction of new functionality
- Extensive use of gaseous reagents
- High selectivity of chemical steps by utilization of catalytic materials, therefore reducing the need for chemical derivatisation for transformation
- High conversion of chemical steps by utilization of catalytic materials

2.3 Biomass based industrial products

While most of the chemicals are derived from a petrochemical origin an important example of a chemical, produced in bulk, from a non-petrochemical origin is ethanol. Ethanol, produced by the fermentation of molasses etc., has been most extensively used in the food and beverage industry, however, increased amounts are also used in bio-based transportation fuels and to prepare non-food industrial chemical products.

While ethanol is perhaps the most widely known example of a bio-based chemical product both in the Netherlands and worldwide, there is a range of other bio-based chemical products produced and used in a variety of industrial applications. These fall into several generic categories:

- Naturally occurring carbohydrate polymers
- Fats and oils from plant origin (and to a lesser extent of animal source)
- Terpene based materials
- Chemical products of carbohydrate containing materials
- Fermentation products of carbohydrate containing sources

A recent study coordinated by the European Renewable Resources & Materials Association (ERRMA) has evaluated the current situation of biomass use as industrial feedstock for chemicals and materials (Ehrenberg, 2002). Table 1 shows the potential of biomass to replace petrochemical based products in the area of polymers, lubricants, solvents and surfactants. Many of those applications, especially in the areas of lubricants, solvents and surfactants, can be achieved by direct extraction of the components from the biomass without additional (bio)conversion steps.

Carbohydrates

Today's bio-based products include commodity and specialty chemicals, fuels, and materials. Some of these products result from the direct physical or chemical processing of biomass cellulose, starch, oils, protein, lignin, and terpenes. The great majority of all biomass consists of natural polymers, and the great majority of all biomass is carbohydrate in nature. This means that the majority of all biomass is in the form of carbohydrate polymers (polysaccharides). These natural polymers can be used both as nature provides them and as the skeletal framework of other derived polymers.

Table 1 Estimated EU potential of major biomass-based products (Ehrenberg 2002)

Market sector	Total consumption market (1998) (kton)	Renewable consumption market (1998) (kton)	Potential renewables in 2010 (kton)	Potential of share in 2010 (%)
Polymers	33000	25	500	1.5
Lubricants	4240	100	200	5
Solvents	4000	60	235	12.5
Surfactants	2260	1180	1450	52

By far the most abundant of these carbohydrate polymers is cellulose, the principal component of cell walls of all higher plants. It is estimated that 75 billion tons of cellulose are biosynthesised and disappear each year, most of the disappearance being through natural decay. Cellulosic plant materials are used as fuel, lumber, mechanical pulps and textiles. Purified cellulose is currently used to make wood-free paper, cellophane, photographic film, membranes, explosives, textile fibres, water-soluble gums, and organic-solvent-soluble polymers used in lacquers and varnishes.

The principal cellulose derivative is cellulose acetate, which is used to make photographic film, acetate rayon, various thermoplastic products, and lacquers. The world's annual consumption of cellulose acetate is about 750,000 tons. Cellulose acetate products are biodegradable. Recently also the commercial production of lyocell, a cellulosic fibre made from a solvent spinning process, which unlike rayon does not require dry cleaning but is washable and very strong. Lyocell is the first new textile fibre to be introduced in 30 years.

At present cotton is the most important non-wood fibre crop and mainly used for weaving and spinning into cloth. Advances in biotechnology and genetic engineering are now enabling development of cotton cultivars with improved pest resistance, yield, and quality, thereby potentially reducing production costs and better matching cotton characteristics to specific applications. Natural fibres other than cotton occupy various niche markets, such as specialty fabrics, fibre reinforced composites, papers, cordage, and horticultural mulches and mixes.

Heightened environmental concerns are helping jute, hemp, flax, sisal, abaca, coir fibres, and products derived from these fibres to find their way into new markets as well. Especially the use of natural fibres in fibre reinforced composites has seen a tremendous growth in Europe over the recent years (van Dam et al, 2004).

Fatty Acids

Fatty acids, readily available from plant oils, are used to make soaps, lubricants, chemical intermediates such as esters, ethoxylates, and amides.

These three important classes of intermediates are used in the manufacture of surfactants, cosmetics, alkyd resins, polyamides, plasticizers, lubricants and greases, paper, and pharmaceuticals (Ahmed and Morris, 1994). Of the approximately 2.5 million tons of fatty acids produced in 1991, about 1.0 million tons (40 percent) were derived from vegetable and natural oils; the remaining 1.5 million tons were produced from petrochemical sources. Twenty-five percent of all plant-derived fatty acids used in the coatings industry comes from tall oil (a byproduct of kraft paper manufacture). At present surfactants are by far the most important outlet for fatty acids (Table 1). In Europe the majority of raw materials used for surfactants production are derived from tropical oils because of their more suitable chemical structure. Besides oil based surfactants there is also a relatively small market (<5%) for starch derived surfactants.

Other

Terpenes, derived from woody materials, also give rise to various chemicals and products. Crude turpentine, isolated from the pulping industry, may be used to isolate "pine oil" commonly used in cleaning products, alternatively its components may be isolated and chemically transformed to materials such as dipentene, which can be polymerised to prepare tacky polymers and used in chewing gum and food packaging coatings.

Although not widely carried out in Western Europe and North America, a number of Eastern European, Asian and South American countries use carbohydrate containing agricultural residues as a raw material in the chemical industry. For example, hydrolysis of starchy materials to glucose with concomitant severe acid catalyzed degradation can result in oxalic acid, which is used in the leather industry. Alternatively, pentoses, found in bagasse and corncobs, for example, can readily undergo acid catalyzed dehydration to furfural. Furfural is a flexible chemical raw material, which can be used as a solvent itself in several applications or can be used to prepare furfuryl alcohol used in resin materials and tetrahydrofuran, a common organic solvent. A large number of other chemical transformations are possible; however their present commercial status remains unclear.

Carbohydrates remain to be a flexible raw material and as well as "classical" chemical transformations, biotechnological transformations have also been explored. For example lactic acid can be used to prepare, a biodegradable polymer with interesting properties, and has a wide range of potential applications including fibres and packaging materials (Sreenath et al. 2001). Other biotech products include citrates to prepare additive chemicals (dyeing, cleaning, and polymer) and fumaric acid in preserving agents and as a component of unsaturated polyesters.

Specialty chemicals can be made using fermentation and enzymatic processes or directly extracted from plants (or aquatic biomass). It has been shown plants can be altered to produce molecules with functionalities and properties not present in existing compounds (e.g., chiral chemicals). Examples of bio-based specialty chemicals include bioherbicides and biopesticides; bulking and thickening agents for food and pharmaceutical products; flavors and fragrances; nutraceuticals (e.g., antioxidants, noncaloric fat replacements, cholesterol-lowering agents, and salt replacements); chiral chemicals; pharmaceuticals (e.g., Taxol); plant growth promoters; essential amino acids; vitamins; industrial biopolymers such as xanthan gum; and enzymes. At present specialty chemical markets represent a wide range of high-value products. These chemicals generally sell for more than 4 €/kg. Although the worldwide market for these chemicals is smaller than those for bulk and intermediate chemicals, the specialty chemicals market now exceed \$3 billion dollars.

It is anticipated that advances in biotechnologies will have significant impacts on the growth of the specialty chemicals market.

2.4 International Perspectives

In a number of industrialized countries (i.e. USA, UK, the Netherlands) government, business, society and science have been engaged in outlining the contours of future developments in the material and chemical industry (American Chemical Society 1996; Molendijk et al. 2004; National Research Council 2000; Okkerse and van Bekkum 1997; Parris 2004; Sims 2004; UK Foresight programme Chemicals Panel 2000; US Department of Energy, 1998, 1999; Weaver 2000). Most of these foresight exercises are led by the view that there will be an increased demand for chemicals and materials, which will place additional pressure on the use of resources and the environment. Accordingly, the thrust is in finding new technologies and creating novel materials, processes and capabilities to bring this growth in line with the societal demand for sustainability.

The perspectives indicate a shared interest in shifting from a sole dependence on fossil resources to a chemical and material industry founded in the application of plant-based resources, either derived from secondary streams (i.e. waste and recycling) or from primary streams (i.e. dedicated production). The discussion suggests that changing the resource base of the chemical and material industries will induce cleaner processes, safer products and a more effective use of scarce resources. The shift to a bio-based chemical and material industry will alter the technological basis of the industry quite radically. To substantiate the sustainable credentials of new products and processes, further research and actual implementation will indicate what specific technological routes in fact contribute to sustainability. This will be necessary for communication with NGOs, the general public, regulators and policy makers about, for example, CO₂ emissions.

From the perspective of the chemical industry striving for sustainability with sound economic foundations draws the attention to three key areas:

- **Production:** The actual production process has a major environmental impact both on efficient use of energy and resources and on emission and waste production; this is especially so in bulk industries. This links the provision of multi-quality biomass and the industrial production process. Due to the large volumes used, it may have a far-reaching impact on the environment. Cost reduction, due to cheaper raw materials or processes with less extreme conditions, will be an important consideration.
- **Integration:** Implementing a strategy for sustainability requires coordination between different levels of a supply chain, product portfolio and fine-tuning between distributed technological capabilities. Key technologies in conversion, extraction and separation will lay the foundation for further improvement in bulk production and the development of products with well defined functionalities.
This requires an integrated view on resource use and a strategic view on technology development. Linking life sciences, chemistry, energy technology and process engineering is required for taking up such a challenge.
- **Use and re-use:** In terms of specific functionality, life cycle and recycling or safety, the actual performance of end-products importantly defines the contours of a market-oriented strategy for sustainable resource use. Increased revenues by generating also high value products will also be an important consideration. This links production process with product design and defines a new terrain for innovative business enterprises. Communicating the sustainability benefits to consumers or users in (new) end-use market will allow them to make better informed choices.

For developing a sustainable perspective for the chemical industry a combinatorial approach integrating functionality provided by new molecules or materials, improved efficiency and safety of production processes, and use and re-use of materials has to be applied. Integrating criteria like design for functionality or recycling properties of new materials will encourage the search for new sustainable solutions in the chemical industry.

3. Biomass: Technology and Sustainability

The chemical industry undergoes fast and important changes inherent to the turmoil resulting from transitions at the end of an industry's current lifecycle. These changes require new technological, organizational and commercial answers from the industry. Moreover, the business strategy of the chemical industry becomes increasingly dependent on the acceptance and rejection of its activities and its conduct by society and consumers. This paragraph brings forward a perspective on a chemical industry that combines technological innovation with a socially acceptable business strategy.

3.1 Transition to a bio-based industry: sectoral integration in the Netherlands

Products from the chemical, material and power industries have become an integral part of our daily lives and the projected demand for these products will increase. A general concern is the intensive usage of finite resources, in particular fossil resources, and, consequently, the industry is in the midst of reconsidering its current resource use. Two major Dutch companies communicated its transition to the general public: The chemical company DSM advertised its transition process to a specialty company while building an image of sustainability and, in 2002, Shell, the energy company, launched a nation-wide advertisement campaign highlighting the future of natural and renewable resources. In this process, industrial R&D seems to (re)discover the variation of quality and specific functionalities in renewable resources; this offers the opportunity to meet the demand for healthy and environmentally friendly end-products. However, the industry has to contend with both established paths of research and development and its extensive infrastructure in terms of production facilities and equipment. As a result, a transition to a bio-based industry requires the development of new chains and persistent crossing of boundaries between disciplines, departments and sectors.

Innovation in the energy sector is an important driver of technology development in the chemical and material industries. Hence, petrochemistry is a constant factor in industrial development, although the use of biomass or renewable resources comes to the fore anticipating rises in oil prices or directive measures related to international agreements, such as the EU directive 2003/30/EC on the promotion of the use of biofuels or other renewable fuels for transport. There are several political drivers for the enforcement of such directives. The most important include:

- the general accepted treat of global warming by the emission of greenhouse gasses
- the unwanted dependency on oil producing countries
- the recent enlargement of the EU with associated political issues especially related to agriculture
- sustainable development of rural areas and creation of employment

The question is whether an integrated energy sector and petrochemical industry is the right or only venue for a transition to a bio-based industry.

Two non-exclusive scenarios can be distinguished:

1. The energy sector and the petrochemical industry integrate further and the oil price remains the major driving force in business and in innovation.
2. The chemical and materials industry dissociate themselves from the petrochemical sector and seeks new potentials of bio-based industrial processes using renewable resources supplied by the agro-sector, leading to environmentally friendly modes of production and to healthy and sustainable end-products with specific qualities (Coombs 1995).

Most likely vertically integrated companies, including Sabic and Shell, will tend to stick towards the first strategy, while companies not involved in exploration, e.g. Dow, DSM, might tend to follow the second strategy. The sell of the polyolefins division of DSM to Sabic and the acquisition of part of Roche can be seen as an example of this strategy. These scenarios (represented in Fig. 2), that were discussed at a number of occasions in the Netherlands, draw the attention to linking the agro-sector and the food and feed processing industry with the chemicals and materials industry (Klerk de et al. 2002).

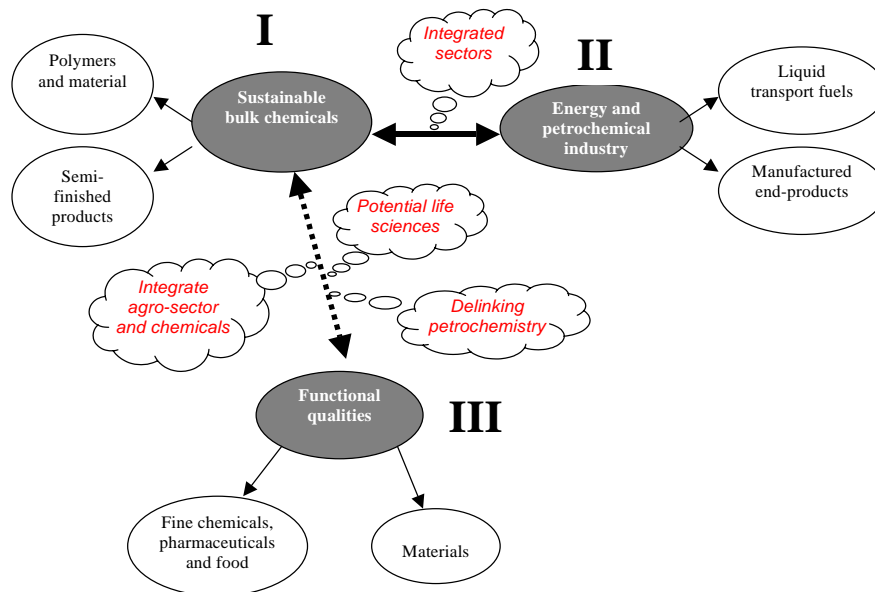


Fig. 2 New synthesis between economic clusters

The Dutch economy still has a strong base in manufacturing, both of food and non-food products. Yet, the agro-sector and the chemicals sector operate remotely and the lack of synergy between these two sectors may hinder progress in developing biorefineries with new manufacturing processes and new products. In the 1980s and 1990s, the agro-sector was involved in a trajectory of so-called „agrification“, i.e. producing industrial crops in rotation with food crops or potatoes, but failed to create ventures with end-users for its resources in the chemical and manufacturing industries (van Roekel and Koster 2000).

Hence, pushing the use of renewable resources without identifying a clear demand, either by industry-based end-users or consumers, appeared to be unproductive and even counterproductive.

Fine-tuning across sectoral boundaries seems to be an important condition for changing current resource use. In the following, we will identify the consequences of this condition for the position of the Dutch agrosector and food industry.

The Dutch agro sector and the food and feed industry are founded not only in primary production of agricultural crops but equally in processing, distributing and transporting primary and secondary flows of agricultural resources. The combination of intensive agricultural production, the transit of commodities in the Rotterdam harbor and an extensive food processing industry is a specific quality of the Dutch economy. Import of resources for the food processing industry, including starch, sugar and vegetable oils, results in a high „biomass intensity“. A related factor is the opportunity to direct secondary flows, side and waste streams, to other industries; without the absorption of these secondary flows, mainly by the feed and alcohol producers, the continuity of the processing industry would be in danger (Rabobank International, 2001). The above sketches a landscape wherein a new synthesis between sectors is possible. This contrasts, however, with the current low-value use of renewable resources, mainly in the feed and power industry. A driver for change in the feed industry might originate in recent scares about the use of slaughter residues and of potentially hazardous fats and oils in feed, bringing these undesired components in the cycle for human consumption. Besides, the European debate on genetically modified crops might result in stricter regulation on the use of these crops in feed and food. Consequently, the composition of feed is affected by public pressures and stricter regulation, which, in combination with the tendency to reduce the intensive livestock industry in the Netherlands, might lead to the disappearance of existing markets for secondary flows. This will place high pressure on food processing industry because secondary or waste streams will become a cost rather than an income generator (Rabobank International, 2001).

The short term question is where the food processing industry and the agrosector can market their secondary resource flows and/or plant-based resources; this is an environmental as well as an economic problem. Therefore, companies, research institutes and government try to address the issue of creating new chances for biomass, which includes finding alternative markets for rest or waste streams. A related question is how to find high-value utilization and application of these renewable resources, in addition to low value energy and bulk products. This will require fine-tuning of the quality, price and quantity of renewable resources with demand in end-user market and functionality requirements of new products. Therefore, we have to turn around the chain and move from demand and functionality to processing and, eventually, to the production or supply of the raw material.

The next section briefly identifies how different social actors perceive healthy and sustainable products and processes, in order to provide a guide for formulating technology agenda's for the chemicals and materials industry.

3.2 Can sustainability drive technology?

One of the more important societal driving forces is the drive for sustainability. Directing innovation and technology development from the perspective on a sustainable, bio-based society is one of the major challenges for the chemicals and materials industries. In response to this widely conceived public concern, companies try to focus their business strategies both on sustainability, including environmental concerns, and on consumer demands for safe products. However, most companies trying to address the three Ps (planet, people, profit) are well aware that profit is always the ultimate driving force.

To develop the technology supporting such an ambition still requires a substantive effort, both in terms of innovative research and in terms of bringing together different disciplines, such as chemistry, biology, energy technology and engineering, and different professional fields, such as design, bulk production of chemicals, and the supply and storage of renewable or plant-based resources. Hence, both from a sustainability and business viewpoint an integral approach to chemical, material, product and energy outlets will need to be addressed in biorefineries creating maximal added value from the selected biomass resources.

A sustainable chemical industry has to strive for a business strategy that integrates social, safety, health and environmental objectives with the technological and economic objectives of its activities. Assembling industry, science and government is one aspect of developing foresight; consulting a wider range of stakeholders, i.e. consumers and citizens, about technology strategies is another pillar. In doing so, interdisciplinary research may be able to contribute to fine-tuning business strategies and technology strategies. Before formulating the contours of such a new perspective, first a selected number of international perspectives on technological change in the materials and chemicals industry will be discussed.

4. The Chemical Industry: Biomass Opportunities – Biorefineries

The earlier paragraphs have shown the scope of chemical products that are currently produced and therefore the targeted product portfolio of biomass based chemical products. It was also shown that drivers for a transition to a bio-based economy lay not only in technological opportunities, but are a complex combination of societal, economic and technological opportunities, challenges and constraints. This paragraph will focus in more detail on the main technological opportunities to transfer biomass, either directly or via chemical intermediates, into chemical products.

4.1 Biomass opportunities

In the realization of a bio-based chemical industry two distinct approaches can be identified. In the first approach, *the value chain approach*, value added compounds in biomass are identified and isolated in different processing and (bio)conversion steps. The remaining biomass is then transformed into a universal substrate from which chemical products can be synthesized. In this approach it is thought that it is technologically and economically beneficial to extract valuable chemicals and polymers from biomass rather than building these compounds from universal building blocks. It can be concluded that the main technological challenges to aid the economic feasibility of this approach lay in the area of biomass refining, separation technology and bioconversion technology. Moreover, a far reaching integration of food, feed and chemical industries is required as well as a major investment in infrastructure.

The second approach, *the integrated process chain approach*, follows the analog of the petrochemical industry. In this scheme a "universal" substrate is first transformed into universal building blocks, based on which chemical products are produced. In this approach it is thought that it is economically and technologically beneficial to build chemicals in highly integrated production facilities. The main technological challenges for this approach lay in the high-efficient transformation of biomass into commonly known building blocks for the petrochemical industry (Tuil van 2002).

The main technologies to produce chemicals from biomass are:

- biomass refining or pretreatment
- thermo-chemical conversion (gasification, pyrolysis, hydro-thermal-upgrading (HTU))
- fermentation and bioconversion
- product separation and upgrading

Five main categories of building blocks can be identified as intermediates for the production of chemical products from biomass:

- Refined biomass, i.e. the biomass in which the valuable components have been made accessible by physical and/or mild thermo-chemical treatment. These components are extracted from the refined biomass. The remaining biomass then undergoes further transformation
- BioSyngas, this gas (mainly CO and H₂) is a multifunctional intermediate for the production of materials, chemicals, transportation fuels, power and/or heat from biomass; it can easily be used in existing industrial infrastructures to substitute the conventional fossil-based fuels and raw materials
- Mixed sugars, these C5 and C6 sugars are further refined substrates for chemical and bioconversion. These substrates mainly originate from side streams in the food industry and potentially from ligno-cellulosic biomass streams
- Pyrolysis oil, this oil is produced in fast and flash pyrolysis processes and can be used for indirect cofiring for power production in conventional power plants, for direct decentral heating purposes, and potentially as high energy density intermediate (important in case of long distance transportation) bio-based intermediate for the final production of chemicals and/or transportation fuels
- Biocrude, this material refers to a fossil oil like mixture of hydrocarbons with low oxygen content. Biocrude results from severe hydro-thermal-upgrading (HTU) of (relatively wet) biomass and potentially can, like its petroleum analog, be used for the production of materials, chemicals, transportation fuels, power and/or heat

4.2 Biorefinery concept

A biorefinery is a facility that integrates biomass conversion processes and equipment to co-produce fuels, power, and chemicals from diverse biomass sources. The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum. Industrial biorefineries have been identified as the most promising routes to the creation of a bio-based economy (Realf and Abbas 2004). Partial biorefineries already exist in some agricultural and forest products facilities (e.g. pulp mills, corn wet milling, starch and sugar beet refining).

These systems can be improved through better utilization of residues and optimization of total added value creation; new biorefineries can be enhanced by applying the lessons learned from existing facilities to comparable situations.

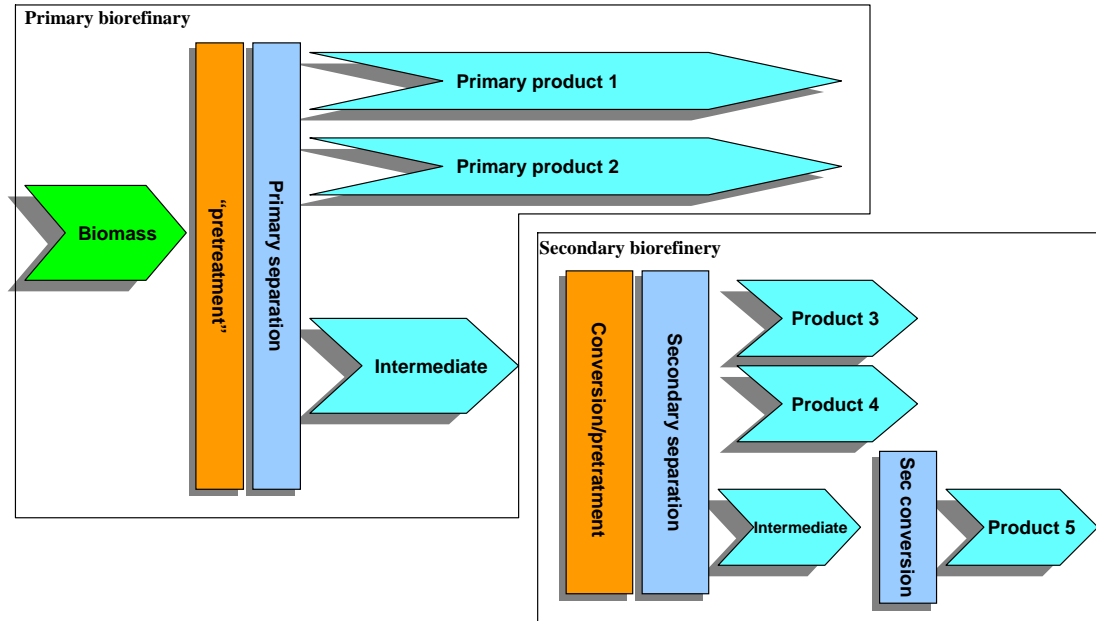


Fig. 3 Schematic overview general integrated biorefinery process

By producing multiple products, a biorefinery can take advantage of the natural complexity and differences in biomass components and intermediates and therefore maximize the value derived from the biomass feedstock. A biorefinery might, for example, produce one or several low-volume, but high-value, chemical products and a low-value, but high-volume, platform chemical and/or liquid transportation fuel; while generating power and heat for its own use, and likely enough for sale of electricity. The high-value products enhance profitability, the high-volume chemicals and/or transportation fuels help to meet European energy needs and CO₂ emission reduction goals; whereas the power and/or heat both reduces overall production costs and greenhouse gas emissions.

4.3 Biomass availability

The Netherlands is a small country where land is scarce. Though the options for primary crop production are limited, the biomass flux of utilized biomass (organic material) is very high (partially imported). An estimated 42 million dry tons of biomass (13 ton/ha) (van Dam et al., in preparation) are used and produced in different sectors of the economy (compare to a biomass flux some 5 tonnes for Germany). As markets change this high turnover of biomass does generate many opportunities for reallocating streams towards biorefinery feedstocks.

One of the largest biomass streams is produced in the agri-industrial complex. A large part of these streams can be considered byproducts. Some 10 million tonnes (as received) of byproducts are currently mostly (90%) used for animal feed (Vis 2002; Elbersen et al. 2002). These byproducts vary from slaughterhouse wastes to discarded frying oil, potato peels, etc. As traditional markets change (diminish) and markets for biobased energy and products increase, a large part of these streams can become partially available for biorefinery. This change in market demand for feed is already apparent in the decline in livestock (from 4.6 in 1995 to 3.6 million in 2003), and pigs (14.5 million in 1995 to 10.7 million in 2003), which leads to a smaller feed demand.

Another estimate has been made of the potentially available (ligno)cellulose biomass feedstocks in The Netherlands that could be used for ethanol production (de Jong et al., 2003). The total amount of these technically suitable feedstocks is approx. 12 Million tons (dry weight) per year (about 220 PJ_{th}/a), excluding import and biomass energy crops. However, the potential feedstocks are highly variable and include a range of agro-industrial residues, agricultural wastes, forestry residues and house hold organic wastes, etc.

As said the domestic (primary) biomass energy crop potential is limited with some 2 million ha of agricultural land of which less than 1 million ha is used arable land. It is hard to estimate the potential for biomass energy crops as competing demands for land are uncertain. Estimates range from 0 to a maximum of 3 million tonnes (300.000 ha at 10 ton dry weight/ha.a, 18 GJ/ton dry weight) equivalent to 50 PJ_{th}/a (Minnesma 2003). In the short term arable agriculture could be an important source of biorefinery feedstocks with more than 1 million tonnes of crop field residues available.

The maximum total Dutch biomass availability (organic residues and crops) will therefore amount to 300 PJ_{th}/a (some 15 million tonnes dry weight). Taking the longer-term (2040) policy ambitions into account, requiring a biomass substitution volume of about 600 – 1000 PJ_{th}/a, it can be concluded that The Netherlands will have to import at least half if not more of its long-term biomass requirements.

The potentially available feedstocks for biorefinery in The Netherlands are highly variable and most streams are dispersed over the country. Though many streams currently have other applications the potential is more than 15 million dry tonnes of biomass. Large scale biorefinery systems will have to use a variety of feedstocks in order to secure feedstock availability ('multi-feedstock plant'). Furthermore, the option to import biomass over longer distances should be available.

For medium term development (<10 years) a focus on feedstocks which have the desirable characteristics (for example homogeneous streams low in lignin and/or low in ash) are desirable. For the longer term (> 10 years), as the production scale increases, the feedstock range should be broadened with additional residues and (woody) energy crops (e.g. willow).

The worldwide average net available biomass potential for non-feed and non-material purposes is expected to amount 200 – 700 EJ_{th}/a (maximally: 1100 EJ_{th}/a) in 2050 (Lysen 2000). Worldwide, enough biomass will be available to fulfil the needs. Because other countries will claim the same biomass, the market price will be internationally settled. Timely participation in the developing international market is a requirement to become an important global player.

4.4 Primary refinery

Deriving a raw material stream with desired specifications (i.e. amount of ash, fermentable sugars, lignin) while simultaneous extract valuable components from the heterogeneous biomass streams is one of the major biorefinery R&D issues. The following five main R&D areas are identified which need to be addressed before an efficient biomass pre-treatment chain can be established:

- Characterization and standardization of raw materials and products.
- Development of a cost-effective infrastructure for production, collection, characterization, storage, identity preservation, pre-processing activities, import and transportation of feedstocks for bio-based products and bioenergy applications.
- Development of economically viable pre-treatment processes for commercial use of a range of current and new bio-based feedstocks.

Biorefineries could potentially use complex processing strategies to efficiently produce a diverse and flexible mix of conventional products, fuels, electricity, heat, chemicals, and material products from all available, environmentally appropriate biomass feedstocks. To achieve economically viable biorefineries it is important that:

- Separation and fractionation technologies for high-throughput systems are developed that produce value-added products and no waste streams.
- Generic solutions have to be identified that will apply across multiple feedstocks while simultaneously achieving a zero-waste production system with either direct use or recycling of all components.

4.5 Secondary thermo-chemical refinery

Thermo-chemical based refinery processes are generally consisting of the following interconnected unit operations: pre-treatment (i.e. drying, size reduction), feeding, conversion (gasification, pyrolysis, HTU), product clean-up and conditioning, and product end-use. In this subparagraph only gasification-related aspects are discussed, because it is expected that gasification will be the key technology in (secondary) thermo-chemical refinery processes.

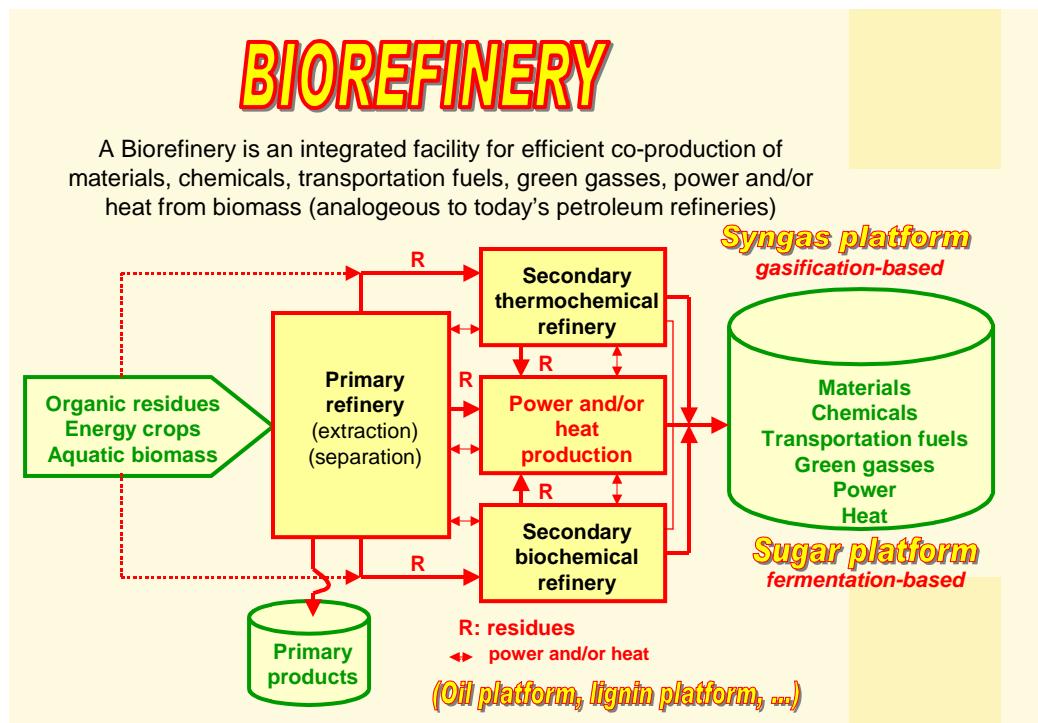


Fig. 4 Detailed overview integrated biorefinery process

Atmospheric air-blown gasification processes, based on fixed bed, (circulating) fluidised bed, or indirect dual reactor technology, are commercially available for product gas (mainly CO, H₂, N₂, impurities) production. After gas clean-up this – so called – fuel gas potentially can be used for heat, power or CHP production in a variety of prime movers. At the moment only direct heat production by coupling of these technologies to conventional (natural gas or diesel fired) furnaces, and power production by indirect cofiring in coal-fired power plants, is technically and economically feasible.

The market implementation of fully integrated gasification-based systems for stand-alone power or CHP production is delayed by the high power/CHP production costs, mainly caused by the relatively high investment costs of these new and emerging technologies, and insufficient financial support from the government.

Oxygen-blown gasification processes, especially applicable for the production of BioSyngas (mainly CO and H₂), based on both bubbling fluidised bed and entrained-flow technology, are technically not available yet for biomass applications. Within the framework of the EU Chrisgas-project, TPS et al., are now trying to modify the air-blown pressurized Varnamo gasification plant (Sweden) for oxygen-blown operation.

Within the 6th Framework Programme of the EU, ECN et al. are currently (October 2004) preparing a large STREP proposal concerning the modification of existing coal-based slagging oxygen-blown entrained-flow based gasification technology for 100% biomass use. Main research areas are: biomass feeding, gasification/slag behaviour, product gas cooling, and the commercial applicability of produced solid waste streams. The final goal is to design, built and operate several MW_{th} pilot plants within 4 years time, so that large commercial implementation can become feasible around 2010. The gasification processes mentioned all require size reduced and relatively dry (about 15-20% moisture maximally) biomass fuels. "Wet" biomass fuels require severe drying before it can be used.

Alternatively these fuels potentially can be converted by means of sub-/supercritical gasification processes (or the fermentative processes, see 4.6). Supercritical biomass gasification is performed at conditions above the critical point of water (374°C, 221 bar), mostly in a temperature range of 500-700°C. At these conditions a H₂-rich product gas is being produced. At subcritical conditions (temperature range of about 350-400°C) a methane-rich gas will be produced. At this condition for full carbon conversion very low dry matter concentrations and a catalyst is required. In spite of the fact that bench/pilot facilities are available – FZK (D): 100 l/hr (since: 2003), University of Twente (NL): 5-30 l/hr (since: 1998) – the ECN opinion is that some years of lab-scale PHD-work will be required, before this technology potentially can be implemented into the market. The technology is expected to be developed for "Green natural gas" (SNG) production; for the production of hydrogen, ECN has the opinion that this technology will not become financially competitive on the longer term. Some main research items are: feeding, heat exchange and catalyst behavior.

Within the framework of the biorefinery concept, two gasification-based pathways can be distinguished:

- Application of the biorefinery concept to increase the financial yield of "conventional" gasification processes. By the separation of highly added-value components from raw biomass fuels before conversion, or afterwards from the raw "products" in the product gas clean-up/conditioning, the overall plant economics could be increased, simplifying market implementation (see also Fig. 4).
- Development of high-efficient advanced gasification-based thermo-chemical secondary biorefining processes. By the development of advanced catalytic supported staged or subcritical gasification processes it is expected that a variety of "products" could be separated from biomass in such a way that the overall process will be market competitive, without the necessity of substantial governmental support.

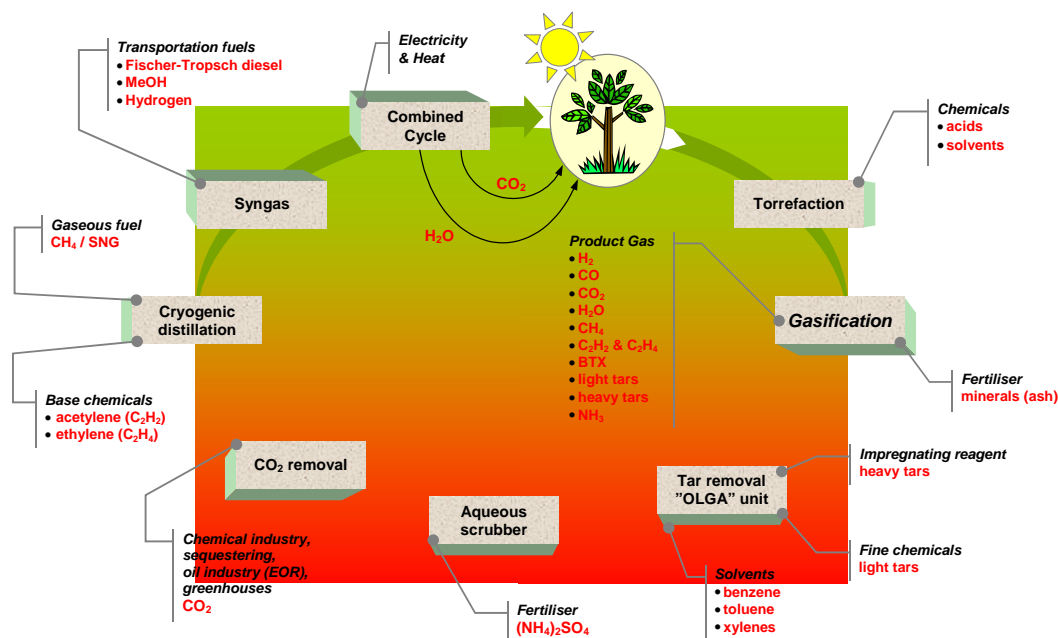


Fig. 4 Thermo-chemical biorefinery concept of ECN to increase the financial yield of “conventional” gasification processes (Boerrigter et al. 2004)

4.6 Secondary biochemical refinery – fermentative processes

This paragraph focuses on fermentation as the main form of bioconversion. At the moment a large number of chemicals are produced by fermentation. These products range from bulk chemicals as ethanol (for food and fuel purposes) (Reith et al. 2002) and lactic acid (as food ingredient or as monomer of polylactic acid) (Datta et al. 1995), via compounds as amino acids, gluconic acid and citric acid, to high value products as antibiotics.

The efficient conversion of sugars into ethanol and lactate by fermentation increases the interest in fermentation technology as a means for production of bulk chemicals. There are several advantages of fermentation over conventional chemical reactions.

- Fermentation processes are usually one-step synthesis which could reduce investment costs
- Microbial biosynthesis offers a control over chemical reactions that is unchallenged by state-of-the-art chemical synthesis resulting in highly functional compounds

However, fermentation has at the moment several disadvantages which have to be solved before fermentation will be able to compete with conventional chemical reactions:

- The costs of fermentation processes for bulk processes are higher than those for the corresponding chemical process
- The natural product spectrum of microorganisms is limited
- In fermentation processes several side streams are formed which can be coped with at small scale but will cause a severe burden at bulk scale

4.6.1 Feedstocks

At the moment most feedstocks used for fermentation processes are based on sugar beet, sugar cane and corn. To reduce costs of the feedstock other substrates have to be used. Several alternative feedstocks are being considered as fruit waste, wood, straw, agricultural waste streams, dung, oils and fatty acids, etc.

Among these the lignocellulosic materials are the most abundant polysaccharide containing biomass available in the world and are therefore an extensively studied feedstock for fermentation processes. For almost all micro-organisms this lignocellulosic material has to be hydrolyzed into its component saccharides by mechanical pretreatment, followed by employing acid or base, heat treatment, organic solvents or wet-oxidation to open the matrix most times followed by enzymatic hydrolysis of the cellulose. The costs of the hydrolytic enzymes are the major expenses in the feedstock pretreatment and hydrolysis.

Hydrolysates from lignocellulosic materials contain beside C6-sugars as glucose also C5-sugars as xylose and inhibitors. The relative amount depends on the type of feedstock and the process used. Bakers' yeast, used in the production of ethanol, is not able to use these C5-sugars. It has been calculated that for a competitive process also these C5-sugars should be converted into ethanol. This probably also holds for other future processes.

4.6.2 Product spectrum

Micro-organisms are able to produce an extreme wide variety of chemical compounds. However, most of these compounds are only intermediates in the overall metabolism and will not be produced in a significant amount. Furthermore, many of the platform chemicals used in the chemical industry are not produced by natural micro-organisms. The new fermentation technology has to interface directly with existing processes and installations in classical chemistry to reduce investment costs, indicating that the biochemical pathways of the micro-organisms have to be modified to be able to produce the existing platform chemicals. Several physiological aspects (yield, productivity, toxicity of product, use of GMOs, byproduct formation etc) have to be taken into account to be able to do this successfully. This shows that the production of non-natural compounds by micro-organisms can be a complex task. However, some successful examples of the modification of metabolic pathways are the production of 1,3 propanediol for the production of Sorona by DuPont, the synthesis of muconic acid as a precursor for adipic acid and the optimization of succinic acid production (Biebl et al. 1999; Chotani et al. 2000; Zeikus et al. 1999).

4.6.3 Side streams and recycling

Fermentation processes are usually considered as 'clean' processes. However, during fermentation some side-streams are created which could form a severe environmental burden on bulk scale. Some examples:

- During ethanol production by bakers' yeast glycerol and fusel oils are produced.
- Lactic acid is removed from the fermentation broth by complexing with calcium ions resulting in the formation of insoluble calcium lactate. Finally this results in the formation of equimolar amounts of gypsum.
- In all fermentations microbial biomass is formed. This can be a considerable fraction. For example in the experimental production of polyhydroxyalkanoates (biopolymers) 20-50% of the product is biomass.

In the case of gypsum production, which could also form a problem in the synthesis of other organic acids, a lot of research has been put in the development of other downstream-processing processes, such as membrane electrodialysis. In the case of microbial biomass formation another solution has to be sought in which the high-added-value components of the microbial biomass such as pigments, vitamins and antioxidants are extracted and the remaining material could then be recycled as feedstock in the fermentation process.

5. Conclusions, Outlook and Perspectives

The aim of this paragraph is to conclude on the former paragraphs by presenting an agenda for further activities in order to facilitate the transition towards the production of chemicals and chemical products from biomass. We believe that if these agendas are addressed the sustainable production of chemicals from biomass will become a realistic future option.

5.1 Biomass - sustainability

A transition towards an increased use of biomass originates from its possible contribution to a sustainable production of energy, fuels, chemicals and materials. Moreover, a number of chemicals can be more easily or energy efficiently produced from biomass than from other feedstock. Many of these products can be directly extracted from the biomass.

The importance of biomass use towards the sustainability of the production of chemicals is directly linked to the scale of production. Moreover, it is often questioned whether the use of biomass for energy, fuels and chemicals can form a symbiosis with the use of the same biomass for the production of food, feed and materials like paper and wood. Also mentioned is the uncertainty of the implication of a change in the main feedstock for energy and fuels industry on the chemical industry.

What will be the main feedstock for energy and fuels in 50 years time; water, sunlight, natural gas or biomass? Are the conversion technologies mentioned in this study elegant ways of waste disposal in the food, feed and cellulose/paper industry? Is biomass mainly of interest for the extraction of valuable chemicals? What will be the impact of a biotechnological revolution on the opportunities and pitfalls of biomass?

Some of these questions have been touched upon in this paper. It is however suggested that further foresighting on the role of biomass for chemicals for the Dutch situation will be done in the form of scenario evaluation. The result of this evaluation will make it possible to choose feedstock/conversion technology combinations that maximize the potential of biomass use for chemicals and chemical products.

5.2 Biomass refining and pre-treatment

A range of standards is needed to verify performance in the industry and to help improve marketability. These include standards for environmental quality of feedstocks and conversion technologies, and accreditation and standards for the energy content and quality of feedstocks and products. Much of the developed technology and products have not been proven under "real world" conditions and/or faces significant certification challenges. These certification challenges are often the result of systems that set standards based on the physical characteristics of petroleum products, rather than on the performance of the end product.

Improved practices in agriculture, silviculture, and aquaculture can play a significant role in increasing yields while reducing required inputs. To achieve the great increases in biomass feedstock availability many issues must be resolved in harvesting, collection, storage, import and transport.

Current methods result in low densities of desired components, high transportation costs, and potential storage stability issues. Pre-processing might be done "on the farm" or even during harvesting or transportation "en route" to densify, dry, and perhaps initially separate biomass components.

New transportation schemes might include pumping a fluid slurry, torrefication, pyrolysis or "pelletizing" biomass locally. All of these advances must be made while maintaining biodiversity and ensuring the safety and sustainability of the technologies utilized.

Most biomass is solid, requiring improved material handling systems at the front end of conversion operations. Breakthroughs in fractionation and separation technology will be required to produce higher value-added products, to reduce processing costs, waste, and environmental impact.

5.3 Conversion technology

Next to already known conventional thermal, chemical and bioconversion technologies this report has shown that the potential in conversion technology is enormous, partly as a result of the ever increasing knowledge on thermo-chemical and biotechnological pathways for the conversion of biomass into chemical products. It is suggested to focus research efforts on the following areas:

- Optimization of thermo-chemical conversion technologies: This paper showed that various technologies are proposed for the thermo-chemical conversion of biomass. Further improvements lay in 1.) The optimization of the efficiency and cost reduction of currently employed conventional technologies and 2.) The development of new advanced technologies, such as catalytic supported staged or subcritical gasification processes.
- (Bio)catalyst development and bioreactor engineering: Metabolic pathway engineering allows for the syntheses of very specific catalysts (both whole cell and enzymes) for the transformation of refined biomass (mainly mixed sugars, fatty acids and syngas) into a variety of chemical intermediates and chemical products. This will lead to the controlled, safe and efficient production of new and existing chemicals and polymers. Important issues for the efficient use of biocatalysts include immobilization, reactor kinetics and design, and separation of the chemical product from the reaction mixture. Like in the pre-treatment of biomass, separation technology also plays an important role in an efficient and cost effective biocatalytic production process.

5.4 Chemicals and Materials Design

The approaches presented in this paragraph to the production of chemicals from biomass are resource based forward integrated approaches. Also a design approach can be suggested in which a backward integrated chemical industry designs chemicals and production methods that fit the application of the chemical product. It is thought that while the resource based approach fits current (petro)chemical business and production models, the design approach will lead to a real transition in the area of the production and design of chemicals and materials. This backward integrated approach will be at first applicable in specialty chemical markets but there are also long term opportunities in bulk chemical markets.

It is thought that with the envisioned development in advanced thermo-chemical and bioconversion technologies the role of biomass as well as a biomimetic approach into the design of chemicals and materials may add to a sustainable production, use and reuse or disposal of chemicals and materials. It is therefore suggested to further examine the role that chemicals and materials design can have on the sustainable use of biomass as well as biomass based resources.

5.5 Dutch Energy Research Strategy (“EOS”)

In The Netherlands, the Ministry of Economic Affairs has defined a national subsidy programme “Energie OnderzoeksStrategie (EOS)” for co-financing long-term (> 10 year) technology developments that support the transition process to a more sustainable society. In this programme (2004 – 2008) an annual subsidy budget of 35 M€ is available for technology development trajectories in some pre-defined areas. Biomass-based technology development in the fields of direct/indirect cofiring in conventional power plants, gasification and biorefineries are selected for co-financing. It is expected that for biorefinery technology development about 10 M€ subsidy will be available for project co-funding for the next 4 years.

The Energy research Centre of the Netherlands (ECN) – Biomass Department, together with Agrotechnology and Food Innovations B.V. (A&F), Wageningen University and Research centre (WUR), University of Twente (UT), Utrecht University (UU), and Groningen University (RUG), have defined an integral biorefinery-based R&D-programme for the coming 4 years. Within this programme joint projects will be defined, based on a common vision, and submitted for co-funding. Research items that will be addressed are: integral chain analysis and scenario studies to identify platform chemicals and provide the framework for the technological developments; primary refining processes, including pre-treatment; secondary thermo-chemical and biological refining processes, including product separation and upgrading, and some site-specific case studies to encourage real market implementation.

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