

Bioethanol in Europe

Overview and comparison of production processes

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Abstract

Bioethanol is regarded as one of the main biofuels for application in the European transport sector. Several processes exist for the production of bioethanol. Currently, in Europe processes using sugar beets or grains as raw material are used, but using residual starch streams is gaining increased attention. Also, bioethanol processes using lignocellulosic biomass are being developed. The best-known process under development, commonly referred to as 'cellulosic ethanol' process, is based on physical/chemical pre-treatment of the biomass feedstock followed by enzymatic hydrolysis of cellulose and fermentation of the released sugars to ethanol. Furthermore, two other processes for bioethanol production from lignocellulose are under development. One process is based on gasification of lignocellulose to syngas (mainly CO and H₂) and subsequent catalytic synthesis, using a metal catalyst, to produce bioethanol or a mixture of alcohols. The other process is also based on gasification, but in this process the syngas is converted to bioethanol by fermentation through microorganisms. This report gives an overview of these different processes and evaluates their economic potential and environmental performance.

Keywords

Bioethanol, biofuels, biomass, enzymatic hydrolysis, fermentation, gasification, greenhouse gas mitigation, production costs, production process

Summary

Objectives

Bioethanol is regarded as one of the main biofuels in Europe, now and in the future. Current production is largely based on fermentation of sugar and starch crops. In 2005, 721.000 tons of bioethanol for transport were produced in Europe, approximately 50% more than in 2004. Fulfilment of the EC Directive target for 2010 to substitute 5.75% of diesel and petrol transport fuels requires an amount of 760 PJ biofuels. Assuming that bioethanol will account for half of that amount, the demand for fuel ethanol in 2010 in Europe will be approximately 14.5 million ton (or 18 million m³).

In order to fulfil the rapidly growing demand for fuel ethanol, several new processes using lignocellulosic biomass as feedstock are being developed. Lignocellulosic biomass is available in large amounts and at low cost in the form of agricultural (e.g. straw) and forestry residues or can be cultivated with a high yield per hectare and low energy inputs as compared to currently used starch and sugar crops. Bioethanol produced from lignocellulose is therefore expected to be more cost-effective in reducing greenhouse gas emissions than current bioethanol production. Currently, three types of new lignocellulose based production processes are under development.

This report gives an overview of the various bioethanol processes and evaluates their economic potential and environmental performance. The evaluated processes are:

- 'Conventional' bioethanol production from sugar beets, grains, potatoes and residual starch streams by fermentation and distillation. These are the main feedstocks currently used in Europe.
- 'Cellulosic' bioethanol production from lignocellulosic biomass by physical-chemical pre-treatment followed by enzymatic hydrolysis, fermentation and distillation.
- The production of bioethanol or a mixture of alcohols from lignocellulosic biomass by gasification and subsequent catalytic conversion of syngas to alcohols.
- The production of bioethanol from lignocellulosic biomass by gasification and subsequent fermentation of syngas to ethanol, a combination of thermochemical and biochemical techniques.

Evaluation of processes

An overview of production costs, greenhouse gas emission reduction and mitigation costs for all evaluated processes is presented in Table 1.1, Table 1.2 and Table 1.3 at the end of this summary.

Conventional bioethanol

The production of 'conventional' bioethanol from sugar and starch crops is widely commercialised. In the past 30 years the ethanol industry has reduced production costs 2 to 3-fold due to an increase in ethanol yield, and a two-fold reduction of energy use by a shift to larger ethanol production plants and adoption of energy-saving technologies. This trend will continue in the coming years as new plants are built with state-of-the-art technology.

For large plants with a capacity of ca. 240.000 m³ bioethanol/year current production costs in Europe are estimated at 0.50-0.55 €/l for sugar beet based processes, 0.55-0.60 €/l for grain based processes, 0.85-0.90 €/l for potato based processes, and 0.45-0.55 €/l for processes using residual starch streams (Table 1.1). Production costs are strongly dependent on the feedstock costs, which make up 50-70% of the overall costs. Future costs are expected to decrease due to process improvements. However, the high demand for bioethanol will likely increase the cost of sugar and starch feedstocks. Bioethanol production costs in 2020 are estimated at 0.45-0.50 €/l for sugar beet based processes, 0.50-0.55 €/l for grain based

processes 0.80-0.85 €/l for potato based processes, and 0.40-0.50 €/l for processes using residual starch streams.

The current reduction of greenhouse gas emissions compared to petrol (Table 1.2) is estimated on average at 40% for bioethanol from sugar beets and 20% for bioethanol from grains. The actual reduction depends on the type of production facility, type of fuel used etc. An improvement to 60% and 40% reduction respectively is possible by using state-of-the-art technology both in farming practices and in the production facilities. For processes using residual starch streams the greenhouse gas reduction compared to petrol is estimated at 40-60% with a possible improvement to 45-75%.

The GHG mitigation costs, i.e. the additional costs to be paid for bioethanol compared to petrol (at petrol production costs of 0.40 €/l, oil price ~50 \$/barrel) divided by the amount of GHG emissions avoided, are given in Table 1.3. The current GHG mitigation costs (Table 1.3) are estimated at 190-450 €/t CO₂-eq. for residual starch streams, 370-450 €/t CO₂-eq. for sugar beets and 900-1070 €/t CO₂-eq. for grains. It is expected that in 2020, the GHG mitigation cost can approximately be halved to at best 110 €/t CO₂-eq. for residual starch streams.

Cellulose ethanol by enzymatic hydrolysis

Bioethanol production using physical-chemical pre-treatment followed by enzymatic hydrolysis and fermentation is close to commercial application. In this process the cellulose and hemicellulose fractions in lignocellulosic biomass and residues (grass, straw, wood etc.) are used as a source of sugars for fermentation. The lignin fraction can be used for combined heat and power generation for the production process and export to the grid. Recent technological developments make it likely that this process is close to commercialisation.

For production in installations of ca. 240.000 m³ bioethanol/year the production costs are estimated in this study at 0.50-0.75 €/l in the short term (i.e. 2010) and 0.30-0.50 €/l in the medium term (2020). The reduction of greenhouse gas emissions for the use of 'cellulosic ethanol' compared to petrol is estimated at 80-85%. The GHG mitigation costs are 180-390 €/t CO₂-eq. for 2010 and 20-170 €/t CO₂-eq. for 2020, and are substantially lower than for 'conventional' bioethanol.

At the current state of development several bottlenecks remain. Development of an efficient pre-treatment process is a topic of active R&D. In the area of fermentation a recent breakthrough is the development of a yeast strain capable of rapid glucose and xylose fermentation. Further work is required to develop a robust industrial process for fermentation of lignocellulose hydrolysates. Other issues include conversion of the lignin fraction and the design of optimal process integration, water treatment and recycle. Presently, several pilot plants are in operation worldwide, using feedstocks such as corn stover, straw and wood. Industrial implementation of technology based on enzymatic hydrolysis is expected to start within 5 years in North America and/or the EU. Multinationals such as Shell, Abengoa and Royal Nedalco have invested in the development and are carrying out active R&D. The first commercial plants are expected around 2010.

Cellulose ethanol by gasification and subsequent catalytic syngas conversion

Production of bioethanol from lignocellulose by gasification and subsequent catalytic conversion of syngas to alcohols is receiving increased attention. The process (also called the HAS [higher alcohol synthesis] process) uses gasification so the lignin fraction of the biomass can be converted to bioethanol as well. Furthermore, no energy intensive separation of ethanol and water is required.

At present, the most suitable gasification technology –entrained flow gasification– is not fully developed yet for the use of biomass and the conversion rate and selectivity of the investigated catalysts is still far from what is required for commercial application. The

process will produce a mixture of alcohols, which could be used as fuel, although the methanol content should be minimised. Alternatively, sales of the co-produced higher alcohols for non-fuel applications –with a relatively high market value– may facilitate commercial implementation.

The estimated production costs (Table 1.1) are comparable with estimates for Fischer Tropsch diesel from biomass and vary from 0.30 - 0.50 €/l bioethanol for very large (several million m³/y) or large installations (ca. 240.000 m³/y). Since the investment costs are a significant part of the production costs, large-scale production is required, up to several million m³/y, in order to make use of scale-effects.

The expected reduction of GHG emissions compared to petrol is 90%, which leads to mitigation costs of 20-160 €/t CO₂-eq. for 2020, lower than for 'conventional' bioethanol and comparable with bioethanol from lignocellulose via enzymatic hydrolysis. Overall, this process seems promising and could be ready for market introduction between 2010 and 2020. Its success depends on the development of suitable catalyst.

Cellulose ethanol by gasification and subsequent syngas fermentation

The production of bioethanol from lignocellulosic biomass by gasification and fermentation of the produced CO and H₂ in syngas to ethanol converts all lignocellulose fractions (incl. lignin) to bioethanol and uses mild temperatures and pressures. R&D on this process has not been very intensive thus far, but there is currently one pilot plant in operation in the USA, which achieves only low bioethanol yields. The process seems far from commercialisation.

The process seems most suitable for small-scale operation (ca. 10.000-50.000 m³/y), as large-scale plants would require extremely large fermentation reactors. A low-temperature gasification technology, such as fixed bed, fluidised bed or indirect gasification should be used in combination with a technology to remove tars from the product gas. To be operated economically on a small scale, low cost, locally available biomass and/or waste is required as feedstock.

An initial cost estimate for this process based on current information is 0.60-0.90 €/l (see Table 1.1). The reduction of GHG emissions compared to petrol is expected to be 80-90%, provided the energy use in this process is not too high. This leads to GHG mitigation costs of 240-510 €/t CO₂-eq. for 2020, which is significantly higher than for other bioethanol processes using lignocellulosic biomass as feedstock.

The current cost projections are relatively high but further R&D might change this prospect. The main topics are: 1) Increase the tolerance of the fermentation organisms to ethanol. Currently, ethanol is toxic to the culture and ethanol concentrations should be kept below 3 % vol. This is too low from an economic and energetic point of view and should be increased to at least 6% vol. 2) Investigate whether small hydrocarbons such as methane present in syngas act as inhibitor to the fermentation process and/or development of resistant strains. 3) Improve the gas-to-liquid mass transfer and scale up of the fermentors. The latter is very important for cost reduction because the fermentation reactors are a major cost driver.

Improvement potential

Optimisation of classical ethanol production from sugars and starch is an ongoing process and will continue in the coming years especially by the construction of new, large-scale production plants with state-of-the art technology. In the long term the potential for reduction of production and GHG mitigation costs for conventional bioethanol is however limited compared with the new technologies using lignocellulose as feedstock. Production of bioethanol from lignocellulosic biomass by physical/chemical pre-treatment and enzymatic hydrolysis is mostly based on new technology and therefore long-term gains will most likely be higher, due to technological learning. This is illustrated by the projected costs for cellulose

ethanol from lignocellulose by this route, which are expected to decrease from 0.50 - 0.75 €/l in 2010 to 0.30 - 0.50 €/l in 2020.

Overall, the main contributors to the production costs of bioethanol are feedstock and investment costs and –to a lesser extent– energy costs. Bioethanol production costs are most sensitive to feedstock costs, which are subjected to market conditions. This applies especially to bioethanol from sugar beets and grains where raw material costs account for 50-70% of total production costs, whereas this is 25-50% for bioethanol processes based on lignocellulose. The capital costs are a more important cost driver for lignocellulose technologies where they account for 30-60% of the production costs. Energy costs are a factor only for conventional bioethanol production with a limited effect on production costs.

The oil price is a major, volatile factor for the competitiveness of bioethanol in the transport fuel market, but this applies equally to all types of bioethanol and other biofuels.

Bioethanol in the European biofuels market

The European Union actively pursues its Directive target of 5.75% substitution of petrol and diesel fuels with biofuels in 2010. This leads to a high demand for biofuels on the European market. It is not necessarily true that only the processes with lowest costs are competitive when demand for bioethanol is high. The current ethanol market where demand exceeds supply illustrates this. At present the European market demand is fulfilled by low-cost Brazilian bioethanol as well as more costly bioethanol and biodiesel produced in Europe.

In the longer term, it is expected that the best performing biofuels in terms of economic, but also environmental performance, will dominate the market. In the longer term the best performing biofuels are lignocellulose gasification-based fuels such as bio- Fischer-Tropsch diesel, bioethanol produced from lignocellulose by physical/chemical pre-treatment and enzymatic hydrolysis, and bioethanol produced from lignocellulose by gasification and catalytic synthesis. The estimated production costs for these two bioethanol processes for 2020 are 0.30 - 0.50 €/l or 15-22 €/GJ which compares well with cost estimates for bio-Fischer-Tropsch diesel. Bioethanol from lignocellulosic biomass is more cost-effective in reducing greenhouse gas emissions than the conventional bioethanol processes. This is mainly due to the better greenhouse gas balance compared to conventional bioethanol. The GHG mitigation costs for cellulosic bioethanol and for bio-Fischer Tropsch diesel are also similar: 20 - 170 €/t CO₂-eq. for 2020 at an oil price of 50 \$/barrel.

Table 1.1 Bioethanol production costs in Europe

Feedstock (& process)	Bioethanol production costs, including profit margin (€/l) *		
	2006	2010	2020
Sugar beets	0.50 - 0.55*	0.50 - 0.55	0.45 - 0.50
Grains	0.55 - 0.60	0.55 - 0.60	0.50 - 0.55
Potatoes	0.85 - 0.90	0.85 - 0.90	0.80 - 0.85
Residual starch streams	0.45 - 0.55	0.45 - 0.55	0.40 - 0.50
Lignocellulose (enzymatic hydrolysis)	-	0.50 - 0.75	0.30 - 0.50
Lignocellulose (gasification & synthesis)	-	-	0.30 - 0.50
Lignocellulose (gasification & fermentation)	-	-	0.60 - 0.90 ?

* 1 €/l bioethanol= 47 €/GJ (LHV)

Table 1.2 GHG emission reduction

Feedstock (& process)	GHG emission reduction compared to petrol		
	2006	2010	2020
Sugar beets	40%	60%	60%
Grains	20%	40%	40%
Potatoes	20%	40%	40%
Residual starch streams	40-60%	40-60%	45-75%
Lignocellulose (enzymatic hydrolysis)	-	80%	85%
Lignocellulose (gasification & synthesis)	-	-	90%
Lignocellulose (gasification & fermentation)	-	-	80-90% ?

Table 1.3 GHG mitigation costs

Feedstock (& process)	GHG mitigation costs (€/t CO ₂ -eq.)*		
	2006	2010	2020
Sugar beets	370 - 450	250 - 300	190 - 250
Grains	900 - 1070	450 - 530	370 - 450
Potatoes	1880 - 2050	940 - 1020	860 - 940
Residual starch streams	190 - 450	190 - 450	110 - 330
Lignocellulose (enzymatic hydrolysis)	-	180 - 390	20 - 170
Lignocellulose (gasification & synthesis)	-	-	20 - 160
Lignocellulose (gasification & fermentation)	-	-	240 - 510 ?

* At petrol production costs of 0.40 €/l (oil price ~50 \$/barrel)

Samenvatting

Doelstelling

Bioethanol wordt beschouwd als één van de belangrijkste biobrandstoffen in Europa voor nu en voor de toekomst. De huidige productie is grotendeels gebaseerd op fermentatie van suiker- en zetmeelgewassen. In 2005 is in Europa 721.000 ton bioethanol geproduceerd voor de transportsector, ongeveer 50% meer dan in 2004. De uitvoering van de EU-richtlijn met de doelstelling van 5,75% vervanging van benzine en diesel door biobrandstoffen in 2010, komt neer op een hoeveelheid van 760 PJ aan biobrandstoffen. Wanneer dit voor ongeveer de helft ingevuld wordt met biobrandstoffen, zal de vraag naar bioethanol voor de transportsector in Europa in 2010 ongeveer 14,5 miljoen ton (of 18 miljoen m³) bedragen.

Om te voldoen aan de snelgroeiende vraag naar bioethanol worden enkele nieuwe processen ontwikkeld die gebruik maken van lignocellulose (hout- of grasachtige gewassen) als grondstof. Lignocellulose is beschikbaar in grote hoeveelheden en tegen lage kosten in de vorm van landbouw- en bosbouwafval of kan verbouwd worden met hoge opbrengst per hectare en lage energie input vergeleken met zetmeel- en suikergewassen. Voor bioethanol productie uit lignocellulose wordt daarom verwacht dat het kosteneffectiever is dan de huidige bioethanol productie als het gaat om de reductie van broeikasgasemissies. Momenteel zijn drie nieuwe op lignocellulose gebaseerde productieprocessen in ontwikkeling.

Dit rapport geeft een overzicht van de verschillende bioethanol processen en beoordeelt het financieel-economisch en milieutechnisch perspectief. De beoordeelde processen zijn:

- 'Conventionele' bioethanol productie uit suikerbieten, graan, aardappelen en zetmeelhoudende reststromen door middel van fermentatie en destillatie. Dit zijn de belangrijkste grondstoffen die momenteel in Europa gebruikt worden voor bioethanol productie.
- 'Cellulose' bioethanol productie uit lignocellulose door fysisch-chemische voorbehandeling gevolgd door enzymatische hydrolyse and destillatie.
- De productie van bioethanol of een mengsel van alcoholen uit lignocellulose via vergassing gevolgd door katalytische conversie van syngas naar alcoholen.
- De productie van bioethanol uit lignocellulose via vergassing gevolgd door fermentatie van syngas naar ethanol, een combinatie van een thermochemisch en een biochemisch proces.

Evaluatie van de processen

Een overzicht van productiekosten, de reductie van broeikasgasemissies en de kosten voor vermeden broeikasgasemissies is voor alle beoordeelde processen weergegeven in respectievelijk Tabel 1.1, Tabel 1.2 en Tabel 1.3.

De productie van 'conventionele' bioethanol uit suiker en zetmeelhoudende grondstoffen wordt commercieel toegepast. In de afgelopen 30 jaar heeft de ethanolindustrie de productiekosten gereduceerd met een factor 2 à 3 door een verhoging van de ethanolopbrengst en door een reductie van het energiegebruik met een factor 2 door het overschakelen naar grotere fabrieken en het toepassen van energiebesparende technologie. Deze trend zal voortgezet worden in de komende jaren wanneer nieuwe fabrieken worden gebouwd met state-of-the-art technologie.

Voor grote fabrieken met een capaciteit van ca. 240.000 m³ bioethanol per jaar worden de huidige productiekosten in Europa geraamd op 0,50-0,55 €/l voor bioethanol uit suikerbieten, 0,55-0,60 €/l voor bioethanol uit granen, 0,85-0,90 €/l voor bioethanol uit

aardappelen, en 0,45-0,55 €/l voor bioethanol uit zetmeelhoudende reststromen (Tabel 1.1). De productiekosten zijn sterk afhankelijk van de grondstofkosten, die 50-70% van de productiekosten bedragen. De verwachting is dat toekomstige bioethanol productie kosten zullen dalen door procesverbeteringen. De toekomstige grote vraag naar bioethanol zal echter waarschijnlijk de prijs van suiker- en zetmeelhoudende grondstoffen opdrijven. De bioethanol productiekosten in 2020 worden geraamd op 0,45-0,50 €/l voor bioethanol uit suikerhoudende grondstoffen, 0,50-0,55 €/l voor bioethanol uit granen, 0,80-0,85 €/l voor bioethanol uit aardappelen, en 0,40-0,50 €/l voor bioethanol uit zetmeelhoudende reststromen.

De huidige reductie van broeikasgasemissies vergeleken met benzine (Tabel 1.2) wordt geraamd op gemiddeld 40% voor bioethanol uit suikerbieten en 20% voor bioethanol uit granen. De werkelijke reductie hangt af van het type productie-installatie, de brandstof, etc. Een verbetering naar respectievelijk 60% and 40% is mogelijk door het toepassen van state-of-the-art technologie zowel voor het verbouwen van gewassen als voor productie installaties. Voor processen gebaseerd op zetmeelhoudende reststromen wordt de broeikasgasemissiereductie vergeleken met benzine geraamd op 40-60%, met een mogelijke verbetering naar 45-75%.

De kosten voor vermeden broeikasgasemissies, d.w.z. de additionele kosten voor de productie van bioethanol vergeleken met benzine (bij benzine productiekosten van 0,40 €/l, olie prijs ~50 \$/vat) gedeeld door de vermeden broeikasgasemissies (in ton CO₂-eq. zijn weergegeven in Tabel 1.3. De huidige kosten van vermeden broeikasgasemissies worden geraamd op 190-450 €/t CO₂-eq. voor bioethanol uit zetmeelhoudende reststromen, 370-450 €/t CO₂-eq. voor suikerbieten en 900-1070 €/t CO₂-eq. voor productie uit granen. De verwachting is dat in 2020, de kosten van vermeden broeikasgasemissies ongeveer gehalveerd kunnen worden tot (als beste optie) 110 €/t CO₂-eq. voor zetmeelhoudende reststromen.

Productie van cellulose ethanol via enzymatische hydrolyse en fermentatie

De productie van bioethanol uit lignocellulose door fysisch-chemische voorbehandeling gevolgd door enzymatische hydrolyse is dicht bij commerciële toepassing. In dit proces worden de cellulose en hemicellulose fracties in lignocellulose biomassa en residuen (gras, stro, hout etc.) gebruikt als bron van suikers voor ethanol fermentatie. De lignine fractie kan worden ingezet worden voor productie van warmte en elektriciteit voor het productieproces en levering aan het net.

Voor productie in installaties met een schaal van ca. 240.000 m³ bioethanol/jaar worden de productiekosten in deze studie geraamd op 0,50-0,75 €/l op korte termijn (2010) en 0,30-0,50 €/l op middenlange termijn (2020).

De reductie van broeikasgasemissies bij gebruik van 'cellulose ethanol' vergeleken met benzine wordt geraamd op 80-85% (Tabel 1.2). De kosten van vermeden broeikasgasemissies worden geraamd op 180-390 €/t CO₂-eq. in 2010 resp. 20-170 €/t CO₂-eq. in 2020. Deze kosten zijn substantieel lager dan voor 'conventionele' bioethanol.

Door recente technologische ontwikkelingen is commercialisatie van dit proces op relatief korte termijn te verwachten. Bij de huidige stand van de ontwikkeling bestaan evenwel nog enkele bottlenecks. Aan de ontwikkeling van een efficiënt voorbehandelingsproces wordt onder meer gewerkt in diverse pilot installaties. Op fermentatiegebied is recent in Nederland een doorbraak bereikt door ontwikkeling van een giststam die in staat is tot snelle fermentatie van glucose en xylose. Verder werk is nodig om een robuust industrieel proces te ontwikkelen voor de fermentatie van lignocellulose hydrolysaten. Andere R&D issues betreffen de conversie van de ligninefractie en het ontwerpen van optimale procesintegratie, waterbehandeling en -recycle. Momenteel zijn wereldwijd diverse pilot plants operationeel, met grondstoffen als maisloof ('corn stover'), stro en hout. Het begin

van de industriële implementatie van de technologie gebaseerd op enzymatische hydrolyse wordt verwacht binnen 5 jaar in Noord Amerika en/of de EU. Multinationals zoals Shell, Abengoa en Koninklijke Nedalco hebben in deze ontwikkeling geïnvesteerd en doen actief onderzoek op dit gebied. De eerste commerciële fabrieken worden verwacht in 2010.

Productie van cellulose ethanol via vergassing en katalytische syngas conversie

Productie van bioethanol uit lignocellulose via vergassing en aansluitende katalytische conversie van syngas naar alcoholen krijgt de laatste jaren meer aandacht. Het proces is gebaseerd op vergassing zodat ook bioethanol kan worden geproduceerd uit de ligninefractie van de biomassa. Daarnaast, is er geen energie intensieve scheiding nodig van ethanol en water. Op dit moment is de meest geschikte vergassingstechnologie voor dit proces -'entrained flow gasification'- nog niet volledig uitontwikkeld voor het gebruik van biomassa als grondstof. Ook de conversiegraad en selectiviteit van de geteste katalysatoren zijn nog ver verwijderd van de eisen voor commerciële toepassing. Het proces produceert een mengsel van alcoholen (waaronder ethanol) die als brandstof gebruikt kunnen worden mits het methanol gehalte wordt geminimaliseerd. Als alternatief kan de afscheiding en verkoop van de hogere alcoholen voor niet-brandstof toepassingen -met een relatief hoge marktwaarde- commerciële implementatie bespoedigen.

De geraamde productiekosten (Tabel 1.1) zijn vergelijkbaar met kosten ramingen voor Fischer-Tropsch diesel uit biomassa en variëren van 0,30-0,50 €/1 bioethanol voor zeer grootschalige (enkele miljoenen m³) of grootschalige installaties (ca. 240.000 m³). Omdat de investeringskosten substantieel bijdragen aan de productiekosten is grootschalige productie, tot enkele miljoenen m³/jaar, noodzakelijk om te kunnen profiteren van schaalvoordelen in de investeringskosten. De verwachte reductie van broeikasgasemissies vergeleken met benzine is 90%, waaruit kosten van vermeden broeikasgasemissies resulteren van 20-160 €/t CO₂-eq. in 2020. Dit is substantieel lager dan voor 'conventionele' bioethanol en vergelijkbaar met bioethanol uit lignocellulose via enzymatische hydrolyse. Dit proces lijkt veelbelovend en de markt introductie kan verwacht worden tussen 2010 en 2020. De slaagkans is afhankelijk van de katalysatorontwikkeling.

Productie van cellulose ethanol via vergassing en syngas fermentatie

Bij de productie van bioethanol uit lignocellulose via vergassing en fermentatie van de geproduceerde CO en H₂ in syngas worden alle biomassa fracties (incl. lignine) omgezet in ethanol bij lagere temperatuur en druk. De R&D inspanning naar dit proces is tot dusver beperkt. Desondanks is al een pilot plant operationeel in de VS, waar momenteel echter lage bioethanol opbrengsten worden behaald. Het proces lijkt het meest geschikt voor kleinschalige bioethanol productie (ca. 10.000-50.000 m³/jaar), omdat op grote schaal extreem grote fermentatie reactoren nodig zullen zijn. Een lage-temperatuur vergassing technologie, zoals vastbed, fluïde bed of indirecte vergassing is benodigd in combinatie met technologie om teren te verwijderen uit het productgas. Om het proces op kleine schaal economisch rendabel te maken is het gebruik van goedkope, lokale biomassa en/of afvalstromen een vereiste.

Een initiële kostenraming voor dit proces (Tabel 1.1) gebaseerd op de beschikbare informatie bedraagt 0,60 - 0,90 €/l. De verwachte reductie van broeikasgasemissies vergeleken met benzine bedraagt 80-90% indien het energiegebruik in het proces kan worden geminimaliseerd. Hieruit volgen kosten van vermeden broeikasgasemissies van 240-510 €/t CO₂-eq. in 2020. Dit is substantieel hoger dan voor andere bioethanol processen die gebruik maken van lignocellulose als grondstof.

De huidige kostenramingen zijn ongunstig, maar verdere ontwikkeling kan hierin mogelijk verbetering brengen. De belangrijkste onderwerpen voor verder onderzoek zijn 1) het verbeteren van de ethanol tolerantie van de fermentatie organismen, waardoor een ethanol concentratie na fermentatie van minimaal 6 vol% kan worden bereikt 2) onderzoek naar mogelijke remmende effecten van kleine koolwaterstoffen (zoals CH₄) en (indien nodig) de

ontwikkeling van resistente stammen en 3) het verbeteren van de gas/vloeistof stofoverdracht in de fermentatie reactoren. Dit laatste is belangrijk om de kosten voor de fermentatie reactoren, die een zeer belangrijke kostenfactor zijn, te reduceren.

Verbeterpotentieel

De optimalisatie van de klassieke ethanolproductie uit suikers en zetmeel is een voortdurend proces dat in de komende jaren doorgezet zal worden met name bij het realiseren van nieuwe grootschalige fabrieken met state-of-the-art technologie. Op de lange termijn is het potentieel om de productiekosten en de kosten voor vermeden broeikasgasemissies te reduceren voor conventionele bioethanol echter beperkt vergeleken met nieuwe technologieën die lignocellulose als grondstof gebruiken. De productie van bioethanol uit lignocellulose via fysisch-chemische voorbehandeling en enzymatische hydrolyse is grotendeels gebaseerd op nieuwe technologieën en vanwege (technische) leereffecten zullen hiervoor de kostenreducties op lange termijn groter zijn. Dit is ook terug te zien in de kosten voor 'cellulose' bioethanol, waarvan verwacht wordt dat deze zullen dalen van 0,50 - 0,75 €/l in 2010 naar 0,30 - 0,50 €/l in 2020.

Voor alle processen zijn de belangrijkste kostenfactoren voor bioethanol productie de grondstofkosten en de investeringskosten en -in mindere mate- energiekosten. De bioethanolkosten zijn het meest gevoelig voor de grondstofkosten, die afhankelijk zijn van marktcondities. Dit geldt met name voor bioethanol uit suikerbieten en granen, omdat de grondstofkosten hiervoor 50-70% van de totale productiekosten bedragen. Dit is 25-50% voor bioethanol geproduceerd uit lignocellulose. De investeringskosten zijn een belangrijke kostenfactor voor bioethanol uit lignocellulose, waar deze 30-60% van de productiekosten bedragen. Energiekosten zijn alleen belangrijk voor conventionele bioethanol, maar hebben slechts een beperkt effect op de productiekosten.

De olieprijs is een belangrijke en instabiele factor voor de kosten van vermeden broeikasgasemissies voor bioethanol, maar dit geldt in gelijke mate voor alle bioethanol processen en voor andere biobrandstoffen

Bioethanol in the Europese biobrandstoffenmarkt

De Europese Unie voert actief beleid om de in een richtlijn vastgelegde doelstelling van 5,75% vervanging van benzine en diesel door biobrandstoffen in 2010 te bewerkstelligen. Hierdoor is er een grote vraag naar biobrandstoffen op de Europese markt, wat betekent dat niet alleen de productieprocessen met de laagste kosten kunnen concurreren. Momenteel wordt aan de bioethanol vraag voldaan door zowel goedkope Braziliaanse bioethanol als de duurere bioethanol en biodiesel die in Europa geproduceerd wordt.

De verwachting is dat op de lange termijn de biobrandstoffenmarkt gedomineerd wordt door de biobrandstoffen die het best presteren wat betreft economische, maar ook milieuprestatie. Dit zullen biobrandstoffen zijn geproduceerd uit lignocellulose via vergassing, zoals bio-Fischer-Tropsch diesel, bioethanol uit lignocellulose geproduceerd door fysisch-chemische voorbehandeling en enzymatische hydrolyse en bioethanol uit lignocellulose geproduceerd via vergassing en katalytische conversie. De geraamde productiekosten voor 2020 voor deze twee bioethanolprocessen bedragen 0,30-0,50 €/l, of 15-22 €/GJ, wat overeenkomt met de verwachte productiekosten voor bio-Fischer-Tropsch diesel. Bioethanol uit lignocellulose is kosteneffectiever in het reduceren van broeikasgasemissies dan de conventionele bioethanol. Dit komt met name door de betere broeikasgasemissiebalans vergeleken met conventionele bioethanol. De kosten voor vermeden broeikasgasemissies zijn voor bioethanol uit lignocellulose en voor bio-Fischer-Tropsch diesel vergelijkbaar: 20 - 170 €/t CO₂-eq. voor 2020 bij een olieprijs van 50 \$/vat.

Tabel 1.1 Bioethanol productiekosten in Europa

Grondstof (& proces)	Bioethanol productie kosten, inclusief winst marge (€/l) *		
	2006	2010	2020
Suikerbieten	0,50 - 0,55	0,50 - 0,55	0,45 - 0,50
Graan	0,55 - 0,60	0,55 - 0,60	0,50 - 0,55
Aardappelen	0,85 - 0,90	0,85 - 0,90	0,80 - 0,85
Zetmeelhoudende reststromen	0,45 - 0,55	0,45 - 0,55	0,40 - 0,50
Lignocellulose (enzymatische hydrolyse)	-	0,50 - 0,75	0,30 - 0,50
Lignocellulose (vergassing & synthese)	-	-	0,30 - 0,50
Lignocellulose (vergassing & fermentatie)	-	-	0,60 - 0,90 ?

* 1 €/l bioethanol= 47 €/GJ (LHV)

Tabel 1.2 Reductie van broeikasgasemissies

Grondstof (& proces)	Reductie van broeikasgasemissies vergeleken met benzine		
	2006	2010	2020
Suikerbieten	40%	60%	60%
Graan	20%	40%	40%
Aardappelen	20%	40%	40%
Zetmeelhoudende reststromen	40-60%	40-60%	45-75%
Lignocellulose (enzymatische hydrolyse)	-	80%	85%
Lignocellulose (vergassing & synthese)	-	-	90%
Lignocellulose (vergassing & fermentatie)	-	-	80-90% ?

Tabel 1.3 Kosten voor vermeden broeikasgasemissies

Grondstof (& proces)	Kosten voor vermeden broeikasgasemissies GHG (€/t CO ₂ -eq.)*		
	2006	2010	2020
Suikerbieten	370 - 450	250 - 300	190 - 250
Graan	900 - 1070	450 - 530	370 - 450
Aardappelen	1880 - 2050	940 - 1020	860 - 940
Zetmeelhoudende reststromen	190 - 450	190 - 450	110 - 330
Lignocellulose (enzymatische hydrolyse)	-	180 - 390	20 - 170
Lignocellulose (vergassing & synthese)	-	-	20 - 160
Lignocellulose (vergassing & fermentatie)	-	-	240 - 510 ?

* Bij benzine productiekosten van 0.40 €/l, olie prijs ~50 \$/vat

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1 Introduction

1.1 Background

In May 2003, the European Union has introduced a Directive with targets to partly substitute diesel and petrol transport fuels with biofuels (EU, 2003). The targets defined are 2% substitution on energy basis in 2005 and 5.75% in 2010. The Directive aims at reduction of greenhouse gas emissions from transport and an increased security of energy supply. Several European countries now use considerable amounts of biofuels, mainly bioethanol and biodiesel, so-called 'first generation' biofuels, which are not very cost-effective in reducing greenhouse gas emissions. However, in the near future 'second generation' biofuels will be produced using new production processes, and these biofuels will be more cost-effective in reducing greenhouse gas emissions.

Bioethanol is currently one of the main biofuels. In Europe it is produced from sugar containing materials such as sugar beets or molasses (by-product in sugar production), but also from starch containing materials, such as grains, and to a lesser extent potatoes. However, there are also processes being developed that can convert lignocellulosic biomass, such as straw, agricultural residues and wood, to bioethanol. The best-known process is commonly referred to as 'cellulosic ethanol' process, and it is based on physical/chemical pre-treatment of the biomass followed by enzymatic hydrolysis of cellulose. Many research institutes and companies are working to get this process ready for the market. However, researchers are also working on the development of two other bioethanol production processes. One process is based on gasification and subsequent catalytic synthesis of bioethanol or a mixture of alcohols using a metal catalyst. The other process also uses gasification, but the synthesis gas is here converted to bioethanol by fermentation by microorganisms. These latter two processes are relatively new, but have the potential to convert all of the lignocellulosic biomass, including the lignin fraction, into bioethanol.

1.2 Problem definition

Several evaluations exist of the different processes. However, the many research activities in the last years, there is no up-to-date overview of all bioethanol production processes. Especially for the two new processes using gasification followed by either catalytic synthesis or fermentation the available information is scarce and fragmented.

1.3 Objective

This report summarises available information and gives an insight in the feasibility of the new processes for the production of bioethanol for transport application. To this purpose, a state-of-the-art process description is given for existing and developed production processes, followed by the national and international parties involved, and an economic and environmental assessment. A comparison is made between the results of the different bioethanol processes and subsequently a comparison with other biofuels and with petrol (based on an oil price of 50 \$/barrel).

1.4 Report outline

A brief overview of the history of bioethanol is given in chapter 2. The process of bioethanol from sugar and starch crops and residues and its economic and environmental performance is described in the chapter 3. Chapter 4 deals with the process of 'cellulosic ethanol', i.e. physical/chemical pre-treatment of the biomass followed by enzymatic hydrolysis of

cellulose. Chapter 5 describes, as a comparison for the processes in later chapters, the production processes for biofuels other than bioethanol produced by gasification of lignocellulosic biomass and subsequent chemical synthesis. The process of bioethanol from lignocellulosic biomass by gasification and chemical synthesis is described in chapter 6 and the process of bioethanol from lignocellulosic biomass by gasification and fermentation in chapter 7. A comparison of the processes in the context of the European bioethanol market is given in chapter 8, followed by conclusions in chapter 9.

2 Brief history of bioethanol

The term 'bioethanol' indicates ethanol produced from biomass, as opposed to synthetic ethanol produced from fossil feedstocks. The production volume of synthetic ethanol is small compared to the amount of bioethanol produced. Generally the term bioethanol is applied specifically for ethanol used as (a component in) transportation fuel.

The use of ethanol for transport started in the beginning of the 20th century, but was abandoned after the Second World War. Interest in bioethanol revived after the first oil crisis. In 1975 Brazil started a large, government-sponsored programme for fuel-ethanol production from sugar cane. . Since then the Brazilian ethanol industry has grown considerably. In the United States large-scale ethanol production from (mainly) corn began in 1978 with steady growth, which has accelerated in recent years due to government policies and financial incentives. More recently countries like Canada, Australia, China, France, Spain, and Sweden started to promote the production and use of bioethanol. In 2005, the total worldwide production of bioethanol, for fuel and non-fuel applications, was 46 billion litres. The distribution over the different regions is shown in Figure 2.1. The development of the production of biofuels in Europe is shown in Figure 2.2. In the EU the production of fuel ethanol will expand substantially in the coming years due to European Commission policies. Various EU countries will either expand existing production capacity (Spain, France, Sweden) or implement new production facilities (e.g. UK, Germany, The Netherlands, Belgium, Poland).

Bioethanol is currently mostly used in transportation fuels blended with petrol in various percentages (E5, E10, E85), or as a component for production of the oxygenate ETBE, which is synthesized from bioethanol and isobutylene, a refinery by-product.

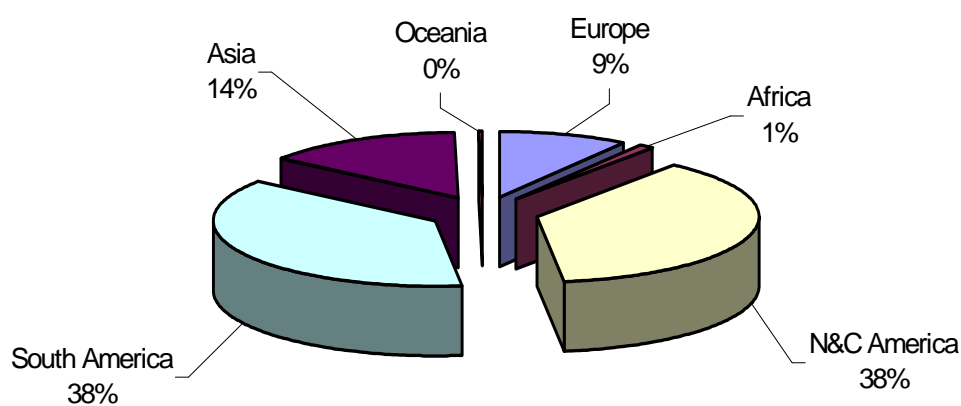


Figure 2.1 Distribution of worldwide bioethanol production (for fuel and non-fuel applications) in 2005.

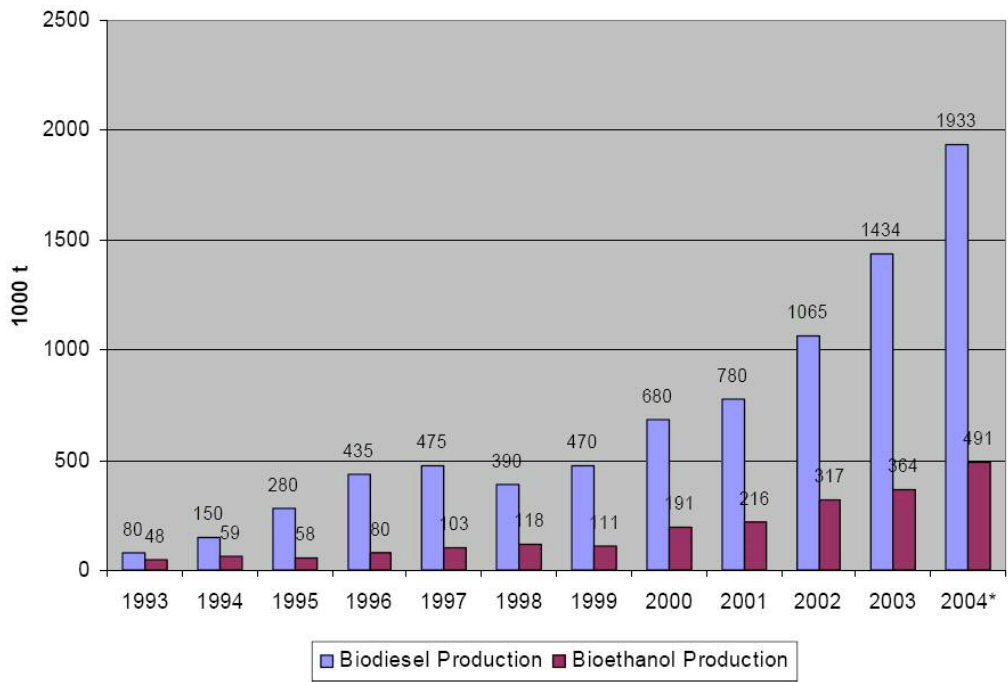


Figure 2.2 Biofuels production in the EU15. The 2004 figures are for the EU25 (Bomb, 2005).

3 Bioethanol from sugar and starch crops and residues

Bioethanol is produced through fermentation of sugars by yeasts or bacteria. Mostly used in the ethanol industry is the yeast *Saccharomyces cerevisiae* ('bakers yeast') which is capable of fermenting glucose, fructose, sucrose, galactose and mannose (Roehr, 2001). Bioethanol can thus be produced from any feedstock that contains significant amounts of these sugars or glucose polymers such as starch and cellulose that can be converted into glucose via hydrolysis (or 'saccharification'). The main sugars and sugar polymers used for ethanol production are depicted in Figure 3.1

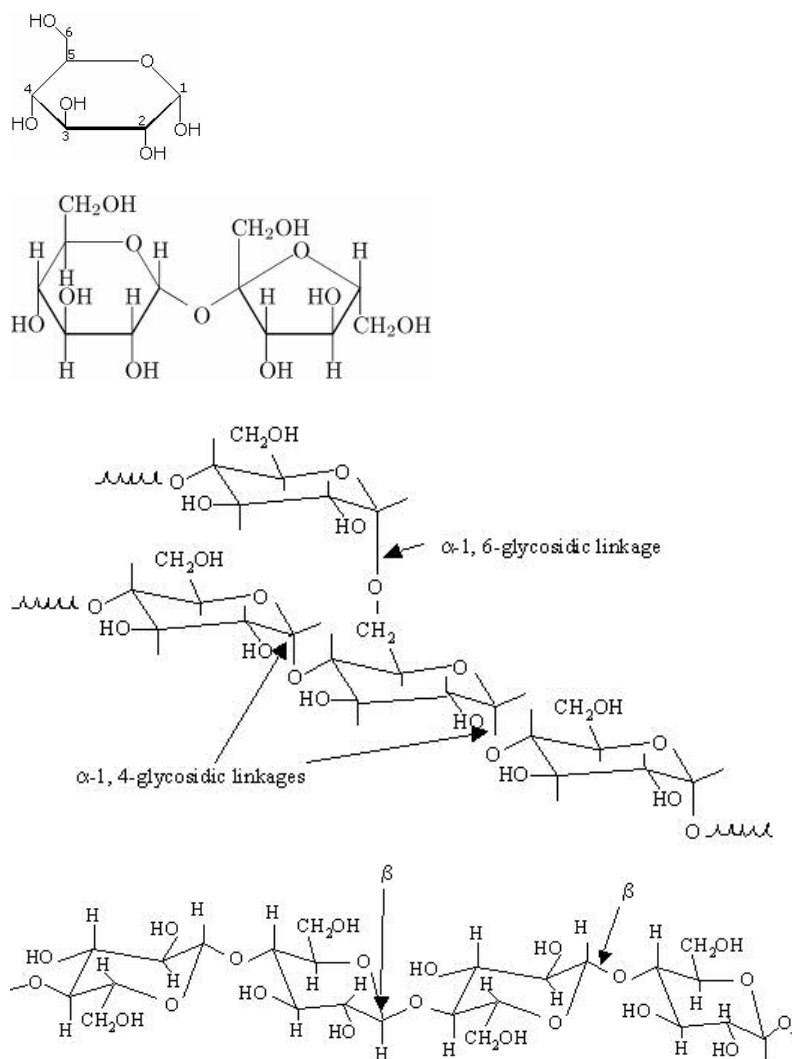


Figure 3.1 Major sugars and sugar polymers for bioethanol production. From the top: glucose, sucrose (or saccharose; a disaccharide composed of a glucose and a fructose monomer), starch (a glucose polymer with a branched structure), and cellulose consisting of linear glucose polymer chains.

Sugar obtained from feedstocks such as sugar beets, sugar cane and 'molasses', a by-product from sugar production, can be fermented directly. Starch from agro-feedstocks such as corn,

potatoes, wheat, rye, barley and sorghum is a glucose polymer that must be enzymatically hydrolysed to glucose monomers prior to fermentation. Production of fermentable sugars from (ligno)cellulose requires more rigorous pre-treatment due to the strong intermeshment of the sugar polymers (cellulose and hemicellulose) with each other and other biomass components.

Residues from agri-processing industries often contain substantial amounts of sugars or starch and are, therefore, also suitable as feedstock for ethanol production. In the Netherlands a production of approximately 2 million hectolitres of ethanol per year from agri-processing residues is feasible. The use of these residues as animal feed is declining, which makes their use as feedstock for ethanol production increasingly attractive. Industrial processes for the production of ethanol from sugars and starch (also referred to as 'conventional' or 'first generation' bioethanol) are today well established. Production of ethanol from (ligno)cellulose sources and residues, such as wood or straw, which are more abundant and cheaper than starch or sugar crops, is not yet realised at a commercial scale. Recent technological developments and the quickly growing demand for biofuels make it likely that industrial production of ethanol from lignocellulose is close to commercialisation. Bioethanol production from lignocellulose is described in chapter 4.

3.1 Process description

3.1.1 Pretreatment of sugar crops

In Brazil, sugar and bioethanol is produced from sugar cane, a crop with a high yield, but only suitable for the tropical climate. Sugar beets are more versatile sugar crops, because they can tolerate a wide range of soil and climatic conditions and consequently they can be produced in most European countries. Sugar beets are used for ethanol production only in Europe. The sucrose content of the beets is typically 15-20 wt% of the dry weight. In the processing plant the beets are washed, sliced and passed into a 'diffuser' to extract the sugar into a hot water solution. The liquid exiting the diffuser is called 'raw juice'. At a certain point, further sugar extraction is not economically attractive. The remaining syrup ('molasses') contains 45 wt% sugar, and can be fermented to ethanol (see paragraph 3.1.3). The remaining pulp contains 95% moisture and can be pressed to recover sugar, which is added to the raw juice. The pressed pulp is dried and sold as animal feed.

Alternatively, sugar syrup may be produced directly from sugar beet by cooking shredded sugar beet for several hours and then pressing the resulting beet mash and concentrating the juice. The raw juice can be used for production of sugar or bioethanol. (Figure 3.2). If the raw juice is used for sugar production, it has to be purified and partly evaporated to produce a concentrated juice, from which the sugar is crystallized.

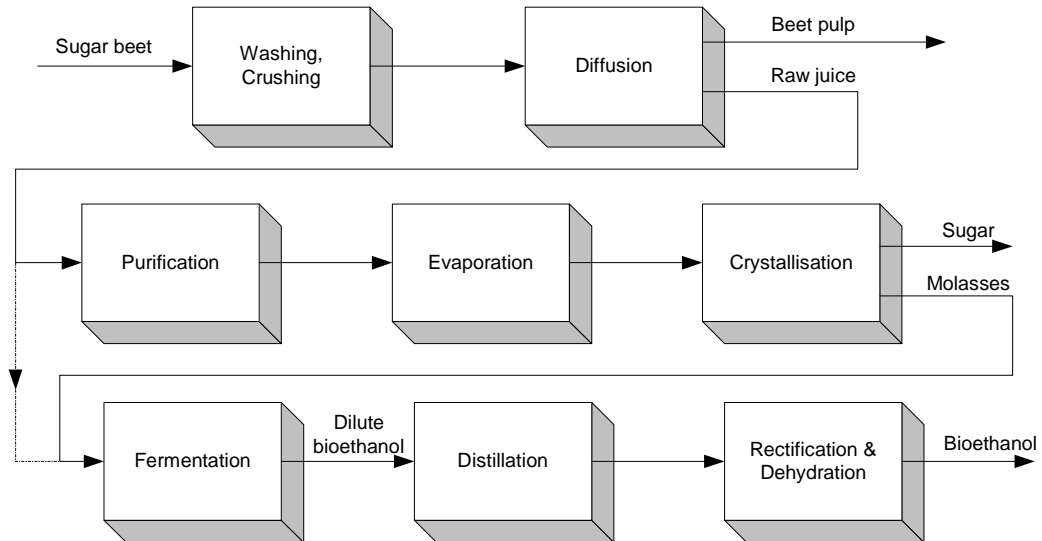


Figure 3.2 Scheme of a combined sugar/bioethanol production process from sugar beet.

3.1.2 Pre-treatment and hydrolysis of starch crops

In the United States and Europe bioethanol is mostly produced from starch crops. In the US this is mainly corn (maize). In Europe wheat, rye, barley and potatoes are used for bioethanol production. In Germany and Eastern Europe potatoes are the most widely used starch source. Wheat, rye and barley grains typically contain 60-70 wt% starch, 15 wt% water; while the remainder consists of mainly proteins, but also some fats, cellulose and minerals. Fresh potatoes generally contain 75 wt% water and approximately 17 wt% starch, with the remainder being proteins, small amounts of sugars and other compounds.

Ethanol processes based on starch are more complicated than those using sugars directly, because the starch has to be hydrolysed to glucose prior to fermentation. The most common process used in Europe is the 'milling and mashing process at higher temperatures'. In this process, first starch is released from the cell material ('liquefaction') and then the starch is converted to fermentable sugars ('saccharification') by addition of enzymes (amylases). The process can use all starch containing raw materials. After washing of the raw materials to remove sand, stones, soil etc., they are reduced in size, generally to 1.5 mm with a hammer mill. Preheated water and liquefaction enzymes are added and the mash is heated with steam to 65-95°C, depending on type of feedstock. The liquefaction takes 30 minutes to several hours. The mash is cooled down for saccharification and cooled down further to the temperature required for fermentation. The performance of this process depends on the efficiency to break up cells during milling and on the efficiency of the enzymes used. The process can be executed as a batch or as a continuous process.

After the starch is converted to glucose, the mash is fermented to ethanol (see paragraph 3.1.3). The fermentation product ('beer'), containing ethanol and solids, is distilled (see paragraph 3.1.4). The water/solids mixture obtained after distillation ('stillage') can be used as animal feed or fertiliser, either in liquid or dried form. The water can be recycled after the solids are mechanically removed, in order to reduce water and energy demand of the production process.

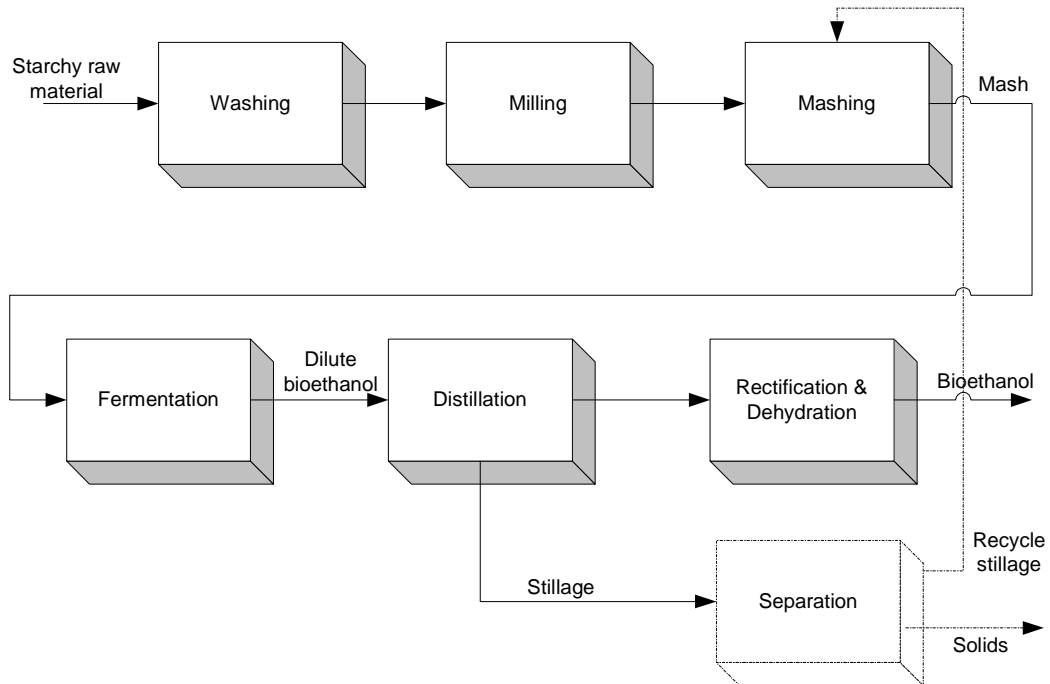


Figure 3.3 Scheme for bioethanol production from starchy raw materials.

3.1.3 Fermentation

Industrial fermentation of sugar to ethanol is generally performed with the yeast *Saccharomyces cerevisiae* at temperatures of 28-35 °C. The fermentation process can only be executed in relatively dilute concentrations, because yeasts are susceptible to ethanol inhibition. Concentrations in the order of 10-20 vol% may completely halt yeast growth in batch fermentations. Continuous processes where yeast is added allow for higher ethanol concentrations up to 20 vol%. Certain species of bacteria can also ferment sugar to ethanol, but they often also produce side products, such as organic acids. Furthermore, infections are more difficult to control in bacterial fermentations.

The fermentation takes place in large cylindrical fermentors, generally in a batch process, for periods of 10-60 hours. Following fermentation the yeast and other solids are often separated from the 'beer' by centrifugation, and may be recycled to the fermentor.

Fermentation can also be executed as a continuous process using continuous stirred tank reactors, which has several advantages over a batch process. Continuous processes may be carried out for a long period without shutdown, have higher productivity and thus require smaller reactor volumes. Continuous fermentations can be fully automated and operated under conditions that give a uniform product. However, a continuous process does require raw materials with uniform quality, as conditions cannot be adapted easily.

As a by-product of the fermentation process carbon dioxide is formed. This off-gas stream (> 90 vol% CO₂) contains appreciable amounts of ethanol vapour, which is recovered by scrubbing. Before venting the off gas to the atmosphere odour compounds must be removed. In some ethanol plants the CO₂ is captured and marketed for application in soft drinks or Enhanced Oil Recovery.

3.1.4 Distillation and final dehydration

Dedicated engines that can use 95 vol% ethanol ('hydrous ethanol') are currently used only in Brazil. In order to be used as a component in blends with petrol, bioethanol has to be purified to more than 99.5 vol% purity. A first distillation or stripping column removes

ethanol from the beer giving an approximately 50/50 water/ethanol mixture. Remaining solids are removed in the 'bottoms' or 'stillage' fraction, if these were not already removed prior to distillation. A second column ('rectifier') removes water up to 95 vol% ethanol. Higher alcohols or 'fusel oils' are also removed in this column. The limit for distillation is 95-96 vol% ethanol due to the water/ethanol azeotropic system. Therefore, the remaining water has to be removed with a different technique, such as dehydration with molecular sieves.

Distillation requires a large amount of energy. Increasing energy costs, especially in Europe, have led to an increased emphasis on heat recovery and reduction of energy use. In practice this is realised by using vapour recompression systems or multiple-stage, high-pressure distillation systems, resulting in a 40-80 % reduction of steam consumption. The investment costs for these systems are higher than for conventional distillation technology. The actual energy usage of the distillation depends strongly on the ethanol concentration after the fermentation process. The higher the ethanol concentration, the lower the energy cost for the distillation, as is shown in Figure 3.4. Final dehydration to 99.5 vol% bioethanol requires additional energy.

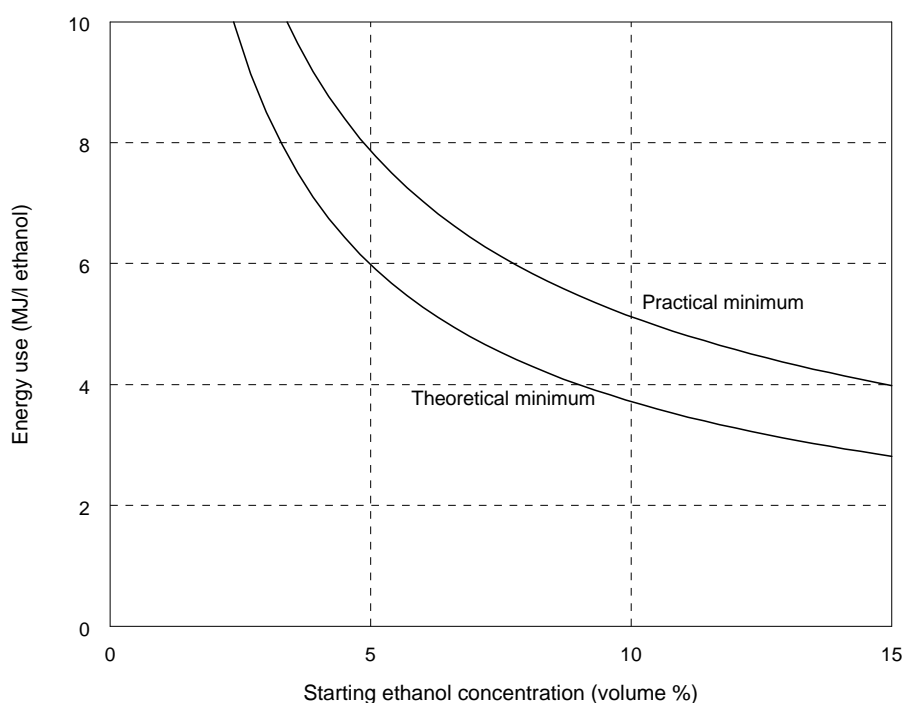


Figure 3.4 Energy requirement for distillation to 95% vol. ethanol. The energy content (LHV) of ethanol is 21.2 MJ/l. The theoretical minimum is based on thermodynamics; the practical minimum takes into account limitations in size for distillation towers. Adapted from (Madson, 2005).

3.2 Technology development

During the last three decades the ethanol industry has directed a substantial effort at improving ethanol yields and reducing production costs. In Brazil ethanol production costs have been reduced by approximately 3% per year through a combination of new, high-yielding sugar cane varieties, improved cultivation and harvesting practices, and improvements in the extraction, fermentation and distillation processes. In the US ethanol production costs have been reduced by two-thirds since the 1980's, due to a substantial increase in ethanol yield, and a two-fold reduction of energy usage by a shift to larger ethanol production plants, and adoption of energy-saving technologies. In addition to improvements of the manufacturing process itself, changes in the use of by-products

(bagasse, stillage) have increased energy efficiency, and reduced production costs. Overall, the ethanol industry has reduced production costs 2 to 3-fold in the past 30 years. Current efforts are mostly focused on improving production yields and lowering energy use, and include improvements of feedstock production, fermentation and distillation (see Table 3.1).

Table 3.1 Recent (and near future) technological innovations in fuel-ethanol production chains. Taken from (Uil, 2003)

Area	Developments
Crop production	High yielding varieties; reduced tillage; decline in fertilisation
Starch hydrolysis	Improved enzyme technology; On-site enzyme propagation
Fermentation	High-concentration wort; CO ₂ ethanol stripping; continuous membrane-bioreactor (removes ethanol, but not yeast); yeast strain selection; continuous fermentation units; yeast immobilisation
Distillation	Pressure-swing adsorption; dehydration with molecular sieves
Process control	System automation; integrated thermal engineering (capture and re-use of process heat)
Co-product use	Bagasse combustion; corn stillage refinery; corn-fibre oil and gum

Much ongoing effort is directed at optimisation and cost reduction of the enzymes required for starch hydrolysis. Since 2004 several corn bioethanol plants in the USA have started to use low temperature 'raw starch hydrolysis' employing newly developed enzymes that can hydrolyse starch while it is not yet liquefied (Williams, 2006). This means that a cooking process is not necessary and that the process can be executed at 30-40 °C, which saves a considerable amount of energy. Furthermore, it reduces capital expenses by reducing the number of unit operations and the requirement for heat exchangers and/or coolers. Other ongoing developments include improved enzymes for hydrolysis of starch from small grains such as wheat that will contribute to better yields and lower production costs.

Performing the fermentation at high yeast concentrations allows for higher ethanol productivity per unit fermentor volume and higher starting ethanol concentration for distillation. In so-called 'Very High Gravity fermentation technology' the dissolved solids are well above 30 wt./vol% leading to more than 16 vol% of ethanol after fermentation (EPM, 2006). In batch processes yeast may be recovered by centrifugation and recycled to the fermentor. Modern plants in the US use continuous processes together with simultaneous saccharification and fermentation (SSF) that can be combined with yeast propagation. This allows a higher concentration of yeasts in the fermentation process thus optimising productivity. Furthermore, modern plants are equipped with computerized process control reducing labour costs.

A recent development is the use of thermophilic microorganisms for ethanol fermentation. Thermophilic bacteria grow and ferment optimally at temperatures of 50°C and higher. They are tolerant to fluctuations in pH and temperature and can ferment a broad range of sugars. They have rapid growth rates and high activity with increased production rates (TMO Biotec, 2006). The high fermentation temperature is an advantage, because the up-stream liquefaction usually takes place at higher temperatures while the downstream distillation takes place at higher temperatures as well. Thus, the use of thermophiles for fermentation will potentially save cooling and heating operations and energy use.

Distillation best practise and current energy use is close to the 'practical minimum' depicted in Figure 3.4, although many current installations do not yet use the best available technology. Further reduction of energy use for distillation is possible by increasing the ethanol concentration in the fermentation. Innovations such as SSF could bring fermentation processes that now produce a 10-12 vol% ethanol solution up to 16 vol%. Another current approach to reduce energy consumption is the development of membrane-based pervaporation for ethanol purification.

3.3 Important actors

The bioethanol market in Europe is mainly controlled by big industrial groups and large agricultural cooperatives of the sugar and alcohol industries (Observ'ER, 2005). The Spanish group Abengoa is the largest producer in Europe with a 150.000 ton ethanol plant in Cartagena, a 176.000 ton plant in Galicia, and a third, 160.000 ton plant being commissioned in Salamanca. It has also tendered in the French bioethanol programme. Other large bioethanol producers are Sauter and Südzucker in Germany, Cristal Union and Tereos in France, and Agroetanol AB and Svensk Etanolkemi in Sweden. Main actors in the transformation of ethanol into ETBE are Total in France and Repsol and Cepsa in Spain.

In the Netherlands, Royal Nedalco has recently announced the construction of an additional fuel ethanol plant at their production site in Sas van Gent. The feedstock will consist of wheat milling residue from the neighbouring Cerestar (Cargill) plant. Furthermore, Futura Petroleum Ltd, a subsidiary of the English company Blue Ocean Associates, has announced plans to build a 110.000 tonnes bio-ethanol from grains plant in the port of Amsterdam. Bio-ethanol Rotterdam B.V. (BER), a cooperation of Chemical Processing Consult (CPC), HES Beheer and Holland Innovation Team, is planning a 100.000 tonnes per year bioethanol plant in the port of Rotterdam. Another 10.000 tonnes of capacity should be added to the site as a pilot project using thermophiles for fermentation, developed by the English company TMO Biotec. At present, there is no ETBE production capacity in the Netherlands, but Lyondell is retrofitting its MTBE plant at Botlek for ETBE production and Sabic has announced plans to start ETBE production.

3.4 Performance

3.4.1 Economics

The costs of bioethanol production are highly dependent on raw material costs, investment and energy costs and the value of by-products. The feedstock contributes 50-70% to the costs of bioethanol, the remainder being mainly investment and energy costs. By-product values depend on the markets available. By-products from bioethanol from grains can be used as animal feed. For small facilities, it might be more useful to convert the by-products to biogas. By-products from bioethanol from sugar beet can in some cases be used as animal feed, but also as fertiliser. However, the upgrading of most by-products requires additional investment and energy costs, mainly for drying.

The capital investment of a bioethanol plant depends on the type of feedstock and the location and scale of the plant. A best estimate for the capital cost of bioethanol plants in Europe is given in Table 3.2. Generally, larger bioethanol plants have lower production costs, as is shown in Figure 3.5. The economy of scale applies both to the investment costs and personnel costs. However, there is an economic maximum to the size of bioethanol plants: for very large plants, the cost advantages associated with the large scale are offset by higher costs for transport of the feedstock.

A best estimate for bioethanol production costs is given in Table 3.3. The higher costs for bioethanol from starch crops as compared to sugar crops is mainly caused by higher investment and energy costs for upgrading of the by-products. Bioethanol from potatoes is especially expensive, because potatoes contain 75% water, which implies that transport from the field to the factory is relatively costly. Furthermore, the energy usage and costs are highest in the production process from potatoes. As average cost figures in this study, 0.50 - 0.55 €/l was used for bioethanol from sugar beets, 0.55 - 0.60 €/l from grains and 0.85 - 0.90 €/l from potatoes. The costs for bioethanol from residual starch streams are estimated at 0.45 - 0.55 €/l (Kampman, 2005). A complete overview of the cost figures selected is given in chapter 8.

Table 3.2 Estimated capital costs for bioethanol plants (Schmitz , 2003)

Feedstock	Small installations (20.000 m ³ /y) M€	Medium-sized installations (60.000 m ³ /y) M€	Large installations (120.000 m ³ /y) M€	Largest installations (240.000 m ³ /y) M€
Sugar beet molasses / raw juice	20	30	40	60
Grains	30	50	70	105
Potatoes	30	50	70	90

Table 3.3 Bioethanol production costs in Europe, including profit margin (Schmitz, 2003)

Feedstock	Feedstock costs (fresh) €/t	Small installations (20.000 m ³ /y) €/m ³	Medium-sized installations (60.000 m ³ /y) €/m ³	Large installations (120.000 m ³ /y) €/m ³	Largest installations (240.000 m ³ /y) €/m ³
Sugar beet molasses	85	657	560	538	532
Sugar beet raw juice	202	643	548	527	522
Wheat	120	805	671	632	610
Rye	85	738	604	565	544
Triticale	105	779	646	607	587
Maize (corn)	105	761	626	585	562
Potatoes	50	1033	928	898	885

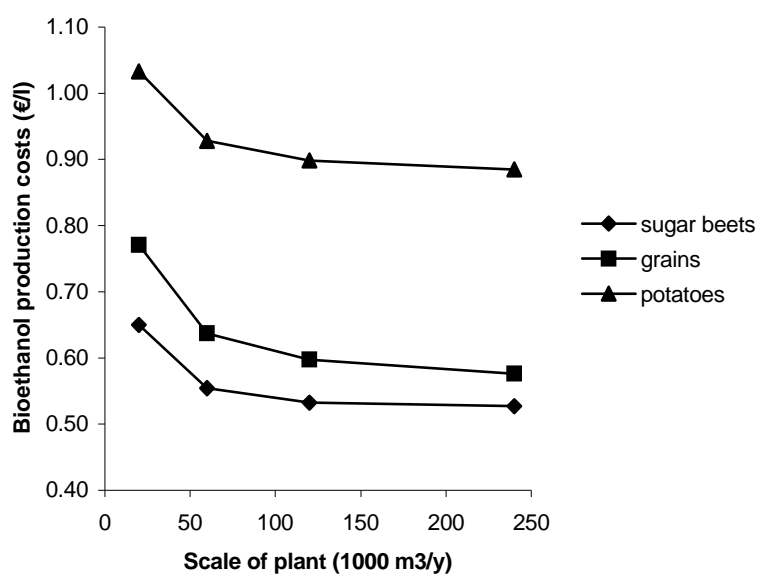


Figure 3.5 Scale dependency of 'conventional' bioethanol production costs.

3.4.2 Energy balance and greenhouse gas emissions

The main energy input in the production of bioethanol from sugar or starch crops is the process energy used in the bioethanol plant. Also important are the energy inputs for the

production of fertilisers and pesticides used for feedstock cultivation. In addition, a very important factor for the greenhouse gas balance is the emission of N₂O (a strong greenhouse gas) from the field during feedstock cultivation, and from fertiliser production. The energy and greenhouse gas balances are dependent on the type of process, plant size and the feedstock used. Calculations of net energy balance are highly sensitive to system boundaries and parameter values. Another important factor in the energy balance is how the energy use is attributed to the by-products. The by-products basically replace other products that would require energy to produce, which should be accounted for.

Several studies from the USA have suggested that the energy balance for bioethanol is negative, i.e. more energy is required to produce the ethanol than is gained by replacing petrol (Patzek, 2004; Pimentel, 2005). The authors also suggest that the net life-cycle greenhouse gas emissions for bioethanol are higher than for petrol. These studies have, however, been widely disputed. In a recent article in Science concerning bioethanol from corn in the USA, it was concluded that the energy balance is clearly positive (Farrell, 2006). However, according to the article, the average reduction of greenhouse gas emissions using corn ethanol is only 14%, whereas in individual cases an increase in greenhouse gas emissions is possible.

A recent Dutch LCA for bioethanol from wheat finds a GHG emission reduction of 30% compared to petrol (SenterNovem, 2005). A Dutch review of European studies indicates that the use of bioethanol reduces greenhouse gas emissions by 41-61% (Uil, 2003). This clearly positive number compared to the US studies was explained by the facts that: 1) in Europe other feedstocks are used, which can be processed more efficiently than corn, 2) energy costs in Europe are higher and, therefore, production processes are more efficient and 3) whereas in the USA many processes use coal for heat production, in Europe, mostly natural gas or oil is used.

Other European studies and reviews give different results with broader ranges, as can be seen in Table 3.4. From these figures it seems that most of the bioethanol production and use from current plants likely reduces greenhouse gas emissions, but some bioethanol plants, e.g. a small number of plants using grain as feedstock and (lignite) coal as heating fuel, could actually have a negative greenhouse gas balance. On average, based on the figures in Table 3.4 with special emphasis on the renowned VIEWLS (values today) and Concawe/EUCAR/JRC studies, for the GHG emission reduction by bioethanol from sugar crops a value of 40% was selected and a value of 20% for bioethanol from grains. Obviously, these figures can vary significantly between different bioethanol plants.

Table 3.4 Reduction of greenhouse gas emissions for European produced bioethanol, compared to petrol. (EC, 2006)

Study by	Bioethanol from sugar crops*	Bioethanol from grain*
VIEWLS (values today)	20 - 73 %	-/- 21 - 32 %
VIEWLS (values for 2010)	35 - 72 %	16 - 64 %
Sheffield Hallam	47 - 54 %	62 - 67 %
Imperial College	-/- 11 - 63 %	5 - 68 %
Concawe/EUCAR/JRC	37 - 44 %	-/- 6 - 43 %
PWC	40 - 60 %	40- 70 %
IEA	34 - 55 %	18 - 46 %
ADEME	75 %	75%

* -/- indicates a negative reduction which actually is an increase in greenhouse gas emissions

For greenhouse gas reduction by the use of bioethanol from residual starch streams from agri-processing industries, the only available estimate is a 40-60% reduction compared to petrol (Kampman, 2005). This is better than for sugar or starch crops because these streams require no or less intensive cultivation of raw materials.

3.4.3 Performance improvements

As described in paragraph 3.4.1, the experience in Brazil and the USA has shown that bioethanol production costs can decrease significantly when the production volume increases. This is due to a shift to larger plants and technological improvements in feedstock production and the manufacturing process. It can be expected that process improvements, such as given in Table 3.1, will be implemented. Furthermore, when many plants of the same type are built, the costs of plant equipment will decrease due to scale advantages in equipment manufacturing.

However, the costs for conventional bioethanol depend for a large part on the feedstock costs, which at present accounts for 50-70% of the cost of bioethanol. Thus, bioethanol production costs are extremely sensitive to changes in feedstock costs. Recently, corn prices have soared by 15-30% in the USA due to the high demand for bioethanol. A similar increase of feedstock cost in Europe would cause an increase in production costs of 0.05-0.10 €/l. Estimates for future bioethanol production costs are difficult to give. Based on the assumptions that process improvements will lower bioethanol cost significantly, but that feedstock costs will rise due to a high demand for bioethanol, it is estimated that the costs of bioethanol production in Europe will decrease, but only slightly by 0.05 €/l.

As described in paragraph 3.4.2, the greenhouse gas emission reduction is at present only 40% for bioethanol currently produced from grain and 20% from sugar beets. However, many of the currently operating bioethanol plants do not use state-of-the-art-technology. Indeed, according to expert judgements, state-of-the-art technology in farming and conversion is better than most of the technology that is used today, see Table 3.5. This is in line with the VIEWLS estimates for 2010 (see Table 3.4). Based on these figures the GHG emission reduction for bioethanol production in new plants will on average be 40% for bioethanol from grains and 60% for bioethanol from sugar beets. These estimates are used in this study for 2010 and 2020.

Table 3.5 Greenhouse gas emissions and reductions of state-of-the-art bioethanol production (Schmitz, 2003)

Feedstock	Farming emissions ¹ (g CO ₂ -eq. / 1 ethanol)	Conversion emissions ² (g CO ₂ -eq. / 1 ethanol)	Total emissions (g CO ₂ -eq. / 1 ethanol)	GHG emission reduction ³
Sugar beet molasses	296	480	776	56 %
Sugar beet raw juice	274	387	661	62 %
Wheat	484	537	1021	42 %
Rye	751	423	1174	33 %
Triticale	634	423	1057	40 %
Maize (corn)	338	368	706	60 %
Potatoes	414	579	993	43 %

1) 10% already deducted and attributed to by-products 2) 20% already deducted and attributed to by-products 3) compared to petrol using heating values of 21.2 MJ/l for bioethanol and 31.0 MJ/l for petrol. Burning petrol results in 72 g CO₂-eq./MJ and its up-stream processing (oil extraction, oil refinery) is estimated at an additional 15% of GHG emissions.

For residual starch streams, an improvement from the current 40-60% reduction to 45-75% in the long-term (2020) is expected, based on process improvements. A complete overview of all the figures selected is given in chapter 8.

4 Bioethanol from lignocellulose via enzymatic hydrolysis

The cellulose and hemicellulose fractions in lignocellulose (grass, straw, wood etc.) are potential sources of sugars for bioethanol production. Bioethanol can be produced from cellulose and hemicellulose by pre-treatment and hydrolysis to sugars, and subsequent fermentation. Lignocellulose is a low cost feedstock with the advantage that it is either available in large amounts as agricultural residues (e.g. straw) or that it can be cultivated with high yield per hectare and low energy inputs. The lignin, also a major constituent of lignocellulose (see Table 4.1), cannot be fermented to ethanol and must be used efficiently for other uses such as heat and power production. The production of bioethanol from lignocellulosic materials is not yet commercialised, but several pilot plants are in operation. Often-used feedstocks include corn stover, straw and wood. Industrial implementation is expected to start within 5 years in North America and/or the EU.

Table 4.1 Typical compositions of lignocellulosic materials (dry weight basis)

Component	Verge grass	Willow tops	Straw
(Hemi) cellulose (wt.%)	61	75	55
Lignin (wt.%)	21.5	23	28
Other organics (wt.%)	10.5	0.5	9
Ash (wt.%)	7	1.5	8

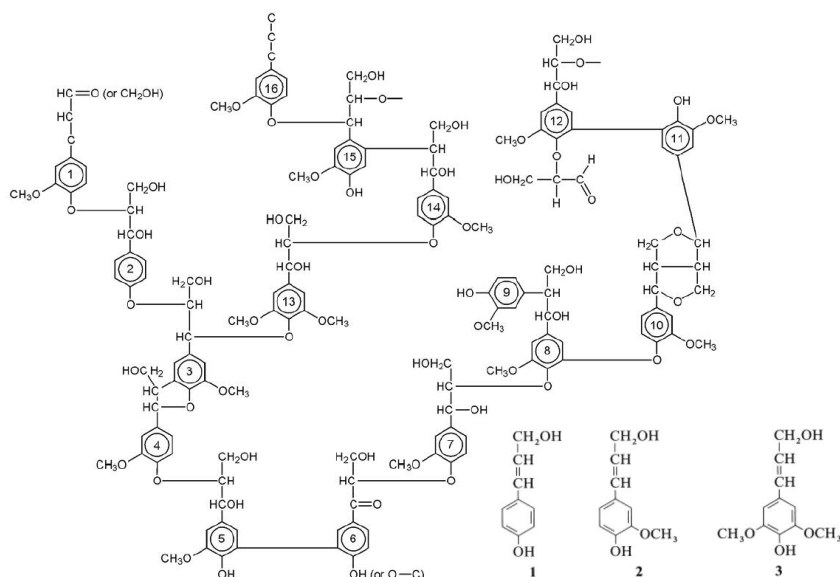


Figure 4.1 Example structure of lignin with the major monomers in the lower right-hand corner.

4.1 Process description

Several process configurations are currently under development. They all share a number of similar process steps (see Figure 4.2), described in the following sections.

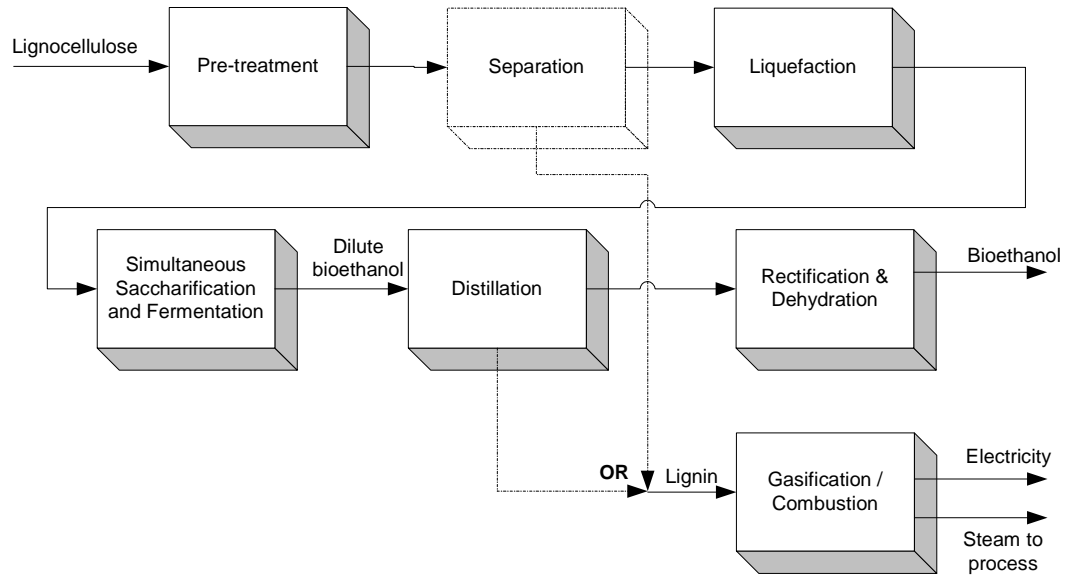


Figure 4.2 Scheme for bioethanol production from lignocellulosic materials.

4.1.1 Pre-treatment and hydrolysis

The first step is size reduction of the biomass through shredding or milling, e.g. using hammer mills. A washing step may be included depending on the feedstock. The feedstock is then subjected to a physical-chemical pre-treatment process, which needs to be more rigorous than for starch crops, due to the strong intermeshment of the sugar polymers with other biomass components (especially lignin), and the highly crystalline structure of the cellulose polymer.

Pre-treatment breaks up the fibre structure and enhances the accessibility of the cellulose polymers to enzymes in the following hydrolysis step. Dependent on the method employed the pre-treatment step also hydrolyses sugars (mainly xylose) from the hemicellulose, which is much easier to hydrolyse than the crystalline cellulose. Several methods are being developed including mechanical, thermal and chemical processes and combinations thereof (see Table 4.2). At the current state of development all methods still show specific drawbacks, such as: the production of undesirable side products that inhibit fermentation (breakdown products derived from sugars or lignin; 'inhibitors'), excessive use of chemicals and associated waste production, high energy use and/or high investment costs. Table 4.2 gives a qualitative evaluation of developed pre-treatment methods. Currently, dilute acid thermal pre-treatment and steam explosion seem closest to industrial implementation.

In order to reach optimal productivity high solids concentration is preferred, causing high viscosity of the pre-treated product. Therefore, the pre-treatment process may be followed by a 'pre-hydrolysis' step where enzymes reduce the viscosity by (partly) breaking down the cellulose. This step is comparable to the liquefaction step in starch to bioethanol plants, although for cellulose other types of enzymes i.e. cellulases are required.

Liquefaction is followed by enzymatic hydrolysis (saccharification) of cellulose either separately or in combination with ethanol fermentation. The process developed by Iogen (Canada) employs separate hydrolysis and fermentation (SHF). Other developed processes are based on simultaneous saccharification and fermentation (SSF) where cellulase enzymes for cellulose hydrolysis to glucose and microorganisms for ethanol fermentation are used in the same vessel. Cellulases are more expensive than industrial amylases to saccharify starch. Through a substantial R&D effort in recent years (subsidized by the US government) major industrial enzyme manufacturers Novozymes and Genencor claim to have realized a large reduction of enzyme costs. In 2005 enzyme manufacturer Novozymes announced a 30-fold

cost reduction for cellulase from over € 1 down to € 0.02-0.04 per produced litre of cellulose ethanol (Novozymes, 2006).

Table 4.2 Qualitative evaluation of pre-treatment processes (Reith, 2002)

Pre-treatment process	Yield of fermentable sugars	Inhibitor production	Recycling of chemicals	Waste production	Investment costs
Dilute acid	++	--	--	-	+/-
Strong acid	++	--	--	-	-
Steam explosion	+	--	++	+	-
Organosolv	++	++	--	+	--
Wet oxidation	+/-	+	++	+	+
Mechanical methods	-	++	++	++	+
Alkaline extraction	++/+	++	--	-	++

The '+' and '-' signs indicate a positive or negative characteristic respectively. For the different categories a '+' score implies: 'high yield of fermentable sugars', 'no or low inhibitor production', 'no requirement for chemicals recycling', 'no/low waste production' and 'low investment costs' respectively.

4.1.2 Fermentation

The fermentation is typically executed at 28-35 °C. The widely used industrial yeast *Saccharomyces cerevisiae* can only ferment C₆ sugars, which are present in cellulose, but not C₅ sugars (e.g. xylose), which make up a large part of the hemicellulose fraction, and need to be converted to ethanol as well in order to achieve acceptable conversion efficiencies. For several decades international R&D has been targeted at development of new fermentation systems e.g. *Zymomonas mobilis* or genetic modification of fermenting bacteria including *E.coli*. These efforts have thus far not led to a robust industrial fermentation system. Recent work performed in the Netherlands by KUN, TUDelft and Bird Engineering has led to an engineered *Saccharomyces* Strain RWB 218 that is capable of rapid consumption of glucose/xylose mixtures, and has high specific growth rates and ethanol production rates under anaerobic conditions (Kuyper, 2005). The authors claim that the kinetics of industrial xylose fermentation are no longer a bottleneck with this fermentation system.

4.1.3 Distillation and dehydration

The purification of the dilute ethanol to motor fuel quality is mostly the same as for the conventional bioethanol process and proceeds through distillation, rectification and dehydration. Depending on the process configuration, the lignin and other solids may still be present in the dilute ethanol at this stage. They can be removed with the water in the distillation, which poses certain restrictions on the design of the distillation column. Also, because of viscosity issues earlier in the process, with current lignocellulose pre-treatment technology there is likely a maximum to the ethanol concentration that can be produced in the fermentation. This lies probably in the order of 6-8 vol%, whereas ethanol concentrations produced from conventional bioethanol processes are generally in the order of 10-16 vol% after fermentation.

4.1.4 Use of lignin

Lignin cannot be fermented and has to be removed from the main process stream and then used for combined heat and power (CHP) production by combustion or gasification. Conversion of the lignin can produce sufficient steam and electricity for the ethanol plant and a surplus of electricity for delivery to the grid. The lignin stream (approx. 20 wt% dry matter) may be removed either after hydrolysis (in the case of SHF) or after distillation. For combustion the lignin must be dewatered and dried to at least 50% dry matter and for gasification to 85% dry matter. A complication is the presence of minerals (ash) from the

feedstock and chemicals that are added in the process. These compounds may cause corrosion and fouling in the CHP installation and may require intensive flue gas clean up. Another important issue is the use of the remaining mineral ashes.

4.2 Research and development

At the current state of development several bottlenecks remain. There is still need for an efficient pre-treatment process that has acceptable costs, high yields, and minimal production of undesired by-products and waste. This is a topic of active R&D both on lab scale and in several pilot plants in the US and Europe. Although the cost of cellulase enzymes has been substantially reduced further reduction would be beneficial. Ongoing R&D focuses among others on enhancement of enzymatic activity and development of thermo tolerant enzymes. In the area of fermentation further work on co-fermentation of C₆ and C₅ sugars is required to develop a robust industrial process for optimal fermentation of actual lignocellulose hydrolysates.

Efficient dewatering and thermal conversion of the lignin residue is a major aspect in current R&D, which also addresses the possibility to use ashes as secondary building materials or fertilizers. Finally optimal process and heat integration and water treatment and recycle are important issues. In the Netherlands these issues are addressed in the EET project 'Bio-ethanol and lactic acid from lignocellulose' (E.E.T., 2006).

Other R&D issues include the integral optimisation of enzymatic hydrolysis and fermentation tailored to specific feedstocks. A long-term R&D objective is development of an integrated microbiological/enzymatic process for combined pre-treatment, hydrolysis and fermentation: 'consolidated bioprocessing'. In such a process all (sequential) steps (pre-treatment, liquefaction, saccharification, fermentation) could be executed simultaneously in one vessel by mixed populations of microorganisms and/or enzymes. This ambitious objective requires a substantial, long-term R&D effort with uncertain outcome.

4.3 Important actors

The Canadian biotechnology firm and enzyme producer Iogen operates a demonstration plant in Ottawa for bioethanol production from straw with a capacity up to 4 million litres bioethanol per year. This plant uses a modified steam explosion pre-treatment process. Besides Iogen, shareholders are Shell Global Solutions, Petro-Canada and the Canadian government. Iogen claims to be three years ahead of the competition. One of these competitors is the multinational Abengoa, which has scheduled a 5 million litres per year plant to be operational in the fall of 2006, located adjacent to a cereal grain-to-ethanol plant in Salamanca in Spain. This plant will use steam-explosion as a pre-treatment process. Abengoa also plans to build a pilot plant in York, Nebraska (USA). In Sweden, in Örnsköldsvik, a pilot plant is in use with a capacity of 150.000 litres bioethanol per year. The plant is owned by ETEK, a joint venture of several energy companies. It currently uses sawdust as raw material and has a dilute acid pre-treatment process. Furthermore, several small research facilities on cellulosic ethanol are or have been in operation in U.S. states such as Louisiana, California, Idaho and Nebraska. In Denmark, Elsam Engineering and the Danish Royal Veterinary and Agricultural University have tested a newly developed wet oxidation pre-treatment process in a pilot plant for 100 kg/h of straw and a 1000 kg/h pre-treatment plant is being built. In the field of enzymes development major actors are Genencor and Novozymes.

In the Netherlands, Royal Nedalco is an active participant in R&D for bioethanol from lignocellulosic materials. Nedalco has recently announced the construction of a new fuel ethanol plant (feedstock wheat milling residue) in which the company is planning to integrate technology for cellulose ethanol production. Royal Nedalco is also patent holder of

the engineered *Saccharomyces* strain, developed by KUN, TUDelft and Bird Engineering, that is capable of rapid glucose and xylose fermentation (see 4.1.2).

4.4 Performance

4.4.1 Economics

Reliable cost estimates for processes that are not yet commercial are difficult to make. A thorough study has been carried out by NREL in the United States. This study finds that the investment costs for a 260.000 m³/y plant are approximately 200 M\$, and that the bioethanol production costs are approximately 0.28 \$/l. (Aden, 2002). The investment costs are much higher than for conventional bioethanol processes, mainly because extensive pre-treatment is necessary and because of the CHP unit for lignin conversion. Since investment costs are an important factor, the bioethanol production costs are strongly dependent on the scale of the plant, as is shown in Figure 4.3. The feedstock costs are lower than in conventional processes, but still an important cost factor.

A Dutch study calculates the costs at 0.47 €/l for the short-term (Hamelinck, 2004). In another Dutch study the capital costs for a 200.000 m³/y plant range from 235 to 313 M€ depending on the type of feedstock used (Reith, 2002). Here, the bioethanol production costs are 0.75 - 0.99 €/l. An important difference with the NREL study is that this study has assumed the actual cost for the cellulase enzyme at that time, whereas the NREL study assumed future (and much lower) cost estimates for cellulases. The Dutch study identifies as the main cost drivers the biomass costs, the investment costs and the costs for the cellulase enzyme. It is concluded that in order to reach a targeted cost of 0.40 €/l, a 10-fold reduction of the costs for the cellulase enzyme is necessary *and* a 30% reduction in capital costs. As mentioned earlier, the costs for cellulase enzymes have since then decreased by even more than 10-fold. As for capital costs, recently announced plans by Iogen for a lignocellulose to bioethanol plant with a capacity of 160.000 m³ per year mention that this would require an investment of approximately 320 M\$. (Zuidema, 2006). This is much higher than the earlier cost estimate of NREL, even when taken into account that a first plant is always more expensive than the next ones. An important reason for the higher investment is the increased price of steel.

Based on current information, it seems that the low cost estimate by NREL was too optimistic, at least for the short/medium term. It is likely that the costs for bioethanol from lignocellulose via enzymatic hydrolysis will be between 0.50 and 0.75 €/l. The main costs factors are investment costs, ca. 30-35%, and raw material costs, ca. 25-30%. As raw material costs are more volatile than investment costs, these cause the highest uncertainty in the production costs. However, the sensitivity of the production costs to the raw material costs is less than for the production of bioethanol from sugar or starch crops, where raw material costs contribute 50-70% to the production costs.

A Dutch consortium (ECN, Shell, Royal Nedalco, Agrotechnology & Food Innovations, Wageningen University, TNO, PURAC biochem) will finalize a 4-year R&D project in September 2006 (E.E.T., 2006). The results will include a conceptual design and economic analysis for a 200.000 m³/y plant.

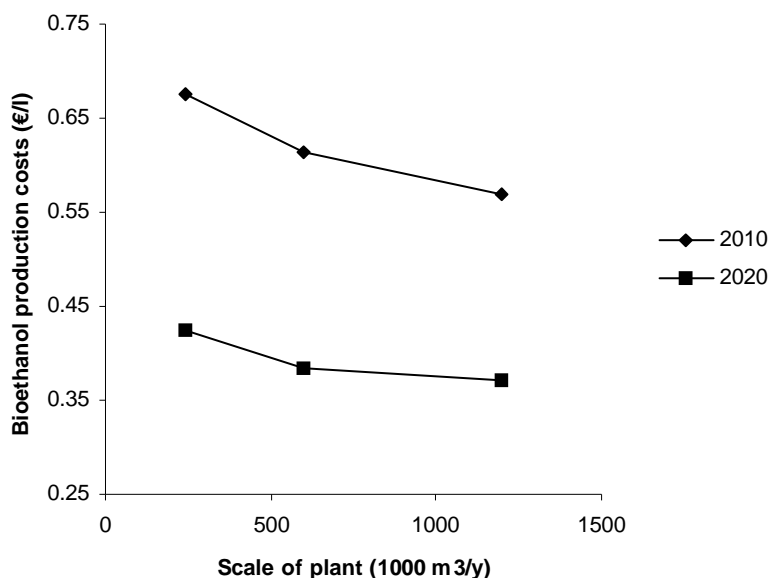


Figure 4.3 Scale dependency of 'cellulosic' ethanol production costs. Trend lines from (Hamelinck, 2004), but different figures used. Depicted figures are estimated averages; see Table 3.1 for the cost ranges.

4.4.2 Greenhouse gas emissions

Several studies have calculated the greenhouse gas emissions balance for the cellulosic ethanol process. Recent studies find a range of approximately 75-90 % GHG emission reduction compared to petrol (see Table 4.3). Earlier studies have even found values higher than 100% arising from the electricity by-product replacing electricity generated by fossil fuels. A value of 80% GHG emission reduction is selected for 2010.

Table 4.3 Reduction of greenhouse gas emissions for cellulosic ethanol compared to petrol.

Study by	GHG emission reduction compared to petrol
VIEWLS, 2005	74 - 82 %
Concawe/EUCAR/JRC, 2006	75 - 88 %
Farell, 2006	88 %

4.4.3 Performance improvements

The first commercial plants are likely to be realised around 2010 and an outlook for future improvements and cost development is therefore difficult to give. Eventually, technology development could lead to 'consolidated bioprocessing' (paragraph 4.2) where pre-treatment, hydrolysis and fermentation are executed in one vessel, resulting in considerable savings on investment costs. However, this ambitious objective requires long-term R&D efforts with uncertain outcome. The production costs in the long term (< 20 years) by 'consolidated bioprocessing' are estimated at 0.23 €/l (Hamelinck, 2004). However, the scope of this study does not go beyond 2020. Considering the uncertainties in the pace of technology development, the production costs for 2020 are estimated at 0.30-0.50 €/l.

Since the GHG emission reduction of cellulose ethanol compared to conventional bioethanol is already considerable for the first commercial plants (ca. 80%), there is only little improvement expected and a figure of 85% is used for the year 2020.

5 Biofuels from lignocellulose via gasification

Besides through biochemical and biological processes bioethanol can also be produced by thermo chemical processes, such as gasification and subsequent catalytic synthesis. The use of these processes for bioethanol production is a fairly new concept, but they are well known, although not yet fully developed, for the production of biofuels such as bio-Fischer-Tropsch diesel (a diesel-like fuel), biomethanol (a liquid with a relatively low energy density), bio-dimethylether (bio-DME, best comparable with LPG) and bio-Synthetic Natural Gas (bio-SNG, similar to natural gas). As an example, the integrated process for bio-Fischer-Tropsch diesel is given in Figure 5.1. The most important process steps of gasification and chemical synthesis are described in respectively paragraph 5.1 and 5.2.

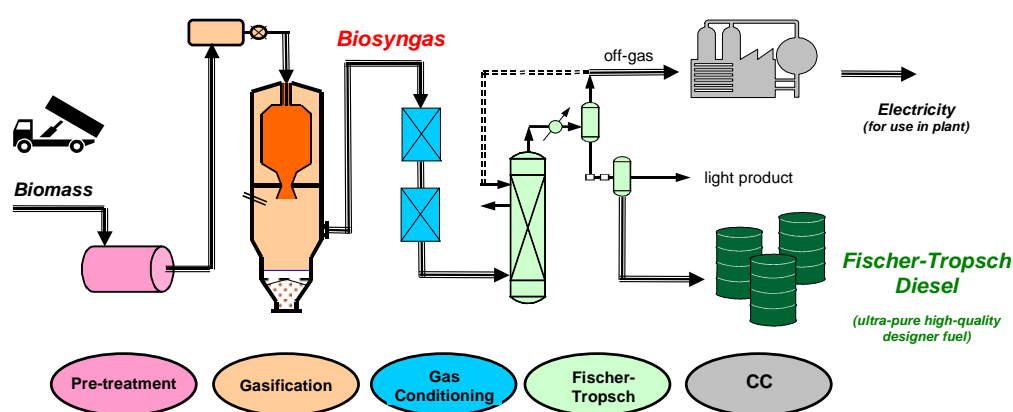


Figure 5.1 Schematic line-up of the integrated Biomass Fischer-Tropsch plant (Boerrigter, 2006a)

5.1 Gasification of biomass

Gasification is the term used for the process of partial oxidation, i.e. partial incineration with a restricted oxygen/air supply. Gasification produces from the fuel a 'synthesis gas' (also 'syngas') consisting of hydrogen and carbon monoxide or a 'product gas' containing besides hydrogen and carbon monoxide also methane and other hydrocarbons. The feedstock can be solid (coal, biomass, waste), liquid (oil) or gaseous (natural gas); and the oxidant pure oxygen, air and/or steam. The syngas can be used for combustion or for the production of chemicals, for example liquid fuels. Whereas gasification of coal is a common technology (Higman, 2003), gasification of biomass has only been developed the last decades (Bridgwater, 2002). At present, a considerable number of biomass gasification plants is operational, based on different technologies. For biomass gasification basically any biomass feedstock can be used, as long as it does not contain too much water. Preferably, for most biomass gasification technologies the water content of the biomass should be 15% or lower. Higher water contents result in poor efficiencies, because all the water has to be vaporised in the process.

For the synthesis of bio-Fischer-Tropsch diesel, biomethanol and bio-DME, not all gasification processes are suitable. The biomass gasification processes at lower temperatures (ca. 600-900 °C) produce product gas, which contains besides hydrogen and carbon monoxide also gaseous hydrocarbons and methane, which cannot be converted to alcohols

in the catalytic process. Thus, gasification technologies that produce hydrocarbons such as methane, ethylene and tars are not suitable. This leaves only gasification technologies operating at high temperatures ($>1000\text{ }^{\circ}\text{C}$). Furthermore, preferably, there should not be any inert gases such as nitrogen in the syngas, because these will increase the size of the catalytic synthesis reactor leading to an increase in investment costs. This means that air cannot be used in the gasification process, but only oxygen and/or steam. In addition, the synthesis reactors are operated at high pressures, which means that also the gasification process used should be executed under high pressure, if high compression costs are to be avoided. Considering these constraints, the obvious choice for gasification technology would be the 'Entrained flow reactor'.

Entrained flow gasification is a well-proven technology for coal gasification. Currently, research is ongoing, e.g. by Shell and ECN, to make the existing entrained flow technology suitable for biomass gasification (Boerrigter, 2004a; Boerrigter, 2004b; Drift, 2004). Biomass has different properties than coal and, therefore, several process modifications are necessary. Entrained flow gasification has a lower efficiency than most lower temperature gasification technologies. However, for applications that require a hydrocarbon free gas, lower efficiency is acceptable, because the overall efficiency to the end product is higher.

For the production of bio-SNG, which mainly consists of methane, preferably a low-temperature gasification process (ca. $600\text{-}900^{\circ}\text{C}$) should be used, because gasification processes at these temperatures already produce a certain amount of methane in the product gas. This is beneficial to the overall process efficiency. However, low-temperature gasification processes also produce tar, which has to be removed from the product gas prior to methanation, because it can foul the catalyst.

5.2 Chemical synthesis of biofuels

After gasification, the syngas or product gas needs to be cooled and conditioned for the chemical synthesis process. Metal catalyst are generally very sensitive to gas impurities. Any components that could deactivate the catalyst, such as in most cases sulphur components, should be removed. Furthermore, if a specific ratio of hydrogen and carbon monoxide is required the gas can be using the 'water gas shift' reaction.

Fischer-Tropsch synthesis processes use an iron or cobalt catalyst and operate at $200\text{-}250\text{ }^{\circ}\text{C}$ and $25\text{-}60\text{ bar}$. The process converts the syngas to FT-wax ($>\text{C}_{20}$) and is then followed by hydrocracking producing Fischer-Tropsch liquids. For biomethanol synthesis processes usually use a copper catalyst and operate at approximately $250\text{ }^{\circ}\text{C}$ and $80\text{-}120\text{ bar}$. The synthesis process for bio-DME is very similar to that of biomethanol, but it is operated at lower pressures. The methanation process for the production of bio-SNG uses a nickel-based catalyst at $5\text{-}40\text{ bar}$ and $300\text{-}600\text{ }^{\circ}\text{C}$. Any remaining off-gas from the synthesis process, containing unconverted but combustible components, can be used to for power generation to meet process demands or produce excess power to the grid.

5.3 Performance

At present, gasification technology for the production of bio-Fischer-Tropsch diesel is not fully developed yet. The Fischer-Tropsch synthesis process, however, is already a commercial process, operated by Shell and Sasol. While Shell operates on synthesis gas obtained from natural gas, Sasol uses synthesis gas obtained from coal gasification. Experience and research have shown that for the Fischer-Tropsch process to be economically viable, it needs to be operated on a very large scale: in the order of $1.000\text{ - }5.000\text{ MW}_{\text{th}}$ (Boerrigter, 2006b).

Detailed costs projections have been made for bio-Fischer-Tropsch diesel based on the costs of commercially used Fischer Tropsch synthesis plants and the costs of entrained flow gasifiers for coal gasification (Boerrigter, 2006a). These costs calculations, given in Figure 5.2, show a strong economy of scale. Currently existing Fischer Tropsch plants based on natural gas have capacities of 34,000 - 75,000 bbl/day (ca. 2-4.5 million m³/y or 2200-4800 MW FT product). This also compares well to the size of oil-refineries. Their investment costs are in the order of 900 -1400 M\$. These costs are approximately 60% higher for coal or biomass based Fischer-Tropsch plants, because solids require more feedstock handling and a more complex process to convert them into synthesis gas. The production costs of Fischer-Tropsch liquids from biomass at these large scales would be ca. 15 €/GJ. For a scale comparable with large bioethanol plants, 240.000 m³/y ethanol, this would be much higher: approximately 22 €/GJ. The greenhouse gas emissions reduction by the use of bio-Fischer-Tropsch diesel is approximately 90% compared to diesel; cf. Table 5.1.

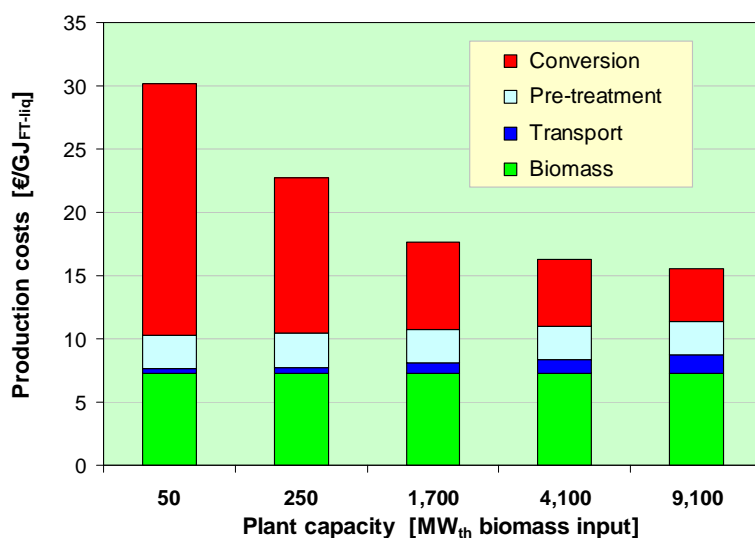


Figure 5.2 Scale dependency of FT fuel production costs for five reference scales. For illustration: 15 €/GJ_{FT} ≈ 0.55 €/l_{FT} (Boerrigter, 2006a).

Table 5.1 Reduction of greenhouse gas emissions for bio-Fischer-Tropsch diesel compared to diesel.

Study by	GHG emission reduction compared to diesel
VIEWLS, 2005	81 - 92 %
Concawe/EUCAR/JRC, 2006	90 - 95 %

At present, there is not much interest to produce bio-methanol for transport purposes, because of its fairly low energy density and its toxicity. For bio-DME there is currently only interest in Sweden, for application in heavy-duty vehicles. The methanation process for bio-SNG production is still in the development phase. The Netherlands, Austria and Sweden are involved in bio-SNG projects, of which some are aimed at transport purposes and others at injection into the natural gas grid.

5.4 Market introduction

The gasification technology for the production of biomass Fischer-Tropsch diesel still requires several years of R&D and demonstration, before it can be used commercially. When the technology will be ready, it needs to be operated on a very large scale to be economically viable. However, there is a good possibility to increase biomass Fischer-Tropsch diesel production gradually, as a transition. This can be done by co-gasification of biomass in coal-fired installations, which allows the production of significant amounts of bio syngas without the requirement of major system modifications. This is illustrated by experiences in the 250 MW_e *power plant* in Buggenum, the Netherlands, which has processed fuel mixtures with up to 30 wt% of various biomass materials, producing approximately 100 MW_{th} of bio syngas. Co-gasification of biomass is an easy and cost-effective approach to bio syngas production on industrial scale in short term. Therefore, biomass Fischer-Tropsch plants should initially be operated on biomass-coal mixtures, increasing the share of biomass in time, to finally operate as dedicated biomass-fired plant. (Boerrigter, 2006b)

6 Bioethanol from lignocellulose via catalytic syngas conversion

Bioethanol can be produced using only thermo chemical processes: by gasification of the biomass and subsequent catalytic conversion of the syngas to bioethanol. However, so far no process has been developed producing ethanol as a single product, but only mixtures of different alcohols. The thermo chemical process of higher alcohol synthesis (HAS) has been investigated early in the 20th century after alcohols were obtained as by-product from the Fischer-Tropsch process when catalysts or conditions were not optimised. BASF patented such a HAS process in 1913, and Fischer and Tropsch developed the 'Synthol'¹ process in 1923, which was used commercially in Germany until 1945 using coal as feedstock (Mills, 1994).

Renewed interest started when oil prices increased because of the 1973 Arab oil embargo and the 1979 Iranian revolution. Several companies, including Snamprogetti, Lurgi, Dow and IFP, have actively pursued HAS research for processes to be used with coal or natural gas as a feedstock (Spath, 2003). All these processes produced a mixture of alcohols. In Italy, petrol blends containing ca. 5% C₁-C₅ alcohols were marketed successfully as a premium fuel called 'Super E' in the 1980's. Most of the projects were discontinued after oil prices fell sharply in the late 1980's. Then again, there was renewed interest in the USA, mainly because of the need for new fuel oxygenates. Biomass is now considered the most interesting feedstock, because of environmental and security of supply considerations. Compared to biochemical processes for the production of bioethanol, this process would have the advantage of also converting the lignin fraction into alcohols. In addition, this is the only bioethanol process that does not require the energy consuming distillation process for separation of ethanol and water.

6.1 Higher alcohols vs. ethanol

The composition of higher alcohols varies depending on the process used and the desired composition of the fuel. Methanol is generally unwanted and much of the catalyst development is aimed at minimising the formation of methanol. The USA Corporation Power Energy Fuels has trademarked its foreseen higher alcohols product as Ecalene™, of which the advertised composition is given in Table 6.1. It has registered the product as a fuel additive at the Environmental Protection Agency (PEFI, 1998)

Table 6.1 Advertised composition of Ecalene™ (WRI, 2000)

Component	Weight %	Mole %
Methanol	0.3	0.4
Ethanol	75.0	81.9
Propanol	9.0	8.1
Butanol	7.0	4.8
Pentanol	5.0	2.8
Hexanol and higher	3.7	2.0

Higher alcohols for use as automotive fuel have several advantages over ethanol. Higher alcohols have a higher octane number and higher energy density than ethanol. In blends

¹ Not the same as the SASOL Synthol process.

with petrol, higher alcohols blend better than ethanol, because of the longer carbon chains of the higher alcohols. However, the higher alcohols should not contain too much methanol, since this could cause a phase separation between the alcohols and the petrol. Furthermore, the vapour pressure of blends of higher alcohols and petrol is generally lower than that of blends of ethanol and petrol, because the higher alcohols have lower vapour pressures. Again, the opposite is true when too much methanol is present. Higher alcohols can also be used as a pure fuel, in which case a higher proportion of methanol is possible than when it is used in blends with petrol. Thus, higher alcohols have some advantage over ethanol when used as a transportation fuel, providing that the methanol content is low.

However, except for Power Energy Fuels, the other companies involved in this field seem to prefer to produce pure ethanol over higher alcohols for the fuel market, because ethanol is one single chemical compound and not a mixture, and therefore its quality and properties are clearly defined and constant. They prefer a synthetic process optimised for ethanol yield and separation of higher alcohols, which can be sold at a higher price than ethanol, although the market for these higher alcohols is limited.

6.2 Process description

The process consists of the main steps of biomass gasification, gas cleaning and catalytic higher alcohol synthesis as depicted in Figure 6.1.

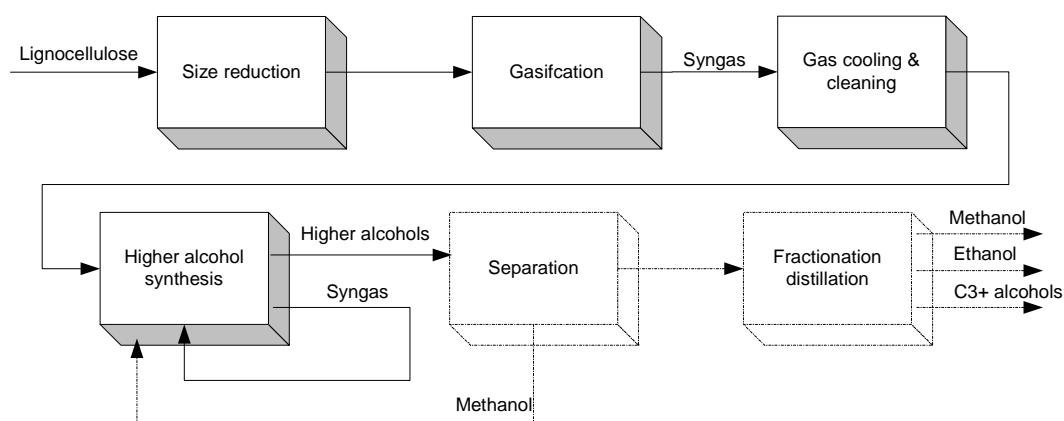


Figure 6.1 Simplified process scheme for bioethanol production via catalytic syngas conversion.

6.2.1 Gasification

Not all gasification processes are suitable for mixed alcohol synthesis. For mixed alcohol synthesis the same reasoning applies as for bio-Fischer-Tropsch synthesis (see paragraph 5.1): that syngas is required at high pressure without any inert gases present. Thus, the most suitable gasification technology would be the 'Entrained flow reactor'.

6.2.2 Gas clean-up requirements

Several different catalyst can be used for HAS, described in paragraph 6.2.3, which require different gas cleanliness. The requirements for the modified FT and modified methanol synthesis catalysts are the same as those for the unmodified catalysts, i.e. low sulphur, low halides and low ammonia. The modified MoS₂ catalyst is already sulphided and, therefore, extremely resistant to poisoning by sulphur in the syngas. The allowed carbon dioxide content is usually limited to a few percent, although there are also studies claiming a positive effect of carbon dioxide for HAS.

6.2.3 Higher alcohol synthesis

Generally, five different types of catalysts for higher alcohol synthesis are distinguished, of which the characteristic are given in Table 6.2. The mechanism for higher alcohol synthesis involves a complex set of simultaneous reactions with multiple pathways leading to a variety of products. For higher alcohol synthesis first methanol has to be produced from the syngas (Reaction 6-1). HAS catalysts are generally also active for the water gas shift reaction (Reaction 6-2), which means that a specific H₂/CO ratio of the syngas is not necessary for HAS. For the production of higher alcohols the formation of C-C bonds is necessary, starting by insertion of CO into CH₃OH (Reaction 6-3). Higher linear alcohols are formed by further CO insertion, also called homologation (Reaction 6-4). However, other pathways to higher alcohols also exist. Branched alcohols can be formed when modified methanol or modified Fischer-Tropsch catalyst are used. Other oxygenates such as acetic acid, dimethylether and methyl esters, can also be formed, as well as olefins and paraffins (Spath, 2003).

Reaction 6-1	Methanol synthesis	$\text{CO} + 2 \text{H}_2 \rightarrow \text{CH}_3\text{OH}$
Reaction 6-2	Water gas shift reaction	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
Reaction 6-3	Ethanol homologation	$\text{CH}_3\text{OH} + \text{CO} + 2 \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH}$
Reaction 6-4	HAS homologation	$\text{C}_n\text{H}_{2n-1}\text{OH} + \text{CO} + 2 \text{H}_2 \rightarrow \text{CH}_3(\text{CH}_2)\text{OH} + \text{H}_2\text{O}$

Table 6.2 Characteristics of HAS catalysts (Mills, 1994; Spath, 2003; Caraballo, 2005)

Characteristic	Modified high-pressure methanol synthesis catalysts	Modified low-pressure methanol synthesis catalysts	Modified Fischer-Tropsch catalysts	Modified hydro-de-sulphurisation catalysts	Rhodium catalysts
Catalyst composition	Alkali/ZnO/Cr ₂ O ₃	Alkali/Cu/ZnO (Al ₂ O ₃)	Alkali/CoO/CuO/Al ₂ O ₃	Alkali/MoS ₂ /Co	Rh/SiO ₂
Pressure (bar)	125-300	50-100	60-200	30-175	50-175
Temperature (°C)	300-425	275-310	260-340	260-350	200-350
Product alcohols	Branched primary alcohols	Primary alcohols	Linear primary alcohols	Linear alcohols (C ₁ -C ₄) methanol can be fully recycled.	Ethanol, methanol, other non-alcohol oxygenates

Methanol formation is favoured at low temperatures and high pressures. When the temperature is increased at high pressures, higher alcohols yield increases and methanol and hydrocarbon products decrease. For some catalysts the methanol product can be recycled, increasing the higher alcohols yield. Thermodynamic constraints limit the theoretical yield of higher alcohols. Very important is that the higher alcohol synthesis is highly exothermic. This makes temperature control a major factor in the reaction system design, which may cause a limitation for the conversion. HAS can be performed in reactors that are similar to methanol and FT synthesis processes. Research and development is being conducted to investigate the use of slurry phase reactors for HAS. Another possibility is a 'double bed' configuration, optimising methanol production from syngas in the first reactor at a lower

temperature and increase the yield of higher alcohols in a second reactor at slightly higher temperatures. Operating temperatures and pressures of the HAS process are dependent on the catalyst used and vary between 250 - 425 °C and 30-300 bar.

Much catalyst research has already been done in the past with renewed efforts in the 1990s (West Virginia University, 1998; Klier, 1999). Currently, there is no commercial application. It is even difficult to predict which catalyst(s) will be the winner(s). Although the modified high-pressure methanol catalyst is very fast, its drawbacks are its high operating temperature and pressure. The advantage of the modified MoS₂ catalyst is its resistance to sulphur poisoning, but for HAS the catalyst is less active than the modified FT and methanol catalysts. The rhodium catalyst could offer a process at mild conditions. The main problem for all catalysts is the selectivity. In most cases a wide range of products is formed, where only higher alcohols are desired. Thus current research is aimed at developing catalysts that favour ethanol formation, and with reasonable conversions. However, most of the research results are kept confidential.

6.3 Research and development

Since the beginning of the 20th century many research programmes have been started, interrupted and discontinued. Current activity in this field takes place mainly in the United States, motivated by the need for new fuel oxygenates, reduction of greenhouse gas emissions and an increased security of energy supply. Since 2002, there is a pilot plant in Mississippi (USA) owned by the Canadian company Ethxx International and based on technology developed by Pearson technologies (Pearson, 2001). Its current status is unknown. In 2002 construction was also to be started of a pilot plant by Power Energy Fuels, a Colorado based company that registered its foreseen mixed alcohol product as 'Ecalene™'. However, no recent information is available on this project.

More projects in the field of higher alcohols have been announced, such as a Starbourn-Triton cooperation in 2005 aimed at building ethanol producing plants in the United Kingdom and the USA, but its first plant will use coal as feedstock and use the syngas for power production. In January 2006, the California based company MEMS has announced a commercial plant for 2010 to be located in Ontario, Canada (Ross, 2006). The plant will use wood and forest waste as feedstocks, should have a capacity of 227 million litres ethanol and is estimated to cost 150 million dollars.

Although quite some project announcements have made the press, actual operational results, although limited, have only been reported by Pearson technologies (TSS Consultants, 2005). It can be concluded that the technology for higher alcohols production is not ready for commercialisation, because the catalyst development is not ready. This is illustrated by the fact that last year, multinational Abengoa and several US research institutes have received a 2.25 million dollar DOE grant for the development of new catalysts for the conversion of bio-based synthesis gas to ethanol. Furthermore, there is at present no commercial biomass-to-syngas technology that can produce a clean syngas that does not deactivate the catalysts.

6.4 Performance

6.4.1 Economics

Not many cost estimates currently exist for the production of bioethanol or higher alcohols via catalytic syngas conversion. In fact, there is only one study with significant details published (Delta T Corp., 2002). This study calculates the capital costs at 48 M\$ for a 60.000 m³/year plant. However, this might be optimistic, certainly considering the relatively small scale for a gasification process. Economies of scale favour larger-scale over smaller-scale

processes, but the actual size will also depend on the costs for logistics of feedstock and products. If low cost (local) biomass is available, a small plant could be considered. Another study, for ethanol synthesis from coal gasification, does assume large scale and estimates capital costs at 563 M\$ for a 636.000 m³/y plant to 3312 M\$ for 5 million m³/y (West Virginia University, 1998).

However, at present, the best method to make a cost estimate is a comparison with bio-Fischer-Tropsch production (see paragraph 5.3), since both processes are very similar. Compared to Fischer-Tropsch production the costs for the synthesis reactor could be somewhat higher because higher pressures are used, but this could be off-set by lower costs for product upgrading, also depending on the type of product, ethanol or mixed alcohols. The production costs of Fischer Tropsch liquids from biomass at very large scales (ca. 2-4.5 million m³/y) would be 15 €/GJ. For bioethanol, with a lower heating value of 21.2 MJ/l, this means a cost of 0.32 €/l bioethanol.

Considering the current state of technology of HAS and, equally important, the huge investment costs and accompanying risks involved for very large scale plants, it is uncertain if these plants will be operational already by 2020. It could very well be that by 2020, only HAS plants of approximately 240.000 m³/y ethanol, the size of the largest (conventional) bioethanol plants today, are operational. However, the production costs are very sensitive to the scale of the plant, illustrated in Figure 6.2. The production costs for bioethanol via HAS for 2020 are estimated at 0.30-0.50 €/l.

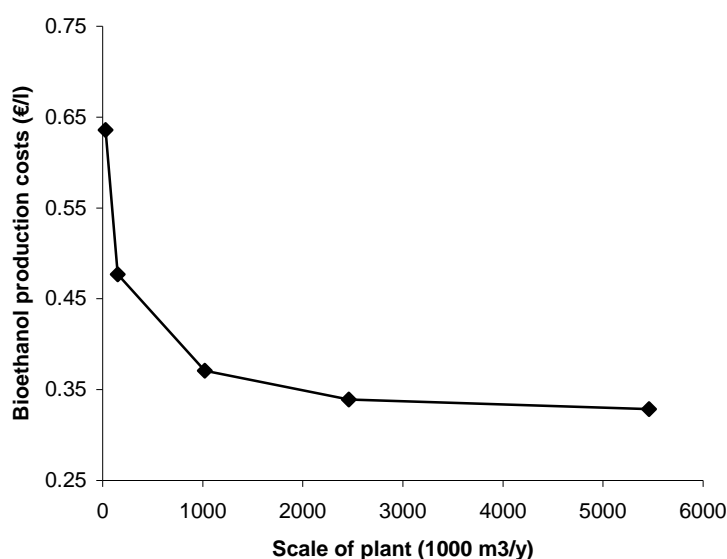


Figure 6.2 Scale dependency of 'gasification and synthesis' bioethanol production costs. Based on bio-Fischer-Tropsch production cost; see Figure 5.2.

Above costs estimates are made under the assumption that the catalyst research for HAS results in almost similar conversions and selectivities as Fischer Tropsch synthesis (which is ca. 71% conversion of syngas to FT products and 8% to lower hydrocarbons). For initial HAS commercialisation, however, lower selectivities to ethanol or higher alcohols can be accepted, if some valuable alcohols are produced as by-product (see Table 6.3) to compensate for the lower production of bioethanol. The bioethanol production costs are, however, very sensitive to the revenues from the higher alcohols sold for non-fuel applications, as the market prices of these alcohols are volatile. Furthermore, in the longer term with expanding volumes, this is not viable, because the market for these valuable alcohols is relatively small.

Table 6.3 Market value of alcohols (Abengoa, 2005)

Alcohol	Market price* (\$/l)
Methanol	0.20
Ethanol	0.35
n-Propanol	1.50
n-Butanol	1.50
iso-Butanol	1.30
Amyl alcohol	1.60

* Market (spot) prices of chemicals can vary strongly; given prices are only for mutual comparison and not should be taken as absolute values.

6.4.2 Greenhouse gas emissions

There no figures available for the greenhouse gas emissions of this process. However, since the process is very comparable with Fischer-Tropsch production from biomass, as a best estimate the greenhouse gas emission reduction of bio-Fischer-Tropsch diesel can be used, which is approximately 90% reduction compared to fossil fuels (see Table 5.1).

6.4.3 Market introduction

To overcome the initial bottleneck of the huge investments for the very large-scale plants that are necessary to achieve low production costs, the market introduction of bioethanol via HAS could be very similar to that of biomass Fischer-Tropsch diesel, i.e. by co-gasification of biomass in coal-fired installations (see paragraph 5.4). However, the market introduction of HAS will be later than for bio-Fischer-Tropsch liquids, because the catalyst development is not as far advanced as for Fischer-Tropsch liquids production. This leads to a second market introduction possibility: using a side stream of syngas of an existing bio-Fischer-Tropsch liquids plant. A third possibility is to start with plants of more moderate sizes, e.g. 240.000 m³/y ethanol, and separate and sell valuable higher alcohols at premium prices to non-fuel markets. However, in the longer term, this is not viable, because the market for these valuable alcohols is relatively small.

7 Bioethanol from lignocellulose via syngas fermentation

A fairly new concept for the production of bioethanol is the combination of gasification and fermentation. The development of thermo chemical gasification followed by the conversion of the produced synthesis gas to bioethanol by microorganisms started late in the 1980's (Klasson, 1990), but during the 1990's only a handful of researchers have worked on this topic. Currently, one pilot plant is operational in Arkansas, USA. Compared to direct fermentation processes, this process has the possibility to convert the lignin fraction to bioethanol as well. Compared to catalytic synthesis processes, this process could offer advantages such as milder temperatures and pressures, tolerance to sulphur compounds and, most importantly, a higher selectivity.

7.1 Process description

The main process steps are biomass gasification, gas cleaning, syngas fermentation and product upgrading, as depicted in Figure 7.1. Since the first step of the process is gasification, the feedstocks that are suitable for this process are identical as for the bioethanol process via gasification and catalytic synthesis.

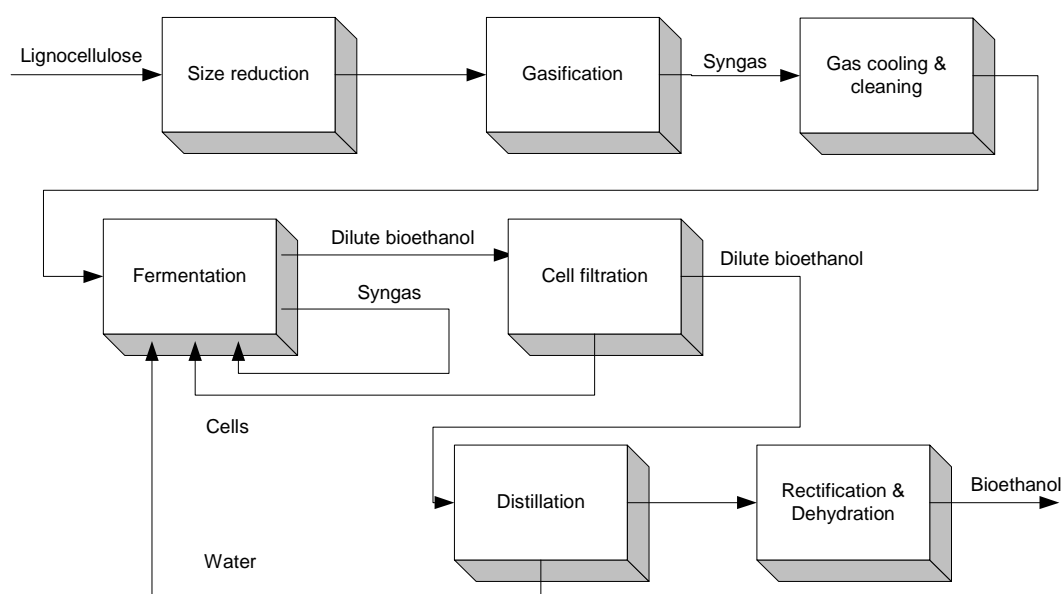


Figure 7.1 Simplified process scheme for bioethanol production via syngas fermentation.

7.1.1 Gasification

A general description of the gasification technology is given in paragraph 5.1. For the syngas fermentation process, not all gasification technologies are suitable, mainly because the fermentation organisms can only use hydrogen, carbon monoxide and carbon dioxide. They cannot ferment hydrocarbons, which are present in the biomass product gas from certain gasification technologies, and these hydrocarbons are possibly even inhibitors to the fermentation process. Furthermore, there should not be any inert gases such as nitrogen in the syngas, because this will increase the size of the downstream fermentor, which will lead

to a considerable increase in investment costs. This implies that air cannot be used in the gasification process, but only oxygen and/or steam. Another restriction is that the fermentation is executed at atmospheric or moderate pressure (up to 3 bar). A high-pressure gasification process is, therefore, not necessary. These three restrictions do not leave an obvious choice for the employed gasification technology. Entrained flow gasification is not a likely candidate for gasification at atmospheric conditions. Fixed bed gasification techniques using oxygen could be used, but their scale-up possibilities are limited and they still produce some hydrocarbons. Another possibility is fluidised bed gasification followed by high-temperature cracking of the hydrocarbons, but the cracking causes a considerable loss in efficiency.

If the fermentation organisms are resistant to smaller hydrocarbons such as methane, ethylene and acetylene, a gasification technique that produces hydrocarbons could be used. These small hydrocarbons would then pass through the fermentor unchanged and can then be used for e.g. electricity production. This would effectively lead to co-production of ethanol and methane or of ethanol and electricity. In this case, indirect gasification technology can be used. Indirect gasification uses two reactors: a gasifier where the product gas is produced and a combustor where the heat that is necessary for gasification is produced. Whereas the combustor uses air, the gasifier uses only steam as a gasifying agent, which means that the product gas does not contain nitrogen. It does, however, contain tars, which should be removed, e.g. by OLGA technology (Boerrigter, 2005).

7.1.2 Gas clean-up requirements

Following gasification the gas needs to be cooled and purified to remove compounds that might be harmful for the fermenting organisms. This includes tars, if present in the product gas, and possibly smaller hydrocarbons. Sulphur compounds such as H₂S do not have to be removed, since the fermentation process is very tolerant to sulphur: without optimisation, concentrations of H₂S up to 2.5% are no threat to the fermentation microorganisms and the rate of reaction (Klasson, 1993). The amount of sulphur in biomass syngas, but even coal syngas, stays well below this limit. Thus, it seems that only ash and residual char should be removed with a cyclone. However, in actual tests with biomass product gas cleaned of tars cells did not grow, although they did not die either (Datar, 2004). It is not known which compound caused this effect, but it is suspected that this is due to the presence of nitric oxides and/or acetylene.

7.1.3 Fermentation

Fermentation is a biological process in which microorganisms convert organic compounds to other organic compounds such as lactate, acetic acid and ethanol in a series of reactions that release energy. It is executed in the absence of oxygen and usually in aqueous environment. The most promising organisms for syngas to bioethanol fermentation are the bacteria *Butyribacterium methylotrophicum* and *Clostridium* species (Kasteren, 2005). These bacteria use a heterofermentative version of the acetyl-CoA pathway for acetogenesis. *Butyribacterium methylotrophicum* can produce acetic acid, butyric acid, ethanol and butanol, although the production of ethanol and butanol is usually low. Butanol is dominant when production of ethanol and butanol is increased. *Clostridium* species are regarded to have more potential. *Clostridium ljungdahlii* is the most studied species for this purpose and produces a mixture of acetate and ethanol from syngas. The ratio of these products can be adjusted by pH. Almost complete elimination of acetate production has been reported and a final ethanol concentration of 48 g/l, (Klasson, 1993). Possibly even more promising is *Clostridium carboxidovorans* (P7), which converts syngas into a mixture of acetate, butanol and ethanol. Further developments are expected to include hydrogen uptake and inhibition of butanol production.

The fermentation takes place at 37-39 °C and can be executed at atmospheric or moderate pressure (1-3 bar). Operation under pressure should increase the reaction rate, because the

transfer of syngas to the liquid phase increases at higher pressures. The fermentation medium consists of various minerals, trace metals and vitamins (Phillips, 1994).

The final ethanol concentration should be as high as possible in order to minimize distillation costs. A concentration of 48 g/l, equivalent to 6% volume has been reached, but only after 25 days in batch operation (Klasson, 1993). However, it has also been reported that ethanol is toxic to the culture and ethanol concentrations should be kept below 3 % vol. (McCloy, 1999). The pilot plant of BRI Energy in Arkansas aims at production of 2% vol. ethanol. Distillation of water/ethanol mixtures with only 2% vol. ethanol, does, however, not seem economically feasible, not even in the USA where energy prices are generally lower than in Europe. An ethanol concentration of at least 6% vol. is more favourable. Thus, the energy balance of the overall process is greatly affected by the ethanol concentration, because of the energy required for distillation (see Figure 3.4).

7.1.4 Fermentor design

The fermentation process converts a gas into a liquid and is executed in aqueous phase. The rate-limiting step in the process is the gas-to-liquid transfer of the syngas. This implies that the reaction rate of bioethanol production will increase when the gas is taken up more rapidly into the liquid phase. Usually, stirred tanks are used to enhance gas-to-liquid mass transfer, but this might not be commercially feasible, because of excessive power costs for stirring. A trickle-bed reactor, a columnar packed bed gas continuous reactor where the liquid phase trickles downward over the packing, could provide more energy-efficient mass transfer, because it does not require mechanical agitation.

Due to the novelty of the process, much is unknown about scale-up of fermentation. In laboratory research different reactor types have been used. The only existing pilot plant uses a continuous stirred tank reactor (CSTR).

7.2 Research and development

Research in this field has started already late in the 1980's, and during the 1990's a handful of researchers in the USA states of Arkansas, Oklahoma, Mississippi and Michigan have worked on this topic. Currently, one pilot plant is operational in Arkansas belonging to BRI Energy LLC, using technology of Bioengineering Resources Inc., developed at the University of Arkansas (BRI Energy, 2005). The capacity is 1500 kg per day. It has a two-stage gasifier of which the second 'cracking' stage has a temperature higher than 1100 °C in order to convert hydrocarbons formed in the first stage to syngas. The first (low-temperature) stage of the gasifier uses air and the second stage oxygen, thus limiting the amount of nitrogen in the product gas somewhat. The fermentation is performed in a CSTR. The organism used is *Clostridium ljungdahlii* that uses most of the carbon monoxide to produce dilute aqueous ethanol at 2% vol. concentration. Most of the hydrogen leaves the fermentor unprocessed. The cells are separated from the dilute ethanol solution by a membrane. The ethanol/water mixture is purified to 99.5% ethanol by distillation and dehydration with molecular sieves. The entire process from gasification to distillation is claimed to take 7 minutes.

The company Mississippi Ethanol LLC has also been planning, together with Mississippi State University, to start a pilot facility. At the end of 2005 the US Department of Energy (DOE) has defined syngas fermentation as a scientifically recognized method of producing cellulosic ethanol, effectively meaning that its R&D will be supported. The main reason for the support is that, according to DOE, the technology promises to be applicable to the conversion of a very broad range of feedstock, including urban, agricultural, and forestry waste.

Besides the before mentioned projects, other research groups in the United States are working in this field including Oklahoma State University and Michigan State University. In Europe

at least the Finnish VTT (Heiskanen, 2004) and Eindhoven University of Technology in The Netherlands are active in this field (Schijndel, 2004).

7.3 Performance

7.3.1 Plant scale

The most suitable scale for this process is not obvious. On the one hand most gasification technologies are costly when operated on a small scale, on the other hand the choice for a large-scale gasifier will likely pose significant problems, because this requires extremely large fermentors. Thus, the most likely option would be a small-scale plant, which in order to be operated economically, requires low cost, locally available biomass and/or waste as feedstock.

Since the fermentation process can only convert syngas to bioethanol and not hydrocarbons that are present in product gas, a high temperature gasification process (entrained flow) would be most suitable. However, entrained flow reactors are very costly for small-scale application. Thus, low-temperature gasification technology, such as fixed bed, fluidised bed or indirect gasification should be used in combination with technology to remove tars from the product gas, such as a subsequent high-temperature 'cracking' stage, applied in the BRI pilot plant (see paragraph 7.2) or OLGA tar removal technology (Boerrigter, 2005). The latter is indeed included in a conceptual plant design for a small-scale plant (Kasteren, 2005). In both cases, small hydrocarbons, mainly methane, will remain in the product gas. These cannot be converted to bioethanol and at present it is unknown whether the fermentation organisms can tolerate these compounds.

7.3.2 Economics

At present, only one cost calculation is publicly available for this process, reporting a cost range of 0.56 - 0.88 €/l (Kasteren, 2005). This applies to an 11.000 m³/y bioethanol plant that uses cheap biomass or waste feedstock. The process design includes a circulating fluidised bed gasifier and OLGA technology for tar removal; it is not mentioned how the methane in the product gas is utilised. The study assumes that 6% vol. ethanol in water can be reached in the fermentation process.

The authors conclude that production costs of 0.60 €/l are possible in a small scale plant. This seems fairly optimistic, because their lower estimate of the 0.56 - 0.88 €/l range does not include any return on investment. Moreover, the economic evaluation is incomplete because ethanol purification to the required 99.5% vol. is not accounted for and the costs for steam usage and wastewater treatment are likely underestimated. A valid conclusion from the study is that the fermentors are a major cost driver due to the low solubility of syngas in water. The fermentors account for ca. 75% of the investment costs, whereas the investment costs contribute 30-35% to the overall production costs.

Based on the available information, an estimate of 0.60 - 0.90 €/l is used for 2020 for bioethanol produced by gasification and fermentation.

7.3.3 Greenhouse Gas Emissions

No well-founded estimates are available for the greenhouse gas emission reduction of bioethanol produced by gasification and fermentation compared to petrol. However, since the process uses lignocellulosic biomass the GHG emission reduction may be estimated at 80-90%, similar to bioethanol from lignocellulose produced by other processes, provided that the energy use in the process is not too high. This implies that an ethanol concentration of approx. 6% vol. should be reached in the fermentation process in order to avoid excessive

energy use for distillation and that energy use in the fermentation section should be minimised.

7.3.4 Technology development

Although the current cost estimates are not very promising, further R&D may change this prospect. The main topics for further R&D are:

- Increase the tolerance of the fermentation organisms to ethanol. Currently, ethanol is toxic to the culture and ethanol concentrations should be kept below 3 % vol. This is too low from an economic and energetic point of view and should be increased to at least 6% vol.
- Investigate whether small hydrocarbons such as methane act as inhibitor to the fermentation process and the development of resistant stains.
- Improve the gas-to-liquid mass transfer in the fermentors. The scale-up of the fermentation reactors requires further R&D as well.

Considering these issues for further R&D, it is surprising that there is already a pilot plant running. However, it must be noted that this pilot plant produces dilute ethanol at only 2% vol. concentration and that the conversion efficiency is still very low, as most of the hydrogen leaves the fermentor unprocessed. Commercialisation is still far off.

8 Comparison of bioethanol processes

8.1 Economics

8.1.1 Bioethanol costs

Based on the assessments in the previous chapters the best estimates for the bioethanol production costs for each production chain are given in Table 8.1. These costs are to some extent difficult to compare, because:

- The timeframe considered for the different processes. Some processes will still take more time before their introduction into the market than others. Therefore, in the table a distinction is made in different timeframes.
- The learning effect of new technology will reduce costs. This is described in more detail in paragraph 8.2.1.
- The costs depend on the scale of the installation. For conventional bioethanol processes a typical scale is ca. 240.000 m³/y. For bioethanol from lignocellulose by enzymatic hydrolysis or gasification and synthesis the scale of installation must be at least 240.000 m³/y and can be up to several million m³/y. Bioethanol from lignocellulose by gasification and fermentation is likely to be produced at small scale (e.g. 10.000-50.000 m³/y).
- Costs are different for every single installation, even if they are based on identical technology and feedstock, because of location specific conditions, feedstock logistics, etc.

Table 8.1 Estimated bioethanol production costs for the different processes

Feedstock (& process)	Bioethanol production costs*, including profit margin (€/l)		
	2006	2010	2020
Sugar beets	0.50 - 0.55	0.50 - 0.55	0.45 - 0.50
Grains	0.55 - 0.60	0.55 - 0.60	0.50 - 0.55
Potatoes	0.85 - 0.90	0.85 - 0.90	0.80 - 0.85
Residual starch streams	0.45 - 0.55	0.45 - 0.55	0.40 - 0.50
Lignocellulose (enzymatic hydrolysis)	-	0.50 - 0.75	0.30 - 0.50
Lignocellulose (gasification & synthesis)	-	-	0.30 - 0.50
Lignocellulose (gasification & fermentation)	-	-	0.60 - 0.90 ?

* For comparison: bio-Fischer Tropsch diesel production costs are estimated at 15-22 €/GJ for 2020, which compares (corrected for the different volumetric energy densities) with 0.30 - 0.50 €/l bioethanol; off-refinery costs of petrol have been between 0.18 and 0.51 €/l in the last few years, which compares (corrected for the different volumetric energy densities) with 0.12 - 0.35 €/l.

The main contributors to the production costs of bioethanol are:

- The raw material price, accounting for 50-70% of the production costs of bioethanol from sugar, beets, grains and potatoes, for 25-30% for bioethanol from lignocellulose by enzymatic hydrolysis and up to 50% for bioethanol from lignocellulose by gasification and synthesis, (depending on the scale of the plant).

- Capital costs, accounting for ca. 30-35% of the production costs of bioethanol from lignocellulose by enzymatic hydrolysis and 30-60 % for bioethanol from lignocellulose by gasification and synthesis (depending on the scale of the plant).
- Energy price, only in the processes for bioethanol from sugar, beets, grains and potatoes and less important than the other two factors.

The bioethanol production costs are very sensitive to raw material prices as these make up an important part of the costs and are generally volatile, and, to a lesser extent, to the capital costs, which are partly dependent on the steel price.

Finally, it is not necessarily true that only the process with the lowest cost can be competitive, certainly not when the processes have different biomass feedstocks. Currently, bioethanol plants based on different technology and feedstocks exist simultaneously and demand for bioethanol greatly exceeds supply. In paragraph 8.1.3 the market for bioethanol is described in more detail in relation to bioethanol production costs.

8.1.2 Learning effects

New technology is always expensive compared to existing technologies. However, the more a technology is applied, the more it improves and decreases in costs. Once a process has gained momentum, the gains in costs reduction can be considerable. Examples are the bioethanol from corn in the USA and bioethanol from sugar cane in Brazil. In the USA, plant construction costs per litre of bioethanol have more than halved since the early 1980's. This is a result of incremental improvements in the design for each new plant, the optimisation of the process, and the ability to negotiate lower costs with suppliers because of the increasing volumes (BBI, 2005). Further, the construction time has decreased from 16-24 months in the mid-1990s to 12 months or less today. The Brazilian bioethanol programme started before 1980 and the production costs have decreased dramatically since then (see Figure 8.1).

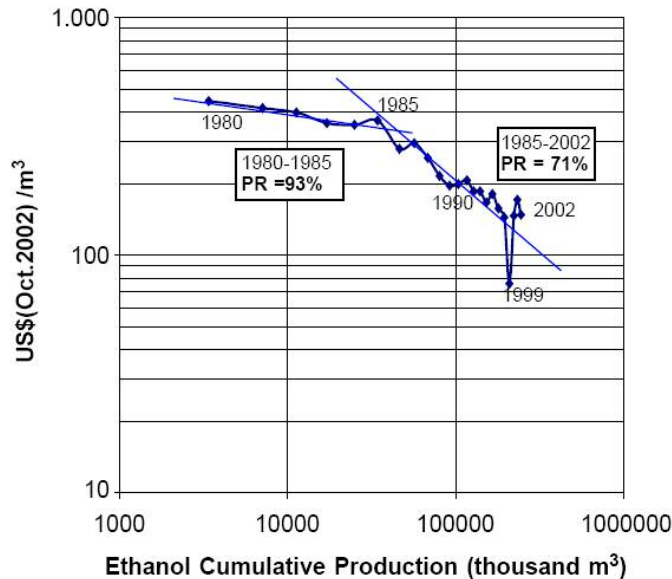


Figure 8.1 Brazilian ethanol learning curve: prices, trends and progress ratios (Goldemberg, 2004)

The learning effect applies for all bioethanol production processes, but probably not to the same extent. The production of bioethanol from sugar beets and grains exists already for a long-time, although the increase in production volumes started only recently in Europe. However, production of bioethanol from lignocellulosic by enzymatic hydrolysis is for most part based on completely new technology and gains will likely be higher in this case. These costs might be halved on the long-term (Hamelinck, 2004). A learning effect could also be

applicable to the production process from lignocellulosic by gasification & synthesis, but the cost estimates made are already partly based on existing technologies which limits the gains in further cost reduction.

8.1.3 Bioethanol market

The petrol price has increased dramatically in the last years, because of the increasing oil price. At the beginning of 2002 the oil price was 23 \$/barrel which has increased to 63 \$/barrel in September 2005 (DOE, 2006). In the same period, petrol prices in the Netherlands, excluding duties and taxes, have ranged from 0.29 to 0.62 €/l (DG-TREN, 2006). However, the actual production cost of petrol at the refineries is lower, because the mentioned prices also include storage and transport (ca. 0.06 €/l) and retailer cost and profits (ca. 0.05 €/l). Thus, off-refinery costs for petrol, which are basically the production costs, have been between 0.18 and 0.51 €/l in the last few years. The energy density of bioethanol is lower than for petrol (21.2 MJ/l vs. 31.0 MJ/l), which means that more litres of bioethanol than litres of petrol are necessary to drive the same distance. Thus, in order for bioethanol to be competitive with petrol, a production cost as low as 0.12 - 0.35 €/l is necessary.

However, the European Union actively pursues the aim of its 2003 Directive to substitute 5.75% of petrol and diesel fuels with biofuels in 2010 (EC, 2005). Therefore, bioethanol does not have to compete with petrol, but more important is its price in relation to other biofuels. Biodiesel currently has a production costs in the order of 0.70 - 0.75 €/l, but also biodiesel has a higher energy density than bioethanol (i.e. 32.8 MJ/l), thus this price compares with a bioethanol price of 0.46 - 0.49 €/l. Future costs estimates for bio- Fischer-Tropsch diesel compare with bioethanol prices of 0.32 - 0.47 €/l, depending on the scale of the Fischer-Tropsch diesel production facilities. However, biomass Fischer-Tropsch diesel is not ready for commercialisation yet.

Currently, there is not really a competition between biofuels, because demand is higher than supply. In March 2006, European spot prices for (fuel) bioethanol have risen due to the high demand to 0.63 €/l compared to 57 €/l six months earlier (F.O. Lights, 2006). The world cost-supply curve shown in Figure 8.2 shows that, although currently only Brazilian bioethanol from sugar cane can compete with petrol prices, due to the high bioethanol demand, other bioethanol producers can also make a profit in the current bioethanol market. Thus, even though some bioethanol production processes are more expensive than others, as long as they can produce under the market price, they are competitive. However, higher demand for biofuels and bioethanol will likely also increase the market price for current feedstocks sugar beets and grains. This will make processes based on 'new' raw materials, such as agricultural residues, food industry residues, or wood, even more attractive.

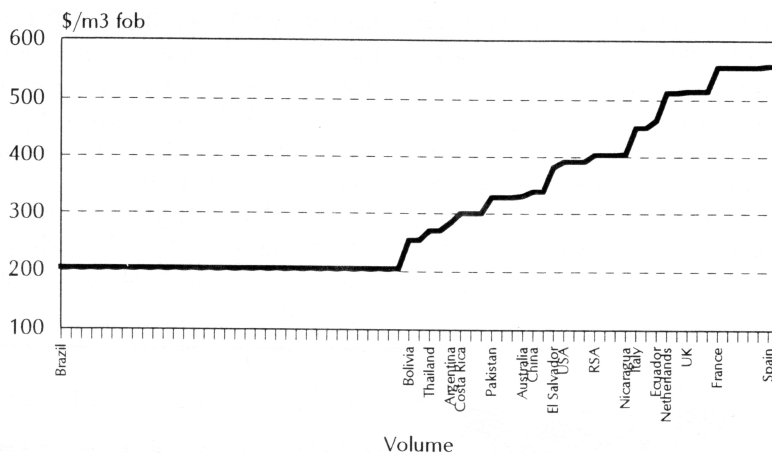


Figure 8.2 World supply curve for bioethanol in 2004 (F.O. Lights, 2005)

8.2 Environmental performance

8.2.1 Greenhouse gas mitigation costs

The greenhouse gas mitigation costs indicate the cost-efficiency of the use of money for a certain application that reduces greenhouse gas emissions. For biofuels, greenhouse gas mitigation costs are generally high compared to other measures to reduce greenhouse gas emissions, such as increasing energy efficiency or biomass co-firing. However, the motivation to use biofuels in Europe is not only to reduce greenhouse gas emissions, but also to increase security of energy supply and to create socio-economic opportunities for the agricultural sector. For many national and local authorities, the reduction of exhaust emissions such as fine dust is also a motivation to use biofuels.

Greenhouse gas mitigation costs were calculated for the bioethanol processes considered, based on the costs data in Table 8.1 and the estimates for greenhouse gas emission reductions in Table 8.2, based on figures earlier in the report. The figures shown depend on several factors that have a large uncertainty of which the bioethanol costs is the most important. Therefore, the results should be regarded only as indication.

Table 8.2 Estimated GHG emission reductions for the bioethanol from different processes

Feedstock (& process)	GHG emission reduction compared to petrol*		
	2006	2010	2020
Sugar beets	40%	60%	60%
Grains	20%	40%	40%
Potatoes	20%	40%	40%
Residual starch streams	40-60%	40-60%	45-75%
Lignocellulose (enzymatic hydrolysis)	-	80%	85%
Lignocellulose (gasification & synthesis)	-	-	90%
Lignocellulose (gasification & fermentation)	-	-	80-90% ?

* For comparison: The GHG emission reduction for bio-Fischer Tropsch diesel compared to diesel is estimated at 90%.

Table 8.3 Indication of GHG mitigation costs for the different bioethanol processes

Feedstock (& process)	GHG mitigation costs (€/t CO ₂ -eq.)*,**		
	2006	2010	2020
Sugar beets	370 - 450	250 - 300	190 - 250
Grains	900 - 1070	450 - 530	370 - 450
Potatoes	1880 - 2050	940 - 1020	860 - 940
Residual starch streams	190 - 450	190 - 450	110 - 330
Lignocellulose (enzymatic hydrolysis)	-	180 - 390	20 - 170
Lignocellulose (gasification & synthesis)	-	-	20 - 160
Lignocellulose (gasification & fermentation)	-	-	240 - 510 ?

* Assuming production costs for petrol of 0.40 €/l (oil price ~50 \$/barrel)

** For comparison: The GHG mitigation costs for bio-Fischer Tropsch diesel compared to diesel are estimated at 20 - 160 €/t CO₂-eq. for 2020.

8.2.2 Other environmental aspects

Environmental aspects other than greenhouse emissions likely concern mainly the biomass cultivation and the bioethanol use in the car and not so much the conversion process. There are not many Life Cycle Assessments (LCAs) for bioethanol that take into account environmental aspects other than greenhouse gas emissions and fossil energy use. A LCA study on bioethanol from sugar beet and grains shows these have, compared to petrol, lower environmental impact in most of the eleven categories that were considered, except for acidification and eutrophication (Malça, 2005). A Dutch LCA for bioethanol from wheat finds an increase for acidification (33% increase) and eutrophication (100% increase) compared to petrol, caused by the agricultural emissions of ammonia, NO_x, SO_x, and phosphates.

Tailpipe and evaporative emissions are generally excluded in biofuel LCAs. These emissions depend very much on the way bioethanol is used in the car, such as neat or in a mixture, in an existing or a dedicated engine. Of course, these emissions are not dependent on which bioethanol production process is used, because the fuel is the same, except when higher alcohols are used. Existing data on tailpipe emissions from bioethanol use is scarce, fragmented and ambiguous. A review for bioethanol blended as 10% mixture in petrol finds that emissions of acetaldehyde, ethanol and NO_x are increased, whereas carbon dioxide and particulate emissions are reduced (Niven, 2005). However, the increased emissions can be reduced by fine-tuning the engines to the fuels and by the use of exhaust gas catalysts.

9 Conclusions

9.1 Comparison of production processes

9.1.1 Bioethanol from sugar and starch crops and residues

The production of 'conventional' bioethanol from sugar and starch containing feedstocks is widely commercialised. Overall, the ethanol industry has reduced production costs 2 to 3-fold in the past 30 years due to a substantial increase in ethanol yield, and a two-fold reduction of energy usage by a shift to larger ethanol production plants, and adoption of energy-saving technologies. Furthermore, changes in the use of by-products (bagasse, stillage) have increased energy efficiency and reduced production costs. Cost gains are also achieved by a shift to larger production installations. This trend will no doubt continue in the coming years.

For large plants with a capacity of ca. 240.000 m³ bioethanol/year current production costs in Europe are estimated at 0.50-0.55 €/l for sugar based processes, 0.55-0.60 €/l for grain based processes, 0.85-0.90 €/l for potato based processes, and 0.45-0.55 €/l for processes using residual starch streams. These costs are strongly dependent on the feedstock costs, which make up 50-70% of the overall costs. Future costs are expected to decrease due to process improvements. However, higher demand for bioethanol will likely also increase the market price for sugar and starch feedstocks. Ethanol production costs in 2020 are estimated at 0.45-0.50 €/l for sugar based processes, 0.50-0.55 €/l for grain based processes 0.80-0.85 €/l for potato based processes, and 0.40-0.50 €/l for processes using residual starch streams.

The current reduction of greenhouse gas emissions compared to petrol is estimated on average at 40% for bioethanol from sugar crops and 20% for bioethanol from grains. The actual reduction is strongly dependent on the type of production facility, type of fuel used etc. An improvement to 60% and 40% reduction respectively is possible by using state-of-the-art technology both in farming practices and in the production facilities. For processes using residual starch streams the greenhouse gas reduction compared to petrol is estimated at 40-60% with a possible improvement to 45-75%. The current GHG mitigation costs are estimated at 190-450 €/t CO₂-eq. for residual starch streams, 370-450 €/t CO₂-eq. for sugar beets and 900-1070 €/t CO₂-eq. for grains. It is expected that in 2020, the GHG mitigation cost can approximately be halved with at best 110 €/t CO₂-eq. for residual starch streams.

9.1.2 Bioethanol from lignocellulose via enzymatic hydrolysis

The cellulose and hemicellulose fractions in lignocellulose biomass and residues (grass, straw, wood etc.) are potential sources of sugars for bioethanol production. The lignin fraction can be used for combined heat and power generation for the production process and export of surplus electricity to the grid. Recent technological developments make it likely that industrial production of ethanol from lignocellulose is close to commercialisation. Currently several pilot plants are in operation worldwide, using feedstocks such as corn stover, straw and wood. Industrial implementation of technology based on enzymatic hydrolysis is expected to start within 5 years in North America and/or the EU.

Previous cost estimates for 'cellulosic ethanol' ranged from ca. 0.25 - 1 €/l. However, the lower costs estimate may only be reached in the long term (>2020) and the higher cost estimate seems outdated, because of recent progress, e.g. a 30-fold reduction in enzyme costs. For production in installations of ca. 240.000 m³ bioethanol/year the production costs are estimated in this study at 0.50-0.75 €/l in the short term (i.e. 2010) and 0.30-0.50 €/l in the medium term (2020).

The reduction of greenhouse gas emissions for the use of 'cellulosic ethanol' compared to petrol is estimated at 80-85%. The GHG mitigation costs are 180-390 €/t CO₂-eq. for 2010 and 20-170 €/t CO₂-eq. for 2020, and are substantially lower than for 'conventional' bioethanol.

At the current state of development several bottlenecks remain. Development of an efficient pre-treatment process is a topic of active R&D on lab scale and in pilot plants in the US and Europe. In the area of fermentation a recent breakthrough is the development of a yeast strain capable of rapid glucose and xylose fermentation. Further work is required to develop a robust industrial process for fermentation of lignocellulose hydrolysates. Other issues include conversion of the lignin fraction and the design of optimal process integration, water treatment and recycle. Overall, process development is gaining momentum and the prospects are good. Multinationals such as Shell, Abengoa and Royal Nedalco have invested in the development and are carrying out active R&D. The first commercial plants are expected around 2010.

9.1.3 Bioethanol from lignocellulose via catalytic syngas conversion

The production of bioethanol or a mixture of alcohols from lignocellulosic biomass by gasification and subsequent catalytic conversion of syngas to alcohols has been known for a long time, and is receiving more attention in recent years. Because this process uses gasification, the lignin fraction of the biomass can be converted to bioethanol as well. Furthermore, this is the only bioethanol production process that does not require energy intensive separation of water and ethanol by distillation. However, at present, the most suitable gasification technology –entrained flow gasification– is not fully developed yet for the use of biomass. Furthermore the conversion rate and selectivity of the various catalysts investigated is still far from what is required for commercial application. It is unlikely that the process will produce bioethanol only, but a mixture of alcohols could be used as fuel as well, although the methanol content should be minimised. Alternatively, the separation and sales of co-produced higher alcohols for non-fuel applications –with a relatively high market value– may facilitate commercial implementation.

The estimated production costs are comparable with cost estimates for Fischer Tropsch diesel from biomass. They vary from 0.30 - 0.50 €/l bioethanol for very large (several million m³/y) or large installations (ca. 240.000 m³/y) respectively. The expected reduction of GHG emissions compared to petrol is 90%, which leads to mitigation costs of 20-160 €/t CO₂-eq. for 2020, lower than for 'conventional' bioethanol and comparable with bioethanol from lignocellulose via enzymatic hydrolysis.

The process for bioethanol production from lignocellulosic biomass by gasification and catalytic synthesis seems promising and could be ready for market introduction between 2010 and 2020. Its success depends on the development of a catalyst with acceptable conversion rate and high selectivity towards ethanol and higher alcohols. The required gasification technology, biomass entrained flow gasification, is being developed simultaneously for the production of bio-Fischer-Tropsch diesel. Integral testing, i.e. the integral line-up from biomass gasification to the higher alcohols end product, should demonstrate which gas-cleaning methods are required.

9.1.4 Bioethanol from lignocellulose via syngas fermentation

The process for bioethanol production from lignocellulosic biomass by gasification and fermentation combines thermochemical and biochemical techniques. The advantage of the process is that it can convert the lignin fraction in the biomass to bioethanol as well and that it operates at mild temperature and pressure. R&D on this process has not been very intensive yet, but there is currently one pilot plant in operation in the USA, which at present achieves only low bioethanol yields. Commercialisation is still far off.

The process seems most suitable for small-scale operation (ca. 10.000-50.000 m³/y), as large-scale plants would require extremely large fermentation reactors. A low-temperature gasification technology, such as fixed bed, fluidised bed or indirect gasification should be used in combination with a technology to remove tars from the product gas. To be operated economically on a small scale, low cost, locally available biomass and/or waste is required as feedstock.

A first estimate of the production costs is 0.60-0.90 €/l, based on the currently available information. The reduction of GHG emissions compared to petrol is expected to be 80-90%, provided the energy use in this process is not too high. This leads to GHG mitigation costs of 240-510 €/t CO₂-eq. for 2020, which is significantly higher than for other bioethanol processes using lignocellulosic biomass as feedstock.

Although the current cost estimates are not very promising, further R&D may change this prospect. The main topics are: 1) Increase the tolerance of the fermentation organisms to ethanol. Currently, ethanol is toxic to the culture and ethanol concentrations should be kept below 3 % vol. This is too low from an economic and energetic point of view and should be increased to at least 6% vol. 2) Investigate whether small hydrocarbons such as methane present in syngas act as inhibitor to the fermentation process and/or the development of resistant stains. 3) Improve the gas-to-liquid mass transfer in the fermentors. The scale-up of the fermentation reactors requires further R&D as well.

9.2 Improvement potential

Optimisation of classical ethanol production from sugars and starch is an ongoing process. Current optimisation efforts are focused on improving production yields and lowering energy use, and include improvements of feedstock production, cost reduction of enzymes for starch hydrolysis, and optimisation of the fermentation and distillation process. This trend will continue in the coming years especially by the construction of new, large-scale production plants that use state-of-the art technology. In the long term the potential for reduction of production costs and GHG mitigation costs for conventional bioethanol is however limited compared with the new technologies using lignocellulose as feedstock.

Production of bioethanol from lignocellulosic biomass by enzymatic hydrolysis is for most part based on completely new technology and gains in the long term will likely be higher in this case, due to technological learning. This is illustrated by the projected costs for bioethanol from lignocellulose by physical/chemical pre-treatment and enzymatic hydrolysis, which are expected to decrease from 0.50 - 0.75 €/l in 2010 to 0.30 - 0.50 €/l in 2020. A learning effect could also be applicable to the production process based on gasification & catalytic synthesis, but the cost estimates presented in this study are partly based on existing technologies (e.g. coal gasification) which limits the potential for further reduction of production and GHG mitigation costs.

The main contributors to the production costs of bioethanol are feedstock and investment costs and –to a lesser extent– energy costs. Bioethanol production costs are most sensitive to feedstock costs, which are subjected to market conditions. This applies especially to bioethanol production from sugar beets and grains where raw material costs account for 50-70% of total production costs, whereas this is 25-50% for bioethanol processes based on lignocellulosic biomass. The capital costs are more important for processes based on lignocellulosic biomass where they account for 30-60% of the production costs. Energy costs are a cost factor only for conventional bioethanol production with a limited effect on production costs. The oil price is a major, volatile factor for the competitiveness of bioethanol in the transport fuel market, but this applies equally to all types of bioethanol and other biofuels.

9.2.1 Bioethanol in the European biofuels market

The European Union actively pursues its Directive target of 5.75% substitution of petrol and diesel fuels with biofuels in 2010. This leads to a high demand for biofuels on the European market. At present this demand is fulfilled by imported low-cost Brazilian bioethanol as well as the more costly (conventional) bioethanol and biodiesel produced in Europe. However, in the longer term, it is expected that the best performing biofuels in terms of economic, but also environmental performance, will dominate the market, certainly if biofuels are still more expensive than fossil fuels. In the longer term the best performing biofuels are lignocellulose gasification-based fuels such as bio- Fischer-Tropsch diesel, but also bioethanol produced from lignocellulose either by physical/chemical pre-treatment and enzymatic hydrolysis or by gasification and catalytic synthesis. The estimated production costs for these two bioethanol processes for 2020 are 0.30 - 0.50 €/l or 15-22 €/GJ which compares well with cost estimates for bio- Fischer-Tropsch diesel. The GHG mitigation costs for bioethanol from these processes and for bio-Fischer Tropsch diesel are also similar: 20 - 170 €/t CO₂-eq. for 2020 at an oil price of 50 \$/barrel.

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