Identifying breakthrough technologies for the production of basic chemicals

A long term view on the sustainable production of ammonia, olefins and aromatics in the European region

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CE Delft
Committed to the Environment

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CE Delft's solutions are characterised in being politically feasible, technologically sound, economically prudent and socially equitable.

Contents

Executive Summary

Background of the report

The European Commission's *Roadmap for a competitive and low carbon economy in 2050* indicates that greenhouse gas (GHG) emissions in all sectors should be significantly reduced to meet the European Union (EU) objective of 80 to 95% greenhouse gas emission reductions by 2050 compared to 1990 levels. The European Commission indicated in the Roadmap that the EU's industrial sectors should reduce emissions by 83 to 87% domestically by 2050 compared to 1990 levels.

The objective of this study is to explore breakthrough abatement technologies in three processes in the European chemical industry that can considerably contribute to achieving the required greenhouse gas emission reductions.

Specific processes studied

In this context we have assessed the processes for the production of:

- ammonia;
- olefins;
- aromatics (BTX).

These chemicals are expected to remain an important part of the mixtures of chemicals that may be produced in 2050, since these chemicals are so-called basic chemicals and form as such the building blocks of a wide variety of chemical compounds. Furthermore, these three processes currently account for 20% of the GHG emission of the European chemical industry.

Current best available technology references (BAT REFs) would allow for maximally 30% reduction in GHG emissions in these processes.

Methodology

Of each process an introduction to the current technology is made, including the current market situation, the expected future demand, a description of the current production process and the current GHG emissions.

For each production process breakthrough technologies were identified. Each of these alternative production methods are currently tested on pilot scale or are already offered on a commercial basis.

Per breakthrough technology a factsheet on the technology has been drawn up comprising a description of the applied technology the related GHG emissions and an estimate of investments and operational costs.

Economic assessment of breakthrough technologies

When assessing the economic feasibility of the presented breakthrough abatement technologies one should bare the following in mind:

- Prices for alternatives are consequently overestimated while the prices for the conventional technologies are underestimated.
- This study focuses on the requirements within the current way of organising production. For a decentralised small scale production integrated with other functions the outcomes may be different.
- The effect of the price of basic chemicals on the price of a consumer product is typically below 1%.

In other words the estimates of the feasibility of the presented alternatives are rather conservative.

Since the projected CO_2 reduction costs in 2050 varies between 28-70 €/tonne (UMWE(2011), Table 3-2), the additional costs of most alternatives will be compensated by the EU-ETS. In addition the cost impact of olefins and aromatics in the final consumer product is typically 1%. Therefore cost issues do not seem to be a major obstacle for implementation of the suggested alternative processes for the production of ammonia, aromatics and olefins.

Outcomes of inventory of breakthrough technologies

For all three processes possible breakthrough abatement technologies were found allowing for reductions in GHG emissions varying between 50 and 100% compared to the conventional processes to produce ammonia, olefins and aromatics (BTX).

The use of biomass as a raw material or processes powered by renewable power are essential to prevent greenhouse gas emissions in the three processes assessed. However, for the use of biomass as a raw material it is crucial to prevent perverse effects such as increased greenhouse gas emissions as a result of unsustainable sourcing. An integrated EU resource-efficiency framework and robust biomass sustainability standards are vital to ensure real emission reductions.

Policy measures to encourage the transition to a low carbon chemical industry

Our finding regarding the chemical industry and our earlier findings regarding options in the steel, cement and pulp and paper industries (CE, 2010) show that promising breakthrough abatement technologies are available for European energy-intensive industries to contribute to a low-carbon economy. However, large scale deployment requires an integrated EU industry and energy policy allowing for a resource efficient and sustainable use of available biomass and renewable energy capacity.

In this policy choices have to be made in order to prevent unsustainable mechanisms. The following measures are suggested to realise these choices:

- The influence of the EU ETS as a mechanism to provide a reward on GHG emission reduction has been mentioned before. The range of reduction costs for CO_2 as projected in a number of scenario studies allows breakeven for most biobased alternatives. The question is whether price leverage mechanisms are enough to realise a sustainable industry.
- To prevent a too high stress on biomass demand which could lead to unsustainable mechanisms, policy measures could aim to reduce use, and demand minimum sustainability standards on sourcing of biomass. In addition, alternatives for biomass use like the renewable power based ammonia production could be favoured over biomass intensive alternatives.
- To prevent lock-in effects policy makers may consider to secure access to the limited CCS storage capacity to those industries that do not have an alternative to comply with the targets for 83-87% reduction in greenhouse gas (GHG) emissions.

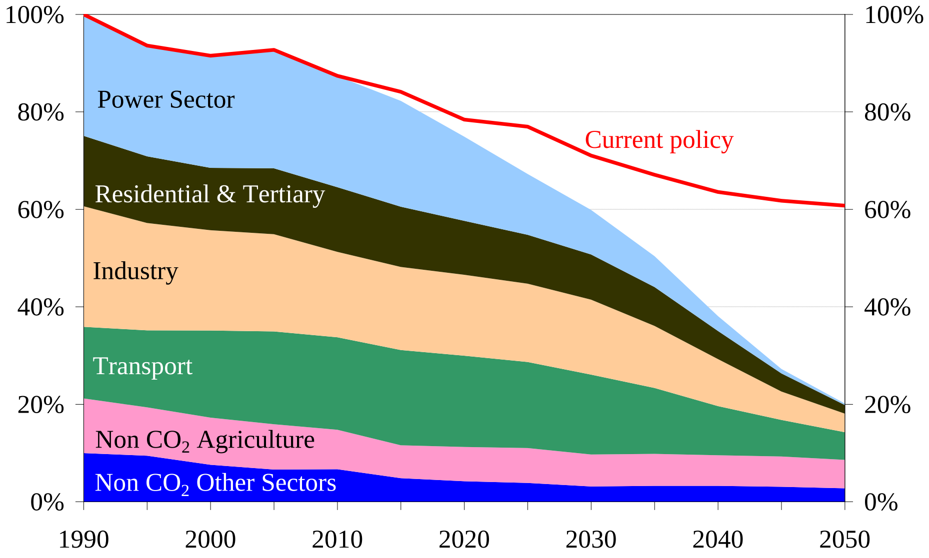
1 Introduction

1.1 Background

In order to keep climate change below two degrees Celsius (2°C) temperature increase EU heads of state and government reconfirmed in February 2011 the objective of reducing EU greenhouse gas (GHG) emissions by 80 to 95% by 2050 compared to 1990 levels, in the context of necessary reductions according to the Intergovernmental Panel on Climate Change (IPCC) by developed countries as a group.

On March 8th, 2011, the European Commission launched, building on this agreement, the Communication *Roadmap for moving to a competitive low carbon economy in 2050*. The European Commission assumed in this Communication that 80% domestic emission reductions in the EU are required by 2050. The Communication shows that all sectors should contribute to the proposed decarbonisation of the EU's economy.

Figure 1 **EU GHG emissions towards an 80% domestic reduction (100% =1990)**



Source: EC, 2011a.

Furthermore, the European Commission has indicated greenhouse gas emission reduction milestones for different sectors of the economy, including industrial sectors (EC, 2011a), see Table 1.

The Commission's analysis shows that GHG emissions in the industrial sectors could be reduced by 83 to 87% in 2050 compared to 1990 levels. But as solutions are sector-specific, it is recognised more detailed Roadmaps for the specific sectors are needed.

For a reduction of industrial emissions, the Commission also refers to the need for more resource-efficiency and increased recycling. It should therefore be underlined that *A Roadmap for moving to a competitive low carbon economy in 2050* was published in the context of the Europe 2020 flagship initiative for a resource-efficient Europe. Part of this flagship initiative is the Communication titled *Roadmap to a Resource Efficient Europe*. In this Communication the Commission outlines the importance of changing consumption patterns, innovative product design, reuse and recycling in order to achieve greenhouse gas emission reductions and other EU goals (competitiveness, raw material access, biodiversity, air and water quality).

Table 1 **Sectoral reductions in greenhouse gas (GHG) emissions**

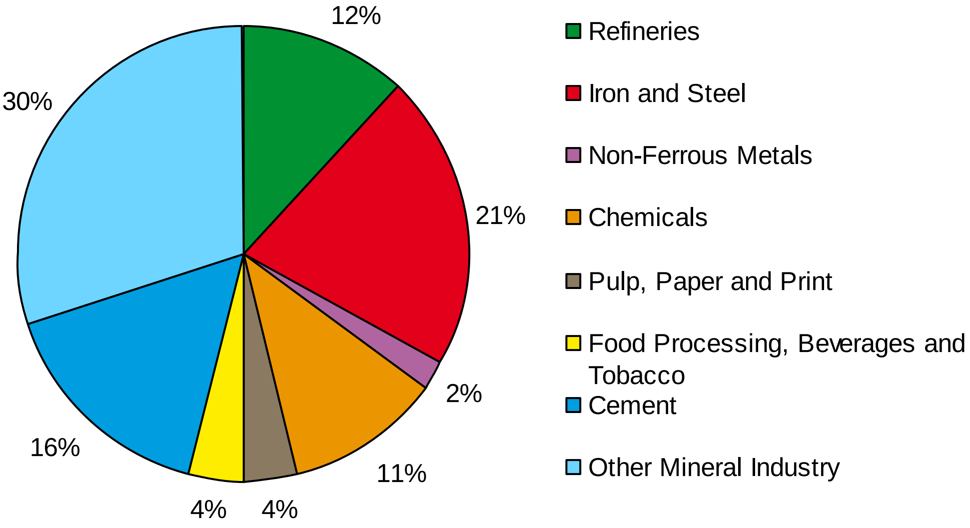
GHG reductions compared to 1990	2005	2030	2050
Total	-7%	-40 to 44%	-79 to -82%
Sectors			
Power (CO_2)	-7%	-54 to -68%	-93 to -99%
Industry (CO_2)	-20%	-34 to -54%	-83 to -87%
Transport (incl. CO_2 aviation excl. maritime)	+30%	+20 to -9%	-54 to -67%
Residential and services (CO_2)	-12%	-37 to -53%	-88 to -91%
Agriculture (non-CO_2)	-20%	-36 to -37%	-42 to -49%
Power (CO_2)	-30%	-72 to -73%	-70 to -78%

Source: EC, 2011a.

Climate Action Network Europe (CAN-Europe) asked CE Delft to present an inventory of different breakthrough abatement technologies at plant level for the production of basic chemicals, and to assess the contribution of these technologies to the required greenhouse gas emission reductions in the *Roadmap for moving to a competitive low carbon economy in 2050* (EC, 2011a). Beside the abatement technologies explored in this report, CE Delft recognises the role that innovative product design, reuse and recycling could play in greenhouse gas emission reductions in energy-intensive sectors, including the chemical industry.

In June 2010, we assessed on request of CAN-Europe, breakthrough technologies in the following three industrial sectors: Iron and Steel, Cement, Paper and Pulp. The results of this analysis are published in the report *Technological developments in Europe: a long-term view of CO_2 efficient manufacturing in the European region* (CE, 2010).

Figure 2 **Greenhouse gas emissions by the European industry as reported in 2007**



1.2 Objective and scope

The objective of this study is to explore breakthrough abatement technologies at plant level in three processes in the European chemical industry that allow for significant reduction in greenhouse gas emissions for these processes in Europe. The report does not assess greenhouse gas emission reduction options in the context of a broader European resource-efficiency strategy.

Definition breakthrough abatement technologies
Breakthrough technologies are, in the context of this study:
'Technologies that reduce CO_2/GHG emission by at least 25% compared to the benchmark, will be widely commercially available in 2020-2030 at the latest and are economically competitive compared to reference and alternative technologies.'

Carbon Capture and Storage (CCS) and biomass use are included in this inventory of technologies. However, we do recognise that CCS still has to be proven to a certain extent, and that storage capacity for CO_2 is limited. These issues are further detailed in Annex A. Regarding biomass, we do recognise the important outstanding issues around sustainability, greenhouse gas balance and indirect land use related to specific types of biomass. These issues are further detailed in Annex B.

1.3 Selection of chemical processes to be studied

CE Delft has applied the following criteria for selecting the chemical processes for this report:

a Processes have a higher likelihood of relevance in 2050.
b The processes have significant greenhouse gas emissions.
c Breakthrough abatement technologies are required (for a number of chemical processes commercially available technologies are already obtainable).

Using these criteria, which are further outlined below, the following chemical processes were selected. The production methods of (in alphabetic order):
- ammonia;
- aromatics or so-called BTX (benzene, toluene and xylene);
- olefins (ethylene, propylene, butadiene).

1.3.1 Relevance for 2050

For this study the selected industrial processes have to be relevant in 2050.

This does not imply the selected processes are regarded as a part of a sustainable future, it only means that we expect that in 2050 ammonia, aromatics and olefins are required for specific (partly yet unknown) products.

In the production of chemicals one can discriminate between final products and basic chemicals. Basic chemicals are those chemicals that are used as precursors or building blocks for other chemical components. To understand the difference one could compare basic chemicals with ingredients like milk, sugar, eggs and flour, and final products with pastry. You do not know what pastry will be eaten in 2050 but it is not a wild guess that sugar or flour will be used.

Well known basic chemicals are olefins like ethylene or aromatics like benzene. APPE, Association of Petrochemical Producers in Europe, has developed a virtual tour explaining the relation between different olefins and aromatics and the many different type of plastic materials that are made of them (http://www.petrochemistry.net/flowchart/flowchart.htm). In 2004, basic petrochemicals accounted worldwide for more process energy use (about 3 million TJ fuels combusted) and CO_2 emissions (about 200 million tons) in total than any other type of chemical.

Another basic chemical is ammonia, which has a number of applications as such but is also widely used as a precursor for a wide variety of nitrogenous products of which the best known are fertilizer and dynamite.

Both examples show basic chemicals produced in highly energy intensive processes on the basis of fossil fuels (naphtha for the petrochemicals and methane for the ammonia production). Like all other highly energy intensive industries both the petrochemical industry and the ammonia industry are facing the dual challenge of climate change and security of energy supply. Therefore, it is in the interest of both policymakers and chemical engineers to gain a greater understanding of the potential of energy efficiency improvement and the options of using alternative primary sources (including biomass).

1.3.2 Significant GHG emissions

Ecofys and partners gave in their sector report for the chemical industry an overview of the most emission intensive activities in the chemical industry. This overview is reproduced in Table 1.

Breakthrough technologies that allow for a significant reduction of emissions related to production of the chemicals listed in this table potentially have a significant effect on the reduction of the chemical industry as a whole. Thus the products of the chemical processes to be selected have to be mentioned in Table 2.

Table 2 **Ranking of the most emission intensive activities in the chemical industry**

No.	Product/process[1]	Process *and* steam emissions (Mt CO_2 equivalents	Share	Cumulative share
1	Nitric Acid	41 [4]	21.6%	21.6%
2	Cracker products (HVC)	35	18.4%	40.0%
3	Ammonia	30	15.8%	55.8%
4	Adipic acid	13 [4]	6.8%	62.6%
5	Hydrogen/Syngas (incl. Methanol)[2]	12.6	6.6%	69.3%
6	Soda ash	10	5.3%	74.5%
7	Aromatics (BTX)	6.6	3.5%	78.0%
8	Carbon black	4.6	2.4%	80.4%
9	Etylene dichloride/Vinyl chloride/PVC	4	2.1%	82.5%
10	Ethylbenzene/Styrene	3.6	1.9%	84.4%
11	Ethylene oxide/Monoethylene glycol	3.6	1.9%	86.3%
12	Cumene/Phenol/Acetone	1.2	0.6%	86.9%
13	Glyoxal/Glyoxylic acid[3]	0.4 [4]	0.2%	87.2%
14	*Polyolefins (PE/PP/PS)*	1.1	0.6%	87.7%
15	*Butadiene*	0.6	0.3%	88.1%
16	*Dimethyl therephthalate/Terephthalic acid/Polyethylene terephthalate*	0.6	0.3%	88.4%
17	*Propylene oxide*	0.5	0.3%	88.6%
18	Others		11.4%	100.0%
	Total upper processes (1-18)	168.4	88.6%	
	Total chemical industry[5]	190	100.0%	

[1] In Italics, production processes with steam consumption only. Other emissions have direct emission from the process and emissions from steam consumption.

[2] This figure includes 3.8 Mt CO_2 from gas producers, who supply refineries. Hydrogen production in refineries accounts for 44 Mt CO_2.

[3] This figure is based on the Registre Français des Emissions Polluantes (IREP), year 2005.

[4] Carbon dioxide and nitrous oxide.

[5] This figure includes N_2O and CO_2 emissions phrased as Mt CO_2 equivalents and is based on the greenhouse gas inventory, see Table 4 in source document.

Source: http://ec.europa.eu/clima/studies/ets/docs/bm_study_-_chemicals_en.pdf.

The cracker products or High Value Chemicals (HVC) in this overview are a mix of varying composition of olefins, aromatics and syngas (a gas mixture of hydrogen and carbon monoxide) of which the olefin ethylene is a major component (the size of production locations is expressed in tonne ethylene/year).

1.3.3 Breakthrough technologies are required to reach the climate goals

Based on absolute emission levels the processes producing nitric acid and adipic acid do classify as relevant. However, based on the existing best available technology references these emissions can be reduced with over 80%. Technology is not the bottle-neck in this situation. Therefore we expect that other processes will be more relevant to the 2050 low carbon roadmap.

1.4 Data availability

The execution of this project has been conditional on the availability and reliability of data on the evaluated technologies that are at different stages of development. Some published information on energy consumption, CO_2 emissions and costs consist of early results stemming from pilot phases whereas other technologies are already on the market and figures are less uncertain. Besides, strategic behaviour in the provision of data might play a role. Companies might have an incentive to be optimistic on CO_2 efficiency, as they want to present themselves as frontrunners. On the other hand, stakeholders might be more negative on attainable CO_2 efficiency in the sector in the light of the broader political context (for example, debates on benchmarks). The figures in this report are based on the best information available at the moment of writing.

1.5 Structure of the report

In this report, breakthrough technologies are discussed of production processes of the following three categories of chemicals:
- ammonia;
- olefins;
- aromatics.

These processes are described in the above mentioned order, using two chapters per process:
The first chapter is dedicated to the description of the current production method(s), the current emission levels CO_2 and GHG emissions, and the benchmark for emissions suggested for the post-2012 EU ETS.

The second chapter describes alternative processes and the emission reductions possible when replacing the existing processes by the alternative processes and compares the current production costs with (expected) production costs of the alternative route.

The last chapter is dedicated to conclusions and recommendations.

Annex A discusses the potential of capturing of CO_2 combined with storage (CCS) or use in other processes.

Biomass based chemistry appears to play a key role for all three processes. The limited availability and some indications for policymakers are discussed in Annex B.

Footnotes are used in this report to suggest further reading, all sources are put between brackets. Under References the sources are listed first, the footnotes are listed separately under Websites.

2 Conventional ammonia production

2.1 Current production volumes and applications

Annual ammonia production amounts to approximately 125 Mt, approximately 14 Mt/year of which are being produced within the EU (see Table 3).

Table 3 Annual ammonia production per region (figures in Mt/year)

Process description	Amount of woody biomass (Mtonne/year)	Amount of bio-ethanol (Mtonne/year)
Water electrolysis based NH_3	0	0
Biomass gasification based NH_3	38	0
Bioethanol based ethylene	0	34
Bioethanol based propylene	0	28
Bioethanol based aromatics (BTX)	0	21
Biogasification based aromatics (BTX)	25	0

Source: IFA website.

Globally approximately 85% (as of 2004) of ammonia is used as a raw material for fertilizers, such as urea and nitrate salts. For plants, nitrogen is an essential mineral for growth and is transformed in the plant into proteins and of enzymes. Most plants can only take up nitrogen from the soil, mostly as nitrate[1].

Fertilizers produced from ammonia currently dominate the market for nitrogen fertilizers. Before the nineteen twenties, nitrogen fertilizers mainly concerned natural nitrate salts, mined in Chile[2].

Other major applications concern utilisation as a cleaning agent in households and use as a pH controlling agent in fermentation processes (e.g. brewing, wine making).

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[1] See e.g.: http://www.efma.org/documents/file/publications/EFMANitrogenbooklet.pdf.

[2] See e.g. http://en.wikipedia.org/wiki/Caliche_(mineral)#Chilean_Caliche and http://en.wikipedia.org/wiki/Sodium_nitrate.

2.2 Future demand

2.2.1 Factors and issues influencing future demand

As illustrated in the previous paragraph, global - and regional - demand for ammonia is strongly linked to agricultural applications, this being the main market of ammonia.

Demand by the agricultural sector will be determined by:

- type of crops cultivated;
- the area of the different cultivated crops;
- the yield aimed at (metric ton per hectare);
- agronomic practices applied in cultivation and the resulting efficiency with which nutrients are taken up by the crop.

The type of crops being cultivated and the amounts produced in turn are related to food consumption patterns - the amount of food consumed and the types of products consumed (meat, dairy, vegetables, staple food).

Table 4 **Annual ammonia production per region (figures in Mt/year)**

	2005	2006	2007	2008	2009
EU	14	13	14	14	13
Stranded gas and associated gas	11	11	12	11	12
China	38	41	42	41	42
India	11	11	11	11	11
Indonesia	4	4	4	5	5
Russia	10	11	11	10	10
Ukraine	4	4	4	4	4
USA+Canada	12	12	13	13	12
Others	18	20	20	21	21
	122	126	131	130	130

Source: IFA website.

Current consumption patterns and agricultural practices in the EU are not yet sustainable:

- Part of the EU population suffers from overweight and cardiac diseases because of overconsumption of food compared with daily food intake requirements.
- Agricultural practices in the intensive agricultural sector in North-West Europe in the nineteen fifties to nineteen eighties relied on application of surpluses of fertilizers and manure. This resulted in a number of environmental problems such as eutrophication of surface and groundwater, reduced soil fertility and air pollution by ammonia. Agricultural practices have since been significantly improved. There is however still room for improvement in agricultural practices and nutrient application efficiencies. The agricultural sector aims to achieve these improvements and to become more sustainable. This is encouraged by the EU and national governments.

Policies on EU and national level are being developed to tackle these issues. For example:

- The Commission is developing strategies to reduce health impacts due to unhealthy diets[3]. Insurance companies are more and more taking into account live style in insurance contributions.
- The agricultural sector, research institutes and legislators are developing more sustainable agricultural practices, which will be included in the Common Agricultural Policy. Focus is on:
    - increasing the capacity of the soil to retain nutrients (and water) by increasing the carbon content of the soil. This can be achieved by leaving crop residues on the field, by growing green manure, adding organic fertilizers and by reducing tillage;
    - utilisation of more efficient agricultural practices such as only applying fertilizer in the crop rows and not indiscriminately distributing fertilizer over the entire crop field.

These developments will have a mitigating effect on demand for nitrogen fertilizer in the intensive North-West EU agricultural sector.

However, in parts of Central and Eastern Europe the situation is quite different. Much of the agricultural sector in this region still consists of subsistence farms with traditional agricultural practices, which have a hard time competing on an increasingly liberal market[4]. Because of the traditional agricultural practices, agriculture – and the associated limited nutrient gift - is depleting the soil of nutrients[5]. It can therefore not be excluded that for these regions fertilizer use will increase in the next decades.

2.2.2 The European ammonia industry and European ammonia demand

As illustrated by IFA's trade map, the EU is a partly self supplying market, annually producing 14 Mtonne of ammonia. Another 3.26 Mtonne of ammonia is imported directly (1.87 Mtonne/year) or as DAP (0.1 Mtonne NH_3 eq./year) or urea (1.29 Mtonnes NH_3 eq./year).
The main challenges for the EU ammonia industry and fertilizer industry in general are linked to:

- The cost and availability of natural gas, the principal energy carrier and raw material. Natural gas is mainly imported into the EU. Prices in the EU are high compared to regions with high reserves, especially in regions with large reserves of associated gas or stranded gas.
- The obligation to reduce emissions. Regulation concerning CO_2 emissions, pollution prevention and control, and waste have been strengthened over the years.
- Competition from third country producers (Russia, North Africa, Middle East), operating under a different legislative framework.

European fertilizer production has been declining within the EU according to EFMA, mainly because of decreasing demand from agriculture, the lack of natural gas within the EU and its high price from abroad. The extra cost of ETS III are expected by EFMA to cause this long term decline to continue and to enhance imports.

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[3] See e.g: http://europa.eu/legislation_summaries/public_health/health_determinants_lifestyle/c11542c_nl.htm.

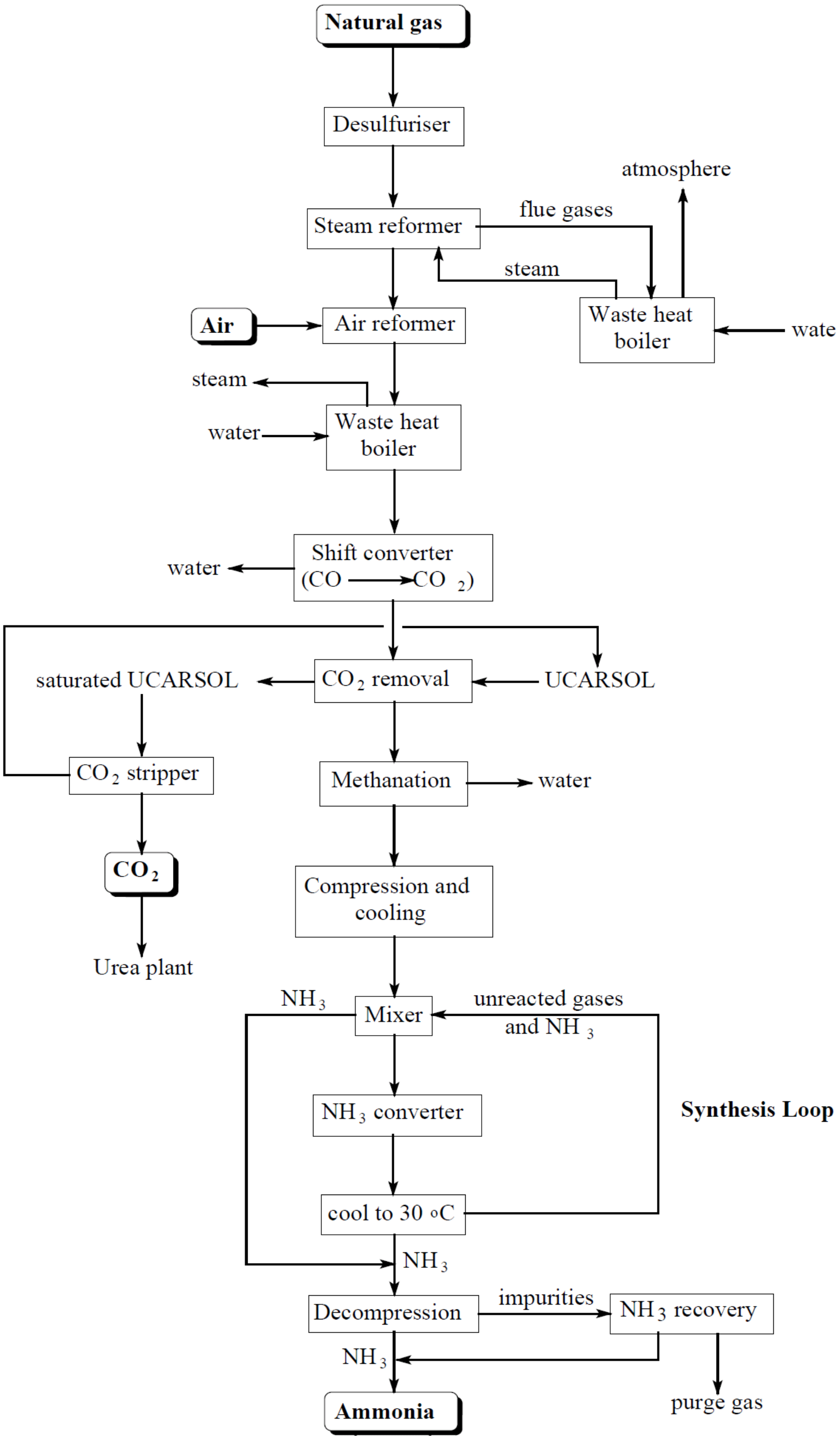
[4] See e.g.: http://www.scarled.eu/fileadmin/scarled/publications/Poster_-_Lena_Fredriksson.pdf, http://ageconsearch.umn.edu/bitstream/93082/2/sr_vol22.pdf.

[5] See e.g. Alterra reports for EU.

Figure 3 Mineral streams from, to and inside Europe

2.3 Production process

Figure 4 Schematic representation of the ammonia production process



Source: http://nzic.org.nz/ChemProcesses/production/1A.pdf.

2.3.1 Applied technology

Currently, ammonia is globally produced almost exclusively via the Haber-Bosch process. The Haber-Bosch process is a catalytic process in which hydrogen reacts with nitrogen:

N_2 (g) + 3 H_2 (g) ↔ 2 NH_3 (g) (equilibrium) $K_{eq} = \frac{p^2_{NH_3}}{p_{N_2} \cdot p^3_{H_2}}$

The process is typically operated at 15–25 MPa (150–250 bar) and between 300 and 550°C, the reactants passing over four beds of catalyst, with cooling between each pass. On each pass only about 15% conversion occurs, but any unreacted gases are recycled, so that eventually an overall conversion of 97% can be achieved.
The pressure is kept high to force the equilibrium to the ammonia side. Next to this, ammonia is removed from the equilibrium mixture of gases leaving the reaction vessel by condensing produced ammonia between each catalyst bed by cooling the gas stream. Unreacted hydrogen and nitrogen gases are then returned to the reaction vessel to undergo further reaction.

The required hydrogen is commonly produced by gasification of natural gas with steam and air:

$CH_4 + H_2O \rightarrow CO + 3\ H_2$
$2\ CH_4 + O_2 \rightarrow 2\ CO + 4\ H_2$
$CO + H_2O \rightarrow CO_2 + H_2$

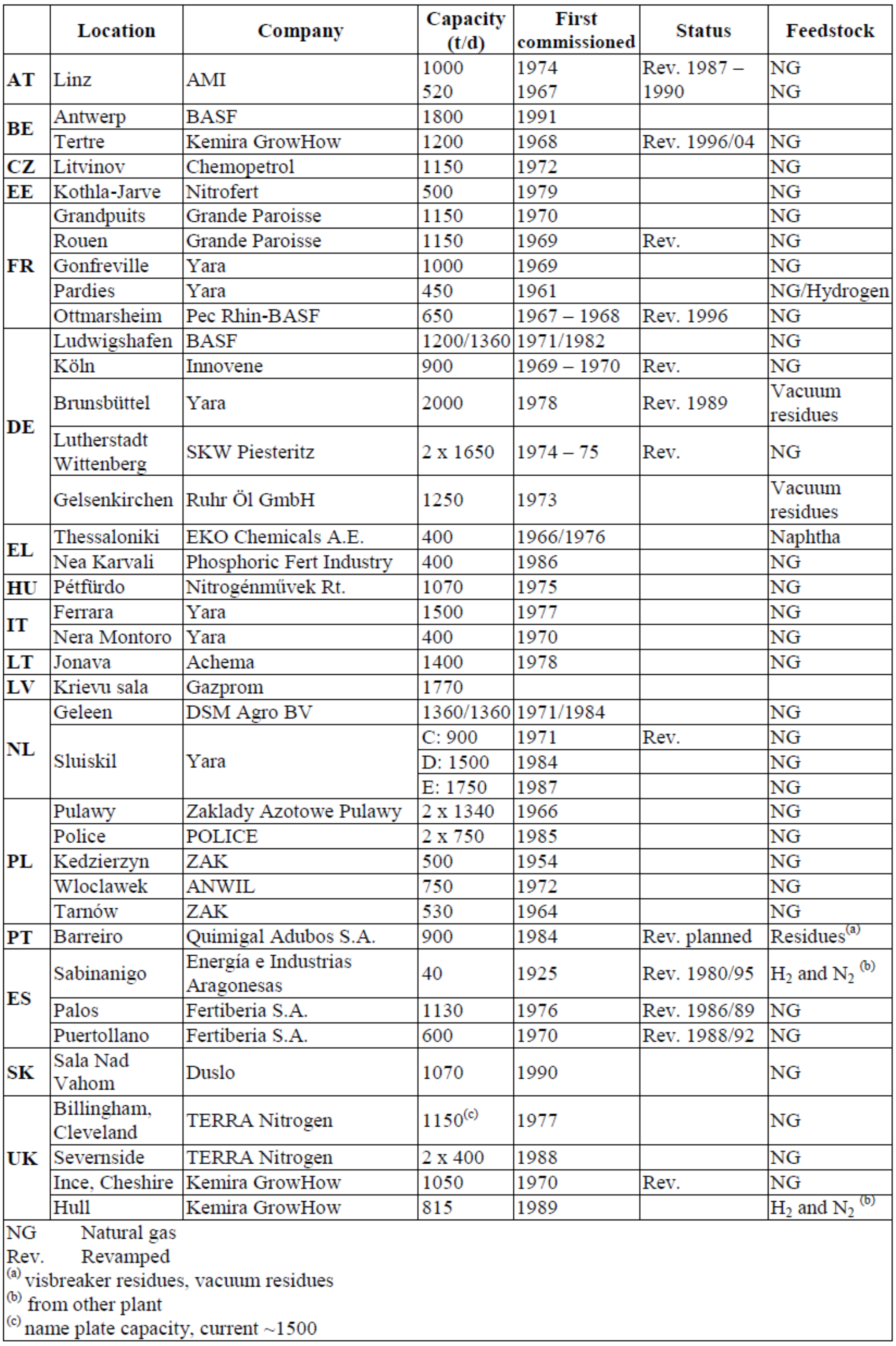
The air also provides the nitrogen required in the Haber-Bosch reaction.

Figure 5 **The Vemork power station at the Norsk H Rjukan reservoir**

Source: http://thefreeonline.wordpress.com/2011/07/04/co2-free-nh3-from-rjukan-waterfall1913/.

As an alternative to natural gas, approximately 4% of global ammonia production is based on hydrogen produced from heavy residual oil and coal which is gasified with oxygen. An alternative for residual oil and coal could be (and has been) biomass and/or peat. In Oulu in Finland a peat and biomass based ammonia plant was operated in the nineteen eighties.

Table 5 **Overview of current production facilities for ammonia in EU27**



	Location	Company	Capacity (t/d)	First commissioned	Status	Feedstock
AT	Linz	AMI	1000 520	1974 1967	Rev. 1987 – 1990	NG NG
BE	Antwerp	BASF	1800	1991		
	Tertre	Kemira GrowHow	1200	1968	Rev. 1996/04	NG
CZ	Litvinov	Chemopetrol	1150	1972		NG
EE	Kothla-Jarve	Nitrofert	500	1979		NG
FR	Grandpuits	Grande Paroisse	1150	1970		NG
	Rouen	Grande Paroisse	1150	1969	Rev.	NG
	Gonfreville	Yara	1000	1969		NG
	Pardies	Yara	450	1961		NG/Hydrogen
	Ottmarsheim	Pec Rhin-BASF	650	1967 – 1968	Rev. 1996	NG
DE	Ludwigshafen	BASF	1200/1360	1971/1982		NG
	Köln	Innovene	900	1969 – 1970	Rev.	NG
	Brunsbüttel	Yara	2000	1978	Rev. 1989	Vacuum residues
	Lutherstadt Wittenberg	SKW Piesteritz	2 x 1650	1974 – 75	Rev.	NG
	Gelsenkirchen	Ruhr Öl GmbH	1250	1973		Vacuum residues
EL	Thessaloniki	EKO Chemicals A.E.	400	1966/1976		Naphtha
	Nea Karvali	Phosphoric Fert Industry	400	1986		NG
HU	Pétfürdo	Nitrogénművek Rt.	1070	1975		NG
IT	Ferrara	Yara	1500	1977		NG
	Nera Montoro	Yara	400	1970		NG
LT	Jonava	Achema	1400	1978		NG
LV	Krievu sala	Gazprom	1770			
NL	Geleen	DSM Agro BV	1360/1360	1971/1984		NG
	Sluiskil	Yara	C: 900	1971	Rev.	NG
			D: 1500	1984		NG
			E: 1750	1987		NG
PL	Pulawy	Zaklady Azotowe Pulawy	2 x 1340	1966		NG
	Police	POLICE	2 x 750	1985		NG
	Kedzierzyn	ZAK	500	1954		NG
	Wloclawek	ANWIL	750	1972		NG
	Tarnów	ZAK	530	1964		NG
PT	Barreiro	Quimigal Adubos S.A.	900	1984	Rev. planned	Residues(a)
ES	Sabinanigo	Energía e Industrias Aragonesas	40	1925	Rev. 1980/95	H_2 and N_2 (b)
	Palos	Fertiberia S.A.	1130	1976	Rev. 1986/89	NG
	Puertollano	Fertiberia S.A.	600	1970	Rev. 1988/92	NG
SK	Sala Nad Vahom	Duslo	1070	1990		NG
UK	Billingham, Cleveland	TERRA Nitrogen	1150(c)	1977		NG
	Severnside	TERRA Nitrogen	2 x 400	1988		NG
	Ince, Cheshire	Kemira GrowHow	1050	1970	Rev.	NG
	Hull	Kemira GrowHow	815	1989		H_2 and N_2 (b)

NG Natural gas
Rev. Revamped
(a) visbreaker residues, vacuum residues
(b) from other plant
(c) name plate capacity, current ~1500

Source: BAT REF dochttp://eippcb.jrc.es/reference/lvic-aaf.html

Historically, BASF and Norsk Hydrogen first produced hydrogen for ammonia production by water electrolysis[6]. The 60 MW Rjukan hydropower dam in Telemark, Norway produced ammonia via electrolysis of water for many years, from 1913 producing fertilizer for much of Europe.
Currently approximately 1% of global ammonium is still produced from hydrogen from electrolysis, the applied hydrogen being a by-product of the chlor-alkali process.

In Europe all kinds of processes are applied.

2.3.2 Current level of energy requirement and greenhouse gas emissions

According to EFMA (1999) a modern ammonia plant without steam export will consume:

- 22.1 GJ/tonne NH_3 for feedstock;
- 7.2-9,0 GJ/tonne NH_3 for fuel.

The associated CO_2 emission would amount to 1.2 tonne/tonne NH_3 and 0.4-0.5 tonne CO_2/tonne NH_3 respectively.
These figures concur with data mentioned in IPPC BAT REF document and Ecofys benchmark report. In accordance with this, the proposed benchmark level for emissions per tonne ammonia amounts to 1.61 tonne CO_2/tonne ammonia.

Fuel is utilised in the fired primary reformer for supplying heat required for the chemical reactions in the primary reformer. Heat of off-gases of the primary reformer and heat from the exothermal reactions in the secondary reformer and ammonia synthesis is utilised for preheating natural gas feedstock and air, for desulphurisation and for generation of superheated steam. Superheated steam is utilised for driving compressors and other mechanical installations.

In less optimised plants especially fuel consumptions and associated CO_2 emissions will be higher.

2.3.3 Opportunities for energy improvements and CO_2 reduction

The process itself is said to be close to its thermodynamic optimum leaving little opportunities for process improvements and savings in energy consumption[7]. Potential measures mentioned in literature include:

- preheat combustion air;
- integration of a primary reformer;
- lower excess air in heater of primary reformer;
- utilisation of optimised absorbens in CO_2 capture;
- integration of a gas turbine providing combustion air to the primary reformer furnace.

Natural gas purchase costs are estimated to make up 70-90% of total production costs[8], which implies that there is a strong autonomous drive to optimise energy consumption.

A directly implementable option that could reduce process emissions significantly is CCS of process CO_2.

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[6] See e.g. http://en.wikipedia.org/wiki/Ammonia#Uses and http://en.wikipedia.org/wiki/Haber-Bosch_process.

[7] See e.g. http://oee.nrcan.gc.ca/industrial/technical-info/benchmarking/ammonia/results.cfm?attr=24.

[8] See e.g. http://climatetechwiki.org/technology/ammonia-industry.

The CO_2 from the process (70-75% of total emissions) is routinely captured and is frequently applied as a raw material or commodity. The International Fertilizer Association reports that the industry globally utilises around 36% of the CO_2 removed. Of this, around 33% is used for the synthesis of ammonia into urea, whilst the remaining 2.2% is sold on to other uses (5.2 Mtonne CO_2 globally), such as CO_2 use for enhanced oil recovery or soft drink carbonation[9].

Preparation of captured process intrinsic CO_2 for CCS would require € 10-15 per tonne CO_2, mainly for compression to pressures required for transport and deep geological storage. Transport and storage will require an additional fee of € 5-10 per tonne CO_2. Total costs per tonne avoided CO_2 would be comparable to current and medium term trade prices in the ETS, which implies that under the right market conditions on the carbon market CCS would probably be an autonomous development.

Capture and storage of fuel related CO_2 would require installation of a post combustion capture plant and would require additional heat to be supplied by the steam cycle of the ammonia plant. Costs associated with capture of fuel associated CO_2 are estimated to amount to € 45-50 per tonne – higher than e.g. capture costs at coal fired power stations.

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[9] See http://www.unido.org/fileadmin/user_media/Services/Energy_and_Climate_Change/Energy_Efficiency/CCS_%20industry_%20synthesis_final.pdf.

3 Low carbon ammonia

As described in the previous chapter the energy use and greenhouse gas (GHG) emissions related to the production of ammonia are mostly caused by the production of the hydrogen required to make ammonia (NH_3).

As far as could be conducted from publicly available information the ammonia industry and national authorities are not focussing on development of alternatives for the conventional fossil fuel intensive hydrogen production (gasification of natural gas as the mean source of hydrogen).

All alternatives mentioned in literature were discussed in desktop studies prepared by university researchers. These studies focussed on two routes:
- ammonia production based on hydrogen produced from water electrolysis;
- ammonia production based on hydrogen produced by biomass gasification.

Efforts for further development of these hydrogen production technologies within and outside the EU are discussed below.

3.1 European efforts

Hydrogen from water electrolysis

Further development of electrolyser technology is stimulated in the EU under the Fuel Cells and Hydrogen (FCH) Joint Technology Initiative with a total budget of M€ 1,000, of which M€ 500 from private investors. The program will run between 2008 and 2017. This program includes all aspects involved in utilisation of hydrogen as a fuel in transportation: production, storage and utilisation in vehicles.

Under the Seventh Framework Program (FP7) a number of smaller and more basic research projects are and have been financed. Projects currently being executed include ADEL, HYSTRUC, SusGhen and RELHY with a total budget of approximately M€ 10. Except for HYSTRUC these projects concern fundamental research projects focusing on aspects such as development of new membrane materials.
The HYSTRUC project on the other hand is aimed at ‘development and testing of an innovative 30 Bar low cost, small size pressure module electrolyser (pme) in the MW power range for the cost efficient production of electrolytic hydrogen’. Apart from the aimed at scale the technology would fit the specifications of the Haber-Bosch process very well. The project is conducted by a consortium of Norwegian NORSK HYDRO, MTU Friedrichshafen GmbH from Germany and Prime Membrane Technologies NV from Flanders.

Biomass gasification

Development of biomass gasification is stimulated with widely orientated programs such as EUBIA, which focuses on different kinds of aspects (gasification technology, tar removal, syngas applications).

Most efforts in the EU are focussed on production of hydrogen based on the gasification of biomass to fuel in the form of so-called bio-SNG (synthetic natural gas). There is no specific focus on integration of biomass gasification with ammonia production.

However, as indicated in Section 3.5, integrated biomass gasification and ammonia production has already been demonstrated in Oulu, Finland in the nineteen eighties.

3.2 Non-EU efforts

Hydrogen from water electrolysis

In the USA a large program with a M$ 250 budget is run by the Department of Energy (DOE) since 2004. As in the EU FCH program this program includes all aspects involved in utilisation of hydrogen as a fuel in transportation.

The DOE hydrogen program has developed a number of specific performance targets for production costs of hydrogen and for investment costs for electrolysers. For large and central electrolysis plants with 20 kt/year production capacity, the targets are given in Table 6.

Table 6 **Technical targets of wind powered electrolysis**

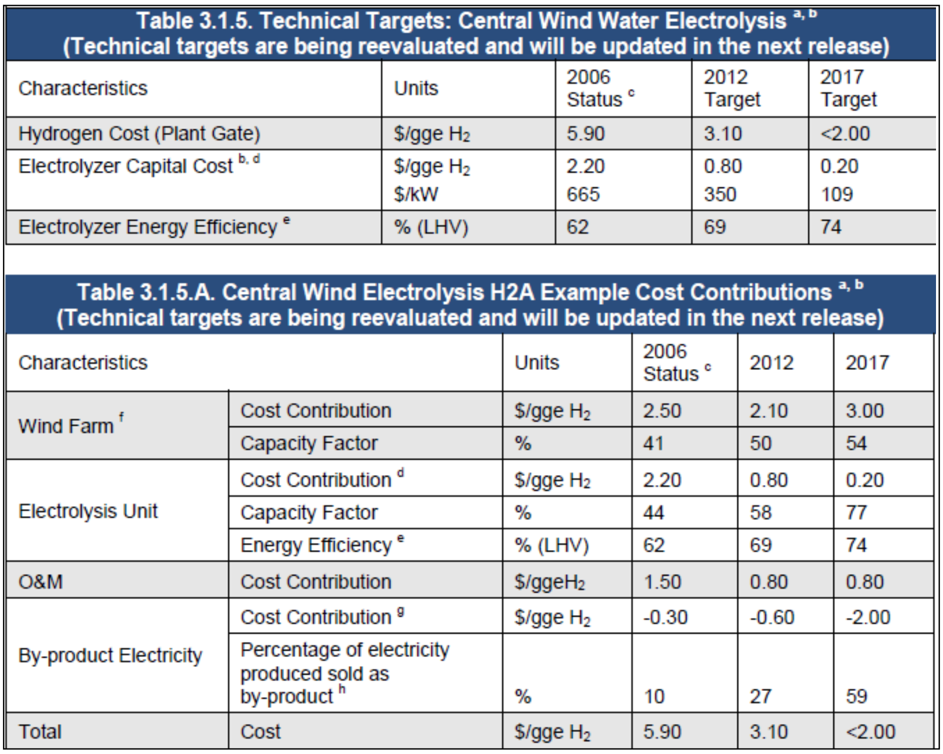


Table 3.1.5. Technical Targets: Central Wind Water Electrolysis[a, b]
(Technical targets are being reevaluated and will be updated in the next release)

Characteristics	Units	2006 Status[c]	2012 Target	2017 Target
Hydrogen Cost (Plant Gate)	$/gge H_2	5.90	3.10	<2.00
Electrolyzer Capital Cost[b, d]	$/gge H_2 $/kW	2.20 665	0.80 350	0.20 109
Electrolyzer Energy Efficiency[e]	% (LHV)	62	69	74

Table 3.1.5.A. Central Wind Electrolysis H2A Example Cost Contributions[a, b]
(Technical targets are being reevaluated and will be updated in the next release)

Characteristics		Units	2006 Status[c]	2012	2017
Wind Farm[f]	Cost Contribution	$/gge H_2	2.50	2.10	3.00
	Capacity Factor	%	41	50	54
Electrolysis Unit	Cost Contribution[d]	$/gge H_2	2.20	0.80	0.20
	Capacity Factor	%	44	58	77
	Energy Efficiency[e]	% (LHV)	62	69	74
O&M	Cost Contribution	$/gge$H_2$	1.50	0.80	0.80
By-product Electricity	Cost Contribution[g]	$/gge H_2	-0.30	-0.60	-2.00
	Percentage of electricity produced sold as by-product[h]	%	10	27	59
Total	Cost	$/gge H_2	5.90	3.10	<2.00

Source: NREL, 2010b

Total capital costs for this 20 ktonne/year plant are estimated at M$ 60, for green field situation in the USA. Fixed operational costs are estimated at M$ 3.3/year.

Biomass gasification

Similar to the situation in the EU, the further technological development of gasification of biomass in developed countries such as the USA is primarily focused at production of biofuels (Fischer-Tropsch products and SNG) and not on integrated gasification and ammonia production.

3.3 Breakthrough technologies selection

Based on the referred to desk top studies and on our own analysis of the historical developments in ammonia production technologies we identified two ‘breakthrough’ technologies, which both actually concern technologies operated historically:

- ammonia production based on hydrogen produced from water electrolysis;
- ammonia production based on hydrogen produced by biomass gasification.

The reason for selecting biomass gasification is that this route has already been demonstrated on commercial scale in Oulu, Finland. The reason for selecting ammonia production based on hydrogen from water electrolysis is

a The fact that a (small) fraction of global ammonia production is already based on hydrogen from electrolysis. And

b The fact that much effort and money is put into improving water electrolysis for hydrogen production.

3.4 Water electrolysis

3.4.1 Generalised process description

For industrial ammonia synthesis a centralised electrolyser system is required, producing ten thousands tonnes per year of hydrogen. Such a plant will be constructed by combination of tens to hundreds of electrolysis cells, comparable with the situation at an aluminium smelter. Such plants have already been demonstrated (and are partly still operational) in Zimbabwe, Canada and Peru.

The electrolyser units will use process water and electricity input for electrolysis. Cooling water for cooling and potassium hydroxide (KOH, or Lye) is needed for the electrolyte in the system.

When connected to the grid, the electrolyser system receives AC grid electricity which is converted via transformer and rectifier sub-systems into DC electricity for use by the electrolyser stack.

Process water is de-mineralised and softened to a specific resistance of 1 to 2 megaohm/cm in the Water Demineralizer Unit. The system requires one liter per normal cubic meter (Nm^3) of hydrogen produced. This translates to roughly 1.5 tonne of water per tonne of ammonia produced.

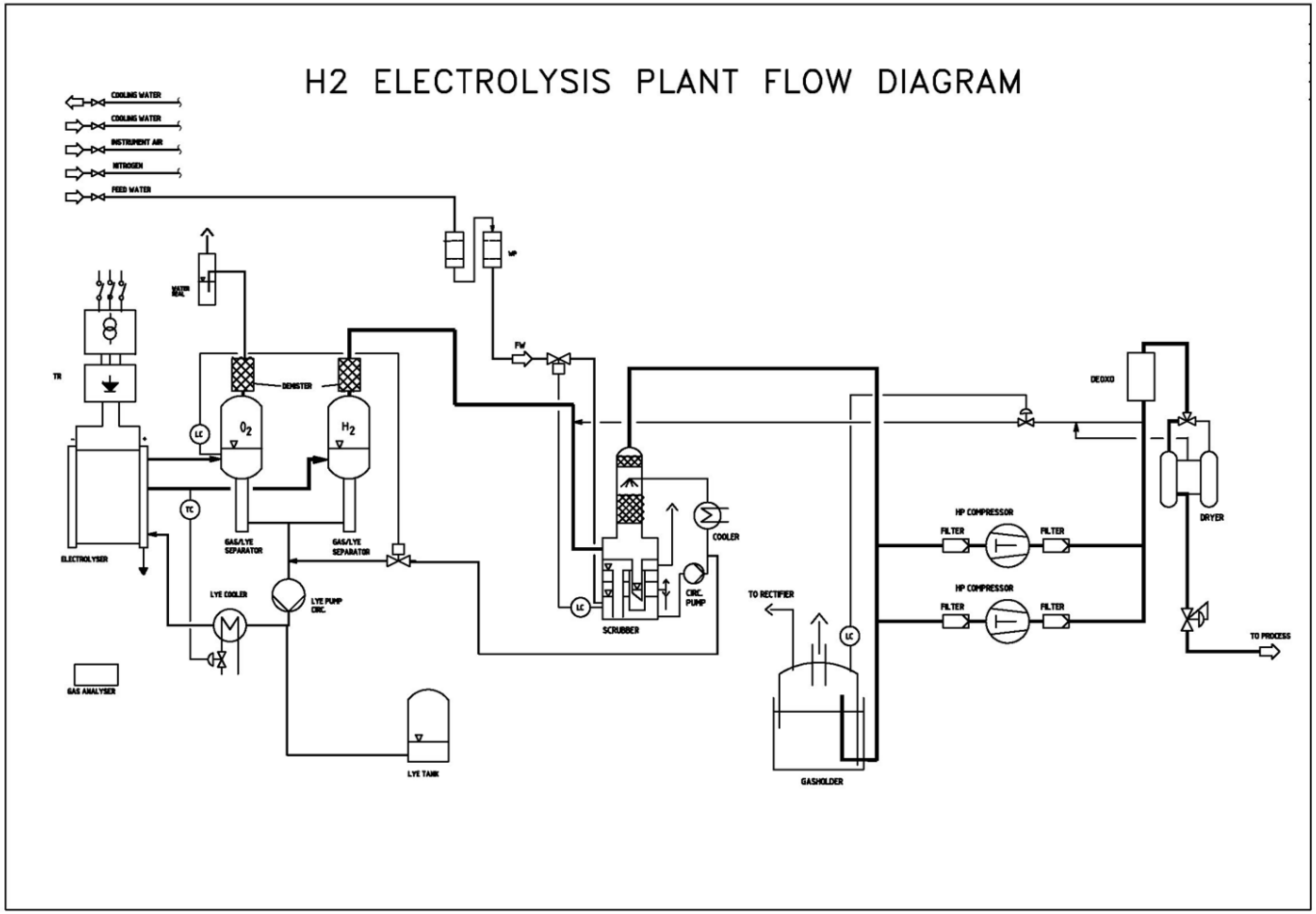
The purity of the hydrogen gas coming off the electrolyser stack is 99.9%. Following the gas purifer, deoxidizer and dryer stages, the purity of hydrogen increases to 99.9998% (2 ppm).

Oxygen is removed from the lye in the Oxygen/Lye separator. The system modelled does not capture the oxygen gas, but capture of the high-purity oxygen gas is a possibility, allowing for oxygen to be supplied as a by-product.

The purified hydrogen will have atmospheric pressure or limited elevated pressure. For ammonia synthesis the hydrogen is compressed additionally to 150–250 bar.

The hydrogen and nitrogen produced by a standard cryogenic ASU (Air Separation Unit) will be processed by a standard ammonia synthesis process with several serially placed reactors with intercoolers and recirculation of unreacted reactants (synloop). Synloop and ASU consume approximately 390 kWh_e/tonne NH_3 for compression.

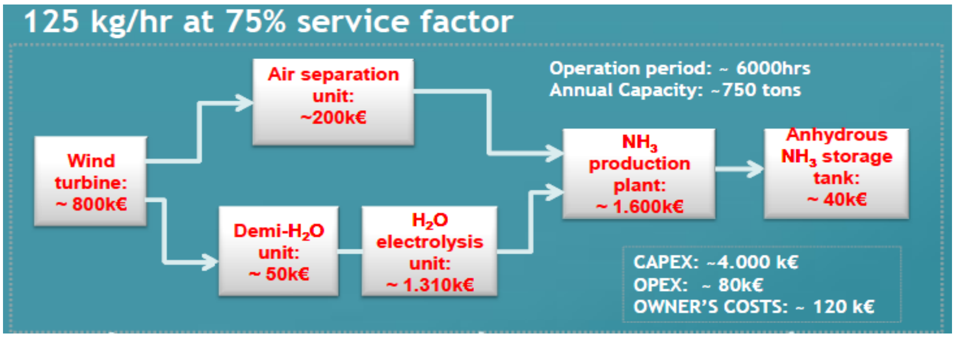
Figure 6 **Flow sheet for water electrolysis based hydrogen production**



Source: http://ieahia.org/pdfs/Task25/alkaline-electrolysis.pdf.

Alternatively, a Dutch firm, Proton Ventures claims it can supply small scale skid mounted water electrolyser based ammonia production units, which can be combined with an individual windmill or other type of decentralised renewable power source.

Figure 7 Flow sheet of skid mounted water electrolyser based ammonia production unit offered by Proton Ventures



Source: Proton Ventures, 2010.

3.4.2 Benchmark on the GHG emissions

The proposed benchmark level for emissions per tonne ammonia amounts to 1.61 tonne CO_2 eq. per tonne NH_3 for conventional ammonia production.
As described above the water electrolysis route consist of two steps:

- the production of hydrogen based on electrolysis of water using renewable power;
- the synthesis of ammonia from hydrogen and nitrogen by means of the Haber-Bosch process.

If the hydrogen is produced using additional windpower and hydropower, there are no GHG emissions related to the production of hydrogen.
The Haber-Bosch process is an exothermic process, which means that it generates heat, it only needs cooling and therefore it does not generate GHG emissions. Therefore the water electrolysis based ammonia production based on renewable power is a way to realise 100% reduction in GHG emissions related to ammonia production.

3.4.3 Current state of development of technology and technological development targets

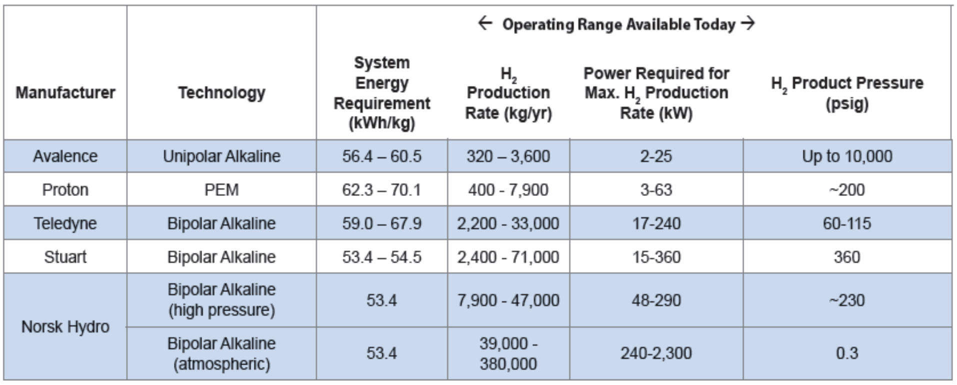
As illustrated by Table 7 and Table 8, water electrolysis for hydrogen production actually already is an off-the-shelf commercially available technology.

However, there is still much opportunity for optimisation with respect to costs and energy efficiency:

- Current electrolyser investment costs range from € 700 to 1,300/kW (based on Lower Heating Value). The overall cost taking into account the complete installation is around 50% for a single electrolyser and decreases to ~10% for large plants (~100 electrolyser units).
- Targets mentioned for future specific investment costs amount to € 500/kW_e for the EU HYSTRUC program to € 250/kW_e as assumed in the NREL hydrogen program for a 2017 central electrolysis plant.
- The current energy efficiency is approximately 60%, targets for future improved electrolysis cells amount to 75-80%.

As indicated, several programs aim at achieving these goals at about 2020-2025 (see DOE's program).

Table 7 Overviews of commercially available technology for hydrogen production (part 1)



Manufacturer	Technology	← Operating Range Available Today →			
		System Energy Requirement (kWh/kg)	H_2 Production Rate (kg/yr)	Power Required for Max. H_2 Production Rate (kW)	H_2 Product Pressure (psig)
Avalence	Unipolar Alkaline	56.4 – 60.5	320 – 3,600	2-25	Up to 10,000
Proton	PEM	62.3 – 70.1	400 - 7,900	3-63	~200
Teledyne	Bipolar Alkaline	59.0 – 67.9	2,200 - 33,000	17-240	60-115
Stuart	Bipolar Alkaline	53.4 – 54.5	2,400 - 71,000	15-360	360
Norsk Hydro	Bipolar Alkaline (high pressure)	53.4	7,900 - 47,000	48-290	~230
	Bipolar Alkaline (atmospheric)	53.4	39,000 - 380,000	240-2,300	0.3

Source: http://www.nrel.gov/docs/fy04osti/36705.pdf , Norsk Hydro is now: NEL.

Table 8 Overviews of commercially available technology for hydrogen production (part 2)

Manufacturer	Country of origin	Model	Capacity range Nm^3/h	Pressure Bar g	Energy cons. kWh/Nm^3	Type of electrolyser
Hydrogenics	US/EU	IMET 300	1-3	25	4.2	Alkaline
		IMET 1000	4-15, 26-30, 31-45, 46-60	10 or 25	4.2	Alkaline
Teledyne	US	Titan™ HP	75,100,125,150	8-16	5.6	Alkaline
		Titan™ EC	28,33.5,42,56	4.2-8.1	5.6	Alkaline
		Titan™ HM	2.8, 5.5, 7, 8.4, 11.2	5.0	6.1-5.3	Alkaline
Norsk Hydro Electrolyser	N	Atm. (4000A)	0-377	0.02	4.1	Alkaline
		Atm. (5150A)	0-485	0.02	4.3	Alkaline
		HPE	10-65	12	4.8	Alkaline
IHT	CH	Lurgi system	110-760	32 atm	4.3-4.6	Alkaline
		Bamag system	3-330		3.9-4.5	Alkaline
Accagen	CH	Standard	1-100	10	4.4-6.3	Alkaline
		HP		30		
		VHP		200		
Idroenergy	IT		0.4-64	1.8-3.9	5-6	Alkaline
Proton	US	HOGEN S	0.53, 1.05	13.8	6.7(*)	PEM
		HOGEN H	2, 4, 6	15	7.3-6.6(*)	PEM

Source: http://www.empa.ch/plugin/template/empa/*/73305.

3.4.4 Indicative assessment of future centralised electrolysis plants

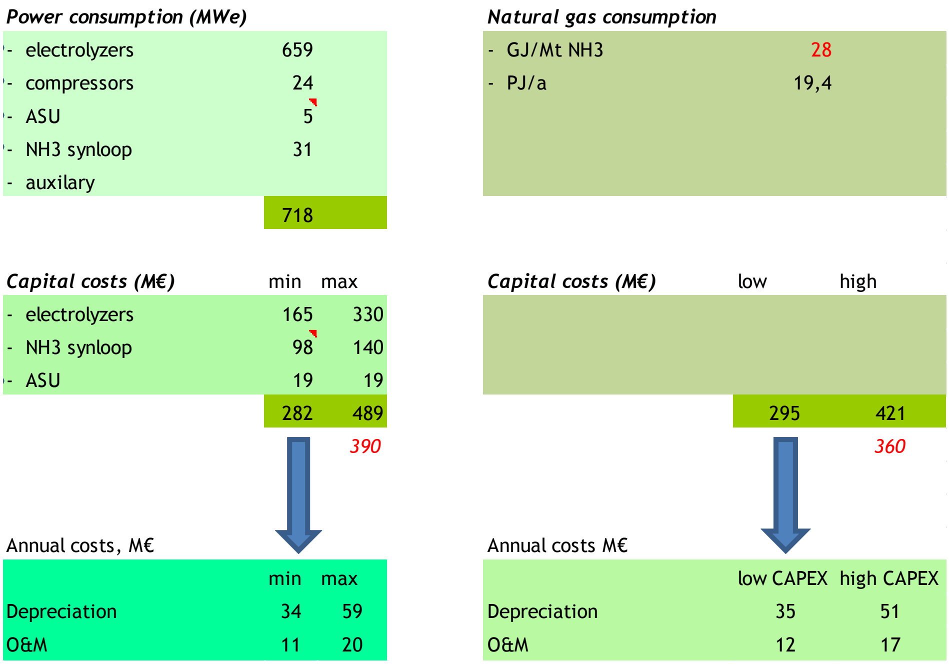
Based on an investment of € 250/kW_e to € 500/kW_e for the electrolysers and associated systems and a specific power requirement of 4 kWhe/Nm^3 hydrogen following comparison was made between electrolysis based ammonia production and natural gas based ammonia production (see Figure 8).

For a centralised water electrolysis plant, investment costs are estimated as being one third of the investment costs of a conventional natural gas based plant of equivalent production capacity.

Investments for a natural gas based plant were adopted from several literature sources. According to Bartels (2008) investment costs for the ammonia synloop amount to approximately one third of total plant costs.

Investment costs for a water electrolysis based plant were estimated on the basis of assumed electrolyser cell costs and synloop costs for a conventional ammonia plant. The estimated investment costs concern a broad estimate, in accordance with the depth of the commissioned study.

Figure 8 **Comparison of fuel/power consumption and CAPEX/OPEX for conventional and water electrolysis based ammonia production for a 2,000 tpd ammonia plant at 95% availability**



Power consumption (MWe)	
- electrolyzers	659
- compressors	24
- ASU	5
- NH3 synloop	31
- auxilary	
	718

Natural gas consumption	
- GJ/Mt NH3	28
- PJ/a	19,4

Capital costs (M€)	min	max
- electrolyzers	165	330
- NH3 synloop	98	140
- ASU	19	19
	282	489
		390

Capital costs (M€)	low	high
	295	421
		360

Annual costs, M€	min	max
Depreciation	34	59
O&M	11	20

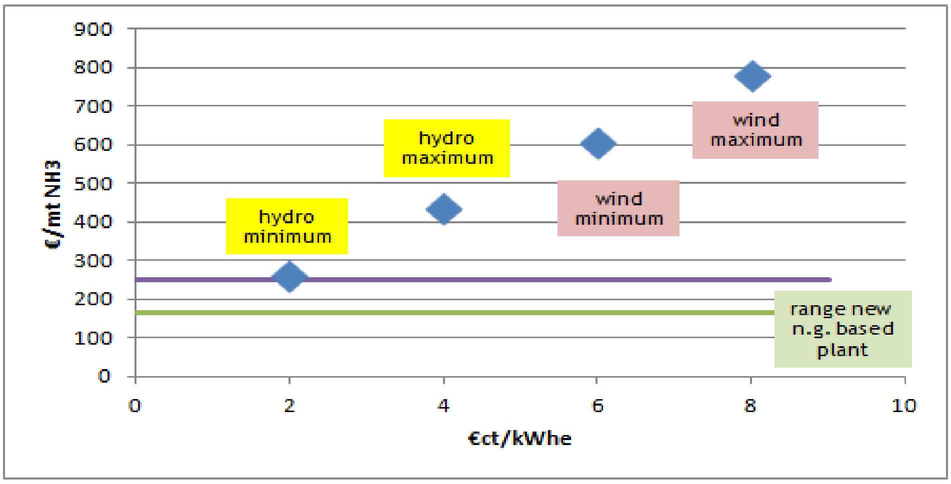
Annual costs M€	low CAPEX	high CAPEX
Depreciation	35	51
O&M	12	17

Source: CE Delft, own calculations.

Depreciation costs and OPEX were estimated at 12 and 4% of investments respectively.

Total specific production costs per tonne of ammonia were estimated based on estimated power production costs for hydropower and wind power in 2050 given in the recent SRREN report and by EWEA.

Figure 9 **Specific production costs for water electrolysis based ammonia in 2050**



Source: CE Delft, own calculations.

Production costs for natural gas based ammonia are given as a range, representing production costs for low and high investments and for a future natural gas price ranging between € 3 and 6 per GJ natural gas (see PWC, 2009). This is lower than the current natural gas price of € 6-8/GJ and excluding a possible future European energy tax.

Even at the low future estimate of natural gas of € 6/GJ, cheap hydropower can compete on price with conventional ammonia production provided that the decrease in capital costs as mentioned above is realised.

In all other cases the power availability is too low for a commercially operated ammonia plant and there is a surcharge for the production of ammonia varying between € 0–175/tonne NH_3 in case of hydropower based production and € 350-500/tonne NH_3 in case of wind-power based production (CO_2 prices of respectively € 0-100 and >€ 200/tonne CO_2).

In addition the fully commercially operated ammonia plant assumed in the assement requires a power availability of 95%. The system supplying the required power will have to be significant in size: approximately 700 MW_e. Both minima for hydropower and wind power refer to power generation with an insufficient high availability, 60% for hydropower and 50% for wind energy.

Such cheap and large renewable power resources with very high availability are scarce although they exist on Iceland[10], where cheap hydropower (€ct 2–3/kWh) could be harnessed.
An alternative to Iceland would be an integrated network with renewables that guarantees the high availability of sustainable power. However such high availability comes with a higher price, see Figure 9.

3.4.5 Limitations of this study

This assessment described above depends heavily on reliable future estimates for both the prices of both natural gas and renewable power. Based on the thorough special report on pathways towards a 100% renewable electricity system of the German Advisory Council on the environment, we can distinguish the following trends:

– The rise in oil prices is structurally underestimated by the IEA (UMWE (2011), Figure 3-8). This may be true for the gas price either.
– The growth of the renewable power is structurally underestimated in studies by IEA and the European Commission (UMWE (2011), Figure 3-4 and 3-5).

This indicates that our estimate of the feasibility of water electrolysis based ammonia production is likely to be conservative.

In addition this study focuses on the requirements within the current way of organising ammonia production. When decentralised small scale production of ammonia is considered the outcome may be different since at one hand one can benefit of peak-shaving tariffs for wind power. At the other hand limited use of production capacity due to limited availability of renewable power causes higher operational costs of the ammonia production plant since the capital costs of the installation have to be compensated by a considerably smaller production. Nevertheless, it may be interesting to look further into the combination of off-peak wind power and ammonia production.

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[10] See http://www.icelandexport.is/english/industry_sectors_in_iceland/energy_in_iceland/.

3.4.6 Conclusions on water electrolysis based ammonia

Ammonia production based on water electrolysis driven by renewable power sources is a proven technology to produce ammonia without causing GHG emissions.

Currently the production process is relatively capital intensive but given the research programs to decrease the capital intensity, it is fair to assume that by 2020 the capital costs involved with the production of ammonia are equal for a modern version of a conventional ammonia plant and a water electrolysis based ammonia plant.
This comparison excludes operational costs for the use of respectively natural gas and sustainably produced electric power. Only when cheap electric power is available (€ct 2-3/kWh) in abundance (700 MW_e) the price difference may be negligible.

Currently this situation exists on Iceland. In the future integrated network with renewables that guarantee the high availability of sustainable power may provide a solution.

This study focuses on the requirements within the current way of organising ammonia production. It may be interesting to look further into the combination of off-peak wind power and ammonia production.

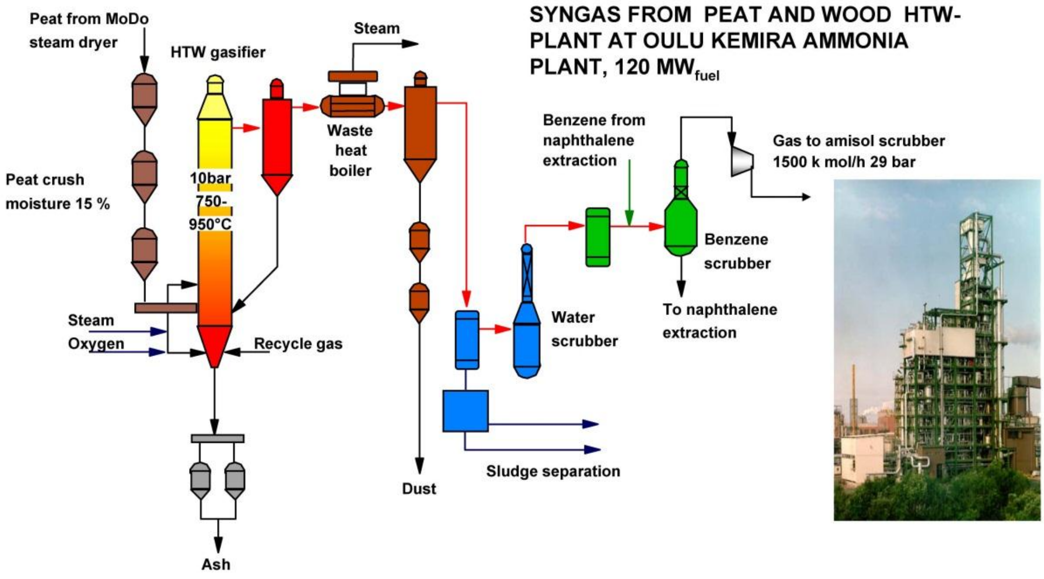
3.5 Biomass gasification and ammonia production from syngas

3.5.1 The production process

Biomass based ammonia production will consist of two largely separate steps:

- biomass gasification with oxygen and steam and subsequent production of hydrogen from the produced syngas;
- ammonia production with the Haber-Bosch process from hydrogen and nitrogen.

Figure 10 Oulu Kemira plant lay out



Source: CE, 2008.

Industrial scale biomass and peat gasification and associated ammonia production has already been proved technically feasible in the late eighties at the Kemira Oulu ammonia production plant in Finland. The gasification technology concerned a pressurised bubbling fluidised bed with oxygen and steam as oxidising reactants. The plant was shut down after cheap Russian natural gas became available at the Finnish market.
A second large (>100 MW_{th}) unit was realised in Berrenrath, Germany and produced syngas for commercial methanol production.

The applied HT Winkler gasification technology is still available and is owned by the German firm Krupp-UHDE. A 250 MW_{th} gasification plant is planned to be realised in the Värmland province in Sweden.
GTI is another technology supplier and can supply pressurised bubbling fluidised bed gasifiers of several tens of MW's. Its largest plant is the Skyde CHP plant in Denmark.

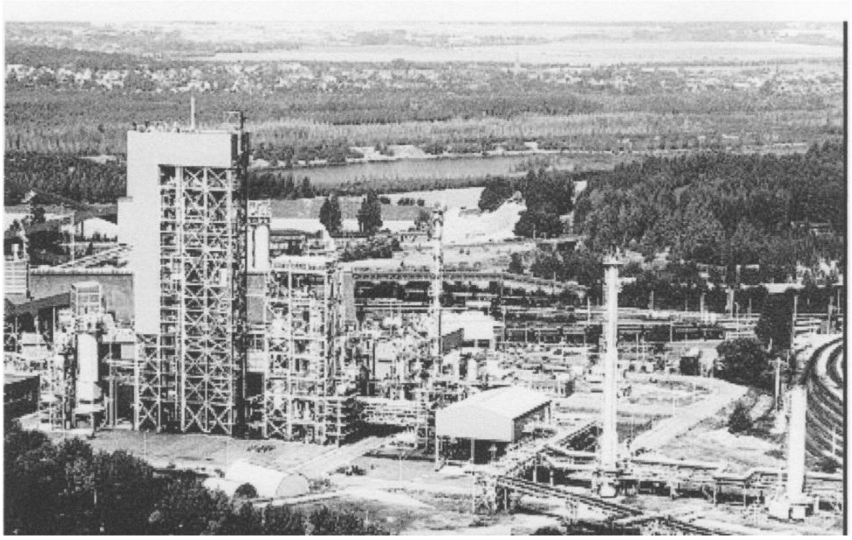
As indicated by both examples the technology has been available on a commercial scale.

A biomass gasification system with associated ammonia plant would include:

- a high temperature syngas cleaning (ceramic filter, sulphur and halogens absorbens);
- a reformer for conversion of the methane present in the product gas;
- a shift reactor for production of additional hydrogen production by conversion of CO into CO_2 by a reaction with steam;
- a high pressure membrane for hydrogen isolation;
- waste heat recovery heat exchangers for high pressure steam generation;
- an air separation plant for providing oxygen to the gasifier and nitrogen to the Haber-Bosch process;
- a gas turbine power island for generation of required power.

Given the size of gasifiers that have been operational, a 2,000 tonne per day world scale ammonia plant would probably require two 400 MW_{th} gasifiers.

Figure 11 **HT Winkler gasifier at Berrenrath**



Source: CE, 2008.

According to literature the total gasification-ammonia synthesis process will have a net energy efficiency of approximately 60% (compared with 65-70% for a new natural gas based plant) and will require 2.7 metric tonne of biomass per tonne of ammonia. At the current annual ammonia production in Europe of 14 Mtonne this would require 38 Mtonne of biomass. What this means in terms of availability of sustainable biomass in Europe is addressed in Annex B. For gasification clean wood is the preferred fuel/feedstock.

3.5.2 Benchmark on the GHG emissions

The proposed benchmark level for emissions per tonne ammonia amounts to 1.61 tonne CO_2 eq. per tonne NH_3 for conventional ammonia production.
As described above the water electrolysis route consists of two steps:

- the production of hydrogen based on electrolysis of water using renewable power;
- the synthesis of ammonia from hydrogen and nitrogen by means of the Haber-Bosch process.

If the hydrogen is produced by gasification of clean sustainable sourced biomass, there are no GHG emissions related to the production of hydrogen. The Haber-Bosch process is an exothermic process, which means that it generates heat, it only needs cooling and therefore it does not generate GHG emissions. Therefore the biomass gasification based ammonia production is a way to realise 100% reduction in GHG emissions.

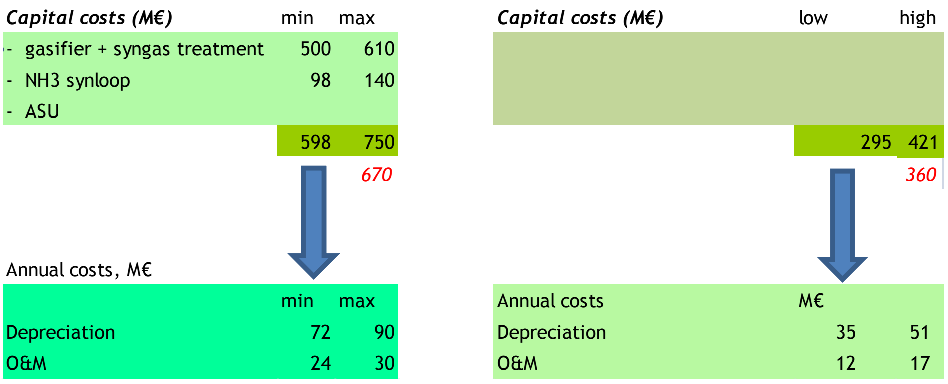
3.5.3 Indicative assessment of future biomass gasification based plants

As described in Section 3.1 on the development of the price of biomass in relation to fossil fuel prices the actual price development is very insecure. However, in most studies the price of biomass technology is expected to decrease moderately, but at the same time the prices of energy crops and forestry fuels are expected to evolve similarly to conventional fuel price (UMWE (2011), Figure 3-10).

The above indicates that in general the current price ratios are assumed.

We therefore adopted current market prices as an indication of the 2050 prices to make the assessment. If fossil fuel prices increase faster than the prices for biomass this is a conservative estimate. However, strong rises in fossil fuel prices only occur on the long term if fossil fuels become scarce, in that case it is fair to assume a battle for biomass. In that situation biomass also will show a sharp price rise if all sourcing occurs sustainable.

Figure 12 **Comparison of fuel/power consumption and CAPEX/OPEX for conventional and biomass based ammonia production for a 2,000 tpd ammonia plant at 95% availability**



Capital costs (M€)	min	max
- gasifier + syngas treatment	500	610
- NH3 synloop	98	140
- ASU		
	598	750
		670

Annual costs, M€

	min	max
Depreciation	72	90
O&M	24	30

Capital costs (M€)	low	high
	295	421
		360

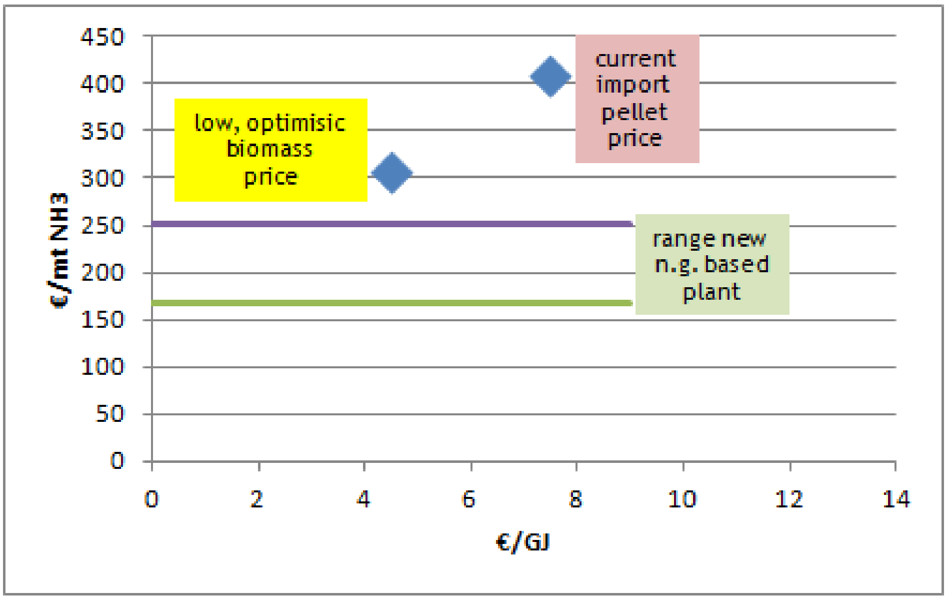
Annual costs	M€	
Depreciation	35	51
O&M	12	17

Source: CE Delft, own calculations.

The capital costs related to the production of ammonia are estimated as follows. For a 2,000 tonne per day of ammonia sized plant, investment costs for gasifiers and syngas treatment are estimated to amount to M€ 500-610[11], double that of a world scale natural gas based plant of the same production capacity.
This makes that the annual costs for depreciation, operation and management are double as high in a biomass gasification based ammonia plant as in a conventional ammonia plant.

In addition there are the raw material based costs.
Taking into account biomass costs of € 4.5-7.5 per GJ for clean wood total production costs are estimated at € 300-400 per Mtonne NH_3.
A price of € 4.5 per GJ is representative for market prices for EU domestic wood chips and for **production costs** for pellets imported from Brazil.
A € 7.5/GJ fee is representative for current market prices for pellets imported from North America.

Figure 13 **Specific production costs for biomass based ammonia**



Source: CE, own calculations.

The current price for natural gas varies between € 6-8/GJ. Therefore we used the average value of € 7/GJ in our calculations.
Based on these assumptions the production of ammonia based on biomass gasification has a surcharge of € 50-150/tonne NH_3 depending on the price of the biomass.
At a benchmark emission of 1.6 tonnes of CO_2 eq./tonne this requires a CO_2 price varying between € 31-93/tonne of CO_2 eq. to reach breakeven. This implies that even when competing with the very advanced ammonia plants that meet the benchmark emission of 1.6 tonnes of CO_2 eq./tonne of NH_3 produced the breakeven point may be at a CO_2 eq. price of € 31/tonne. This may be feasible if the gasification plant is integrated with other wood based industries.

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[11] See Hamelick (2004), BAL-fuel (1997), Rollins (2002).

3.5.4 Potential bottlenecks

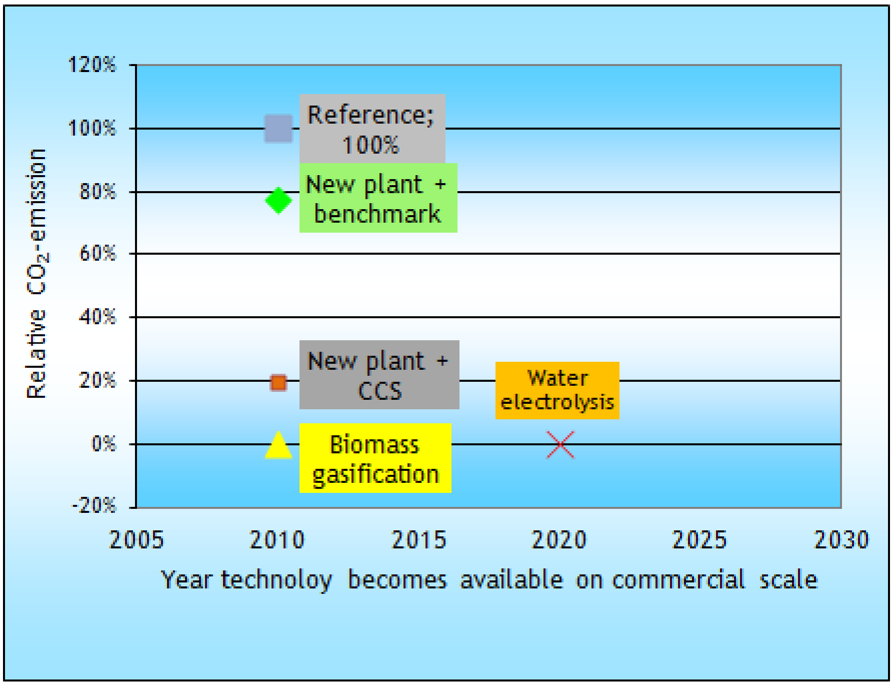
As described in the chapter on the battle of biomass we already described that when sourcing biomass one should be aware of biodiversity loss due to indirect land use, see Section 3.1.

We assume that biomass may be considered carbon natural if it is derived from sustainably managed forests as the amount of biomass harvested from sustainably managed forests is smaller or equal to regrowth.
However, reports such as 'The upfront carbon debt of biomass' suggest that looking from a different perspective - the individual tree at a certain location - it takes decades for biomass from an elder tree to become carbon natural.

3.6 Conclusions on ammonia

The main characteristics and scores of the different technologies discussed in this chapter are summarised in Figure 14 and Table 9.

Figure 14 Schematic overview of what options there are to lower the carbon footprint of an ammonia plant compared to the reference



Source: CE Delft, own calculations.

Table 9 **Overview of environmental and economic aspects for different types of ammonia production**

Current EU: average ammonia plant		New EU		Water electrolysing		Biomass gasification
		New plant BAT REF	New plant BAT REF + CCS	Cheap hydropower 2-4 €ct/kWh	Wind power 6-7.5 €ct/kWh	
Production capacity (ktonne/y)	200-700	500-1,000	500-1,000	694	694	694
Environmental aspects						
Fossil and biomass fuel and feedstock consumption	100% 36 GJ/tonne NH_3	80%	20%	0	0	0
Electricity consumption (kWh/tonne-NH_3)	0	0	0		8.620	0
CO_2 emission (tonne/tonne NH_3)	2,1	1,6 -22%	0,4 -81%	0 -100%	0 -100%	0 -100%
Economic aspects						
CAPEX (greenfield, M€)	Not relevant	360[12]	400	280-490	500-610	
OPEX (incl. energy, excl. depreciation costs)	100%	80%	90%	80-150%	250-350%	150-200%

Source: CE Delft, own calculations.

Table 9 and Figure 14 show that both biomass gasification and wind powered electrolysis based ammonia production have the potential to produce ammonia on a large scale without emission of GHG.
At a carbon price of € 30/tonne CO_2 eq. the breakeven point of ammonia production based on low cost biomass is reached. In this case the source of biomass necessarily is a rest stream of other wood based industries. Biomass from other sources may from a sustainability point of view be less attractive because of alleged ILUC aspects, see Section **Fout! Verwijzingsbron niet gevonden.**

The capital costs related to large scale electrolysis based ammonia production are expected to be enough decreased by 2020 to be a viable alternative, without other sustainability issues related to it. However, the high availability of low cost sustainably produced electricity may remain a bottleneck.

Nevertheless, Iceland offers the required availability of cheap renewable energy. Given the low energy prices the production of ammonia on Iceland based on water electrolysis may prove even cheaper than conventional ammonia production.

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[12] For a 700 ktonne/year plant.

4 Conventional olefins production

4.1 Introduction to the sector and market

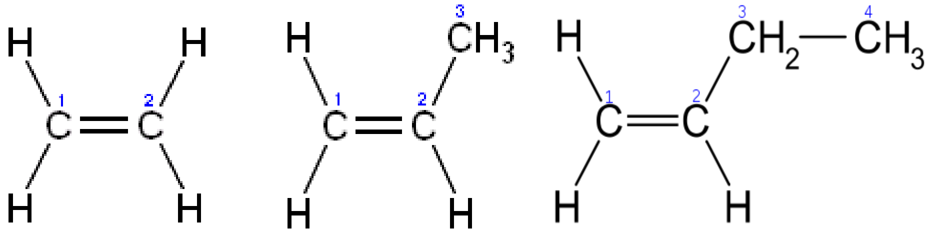
Current production volumes and applications

Olefins are basic chemical compounds, such as ethylene (C_2H_4), propylene (C_3H_6) and various butylene (C_4H_8) isomers. These chemicals are used as a building block in a broad range of plastic materials.

Ethylene is the most important basic petrochemical for making plastics ethylene oxides and other chemicals, in 2006 one third of the basic petrochemicals produced worldwide was ethylene. Propylene was the second most produced basic petrochemical. The Western European production of ethylene and propylene varied between 2006 and 2010 around the 20.3 +/- 1.5 million tonnes of ethylene per year and around the 15 +/- 0.5 million tonnes of propylene[13]. Over the last five years the productions capacity in Western Europe of these basic chemicals seems to have stabilised.

Significant expansion of capacity is reported to be under construction in India and China.

Figure 15 Chemical formula's of respectively ethylene (C_2H_4), propylene (C_3H_6) and 1-butylene (C_4H_8)



4.2 Production process

Most of the olefins and a considerable part of the aromatics in Europe are produced by steam cracking of naphtha (73%), gasoil (10%) and gaseous feedstock (17%) like LPG (butane and propane) and ethane.

Steam cracking of naphtha[14]

Steam cracking of naphtha is a petrochemical process in which naphtha is broken down into olefins and aromatics.

During the steam cracking the naphtha is diluted with steam and briefly heated in a furnace without the presence of oxygen. Typically, the reaction temperature is very high, at around 850°C, but the reaction is only allowed to

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[13] APPE site (Oct 3rd, 2011), http://www.petrochemistry.net/capacity-and-production-propylene-and-derivatives.html. These numbers are the production numbers of pure ethylene and propylene, all derivates are excluded.

[14] Sources: http://en.wikipedia.org/wiki/Steam_cracking#Steam_cracking and 'Petrochemicals from oil, natural gas, coal and biomass: energy use, economics and innovation' PhD thesis by Tao Ren, Utrecht University, The Netherlands, 2009.

take place very briefly. In modern cracking furnaces, the residence time is reduced to milliseconds to improve yield, resulting in gas velocities faster than the speed of sound. After the cracking temperature has been reached, the gas is quickly quenched to stop the reaction in a transfer line heat exchanger or inside a quenching header using quench oil.

The products produced in the reaction depend on the composition of the feed, the hydrocarbon to steam ratio and on the cracking temperature and furnace residence time.

Light naphtha gives product streams rich in olefines such as ethylene, propylene and butadiene. Full range and heavy naphtha feeds give some of these, but also give products rich in aromatics like benzene, toluene and xylene. The higher cracking temperature (also referred to as severity) favours the production of ethylene and benzene, whereas lower severity produces higher amounts of propylene, C4-hydrocarbons and liquid products. The process also results in the slow deposition of coke, a form of carbon, on the reactor walls. This degrades the efficiency of the reactor, so reaction conditions are designed to minimise this. Nonetheless, a steam cracking furnace can usually only run for a few months at a time between decokings. Decokes require the furnace to be isolated from the process and then a flow of steam or a steam/air mixture is passed through the furnace coils. This converts the hard solid carbon layer to carbon monoxide and carbon dioxide. Once this reaction is complete, the furnace can be returned to service.

Naphtha

Naphtha is currently obtained in oil refineries as one of the intermediate products from the distillation of crude oil. It is an intermediate between the lighter gasoline and the heavier kerosene. In the world market, several types of naphtha are being traded. The kinds of naphtha that are being used in steam cracking are:

- Light naphtha, also called paraffinic naphtha (in the range C_5H_{12}-C_6H_{14}) is a by-product of oil refinery. A small amount of light naphtha also comes from natural gas condensates in oil and natural gas fields. Steam cracking of light naphtha leads to a high yield of light olefins. Naphtha made from Fischer-Tropsch (FT) processes, or FT naphtha, is also a light naphtha that leads to an higher ethylene yield than regular light naphtha.
- Full range naphtha: This is a mixture of light and heavy naphtha (in the range of C_5H_{12}-C_9H_{20}). It is the most common type of naphtha used in steam cracking.

4.3 Current level of energy requirement and greenhouse gas emissions

The combined process and steam emissions related to this process are estimated to add up to 35 Mtonne of CO_2 equivalents, accounting for about 18% of the total GHG emissions from the chemical industry in the EU[15]. This is partly explained by the high amounts of olefins produced, partly by the significant energy use related to steam cracking.

Opportunities for energy improvements and GHG emission reduction

According to the report of Ecofys and others the benchmark should be put between 0.5 and 0.7 tonne CO_2 eq./tonne product (mix of olefins and aromatics but primarily ethylene).

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[15] Methodology for the free allocation of emission allowances in the EU ETS post-2012; report ordered by the European Commission and carried out by Ecofys and partners.

Tao Ren and others[16] compared the energy use in conventional steam cracking with more innovative olefin technologies to get an indication for the room for energy efficiency increase. The main findings were:

- State-of-the-art naphtha steam cracking technologies can lead to savings of about 20% compared to the current world average energy use in steam cracking (0.84 tonne CO_2/tonne olefins[17]).
- Catalytic olefin technologies as an alternative processes utilising naphtha, can lead to savings of 10-20% compared to the energy use in state-of-the-art naphtha steam cracking technologies.
- Advanced naphtha steam cracking technologies in the pyrolysis section, such as advanced coil and furnace materials, can together lead to savings of up to about 20% compared to the energy use in state-of-the-art naphtha steam cracking technologies (0.67 tonne CO_2/tonne olefins. Together with the potential improvements in the compression and separation sections, savings of up to 30% are possible compared to the energy use in state-of-the-art naphtha steam cracking technologies (0.59 tonne CO_2/tonne olefins.

The state-of-the-art naphtha steam cracking is already been applied and alternative and advanced processes are already been applied to a certain extend or are being offered for commercialisation and can be widely used in the coming decades.

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[16] Ren T, Patel M, Blok K. 'Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes' Energy, 2006;31(4): 425-451.

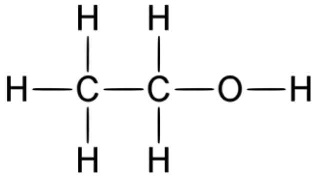
[17] 63% ethylene and 27% propene.

5 Low carbon olefins

5.1 Bioethanol as the key to low carbon olefins

When looking for breakthrough technologies to produce olefins, ethanol appears to be the key. Ethylene is easily made from ethanol and from ethylene all other olefins can be derived. Therefore below the production of ethylene from ethanol is discussed followed by additional information on the conversion of ethylene to propylene and butylene.

Figure 16 Chemical formula of ethanol



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-H$$

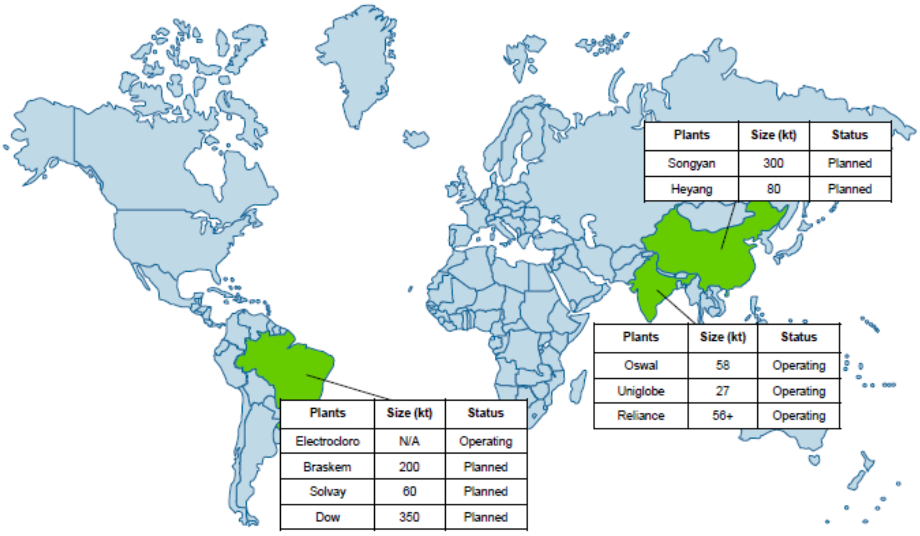
5.2 Ethylene from bioethanol

Sugarcane and sugar beets are the most efficient producers of bioethanol with a crop yield of >5 m^3/ha. Most experience is based on Brazilian sugarcane. This because of the long standing Brazilian policy to produce bioethanol based on sugarcane to decrease dependency on foreign oil.
Large scale bioethanol production on the basis of European grown sugar beets is possible for the same market price.

5.2.1 Status of the technology

Dehydration of bioethanol is a commercially offered technology (see Table 10).

Figure 17 Overview of bioethylene from ethanol initiatives



Plants	Size (kt)	Status
Songyan	300	Planned
Heyang	80	Planned

Plants	Size (kt)	Status
Oswal	58	Operating
Uniglobe	27	Operating
Reliance	56+	Operating

Plants	Size (kt)	Status
Electrocloro	N/A	Operating
Braskem	200	Planned
Solvay	60	Planned
Dow	350	Planned

Source: Accenture, 2009.

The technology was applied for commercial production of ethylene in the 1950s and 1960s, but was in most parts of the world abandoned when cheaper naphtha based ethylene became available. With the desire of substituting fossil fuels, reducing greenhouse gas emissions and creating a green image, there is renewed interest in this technology. A number of initiatives is already operational or has been announced (see Figure 17).

Many initiatives are being developed by local authorities to increase capacity. For example in the Rotterdam area the Rotterdam Climate Initiative is aiming at realisation of a 500 ktonnes/year bioethylene plant and injection of the produced bioethylene in the regional ARG ethylene pipeline network. An advice to the national government recommends support for this initiative.

5.2.2 Benchmark on CO_2 and GHG emissions

According to the report of Ecofys (2009) the benchmark should be put between 0.5 and 0.7 tonne CO_2 eq./tonne product (mix of olefins and aromatics but primarily ethylene). Tao Ren and others[18] mentioned emissions of 0.59-0.67 tonne CO_2 eq./tonne product for advanced ethylene production methods (20-30% more energy efficient than the current state-of-the-art methods).

5.2.3 Achievable reduction in energy consumption and GHG emissions

When producing ethylene from bioethanol the energy consumption related to the production of ethylene is 1 GJ/ton. When assuming that the required energy was supplied by natural gas the related GHG emissions are 0.057 tonne CO_2 eq./tonne product. This is a reduction of 90% in GHG emissions compared to the benchmark of 0.5 tonne CO_2 eq./tonne product mentioned by Ecofys.

Since GHG are a global problem one should not only compare the production steps in the European industry but also take into account the energy content of the raw materials to account for their production too.

Carbon footprint of naphtha based ethylene

Therefore we compare carbon footprints. According to Ecoinvent the carbon footprint and energy demand of the European fossil fuel based ethylene production amounts to 4.6 tonne CO_2 eq./tonne and 69 GJ/ton, of which 9.9 GJ/tonne are related to the production of ethylene and can be lowered by maximally 50%. The carbon footprint related to naphtha is 3.12 tonne CO_2 eq./tonne (JEC, 2007)[19].
This means that the benchmark footprint and energy use for European fossil fuel based ethylene amounts to 3.9 tonne CO_2 eq./tonne and 64 GJ/ton.

Carbon footprint of bioethanol based ethylene

The estimation of the carbon footprint and the energy demand are based on the assumption that ethylene will be produced from imported Brazilian ethanol.
According to the RED[20] and associated information from JEC (2007) and the Biograce GHG calculation tool, sugarcane based ethanol has a carbon footprint of 0.65 tonne CO_2 eq./tonne and has an energy demand of 28 GJ/ton, of which

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[18] Ren, T., Patel, M., Blok, K. 'Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes' Energy, 2006;31(4): 425-451.

[19] JEC, 2007 (http://ies.jrc.ec.europa.eu/uploads/media/WTT_App_1_010307.pdf) says the carbon content of naphta is 85%, equivalent with 3.12 tonne CO_2 eq./ton. Accoridng to list of GHG emission factors used by the Dutch government (http://www.broeikasgassen.nl/docs/Nederlandse%20lijst%20energiedragerlijst%20publicatieversie.pdf) the emission factor of naphta equals 3.225 tonne CO_2 eq./tonne nafta.

[20] Renewable Energy Directive.

27 biobased. Production of bioethylene from ethanol requires an additional 1 GJ/tonne of sugarcane (Ren, 2009) and will proceed with an efficiency of approximately 97%. The total carbon footprint and energy demand amount to respectively 1.22 tonne CO_2 eq./tonne and 49.7 GJ/ton, of which 5 GJ is of fossil origin.

Achievable reduction

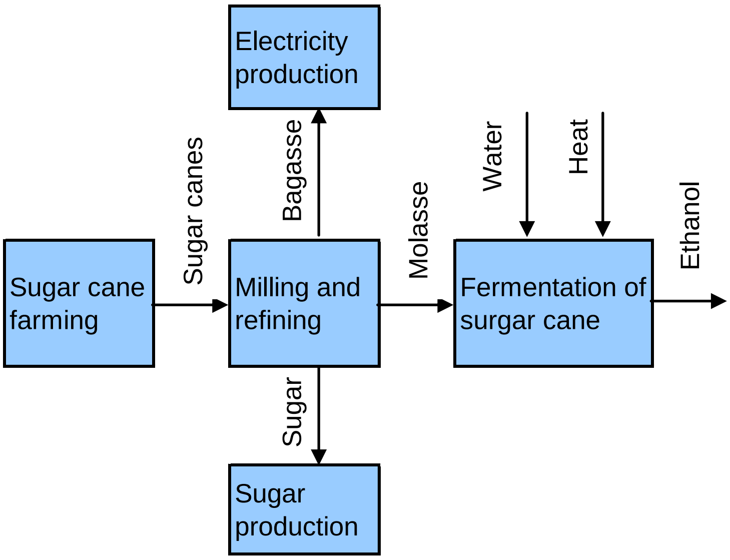
This means that a shift to bioethanol would allow for a reduction of 80-90% in GHG emissions compared to the current state-of-the-art and a reduction of 69% compared to the most advanced naphtha cracking options mentioned in Section 4.3.

This reduction can increase even more since the production of ethanol from sugarcane shows significant potential for improvement according to studies by Macedo et al. (2004)[21] and Oliviera (2005)[22].

5.2.4 Production of bioethanol from sugarcane [23]

Most of the industrial processing of sugarcane in Brazil is done through an integrated production chain, allowing sugar production, industrial ethanol processing, and electricity generation from by-products. The typical steps for the production of ethylene from sugarcane include milling and refining, fermentation and distillation to produce ethanol, see Figure 18.

Figure 18 **Schematic representation of the production process from sugarcane to ethanol**



Milling and Refining

Once harvested, sugarcane is usually transported to the plant by semi-trailer trucks. After quality control sugarcane is washed, chopped and shredded by revolving knives. The feedstock is fed to and extracted by a set of mill combinations to collect a juice, called garapa in Brazil, that contains 10–15% sucrose and bagasse, the fiber residue. The main objective of the milling process is to extract the largest possible amount of sucrose from the cane, and

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[21] Macedo, I. d. C., M. R. L. V. Leal and J. E. A. R. Da Silva: 2004, Assessment of greenhouse gas emissions in the production and use of fuel ethanol in Brazil. Accessible via: Secretariat of the Environment of the State of São Paulo, Brazil.

[22] Dias de Oliveira, M.E., Vaughan, B. E., Rykiel, E. J. 2005. ‘Ethanol as fuel: Energy, carbon dioxide balances, and ecological footprint.’ BioScience 55(7): 593-602.

[23] Source: http://en.wikipedia.org/wiki/Biofuel_in_Brazil.

a secondary but important objective is the production of bagasse with a low moisture content as boiler fuel, as bagasse is burned for electricity generation (see below), allowing the plant to be self-sufficient in energy and to generate electricity for the local power grid. The cane juice or garapa is then filtered and treated by chemicals and pasteurised. Before evaporation, the juice is filtered once again, producing vinasse, a fluid rich in organic compounds. The syrup resulting from evaporation is then precipitated by crystallisation producing a mixture of clear crystals surrounded by molasses. A centrifuge is used to separate the sugar from molasses, and the crystals are washed by addition of steam, after which the crystals are dried by an airflow. Upon cooling, sugar crystallises out of the syrup. From this point, the sugar refining process continues to produce different grades of sugar, and the molasses continue a separate process to produce ethanol.

Fermentation and distillation

The resulting molasses are treated to become a sterilised molasse free of impurities, ready to be fermented. In the fermentation process sugars are transformed into ethanol by addition of yeast. Fermentation time varies from four to twelve hours resulting in an alcohol content of 7-10% by total volume (°GL), called fermented wine. The yeast is recovered from this wine through a centrifuge. Making use of the different boiling points the alcohol in the fermented wine is separated from the main resting solid components. Fractional distillation can concentrate ethanol to 95.6% by weight (89.5 mole%). The mixture of 95.6% ethanol and 4.4% water (percentage by weight) is an azeotrope with a boiling point of 78.2°C, and cannot be further purified by distillation. Because of the difficulty of further purification, 95% ethanol/ 5% water is a fairly common solvent.

5.2.5 Production of ethylene from ethanol

Dehydration of bioethanol to ethylene

Ethanol is catalytically dehydrated to produce ethylene according to the following chemical reaction.

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$

The reaction is endothermic. Also the reaction is reversible with the equilibrium being favoured by higher temperatures (>375°C at a pressure 3.5 bar) and hindered by higher pressures and water vapour in the feed. As recovery of unconverted ethanol for recycle is energy and capital intensive, reaction conditions enabling >99% conversion of ethanol are usually preferred. The selectivity for ethylene varies with the type of process applied between 94-98% in commercial installations, see Table 10.

Table 10 Ethanol dehydrogenation technology suppliers

Technology supplier and process	Type of proces	Ethylene yield	Status
Lummus fixed bed process	Isothermal	94%	Commercial
Lummus fluidised bed process	Isothermal	99%	Pilot plant
Halcon/SD fixed bed process	Isothermal	96%	Commercial
NIKKI/JGC process	Isothermal	97%	Pilot plant
Petrobras process	Adiabatic	98%	Commercial

A typical selectivity breakdown at >99% conversion is shown in Table 11.

Table 11 Conversion selectivity for chemicals during a >99% conversion of ethanol by dehydrogenation

Ethanol selectivity	%
Ethylene	96.80
Ethane	0.50
Propylene	0.06
Butylenes	2.40
Acetaldehyde	0.20

Minor amounts of methane, carbon monoxide and dioxide, ethyl ethers and hydrogen are also formed.

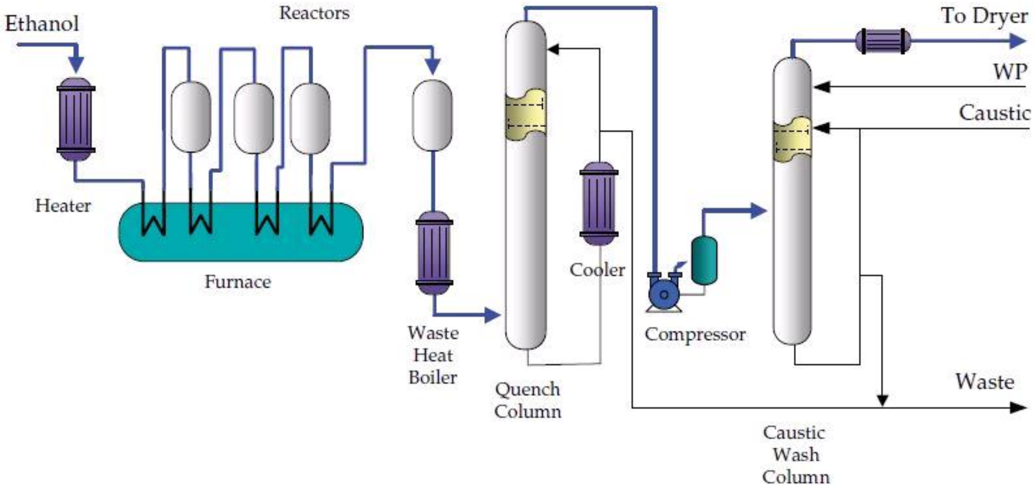
Raw material requirements and specifications

Table 12 Raw material specifications

Raw material specifications	
Ethanol (typical composition)	Ethanol 95% vol
Acetaldehyde	100 ppm wt
Fusel oil	100 mg/l
Acids	10 mg/l
Methanol	0.3 vol%
Sulphur compounds (as S)	0.5 ppm wt
Catalyst	Alumina or Silveroxide catalysts

Process flow sheets

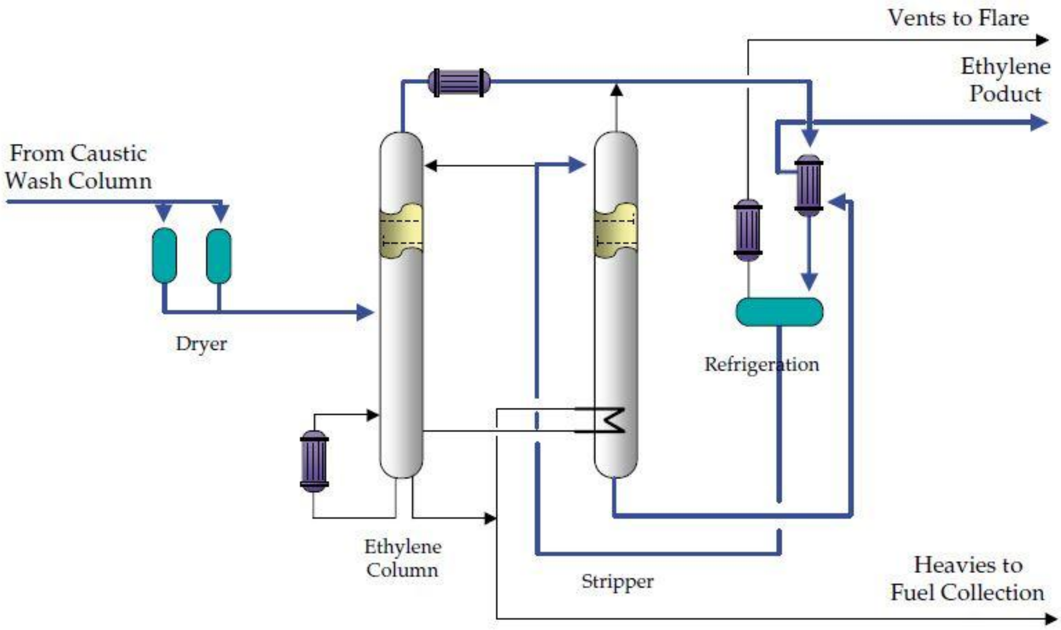
Figure 19 Flow sheet of the conversion of ethanol to ethylene by dehydrogenation



Source: Chematur brochure: Ethylene from Ethanol.

The plants can be designed for crude, intermediate and polymer grade ethylene depending on the product application.
The flow sheets in Figure 19 and Figure 20 show a typical polymer grade application. The process train for intermediate grade ethylene will be the same except that the caustic wash column and the stripper will be deleted. Crude grade ethylene is taken out after the quench column.

Figure 20 Flow sheet of the additional columns required for high purity polymerisation grade ethylene



Source: Chematur brochure: Ethylene from Ethanol.

There are no regeneration facilities for the catalyst included in the plant design, since these are considered obsolete because of the expected long life time of the catalyst.

5.2.6 (Estimated) investments and operational costs

A broad estimation of production costs and profitability

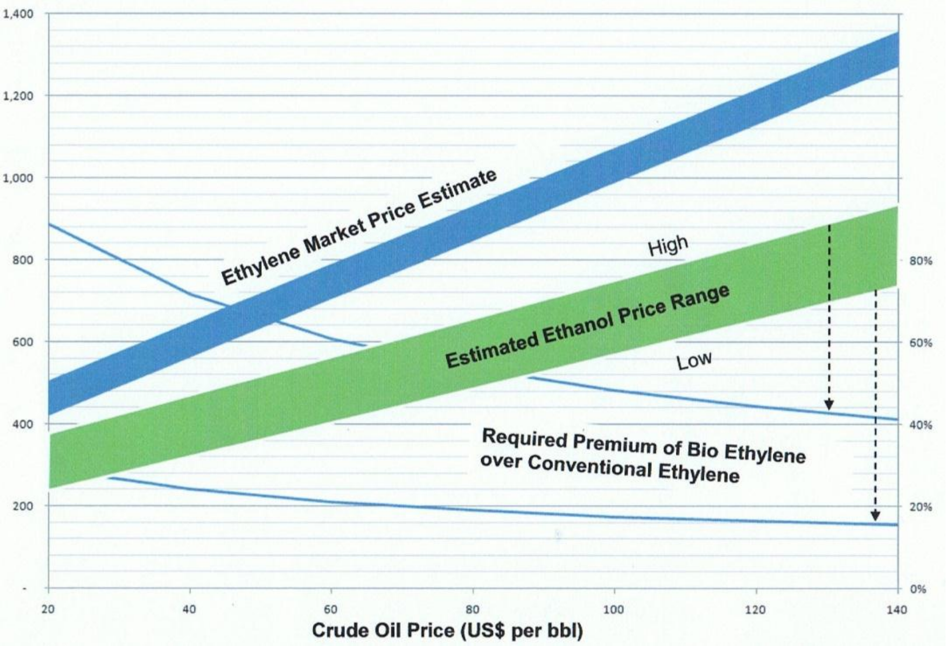
According to an economic feasibility study commissioned by Deltalinques and the Rotterdam Climate Initiative bioethylene could be produced in the Rotterdam area at prices that range from 20-50% above that of fossil based ethylene: approximately € 200-500 per tonne higher than the price of conventional ethylene – assuming a crude price of US$ 90/barrel.

The analysis refers to imported Brazilian ethanol with current import taxation. Given the considered amount of ethanol, the authors concluded that currently import of Brazilian ethanol was the only realistic option.

The authors of the Accenture study (2009) used conservative basic assumptions. For example, for the selectivity for dehydrogenation of ethanol a value of 91% was considered, while suppliers of commercial technology indicate that the selectivity of modern processes ranges between 94-99%.

Therefore we made our own calculation for an imaginary plant of 500 ktonne/year in the Rotterdam area, as is illustrated in Figure 22.

Figure 21 **Premium on price of bioethylene over conventional ethylene as a function of crude price**



Source: Accenture, 2009.

As described in Section 3.1 on the development of the price of biomass in relation to fossil fuel prices the actual price development is very insecure. However, in most studies the price of biomass technology is expected to decrease moderately, but at the same time the prices of energy crops and forestry fuels are expected to evolve similarly to conventional fuel price (UMWE (2011), Figure 3-10).

The above indicates that in general the current price ratios are assumed

This is in line with our analysis that for projections of the post-2020 prices for biomass in general current price ratios with fossil based fuels are assumed. We therefore adopted current market prices as an indication of the 2050 prices to make the assessment. If fossil fuel prices increase faster than the prices for biomass this is a conservative estimate. However, strong price rises in fossil fuel prices only occur on the long term if fossil fuels become scarce, in that case it is fair to assume a battle for biomass. In that situation biomass also will show a sharp price rise if all sourcing occurs sustainable.

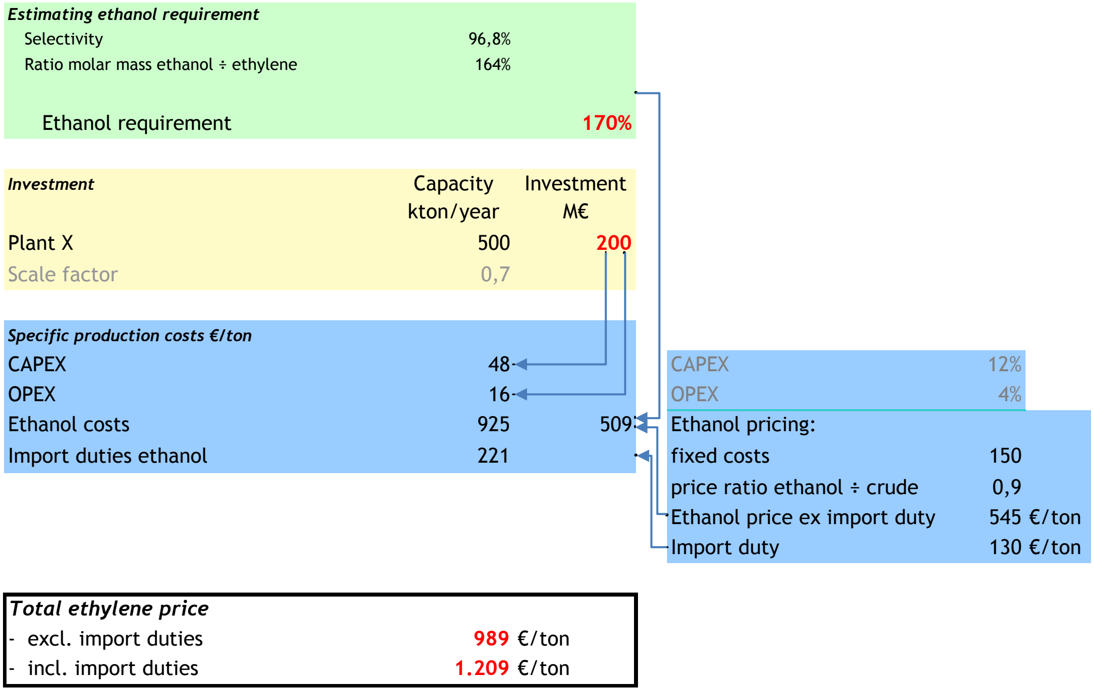
The ethanol requirement is determined by the stoichiometrical relation resulting from the reaction equation describing the conversion of ethanol to ethylene and the selectivity of the conversion to ethylene.
Investments related to a plant with a production capacity of 500 ktonne/year are reported to be € 200 million (Accenture, 2009).

The operational costs exclusive the ethanol and import duties, i.e. the CAPEX and OPEX follow from the investment of € 200 million, respectively 12 and 4%.

The operational costs related to the ethanol are 170% of the ethanol price, since you need 170 tonne ethanol per tonne ethylene produced. The same logic applies to the operational costs caused by import duties.

The current bioethanol prices are significant higher than the production costs in Brazil. If one only had to pay the production costs of ethanol the price would be 509 €/tonne bioethanol instead of 925 €/tonne.

Figure 22 Calculation of bioethylene production costs



Estimating ethanol requirement	
Selectivity	96,8%
Ratio molar mass ethanol ÷ ethylene	164%
Ethanol requirement	170%

Investment	Capacity kton/year	Investment M€
Plant X	500	200
Scale factor	0,7	

Specific production costs €/ton		
CAPEX	48	
OPEX	16	
Ethanol costs	925	509
Import duties ethanol	221	

CAPEX	12%
OPEX	4%
Ethanol pricing:	
fixed costs	150
price ratio ethanol ÷ crude	0,9
Ethanol price ex import duty	545 €/ton
Import duty	130 €/ton

Total ethylene price	
- excl. import duties	989 €/ton
- incl. import duties	1.209 €/ton

Source: CE, own calculations, in this figure ton implies metric ton = tonne.

For the following reasons we decided to work with the bioethanol price exclusive import duties:

1. In Europe production costs of bioethanol based on sugar beet are currently about 500 €/tonne (FAO, 2008). Large scale production of bioethanol is emerging in the European Union, predominately in France.
2. Import duties are put in place to protect the European market, this is no longer necessary at the current price levels.

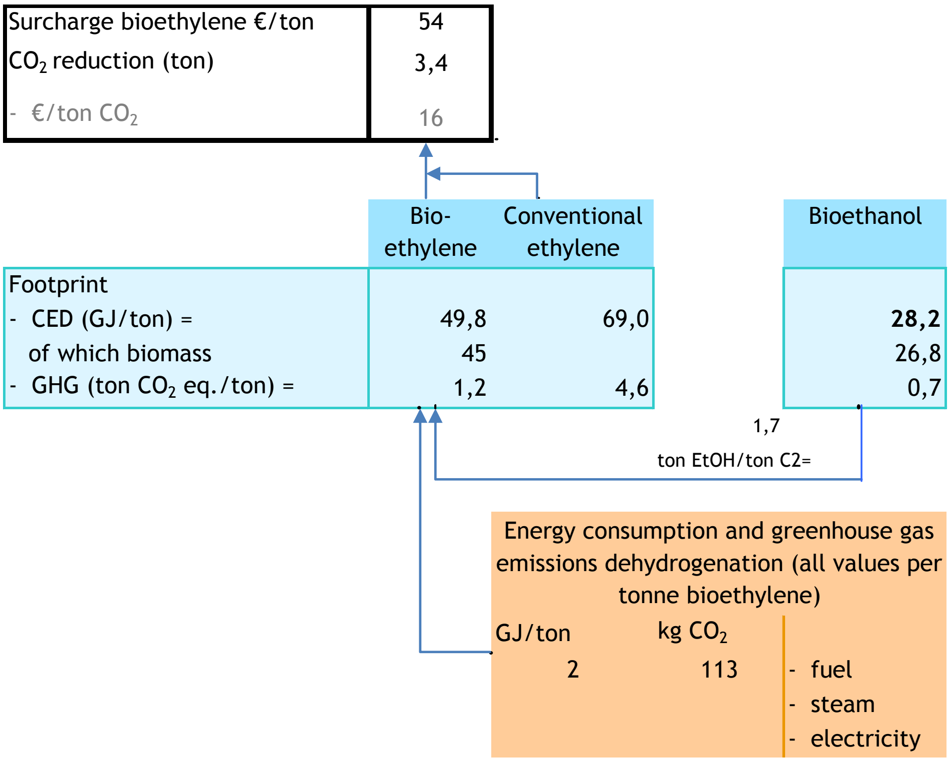
Feasibility surcharge bioethylene

At a price for bioethanol of 545 €/tonne bioethylene has a surcharge of € 54/tonne ethylene compared to naphtha based ethylene. This surcharge is caused by the higher price of bioethanol compared to naphtha.

There are different ways of looking at this:

1. CO_2 rights are expected to solve the price difference between bioethanol and naphtha. At a bioethanol price of 545 €/tonne the required CO_2 reduction cost is 16 €/tonne. The current price of CO_2 rights varies between € 12-13 per tonne. The projected CO_2 reduction costs in 2050 varies between 28-70 €/tonne (UMWE(2011), Table 3-2). The calculation of the CO_2 reduction costs is explained in Figure 23.
2. The cost impact of bioethylene in the final consumer product is typically 1%. This implies that when targeting the right applications will allow to obtain 'Green' branding at a very small cost impact to end customer.

Figure 23 Schematic representation of calculation CO_2 reduction costs



Source: CE, own calculations.

5.2.7 Sustainability aspects of the bioethanol production in Brazil[24]

The rapid expansion of ethanol production from sugarcane in Brazil has raised a number of questions regarding its negative consequences and sustainability. Negative impacts such as future large-scale ethanol production from sugarcane might lead to the destruction or damage of high-biodiversity areas, deforestation, degradation or damaging of soils through the use of chemicals and soil decarbonisation, water resources contamination or depletion, competition between food and fuel production decreasing food security and a worsening of labour conditions on the fields.

The above mentioned aspects have the attention of both the Brazilian government and the sugarcane industry. The increased demand for bioethanol may as well solve most of these threats since it results in the cash flow required to make improvements in current practices.
However, the changes for damage or destruction of high-biodiversity areas due to irreversible conversion of virgin ecosystems also increase with increasing demand for bioethanol. Deforestation, for example, causes the extinction of species and their habitats, and the loss of ecosystem functions. Studies reveal that wide-scale destruction of forests can affect the hydrologic cycle and the climate, reducing regional precipitation and increasing temperatures.

In Brazil, the expansion of sugarcane is limited by the quality of the soil, pluviometric precipitation (sugarcane requires year round sufficient rain fall) and logistics. These requirements make it less likely that sugarcane will replace high-biodiversity areas.

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[24] The sustainability of ethanol production from sugarcane, Energy Policy, Volume 36, Issue 6, June 2008, Pages 2086-2097, José Goldemberg, Suani Teixeira Coelho, Patricia Guardabassi.

However, deforestation in the Amazon region due to indirect land use change (ILUC) remains a possible threat. Increased pressure on existing farm land suitable for sugarcane farming may press farmers of other crops/cattle into the Amazon region.

5.2.8 Conclusions on the production of bioethylene

The production of ethylene on the basis of bioethanol is a commercial available technique. The ethylene can be produced in grades fully compatible with conventional ethylene required for regular plastic applications. Plastic made on the basis op bioethanol could/should be part of the regular plastic recycling.

The current price difference is small and is not considered a major obstacle for the large scale adoption of this technology.

Sustainability effects related to large scale bioethanol use without additional policy measures may form a bottleneck, as discussed in Chapter 3.

5.3 Bio-based alternative: Propylene and butylene from bioethanol

5.3.1 Current status of technology and policy

Biopropylene could be produced on the basis of bioethylene. Production of bioethylene can be achieved by dehydrogenation of bioethanol. Dehydrogenation of bioethanol is a commercially offered technology (see previous paragraph).

The production chain would require dimerisation of part of the ethylene into butylenes (see Figure 24) and subsequent reaction of ethylene and formed butylenes by a metathesis reaction (see Figure 25). Both processes are offered commercially by e.g. Lummus and Axens.

A recent world scale example is the 725 ktonnes/year of propylene combination of dimerisation and metathesis being build for Borouge in the United Arab Emirates[25]. The unit, which will convert ethylene into propylene to feed two new Borstar® technology polypropylene plants, will be the world’s largest using ABB Lummus licensed technology. Total annual output from the metathesis plant will be 752 kilotonnes of propylene plus 39 kilotonnes of butylene totalling 791 kilotonnes.

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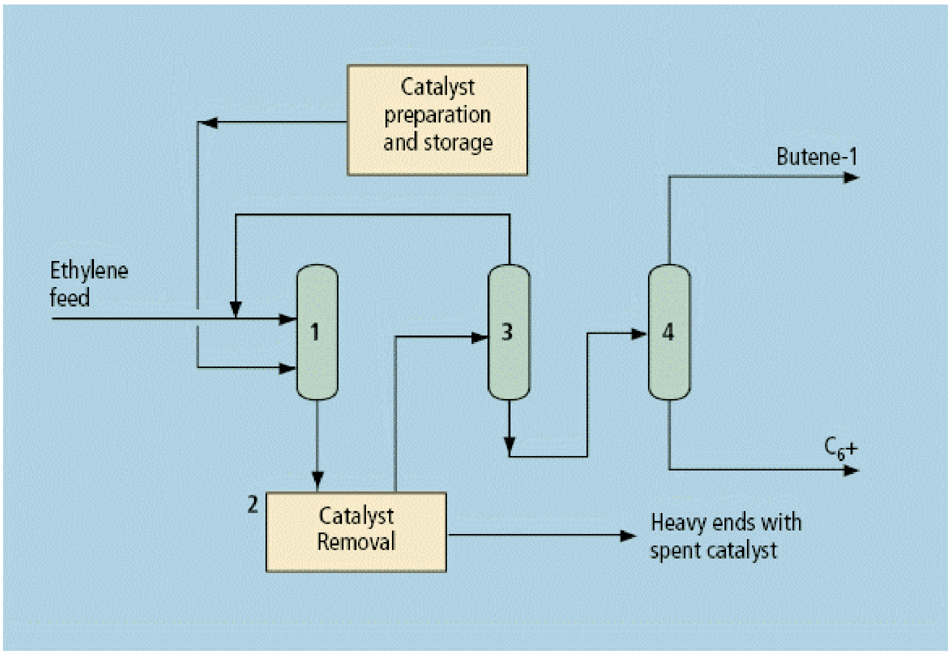
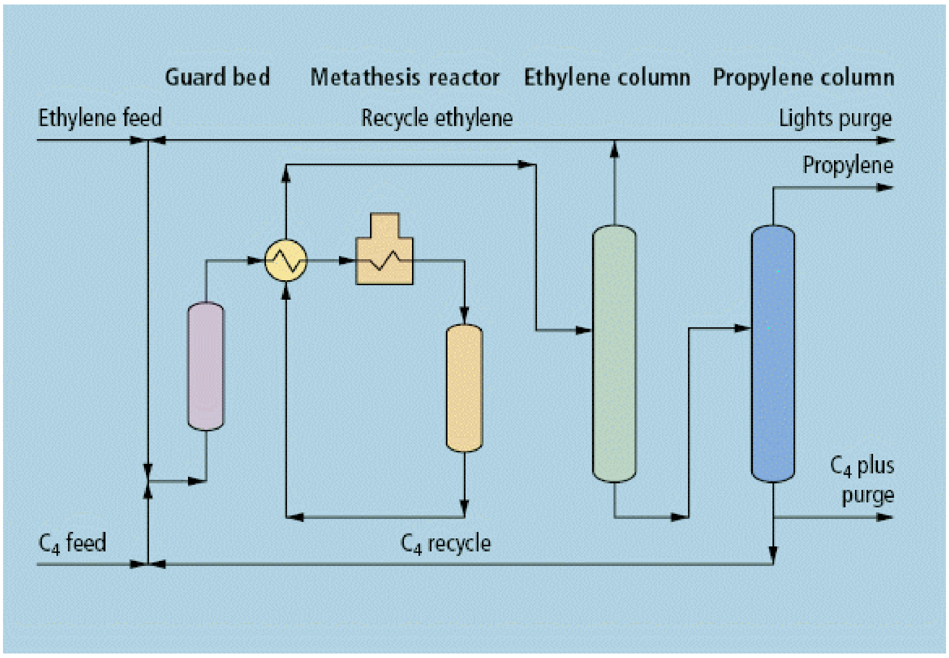
[25] Borouge is a joint venture between the Abu Dhabi National Oil Company (ADNOC) and Austria based Borealis.

Figure 24 Flowsheet of Lummus dimerisation process



Source: Plantas.

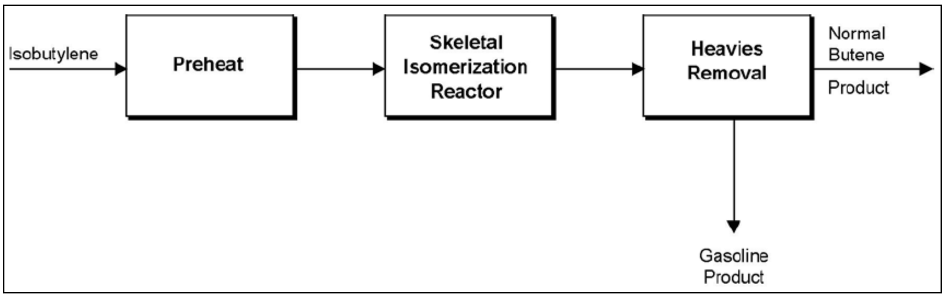
Figure 25 Flowsheet of Lummus metathesis process (Olefin Conversion Technology-OCT)



Source: Plantas.

The Lummus's OCT technology has a selectivity for ethylene of nearly 100%, the selectivity for butylene is 97%.

Figure 26 **Schematic representation of skeleton isomerisation of isobutylene**



Source: Plantas.

5.3.2 Economics

The aforementioned project for Borouge also gives an up-to-date indication of the investments involved for a combination of dimerisation and metathesis. The combination requires an investment of M$ 300, approximately M€ 215[26]. Assuming no differences in costs between the Middle East and North-West Europe. Our calculation is illustrated in Figure 29.

Given the selectivity of the dimerisation process and metathesis process for butylenes and given the investment costs, the resulting production costs for propylene from bioethylene will amount to € 1,117 per tonne at a bioethanol price of € 545 per tonne.

5.3.3 Energy balance and CO_2 emissions

The estimation of the carbon footprint and the energy demand are based on the assumption that ethylene will be produced from imported Brazilian ethanol, as was assumed in the previous paragraph.

Production of biopropylene requires fuel, steam and electricity (Plantas Quimicas, 2009). The total carbon footprint and energy demand amount to respectively 1.44 tonne CO_2 eq./tonne and 55.6 GJ/ton, of which 5.8 GJ is of fossil origin.

For comparison, the average carbon footprint and energy demand given by Ecoinvent for average European fossil fuel based production amount to 4.74 tonne CO_2 eq./tonne and 73 GJ/ton, of which 6.8 GJ/tonne are related to the production of propylene and can be lowered by maximally 50%. The carbon footprint related to naphtha is 3.12 tonne CO_2 eq./tonne (JEC, 2007)[27]. This means that the carbon footprint of propylene based on the most advanced naphtha cracking, amounts to 3.93 tonne CO_2 eq./tonne and 70 GJ/ton.

This implies a reduction in GHG emissions of 63% when producing propylene on the basis of bioethanol compared to the BAT REFs of naptha steam cracking based propylene production.

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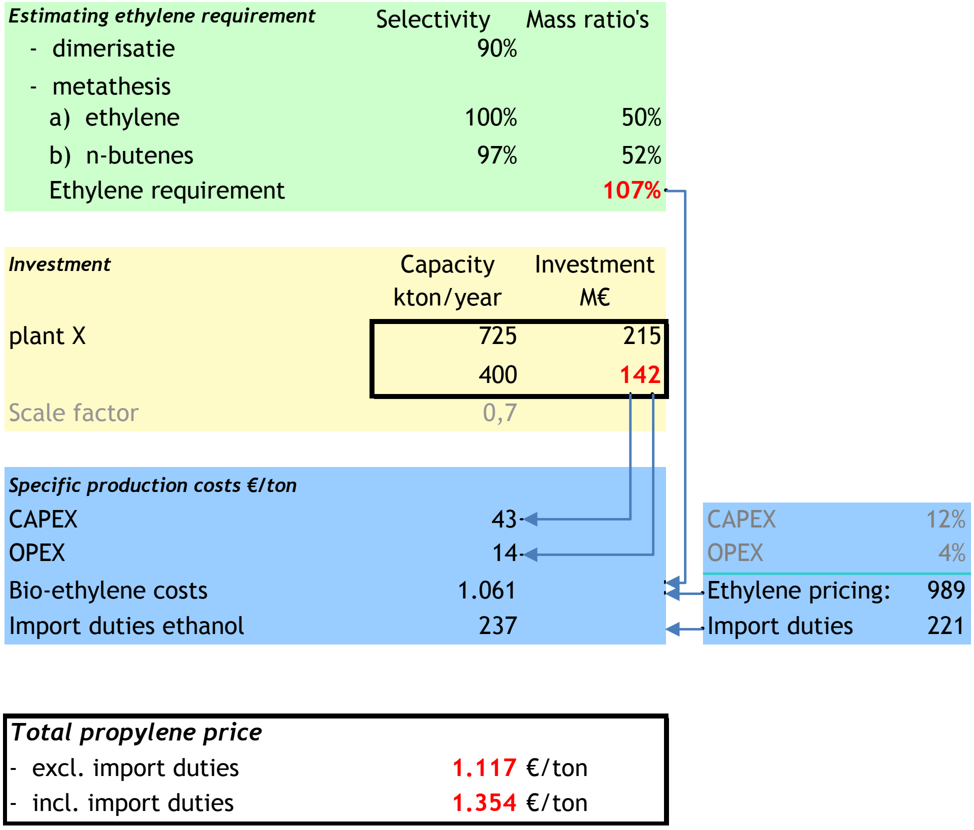
[26] See http://www.borealisgroup.com/news-and-events/company-news/2007/olefins-conversion-unit.

[27] JEC, 2007 (http://ies.jrc.ec.europa.eu/uploads/media/WTT_App_1_010307.pdf) says the carbon content of naphta is 85%, equivalent with 3.12 tonne CO_2 eq./ton. According to list of GHG emission factors used by the Dutch government (http://www.broeikasgassen.nl/docs/Nederlandse%20lijst%20energiedragerlijst%20publicatieversie.pdf) the emission factor of naphta equals 3.225 tonne CO_2 eq./tonne naphta.

Figure 27 Calculation of production costs for biopropylene



Estimating ethylene requirement	Selectivity	Mass ratio's
- dimerisatie	90%	
- metathesis		
a) ethylene	100%	50%
b) n-butenes	97%	52%
Ethylene requirement		107%

Investment	Capacity kton/year	Investment M€
plant X	725	215
	400	142
Scale factor	0,7	

Specific production costs €/ton	
CAPEX	43
OPEX	14
Bio-ethylene costs	1.061
Import duties ethanol	237

CAPEX	12%
OPEX	4%
Ethylene pricing:	989
Import duties	221

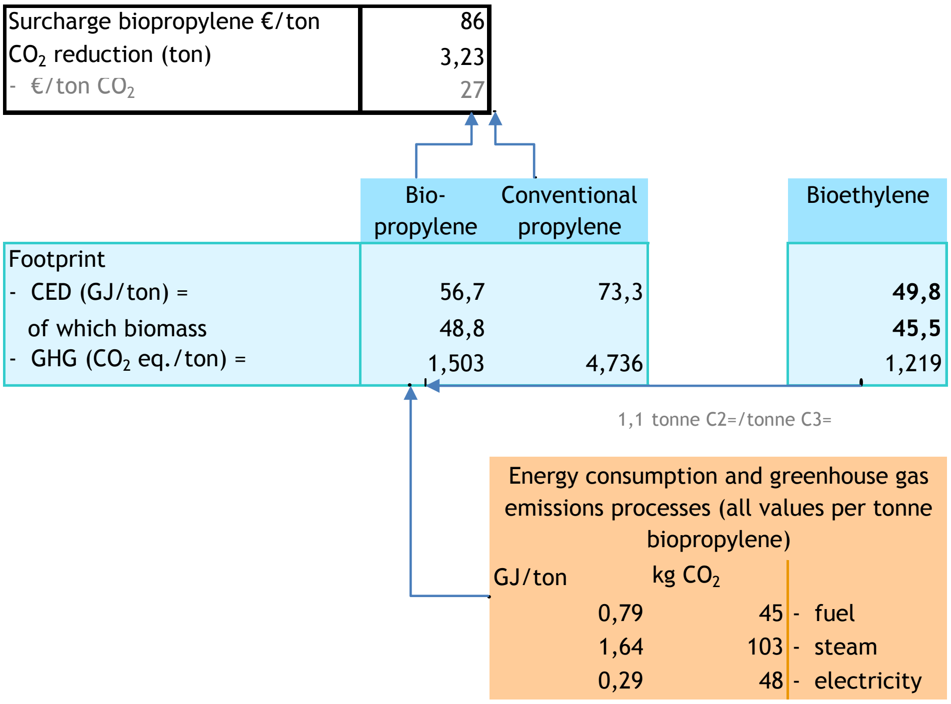
Total propylene price	
- excl. import duties	1.117 €/ton
- incl. import duties	1.354 €/ton

Source: CE, own calculations.

The calculation of the CO_2 reduction price based on the comparison in annual production costs and the carbon footprint of each production method are illustrated in Figure 28.
For comparison, the average carbon footprint and energy demand given by Ecoinvent for average European fossil fuel based production amount to 4.74 tonne CO_2 eq./tonne and 73 GJ/ton, of which 6.8 GJ/tonne are related to the production of propylene and can be lowered by maximally 50%. The carbon footprint related to naphtha is 3.12 tonne CO_2 eq./tonne (JEC, 2007).
This means that the carbon footprint of propylene based on the most advanced naphtha cracking, amounts to 3.93 tonne CO_2 eq./tonne and 70 GJ/ton.

At a bioethanol production price of 545 €/tonne the CO_2 reduction costs associated with utilization of propylene produced from bioethanol would amount to € 27 per tonne CO_2 at the current average production footprint. Projected prices for CO_2 rights in 2050 vary with projected scenario between 28-70 €/tonne CO_2 (UMWE (2011), Table 3-2).

Figure 28 Calculation of carbon footprint and energy savings for biopropylene



Source: Own calculations.

Elucidation: The energy content and carbon footprint of bioethylene and fuel, steam and electricity purchased from outside sources are aggregated, e.g. for CO_2: (45 + 103 + 48)/1,000 + 1.07 x 1,162 = 1,443 kg/tonne C3=).
Next, the difference with the substituted raw material is calculated, per tonne product and annually.

5.3.4 Conclusions on the production of biopropylene and butylene

In general the same applies to the production of propylene and butylene on the basis of bioethanol as applies for ethanol.

The required technology is commercially available and allows for significant reductions in GHG emissions (>63%). The products are produced in grades fully compatible with conventional plastic applications. Plastic made on the basis of biopropylene or biobutylene could/should be part of the regular plastic recycling. The possible negative effects of large scale bioethanol requires attention of policy makers.

At a price of bioethanol of € 545/tonne (possible for European sugar beet based bioethanol) a CO_2 price of € 27/tonne CO_2 eq. is required to equal costs compared with conventional propylene production. In 2050 the projected CO_2 price varies between 28-70 €/tonne CO_2 eq.

In the mean time one could argue that given the low price impact of olefins on consumer products, it is a low price for a green image.

5.4 Conclusions on olefins

Bioethanol seems the key to a carbon low olefins production. The reduction in GHG for ethylene is 90% compared to the current situation and 69% compared to the industry benchmark. For ethylene alone this represents a reduction potential of 51 Mtonnes CO_2 eq./year compared to the current production average and 40.5 Mtonnes CO_2 eq./year compared to the industry benchmark. The reduction potential for propylene and butylene is smaller but still >63% more efficient than the industry benchmark.

The production costs of biobased olefins are currently higher than the production price of conventional olefins. This is mainly due to the costs related to the use of bioethanol. Since the demand for biobased materials is expected to raise no price decrease is anticipated for the period after 2050.

The price difference is compensated by CO_2 rights at a price of 16 €/tonne CO_2 eq. for ethylene and 27 €/tonne CO_2 eq. for propylene. The current price for CO_2 rights varies between 10-15 €/tonne CO_2. Projected prices for CO_2 rights in 2050 vary with projected scenario between 28-70 €/tonne CO_2 (UMWE (2011), Table 3-2).
Even before the CO_2 reduction prices are sufficiently high the price difference does not need to be a major obstacle since for most consumer applications the impact of the olefins price is <1%.

Since plastic made on the basis of bioethanol has the same properties as plastic based on ethylene from naphtha cracking this plastic could/should be part of the regular plastic recycling. More on possible sustainability effects related to large scale bioethanol use in Chapter 3.

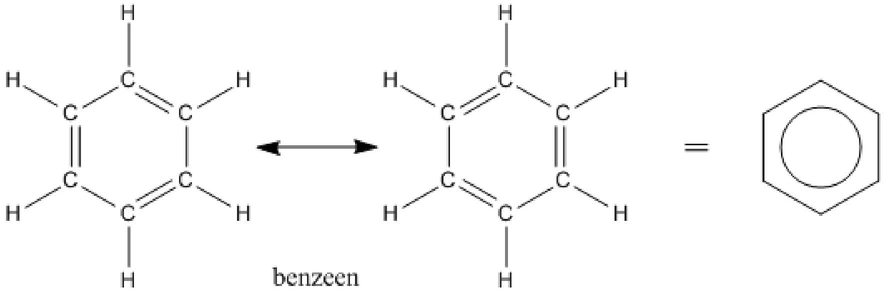
6 Conventional aromatics (BTX) production

6.1 Introduction to the sector and market

Current production volumes and applications

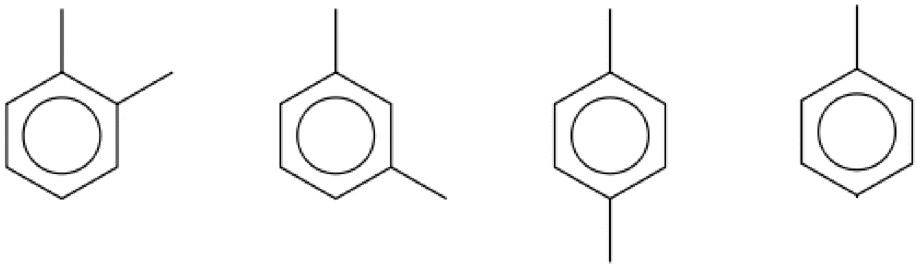
Benzene, toluene and xylenes (BTX) are the basic aromatics intermediates used for the manufacture of other chemicals. The two main sources of feedstocks for the production of aromatics are naphtha steam crackers (see Chapter 6), and reformate from reformers.

Figure 29 Chemical formula of benzene (C_6H_6), showing the special nature of benzene molecules[28]



Reformers are typically found in refineries, so refineries produce a significant proportion of the overall aromatics production. Particularly xylenes are more conveniently produced from reformers than from steam crackers due to the higher yields that are obtained with this type of processes.

Figure 30 Chemical formula’s of ortho-xylene, metha-xylene, para-xylene (C_8H_{10}) and toluene (C_7H_8)



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[28] More information on the special chemical characteristics of aromatics: http://en.wikipedia.org/wiki/Aromaticity.

Benzene is the most important aromatic. The Western European production of benzene, toluene and xylene (para and ortho combined) over the period from 2006 to 2011 was 20-25% lower than the reported production capacity. The yearly production varied +/- 10% around the following average numbers:

- benzene: 7.9 Mtonnes/year;
- toluene : 1.9 Mtonnes/year;
- xylenes[29]: 2.4 Mtonnes/year.

These production numbers exclude the production of derivates like cyclohexane, nitrobenzene, aniline and alkylbenzenes.

6.2 Process

The source of feedstock has an important impact on the process used for extraction of aromatics. In this sense we can distinguish four main process schemes for recovering aromatics based on the type of feed and product desired:

- benzene and/or toluene from naphta cracking;
- benzene and/or toluene extraction from reformate;
- mixed xylenes produced from reformate;
- para-xylene and/or ortho-xylene extraction and isomerisation from reformate (mixed xylenes).

Within these four main options there may be a lot of variations in the process scheme to accommodate to the particularities of each case; however the following description gives a generic indication of the required process.

Benzene and/or toluene from steam cracking

Raw product stream resulting from steam crackers is referred to as pygas and contains a large quantity of diolefins and olefins that need to be hydrogenate before extracting the aromatics. Also some other impurities such as sulphur need to be removed to obtain the specifications required in the aromatics. These requirements as well as the need to fractionate by distillation the desired cut (C6 cut for benzene and/or C7 cut for toluene) determine the required process scheme, which in general will contain the following stages:

- A first stage hydrogenation of pygas for the conversion of diolefins and other very reactive species in olefins or other more stable compounds. This is done in a catalytic reactor at temperatures below 200°C and under a hydrogen pressure typically between 20-50 bars.
- A series of distillation operations to prepare the desired cut for the extraction. These distillation operations may include depentanizers, dehexanizers, deheptanizers, deoctanizers and rerun columns according to the particular scheme.
- A second stage hydrogenation to convert olefins in saturated species as well as to transform sulphur species in H_2S that is further stripped in a column associated to the catalytic reactor. This reactor is operated at temperatures between 240 and 350°C and at pressures typically below 50 bars. Some additional distillation may be required before extraction in some cases to remove heavies formed in the reactor.
- Aromatics extraction using either liquid-liquid extraction technologies or extractive distillation technologies. In both cases a solvent is needed to facilitate the separation of the aromatics from other species with very close boiling points, which prevents the use of conventional distillation.

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[29] APPE site (Oct. 3rd, 2011), http://www.petrochemistry.net/capacity-and-production-propylene-and-derivatives.html. These numbers are the production numbers of pure BTX, all derivates are excluded. For xylenes the combined production of ortho- and para-xylenes is reported.

  Most common solvents used are sulfolane, n-methylpyrrolidone (NMP), n-formyl-morpholyne (NFM) dimethyl-sulfoxyde (DMSO) or variations of molecules similar to sulfolane.
- Final distillations of the extracted aromatics when benzene and toluene (or even some xylenes) are extracted together to separate each aromatics species.

Benzene and/or toluene extraction from reformate

Reformate products contain much lower quantities of olefins than pygas with no sulphur impurities so hydrogenation is not required. In this case the following steps are typically used:

- fractionation of reformate by distillation to produce the desired cut for extraction;
- extraction of aromatics in the same fashion as described in the case of pygas;
- clay treating to remove traces of olefins in the extracted product. This is typically done heating the product at about 200°C in the presence of specific clays;
- distillation of extracted aromatics when various species are extracted together. In some cases aromatics can be extracted jointly from reformate and pygas, which obliges to use a combination of both sequences of processes, previously described.

Mixed xylenes from reformate

A mixture of the three xylenes can be produced in some sites to be used either as solvents or as feed for further PX or OX extraction elsewhere. In this case the required steps are:

- fractionation of reformate to produce the C8 cut rich in xylenes. This typically involves a deheptanizer column and another column to remove heavier molecules than the C8s;
- clay treater to remove traces of olefins;
- when the reformate is coming from a reformer operating at low severity, it may contain significant quantities of non-aromatics C8 species that may require solvent extraction as described in the previous sections.

Para-xylene and/or ortho-xylene from reformate

Para-xylene (PX) and/or ortho-xylene (OX) are normally diluted in reformate C8 streams to about 20% each, being the meta-xylene (MX) the most concentrated compound also with important amounts of ethyl-benzene.
So the process is designed to convert as much as possible of the MX to PX/OX (when both products are desired) or MX/OX to PX when only this last one is the desired product. This is realised within the so-called xylenes loop:

- The C8 reformate cut is processed in a first column (xylenes column) where a purified C8 cut is obtained in the top. This distillation column is a very severe distillation that requires a lot of energy, which usually is heat-integrated with other units of the aromatics complex. When OX is also produced, the OX is separated in the bottom of the xylenes column with the C9 and heavies. In this case the column is even bigger and is usually referred as a super-fractionation unit.
- The C8 cut from the xylenes column is then processed in a special unit for recovering pure PX. C8 aromatic isomers have very close boiling points and chemical properties, so the separation of PX from other C8 aromatics needs to use other techniques. Two type of technologies are used for separating PX from the other C8 isomers:
  - shape selective adsorption of PX in a simulated moving bed adsorber taking benefit of the particular physical shape of this molecule;

  - crystallisation of the PX molecule at temperatures between -4 to -60°C, taking advantage of the higher melting point of the PX in relation to other isomers.
- The remaining C8 aromatics isomers after extraction of PX are sent to a xylenes isomerization unit where some more PX is produced from MX and OX. In this unit also the ethyl-benzene is dealkylated producing benzene that is recovered in a deheptanizer column and exported out of the xylenes loop. The isomerized C8 are recycled back to the xylenes column where they are mixed with the C8 reformate feed. Light decomposition products (mainly ethane) from the isom section are extracted as isom gas which is mainly used to fire furnaces within the PX/OX unit.

Additional processes: HDA and TDP

In some aromatics complexes there may be some additional processes for inter-conversion of aromatics molecules, especially from toluene, which is typically a less desired product, or from C9 aromatic molecules to obtain the most interesting benzene and xylenes products. The main processes used for that purpose are:

- Toluene Disproportionation (TDP) that takes place in presence of a catalyst to yield additional benzene and xylenes that are recovered somewhere else in distillation columns;
- Selective Toluene Disproportionation (STDP) similar to the previous process but a shape selective catalyst allows to produce preferentially PX instead of the other isomers;
- Toluene/C9 Aromatics transalkylation to produce also benzene and xylenes but in this case putting in the feed to this process also heavier aromatics as C9 or even C10s;
- Hydro-dealkylation (HDA) of toluene and/or xylenes to yield benzene.
- Thermal process that removes alkyl groups from the aromatic ring.

6.3 Current level of energy requirement and greenhouse gas emissions

The combined process and steam emissions related to the above described processes are estimated to add up to 6.6 Mtonne of CO_2 equivalents, accounting for about 3.5% of the total GHG emissions from the chemical industry in the EU[30].

Each of the above mentioned processes have different benchmark emissions, the correct method and therefore the exact outcome is still debated. The current status is summarised in Table 13.

Table 13 **Benchmark values for BTX production in Europe**

Process	Process, heat and electricity related emissions (t CO_2/t)
Benzene and/or toluene from steam cracking	0.37-0.43
Benzene and/or toluene extraction from reformate	0.27-0.28
Para-xylene and/or ortho-xylene from reformate	0.65
HDA and TPD	0.38-0.40

Source: Ecofys et al., 2009.

The current industry average is 6.6 Mtonnes CO_2 eq. on a BTX production of 11.9 Mtonnes, which equals an average value of 0.55 t CO_2 eq./t BTX.

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[30] Methodology for the free allocation of emission allowances in the EU ETS post-2012; report ordered by the European Commission and carried out by Ecofys and partners.

7 Low carbon aromatics

7.1 Introduction

Sustainable production of aromatics will require the use of a carbon containing feedstock.

In this study we briefly describe two potential breakthrough technologies that are still in their early developments:
- catalytic pyrolysis of lignin;
- catalytic conversion of ethanol.

Of these two routes, lignin conversion would have the benefit that it could utilise residues and by-products from existing conventional biomass conversion processes such as pulp production and residues from second generation bioethanol production from lignocellulosic raw materials.

Both routes are however still being developed and will probably not be roled out in time to allow significant reductions in aromatic production related greenhouse gas emissions.
Because of the early stage of development both routes are in, energy requirements, potential for reduction of greenhouse gas emissions per unit of aromatics and costs were only broadly assessed.

7.2 Lignin based production routes

The easiest way of production would be utilisation of a biomass feedstock already containing aromatics. In principle such a feedstock is amply available in the shape of lignin, the component that gives wood its mechanical strength. Lignin is part of the residual black liquor produced during wood pulping and conversion of lingo-cellulosic materials into bioethanol. Lignoboost technology developed by innventia allows isolation of lignin from the black liquor. Lignin production at pulp mills in the EU amounts to approximately 20 Mtonne/year[31]. Two sulphite pulping mills - one in Sweden and one in Norway produce pure lignin for utilisation as a raw material.

However, although isolation of lignin is quite feasible, conversion into aromatic monomers is more difficult.

Lignin has a complex structure consisting of a wide range of monomers which are linked by a wide range of different bonds. As a result of its complex nature no technology has yet been developed and demonstrated at any scale larger than laboratory scale that allows breaking this complex structure in monomers or dimmers.

In fact conversion of lignin into aromatic monomers requires development of new technologies, as illustrated in Figure 32.

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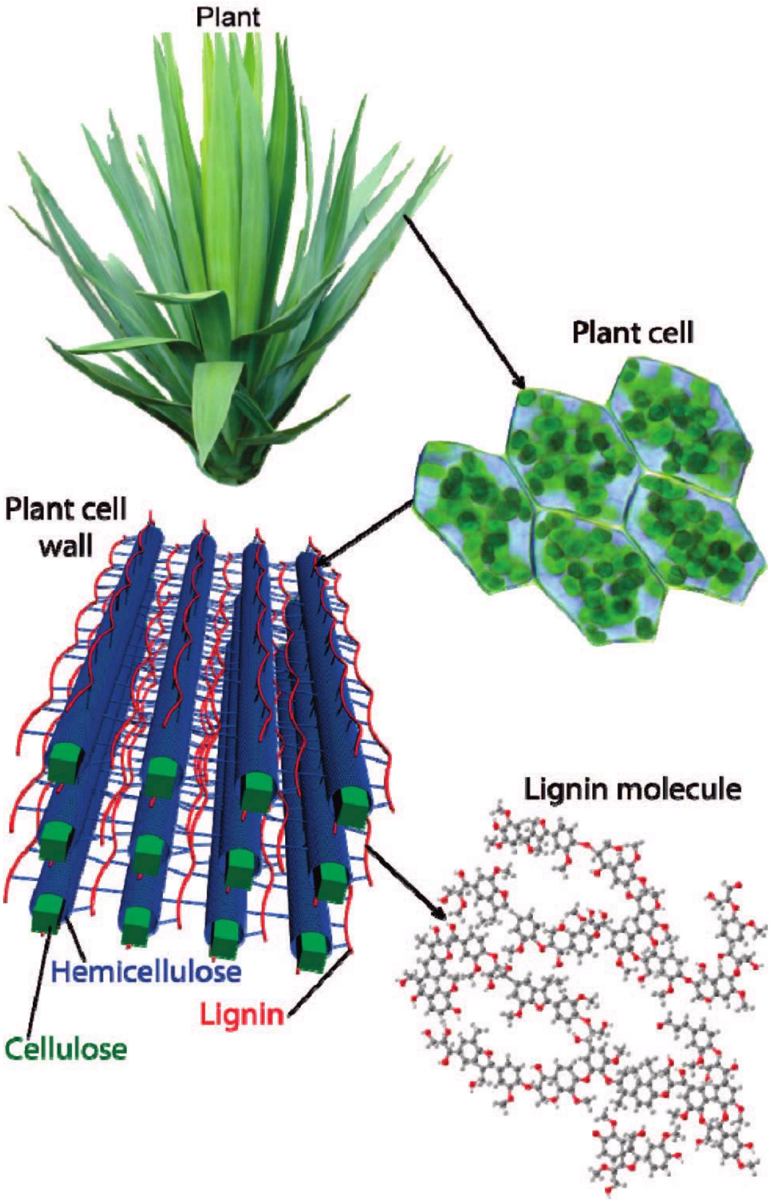
[31] See: http://cordis.europa.eu/documents/documentlibrary/120695511EN6.pdf.

Figure 31 Structure of wood and lignin



Source: http://pubs.acs.org/action/showImage?doi=10.1021%2Fcr900354u&iName=master.img-001.jpg&type=master.

Some promising routes currently being explored include:

- catalytic hydrocracking, tested by e.g. UOP[32] and at the Institut für Holztechnologie und Holzbiologie;
- catalytic pyrolysis over a zeolite (ZSM-5) catalyst, as being developed by e.g. Anellotech[33];
- liquefaction with a mixture of supercritical water and phenol[34].

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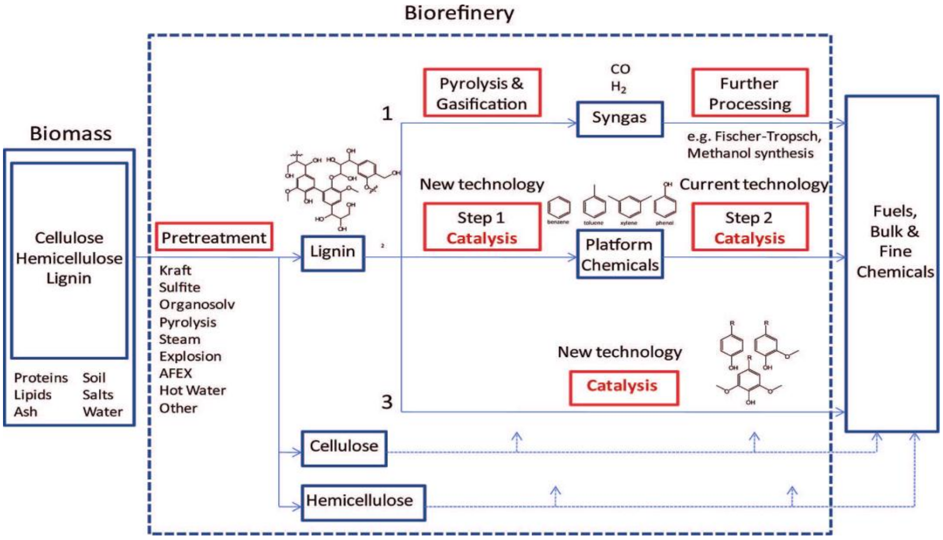
[32] See http://www.nrel.gov/docs/fy11osti/46586.pdf.

[33] Seehttp://anellotech.com/tech.html.

[34] See: http://www.cellulosechemtechnol.ro/pdf/CCT9(2010)/P.353-363.pdf.

Of these routes, catalytic fluidised bed pyrolysis seems the most advanced. The firm Anellotech claims it could build a first commercial plant for conversion of wood dust (not lignin) that would be operational by 2015 and is now trying to find the funds for this plant.
A similar route is developed in the Netherlands by BTG and ECN, but the development of this route seems less far[35].

Figure 32 Technology development requirement



Source: http://pubs.acs.org/action/showImage?doi=10.1021%2Fcr900354u&iName=master.img-006.jpg&type=master.

Figure 33 Impression of current catalytic pyrolysis plant

Source: http://newenergyandfuel.com/wp-content/uploads/2010/11/Huber-Pyrolysis-Plant.jpg.

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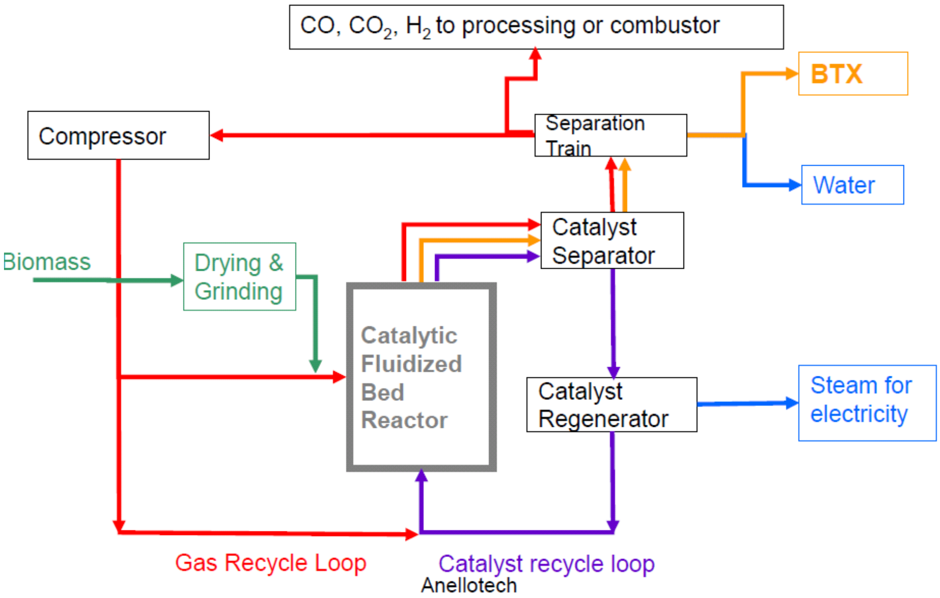
[35] See: http://www.biorefinery.nl/fileadmin/biosynergy/user/docs/LignocellulosicFeedstockBiorefinery-Reith.pdf.

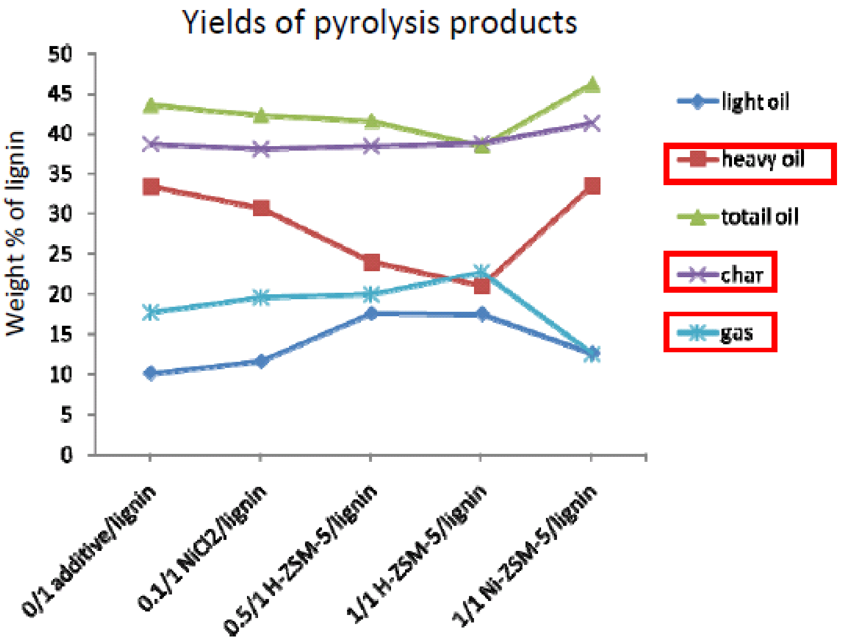
The efficiency of the process would be 40% (energy basis). The process would further yield light gases and coke, the latter being utilised to fuel the process. Given the role of coke, the process may be comparable with fluid catalytic cracking of heavy crude oil residues, a process applied at large scale at crude oil refineries.
Other sources[36] give following indications of products ranges for pyrolysis of lignin (see Figure 35).

Figure 34 **Flow sheet of Anellotech's process**



Source: http://cnse.albany.edu/download/Anellotech.pdf.

Figure 35 **Indicative composition of products of catalytic pyrolysis of lignin**



Source: http://www.tappi.org/content/Events/11BIOPRO/26.2Ben.pdf.

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[36] See: http://www.tappi.org/content/Events/11BIOPRO/26.2Ben.pdf.

Anellotech claims aromatics production costs could be as low as $ 1.05/gallon (approximately € 170/tonne), assuming biomass costs of $ 50/tonne. The investment in a 2,500 tonne/day plant would amount to M$ 220. The plant would be self-supplying in energy[37], [38].

7.3 Ethanol to aromatics

The alternative production route would be to convert ethanol – or probably some other well defined and pure biomass derived hydrocarbon – into aromatics. For this route the same or a very similar catalyst would be applied: a ZSM-5 catalyst. The route has been known for decades and prove of principle is as old as thirty years[39].

The technology is part of Virent's[40] Bioforming technology in which monomer sugars are converted into gasoline, kerosin and diesel. This technology applies the (H)ZSM-5 catalyst, too. However, this process is not focussed on production of aromatics and aromatics make up approximately 20% of the products slate.

However, other production routes, more focussed on aromatics production do not seem to be under development. This situation prohibits a direct evaluation of the financial aspects of aromatics production based on ethanol. Only an indirect evaluation of the process costs related to the production of biofuels can be given.

Current scale of technology concerns a 10,000 gallon of product per year pilot plant (± 30 ktpy).

Production costs per gallon of gasoline are estimated at $ 2.25-2.50. The gasoline is indicated to contain more than 90% of the energy content of the processed biomass.
Shell, Cargill and Honda are involved in rolling out of this technology.

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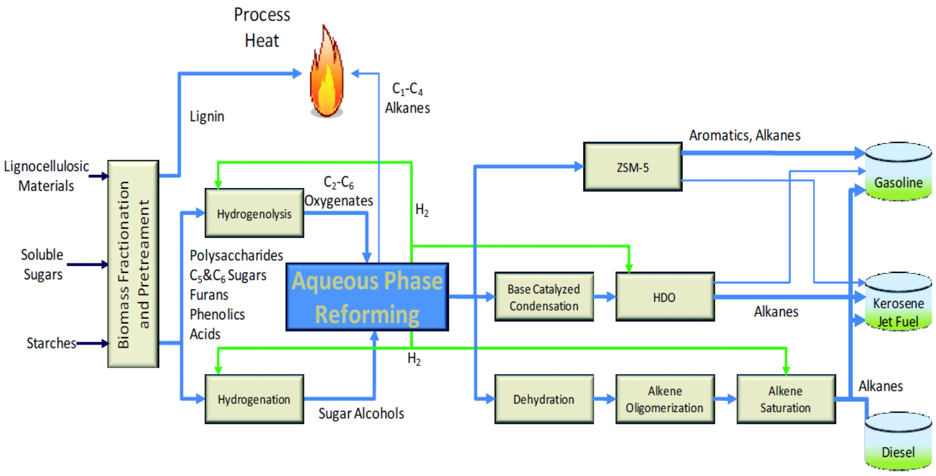
[37] See: cnse.albany.edu/download/Anellotech.pdf.

[38] See: http://www.sari-energy.org/PageFiles/What_We_Do/activities/worldbiofuelsmarkets/Presentations/Bio-basedChemicalsCongress/David_Sudolsky.pdf.

[39] See: http://www.sciencedirect.com/science/article/pii/0166983482800845.

[40] See: http://www.virent.com/BioForming/Virent_Technology_Whitepaper.pdf.

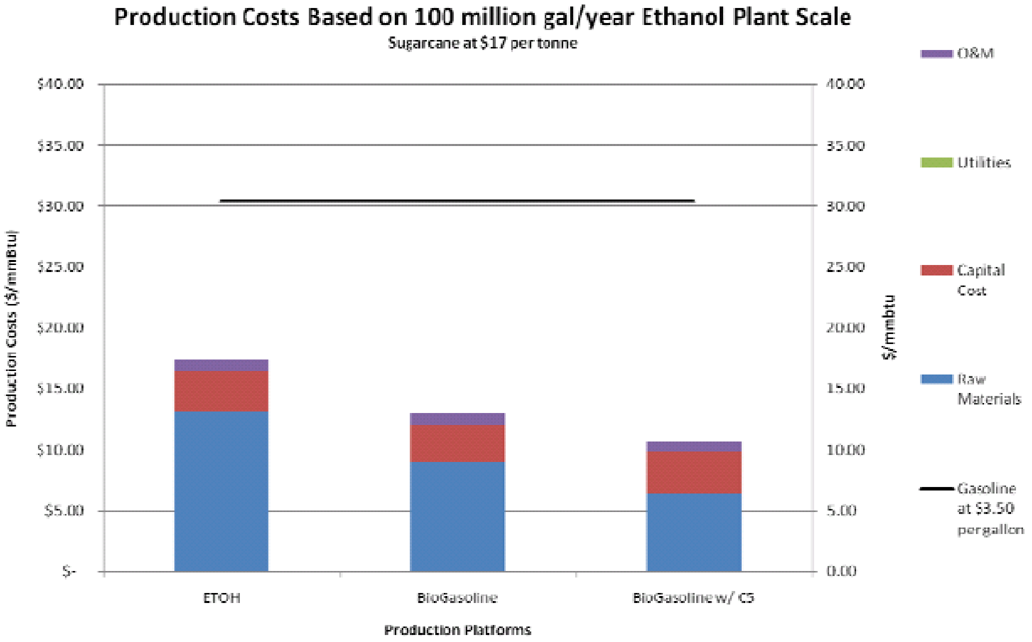
Figure 36 **Flow sheet of Virent's Bioforming sugar to fuel technology**



Source: http://www.virent.com/News/in_the_media/catalytic_conversion_of_sugar.pdf and http://www.wbi.wisc.edu/wp-content/uploads/2009/11/Aqueous-phase-reforming-process-Randy-Cortright-Virent-Energy-Systems.pdf.

An indication of the structure of production costs is given in Figure 37.

Figure 37 **Overview of structure of production costs of conventional bioethanol production and production of biogasoline**



Source: http://files.eesi.org/Blanchard_073108.pdf.

7.3.1 Conclusions on aromatics

In principle there are two routes available to produce climate neutral aromatics, based on biomass:

1. Gasification of lignin (remains of a number of conventional plant based processes). When this method is integrated with conventional plant/wood based processes like papermaking this may have the advantage of using remains and thus less prone to ILUC effects. However, this requires that the energy efficiency of these conventional plant/wood based processes increases since most of the lignin currently is used as a biofuel for these processes.
2. Conversion of ethanol over a zeolite catalyst to aromatics (mixture of BTX). This process has the advantage that bioethanol as a raw material is available at a large scale, but comes with the possible sustainability consequences related to bioethanol use as discussed in Chapter 3.

Currently we can only do a very rough assessment on process costs since the only pilot process applying these insights is optimised for the production of biofuels instead of biochemistry. Based on the type of process we expect a surcharge comparable to the surcharge of propylene production.

8 Conclusions and recommendations

On the basis of likely relevance in 2050, current greenhouse gas emissions of the process and need for breakthrough abatement technologies, we identified the options for emission reductions in the production of the following basic chemicals:

- ammonia (NH_3);
- olefins (the group of small ketenes, i.e. ethylene (C_2H_4), propylene (C_3H_6) and various types of butylenes (C_4H_8) of which ethylene is the most produced);
- aromatics or BTX (benzene (C_6H_6), various types of xylenes (C_8H_{10}) and toluene (C_7H_8)).

We found that breakthrough abatement technologies are available for the production of these three basic chemicals.

For all three processes alternatives were found allowing for reductions in GHG emissions varying between 50 and 100% compared to the current practice.

This means the technologies can significantly contribute to a greenhouse gas reduction pathway of 83 to 87% by 2050 compared to 1990 levels for industrial sectors, as indicated by the European Commission in the *Roadmap for moving to a competitive low carbon economy in 2050* (EC, 2011a).

The identified breakthrough abatement technologies are based on renewable power and/or biomass. However, additional demand for biomass could compete with demand for biomass intended for food, feed, construction material and fuel. Without an ambitious EU resource-efficiency framework (as advocated by the *Roadmap to a resource efficient Europe*) and strict sustainability and indirect land-use criteria for the use of biomass, there is an increasing risk for adverse effects on the environment, including net increasing GHG emissions.

8.1 Outcomes of inventory of breakthrough technologies

8.1.1 Ammonia production

The synthesis of ammonia from nitrogen and hydrogen is an energy producing (exothermic) reaction. Therefore, only alternatives to the current production method of hydrogen production by gasification of natural gas are required to realise a GHG neutral ammonia production. Two GHG neutral alternatives to produce hydrogen were found:

- water electrolysis powered by renewable power;
- biomass gasification.

Both pathways allow for a GHG neutral ammonia production, i.e. allowing for a GHG emissions reduction of 1.6 tonne CO_2 eq./ton NH_3 produced

Water electrolysis based ammonia production

Water electrolysis based ammonia production requires:

- roughly 1.5 tonne of water per tonne of ammonia produced; and
- 50-70 MWh renewable power per tonne of ammonia produced.

At the current European ammonia production of 14 Mtonne/year this translates to 21 Mtonne of water and 700-980 MWh renewable power.

The costs related to large scale production of ammonia in 2050 were assessed in comparison to the expected costs of conventional production in 2050. Even at the low future estimate of natural gas of 6 €/GJ, cheap hydropower can compete on price with conventional ammonia production provided that the foreseen decrease in capital costs for the electrolysis plants to 250-500 €/kWe is realised by 2020.

In all other cases there is a surcharge for the production of ammonia varying between 0–175 €/tonne NH_3 in case of hydropower based production and 350-500 €/tonne NH_3 in case of windpower based production (CO_2 prices of respectively € 0-€ 100 and > € 200/tonne CO_2).

Biomass gasification based ammonia production

Biomass gasification based ammonia production requires roughly 1.8 tonne of biomass per tonne of ammonia produced. Since part of the biomass is burned to fuel the gasification this process is also a net heat producer.
At the current European ammonia production of 14 Mtonne/year this translates to 25 Mtonne of clean wood.

We estimated the costs related to large scale production of ammonia in 2050. The production of ammonia based on biomass gasification has a surcharge of 50-150 €/tonne NH_3 depending on the price of the biomass.

At a benchmark emission of 1.6 tonnes of CO_2 eq./tonne this requires a CO_2 price varying between 31-93 €/tonne of CO_2 eq. to reach breakeven. This implies that even when competing with the very advanced ammonia plants that meet the benchmark emission of 1.6 tonnes of CO_2 eq./tonne of NH_3 produced the breakeven point may be at a price of 31 €/tonne CO_2 eq. This may be feasible if the gasification plant is integrated with other wood based industries.

8.1.2 Olefins production

The least GHG emitting alternative production methods for olefins are bioethanol based. The final reduction in GHG emissions is determined by the following factors, in order of possible effect on magnitude:

- Emissions related to the bioethanol production.
- Specific compound produced: bioethanol is conversed to ethylene, which can be conversed to the other olefins. Each reaction step requires energy.
- The efficiency of the conversion process from bioethanol to the required olefins.

At the current European olefins production this translates to a demand of 65 Mtonne of bioethanol per year to replace the current European olefins production.

Ethylene production based on bioethanol
The production of 1 tonne of ethylene requires:

- 1.7 tonne bioethanol; and
- 48.7 GJ/tonne ethylene produced of which 5 GJ is of fossil origin.

The GHG emissions related to the production of ethylene from efficiently and sustainably produced bioethanol are 90% lower than the current industry average and 69% lower than the post-2012 ETS industry benchmark. This is because of the lower energy need of the conversion process from bioethanol to ethylene than from naphta to ethylene and the lower carbon footprint related to bioethanol compared to naphta as a raw material.

We estimated the costs related to large scale production of ethylene in 2050. At a bioethanol price of 545 €/tonne, this implies a surcharge of 54 €/tonne ethylene. This requires a CO_2 price of 16 €/tonne of CO_2 eq. to reach breakeven.

Propylene production based on bioethanol
The production of 1 tonne of propylene requires:

- 1.9 tonne bioethanol; and
- 55.6 GJ/tonne propylene produced of which 5.8 GJ is of fossil origin.

The GHG emissions related to the production of propylene from efficiently and sustainably produced bioethanol are 63% lower than the post-2012 ETS industry benchmark.

We estimated the costs related to large scale production of propylene in 2050. At a bioethanol price of 545 €/tonne, this implies a surcharge of 90 €/tonne ethylene. This requires a CO_2 price of 27 €/tonne of CO_2 eq. to reach breakeven.

8.1.3 Aromatics production

Two alternatives routes to produce low carbon aromatics were found:

- direct conversion of ethanol to aromatics;
- biomass gasification.

Both routes allow for significant reduction in GHG emissions, although no exact estimate could be made due to a lack of pilot plants dedicated to the production of aromatics. All pilot plants were dedicated to biofuel production. However, based on a comparison in process characteristics we can offer the following rough indications:

The direct conversion of bioethanol to aromatics should yield a GHG emission reduction of over 60%, at a surcharge comparable to the production of propylene from bioethanol, i.e. breakeven at a GHG reduction cost of 30 €/tonne of CO_2 eq.

The biomass gasification method should yield a GHG neutral alternative provided that the biomass is sustainably sourced. At a surcharge comparable to the surcharge of ammonia, i.e. breakeven at a GHG reduction cost of 30-90 €/tonne of CO_2 eq. depending on the wood price.

8.2 Economic assessment of breakthrough technologies

When assessing the economic feasibility of the presented breakthrough technologies one should bare the following in mind:

- Projected CO_2 reduction costs for 2050 are estimated to range between 28 and 70 €/tonne CO_2 eq. in 2050 (UMWE (2011), Table 2-3). This seems sufficient to make all biobased options economically feasible.

- The rise in oil prices is structurally underestimated by the International Energy Agency (UMWE (2011), Figure 3-8). This may also be true for the gas price.
- The growth of the renewable power is structurally underestimated in studies by International Energy Agency and the European Commission (UMWE (2011), Figure 3-4 and 3-5).
- The effect of the price of basic chemicals on the price of a consumer product is typically below 1%.

8.2.1 Policy measures to encourage the transition to a low carbon chemical industry

This study on the chemical industry and an earlier CE Delft publication on breakthrough technologies in the steel, cement and pulp and paper industries show innovative emission reduction options are in reach for the EU's energy-intensive industries. However, the deployment of these technologies on a large scale requires an integrated EU industry and energy policy framework. Moreover, resource-efficiency policies and robust sustainability standards are required to prevent unsustainable and perverse effects.

CE Delft recommends exploring the following options in more detail:
- The influence of the EU ETS as a mechanism to provide a reward on GHG emission reduction has been mentioned before. The range of reduction costs for CO_2 as projected in a number of scenario studies allows breakeven for most biobased alternatives. The question is whether price leverage mechanisms are enough to realise a sustainable industry.
- To prevent a too high stress on biomass demand which could lead to unsustainable mechanisms, policy measures could aim to reduce use, and demand minimum sustainability standards on sourcing of biomass. In addition, alternatives for biomass use like the renewable power based ammonia production could be favoured over biomass intensive alternatives.
- To prevent lock-in effects policy makers may consider to secure access to the limited CCS storage capacity to those industries that do not have an alternative to comply with the targets for 83-87% reduction in greenhouse gas (GHG) emissions.

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Annex A Carbon capture and storage

A.1 Availability of CCS

Carbon Capture and Storage (CCS) alternatively referred to as carbon capture and sequestration, is a technology to prevent large quantities of CO_2 from being released into the atmosphere from the use of fossil fuel in power generation and other industries. It is often regarded as a means of mitigating the contribution of fossil fuel emissions to global warming. The process is based on capturing carbon dioxide (CO_2) from large point sources, such as fossil fuel power plants, and storing it in such a way that it does not enter the atmosphere.

The concept of Carbon Capture and Storage (CCS) still has to be proven to a certain extent.
The individual steps have all been applied in commercial activities, often for a long time[41] and partly in combination with each other. However, perpetual storage of CO_2 is new and has not been demonstrated in practice before. There is some uncertainty if and how it can be guaranteed that CO_2 injected in deep geological gas fields and aquifers will actually stay there for thousands of years. This can only be estimated using model simulations, and the chance maximised by the application of a stringent set of storage site selection criteria and storage reservoir closure and abandonment criteria. The probability is more predictable and the criteria can more easily be met for geologically intensively explored, intrinsically gas-tight natural gas fields than for aquifers.
Criteria and protocols for reservoir behaviour modelling, injection, abandonment and monitoring are currently being developed and embedded in legislation. Initiators will have to prove that the probability of CO_2 escaping is similar to the probability of accidents at industrial facilities[42].

This lack of solid proof of the viability, reliability and safety of the concept has resulted in public concern and hesitation by environmental NGOs to rely on such a technology. Besides, the potential of CCS is probably not sufficient enough to reach an economy-wide reduction of 80-95% in industrial CO_2 emissions as required in the period up to 2050. The latter is due to:

- the limited capacity of sufficiently safe deep geological storage reservoirs;
- competition with the power sector to acquire storage capacity.

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[41] The capture of CO_2 has been commercially applied for decades in hydrogen production, ammonia production, beer brewing, ethanol production and coal fired power plants (e.g.). Transports by pipeline, by road and by rail have been applied commercially as part of respectively CO_2 utilisation in enhanced oil recovery and use of CO_2 in for example beverage industries and horticulture. CO_2 injection has been applied commercially as part of enhanced oil recovery in numerous projects in the USA, Venezuela and Algeria.

[42] Both IPCC report and Australian legislation demand a probability of 20% or less that a maximum of 1% of the stored CO_2 escapes within a 1,000 year period. This is equivalent to a possibility of approximately 1~~-~~x10^{-6} that CO_2 escapes.

Estimations by the EU financed GESTCO and Geocapacity projects of deep geological storage capacity for CO_2 in the EU amount to a capacity of approximately 120 Gtonne CO_2: 96 Gtonne CO_2 capacity in deep saline aquifers, 20 Gtonne in oil and gas fields and 1 Gtonne in unmineable coal fields. This estimate is said to be conservative. Total EU CO_2 emissions from large point sources (>0.1 Mtonne/year) are estimated at 2 Gtonne/year, approximately 50% of which is emitted by power plants. This would imply that the storage capacity in the EU corresponds to 60 years of current annual CO_2 production from large point sources.

It should be noted, however, that these estimates are shrouded in some uncertainty as they are based on a limited amount of data. In addition, it is not possible to estimate which part of these storage sites meet the safety and geology related site selection criteria such as:
- cap rock thickness;
- physical characteristics of the cap rock (plasticity and response to pressure changes);
- chemical characteristics of the cap rock, e.g. resistance of cap rock to chemical reaction with CO_2;
- faults in or just above the cap rock.

Additionally, for gas and oil fields there is no indication concerning:
- the number of existing or abandoned wells;
- the accessibility of the wells for monitoring;
- the suitability of well casings and well plugs for long-term storage of chemically reactive and corrosive high pressure CO_2;
- use for evaluation of field suitability for storage.

As a consequence no indication can be given about the actual suitability of the identified potential reservoirs.

Finally, there is also some discussion about the attractiveness of storage in aquifers. In general, storage in depleted and abandoned gas fields seems more attractive compared to storage in aquifers (Amesco, 2007):
- Available information:
  Storage in depleted gas fields can make use of a long track record of site characterisation with the main focus on the static and dynamic properties of the reservoir. It has been shown that the behaviour of the reservoir during CO_2 injection can be well predicted from the gas production history. These data and information are mostly missing for aquifers.
- Proof of containment:
  The very presence of gas trapped in reservoirs for geological time periods indicates that these structures can contain CO_2 as well, provided that the sealing properties of the cap rock and bounding faults have not changed due to gas production, the cap rock entry pressure for CO_2 is not exceeded, and the sealing properties are not affected by chemical reactions with CO_2 loaded fluids. The containment of CO_2 in aquifers would have to be proven with the help of additional field and laboratory measurements.
- Reservoir conditions:
  In most abandoned gas reservoirs in the Netherlands, for example, the pressure has dropped to very low levels, 30 to 50 bar, which is 100 to 300 bar below the initial reservoir pressure. This pressure window can be used for injecting CO_2 until the initial reservoir pressure is reached, preventing any negative effect on the seal, e.g. fracturing will be prevented. Injection in aquifers starts at the initial (hydrostatic) pressure and builds up pressure well above it, with potential adverse consequences for the seals.

- Reservoir properties:
  In general, the porosity and permeability of gas reservoirs is higher than those of the water-saturated alternatives. This will result in a larger capacity and better injectivity for CO_2 storage than in aquifers. In gas reservoirs there is less free water than in aquifers, which will limit the corrosion of well casing and degradation of the well cement. On the other hand, the high water saturation of aquifers promotes the dissolution of CO_2 in water, making the CO_2 less mobile.

A.2 Suitability of CCS

Given the uncertainties about actual suitability of the identified reservoirs and the question whether storage in aquifers is desirable, as described in the previous paragraph, the estimated storage potential of 120 Gtonne in the EU seems optimistic.
This implies that the available capacity should be reserved for processes that currently have no alternative like the steel industry (CE, 2010).
From the point of view of both a company manager and a policy maker, a scenario in which dependence on CCS can be avoided by applying a breakthrough technology may be attractive. Even more policy makers may want to consider whether industries in which breakthrough technologies are available, are entitled to use this limited storage potential.

A.3 Economics of CCS

Costs related to CCS for chemical processes are estimated to range between US$ 50-60/tonne CO_2 (IPPC, 2005). Future forecasts on CCS are based on the following aspects influencing price:

1. The initial cost of the installation capturing the CO_2 from the flue gas. Experience with flue gas desulphurisation learns that this type of large scale end of line solutions tend to decrease with ca. 12% every time that the installed capacity doubles.
2. The operational costs related to the required electricity use. In most situations this is 50% of the costs related to CCS.
3. The availability of storage capacity which is limited as explained above.

Because of the above mentioned aspects no significant decrease in the cost of CCS is expected for the period after 2020.

A.4 Commercial use of carbon dioxide instead of storage

Carbon dioxide (CO_2) is the product of two types of processes:

1. Burning fossil fuels or biomass or in more general terms: full oxidation of carbon hydrates. And
2. Fermentation like occurs during brewing of beer.

A.4.1 Direct use at the production location

Most of the commercial use of CO_2 occurs at the location where it is generated.

- About a third of the carbon dioxide produced as by-product of the hydgrogen generation required for the ammonia process is used to produce ureum (a fertilizer) from ammonia.
- Carbon dioxide produced during the brewing of beer is used to carbonise the beer.
- Carbon dioxide produced in combined power heat generation units of glass houses and softdrink plants is used to respectively feed the plants and carbonise the drinks[43]. In the first application generating carbon dioxide is so important that these units are said to be fired up in summer for the purpose of the carbon dioxide alone.

Apart from the urea production the CO_2 is not chemically bound and therefore is known to be emitted later to the air (in case of glass houses 5% of the added CO_2 is absorbed by the plants (chemically bound) the rest will be directly emitted. The high concentrations are necessary to push the plants to take up more than under normal conditions and thus grow faster).

A.4.2 Merchants market

CO_2 is used in many consumer products that require pressurised gas because it is inexpensive and non-flammable, and because it undergoes a phase transition from gas to liquid at room temperature at an attainable pressure of approximately 60 bar (870 psi, 59 atm), allowing far more carbon dioxide to fit in a given container than otherwise would. Life jackets often contain canisters of pressured carbon dioxide for quick inflation. Aluminium capsules of CO_2 are also sold as supplies of compressed gas for airguns, paintball markers, inflating bicycle tires, and for making carbonated water and soft drinks. Rapid vaporisation of liquid carbon dioxide is used for blasting in coal mines. High concentrations of carbon dioxide can also be used to kill pests. As mentioned before, plants need CO_2 in order to grow.

The captured CO_2 commercially offered on the market is typically captured during hydrogen production by means of the Haber-Bosch process (gasification of methane) in which CO_2 is produced in high concentrations (>98%). The amount of captured CO_2 that is reused in this way is very low. This is illustrated by the case of the International Fertilizer Association. They report that the industry globally sells 2.2% of the CO_2 produced in the Haber-Bosch process to other uses (5.2 Mt CO_2 globally).
This is a rather small amount when taking into account that the current emission of CO_2 for the production of ammonia, olefins and aromatics in Europe alone account for respectively 30, 35 and 6.6 Mtonnes CO_2/year.

A.4.3 Using CO_2 as a chemical building block

Use of CO_2 as a chemical building block is possible in the following ways:

1. Production of algae containing valuable proteins, amines and oils. As part of the carbon cycle known as photosynthesis, plants, algae and cyanobacteria absorb carbon dioxide, light and water to produce carbohydrate energy for themselves and oxygen as a waste product. This process requires energy (sun light) and very complex catalysts (chlorophyll) and time. Currently numerous pilot scale projects are under ways to develop means to reach the required scale.

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[43] An example of softdrinks carbonised by the plant CPU: http://www.contourglobal.com/portfolio/?id=7.

2. Dedicated production of pure chemical components:
   a Urea (the International Fertilizer Association reports that the industry globally utilises around 36% of the CO_2 removed. More than 90% is used for the synthesis of ammonia into urea).
   b Polyurethanes (pilot plant on kilogram scale by Bayer in cooperation RWTH Aachen).

   The limitation of using CO_2 as a basic chemical is that it is a very stable compound. Therefore, most reactions involving CO_2 are endothermic. Nature has solved this by the development of very sophisticated catalysts (chlorophyll) in order to be able to use sunlight as an energy source. Scientists are able to copy this reaction for a number of chemicals. However, in most applications the speed of reaction currently is a factor 100-10,000 to low to make production on industrial scale feasible. This means that this technology is far away from large scale application. Therefore this can not be regarded as an alternative to CCS in the period until 2050.

A.5 Conclusions

CCS is limited available and therefore should be used for those processes that do not have an alternative like the steel industry as shown in our previous report.

Policymakers may want to reconsider access to the limited storage capacity for CCS for those industries that currently have alternative options.

The use of CO_2 as a basic chemical is put forward as an alternative to the limited available storage capacity for CO_2. Elegant as this option may seem, the reuse of CO_2 is still the area of fundamental research with a limited number of applications that are or may be commercially available by 2050. There are no indications that this market will grow to such a level that it may provide an alternative to CCS.

Annex B Biomass use

B.1 Availability and demand

Based on the current production numbers for ammonia and for olefins and aromatics considerable amounts of woody biomass and/or bioethanol are required. The alternative biomass based production routes for ammonia and for olefins and aromatics discussed in this report would require respectively approximately 25-65 Mtonne/year of woody biomass and approximately 80-85 Mtonne/year of ethanol. Depending on the alternative method selected as is shown in Table 14.

Table 14 Required amounts of biomass per alternative production method assuming current production levels

Process description	Amount of woody biomass (Mtonne/year)	Amount of bioethanol (Mtonne/year)
Water electrolysis based NH_3	0	0
Biomass gasification based NH_3	38	0
Bioethanol based ethylene	0	34
Bioethanol based propylene	0	28
Bioethanol based aromatics (BTX)	0	21
Biogasification based aromatics (BTX)	25	0

For comparison, current consumption of woody biomass for energy in the EU amounts to 173 Mtonne/year, while demand is expected to increase to 350 Mtonne/year in 2030 as a result of EU’s renewable energy policy.

In this perspective demand for woody biomass for production of ammonia seems modest compared to demand for utilisation as a renewable fuel. The amount of ethanol required for production of olefins and aromatics is of the same magnitude compared with the 2020 demand for biofuels under the RED.

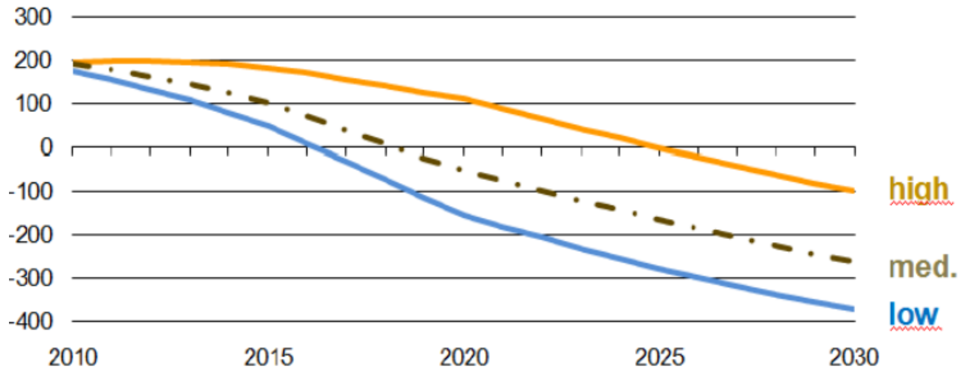
However, there is raising concern for the global stress on biodiversity caused by European energy policies. For example wood pellet exports from Canadian forests to Europe have grown sharply since 2002 (Bradley, 2010).From this point of view an addition in the demand of biomass may result in unsustainable mechanisms.

B.1.1 Future forecast of demand and risk of unsustainable mechanisms

Studies on global agricultural markets clearly predict that new arable land will be required to meet future global demand for food and feed (BUBE, 2010). Although there will be increased productivity on current arable land (intensification), food and feed demand will probably grow faster, which means that mobilisation of new land is likely to occur.

In addition, the policies on heat, power and fuel from biomass add to the deficit in sustainably grown biomass. For bioenergy (heat and power) and biofuels the EU is unable to supply the required amounts. The expected deficit between sustainable supply and demand for wood is illustrated by the development of the EU wood balance, Figure 38.

Figure 38 **Net balance of woody biomass (Mm3) development in the next decades**



Source: Mantau et al., 2010. 1 Mm^3 = 0.5 Mtonne.

If no additional policies are implemented to reduce demand or if targets are not adjusted, the gap between demand and availability will be filled up with imports and/or by unsustainable forest management and reserving cropland for cultivation of sugar and starch containing crops.

In both cases meeting demand will clearly result in deforestation directly due to import of unsustainably obtained wood or indirectly due to indirect land use change due to shifting of crop cultivation for food to other parts of the world.

Utilisation of woody biomass and ethanol as a raw material for the platform chemicals considered in this report will only add to the deficit, unless additional policies are adopted.

The risks mentioned above are not imaginary: current policies to stop biodiversity have failed as is reported in 2009 by the EEA, the European Commission and the Deutscher Bundestag (UMWE (2011), Par. 2.2.3).

B.1.2 Future price developments of biomass

An indicative assessment of future biomass gasification based plant implies some estimates on biomass futures beyond 2020. The problem is that there is profound insecurity on biomass futures beyond 2020 or to predict what will influence these prices. This is caused by the structural uncertainty both with respect to market mechanisms (e.g. is the price for natural gas and other fuels still coupled to that of heating oil and crude?) and to the uncertainty about volumes of sustainably sourced biomass available.

Based on the thorough special report on pathways towards a 100% renewable electricity system of the German Advisory Council on the environment we can distinguish the following trends:

- The price of biomass technology is expected to decrease moderately, but at the same time the prices of energy crops and forestry fuels are expected to evolve similarly to conventional fuel price (UMWE (2011), Figure 3-10).
- The rise in oil prices is structurally underestimated by the IEA (UMWE (2011), Figure 3-8).

The above indicates that in general the current price ratios are assumed.

We therefore adopted current market prices as an indication of the 2050 prices to make the assessment. If fossil fuel prices increase faster than the prices for biomass this is a conservative estimate. However, strong price rises in fossil fuel prices only occur on the long term if fossil fuels become scarce, in that case it is fair to assume a battle for biomass. In that situation biomass also will show a sharp price rise if all sourcing occurs sustainably.

B.1.3 European sugar beet based olefins and aromatics production

Sugar beet can be cultivated in almost the entire EU (IIASA, 2002) and could be combined with cereals cultivation in the conventional four crop rotation cycle as a breaking crop (see e.g. GM, 2002).
However, the required area is probably prohibitive and limitative with respect to the amount of sugar that can be produced from these crops.

Yields in the traditional sugar beet areas in the EU amount to approximately 10 tonne/year/ha of sugar. Sugar beets will probably yield another 2.5 tonne/year/ha of molasse (50% glucose) on average.
These yields give – at a fermentation efficiency of 90% - a total of approximately 5 tonne/year/ha of ethanol. At such average yield, complete substitution of naphtha and other fossil fuel based feedstocks for the EU olefins and aromatics production would require an area of approximately 16 Mhas.

Given a total area of arable land for cereals and oilseeds - which is partly utilised for growing biofuels feedstocks – of approximately 70 Mha there is theoretically enough area available for inclusion of 16 Mha in a four crops rotation system of cereals with sugar beet. However, this would have the following consequences:
- no crop based bioethanol production in the EU for fuel use;
- replacement of all rape seed cultivated for biodiesel production (4.5 Mha);
- replacement of all oil seeds cultivated for edible oil production and other food and feed uses;
- all the above mentioned effects may cause deforestation or other ways of biodiversity loss due to indirect land use change.

In short, there is not enough land available in the EU for the production of biobased petrochemistry in addition to the current demands for biomass.

A first, broad analysis of available residues and cropland in the EU indicates that residues will not help us out either. Availability of crop residues that are logical as a feedstock for ethanol production seems limited. According to JEC (2007) the potential in the EU of straw that can be collected at a reasonable price amounts to approximately 230 PJ/year and can yield approximately 4 Mtonne/year of ethanol.

Based on the above one may conclude that a sustainable solution requires a combination of production of ethanol from high yield crops, use of available residues and significant decrease in demand.

B.1.4 European biomass based ammonia and aromatics production

In the case of a shift of the current ammonia production to wood-based ammonia production this results in an extra demand of 60-65 Mtonne/year for ammonia and aromatics production in the EU on a global market for industrial round wood of approximately 1,500 Mm^3/year (750 Mtonne/year). This will likely mean a significant increase in pressure on this market.

The European pulp industry, and panel and board industry already indicate that they see their raw materials being redirected to energy applications. This is likely to cause an increased demand for the realisation of large scale monoculture wood plantations with short rotation Eucalyptus trees on land that was previously natural land or cropland. And thus increasing the risk for deforestation caused by indirect land use change.

B.1.5 Effect of obliged use of biofuels

The transport sector has an obligation to use an increasing percentage of biofuel. The obliged use of biofuel has increased demand for bioethanol and other biomass based fuels. This has allowed for example the Brazilian sugarcane based bioethanol industry to become more sustainable, while at the same time the risk for biodiversity loss due to indirect land use change has increased, see Section 7.2.4.

The policy also seems to have inspired both the capacity increase for bioethanol production in Europe and pilot projects in which among others aromatics were produced for biofuels based on biomass. Similar trends were found for gasification of biomass. Both in the USA and the EU, the further technological development of gasification of biomass is primarily focused at production of biofuels (gasification as feed for Fischer-Tropsch process may yield biodiesel and SNG) and not on integrated gasification and ammonia production.

Since we did not find research initiatives aiming on greening the (petro-) chemical industry we expect that the current focus on biofuels is caused by the obliged addition of biofuels in fuel for cars in the EU 27. Allowing for funding both by governments and private parties.

B.2 Technical and policy options to mitigate sustainability risks

In general policy options for mitigating land use change risks related to utilisation of biomass are:

- decrease in demand;
- minimal sustainability standards for the biomass sourcing;
- optimisation of the existing use of biomass;
- increasing the supply and production efficiency (within the limits of sustainable production).

Decrease in demand

Decrease in demand can be achieved by policies aiming for changes in consumption, reuse and recycling. In relation to this it is of interest to explore the potential of demand reduction in olefins by for example plastic recycle programs.

Another option to decrease demand for biomass is to focus on other energy or raw material sources for competing potential biomass applications. For wood the competing fossil fuel applications are heat and/or power generation. For these applications, the EU has still a significant unutilised potential of energy savings and renewable sources (SSREN, 2011), such as hydropower, sun, wind power and geothermal heat or even excess heat from industry.

For example in the case of low carbon ammonia production there are two potential low carbon alternatives to the conventional technology, one wood based and the other based on renewable electricity.

Minimal sustainability standards for the biomass sourcing

Minimum sustainability standards on biomass sourcing. This to prevent direct deforestation and other net green house gas emission increasing activities as well as negative effects on biodiversity and land use.

Optimisation of the existing use of biomass

Utilisation of residues that are not in demand for feed, raw material applications, or are not required for maintaining soil fertility and structure.

Increase the supply and production efficiency

Utilisation of crops and plants and conversion routes which yield maximum amount of energy or raw material per unit of area. Here an optimisation between high yield and environmental impact has to be found. We refer to the ongoing discussion on the road to sustainable agriculture and/or forest management within the framework of the common agriculture policy (CAP) post-2012.

B.3 Conclusions on side-effects of biobased chemistry

Apart from the options mentioned in this study there are several functions that increasingly depend on the use of sustainably grown biomass when the use of fossil fuels is phased out. Since the amount of sustainable biomass is limited this requires clear policies to prevent unsustainable land use.

Policy measures could aim to reduce use, demand minimum sustainability standards on production of bioethanol, focus on the optimisation of existing biomass uses and increase the supply and production efficiency.