Biomass for the Dutch Chemical Industry

Opportunities for agriculture

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Colophon

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1 Introduction

1.1 Motivation

The government vision on the Biobased Economy was published on October 8th 2007. One of the conclusions of this vision is that, for the Netherlands, cooperation between the chemical industry and the agrifood sector has a large potential for both economic opportunities and sustainable development.
The study '*Biobased Economy: state-of-the-art assessment*' (BO-03-07-02) performed by WUR/LEI and WUR/A&F in 2007 also concludes that there is a good economic potential for the development of a biobased economy in the Netherlands. This study concludes that large opportunities lie in the field of the use of biomass to produce building blocks for the chemical industry.
Following this last study, the Ministry of Agriculture, Nature and Food Quality (Ministerie van LNV) has asked WUR/A&F to make an overview of the size and structure of the Dutch chemical industry and to address the potential uses of biomass within this industry. This study was financed by the theme 'concurrentiekracht', of the policy support research cluster EPA (BO-03-04).

1.2 Aspects addressed

This report addresses more specifically the structure and size and economic value of the Dutch chemical industry, also in a European perspective, and briefly describes the raw material streams involved. It gives a general picture of the technological possibilities of biomass based feedstocks to be incorporated in the current petrochemical industry and requirements needed to enable this.
Main focus will be on the *organic* chemical industry, since biomass has most potential there.

2 The Dutch chemical industry

2.1 Background: From crude oil to petrochemicals

Synthetic organic materials are nowadays predominantly produced from fossil resources. Bio-based raw materials are used to a relatively small extent (less than 10%). Oil products are by far the most important feedstock for chemicals for non-energy purposes, accounting for almost 95% of the total input in OECD countries. Natural gas follows in importance (< 5%) while coal plays a marginal role (< 0.5%).
Crude oil refineries separate the oil into several fractions. Most of these, such as the LPG, gasoline and kerosene fractions, are used as combustion and transportation fuels, *i.e.* for the creation of energy. The so-called naphtha fraction, on the other hand, is converted by steam crackers into only six base chemicals or 'platform chemicals' that contain two, three, four, six, seven and eight carbon atoms, respectively: ethylene, propylene, butadiene, and the aromatics benzene, toluene and xylenes (BTX). These six compounds are then used as a feedstock for the production of an array of bulk chemicals.
Natural gas is used to produce synthesis gas (carbon monoxide and hydrogen gas). Carbon monoxide is required as raw material for chemicals such as acetic acid and methanol. Hydrogen gas is reacted with nitrogen gas to produce ammonia.

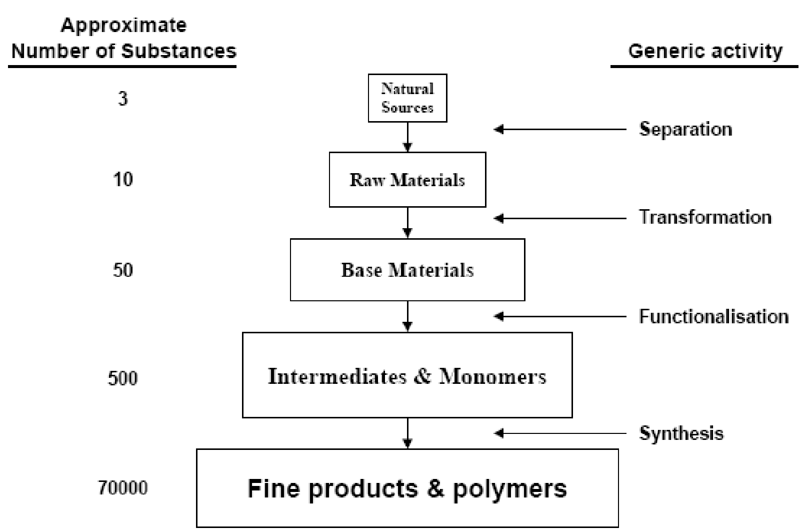


Figure 2.1. Structure of industrial organic chemistry.

The hydrocarbon processing industry thus produces about ten base chemicals: six platform chemicals from crude oil and four natural gas derived base chemicals (carbon monoxide, hydrogen, methanol and ammonia). These are the basic building blocks for the basic petrochemical industry, which produces a wide variety of commodity chemicals. These commodity or bulk chemicals, in turn, are used for an even wider array of fine chemicals and polymers (*Figure 2.1*). Crude oil and natural gas thus form the feedstock of a wide range of products like plastics, rubbers, fibres, resins, paints, glues, additives, etc., which form an important part of everyday life.

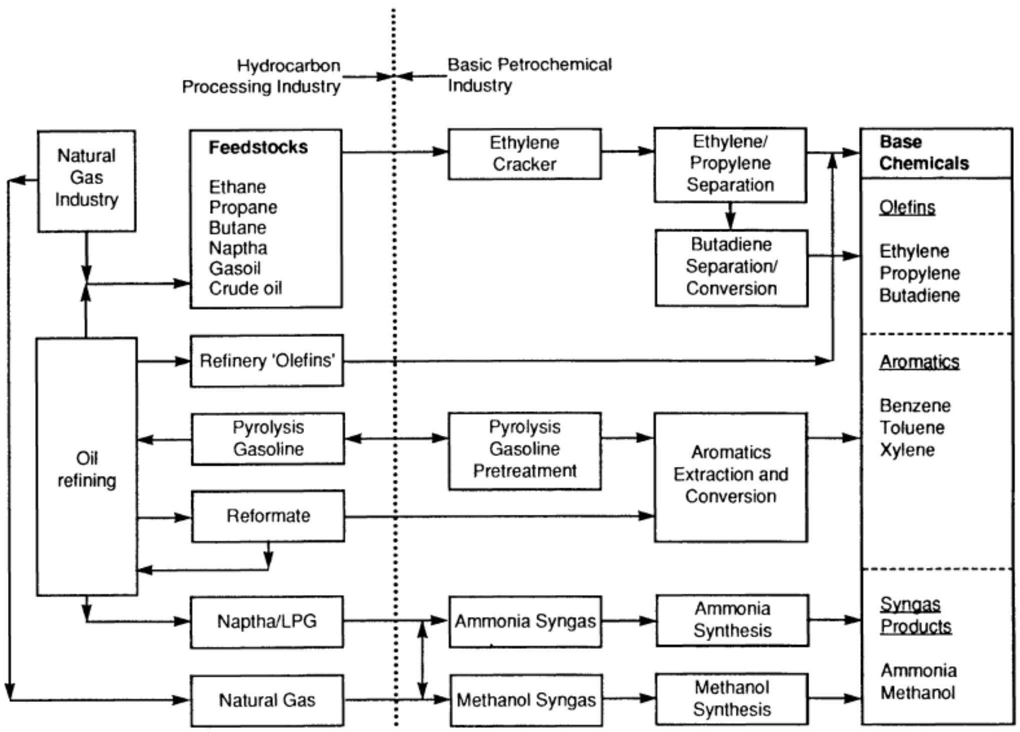


Figure 2.2. Interface between petrochemical and hydrocarbon industries [EC, 1993].

The interface between oil refineries and natural gas plants on the one hand and the basic petrochemical industry on the other is shown in *Figure 2.2*. An overview of base and bulk chemicals, and polymers derived there from is depicted in *Figure 2.3*.
The next sections will briefly describe on what scale this petrochemical industry operates in various geographical regions and what its economic value is.

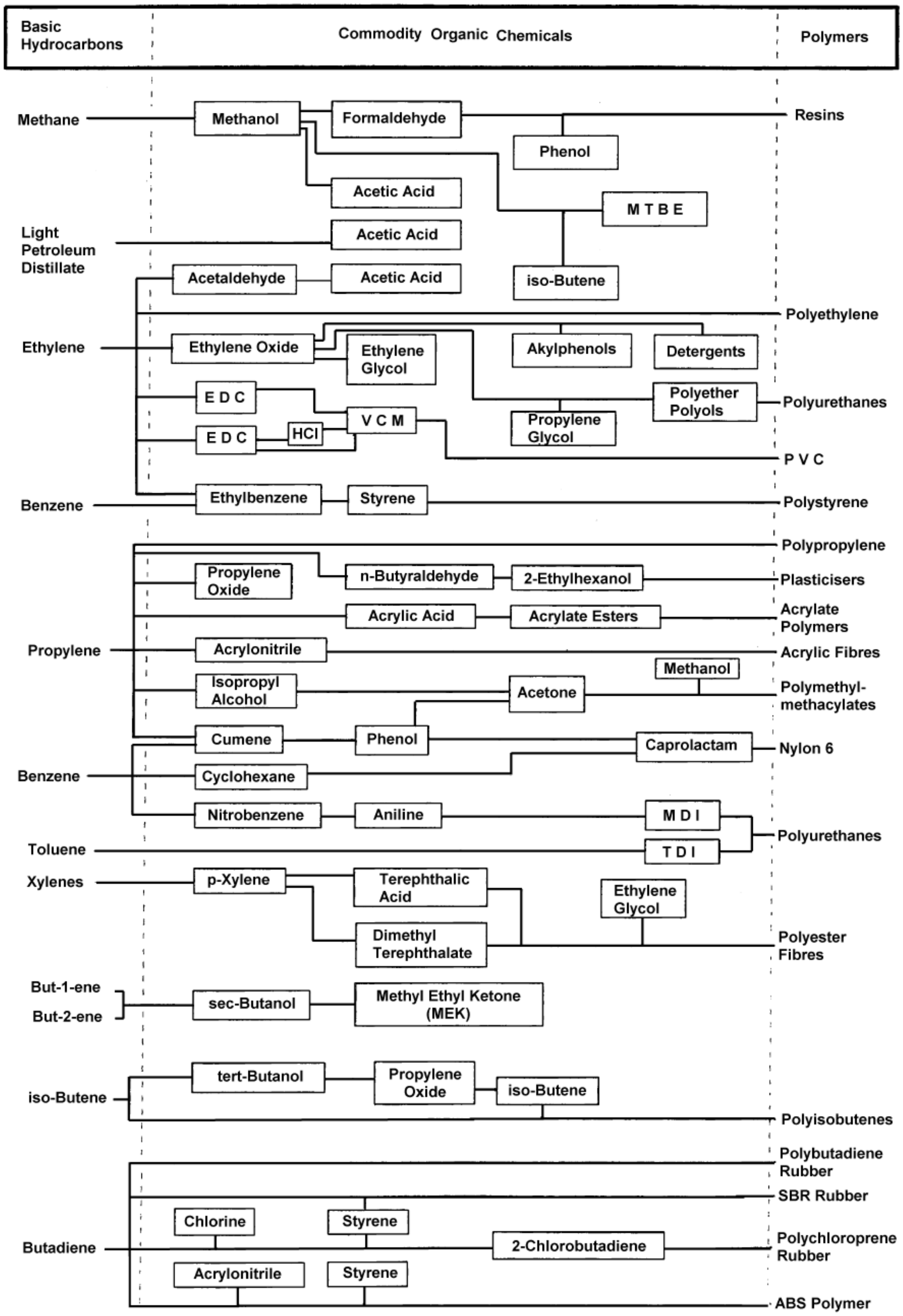


Figure 2.3. Pathways in the organic chemical industry [EC, 1992].

2.2 Size and structure of the European chemical industry

The energy and chemical industries are one of Europe's largest and most competitive industries. More specifically, the chemical industry is Europe's third largest manufacturing industry. It employs 1.7 million people directly and up to 3 million jobs are dependent on it. In addition to several leading global (petro-)chemical companies, this industry also comprises around 36,000 Small- and Medium-sized Enterprises (SMEs). The SMEs represent 96% of the total number of enterprises and account for 28% of the production activities.

Compared to other industrial sectors, the importance of the chemical and energy-related industries is quite likely to grow because the production and demand for *e.g.* transportation fuels, bulk chemicals and fine chemicals/pharmaceuticals outpaces that of most other bulk materials. This is illustrated in *Figure 2.4*, where a comparison is made between the worldwide production of a typical bulk chemical, namely polymers, and crude steel for the period 1950-2002.

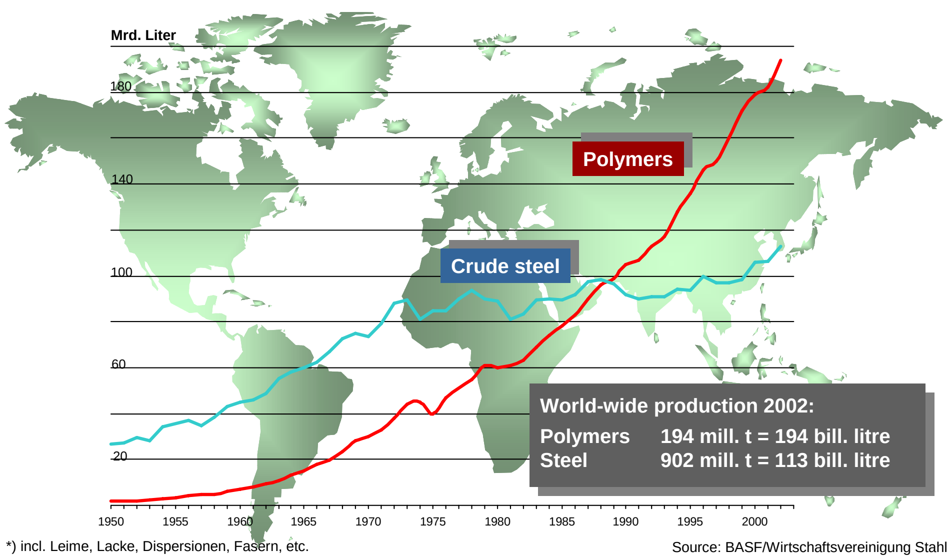


Figure 2.4. Worldwide production of polymers and crude steel in the period 1950 to 2002 expressed in volume terms; 1 kg polymers = 1 L and 8 kg crude steel = 1 L).
Whereas in 2000 the world production of base chemicals (mostly used for the production of a large variety of polymeric materials) was about 200 million tonnes/annum, in 2006 this was already 300 million tonnes.

The chemical and energy-related industries are still very much dependent on crude oil, natural gas and coal. For example, in 2005, the annual imports of crude oil into the European Union (EU25) equaled 4.1 billion barrels (1 bbl = 159 liters) [EC, 2008], which

is 560 megatons (Mt). Most imports came from Russia (30%), Norway (17%), Saudi Arabia (11%) and Libya (9%). About 15% of oil imports was used as chemical feedstock (84.2 M ton of oil equivalents [Mtoe]) for various industrial chemical processes. An additional 82.1 Mtoe was used as energy source for high-temperature and high-pressure processes in these chemical industries. Adding up the energy use as feedstock and for process energy, the EU chemical industry is by far the most energy intensive industrial sector. In addition to this strong dependence on foreign oil imports, the chemical industry is also a major producer of greenhouse gases. According to the Organization for Economic Co-operation and Development (OECD) the total direct emissions of CO_2 from the chemical sector as a whole are in the range of 1 Gt (*i.e.* 1 Gigatons = 10^9 tons) or 4% of the global CO_2 emissions [OECD, 2001]. Needless to say that saving fossil-based resources in the chemical and energy-related industries would not only avoid the impact of global warming, it would also significantly reduce Europe's dependence on foreign crude oil imports.
In 2006, about 172 Mt of CO_2 were emitted in the Netherlands [Emissieregistratie, 2008]. The share of the chemical industry (excluding refineries) was about 10% (ca. 16 Mt). Refineries in the Netherlands emitted more than 11 Mt of CO_2 in 2006.

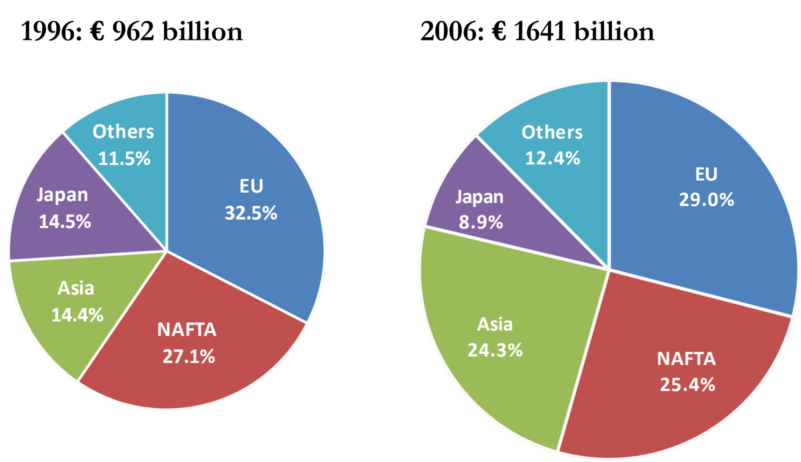


Figure 2.5. World chemicals sales 1996 and 2006 [CEFIC, 2007].

Put into a global perspective, the European chemical industry traditionally has been leading and still is. As shown in *Figure 2.5*, in 1996, the EU was selling 32.5% of global chemicals, with the NAFTA (U.S., Canada and Mexico) second at 27.1%. Japan and Asia-minus Japan each produced about 14%. In 2006, the EU share was still highest at 29%, although Asia (particularly India and China) is showing a rapid increase. The chemical sector supplies virtually all other sectors of European industry, and chemicals are an important part of the

broader industrial value chain. To illustrate this: chemical products account for nearly one third of the material costs in the manufacturing of an automobile.
Although on a relative scale the European chemical industry is showing decline compared to Asia, on an absolute base it is still showing growth.

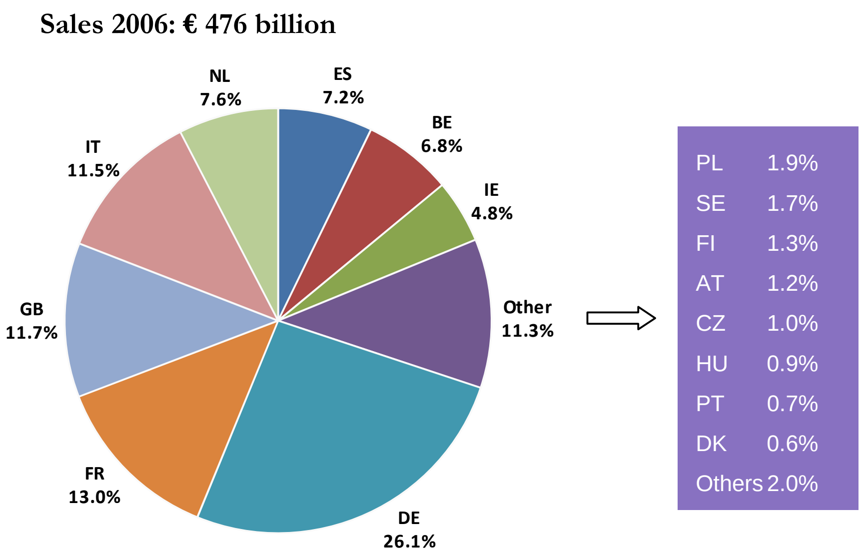
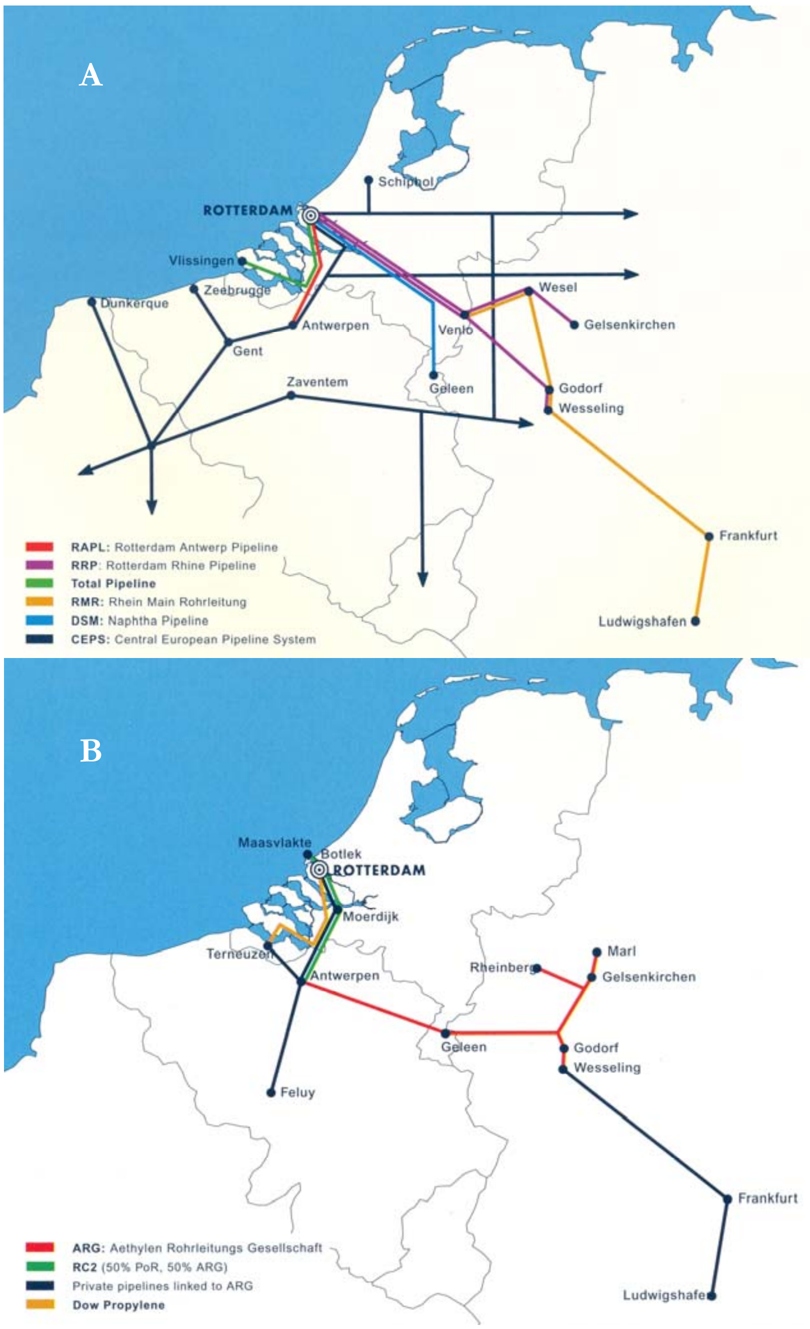


Figure 2.6. Geographic breakdown of EU chemical industry sales [CEFIC, 2007].

2.3 Size and structure of the Dutch chemical industry

Whereas the European chemical industry is large, seen from a global perspective, the same holds for the Dutch chemical industry in a European perspective. Dutch chemicals sales in 2006 was 36 billion Euros, 7.6% of EU sales (*Figure 2.6*).
In the Netherlands, many favourable conditions exist for the chemical industry: availability of raw materials such as salt and natural gas ('aardgas'), large harbours for the supply of raw materials, and a huge transportation network to a densely populated European hinterland with a high standard of living and a huge chemical industry. This all has led to the creation of several large, integrated chemical complexes in the Netherlands and its immediate surroundings. Besides all this 'hardware', the Dutch chemical R&D and chemical education are generally agreed to be of world class quality.
The Netherlands and Belgium account for almost 15% of European chemicals sales [CEFIC, 2007]. The triangle of ports Antwerp–Terneuzen–Rotterdam has the highest density of chemical and energy-related companies worldwide (so far only rivaled by the area Houston–Baton Rouge in the U.S), making the Netherlands a big exporter and key

player in the production of transportation fuels, bulk chemicals as well as fine chemicals and pharmaceuticals.
The huge concentration of chemical activities in this area is also apparent from *Figures 2.7a–c*, which show the important pipeline transportation network for crude oil, naphtha, primary base chemicals (ethylene and propylene) and industrial gases between the different petrochemical complexes.



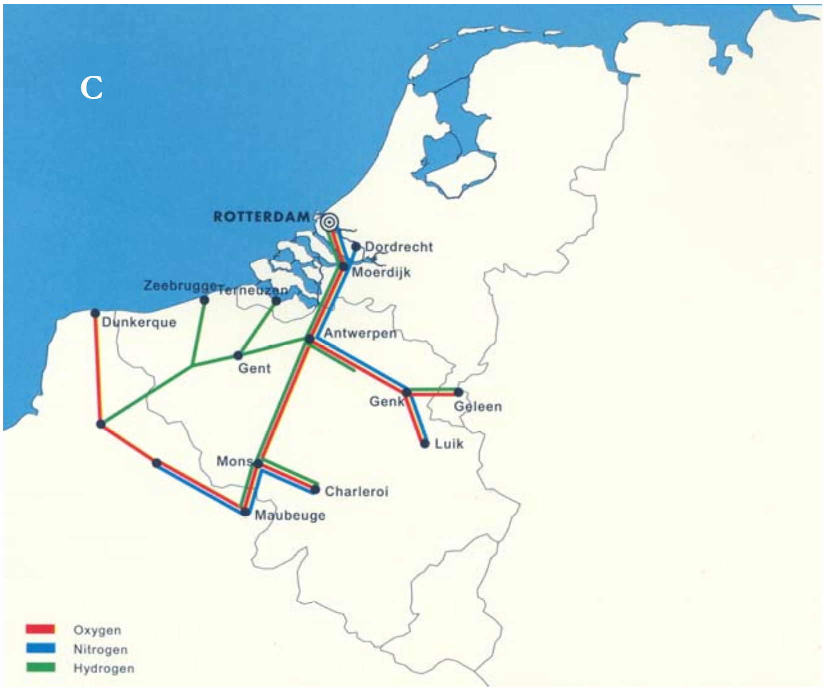


Figure 2.7. Network of pipelines relevant for the Dutch petrochemicals industry. A: crude oil and mineral oil products; B: ethylene and propylene; C: industrial gases [Port of Rotterdam, 2004].

The turnover of the Dutch chemical industry increased significantly over the past years, leading to a turnover of 46 billion Euros in 2006, which is 13% more than in 2005. The Dutch chemical industry generates over 2.3% of the Dutch Gross National Product (GNP) in its direct activities [VNCI, 2006]. More than 100,000 FTEs are working in the chemical (petroleum, chemical, rubber and synthetics) sector [CBS, 2007].
About three quarters of the chemicals produced in the Netherlands are exported; 82% of export goes to countries within Europe. In 2006, total value of exports equalled 53 billion Euros, 11% more than in 2005. The importance of the Dutch chemical industry is furthermore illustrated by the fact that the Dutch chemical industry accounts for 22% of all the chemical exports in the EU, making a very significant contribution to the positive Dutch trade balance.

2.3.1 Locations and capacities of refineries and steam crackers

In the Netherlands, the far majority of all base chemicals are produced in a limited amount of *integrated chemical complexes*. Main locations for the production of these base chemicals are:

1) The Rijnmond area (Maasvlakte, Europoort, Botlek and Pernis, and including the complexes at Moerdijk)
2) The Terneuzen area (including the canal zone till Sas van Gent and the chemical complexes at Vlissingen-Oost)
3) The Delfzijl area
4) The area around Geleen–Sittard in Southern Limburg
5) Smaller concentrations around *e.g.* Amsterdam and Arnhem

Currently, an overwhelming part of these chemicals are produced from inorganic materials (*e.g.* salt) or from fossil feedstocks (mostly crude oil; natural gas and coal is mostly used as energy carrier). In a typical integrated chemical complex such as that in the Port of Rotterdam (see *Figure 2.8*), crude oil is converted into various base fractions including a naphtha fraction, and gasoline, LPG and kerosene which are used as fuels. This conversion is achieved by using numerous cracking and refining catalysts and using distillation as the dominant separation process. The relative volumes of the fractions formed depend on the processing conditions and the composition of the crude oil.

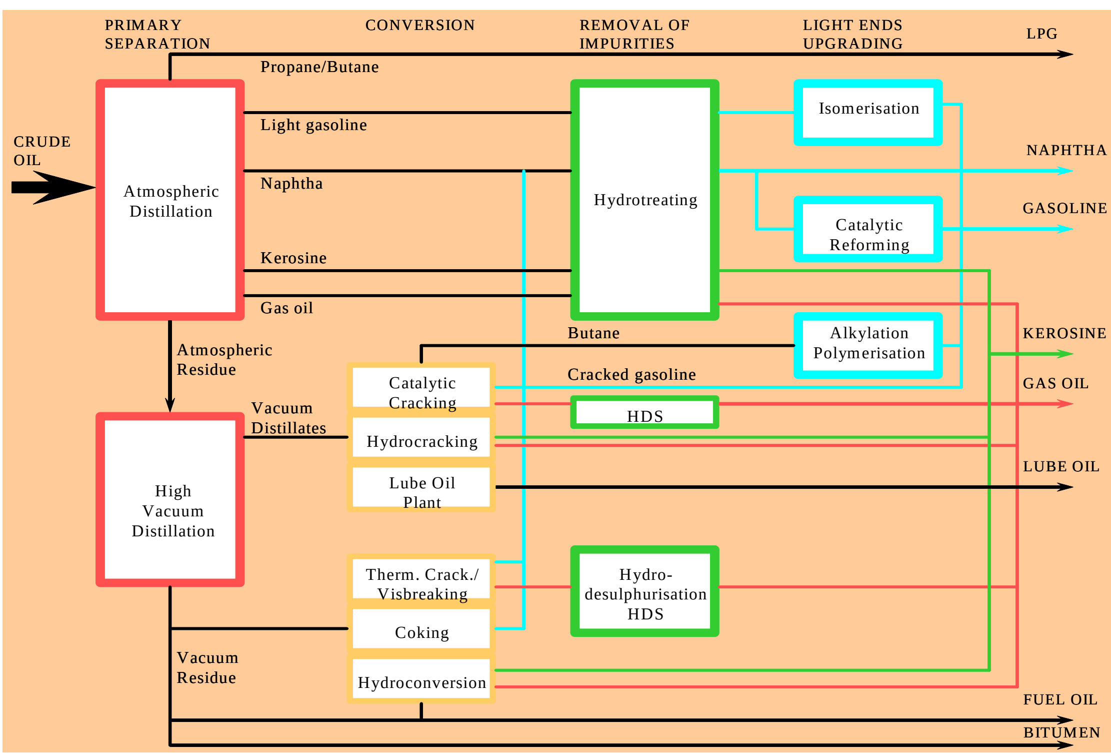


Figure 2.8. Scheme of crude oil refining.

Table 2.1. Crude oil refinery locations and capacities [Oil & Gas Journal] Conversion (http://www.chemlink.com.au/conversions.htm): 1 barrel = 0.1364 tonnes (100,000 bpd = 4.98 Mtpa)

Location	*Company*	*Capacity in bpd*	*(Mtpa)*
Pernis	Shell Nederland Raffinaderij	416,000	(20.7)
Europoort	Netherlands Refining Co. (BP-Texaco)	400,000	(19.9)
Europoort	Kuwait Petroleum Europort BV	80,000	(4.0)
Botlek	Esso Nederland BV	195,000	(9.7)
Vlissingen	Total Raffinaderij Nederland NV (TotalFinaElf)	160,000	(8.0)
	TOTAL:	1,251,000	(62.3)

The Rijnmond and Terneuzen areas are where the oil refineries are located (*Table 2.1*). According to the Dutch Bureau for Statistics (CBS), more than 60 million tons of crude oil were processed in 2006 by the refineries in the Netherlands, as shown in *Table 2.2* [CBS, 2007]. One of the fractions coming out of the refineries is the so-called naphtha fraction. Naphtha is fed to steam crackers (*Table 2.3*) for the production of just a few base petrochemicals or platform chemicals from which all the major bulk chemicals are subsequently derived (see also paragraph 2.1). An important characteristic of the naphtha feedstock is that, in contrast to biomass, it is very low in oxygen content. The majority of bulk chemicals produced in a typical chemical complex such as the one in the Port of Rotterdam, can be produced based on just six platform chemicals (ethylene, propylene, C4-olefins, and the aromatics benzene, toluene and xylene [BTX]). Estimated production capacity of these base petrochemicals in the Netherlands is about 9 million tonnes [Port of Rotterdam, 2004][Dow, 2007][SABIC Europe, 2006] (*Figure 2.9*). Compared to a worldwide production volume of about 250 million tonnes of base chemicals, the Netherlands produce as much as 3–4% of the total world production of these chemicals!

Table 2.2. Petroleum balance sheet. Amounts in kilotons [CBS, 2007]

	1995	2000	2005	2006
Initial stock	3,496	2,808	3,431	3,673
Extraction	3,523	2,351	2,269	2,022
Imports	52,677	54,308	54,178	49,909
From warehouses	7,144	5,998	7,554	9,450
Exports (–)	1,205	184	1,138	671
Processing (–)	62,534	61,788	62,621	61,034
Final stock	3,101	3,492	3,673	3,350

The Port of Rotterdam has the largest share of base petrochemicals production with about 4 million tonnes [Port of Rotterdam, 2004]. In comparison; in 2006 the amount of biomass *transsbipped* by the Port of Rotterdam was about 2 million tonnes (about 300,000 tonnes of vegetable oils, < 500,000 tonnes of woody biomass, about 1 million tonnes of bioethanol and approximately 170,000 tonnes of biodiesel [EUBIONET II, 2007].

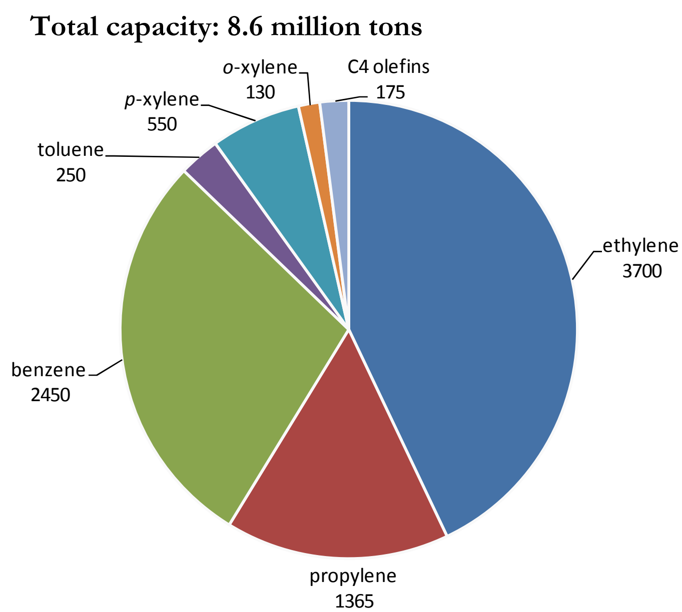


Figure 2.9. Estimated annual production capacities (ktons) of base petrochemicals in the Netherlands [Port of Rotterdam, 2004][Dow, 2007][SABIC Europe, 2006].

In the Terneuzen area, no crude oil crackers are present, but Dow annually processes about 8 million tonnes of naptha into 1.8 million tonnes of ethylene, with propylene, C4 olefins en B,T,X as side products. [Dow, 2007].

SABIC owns two naphtha steam crackers in Geleen that convert naphtha into ethylene, propylene, and co-products. The combined annual capacity is over one million tons of ethylene and approximately 650 thousand tons of propylene. Cracker co-products such as benzene, butadiene, MTBE, ETBE, gasoline components, styrene, C9 resinfeeds, cracked distillate and carbon black oil are produced in co-product upgrading units. The cracker products are key feedstock for derivatives such as PE (polyethylene), PP (polypropylene), styrene, ACN (acrylonitrile), PVC, glycols, rubber and gasoline. Imports from Saudi Arabia consist primarily of glycols, methanol and MTBE, which are used to produce other chemicals and polymers such as textile, PET, formaldehyde and gasoline blends. SABIC is the major importer of these three products into Western Europe and the second largest producer worldwide [SABIC Europe, 2006].

In the Delfzijl Area, the majority of chemicals produced contain chlorine. Approximately 2.2 million tonnes of salt (NaCl) are annually produced at this location. Part is used as road salt, but most is converted by electrolysis into chlorine, sodium hydroxide and soda. Nowadays, chlorine transports no longer occur, and all chlorine is used on site for the production of chemicals such as ethylene dichloride (starting material for production of polyvinylchloride), chloroacetic acid and amines. Furthermore, the site contains a factory suitable for methanol production –until a few years ago about 0.5 million tonnes of methanol starting from natural gas (aardgas) was produced by this plant each year. This process has now become (too) expensive. The factory has plans to start producing methanol from glycerol.

Table 2.3. Steam crackers in the Netherlands

Company	*Location*	*Product capacities (kt/y)*[a]
Dow	Terneuzen (2 crackers)	Ethylene (1700)
		Benzene (900)
Shell	Moerdijk (1 cracker)	Ethylene (900)
		Propylene (500)
		Butadiene (115)
		Pyrolysis gasoline (750)
ExxonMobil	Rotterdam (cracker and refinery)	Benzene (500)
		Toluene (250)
		p-Xylene (510)
		o-Xylene (110)
SABIC	Geleen (2 crackers)	Ethylene (1100)
		Propylene (650)
		Butadiene (130)
		Benzene (350)

[a] Total capacities of propylene and aromatics in the Netherlands are higher, since these are also produced at refineries.

When inorganic base chemicals and gases are included, it is estimated that within the Netherlands approximately 20–25 million tonnes of base chemicals and higher functionlised chemicals derived thereof are produced each year. This amounts to an amazing 5–10% of the total world production!

These hydrogen and carbon containing platform chemicals are either used as solvents (*e.g.* benzene, toluene), as starting material for polymers (*e.g.* ethylene, propylene, butadiene) or are further functionalised with elements such as oxygen, nitrogen or chlorine. *Figure 2.3* gives a summary of how this functionalisation is achieved.

Via such operations the chemicals are entering the next part of the value chain, ultimately leading to products used by companies or consumers. *Figure 2.10* depicts how crude oil derived platform chemicals enter the value chain and can be converted into *e.g.* packaging plastics. It also shows what similar value chains for biobased alternatives that are currently in a market introduction stage would look like.

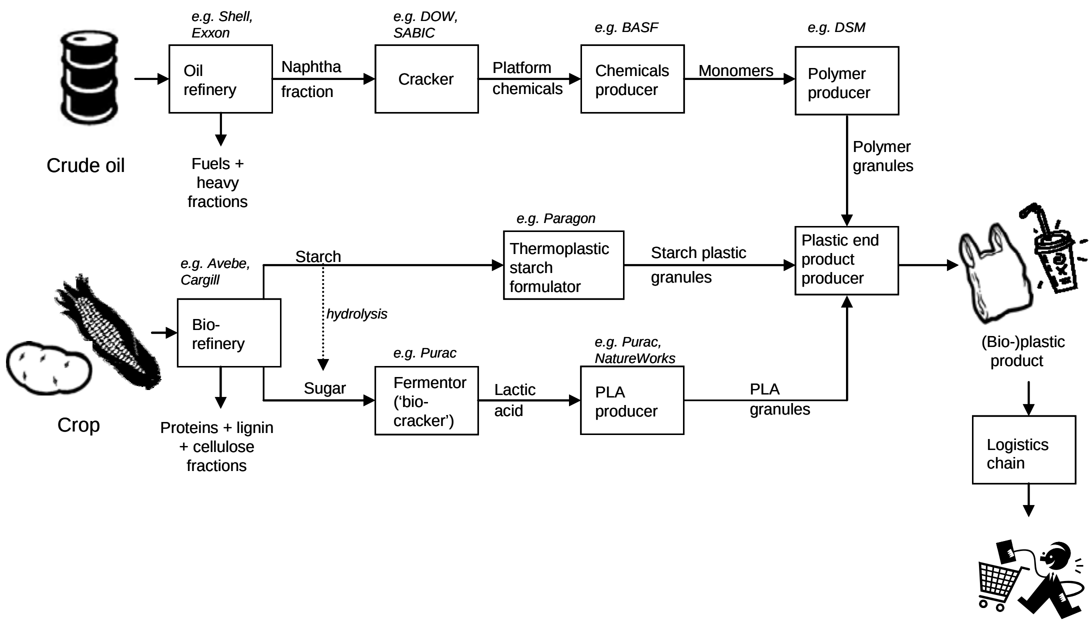


Figure 2.10. Chemical value chain of current production of petrochemical plastics (*e.g.* polyethylene, polystyrene) versus bioplastics (*e.g.* thermoplastic starch, polylactic acid).

3 Development strategies of the Dutch chemical industry – opportunities for biomass

3.1 General developments

Drivers for development of chemical companies are very diverse, and the desire for sustainable products and processes is only one of them.
In general, in contrast to *e.g.* the ICT industry, the chemical sector as a whole can be regarded as a very mature industry. Where large new major players appeared in the sector, they were mostly the result of restructuring (acquisitions and divestments) of existing chemical industries, *i.e.* name changes rather than the appearance of completely new companies. Some well-known names have disappeared, such as Hoechst, Rhone Poulenc, Sandoz, Hüls and, in 2008, probably ICI. Where completely new chemical companies were established in the Netherlands, they were often spin-offs of university departments (*e.g.* Syncom, Suprapolix) or companies active in the field of biotechnology. The underlying trends can be summarised as:

1. Focus of major chemical industries on specific core activities (the need to be number 1–3 on a European or global scale);
2. Splitting up of companies that were back-integrated with regard to feedstock supply and production of chemicals;
3. Higher investments in upcoming economies (especially Asia) than in Europe;
4. A general shift form bulk chemicals to 'high performance chemicals';
5. More attention for sustainable production methods;
6. Recently, more attention for alternative feedstock in general and more biofuels in particular
7. A reduction in fossil feedstock use, both by using less energy intensive processes, and by using less raw materials.

A good example of how major chemical companies transformed themselves during the past ten years is DSM. By *e.g.* acquisition of Gist Brocades and (part of) Hofmann La Roche, and divestment of steam cracking and polyolefin activities to SABIC, the company transformed itself from a bulk chemical industry to a company focusing on life sciences and high performance chemicals. Unilever has split off its oleochemical activities (Uniqema, now Croda), focusing on food and personal care products. Akzo Nobel sold most of its chemical and fibre activities, *e.g.* Acordis, its fibre business unit to Teijin Twaron, its catalyst activities to Albemarle, and more recently its pharmaceutical activities (Organon) to Schering-Plough, and is now focusing on formulating and marketing coatings. Shell transformed into an energy company, having split off most of its polymer activities (*e.g.* Kraton Polymers).

3.2 Developments of the Dutch chemical industry towards a bio-based economy

As already mentioned in section 2.3, the Netherlands have many favourable conditions for the chemical industry. These include the availability of raw materials such as salt and natural gas, large harbours for the supply of raw materials, a huge transportation network to the European hinterland, and integrated chemical complexes in both the Netherlands and its immediate surroundings. Nevertheless, the transformation to a bio-based chemical industry offers new challenges to the Dutch chemical industry and facilitating organisations like the Port of Rotterdam, Chemiepark Delfzijl and other integrated chemical complexes. Major considerations include:

- which raw materials will be needed in the new situation?
- how will biomass be processed?
- how will feedstock be made available at the appropriate location?
- what kind of storage facilities are needed?
- how can the production of bio-based bulk chemicals be integrated?
- how will products be shipped to the (geographic) area covered by the Port?
- which are the most likely companies to produce new bio-based bulk chemicals?

The answers to these questions depend to a large extent on which of the currently envisioned transition scenarios will become the dominant one.

3.2.1 Transition scenarios

Two extremes can be envisioned by which the transformation to a biomass based chemical industry may take place:

1. Biomass will be refined and 'cracked' into the familiar platform chemicals (*i.e.* ethylene, propylene, C4-olefines and BTX) and synthesis gas ('syngas', a mixture of mainly carbon monoxide and hydrogen gas). From these one- to six-carbon building blocks, all other chemicals and materials can be produced. Provided that efficient processes will become available by which oxygen-rich biomass of a varying composition can be transformed into basic hydrocarbon building blocks, the big advantage is that the current petrochemicals infrastructure and processes can be used. The fossil feedstock refining companies of today may then become the biorefineries of tomorrow.
2. A wide range of bio-based building blocks, in which as much of the functionality of biomass as possible has been retained, become the raw materials from which all other chemicals and materials are made. Not a few refineries that produce a limited number of platform chemicals will be present, but a large number of (smaller scale) biorefineries that produce a whole array of building blocks.

Between these two extremes lies a whole spectrum of non-exclusive scenarios that are perhaps more realistic. As a less extreme example of the first scenario: ethylene, one of the current platform chemicals, can be produced from (bio)ethanol. In fact, the Brazilian

company Braskem and US based Dow Chemical will each start commercial production of polyethylene from bioethanol. Both companies will locate their plants in Brazil, the world's most competitive bioethanol producing country. Bioethanol is currently made from sugar or starch. In the future, it is expected that ethanol will be made from the more abundant lignocellulosic or 'woody' biomass.
A scheme that illustrates that the real transformation to a bio-based chemical industry is going to have aspects of both extreme scenarios is shown in *Figure 3.1*. The different components of biomass are transformed by many different processes into many different intermediates. Some are first broken down into one- to six-carbon building blocks, others are directly converted into polymers.

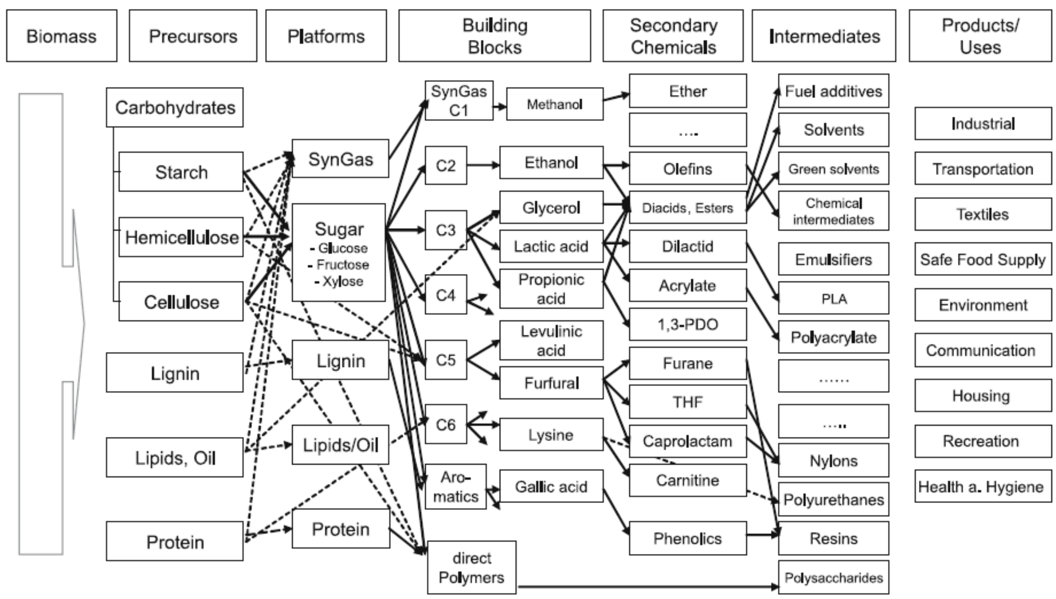


Figure 3.1. Schematic flow-chart of a selected number of current and future biomass transformations [Kamm, 2007].

3.2.2 Bulk chemicals

Recent work carried out by Wageningen UR [Haveren, van *et al.*, 2008] already concluded that with regard to the bulk chemicals produced by a typical integrated chemical complex such as the one based in the Port of Rotterdam, biomass based routes have the potential to make a significant impact on bulk chemicals production within 10 years and a huge impact within 20–30 years from now:

- There is a clear short-term (0–10 years) substitution potential for oxygenated bulk chemicals such as ethylene glycol and propylene glycol, iso-propanol and acetone, butylene and methylethylketone and for replacement of MTBE by ETBE. This implies that, given an estimated production volume of 12,000,000 tonnes of bulk chemicals by the Port of Rotterdam, there is a short term substitution potential of about 10–15% of fossil based bulk chemicals by biomass based bulk chemicals. Since glycerol, a by-product of biodiesel production, is a highly suitable starting material for the production of ethylene glycols and propylene glycols (*vide infra*), this is a very favourable short-term option. Next to glycerol also various sugars offer similar potential.

- On the mid term (10–20 years) there is a clear potential for a bio-based production of acrylic acid and nitrogen-containing bulk chemicals such as acrylonitrile, acrylamide and *ε*-caprolactam. As proteins, a by-product from biofuel production, become increasingly available at decreasing prices, they can become good starting points for such N-containing chemicals.
- On the short to mid term (0–20 years) there is surely a huge potential for a bio-based production of ethylene and vinylchloride. Commercial implementation will most probably first take place in areas with access to cheap ethanol and where production of ethylene is not largely integrated with the production of other platform chemicals.
- Direct isolation of aromatic building blocks from lignocellulosic biomass or conversion of sugars to aromatics is technologically still in its infancy and is mostly related to functionalised aromatics (*e.g.* phenols, styrene) instead of BTX. Here, further development of (biomass) based gas-to-liquid processes are likely to influence the current production of aromatics (benzene, toluene, xylene) in 20–30 years from now.
- Biorefineries that are being started up today, using conversions such as wheat starch to ethanol and rapeseed oil to biodiesel, will form the stepping stones towards the chemicals mentioned above if we learn to upgrade the side streams that will be available abundantly in the port.

These conclusions are further strengthened by announcements made in 2006 and 2007 by companies such as DOW, Solvay and Cargill/Ashland, that they will build production capacity for bio-based commodities at locations in Europe. The bio-based starting material is glycerol (or glycerine).

Whereas until just 5–10 years ago a significant part of glycerol was produced synthetically using epichlorohydrin as an intermediate, both DOW and Solvay have recently announced that they will start producing epichlorohydrin (ECH) from glycerol (from biodiesel production). Solvay has started producing ECH from glycerol (see *Figure 3.2*) from mid 2007 using the new Epicerol™ process [Solvay Chemicals, 2008]. A 10–50 ktonne production plant is based in Europe and 100 ktonne production potential is planned in China.

The Epicerol technology relies on the known conversion of glycerol into 1,3-dichloro-2-propanol (*Figure 3.2*). Solvay claims to have developed improved technology leading to less byproduct formation and less water consumption.

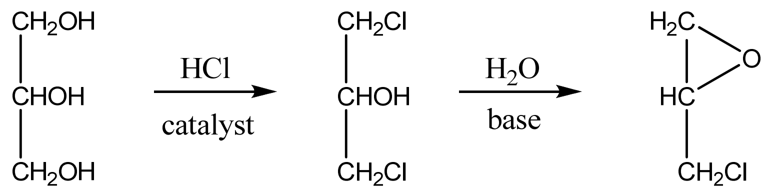


Figure 3.2. Conversion of glycerol into epichlorohydrin according to Solvay's Epicerol™ process.

In May 2007, Ashland and Cargill [Cargill, 2007] have announced that they have agreed to create a new joint venture to develop bio-based chemicals. The venture's first product will be propylene glycol (*Figure 3.3*). Using both licensed [Tuck, 2008] and proprietary technology, the joint venture will start producing propylene glycol from glycerine, at a location yet to be finalised in Europe. The cooperation between agro-food company Cargill and chemical company Ashland is a good example of the type of new alliances that will be necessary in a more bio-based economy.

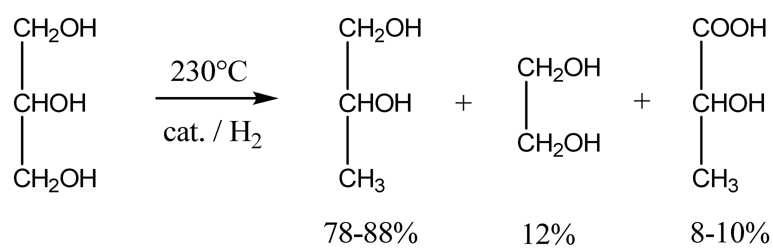


Figure 3.3. Conversion of glycerol to ethylene- and propylene glycol according to Werphy *et al.* (2003).

3.2.3 Fine chemicals

A transition to a society where much more of our fine chemicals are based on biomass is already under way. Examples are the biotechnological production of vitamins and other food-additives and pharmaceuticals (inspired by technological advances). This leads to a bio-based fine chemicals sector which is small in terms of volumes, but large in terms of turnover/sales. In the Netherlands, DSM and Organon (the latter now part of Schering-

Plough) are leading companies in this area. DSM claims to already generate one quarter of its turnover in this area on processes based on biomass.

3.3 Potential players in the bio-based chemical industry

A more bio-based chemistry will almost surely lead to new alliances between the chemical industry and the agro-food sector. New alliances will be made, broken up and restored in different formats. Examples of such alliances are the cooperation (until recently) between Dow Chemical and Cargill in the field of polylactic acid chemistry ('NatureWorks®') and product launching. This alliance was broken up, but recently a new alliance between Cargill and Teijin was established, with the aim to further promote market potential of PLA based products. Other examples are the cooperation between Dupont and Genencor on the development of 1,3-propanediol for fibres and the cooperation between Roquette (French starch manufacturer) and Dupont on isosorbide, with the aim to produce more bio-based PET plastics. Also, new trade relations are being established, such as Shell and SABIC buying bio-ethanol for ETBE production.

In this transition process both existing multinational industries as well as newcomers are likely to be willing to invest in building new chains and product portfolios. In this respect, the interest of established Dutch based chemical industries such as DSM, Shell, SABIC, Akzo Nobel and Dow is also reflected in their contribution to national biomass related research activities such as the B-BASIC programme, the CATCHBIO programme and the biomass activities of the Dutch Polymer Institute.

Newcomers in the area of (precursors for) bulk chemical production will almost surely also be companies from the agro-food sector such as ADM, Cargill, Tate & Lyle, Abengoa, Cosun, Roquette, Südzucker, Campina, KEMIRA, BER, Blue Ocean, and Danisco/ Genencor. All these companies are in the process of defining their future strategy towards non-food products and intensifying their activities with regard to the potential production of bulk chemicals.

In addition to the established chemical companies and the agro-food sector, a third sector will be the catalyst producers, currently offering 'enabling' technologies to the chemical industries. These include producers of biocatalysts (enzymes, micro-organisms) and producers of catalysts for the petrochemical industry, such as Engelhardt (BASF), Albemarle and Grace Davison. These companies will increasingly become interested in exploring the possibilities of catalytic conversion of biomass and the development of new optimised catalysts.

A fourth class of companies will be (new start-up) companies that today have neither a business in the agro-food sector nor the chemical sector.

Apart from the examples given earlier, it is currently too early to predict what the new chemical value chains will look like. Agro-food companies may become producers of bulk chemicals, established chemicals producers may keep this role, or both. It is important to develop realistic scenarios and analyse their potential.

3.4 Feedstock requirements

It is envisaged that there will be a number of inter-related (and complex) technical, economic and geographical issues that need to be addressed in the use of biomass in industry, specifically the chemical industry, ranging from the initial production location of the biomass, (pre-)processing and conversion. The choice of product as well as the biomass chosen is important for development success. Due to the complex nature of these issues, a simple answer to 'feedstock requirements' is not currently available and will require further attention in the future. A possible approach to address this aspect is presented in the following paragraphs.

3.4.1 Biomass complexity and the petrochemical industry

Biomass consists mostly of solid materials consisting of carbohydrates, oils and fats, proteins and lignin as well as other minor organic compounds. In other words, the vast majority of the elements in biomass are C (carbon), H (hydrogen), O (oxygen) with some N (nitrogen) and S (sulphur). This implies that, in principle, current transportation fuels and organic bulk chemicals could be derived from biomass.

However, biomass is a very wide term, covering all organic matter of plant and animal origin. This results in a large variety of materials, derived from diffuse origins, with varying (and complex) chemical structures and composition, water content, seasonality, storability, and transportability. In other words biomass is complex. It is this complexity that leads to the challenges in the application of biomass as a resource for the production of fuels and chemicals.

If one considers the current petrochemical industry, it relies on fossil feedstocks (in liquid or gaseous form) containing only carbon and hydrogen as elements. With nearly 100 years experience, prolonged large investments and technology where conversions are carried out in the absence of water and separations can be performed with the aid of distillation, the application of biomass in these industries requires major changes in technology, as well as a change in attitude.

3.4.2 Which biomass? What product?

Biomass of diverse type, composition and availability [Rabou, 2006] has been well documented. The question arises which biomass should be used to make which product? Biomass has already found use in technical applications. For example, a derivative of soybean oil is used as an additive for poly(vinyl chloride) (PVC), while other fatty oils have been used to make derivatives which can be used as surfactants or a specific kind of nylon (nylon-11). Even so, the direct application of naturally occurring structure(s) or biomass raw materials in technical materials, is more limited if one considers the production of specific chemicals for a particular product.

Effort to produce chemicals with more control over constant quality and performance has been addressed. Mainly, this has focused on the use of carbohydrates as raw materials and use of biotechnology for conversion. For example, the production of lactic acid is well established by both Purac and Cargill and applications are found in many industries. With the advent of successful (large scale) fermentation, technology has also been developed for the synthesis for lactide (from lactic acid) to allow synthesis of poly(lactic acid) (PLA). In the mid 90s, Cargill Dow started production of NatureWorks® which is promoted as a bio-based and bio-degradable material. Other monomers include 1,3-propanediol, a co-monomer in the synthesis of poly(propylene terephthalate) (Sorona®). Biotechnological preparation of 1,3-propanediol has been known for some time, but in recent years developments in metabolic engineering by DuPont and Genencor, allowing glucose to be used as a feedstock, has led to successful commercial production. These technologies focus on 'new' types of chemicals and materials, with new or specific properties, and do not examine the use of biomass as an alternative for the production of chemicals traditionally obtained from the petrochemical industry. The (long) timescales involved for these types of new developments and products are caused by the need to develop both new products and markets, as well as new properties and technologies.

Thus, the production of traditional chemicals from biomass would seem a more logical, much quicker, starting point. But what biomass or component should be used? Biomass consists of more than carbohydrates alone, and perhaps these other components would make more suitable precursors to chemical production than carbohydrates alone. Why? The petrochemical industry utilises simple hydrocarbons such as ethylene to prepare (chemical) products and materials. Here, various process steps together with the use of co-reagents, catalysts and other processing aids are used to convert the simple structures to more functionalised materials. The production of ethylene from biomass derived ethanol is known. Using this approach, bio-based alternatives to fossil derived hydrocarbons are generated. However, it still requires the use of reagents, process steps, energy and hence fossil resources to convert this to more functionalised products. It is already known that lower raw material costs and capital investment costs are incurred in the production of non-functionalised chemicals, compared to more functionalised compounds [Lange, 2001]. Hence, more efficient use of the functionality of biomass may be exploited to make functionalised chemicals. Thus, one should define biomass in terms of the specific components that are present and couple this with the desired end product. For example, some biomass such as potato is poor in proteins but rich in carbohydrates (starch), while others such as alphalpha are richer in proteins. It is the functionality of these specific components, such as the N (nitrogen) functionality in proteins or O (oxygen) functionality in carbohydrates, which will define their use for the synthesis of particular generic chemical species. For example, *amino acids* may be used as a source for amines and other N containing compounds such as ε-caprolactam, some O containing components e.g. *fatty acids*, may be used as a source of carboxylic acids, and *carbohydrates* as a source for alcohols. This is outlined in *Figure 3.4*. The advantage of this approach is that the incorporation of the functionality, e.g. N, in the plant lessens the external energy required to incorporate the functionality in the process to the end product.

Hence, from a practical perspective, once the type of compound or generic species to be synthesised is known, then the general type of biomass to be employed may be identified. At this stage technical considerations such as: specific biomass, cultivation, pre-treatments and conversion techniques and energy use, as well as socio-economic aspects such as land use and supply and demand play a role in the complete strategy for chemical production from biomass. Thus the choice of product as well as the biomass chosen is important for development success. Due to the complex nature of all these issues, a simple answer to 'feedstock requirements' is not currently available and requires further attention.

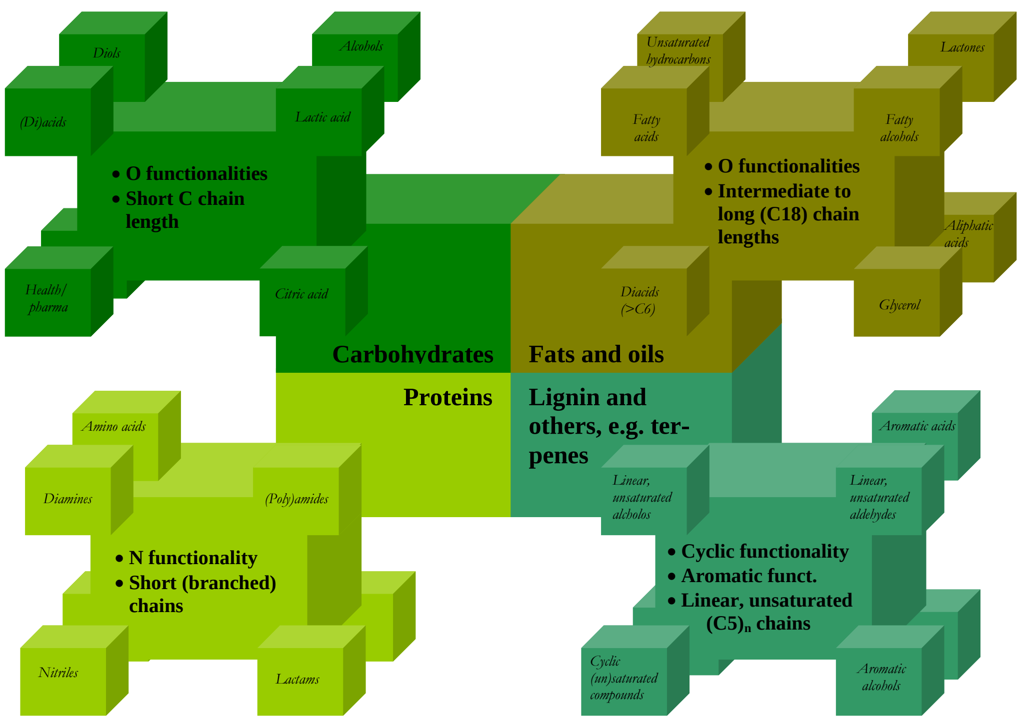


Figure 3.4. Approach for the synthesis of chemicals from biomass. Biomass components such as carbohydrates and proteins (centre, big blocks) are converted based on their main functionalities into chemical products (small cubes).

4 Conclusions

In the Netherlands, a large chemical industry is present, due to the many favourable conditions that exist in the Netherlands, which include the availability of raw materials such as salt and natural gas, large harbours for the supply of raw materials and a huge transportation network to a densely populated European back land with a high standard of living.
Although growth numbers in Asia and other developing countries are higher than in Europe, the European chemical industry is still very large on a world scale. After huge restructuring in the past 10–15 years the Dutch and European chemical industry are doing well and invest in growth areas such as life sciences, fine chemicals, high performance materials (including nanotechnology) and sustainable technology in general.
In the current situation the petrochemical industry almost exclusively relies on crude oil for the production of chemicals, and biomass is only used to a small extent (< 10%).
Many simultaneously acting driving forces will lead to an increased use of biomass for both (transportation) fuels and chemicals production in years to come. This is already demonstrated by announcements of several companies that they will start producing commodity chemicals from biomass. In order to be able to profit as much as possible from the existing infrastructure, further technology development is needed to convert biomass into the proper liquid or gaseous form. Alternatively, it may be needed to partly built a new infra structure.
Biomass consists mainly of a combination of carbohydrates (sugars, starch and cellulose), lignin, proteins and in some cases oil. All these molecules are in principle of interest for the chemical industry, since they have built in functionalities, like oxygen or nitrogen atoms. However, the chances of development success depend on the choice of end-product as well as on the biomass and processing infrastructure available, and are thus case-specific. It is therefore difficult to generally determine the requirements the chemical industry will place on biomass feedstock. This issue requires further attention.
To what extent the Netherlands will be able to profit from its current favourable position in a more bio-based economy will depend on many factors, among which the ability of governmental agencies on various levels to create favourable circumstances for new investments, and the willingness of traditional agro-food related companies to team up with traditional petrochemical industries.

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