

Feasibility study of a value chain around isobutanol

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Isobutanol Platform Rotterdam (IBPR) consortium

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Summary

All kind of different options to use of biomass for producing commodity chemicals are being explored because of potential economic and ecologic benefits. In line with a choice made in an earlier stage, this report discusses the feasibility of setting up a bio-based value chain around isobutanol in the Rotterdam region. The selected feedstocks are beet sugar and beet sugar pulp. The latter should be converted into fermentable sugars, with protein being a valuable side product. Via fermentation isobutanol can be obtained, which can be converted into various products: p-xylene, jet fuel, and glycerol tertiary butyl ether.

Processes were conceptually designed for converting 1.2 million t/a sugar or 1.5 million t/a sugar beet pulp, based on their estimated availability. Despite this scale, the achievable production, mainly 0.1 million t/a p-xylene with 0.15 million t/a jet fuel, is modest when compared to the demand for these products.

There are no major technical hurdles for the process, but most steps require testing, and several steps require significant improvement before the process can be economically feasible. Feedstock costs are too high when using thick juice, and when beet pulp is used, its enzymatic hydrolysis is too expensive. This implies that for the sugar beet pulp case a rigorous technical development is required to lower the total enzyme costs, which may be reached by lower intrinsic enzyme costs and enzyme recycle scenarios.

According to a life cycle analysis, the designed processes significantly decrease both the non-renewable energy use (NREU) and the greenhouse gas (GHG) emission as compared to a fossil-based counterpart. The GHG emissions decrease about 70% or 60% when using crystallized sugar or beet pulp, respectively. In the case of the NREU, the reduction is about 35% or 60% when using crystallized sugar or beet pulp, respectively. The difference is due to the impact of enzyme production for hydrolyzing beet pulp.

A selection has been made of research topics to be addressed and technology providers to be involved for the next stage of the project.

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1 Introduction

1.1 Background and motivation

Our world is addicted to oil. However, oil and gas reserves in limited supply, combined with increased demand for petroleum by emerging economies, and political and environmental concerns about fossil fuels, have stimulated an intensive effort in the development of economic and energy-efficient processes for the sustainable production of fuels and chemicals intermediates from renewable biomass resources. The Rotterdam Climate Initiative (RCI) is aiming at 50 % CO₂ reduction by 2025 in the port and city of Rotterdam. Consequently, the use of biomass is an indispensable element of the RCI programme where there is a particular focus on bio-based chemicals production to replace petrochemical production. In an earlier stage (2012), one target product that has been selected for bio-based production is 2-methyl-1-propanol (isobutanol). Isobutanol is a naturally occurring product of the fermentation process, found in many items such as bread and scotch whiskey; however, its commercial use to date has been limited. Through innovations in microbiology and biochemistry, traditional yeasts have been modified, making possible a much higher selectivity in producing isobutanol, i.e., turning up the yeast's ability to make isobutanol while also limiting the ethanol production pathway.

Butanol or butyl alcohol (also called “biobutanol” when bio-based) is one of the alcohol isomers with the molecular formula C₄H₉OH shown in Figure 1-1. The term “butanol” usually refers to n-butanol (or 1-butanol), which is already produced on large scale by fermentation, but this project focuses on isobutanol.

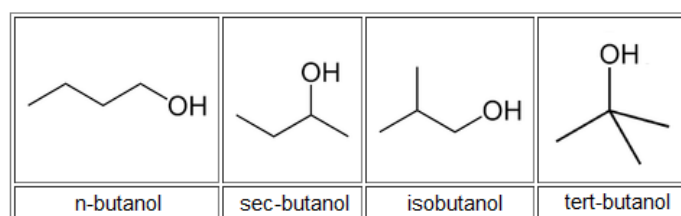


Figure 1-1. The four isomeric structures of butanol.

The fields of application of isobutanol closely resemble those of 1-butanol. Isobutanol has attracted considerable interest as a potential fuel additive since it has a number of advantages over other common alcohols used for improving octane rating. In addition, and unlike traditional oxo-alcohol products, isobutanol is widely regarded as feedstock for the production of C₄ olefins via established dehydration chemistry. Dehydration of isobutanol to 2-methylpropene (isobutylene or isobutene) generates a versatile platform molecule that can be further processed into other high-value hydrocarbon products using conventional petrochemical catalysis.

The prevailing process to manufacture these hydrocarbon products today is through the practice of cracking oil fractions such as naphtha and natural gas liquids (ethane, LPG etc.). Naphtha crackers produce butenes as a co-product and the butenes market has tightened as these crackers have shut down and or shifted from oil to lighter feed such as natural gas liquids thus reducing the available supply of butenes. As a result, we expect the hydrocarbons derived from isobutanol to provide chemical and fuel producers with both supply chain diversity and alternatives to current petroleum-derived products which can be particularly important in a tight petrochemical's environment.

Previous attempts to create renewable, cost-effective alternatives to petroleum-based products have faced several challenges, for example the first generation renewable products are not drop-in solutions for existing markets. It is of crucial importance to establish a product portfolio that has considered effective alternatives to conventional petroleum. Several markets can be foreseen as shown in Figure 1-2. All types of non-food biomass could be considered in the isobutanol platform ranging from forest products and energy crops to aquatic plants.

Much of the technology necessary to convert isobutanol into plastics, fibers, rubber, other polymers and hydrocarbon fuels is known and practiced in the chemicals industry today. The establishment of an isobutanol platform will enhance the access to these large target markets by delivering isobutanol

at a cost structure that allows for the adoption of renewable products into markets that were once the exclusive domain of petroleum-based chemicals and fuels.

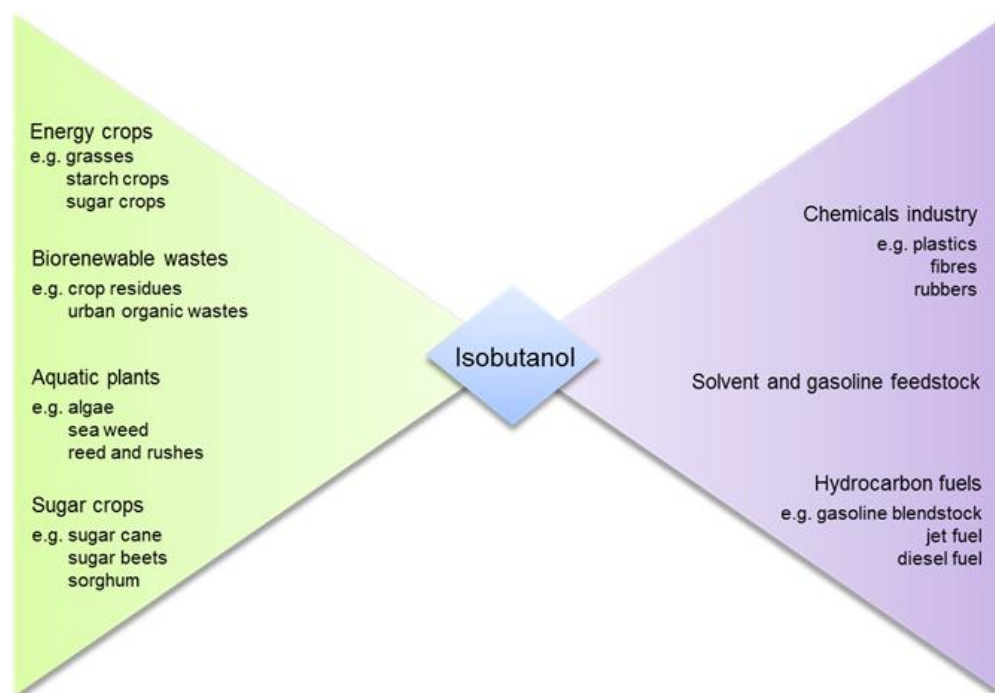


Figure 1-2. Feedstock and product portfolio that could be considered in the isobutanol biorefinery

1.2 Aim and approach

This study aims to determine

- the techno-economic feasibility of developing an industrial value chain centered around bio-isobutanol at the Port of Rotterdam
- how to address the main technical bottlenecks in a next project phase

To achieve the aim, this report contains:

- An overview of the literature on the different steps in the conversion of biomass to isobutanol and of isobutanol to important scalable products, in particular the production of p-xylene, jet fuel and GTBE;
- On the basis of the literature, a selection of a number of process options, and logistics scenarios
- Design of the selected processes using process models, including preliminary mass and energy balances, equipment sizing
- The evaluation of the designed process chains and selected logistics scenarios with respect to economics and life-cycle
- An assessment of the prospects of feasibility at full scale
- A plan towards full scale implementation, including screening of possible technology providers and experimental research to be done

1.3 Short description of the process

The process around isobutanol will resemble a biorefinery. The American National Renewable Energy Laboratory (NREL) describes a biorefinery as follows: "A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass sources. The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum. Industrial biorefineries have been identified as the most promising routes to the creation of a bio-based economy" (NREL 2009).

By producing multiple products, a biorefinery can take advantage of the differences in biomass components and intermediates therefore maximizing the value derived from the biomass feedstock. A biorefinery might, for example, produce one or several low-volume, but high-value, chemical products and a low-value, but high-volume, liquid transportation fuel; while generating power and heat for its own use. A scheme of the isobutanol biorefinery can be seen in Figure 1-4.

As mentioned before, the platform molecule of the biorefinery is isobutanol. Isobutanol is an important platform chemical with broad applications in many chemicals and fuels markets. We focus our feasibility study on four main products:

- Fuels:
 - isobutanol as a blendstock for gasoline and
 - jet fuel;
- Downstream chemicals as shown in Figure 1-3:
 - p-xylene via isooctene dehydrocyclization and
 - glycerol-tertiary-butyl-ether via reaction of isobutylene with glycerol.

The relative amounts of product outputs produced in the isobutanol biorefinery can be flexibly adjusted in various ways to adjust to e.g. changing market demand for specific product streams or to maximize the overall value of the products produced.

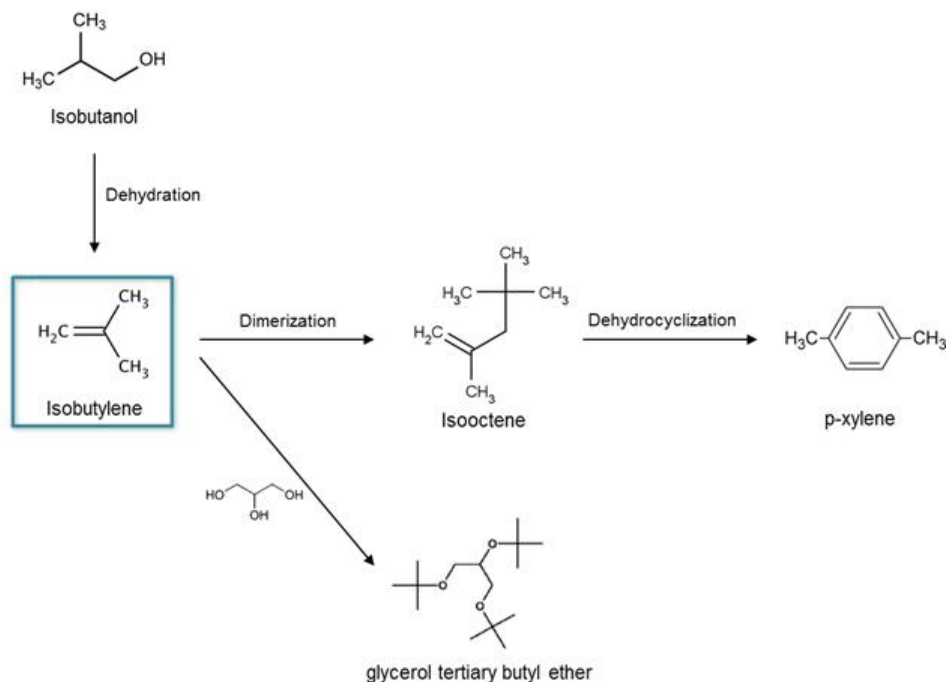


Figure 1-3. Downstream chemicals obtained via isobutanol dehydration. Isobutylene market: rubbers and p-xylene market (e.g. PET).

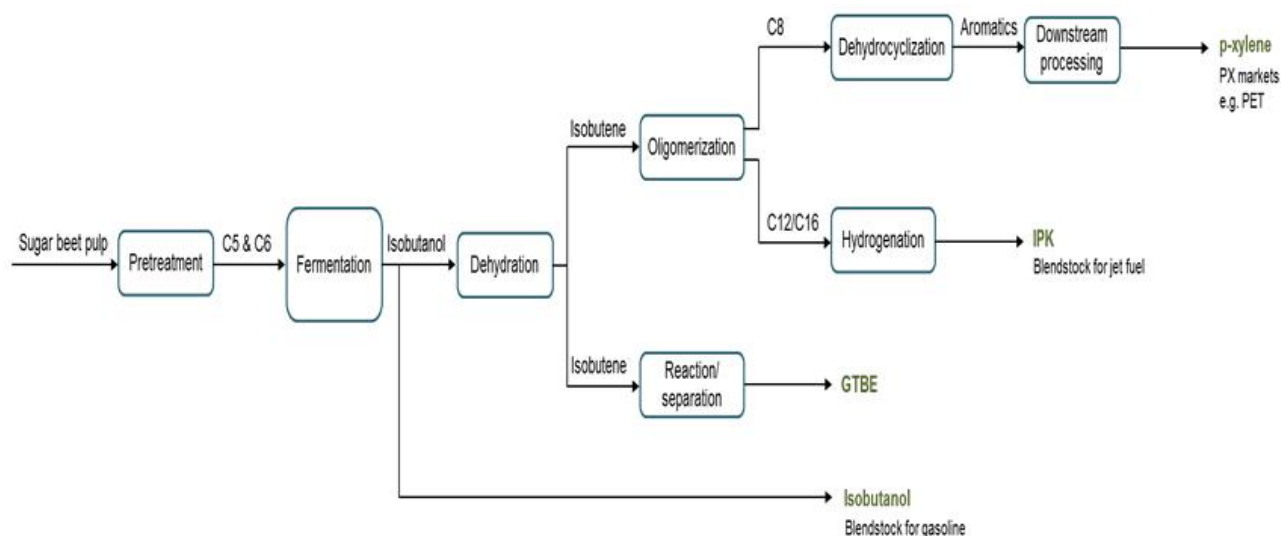


Figure 1-4. Scheme of the isobutanol platform refinery.

2 Design basis and conventions

2.1 Plant size

Because of several feedstock options and product options, the plant size is expressed in amount of isobutanol produced. This is limited by availability of biomass but should be at least 0.2 million t/a for a reasonable scale of economy at the downstream side. Therefore, the plant is designed at 0.2 million t/a.

The proposed product spectrum consists on isobutylene, jet fuel components, and p-xylene in mass proportions of 1:6:3. This product spectrum must be adjusted according to different scenarios of economic performance.

2.2 Scope of the design (battery limits)

For definition of the scope of the design a block scheme will be used (Figure 2-1). The dashed red line shows the battery limit of the current study. Inside the battery limits are kept the pretreatment and fermentation, the recovery of isobutanol from the broth and its dehydration to isobutene, the oligomerization of isobutene and separation of C8 and C12 fractions and their further processing to obtain p-xylene (aromatization) and jet fuel (hydrogenation). Out of the scope of this study remain the further chemical process carried by the companies involved in order to obtain their final products from the products of this biorefinery. The waste treatment and utility generation are also considered out of the scope of this design, and thus they will be considered as a cost per stream disposed or bought, respectively. The streams crossing the battery limits are described in Table 2-1.

The scope drawn corresponds to the selected at the beginning of this study. However, due to the complexity, capital cost required and economy of scale of the aromatization unit, it is still a matter for discussion whether to include it or to move it outside battery limits. In case the second option is chosen, the isooctane stream will be sent to an external partner, which will perform the aromatization to p-xylene.

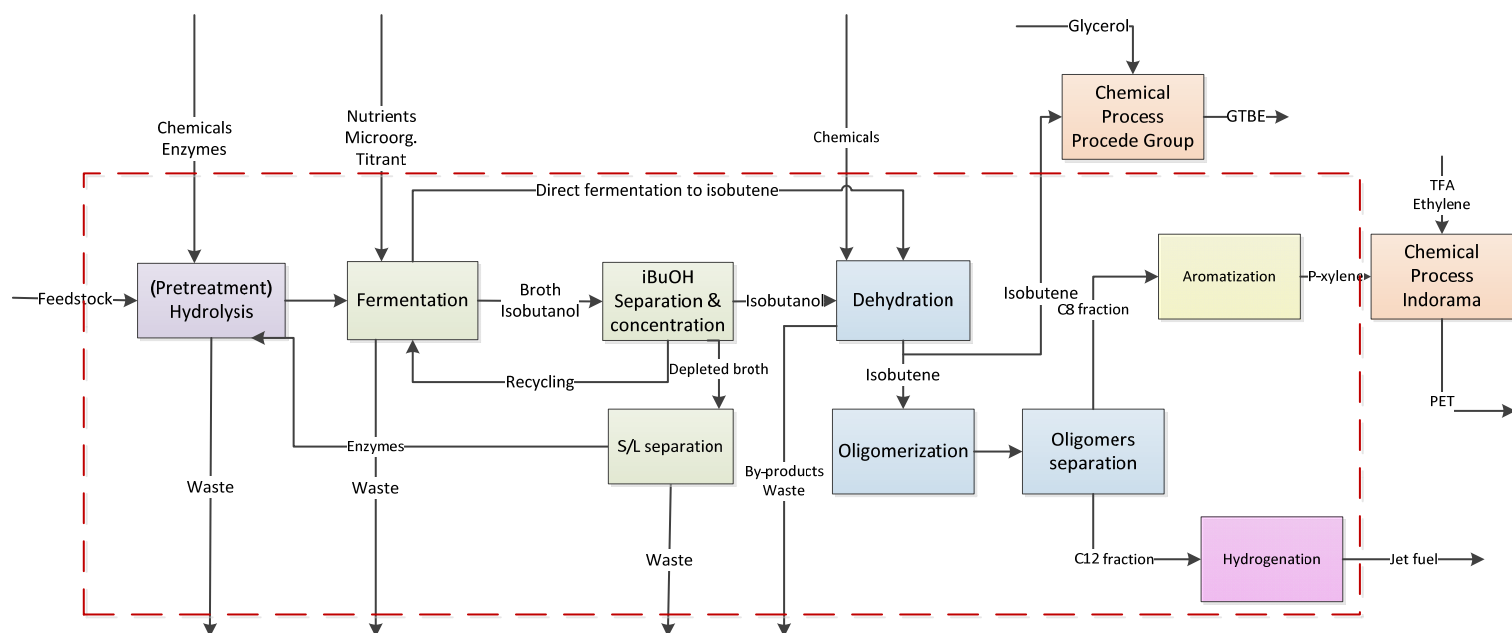


Figure 2-1: Block scheme and battery limits. In case of a direct fermentation of isobutene, it should directly go from fermentation to the oligo en GTBE reactors.

Table 2-1: Overview of streams crossing through the battery limits

Stream	Direction	Project involved	partner
Feedstock	IN	SuikerUnie.	
Chemicals, enzymes	IN	External party	
Nutrients, MO, titrant	IN	External party	
Chemicals/Catalyst	IN	External party	
Waste 1; insolubles after pretreatment/hydrolysis	OUT	t.b.d.	
Waste 2; fermentation waste	OUT	t.b.d.	
Waste 3; mixed stream, liquid: broth after i-BuOH recovery, solid: microorganisms and enzymes	OUT	t.b.d.	
By-products waste	OUT	t.b.d.	
Isobutene 10% total i-butene. 99%purity	OUT	Procede Group	
p-Xylene	OUT	Indorama	
Jet fuel components	OUT	SkyNRG	

2.3 Feedstock

2.3.1 Sugar beet as a feedstock

Sugar beets contain approximately 17% sugar (w/w) and are cultivated in the northwest of Europe (in the so-called "sugar beet-belt"). During the sugar beet campaign, which lasts from September to January, Suiker Unie processes sugar beet into crystalline white sugar in sugar factories in The Netherlands and Germany. During the sugar production process (Figure 2-2) sugar beets are harvested from the land and transported to the sugar factories. After washing and slicing of the sugar beet, sugar juice is extracted by diffusion in warm water. The left over beet material is called sugar beet pulp and is pressed toward approximately 25% dry matter (w/w).

The sugar juice, raw juice, is purified in several steps and concentrated to the process intermediate "thick juice" that contains approximately 68% sugar. The thick juice is then further concentrated until sugar crystals are formed. These are separated from the sugar syrup by multiple centrifugation steps. The syrup that is left over after obtaining crystalline white sugar is called molasses.

In addition to sugar beet Suiker Unie also processes raw cane sugar from the world market that is refined to crystalline white sugar. In 2012 Suiker Unie has started to store thick juice in large storage tanks. Thick juice is processed into white sugar outside the sugar beet campaign during the so-called “thick juice” campaign. Alternatively thick juice can be directly used as a liquid fermentation feed stock.

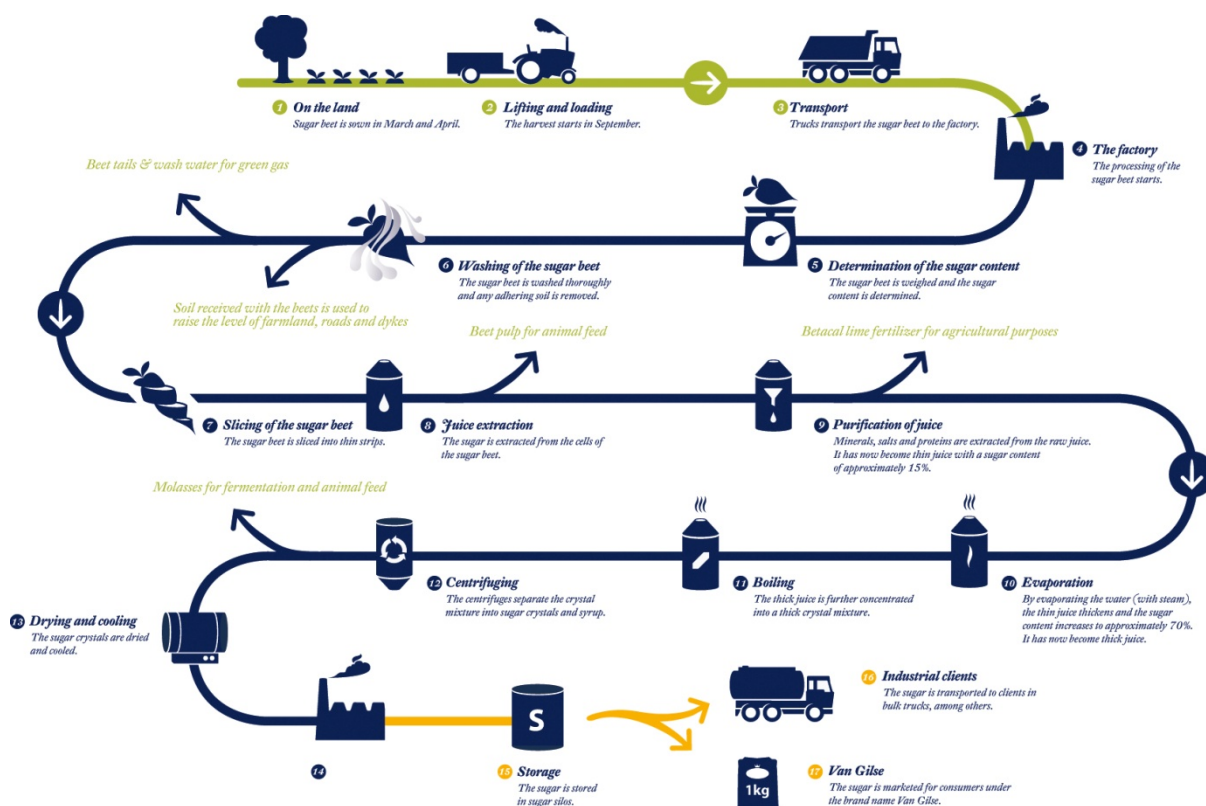


Figure 2-2. The sugar production process

2.3.2 Biomass availability

Currently Suiker Unie produces approximately one million metric tonnes of sugar per year. At this moment the sugar industry in Europe is regulated by the EU Common Agriculture Policy (CAP) (http://ec.europa.eu/agriculture/cap-post-2013/index_en.htm) which limits sugar production for food by a quota system. As of September 2017 this quota system will end and sugar companies in Europe can produce and market unlimited amounts of sugar. Worldwide sugar consumption is expected to grow due to increased consumption in developing countries and the need for renewable feed stocks as a feed stock for biobased fuels, chemicals and materials. Therefore Suiker Unie invests heavily in capacity increase and expects to double its annual production capacity to approximately 2 million tonnes of sugar per year in 2020. The current and future availability of biomass feed stocks as produced by Suiker Unie in The Netherlands and Germany is given in Table 2-2.

Table 2-2. Current and estimated future biomass availability by Suiker Unie (million tonnes)

Biomass feed stock	2012	2020
Quota sugar	0.9	-
Out of quota sugar*	0.3	2.0
Sugar beet pulp (25% d.m.)	1.0	2.0

*or sugar equivalents in thick juice

2.3.3 Biomass composition

Sugar beet contains approximately 17% saccharose (sucrose) that is extracted in the sugar production process. Thick juice contains about 68% sugar and additional components that could be

beneficial as nutrients for fermentation. Sugar beet pulp mainly consists of polysaccharides. Table 2-3 shows the complete composition of the different biomass feed stocks.

Table 2-3. Composition of sugar beet based biomass feed stocks

	Sugar	Thick juice	Sugar beet pulp
Dry matter content (% w/w)	100	70	25
Composition dry matter (% w/w)			
Sucrose	100	95	
Cellulose			24
Hemicellulose			24
Pectin			23
Proteins			10
Other (minerals, acids, ashes)		5	19

2.4 Modeling strategy

General description of the modeling strategy:

Processes were modeled after the closest commercially practiced technology for which in the open literature numbers could be found. (HydrocarbonProcessing 2008; HydrocarbonProcessing 2010; HydrocarbonProcessing 2011) There may be technologies which are more suitable for this modeling, but that requires negotiations with the vendors.

Once a suitable technology had been found, the numbers were adjusted to reflect a common standard. The time of reference was July 1, 2012, and all CAPEX numbers were adjusted using the IPEX index from ICIS (appendix). For reasons of simplicity, 1 euro was assumed to be 1 US\$. Capacities were scaled using a 0.6 scaling factor. For all technologies found, the CAPEX was assumed to be the ISBL erected costs at a general site (that is, no location factor was included). No new process factor was used either. Utilities use assumptions can be found with each process step. We assumed a 300 day/year up-time.

The model uses a rule of thumb cost breakdown, which is (in percentages) listed in Table 2-4. OPEX assumptions are given in Table 2-5. Prices used for feedstocks, products, utilities, and consumables are given in Table 2-6.

Table 2-4. CAPEX cost break-down used

Installed equipment	61%
Spares and storage	1%
Site preparation	2%
Facilities	1%
Allocated cost for utility plants	9%
Contingencies en contractor fees	4%
Cost of Land	2%
Royalties	2%
Cost of Start-Up	6%
Working Capital	13%

Table 2-5. OPEX assumptions used.

Labor Cost	
Operators/Shift	10
Number of Shifts	5
Hours/Year	2080
Wages/Hour	100
Supervisory and engineering personel (% of DW&B)	15%
Operating Supplies	0.60%
QA Lab per year per operators per shift	57000
Plant Cost	
Maintenance (% of Total CAPEX)	3%
Plant overhead	1%
Taxes and Insurance	1%
General Expenses	1%

Table 2-6. Prices used for feedstocks, products, utilities, and consumables.

Item	\$/t	Item	\$/unit
Sugar		<i>Utilities and consumables</i>	
Thick Juice		Natural gas	28 \$/m ³
Beet pulp		Electricity	0.07 \$/kWh
Hydrogen		Process water	0.7 \$/t
Products		Steam	31 \$/t
Isobutanol		Waste water	2 \$/t
Isobutene	950	Acid	100 \$/t
p-Xylene	1200	Base	100 \$/t
Jet fuel	1000	Other	100 \$/t
Hydrogen	1500	N ₂	200 \$/t
Ash	200		
Protein	1100		

3 Logistics

This project is planned inside the framework of the Rotterdam Climate Initiative, which aims at a greening of the energy and chemical sector in the major industrial cluster of the Netherlands, the Port of Rotterdam. Hence, the initial location proposed for this plant is the Port of Rotterdam, in the province of Zuid-Holland.

The initial idea was the transportation of all the feedstock to Rotterdam and the construction of a complete biorefinery setup in the Port, using all the infrastructure already available and interacting with the surrounding factories for utilities and waste disposal.

However, due to the dispersion and high volume of raw material needed, other alternatives for the location must be addressed. For this project, the provider of the raw material was agreed to be SuikerUnie, which in the Netherlands owns factories in Dinteloord (40 km from the Port of Rotterdam) and Vierverlaten (250 km from the port of Rotterdam); see Figure 3-1. The raw materials considered for the present design are bulky solids (both in case of sugar and much more for the sugar beet pulp), or diluted liquid (thick juice, with about 30% of water content).

Considering the price of transportation (data expected), and the amount of inerts that would be transported (either with thick juice, but mainly with sugar beet pulp) it became interest the analysis of using at least the initial processing of the biomass closer to the feedstock, so that a more concentrated product can be sent to the final location.

In such a case, the proposed location was in Dinteloord, as SuikerUnie has land available to build the new production facility. However, in that location it is not possible to process ???

Also, the main stakeholders are interested in obtaining their products close to the Port of Rotterdam, where it is their main location. For this reason, another approach for the production will be the building of two plants: one in Dinteloord, which will process the sugar (wastes) up to an intermediate product that will be sent by transportation to Rotterdam, where all the downstream processing will take place.



Figure 3-1: Map of the Netherlands, with locations discussed for this project

Considering the transportation of an intermediate product from Dinteloord to Rotterdam, three options for transportation are:

- The fermentation broth
- The isobutanol recovered from fermentation (concentrated)
- The isobutylene produced after dehydration of isobutanol.

The first option was discarded, as it will create a conflict with the need for in-situ product removal, and the stream to be transported would be too diluted. The third option is still a question, as SuikerUnie may be reluctant to carry the dehydration process in their factory. As for the second option, two alternatives must be analyzed: Transport of the azeotropic mixture obtained by in-situ removal, or transport of a stream after dewatering.

4 Pretreatment/hydrolysis

4.1 Description of technologies (chemical/enzymatic)

4.1.1 Enzymatic hydrolysis of sugar beet pulp

The major components of sugar beet pulp cell walls are polysaccharides (cellulose, hemicellulose and pectin). The composition of sugar beet pulp (dry matter) is shown in Figure 4-1 (Micard et al. 1996; Zheng et al. 2012).

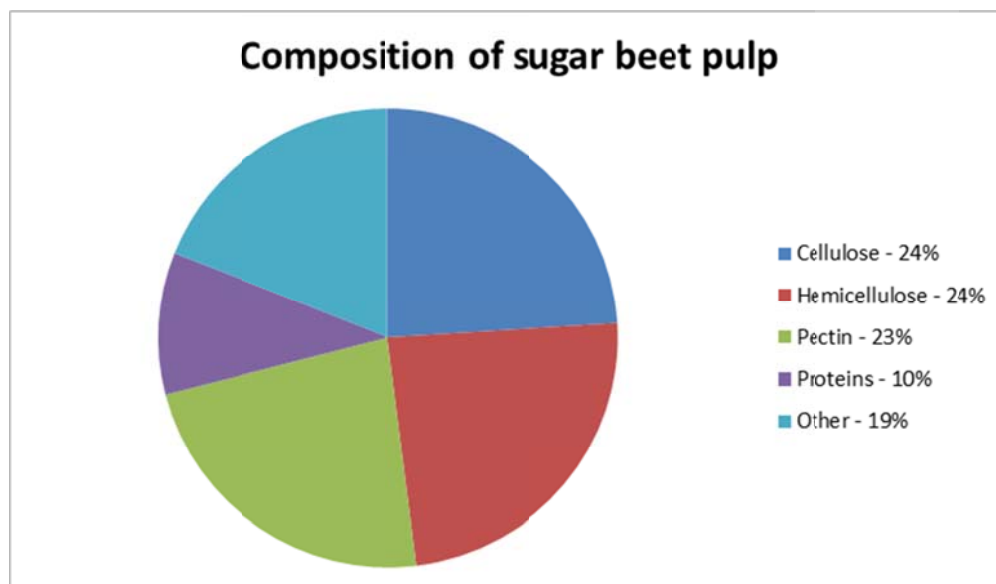


Figure 4-1. Composition of sugar beet pulp dry matter (%)

Unlike lignin-rich biomass streams, sugar beet pulp does not require thermochemical treatment to be degraded, but can be hydrolyzed by enzymatic treatment (Pryor 2008). In the last decades, much research has been performed on the enzymatic hydrolysis of sugar beet pulp into (fermentable) monosaccharides (Beldman et al. 1984; Micard et al. 1996; Micard et al. 1997; Kühnel and Hinz 2008; Kuhnelt et al. 2011). For the production of isobutanol, the polysaccharides in the complex cell wall structures have to be hydrolyzed into fermentable (mono-)saccharides. Multiple enzyme activities are necessary to completely hydrolyze the polysaccharides, e.g. the hydrolysis of pectin requires at least more than 3 different enzyme activities. Synergistic action of different enzymes has been described in scientific literature. Therefore, enzyme cocktails containing a range of hydrolytic activities are used during the hydrolysis (De Baynast De Septfontaines et al. ; Thibault and Rouau 1990; Micard et al. 1996; Micard et al. 1997). Nevertheless, since all commercial enzyme preparations lack 1 or more enzyme activities, 100% complete hydrolysis of the polysaccharides is not possible at this moment and some oligosaccharides will always be present in the hydrolysate. Research must show if these oligosaccharides can directly be fermented. After enzymatic treatment, the main monosaccharides brought into solution are glucose (from cellulose), arabinose (from hemicellulose) and galacturonic acid (from pectin), as shown in Table 4-1. [data from own research within CFTC and from literature]

Note : When dried pulp is used in enzymatic hydrolysis, apart from proteins, crystalline cellulose can also be present as residue. Crystalline cellulose can be attacked after chemical treatments such as persulfate, chlorite or hydrogen peroxide (Thibault and Rouau 1990).

Table 4-1. Composition of solution after enzymatic hydrolysis of sugar beet pulp (Bink, personal communication, 2012, (Micard et al. 1996; Micard et al. 1997; Kühnel and Hinz 2008; Koltermann et al.).

Mono/Oligo-saccharide(s)	Concentration in solution (% of dry matter)	Hydrolysis yield (%)
Galacturonic acid	16	80
Arabinose	17	90
Glucose	23	95
Other monosaccharides (Rha, Gal, Xyl, Man, Fuc)	7	80-85
Oligosaccharides	17	-
Total sugars	80	85-90

Fresh sugar beet pulp is available in large quantities but only during a few months a year (seasonal availability). High levels of water and monosaccharides make it relatively perishable. Therefore, one of the challenges of sugar beet pulp utilization is its stabilization during storage. Because of these potential storage problems, sugar beet pulp is often dried prior to storage. For dry storage, the moisture content should be lower than 15% to prevent fungal growth (Huisman 2003). With regard to biofuel production from sugar beet pulp, the considerable cost contribution of a sugar beet pulp drying process could be a significant concern for the overall economics. At the same time, dry storage may not be advantageous especially when biochemical technologies such as fermentation are used to convert biomass into biofuels and bio-based products because these bioprocesses usually require water. Ensilage is commonly used to preserve sugar beet pulp for prolonged time. Research showed that ensilage can be used both to preserve and treat biomass feedstock for further downstream conversion into chemicals and fuels. In addition, it is reported that ensilage enhances the sugar yield upon enzymatic hydrolysis of the sugar beet pulp, and also might reduce the amount of enzymes needed for the pulp hydrolysis (Zheng et al. 2011). Possible formation of fermentation inhibiting components during the ensilage must be subject of further research. Also, the effect of ensilage on cost price of the pulp feedstock must be calculated to check the economics.

4.2 Freedom to operate (patent tree)

(De Baynast De Septfontaines et al.) : Whole beet is subjected to enzymatic hydrolysis (in combination with acid treatment to reduce pH). A mixture of enzymes is used.

(Beldman et al. 1984): Enzymatic hydrolysis of beet pulp is described using a mix of enzymes for the production of fermentable sugars from the polysaccharides present in the cell wall. A continuous process was investigated in a column reactor connected to a hollow-fiber ultrafiltration unit for enzyme recovery. Cell wall polysaccharides from beet pulp were extensively hydrolyzed: more than 90% conversion was obtained. The synergistic action of cellulases and pectinases is described. Use of a packed column reactor makes a high solid/liquid ratio possible.

(Koltermann et al.) : The liquefaction of (whole sugar beet) biomass is claimed. The liquid fraction can be used in sequent fermentation processes (even after prolonged storage). Adding chemicals or organisms are used to render the liquefied biomass storage stable. Enzymes are used to liquefy the biomass (eg. cellobiohydrolase, beta-glucosidase, polygalacturonase activities, but products are mentioned that include additional enzyme activities, e.g. endo-glucanase, exo-glucanase, endoxylanase, pectin lyase, arabinofucosidase, endo-arabinase, endo-xylanase, pectate lyase, pectinmethylesterase, ...). Chemical stabilization for storage preferably is done with an inorganic acid. Microbiological stabilization to render the liquefied biomass storage-stable is preferably done by using 1 or more strains of lactic acid or ethanol producing bacteria. Final products after bacterial fermentation are mentioned a.o. butanol.

(Baret and Leclerc 1989) : Whole beet is ground, then treatment by mix of enzymes to hydrolyze polysaccharides. No additional water is used. Pretreatment (heat) can be used to make the structure of the polysaccharides less compact and thus more permeable to enzyme diffusion, at the same time providing a larger active surface. The consequences are quicker deviscosification of the product and greater conversion of insolubles. The enzyme dosage can then be reduced, while maintain at least the same process performances. Heat treatment inhibits hydrolysate browning and has a

pasteurization effect. A separation process is included: clarification – microfiltration – pressing – (optional) demineralization.

(Zheng et al. 2012) : Sugar beet pulp is a carbohydrate-rich residue of table sugar processing. It shows promise as a feedstock for fermentable sugar and biofuel production via enzymatic hydrolysis and microbial fermentation.

Note : See also cited references mentioned in section 4.1.1.

4.3 Design basis

The dry matter content of pressed pulp is $\pm$ 25-28% which is too high for good enzymatic hydrolysis because of mixing and enzyme dosing problems. Dilution with water to 10% dry matter gives better hydrolysis results.

After dilution of the pulp the pH needs to be corrected to 4.5 (in case of fresh pulp) and heating to 45 °C. Enzyme solutions can then be added while mixing the pulp slurry to ensure proper distribution of the enzymes. Incubation of the pulp, at 45 °C lasts 48 h. (To reach good hydrolysis in less time, e.g. 24 h, double amounts of enzymes are necessary).

4.4 Byproduct composition and valorization

When sugar beet pulp hydrolysate is directly fermented, the main 'byproduct' is the fermentation broth that contains those components that are not fermented by the organism. The exact composition of this "pulp vinasse" depends on the specificity of the fermentation organism and the yield of the fermentation. The main components that are present include:

- **Oligosaccharides:** After enzymatic hydrolysis an amount of oligosaccharides is present in the hydrolysate. Further research is necessary to find out whether these oligosaccharides can be fermented into isobutanol or have any potential other value.
- **Galacturonic acid:** Depending on the organism selected for the isobutanol production, galacturonic acid may be fermented or left behind after fermentation and valorized separately. When this component is not fermented, the overall fermentation yield in the model should be adjusted.
- **Proteins:** Beet pulp contains approximately 10% proteins (w/w). They are completely denatured since sugar beet pulp is heated to approximately 70 °C in the diffusion tower during the sugar extraction step. Part of the protein fraction might serve as a nutrient for fermentation.

The feed value of the pulp vinasse (per dry matter) equals the feed value of regular pressed beet pulp that is applied as feed. Protein content is enriched in the vinasse fraction, however also other components that have a negative feed value are enriched (e.g. silicates). Alternatively the pulp vinasse could be digested to produce biogas in the biomass digesters and upgraded to green gas quality that can be supplied to the Dutch grid.

Another option would be to first "refine" the sugar beet pulp hydrolysate and extract the protein fraction prior to fermentation. This option would require further knowledge regarding the composition of this (denatured) protein fraction, technologies to extract it from the hydrolysate and insight in potential applications (e.g. technical).

4.5 Equipment design

Hydrolysis of sugar beet pulp requires the following equipment:

- Equipment for washing the pulp to remove contaminations
- Large vessel with mixing equipment, options for heating/cooling and options to dose water, acid and enzyme solution
- Equipment for solid/liquid separation
- Equipment for water evaporation (under reduced pressure)

Scaling up the process could identify the need for additional equipment.

4.6 Identified technology gaps

The main identified technology gaps for this part of the value chain that have been identified:

- Reduction of enzyme costs. Enzyme costs are high and enzymatic hydrolysis is not straightforward due to the required synergistic activities of multiple enzymes needed to degrade pectin. Possible ways to reduce enzyme cost would be:
 - Further optimization of best enzyme cocktail(s) (price/performance)
 - Recycling of enzymes and increase stability. The latter is not particularly the goal of enzyme producing companies, but could reduce costs if enzymes can be used more frequently.
 - Improvement of fermentation yield. Investigate the possibility to ferment oligosaccharides. This way beet pulp polysaccharides do not have to be completely degraded.
 - Higher temperature by in-line hydrolysis during the campaign could speed up the enzymatic reactions, but requires thermostable enzymes.
- Optimizing process conditions for hydrolysis:
 - Evaluation of best dry matter content for hydrolysis. During the sugar beet campaign sugar beet pulp is pressed to a dry matter content of 23-25%. For enzymatic hydrolysis this step might not be necessary.
 - Control of microbiological activity, especially in case the hydrolysate needs storage.
 - Extraction and characterization of byproducts of byproducts streams, especially proteins.
 - Other methods to hydrolyze beet pulp polysaccharides.

5 Fermentation

5.1 Description of technologies (Gevo, Butamax, GBE)

5.1.1 Isobutanol fermentation

Some wild-type microorganisms can produce isobutanol, but only in very small amounts. For example, in beer fermentation the achieved concentration was as low as 16 mg/L (Garcia et al. 1994). Therefore, engineered organisms have to be used.

E. coli is the main organism that has been described for isobutanol production (Atsumi et al. 2008; Bastian et al. 2011; Smith and Liao 2011; Trinh et al. 2011). Many alternatives are being studied because of their robustness or ability to deal with lignocellulosic sugars, for example *S. cerevisiae* (Atsumi et al. 2008; Bastian et al. 2011; Smith and Liao 2011; Trinh et al. 2011; Brat et al. 2012), *C. glutamicum* (Smith et al. 2010; Blombach et al. 2011; Brat et al. 2012; Kondo et al. 2012), *B. subtilis* (Jia et al. 2012), *Clostridium cellulyticum* (Higashide et al. 2011) and *Ralstonia eutropha* (Fei et al. 2013). The metabolic pathway generally used is a modification of the pathway to L-valine. After conversion of carbohydrates to pyruvate, two molecules of pyruvate are coupled to acetolactate by acetolactate synthase, upon release of CO₂. Using NAD(P)H, a reduction occurs to 2,3-dihydroxyisovalerate, which is then dehydrated to 2-ketoisovalerate. A subsequent decarboxylation yields isobutyraldehyde, which is reduced to isobutanol using NAD(P)H. Thus, a maximum of 1 mol isobutanol per mol of glucose (0.41 g/g) or 2 mol isobutanol per mol of sucrose (0.43 g/g) can be achieved if competing reactions are absent. Another requirement is that the type of reduced cofactor (NADH or NADPH) formed during pyruvate formation corresponds to the type required for the subsequent reduction steps. By choosing suitable enzymes, the pathway's dependency on NADPH was removed and the maximum yield of 0.41 g/g was achieved, using anaerobic conditions (Bastian et al. 2011), as shown in Table 5-1.

This table also shows that the highest published isobutanol concentrations are about 22 g/L, achieved at yield on glucose of about 0.35 g/g and with a productivity of about 0.2 g/(L h) (Atsumi et al. 2008; Smith and Liao 2011). The toxicity of isobutanol to *E. coli* limits the production. Using in-situ stripping with gas at non-toxic isobutanol concentrations, a productivity of 0.69 g/(L h) was maintained during 72 h (Baez et al. 2011). This approach also facilitates product recovery, although little is known about the upscaling possibilities of this technique.

Since isobutanol is toxic to the cell, isobutanol production is limited by the toxicity of the final product itself. In this sense, improving the tolerance of the biocatalyst becomes a primary necessity to achieve a process with high product titers.

In any case, the fermentation will be anaerobic or microaerobic. Aerobic conditions are more expensive and not likely to lead to the desired maximum yields.

Table 5-1. Fermentative isobutanol production from sugars in the scientific literature.

Recombinant strain	Isobutanol yield (g/g)	Productivity (g/(L h))	Isobutanol titer (g/L)	Reference
<i>E. coli</i>	0.35	0.19	22	(Atsumi et al. 2008)
	0.32	0.21	21	(Smith and Liao 2011)
	0.29	0.69	11 ^a	(Baez et al. 2011)
	0.38	0.03	5	(Shi et al. 2013)
	0.41	0.56	13	(Bastian et al. 2011)
	0.25	0.45	11	(Shi et al. 2013)
<i>S. cerevisiae</i>	0.015	0.01	0.6	(Brat et al. 2012)
	0.004	0.02	0.6	(Avalos et al. 2013)
<i>C. glutamicum</i>	0.20	0.33	13	(Blombach et al. 2011)
	0.08	0.04	4.9	(Smith et al. 2010)
<i>B. subtilis</i>	0.22	0.06	3.2	(Li et al. 2012)
<i>C. cellulolyticum</i>	0.07 ^b	0.004	0.66	(Higashide et al. 2011)
<i>T. reesei</i> + <i>E. coli</i>	0.25 ^b	0.006	1.9	(Minty et al. 2013)

^a Maintained during 72 h by using in-situ air stripping

^b Isobutanol was formed from cellulose rather than from glucose

Advances in strain development are leading to commercialization by two companies, which are locked in an ongoing legal battle over the production of bio-based isobutanol: Gevo Inc. and ButamaxTM Advanced Biofuels, a joint venture created by BP and DuPont. As it is typical with patents, the patent claims appear to overlap, with both companies stating they have patents on these metabolic pathways in microorganisms that produce isobutanol. Nevertheless, both technologies are very similar. The microorganisms will efficiently convert fermentable sugars into isobutanol, and proper engineering minimizes the production of unwanted by-products to improve isobutanol yield and purity. A brief discussion of the patents tree is given in Section 5.2.

5.1.2 Isobutene fermentation

Fermentative production of isobutene has been patented by the company Global Bioenergies. The advantage of following this fermentation route is that not isobutanol, but instead gaseous isobutene is recovered from the fermenter together with CO₂.

Isobutene is a gas spontaneously volatilizing during fermentation. This characteristic presents two major advantages resulting in lower production costs when comparing to isobutanol production.

- No product-associated toxicity is observed since the product does not accumulate in the fermentation broth. This is critical as toxicity induced by the final product is one of the main constraints in the isobutanol fermentative production process. This difficulty is entirely avoided thanks to the gaseous fermentation approach.

- Downstream purification efforts are dramatically reduced. This confers a major advantage over the production of liquids such as isobutanol, which requires an energy-intensive additional step such as distillation.

These advantages might result in reduced costs and an improved environmental balance, in particular when compared to isobutanol production. Thus, direct isobutene fermentative production seems to be more favorable than fermentative production of isobutanol followed by chemical

dehydration. Van Leeuwen et al. (2012) review several pathways that are able, in theory, to produce 1 mol of isobutene per mol of glucose. The company Global Bioenergies is now concentrating its efforts on the industrialization process: increasing yields and scaling up the process. This way, large scale fermentative production of isobutene might become more competitive with the bio-isobutanol production process.

5.2 Patent situation

In section 5.1 an overview of the main technology providers for fermentative production of isobutanol (or isobutene) was discussed. In this section, their claims will be further analyzed.

5.2.1 Butamax™ Advanced Biofuels

Butamax™ Advanced Biofuels was formed in 2009 to develop biobutanol production, aiming to bring it to market as a cost equivalent to ethanol. The company, based in Wilmington, Delaware (US), is a joint venture created by BP and DuPont, which combines BP's expertise in fuels technology, development and infrastructure with DuPont's leading capabilities in biotechnology (Butamax™ 2013).

Their intellectual property covers a broad range of fermentation techniques to produce isobutanol from sugars, and also to recover the alcohol product from the broth. Regarding fermentation, the main patents or patent applications by the company are summarized in Table 5-2. A complete list of their intellectual property can be found in Appendix 2.

Table 5-2: Butamax patented literature reviewed

Granted US Patents	Title
7,851,188	Fermentative production of four carbon alcohols
7,910,342	Fermentative production of isobutanol using highly active ketol-acid reductoisomerase enzymes
8,372,612	Production of four carbon alcohols using improved strain
Patent applications	Title
20120035398	Process to remove product alcohol from a fermentation by vaporization under vacuum
20110294179	Method for producing butanol using two-phase extractive fermentation
20100120105	Carbon pathway optimized production hosts for the production of isobutanol

In their main patent, *Fermentative production of four carbon alcohols* (Donaldson et al. 2010), isobutanol is produced by fermentative growth of recombinant microbial production hosts, expressing isobutanol biosynthetic pathways. Several hosts are analysed and the results of the fermentations are given under certain conditions, as a proof of principle.

Taking as starting point the claims of this patent, they researched other possibilities. In their newer patent, *Production of four carbon alcohols using improved strain*, (Larossa et al. 2013) a regulatory system in butanol producing bacteria is identified and modified, obtaining a strain with increased tolerance to butanol with which higher titers are claimed (other applications on tolerant resistant microorganisms can be easily found in their database), while in *Fermentative production of isobutanol using highly active ketol-acid reductoisomerase enzymes* (Liao et al. 2011), a recombinant microorganism expressing a highly active ketol-acid reductoisomerase enzyme in addition to other enzymes required for conversion of glucose to isobutanol are cultured, claiming that higher titers were found, while in the patent application *Carbon pathway optimized production hosts for the production of isobutanol* (Anthony et al. 2010) they focus on the maximization of carbon flux in the cell through the Entner-Doudoroff pathway for glucose catabolism into pyruvate (minimizing EMP&PPP routes), aiming to optimize fluxes so that cofactor requirements are balanced.

But their patents not only focus on obtaining appropriate strains for the production of isobutanol, as in *Method for producing butanol using two phase extractive fermentation* (Grady et al. 2011), isobutanol is produced in biphasic fermentation medium with recombinant microorganisms in two

stages: growth (aerobic) & production (anaerobic or microaerobic), while the product is removed *in situ* by extraction into a water immiscible organic extractant during the fermentation, with the option to combine with gas stripping. This approach would increase the productivity, achieving titers of 22-37 g/L of fermentation medium. The further downstream for the recovery of the alcohol, extractant, etc. has also been reported (Grady et al. 2010).

Another reported technology for recovery of the alcohol and integration with fermentation is reported in their patent application *Process to remove product alcohol from a fermentation by vaporization under vacuum* (Grady et al. 2012), in which part of the fermentation broth is removed from the fermenter and sent to a vaporization vessel where it is partially vaporized by vacuum flash or multistage distillation. The vapor stream obtained is then contacted to an absorption liquid under vacuum, so that the vapor stream is absorbed into the liquid, and sent to a multi-stage distillation column.

There are many indications (interviews, discussions about patents issues, job openings, integration with existing ethanol manufacturing) that Butamax is focusing on yeast as microorganism.

5.2.2 Gevo

Gevo is a leading renewable chemicals and advanced biofuels company. Gevo's commercialization efforts are focused on isobutanol for which their Integrated Fermentation Technology® (GIFT®) was designed in order to enable the low cost retrofit of existing ethanol capacity for isobutanol production (Gevo 2013). A proprietary yeast strain is used. The current strain uses 1st generation feedstocks, while future strains and developed with Cargill and will convert 2nd generation feedstocks.

Their intellectual property covers all the stages of the production of isobutanol from corn and lignocellulosic waste, and recovery. As well, they are applying extensive research efforts on the production of chemicals from their isobutanol, such as the targeted in this design project as p-xylene (Peters et al. 2011; Peters et al. 2012a; Peters et al. 2012b) and jet fuel components (Peters 2011). An overview of the patents and patent applications analyzed for this report is shown in Table 5-3.

Table 5-3: Reviewed GEVO intellectual property

Granted US Patent	Title
8,158,404	Reduced by-product accumulation for improved production of isobutanol
8,101,808	Recovery of higher alcohols from dilute aqueous solutions
8,097,440	Engineered microorganisms capable of producing target compounds under anaerobic conditions
8,017,375	Yeast organism producing isobutanol at a high yield
Patent applications	Title
20110172475	Integrated methods of preparing renewable chemicals
20100062505	Butanol production by metabolically engineered yeast
20090215137	Methods for the economical production of biofuel precursor that is also a biofuel from biomass

Gevo is active in further downstream of the isobutanol produced by fermentation, and their patented literature cover also applications such as p-xylene production and jet fuel production, even though at a much earlier stage of development.

5.2.3 Global Bioenergies

Global Bioenergies is a French company founded in October 2008, which is developing a unique process to produce isobutene biologically from renewable resources. In 2009, a proof of concept was obtained for the process leading to the bio-production of isobutene. A lab-scale prototype was built in 2010 (GlobalBioenergies 2012). Currently they are working with LanzaTech in an attempt to combine their technologies (BiofuelsDigest 2011). The company is now concentrating efforts on the industrialization by increasing yields and scaling up the process, but no scale-up facility has been reported yet.

With respect to the process used, it would involve the direct fermentation of sugars and/or CO₂ to isobutene. This would be a promising approach, as it would overcome the two major drawbacks of its production via isobutanol: the need for in situ recovery technologies (isobutene will flash out of the fermentation as it is produced in gas phase), and no need for further purification.

The state of this technology is still too incipient to be considered for the implementation at full-scale in such a short timeframe as described for the IBPR project, and thus it will not be further described in this report. However, if proven feasible at large scale in the future, this direct conversion will only yield in advantages respect the route via isobutanol, and the conversion of the biorefinery to this new technology should be studied.

5.3 Selection of microorganism

For selection of the most suitable strain, Table 5-4 shows a number of criteria than should be taken into account. Tolerance to inhibitors from lignocellulosic hydrolysate (acetate / formate / furanics / phenolics) was not taken into account yet, because the focus here is on sugar beet and insufficient data were gathered on the levels of these compounds and on the organisms.

For different scenario's, different choices might be made:

A. Short term piloting to convert sugar to isobutanol

Short term piloting will have to be done with effective, available strains. The options are the *E. coli* strains for which literature data are available (Table 5-1) and the yeast strains developed according to the patents of Gevo and Butamax. Unfortunately, little is known about the status of semi-commercial yeast fermentations, but probably the performance is of the same order of magnitude as of the best *E. coli* strains. In one recovery patent (Grady et al. 2010), Butamax claims that for isobutanol production with *S. cerevisiae*, the effective titer, the effective rate, and the effective yield, all corrected for the isobutanol lost due to stripping, were 5 g/L, 0.06 g/(L h), and 0.16 g/g, respectively. In another recovery patent (Grady et al. 2012), Butamax performs process calculations with a fermentation that produces 25 g/L 1-butanol or 2-butanol or isobutanol.

If sucrose is to be used for short-term piloting, yeast is more suitable than *E. coli*.

B. Longer term piloting to convert pulp hydrolysate to isobutanol

Organisms that can deal with beet pulp can be engineered for isobutanol production, or organisms that are already good at isobutanol production can be adapted for dealing with beet pulp. The latter will be more difficult, involving more genetic manipulations. Presently, *E. coli* looks reasonable, but it cannot cope with the pH 3-4 reported for the hydrolysate. Changing pH to neutral would consume base and lead to waste salt production, which both would be cost factors that should be prevented.

There are some publications on the use of sugar beet pulp as feedstock for ethanol production (Edwards and Doran-Peterson 2013). Sugar beet pulp is pretreated and hydrolyzed using enzymes to solubilize the sugars and uronic acids. In hydrolysates from sugar beet pulp, glucose, arabinose, uronic acids and galactose were the main components, with concentrations of 9.9, 7.6, 6.5 and 1.7 g/L, respectively (Kuhnel et al. 2011). Uronic acids, mainly galacturonic acid, from pectin are an important component in sugar beet pulp. In order to efficiently utilize the sugars in this biomass to isobutanol, it would be desirable that the microorganism of choice would be able to utilize both the sugars and the galacturonic acid in the sugar beet pulp.

The most studied yeasts species for ethanol production are not able to metabolize galacturonic acid yet (Huisjes et al. 2012). Some recombinant *E. coli* strains are able to utilize uronic acids for ethanol production, although the productivities are relatively low (Edwards and Doran-Peterson 2013). An *E. coli* strain has been modified for the utilization of alginate (polymer of guluronic and mannuronic acids) for production of ethanol via a consolidated bioprocessing approach (Wargacki et al. 2012). This opens the possibilities to use such an approach for isobutanol production from sugar beet pulp, to reduce costs in the enzyme use.

Several species of anaerobic bacteria, including *Thermoanaerobacter*, *Butyvirbio*, *Bacillus* and *Clostridium* have been shown to be able to utilize sugars and uronic acids in biomass resources (Potter and MacCoy 1952; Potter and MacCoy 1955; Hespell 1992). Provided that strains would be genetically accessible, an approach would be to implement the isobutanol pathway in such a strain.

Also, it can be studied how the trade-off may be at higher fermentation temperature between higher isobutanol volatility, which facilitates stripping and decreases DSP costs, versus probably lower isobutanol tolerance and productivity (like for ethanol at high temperature), and maybe also lower pH tolerance.

C. Longer term piloting to convert pulp hydrolysate to isobutene

Here isobutene's volatility is no issue, so high temperature fermentation is no issue here. Also, isobutanol tolerance is no issue. Thus, the organism that can best deal with pulp hydrolysate would have to be chosen and engineered for isobutene production.

Table 5-4. Comparison of strains for isobutanol (IB) fermentation. Empty fields indicate data not yet found.

Recombinant strain	Baker's yeast	<i>E. coli</i>	<i>Clostridium cellulyticum</i>	<i>Corynebacterium glutamicum</i>	<i>Geobacillus thermo-glucosidasius</i>
High IB yield	++?	++		+	
High IB productivity	+?	+?	-	+	
High IB tolerance	+/-	+/-		+/-	
High temperature tolerance	-	-	-	-	+
Fermentation at pH 3-4	+	-	-	-	-
Stripping tolerance	+	+	+		
Tolerance to lignocellulosic inhibitors	+/-				
Genetic accessibility	+	++	+/-	+	+/-
Utilization of sugars					
Sucrose	+	+/-	+		
Pectin	-	-	-	-	+
Cellulose	-	-	+	-	-
Glucose	+	+	+	+	+
Ara/Xyl	+/-	+	+	+	+
GalA	-	+	+	-	
Rha/Gal/Man/Fuc					

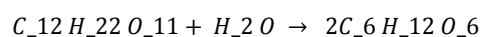
5.4 Design basis

No detailed design of the equipment was performed, but the assumed stoichiometry is discussed below.

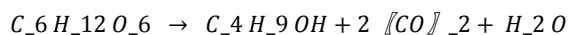
5.4.1 Fermentation

The following stoichiometries have been used in the fermentation:

Sucrose hydrolysis (100 % conversion)

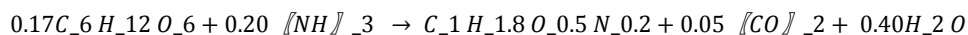


Product formation



Since 90 % of the theoretical yield has been claimed by Gevo and BUTAMAX in the production of isobutanol, it is assumed that the remaining carbon source is used for cell growth following the equations below:

Cell growth



Consequently, the assumed isobutanol yields are 0.39 g/g sucrose and 0.37 g/g beet pulp.

5.4.2 Isobutanol recovery

It is assumed that isobutanol is quantitatively recovered by distillation.

Isobutanol and water are very dissimilar with very large activity coefficients. This produces a heterogeneous azeotrope, as shown in the Txy diagram given in Figure 5-1. The pressure in this figure is 0.066 bar (50 mm Hg) at which the boiling points of pure isobutanol and water are 48.9 and 37.9 °C, respectively. At this pressure the azeotropic composition is 77 mol% water with a temperature of 33.5 °C. The temperature of the azeotrope is lower than the boiling points of both components. The separation of a binary heterogeneous azeotrope is often much easier than the separation of a binary homogeneous azeotrope because the liquid–liquid phase equilibrium in a decanter can be used to facilitate the separation. The organic phase obtained in the decanting is thus used for further isobutanol dehydration while the aqueous phase is sent to a beer column.

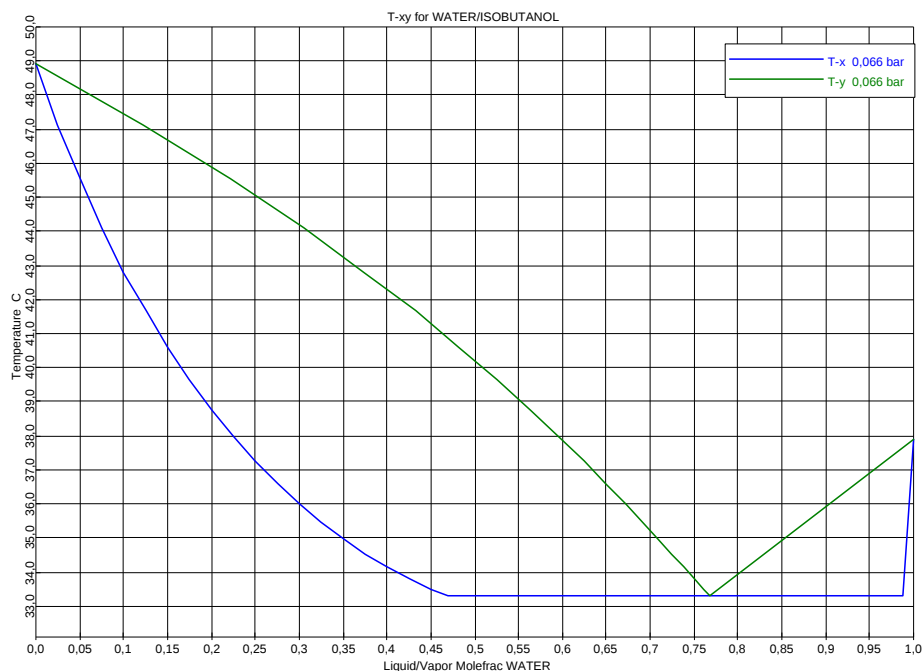


Figure 5-1. Aspen Txy diagram for water/isobutanol at 0.066 bar showing the heterogeneous azeotrope.

5.5 Identified technology gaps

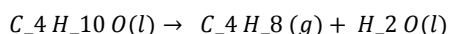
- Knowledge on best producing isobutanol strains is limited. Consultation with the Gevo, Butamax and/or Global Bioenergies is needed to elucidate this point.
- The fermentability of the SBP feedstock by the isobutanol producing-strain needs to be determined.
- Yields and productivity data are not always available.

- Baker's yeast, which is suitable for fermenting glucose to isobutanol, presently cannot ferment galactonic acid, one of the main components of sugar beet.
- The separation of isobutanol from the medium is still an issue that needs improved methods compared to existing technologies. An in-situ product removal approach is expected to be necessary, although it will depend on the tolerance of the host towards the product.

6 Isobutanol dehydration reaction and isobutene recovery

6.1 Description of technologies

Isobutylene (or isobutene) can be obtained by dehydration of isobutanol. Dehydration refers to a chemical reaction that converts the alcohol – isobutanol – into its corresponding alkene – isobutylene.



Isobutanol is essentially completely converted at temperatures from 100 to 300 °C and pressures ranging from 1 to 52 atm (Latshaw 1994). The dehydration reaction of alcohols to alkenes over solid catalysts has been studied and extensively reported in the literature. Isobutanol is most typically dehydrated over mildly acidic gamma-alumina catalysts. However, isobutanol dehydration has been demonstrated over numerous catalysts through the years, including various acid treated and untreated alumina like gamma-alumina, silica catalysts, clays including zeolites, sulfonic acid resins, strong acids, Lewis acids and many different types of metal salts including metal oxides and metal chlorides. Knözinger and co-workers published a series of papers differentiating the dehydration rates of the various butanols and described the reaction mechanism on alumina catalysts with evidence from isotope substitution and surface IR measurements (Knözinger et al. 1968; Knözinger et al. 1972).

A key parameter in the dehydration of isobutanol is the selectivity to isobutylene. Production of diisobutyl ether and linear butenes represents a yield loss on the production of isobutylene. The competing reactions are shown in Figure 6-1. The selectivity for isobutylene is roughly 95 %.

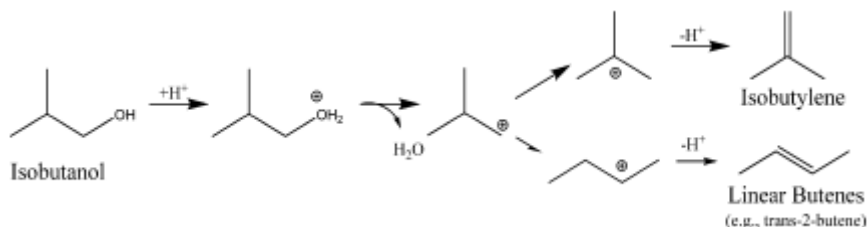


Figure 6-1. Mechanism for dehydration of isobutanol to produce mixed butenes (Taylor et al. 2010)

For the products shown in Figure 1-3, it is desirable to conduct the dehydration such that isobutylene selectivity is maximized. There are other applications where it might be desirable to generate higher concentrations of linear butenes for instance. The reaction can be carried out in both gas and liquid phases and leads to a mixture of 1-butene, cis-2-butene, trans-2-butene, and isobutene. The ratio is determined by the thermodynamics, reaction conditions, and catalysts used, but there is no known method for cleanly dehydrating isobutanol to >99 % isobutylene.

Catalyst

The dehydration mechanism is undoubtedly a function of both the structure of the catalyst as well as the structure of the alcohol. Some of the more acidic catalysts, such as ZSM-5 zeolites, Y-type zeolites, and Amberlyst acidic resins, not only catalyze the dehydration reaction but also catalyze dimerization (or further oligomerization) of the butenes. For the purpose of the design of the isobutanol biorefinery, these catalysts are not considered because the goal is to focus on the dehydration step to produce isobutylene or mixed butenes as a platform molecule that can be used for further production of p-xylene, jet fuel and GTBE. Additionally, it was found that the conditions required for dehydration are not optimal for dimerization, resulting in isomers with inferior fuel/chemical properties to the ones obtained when the two reactions are carried out in series (Taylor et al. 2010).

According to the literature, alumina appears to have been the most widely used dehydration catalyst and therefore, the most widely studied. Isobutanol can be dehydrated over commercial gamma-alumina catalysts at high conversion and with good selectivity to isobutylene. According to Taylor et al. (2010) the catalyst BASF AL3996 shows excellent selectivity >94 % and nearly 100 % conversion at temperatures above 325 °C, while avoiding dimerization and oligomerization.

Configuration

Isobutanol recovered from a fermentation process will most likely be dried to 1% water (as is typical for fuel grade ethanol) using a conventional beer still, decanter (for the heterogeneous azeotrope), and rectifier column in a modified ethanol facility. It may be economically beneficial to avoid some of the drying steps and feed wet isobutanol directly to a dehydration reactor.

During the dehydration of isobutanol, one mole of alcohol reacts to form one mole of olefin and one mole of water. The water generated by the dehydration reaction exits the reactor with unreacted alcohol and alkene product and is separated by distillation or phase separation. For example, dilute aqueous solutions of ethanol (up to 98 wt% of water) can be dehydrated over a zeolite catalyst with all water removed from the ethylene product stream after the dehydration step occurs (U.S. Pat. 4,698,452 and 4,873,392).

Although isobutanol dehydration reactions over solid catalysts have been studied extensively, little work has focused on issues that are specific to fermented isobutanol. For example, fermented isobutanol is initially dilute in water and can be dried to whatever degree is desired.

The dehydration reaction can be efficiently designed to almost complete conversion, minimizing the downstream complexities of the separation of the isobutylene and water, and the effluence of the water. The isobutanol-water mixture forms a heterogeneous azeotrope so that distillation can be used in combination with decantation to isolate and purify the isobutanol. In this method, the isobutanol containing fermentation broth is distilled to near the azeotropic composition in a flash column. Then, the azeotropic mixture is condensed, and the isobutanol is separated by decantation. The decanted aqueous phase is returned to the first distillation column as reflux. The isobutanol-rich decanted organic phase with 15 wt% of water may be further purified by distillation. However, it has been shown by Taylor et al. (2010) that dehydrating the isobutanol in the presence of water in a gas-phase fixed bed is also effective.

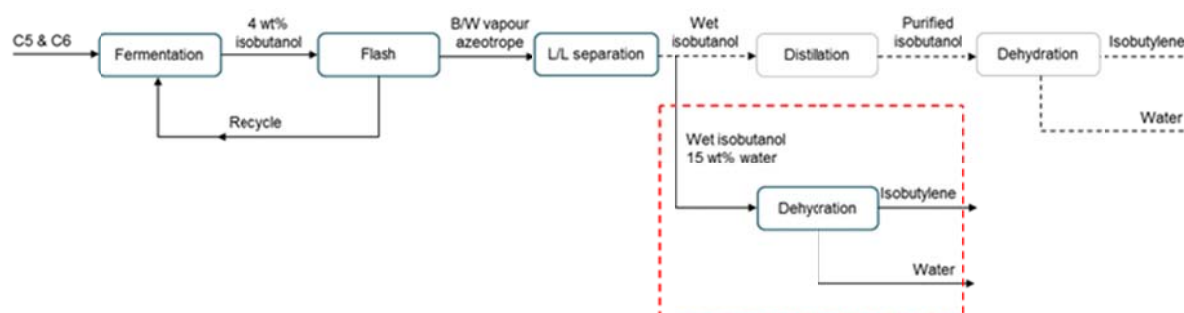


Figure 6-2. Process options regarding the combination of fermentation, product separation /purification and dehydrations steps.

Taylor et al. (2012a) showed that at 285 °C, the water content of the isobutanol negatively impacts the conversion in the dehydration reactor and causes a slight increase in isobutylene selectivity. However, at 325 °C, near-complete conversion is observed for all water contents at 1 bar pressure as well as 4 bar pressure and no significant change in selectivity is observed (Table 6-1). Therefore, if the reactor is run at typical conditions where conversion is high, it is feasible that wet isobutanol can be used directly without the need for a distillation system.

Table 6-1. Impact of isobutanol water content on dehydration reaction (Taylor et al. 2010).

Feed water content	Temperature (°C)	Conversion (%)	Isobutene selectivity (%)
dry	325	99.8	95.2
1 wt%	325	99.8	95.4

15 wt%	325	99.3	95.0
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Process conditions

Although lower pressure is favoured for dehydration, there may be practical benefits to carrying out the reaction at moderate pressures. For example, dimerization of isobutylene is typically carried out at high pressures of 50-70 atm. If the dehydration is carried out at atmospheric pressure, the gas-phase isobutylene is easily separated from the water and then must be compressed in order to condense it prior to pumping up to high pressures. On the other hand, at modest pressures of >3 atm, isobutylene and water can be separated in a decanter as two separate liquid phases and the isobutylene can be pumped directly up to high pressures. Since it is desirable to avoid the use of a compressor in these applications, it is important to understand how pressure affects the dehydration reaction. From experimental work of Taylor and co-workers, it was concluded that it is feasible to run the dehydration with moderate pressure if process energy consumption benefits can be achieved (conversion of 98.8 % and isobutene selectivity of 95 % were obtained at 4 atm; versus 99.0 % and 94.2 % obtained at atmospheric pressure, respectively).

Impurities

Some impurities from the fermentation process may be different from by-products present in petroleum-derived isobutanol; the impurities present in the dehydration reactor arise from metabolic side reactions in the biocatalyst or small levels of contamination by other microorganisms. Table 6-2 shows the results obtained in the dehydration reactor when impurities are added. Ethanol, acetone, and isobutyraldehyde were chosen as model impurities analogous to the fusel alcohol, acetone and acetaldehyde impurities typically found in ethanol fermentations (Knözinger and Scheglil 1970). It is clear from the existing results that none of the impurities have a significant effect on the isobutanol dehydration reaction over short run times.

Table 6-2. Impact of impurities spiked into isobutanol dehydration feed (Taylor et al. 2010).

Feed	Isobutanol conversion (%)	Isobutene selectivity (%)	Impurity conv. (%)
Isobutanol + 1% H ₂ O	99.8	95.7	N.A.
Base + 1% isopentanol	99.7	95.8	99.9
Base + 1% ethanol	99.4	95.5	66.0
Base + 1% acetone	99.5	96.1	99.6
Base + 1% isobutyraldehyde	99.8	96.3	?

Conclusions

Process options and selection regarding isobutanol dehydration are summarized in Table 6-3. The dehydration conversion and selectivity to isobutylene versus temperature is given in Appendix 6.1.

Table 6-3. Process choices in the dehydration of isobutanol.

Parameter	
Water content	- Up to 15 wt% without any changes in conversion and selectivity; - Use the stream after decanting (~15 wt% water)
Catalyst	- Gamma-alumina catalysts; - It is of interest to alter the catalyst selectivity to decrease the production of linear butenes and diisobutyl ether; - Dehydration and oligomerization carried out in series.
Temperature	Optimal temperature 325 °C.
Pressure	- Atmospheric pressure; - Isobutylene is easily separated from water.

6.2 Freedom to operate

6.2.1 Commercial bio-isobutanol to isobutylene (ITI) companies

Production of isobutylene from isobutanol is still being developed. In the past, the dehydration of isobutanol into butenes was not commercially practiced because isobutanol from petroleum was not cost-competitive with other petrochemical processes for generation of butenes. A joint venture of Gevo and LANXESS is currently developing technology for producing isobutylene. Gevo (www.gevo.com) is developing a fermentation process to produce the organic compound isobutanol from the fermentable sugars in biomass, starting with corn. LANXESS (www.lanxess.com) is developing a dehydration process to convert isobutanol into isobutene. LANXESS' dehydration process has not only proven to be successful in the laboratory but also in a small-scale reactor in Leverkusen, Germany, over a period of several months. Tests have shown that the process can deliver biobased butyl rubber that meets the rigorous specifications of the tire industry, which represents roughly 25 percent of LANXESS' sales.

Gevo, Inc. is a renewable chemicals and advanced biofuels company headquartered in unincorporated Douglas County, Colorado in the Denver-Aurora metropolitan area. The company develops bio-based alternatives to petroleum-based products using a combination of biotechnology and classical chemistry. Gevo converts renewable raw materials into isobutanol and renewable hydrocarbons that Gevo believes can be directly integrated on a "drop in" basis into existing fuel and chemical products. Gevo's investors include Burrill & Company, Khosla Ventures, Lanxess, Total, and Virgin Green Fund, among others.

LANXESS is a leading specialty chemicals company with sales of EUR 5.06 billion in 2009 and currently around 14,700 employees in 24 countries. The company is represented at 45 production sites worldwide. The core business of LANXESS is the development, manufacturing and marketing of plastics, rubber, intermediates and specialty chemicals.

In Colorado, Gevo and South Hampton Resources, Inc., a subsidiary of Arabian American Development, have built a demonstration plant to take the bio-isobutanol and processing it further to isoparaaffinic kerosine (IPK) biojet. The demonstration plant was built at a hydrocarbon plant in Silsbee, Texas.

Producing IPK biojet from bio-isobutanol involves three sequential steps:

1. Dehydration of the renewable isobutanol to isobutylene;
2. Oligomerization of the isobutylene to mostly trimers/tetramers to produce C12 and C16 molecules;
3. Hydrogenation of olefins to IPK biojet.

These processes present opportunities for retrofits of existing, underutilized refining/petrochemical assets, in some cases. Commercialization and integration into an existing process plant should be straightforward. This biojet process has been demonstrated in a small (10,000-gallon-per-month-capacity) unit for several months. The alcohol-to-jet (ATJ) product has been sold to the US Air Force as part of the Alternative Fuels Certification Office (AFCO) process.

Dehydration of isobutanol to isobutylene and water is the first step in the process. The reaction is endothermic, with a relatively low operating pressure (< 15 bars) and temperatures of around 325 °C. The operating requirements are similar to semi-regenerative catalytic reforming. Therefore, idled semi-regenerative reformers are possibilities for retrofits to develop the dehydration step. The catalyst for the dehydration has been fully commercialized in similar applications. The dehydration reaction can be efficiently designed to almost complete conversion, minimizing the downstream complexities of the separation of the butylene and water, and the effluence of the water.

The engineering of the downstream processing of isobutanol to paraffinic kerosene (jet fuel) for jet engine testing, airline suitability flights and advancing commercial deployment has been taken care of by Wood Group Mustang (www.mustangeng.com). Mustang is a global project management, engineering, procurement, and construction operations company serving the upstream oil and gas, refining and chemicals, pipeline, automation and control, and industrial markets. Mustang, a Wood

Group company, has offices in the United States, United Kingdom, India, Malaysia, North Africa and the Middle East.

6.2.2 Commercial bio-ethanol to ethylene (ETE) companies

Off-the-shelf technology for the dehydration of bio-isobutanol to isobutylene is not available. Dehydration of bio-ethanol to ethylene, however, is already done on a commercial scale. Key players are Braskem, DOW/Mitsui and Songgyuan Ji'an Biochemical.

Brazilian petrochemical company Braskem (www.braskem.com) inaugurated a new ethylene plant in Triunfo Petrochemical Complex in Triunfo municipality, in Rio Grande do Sul state of Brazil in September 2010. The plant uses ethanol produced from sugarcane as the feedstock. It was the first large-scale ethylene project to use 100 % renewable raw materials. With the capacity to produce 200,000 t/y, it was also the first commercial-scale green ethylene plant in the world. The produced ethylene is converted into equivalent polyethylene resin or green plastic.

Braskem has invested approximately 500 million R\$ (278 million \$) in the plant. It was a collaborative project between Braskem, Triunfo City Hall and the National Service of Industrial Apprenticeship (SENAI) in Rio Grande do Sul. The green ethylene plant is built adjacent to the Basic Petrochemical Unit Plant 2 at the petrochemical complex. The new plant uses the existing polymerisation plants in Triunfo - PE-5 at the complex.

The equipment installed in the bioethylene plant was entirely developed by Braskem. The proprietary technology for converting ethanol into ethylene was developed at the Braskem Technology and Innovation Center, São Paulo in 2007. The ethylene is converted into butylene and then polymerized to produce propylene resins through metathesis process.

Also in Brazil, Dow Chemical (www.dow.com) has teamed with Mitsui (www.mitsui.com) in a joint venture that will produce ethanol and bioplastics from sugarcane, which the companies are saying will be the world's largest biopolymers investment. The project will produce DOWLEXT polyethylene resins, the main building block in polyethylene, from ethanol. The deal includes Mitsui investing 200 million \$, to become a 50 % equity interest partner in Dow's Usina Santa Vitoria sugarcane project in Minas Gerais. The plant is expected to come online by mid-2013, and have a 63 million gallon capacity.

ETE licensors

Dehydration of ethanol can be carried out in the gas phase in either a fixed-bed or fluidized-bed reactor. The fixed-bed route is licensed by Chematur Engineering AB/Halcon Scientific Design and the fluidized bed technology is licensed by ABB Lummus (Yan 2012).

Chematur has developed a polymer grade ethylene production process using the fixed bed system. It uses a new catalyst called Syndol which was developed by Halcon Scientific Design for their production process. Halcon claims that Syndol can stay in continuous operation for eight months without the need of regeneration and is able to handle adiabatic operation (Higashide et al. 2011). This enables the use of a fixed bed reactor and adiabatic operation between temperatures of 315 °C to 425 °C. The reported ethylene yields and ethanol conversion are 99 % and 96.8 %, respectively (Chematur 2012).

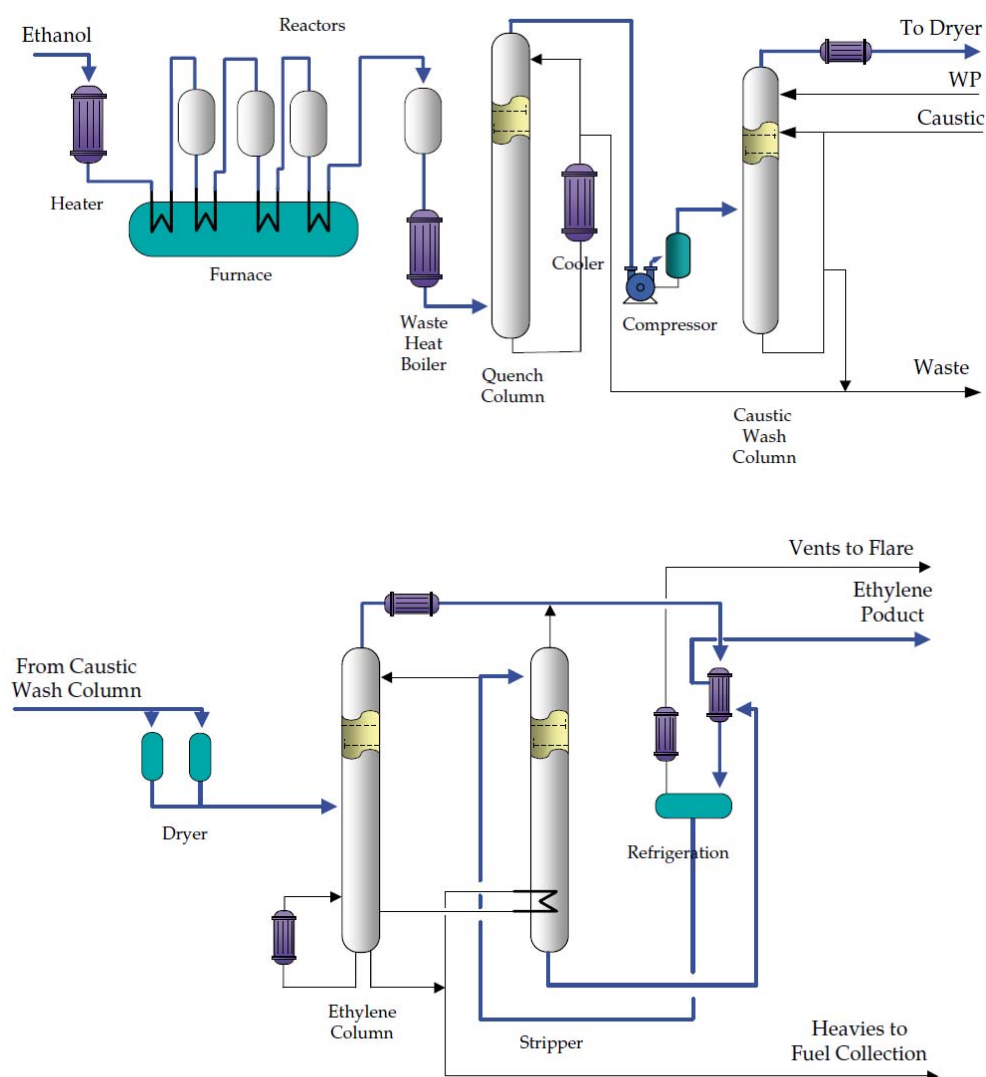


Figure 6-3. Flowsheet of a typical polymer grade application by Chematur.

Syndol is a very stable high yield ethanol dehydration catalyst. A start-of-run, selectivity to ethylene is typically 97 % at 99 % ethanol conversion. Because of the expected long life, no regeneration facilities are included in the battery limits plant design.

ABB Lummus has developed a fluidized bed system to improve the ethylene yield by controlling the temperature and avoiding hot and cold spots. The ethylene yield had increased to 99.5 % with an ethylene selectivity of 99.6 % and an ethanol conversion of 99.6 % (Yan 2012). The applied catalyst can be any dehydration catalyst such as alumina, silica-alumina, activated clay and a zeolite. In this technology, silica-alumina is preferred due to its availability and it is periodically regenerated to remove the carbon and tars formed during the reaction. ABB Lummus has a dedicated pilot plant development program for ethanol dehydration available.

However, one of the authors (JvH) has contacted Dr. Gaffney, then VP R&D at Lummus technology in 2008 about this technology. At that time, she stated that it hadn't been licensed for decades!

Halcon technologies ceased to exist in the 80's and now Scientific Design. The Syndol catalyst is marketed by SD.

In a recent Dow Chemical presentation (Luo et al. 2013), their Brazilian 350 kt/a ethanol to ethylene conversion was discussed. An adiabatic reactor is used, and a really high yield is required to make it worthwhile. With respect to feed impurities on catalyst performance and major factors affecting

catalyst deactivation: The feed contained Fusel oil, 1000-3000 ppm; ethyl acetate 50-200 ppm; acetal 100-300 ppm; acetaldehyde, 0-100 ppm. Aldehyde inactivated the catalyst. There was evidence for aldol condensation and Guerbet reaction over the Al_2O_3 catalyst. The lifetime correlated with NH_3 -TPD.

6.3 Design basis

Process is modeled after an Axens 369 kt/a (diluted) C4-cut input TAME plant, 2010 US Gulf coast investment costs (1 \$ = 1 €). Utilities were assumed to be the same for the dehydration. The numbers can be found in (HydrocarbonProcessing 2010).

Investment is listed as 13 M\$, which is assumed to be erected ISBL costs. These numbers need to be verified with the vendor.

Assumption for the dehydration step were:

- Isobutanol input 468 kt/a
- Molar yield 95 %
- Weight yield 72 %
- Isobutene produced 337 kt/a
- By-products None specified, no use as fuel for them

6.4 Identified technology gaps

There are only a few plants that practice alcohol dehydration, and then only ethanol. Although reports claim that this reaction should be possible, this will have to be experimentally verified with authentic samples of isobutanol with the envisioned commercial catalysts. For instance, some dehydration experiments are performed in the absence of water, whereas other groups report excess steam. Literature indicates that this reaction is technically feasible.

7 Oligomerization

7.1 Description of technologies

The current state of the art technology to oligomerize isobutene is optimized for the production of isooctene/ane which is used as high value high octane gasoline additive. In order to produce jet-fuel, the formed isooctene needs to react further to produce a C12/C16 stream which can then be hydrogenated to meet the jet fuel specifications. The C12 product in the isooctane process is considered a by-product and its formation is suppressed by the addition of alcoholic modifiers. To obtain jet fuel, the process now needs to be converted to produce the C12 stream which used to be an unwanted by-product. Thus far, we have only found a few claims that this is possible.

The oligomerization step is assumed to yield 1/3 C8 and 2/3 C12/C16, with recycle. Or more accurate, it is assumed to yield the desired split. This is thus a common unit for the envisioned complex. For the CAPEX, the unit was modeled after the Axens Dimersol-X process. The listed ISBL unit is 50 kt/a and investment is 8 M\$, 2010 basis. Utilities were estimated from the Refining Hydrocarbon Technologies for the same process. The hydrogenation step was also modeled using these data (chapter 9). Investment was assumed to be erected cost ISBL, which was listed as 5.5 M\$, 1Q US gulf coast basis. Utilities were converted to a per ton basis. Hydrogen usage is not listed, but was assumed to be near stoichiometric. Contact times and equipment sizing were thus assumed to be the same.

In an isooctene or MTBE unit, modifiers are added to maximize the C8 cut. In general, oligomerization is achieved using a polymeric acid catalyst, most commonly Amberlyst™-15. The function of the modifier is to adjust the acid strength of the catalyst, so that only the desired compound is obtained. Changing the amount or type of modifier yields higher oligomerization products. This has been experimentally demonstrated, but not above lab scale.

General references in this area are: Marchionna et al. (2001), Di Girolamo et al. (1999), Yoon et al. (2006; 2007), O'Connor et al. (1985), Alcántara et al. (2000), Ouni et al. (2006), and Kamath et al. (2006).

7.2 Freedom to operate (patent tree)

The steps and conditions have been known for a long time, and industrial published reports date back to 1995 and earlier. We do not foresee any major patent issues for this step.

7.3 Design basis

Assumptions for the oligomerization step:

- Isobutene input 303 kt/a
- Molar yield 95%
- Isooctene produced 91 kt/a
- C12+ produced 182 kt/a
- By-products None specified, no use as fuel for them

Assumption for the product distribution, weight basis, from dehydration unit

- Isobutene to GTBE 10 %
- Isobutene to jet-fuel 60%
- Isobutene to p-Xylene 30%
- By-products None specified, no use as fuel for them

Equipment design: see above.

7.4 Identified technology gaps

As mentioned above, the reaction is tunable to yield the desired product mixture. Furthermore, the envisioned products are produced, albeit at small scale, commercially by Ineos. The main experimental challenges will be to find the correct optimal process conditions, to determine how flexible the process can be, what the catalyst life is, which modifier (if any) to use, and how to manage the heat of reaction. Furthermore, if high purity isobutene is necessary for the production of GTE, then producing for instance MTBE and cracking may be advantageous for the oligomerization step.

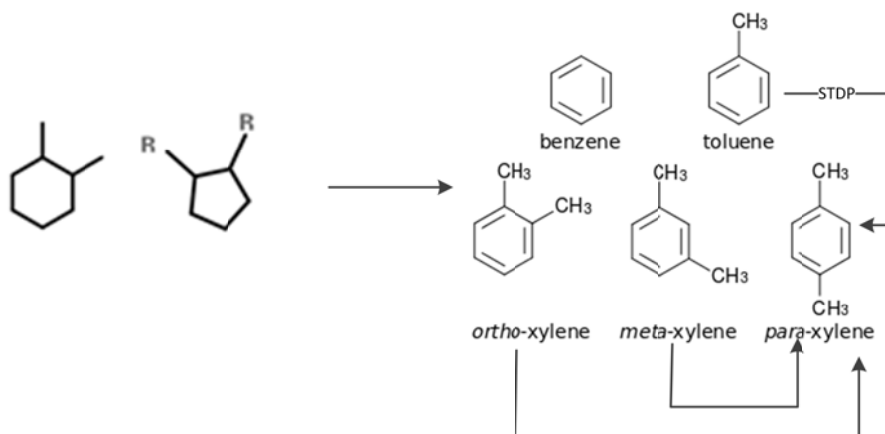
8 p-Xylene formation

8.1 Description of reformer technologies

Reformer case

Starting from naphtha (C5-C10), the reaction is carried on a catalyst of ClAl_2O_3 on Pd or Pt. PIONA numbers must show high quality, high proportion of paraffin and naphtha.

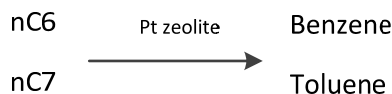
Naphtenes are converted into BTX, which is separated and selectively converted finally to p-xylene through different processes.



AROMAX® process

The Aromax® Process selectively converts light paraffins and naphthenes to hydrogen and aromatic products utilizing conventional fixed-bed reforming equipment.

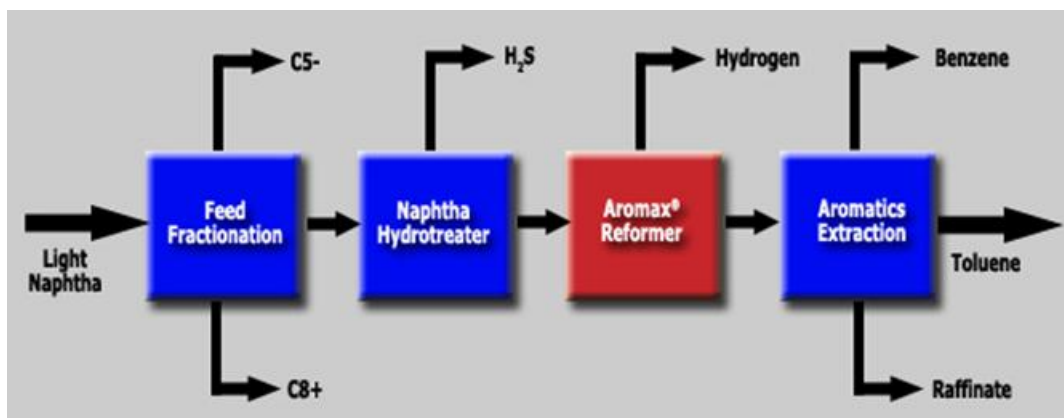
As an overview:



The process has some disadvantages, such as sensitivity to impurities, and restricted application to linear paraffins. Some other facts about the Aromax® Process (ChevronPhilips 2013) are described below.

First reforming process based on a zeolitic catalyst

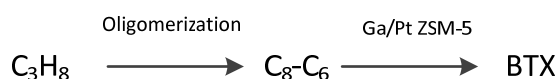
- Best suited for converting C6-C8 hydrocarbons
- Exceptional selectivity for converting C6 and C7 paraffins & naphthenes to benzene, toluene and hydrogen
- Process includes a high efficiency sulfur control system to eliminate catalyst poisoning by sulfur
- Toluene extraction may or may not be required
- Proprietary catalyst technology



CYCLAR process

The UOP Cyclar process converts liquefied petroleum gas (LPG) directly into a liquid, aromatic product in a single processing step. Developed jointly by BP and UOP, the Cyclar process provides a route to upgrade low value propane and butane, recovered from gas fields or petroleum refining operations, into a high value, liquid aromatic concentrate, ideal as feedstock to an aromatics complex (UOP 2013).

An overview of the reaction would be:



It might be suitable to be modified to work on isobutene.

SABIC

Modified technology, related to Cyclar process. Catalyst: Ge ZSM-5. The C8 molecule is selectively and it is converted to xylene. Not applicable for branched paraffins.

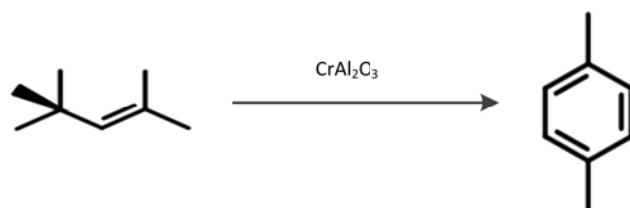
Patents from that might be related:

JAN HAL JAAP W [NL]; STEVENSON SCOTT A [US]; ALLMAN JIM [US]; SULLIVAN DAVID L [US]; CONANT TRAVIS R; US2011263917 (A1) - Process for Producing Propylene and Aromatics from Butenes by Metathesis and Aromatization

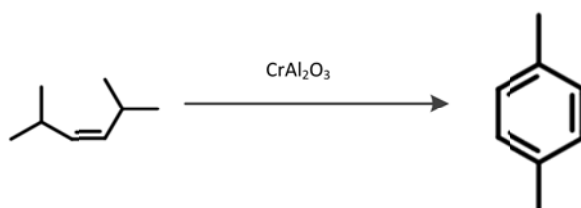
KHANMAMEDOVA ALLA K [US]; MITCHELL SCOTT F [US]; STEVENSON SCOTT A [US]; JUTTU GOPALAKRISHNAN G [US] , Catalyst for Conversion of Hydrocarbons, Process of Making and Process of Using Thereof - Bimetallic Deposition

GEVO

Gevo claims the following direct route (Peters et al. 2012b):



How to achieve this transformation, or its feasibility, is to be discussed. A more reasonable approach would be using the same process but starting from the molecule below, that might be obtained through Axens process (i.e. Axens Dimersol-X process, which transforms butenes to octenes that are ultimately used in the manufacture of plasticizers via isononanol (isononyl alcohol), and diisononyl phthalate (Axens 2013), obtaining indeed p-xylene:



A related patent from Gevo: (Peters et al. 2011)

Axens processes

ParamaX - The BTX Aromatics Technology Suite (Dupraz et al. 2013) is the name of the processes incorporated into Axens aromatics portfolio, which provide a complete suite of advanced technologies for all BTX production goals. The technologies exclusively licensed by Axens in grassroots ParamaX packages are:

- Aromizing – high severity CCR reforming for aromatics production,
- Arofining - reformat saturation for drastically reduced clay consumption,
- Sulfolane (Lyondell) – high purity benzene, toluene and xylenes extraction,
- Morphylane (Krupp Uhde) – toluene and high purity benzene extraction,
- Eluxyl - simulated countercurrent adsorption p-xylene separation,
- Crystallization – enables the production of ultra-high purity p-xylene when combined with Eluxyl in the hybrid version,
- Oparis™ – New generation C8 aromatics (xylenes and ethylbenzene) isomerization,
- XyMaxsm (ExxonMobil) – xylenes isomerization with ethylbenzene dealkylation, using the newly commercialized EM-4500 catalyst with improved activity and selectivity
- PxMaxsm (ExxonMobil) - state-of-the-art Selective Toluene DisProportionation (STDP) technology for the production of a highly p-xylene-enriched xylene stream and benzene,
- TransPlussm (ExxonMobil) – toluene/C9+C10 aromatics transalkylation, with the proven ability to process high amounts of C9 and C10 aromatics, and
- MTDP-3 (ExxonMobil) – toluene disproportionation to benzene and xylenes.

8.2 Description of isobutene/isooctene to xylene technologies

The conversion of isobutene to p-xylene has been a topic of research since the 1950's. However, it does not seem to have progressed beyond the lab scale. Two main tracks of research were adapted, oxidative formation and reforming type formations. The best results suggest that a medium term research goal should be a yield of p-xylene of about 80%. This is in agreement with the best results, but the number of reports with much lower yields is much higher. This should be used for the economic model as current input. No company seems to license the technology.

A research project should answer the question via which intermediate the reaction proceeds (isooctene or 2,5 dimethylhexene or that is forms directly, vide infra) and then focus on designing a catalyst system which optimizes this. The experiments are expected to be challenging as these type of catalysts produce large amounts of by-products. The reaction also involves a large volumetric molar expansion. This adds an extra challenge to the analytical setup. The system must be capable of measuring accurately the volumetric expansion, all hydrocarbons from C1 to C10 (naphthalene) as well as hydrogen, online! Frequent plugging and similar problems should be anticipated in the experimental setup.

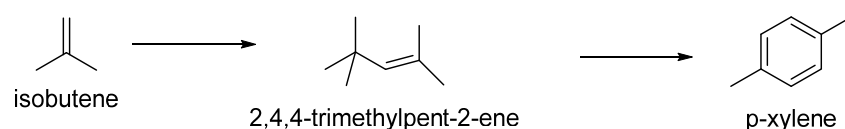
Summary of the open literature

Several ideas on how to convert isobutene (or isooctene) to p-xylene are floating around in the open literature (and seems to be built on ideas in the earlier patent literature, see below). The general ideas are:

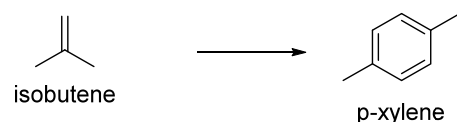
- Oxidative coupling of isobutene to p-xylene
- Dehydrocyclization of octene molecules using
 - Chromium catalysts
 - Pt-catalysts
 - Zeolite based catalysts, ZSM-5 or L were found.

There is disagreement whether the reaction goes through a hexene intermediate or is a result of a direct coupling. Data suggests that isooctene (or isooctane) forms the hexene intermediate first, and then forms the xylene. The different possibilities are shown below.

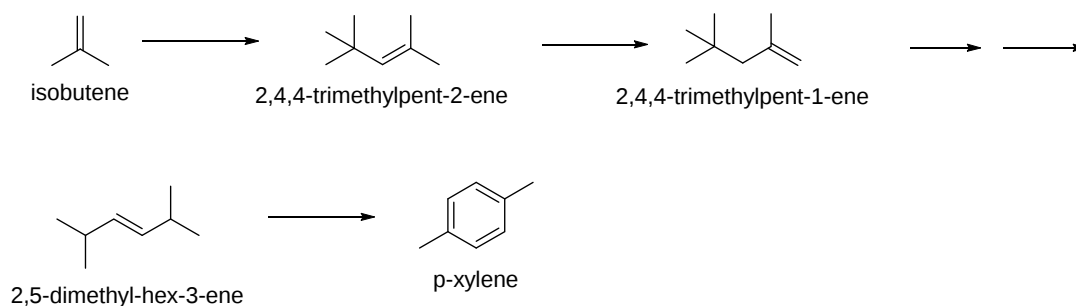
The overall reaction is shown here.



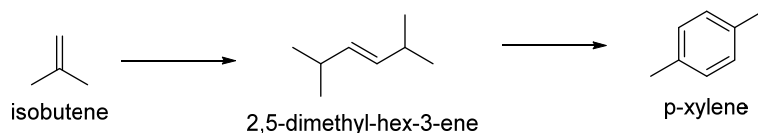
Some data suggests there is a direct (oxidative) pathway to p-xylene from isobutene as shown here:



Other sources (vide infra) suggest a pathway via hexene intermediates, as shown here.



Yet other suggestions include the deliberate formation of the hexene intermediate, as shown here.



This is a summary of a course literature search. Mazumder et al. (2003b; 2003a) describe a bismuth/Sn catalyst for the oxidative coupling of isobutene to 2,5-dimethyl-hexene (DMH) which then forms the desired product. Typical conditions are 500 °C, 0.2 s contact time, isobutene to oxygen 1:0.6, conversions ranging from 5-25 %, with DMH selectivity from 20-55%, aromatics from 0-20% and p-xylene 1-7 %. Their kinetic data suggests that p-xylene is directly formed from isobutene! Bismuth catalysts were known from the patent literature (Beuther et al. 1972; Ondrey and Swift 1972; Ondrey and Swift 1973; Beyerlein et al. 1984).

A good paper about how to run a Cyclar catalysts (and what acid sites do to isooctane) is written by Choudhary (1997) (good name to look at for light paraffin aromatization). Not much on our desired reaction, but useful if we would like to pursue this route.

Goldwasser et al. (1978a; 1978b) describe indium based catalysts, similar to the bismuth catalysts. Conversions range from 10-40%, p-xylene selectivity from 0-30 %. Cuprous oxide was reported to be somewhat effective as well by Del Rosso (1978).

Anders et al. (1982; 1986) describe a system and mechanistic study to form p-xylene from isobutene. One system is a dual catalysts system, where one forms the isooctene, and the other the p-xylene. The dimerization catalysts are molybdenum/rhenium or chromium on alumina (these are also known metathesis catalysts and it is unclear which functionality they have here, and it is in German!). The catalyst for aromatization is K/Cr on Alumina; see also UOP patent (Jan and Frey 2008). Their mechanistic study suggests that isooctene isomerizes to the α -olefin, which then cleaves via a radical mechanism, which then forms the DMH. This forms the p-xylene selectively.

Similar suggestions for the mechanism for the formation were reported by Akimoto (1977). Hydrogen transfer is also suggested as isobutane is formed. Again, rearrangement of the isobutene seems to take place. This then forms DMH type molecules which form the xylenes. Isobutane is also seen in the patent literature (Herron et al. 2001; Manzer et al. 2004).

UOP (Jan and Frey 2008) discloses a process for the conversion of isooctene or isooctane to p-xylene (note, isooctane, trimethylpentane and diisobutane are used interchangeably in the patent literature). Key is the use of non-acidic catalysts. Three types are disclosed: Chromia on neutralized alumina, Pt on neutralized alumina, and neutralized Zeolite L (with Pt). These are two known reforming catalyst and the Aromax catalyst. The Prior art needs to be examined further:

Conversions range from 7 to 99 %, with 0.14 to 52% xylenes with up to 84% p-xylene in the xylenes.

From the UOP patent (Jan and Frey 2008): “Usually para-xylene is produced, in a series of steps, from naphtha fractionated from crude oil. Naphtha is hydrotreated and reformed to yield aromatics, which then are fractionated to separate typically benzene, toluene and C₈ aromatics comprising xylenes from C₉ and heavier aromatics. Toluene and C₉ aromatics may be disproportionated to yield additional xylenes. Xylene isomers, with the usual priority being para-xylene, are separated from the mixed C₈-aromatics stream using one or a combination of adsorptive separation, crystallization and

fractional distillation, with adsorptive separation being most widely used in newer installations for para-xylene production. Other C₈ isomers may be isomerized and returned to the separation unit to yield additional para-xylene.

Although low-value light aliphatics such as butanes and butenes offer a substantial theoretical margin for the production of para-xylene, practical processes to effect this conversion have not been available to date. Butane dehydrogenation and dimerization plus aromatization to yield primarily octane isomers is taught in U.S. Pat. Nos. 5,847,252, 5,856,604 and 6,025,533. U.S. Pat. No. 4,367,356 discloses a combination of butene dimerization and alkylation to obtain C₈ hydrocarbons. These patents, whose relevant teachings are incorporated herein by reference, do not disclose the production of para-xylene.

Pines and Csicsery (1962) disclose the aromatization of trimethylpentanes to xylenes, using a nonacidic chromia-alumina catalyst; 2,2,4-trimethylpentane formed only para-xylene. In the proceedings of the 1962 Radioisotopes Physical Science Industrial Process Conference at pages 205-216, Cannings et al. teach dehydrocyclization of 2,2,4-trimethylpentane over a potassium- and cerium-promoted chromia-alumina catalyst to selectively yield para-xylene. British Patent 795,235 teaches the manufacture of para-xylene from 2,4,4-trimethylpentene using a catalyst comprising a Group VI-A oxide, exemplified as a series of chromia-containing catalysts. U.S. Pat. No. 3,202,725 discloses dehydrogenation of isobutane and recycle di-isobutylene using a chromia-alumina catalyst to yield para-xylene and isobutene, plus dimerization of the isobutene using a silica-alumina, phosphoric acid or sulfuric acid catalyst to yield primarily di-isobutylene recycle. U.S. Pat. No. 3,462,505 discloses the dehydrocyclization of 2,2,4-trimethylpentane to yield para-xylene using a catalyst comprising chromia, magnesia and an alkali metal on activated alumina. U.S. Pat. No. 3,766,291 discloses disproportionation of amylene to 2,5-dimethylhexene, which then is selectively converted to para-xylene over a catalyst comprising a Group II metal (exemplified by Zn) aluminate, tin-group metal, and Group VIII metal. U.S. Pat. No. 4,910,357 teaches the aromatization of dimethylhexanes, especially those contained in alkylate, using a catalyst comprising a dehydrogenation metal and a nonacidic crystalline support containing Sn, Ti, In and/or Pb. U.S. Pat. No. 6,177,601 B1 teaches aromatization of 2,5-dimethylhexane to selectively produce para-xylene, using a nonacidic L-zeolite catalyst. U.S. Publication 2004/0044261A1 teaches production of para-xylene from a feedstock rich in C₈ isoalkanes or isoalkenes using a catalyst comprising a molecular sieve, Group VIII metal and two or more of Si, Al, P, Ge, Ga and Ti. U.S. Publication 2004/0015026 discloses the manufacture of para-xylene from 2,2,4-trimethylpentane using a catalyst comprising chromium. It should be noted that chromium, as a catalyst constituent, is a toxic element.

None of the above references, drawn to the processing of particular feedstocks, discloses the selective process combination of the present invention. The art heretofore has not taught a practical process for the production of para-xylene from light hydrocarbons."

Gevo (Peters et al. 2012b) discloses routes to p-xylene via DMH, which is produces any which way they could think of, including numerous routes which are not industrially viable. Recently Gevo announced that a pilot plant was bought to test production of p-xylene from isobutanol.

Dupont (Herron et al. 2001; Manzer et al. 2004) discloses a chromium catalyst for the selective production of p-xylene from di-isobutene. Catalysts are run in "pulse" more, i.e. 5 minutes reaction time, then regenerated! Isooctene/ane conversion is high (70-85%), with about 25 % overall p-xylene selectivity (although p-xylene is > 95% of the xylenes).

Mobil (Butter 1977) discloses a antimony exchanged zeolite mostly used for the methylation of toluene with methanol. One example describes the aromatization of isobutane. The para-selectivity is high, sometimes 95%. The zeolite is ZSM-5.

Exxon (Beyerlein et al. 1984) discloses a mixed metal oxide. One set of experiments has been performed for the conversion of isobutene. Mostly 2,5 dimethyl hexene is formed with traces of para-xylene. However, the conversions remain below 10%.

Shell Oil (Slaugh 1980) discloses a supported rhenium catalyst. Conversions of isobutene range from 7 to 14%. Para xylene selectivities range from 18 to 40%.

Shell Oil (Kouwenhoven et al. 1980) also discloses a series of Iron based zeolites, used for the selective production of p-xylene from methanol, isobutane, gasoline etc. The yield of liquid product

ranges from 45 to 75%, of which aromatic fraction ranges from 5 to 40%, with the xylenes ranging from 30 to 45%, and the p-xylene in the xylene fraction from 25 to 90%.

In a series of patents Gulf Research (Beuther et al. 1972; Ondrey and Swift 1972; Ondrey and Swift 1973) discloses a bismuth modified Chromia on Alumina catalyst. These show high (~80 %) selectivities to aromatics with the main component being p-xylene. Other products include, unexpectedly, the 2,5-dimethyl-2-hexene (and the like), with very little isooctene. This may mean that isooctene reacts the fastest, or that 2,5-dimethylhexene is formed preferentially and that this forms p-xylene.

8.3 Freedom to operate (patent tree)

Most of the patent literature dates back to the late 1970s and early 1980s. Most of these patents have now expired. The only recent patents are assigned to GEVO, however, they do not disclose novel catalytic routes. The GEVO patent only describes an integrated process. We do not believe that this will interfere with our proposed route. The open and patent literature is described in section 8.2.

8.4 Design basis and equipment design

Assumptions for the aromatization step:

- Isooctene input 91 kt/a
- Molar yield 95%
- p-Xylene produced 80 kt/a
- By-products Hydrogen, stoichiometric, 6 kt/a to jet fuel and sold.

Aromatics in general are produced as by-product in the gasoline production (in the reformer) or steam cracking of heavier naphtha's. There is no commercial process which selectively produces p-xylene from an olefinic precursor. If p-xylene is formed, all the other parts of BTX are always formed as well, most of the time in the thermodynamically predicted ratios. The consortium seeks to identify which technology option is the most suitable for converting isobutene to p-xylene. A coarse screening identified several routes:

- Oligomerization to a C8 olefin and then reforming to BTX
- Aromatization of the above mentioned C8 using a variation of the CYCLAR™ process
- Direct conversion of isobutene to p-Xylene

To produce benzene ring via the C8, an acid catalyst is needed (methyl shift), leads to mixed xylenes and most likely to BTX due to trans-alkylation and dehydroalkylation. Although all the above mentioned processes produce BTX, they have not been attempted with isobutene to our knowledge.

The 1st estimation used the CYCLAR™ process (which does only have two operation plants). The conversion of isobutene to p-xylene is highly speculative, thus an expensive process was chosen. Other options include regular reformers producing BTX, which is then recycled to extinction to form xylene. The formed xylenes are then converted to p-xylene. With no conversion and selectivity data, this is difficult to model at this time. Listed investment is 200-300 \$/t feed, so 300 \$/t was assumed. Utilities were assumed to be the same, minus the fuel credit. The hydrogen produced in the reaction is assumed to be pure enough to be used in the jet fuel part, with the remainder sold to the open market.

We have also assessed this step by assuming that the reformer can be configured in such a way that only p-xylene is formed. Other permutations include processes where mixed xylenes are formed and then separated, isomerized, and recycled to extinction. The results of all these permutations suggest that the secular option is the lowest capital. Therefore, we have chosen this process as basis for our calculations.

8.5 Identified technology gaps

The conversion of isooctane to p-xylene as today only been demonstrated in laboratory reactors. As described in section 8.2, there is still uncertainty over the exact mechanism. Furthermore, no high yields at high conversions have been obtained. We believe that a full-fledged research and development program is needed to implement this step into this process. This will require significant effort as well as breakthrough both in terms of catalyst as well as processes. The aromatization of light olefins to aromatics is notoriously experimentally difficult. The Consortium should realize that this is a high risk proposition. However, recent breakthroughs in the area of the aromatization of

linear alkanes suggest that there is a reasonable possibility that this conversion is technically possible.

9 Jet fuel formation

9.1 Description of technologies

The production of jet fuel from the oligomerized isobutene fraction was modeled after the hydrogenation of isooctene to isooctane. The hydrogenation is described in chapter 7. Hydrogenation of olefins to fuel is a widely used process, for instance in the production of gasoline in a steam cracker.

9.2 Freedom to operate (patent tree)

We do not foresee any intellectual property issues for this step. Technology is available from many suppliers. We foresee that the only have to qualify the catalyst system with our actual feed.

9.3 Design basis and equipment design

Assumptions for the hydrogenation step:

- C12/C16" input 182 kt/a
- H₂ input 2 kt/a from aromatization.
- Molar yield 95%
- Jet fuel produced 175 kt/a
- By-products None specified

Equipment design is the other half, the hydrogenation unit, of an isooctane unit. Contact times, temperature, pressure, etc. was assumed to be the same as for isooctene.

9.4 Identified technology gaps

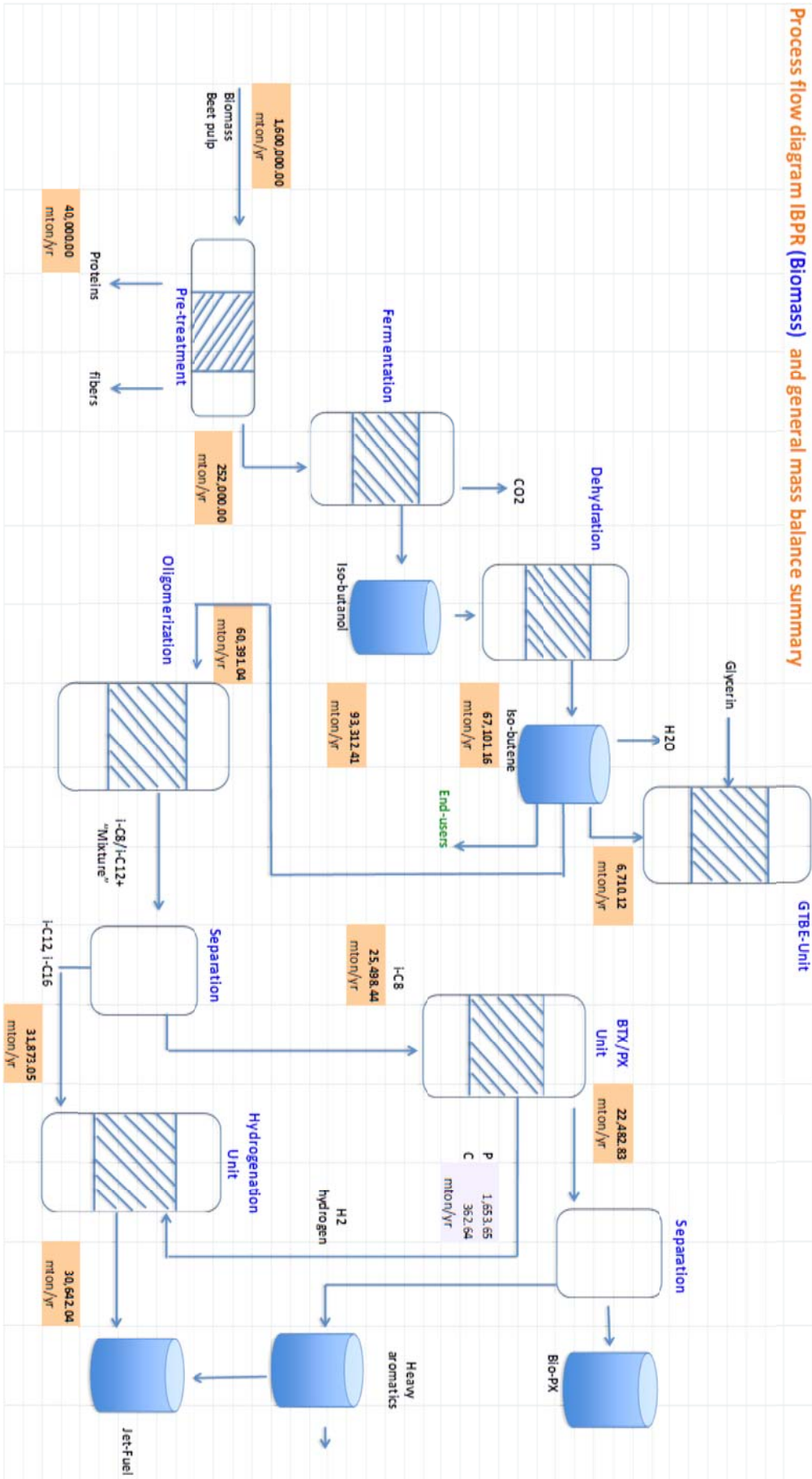
We foresee that, in close corporation with one or more catalyst companies, only commercially available catalysts will have to be qualified with actual feeds produced from isobutanol. No major technical hurdles are expected.

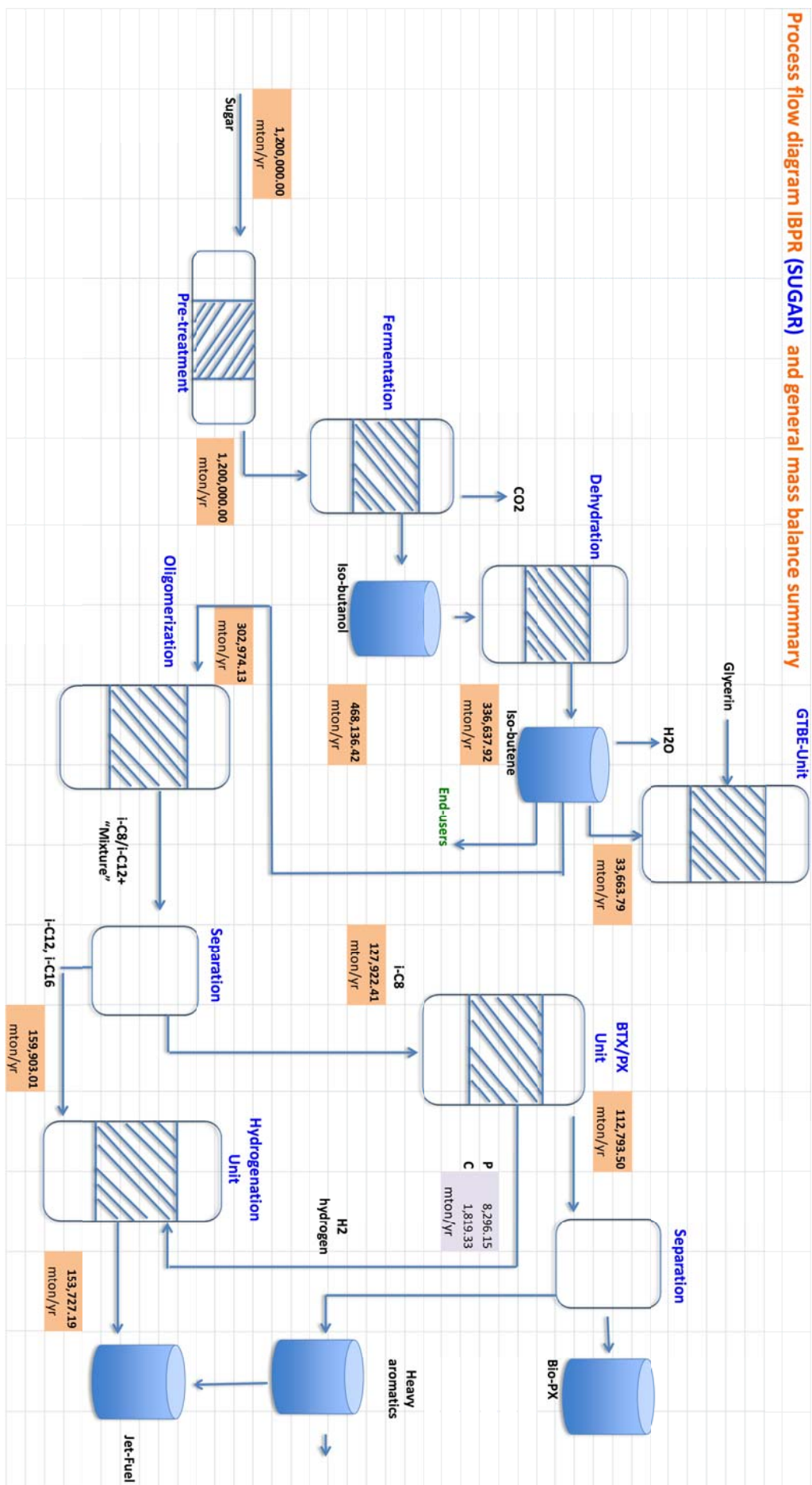
10 Overall process

The overall process comprises a series of steps, which starts with enzymatic hydrolysis of biomass, followed by a fermentation operation. This part is considered by the "upstream process" and utilizes concepts from the biotechnology area, where relatively low temperatures and pressures are required. Moreover these processes uses species like enzymes, yeast, and relatively low risk chemicals.

The downstream steps and processes are characterized to be more thermochemical and catalytic in nature, and generally they use significantly higher temperatures and pressures.

The overall process for the beet pulp case and the sugar case, respectively, are depicted below.





Description of the downstream steps (from proposal and input for 1st estimation of CAPEX and OPEX).

The processes assume that 1.2 Mt/a are available from Suikerunie for the first large scale plant. The pretreatment is assumed to yield 100 % fermentable sugars. For the fermentation, a yield of 90% on carbon basis is assumed. The other 10 % is generally for the growth of the organisms. A significant part of the research needs to be dedicated to the separation of isobutanol from water. ECN develops technology for this, but that is not part of the downstream analysis. Below, we describe the state of the art for each step (see also process flow scheme) and which unit was used to model the conceptual process. The ICS (world) IPEX index was used to extrapolate the CAPEX to July 2012 numbers (with years and quarters averaged if so listed).

Excluded from the estimation are a hydrogen purification unit and a p-Xylene purification unit. At the scales envisioned, the latter needs to be more closely evaluated since the scales may not be sufficient to justify a stand-alone unit. Options that need to be explored are where the p-Xylene should be produced, for instance by sending the C8 cut to a much larger reformer in close proximity.

Dehydration:

The dehydration of alcohols is currently practiced for the production of M/ETBE from t-butanol, for instance by Lyondell in Rotterdam. The dehydration of ethanol to ethylene is making a come-back in Brazil. However, the dehydration of isobutanol has not been commercially practiced and has only been recently demonstrated for the production of one batch by GEVO and partners.

Process is modeled after an Axens 369 kt/a (diluted) C4-cut input TAME plant, 2010 US Gulf coast investment costs (1 \$ = 1 €). Utilities were assumed to be the same for the dehydration. The numbers can be found in the Hydrocarbon Processing 2010 Petrochemicals Processes Licenses handbook. Investment is listed as 13 M\$, which is assumed to be erected ISBL costs. These numbers need to be verified.

Jet fuel:

The current state of the art technology to oligomerize isobutene is optimized for the production of isooctene/ane which is used as high value high octane gasoline additive. In order to produce jet-fuel, the formed isooctene needs to react further to produce a C12/C16 stream which can then be hydrogenated to meet the jet fuel specifications. The C12 product is the isooctane process is considered a by-product and its formation is suppressed by the addition of alcoholic modifiers. To obtain jet fuel, the process now needs to be converted to produce the C12 stream which used to be an unwanted by-product. Thus far, we have only found a few claims that this is possible, but actual performance numbers and process conditions have not been published. The process economics are thus also unknown.

The oligomerization step is assumed to yield 1/3 C8 and 2/3 C12/16, with recycle. Or more accurate, to yield the desired split. This is thus a common unit for the envisioned complex. For the CAPEX, the unit was modeled after the Axens Dimersol-X process. The listed ISBL unit is 50 kt/a and investment is 8 M\$, 2010 basis. Utilities were estimated from the Refining Hydrocarbon Technologies for the same process. The hydrogenation step was also modeled using this data. Investment was assumed to be erected cost ISBL, which was listed as 5.5 M\$, 1Q US gulf coast basis. Utilities were converted to a per ton basis. Hydrogen usage is not listed, but was assumed to be near stoichiometric. Contact times and equipment sizing were thus assumed to be the same.

p-Xylene

Aromatics in general are produced as by-product in the gasoline production (in the reformer) or steam cracking of heavier naphtha's. There is no commercial process which selectively produces p-xylene from an olefinic precursor. If p-xylene is formed, all the other parts of BTX are always formed as well, most of the time in the thermodynamically predicted ratios. The consortium seeks to identify

which technology options are most suitable for converting isobutene to p-xylene. A coarse screening identified several routes:

- Oligomerization to a C8 olefin and then reforming to BTX
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In order to produce benzene ring via the C8, an acid catalyst is needed (methyl shift), leads to mixed xylenes and most likely to BTX due to trans-alkylation and dehydroalkylation. Although all the above mentioned processes produce BTX, they have not been attempted with isobutene to our knowledge.

The 1st estimation used the CYCLAR™ process (which does only have two operation plants). The conversion of isobutene to p-xylene is highly speculative, thus an expensive process was chosen. Other options include regular reformers producing BTX, which is then recycled to extinction to form xylene. The formed xylenes are then converted to p-xylene. With no conversion and selectivity data, this is difficult to model at this time. Listed investment is 200-300 \$/ton feed, so 300 \$ was assumed. Utilities were assumed to be the same, minus the fuel credit. The hydrogen produced in the reaction is assumed to be pure enough to be used in the jet fuel part, with the remainder sold to the open market.

11 Economic analysis

11.1 Base case

Good management consists primarily of making wise decisions; wise decisions in turn involve making a choice between alternatives. Engineering considerations determine the possibility of a project being carried out and point out the alternative ways in which the project could be handled. Economic considerations also largely determine a project's desirability and dictate how it should be carried out. A feasibility study determines either the which or the whether of the proposed project: which way to do it, or whether do it at all. In an engineering sense, feasibility means that the project being considered is technically possible. Economic feasibility, in addition to acknowledging the technical possibility of a project, further implies that it can be justified on an economic basis as well. Economic feasibility measures the overall desirability of the project in financial terms and indicates the superiority of a single approach over others that may be equally feasible in a technical sense.

In this study, the project is considered in an engineering sense. The ultimate objective of the economic analysis is to provide a decision-making tool, which can be used not only for the pilot project but also for demonstration purposes. In this model three different costs are needed to develop an economic model: Capital costs (CAPEX), operational costs (OPEX) and other economical variables (inflation rates, interest rate, weight average cost of capital, and tax rates)

Capital expenditures (CAPEX) are expenditures creating future benefits. A capital expenditure is incurred when a business spends money either to buy fixed assets or to add to the value of an existing fixed asset with a useful life extending beyond the taxable year. In the economical analysis the investments costs for the production units in the chain are considered as CAPEX costs. The investments needed will generate costs such as depreciation and interest costs, which have to be accounted for.

OPEX is an ongoing cost for running a product, or a business. In the economical calculations OPEX costs includes the cost of workers and facility expenses such as rent, utilities, maintenance, logistic costs (Storage and transportation), R&D, depreciation and Administration. In business, an operating expense is a day-to-day expense such as sales and administration, or research & development, as opposed to production, costs, and pricing. In short, this is the money the business spends in order to turn inventory into throughput.

The OPEX and CAPEX costs will be summed up in the "Costs of Goods Sold" (COGS).

When the Revenues from sales and the COGS are known, then the Discounted cash flow analysis can be performed

The discounted cash flow (DCF) analysis is a method of valuing a project, using the concepts of the time value of money. All future cash flows are estimated and discounted to give their present values (PVs)—the sum of all future cash flows, both incoming and outgoing, is the net present value (NPV), which is taken as the value or price of the cash flows in question.

The NPV is a financial indicator of how much value an investment or project adds to the firm. With a particular project, the NPV is a positive value, the project is in the status of positive cash inflow in the time of t . If the NPV is a negative value, the project is in the status of discounted cash outflow in the time of t . Appropriately risked projects with a positive NPV could be accepted. This does not necessarily mean that they should be undertaken since NPV at the cost of capital may not account for opportunity cost, i.e., comparison with other available investments. In financial theory, if there is a choice between two mutually exclusive alternatives, the one yielding the higher NPV should be selected.

In the base case, the cash flow is negative for thick juice as well as for beet pulp (Figure 11-1 and Figure 11-2). Considering the achievable yield of isobutanol on thick juice, the thick juice is just too expensive. In case of beet pulp, the negative cash flow is mainly caused by excessive costs of enzymes for hydrolysis.

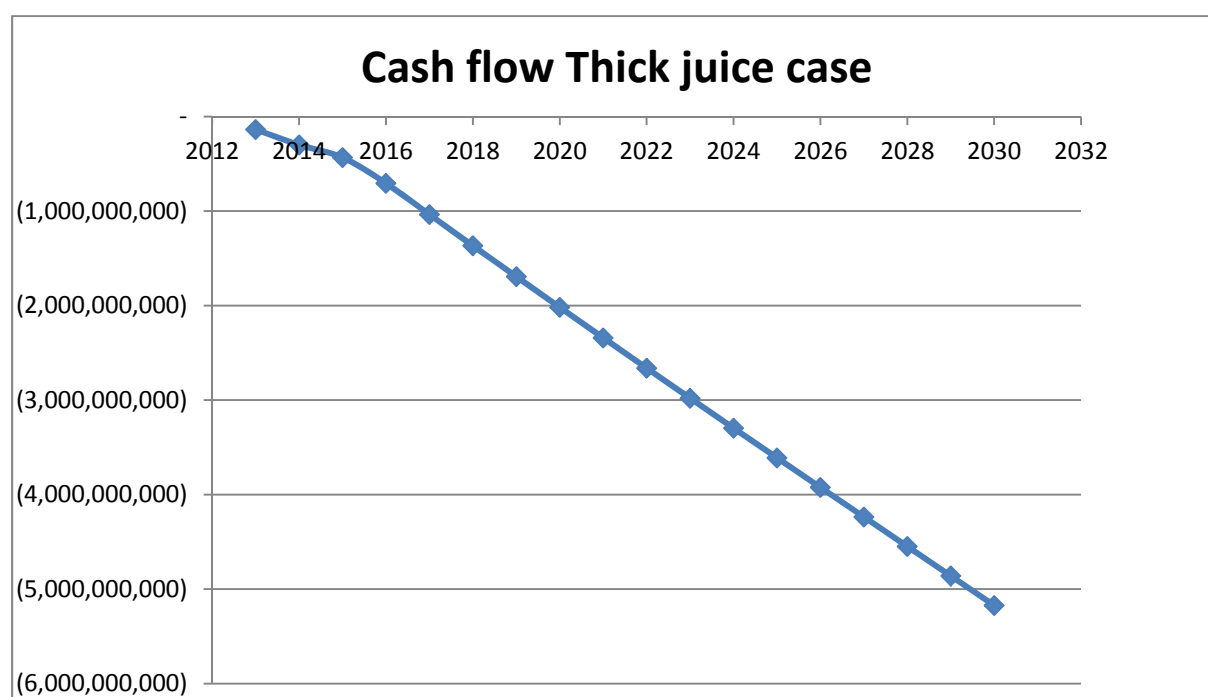


Figure 11-1. Cash flow in US\$ for the thick juice case.

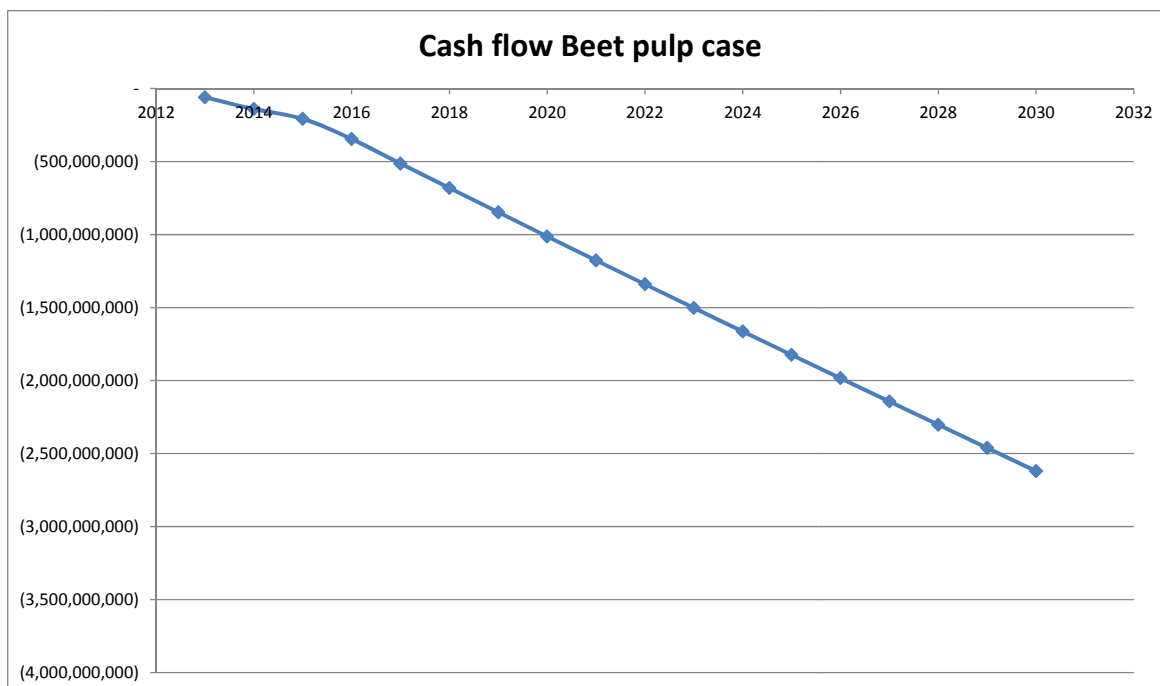


Figure 11-2. Cash flow in US\$ for the beet pulp case.

11.2 Sensitivity analysis

In the economical evaluation sensitivity analysis have been conducted on two types of biomass, i.e. the Sugar case and the Beet Pulp case.

For the Sugar case it became clear that, given the fact that the costs of the sugar biomass in this form has to meet the current “market prices” of EUR 350-400, per metric ton, the NPV-values in all cases remain far negative. This implies that that it is highly unlikely that an economic project to produce GTBE, Jet fuels and bio-PX from this feedstock can be conducted.

For the beet pulp case, a typical sensitivity analysis is shown in Figure 11-3. It shows that a positive NPV can be obtained in several cases, in particular when the costs of enzyme decrease by three-fold.

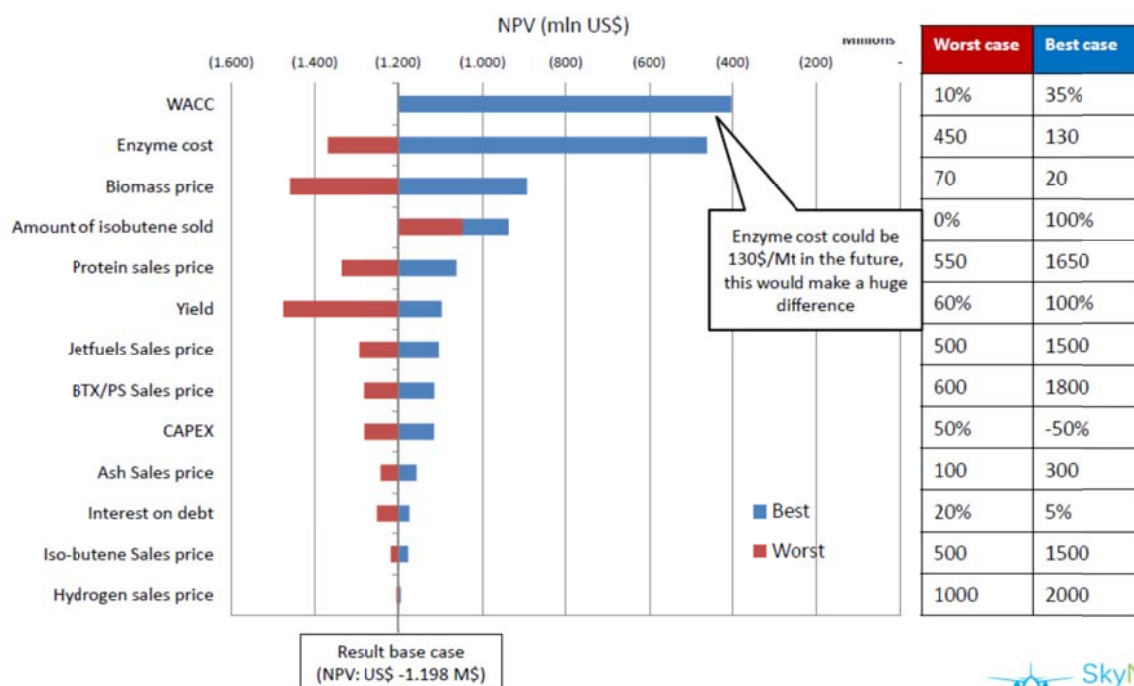


Figure 11-3. Sensitivity of NPV in the beet pulp case.

From the analysis the conclusion can be drawn that the raw materials have the most pronounced effect on the NPV, which is reflected in the Enzyme costs and Biomass price. The yield of the subsequent conversion processes to the desired products is also influencing the NPV significantly.

In a few scenarios a positive NPV was obtained, using the most optimistic case for feedstock and enzyme costs and only producing isobutanol and GTBE from the sugar beet pulp. However when more unit operations, downstream in the chain, are adopted for jet fuels and bio-PX, then the NPV values are significantly negative. What does it mean? One observation is that the volumes for the different products are too low to cover for the CAPEX and OPEX costs for the relevant units. This is more dominant for Bio-PX than Jet fuels, since more unit operations are required to produce Bio-PX.

12 Life cycle assessment

12.1 Goal definition and scoping

The purpose of this LCA study is to calculate the environmental impacts of the IPBR and compare them to an equivalent oil-based platform (i.e., with the same products distribution). Three raw materials are considered: crystalized sugar, thick juice and pressed pulp. A prospective cradle-to-grave LCA for two impact categories is performed here: non-renewable energy use (NREU) and climate change (Global Warming Potential, GWP100), using the LCA databases from SimaPro (PRéConsultants 2006). Other impact factors might be calculated but at this stage of the project probably with insufficient accuracy to draw conclusions.

Two functional units are used for this LCA: i) 1 kg of isobutanol since it is the main intermediate of the analyzed multiproduct-platform and ii) 1 kg of the final mix of products obtained from the multiproduct-platform (i.e., 1 kg of product basket). For all final products the production, relative to isobutanol, was also used for an easier understanding of each processing stage/step. These functional units additionally allowed allocation of the environmental impacts among all final products accordingly. In this case, economic allocation is preferred for material products and system expansion for energy products.

12.2 Inventory analysis

The assumptions and data used are given in Appendix 12.1. These resemble those used for the Economic analysis but are not always identical. The economic and LCA analyses use the same technical data (i.e., yields and raw materials use). However, big differences are found in the use of enzymes. The economic analysis uses 4.3 ton enzymes/ton of isobutanol, while the LCA uses 0.22 ton enzymes/ton of isobutanol. On the other hand, there are small differences among the prices of all raw materials and final products, but these differences do not will lead to significantly different results. Thus, the only critical difference is the use of enzymes.

12.3 Impacts assessment

For easier understanding of the results, the environmental impacts (i.e., NREU and GHG) of each processing step are shown per produced unit of either raw materials (in the case of sugar production and processing) or final products (in the case of isobutanol conversion). For instance, for sugar beet production and processing, the chosen unit is 1 kg of the corresponding raw material (See section 12.3.1) while for isobutanol production and conversion the used unit is 1 kg of isobutanol (See sections 12.3.2 and 12.3.3).

12.3.1 Sugar beet production and processing

Based on Table A- 5 and Table A- 6, the total environmental impacts for sugar beets production and processing were calculated, and credits were given to the energy products, i.e. electricity and biogas. The NREU and GHG emissions for the production of 1 kg of each of the three optional raw materials are shown in Figure 12-1 and Figure 12-2, respectively.

Based on the sale prices of products obtained from the sugar beet milling facilities (Table A- 11) and based on their material flows (Table A- 5), the allocation factors of these products were calculated for each raw material as shown in Figure 12-3. The allocation factors for crystalized sugars and pressed beet pulp are the same because these two products (and also the other by-products) are obtained at the same time in the same ratios. The economic allocation factors were used to

distribute the total environmental burdens among all products of the sugar beet milling process as shown in Figure 12-4 and Figure 12-5, for NREU and GHG emissions respectively.

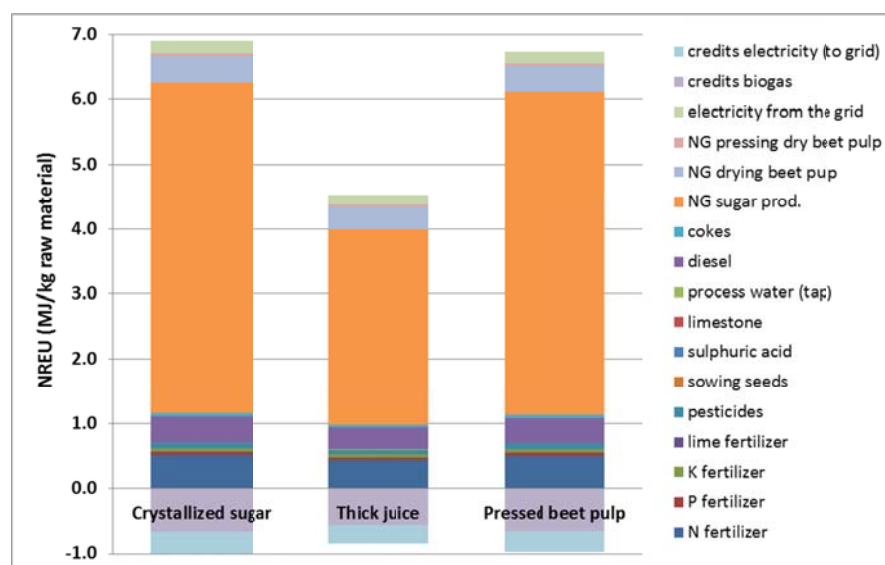


Figure 12-1. Total NREU for raw materials production (with energy credits), system cradle-to-factory gate

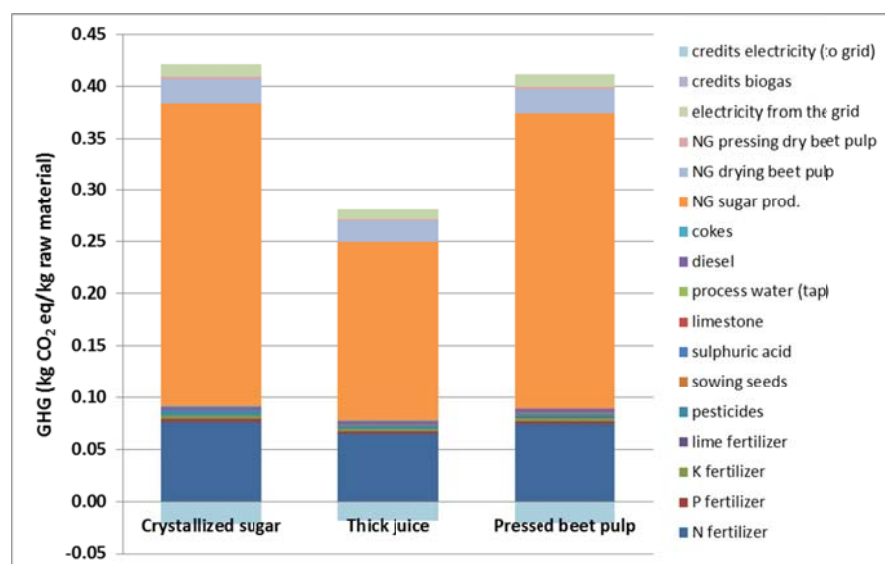


Figure 12-2. Total GHG for raw materials production (with energy credits), system cradle-to-factory gate

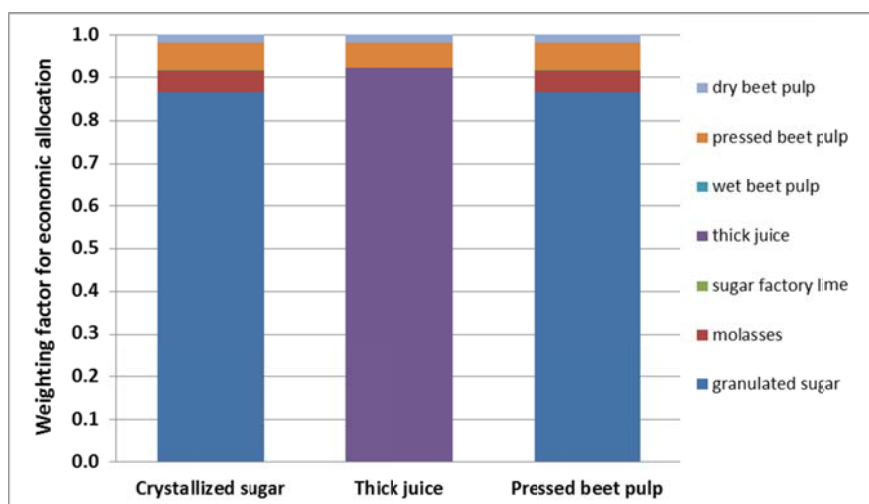


Figure 12-3. Weighting factors for economic allocation of the sugar beet milling process.

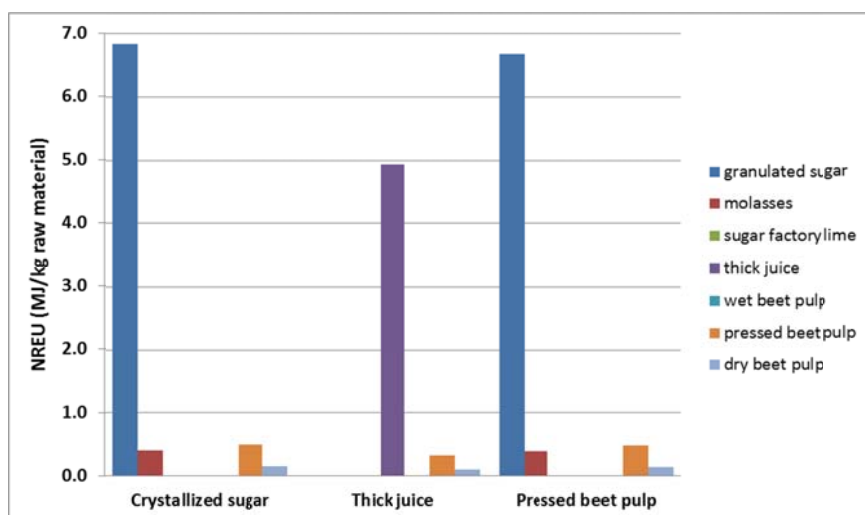


Figure 12-4. NREU for raw materials and by-products (with energy credits and economic allocation), system cradle-to-factory gate

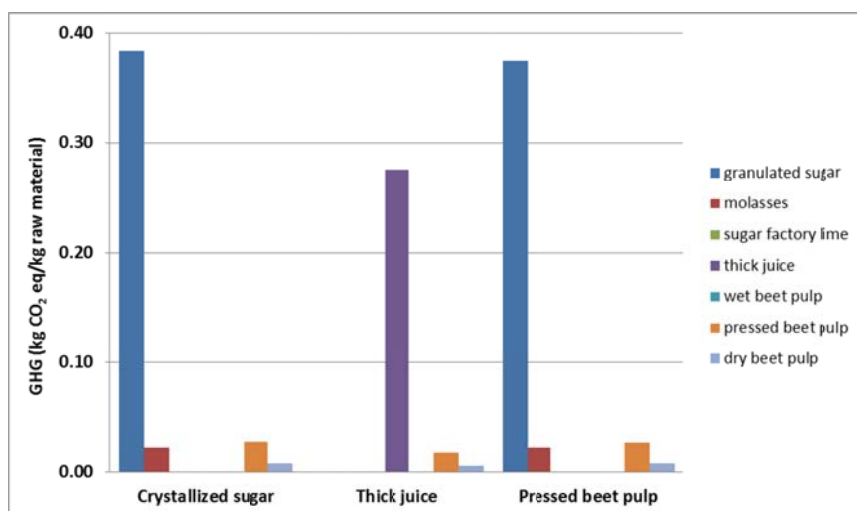


Figure 12-5. GHG emissions for raw materials and by-products (with energy credits and economic allocation), system cradle-to-factory gate

12.3.2 Isobutanol production

Based on Table A- 7 and Table A- 8, the total environmental impacts for isobutanol production were calculated. The analysis of pressed beet pulp as raw material requires additional consideration due to the uncertainties related to the use of enzymes and the environmental impacts associated to their production. The current pretreatment process uses 26 mg enzymes/g biomass¹; however the NREL reports 20 mg enzymes/g biomass (Humbird et al. 2011), and values as low as 9.5 mg enzymes/g biomass have also been reported (Zhu and Zhuang 2012). On the other hand, based on the NREL report, the NREU and GHG emissions for enzymes production were here calculated as 109.4 MJ/kg enzyme and 4.6 kgCO₂ eq/kg enzyme respectively. Novozyme (Nielsen et al. 2007) reported values for enzymes production in the range of 14-125 MJ/kg enzyme and 1-10 kgCO₂ eq/kg enzyme respectively, with 88.9 MJ/kg enzyme and 7.6 kgCO₂ eq/kg enzyme for hydrolysis of cellulosic biomass. Thus, the environmental impacts associated to the enzymes production might be lowered, for instance, by 75% by action of both: decrease of the enzymes usage and improved bio-tech practices. Therefore, two additional cases for reduction of environmental impacts are here considered: i) 50% use of enzymes equivalent to those from NREL and ii) 25% use of enzymes equivalent to those from NREL.

In this case there are no credits for energy or material by-products. The environmental impacts per kg of isobutanol are shown in Figure 12-6 and Figure 12-7 for NREU and GHG emissions respectively. The conversion from the fermentable sugars to isobutanol does not require allocation since only a single product is obtained.

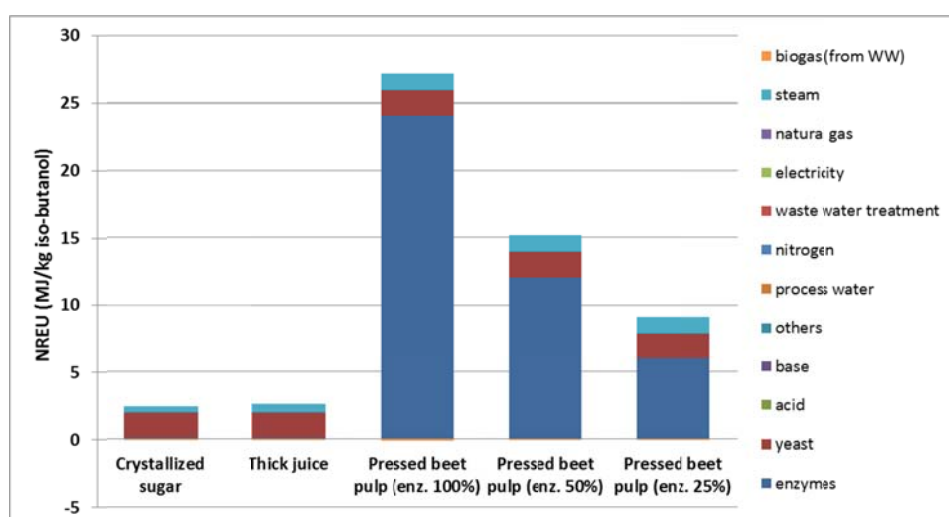


Figure 12-6. NREU for isobutanol production, system factory gate-to-factory gate

¹ Communication with Erik van Hellemond

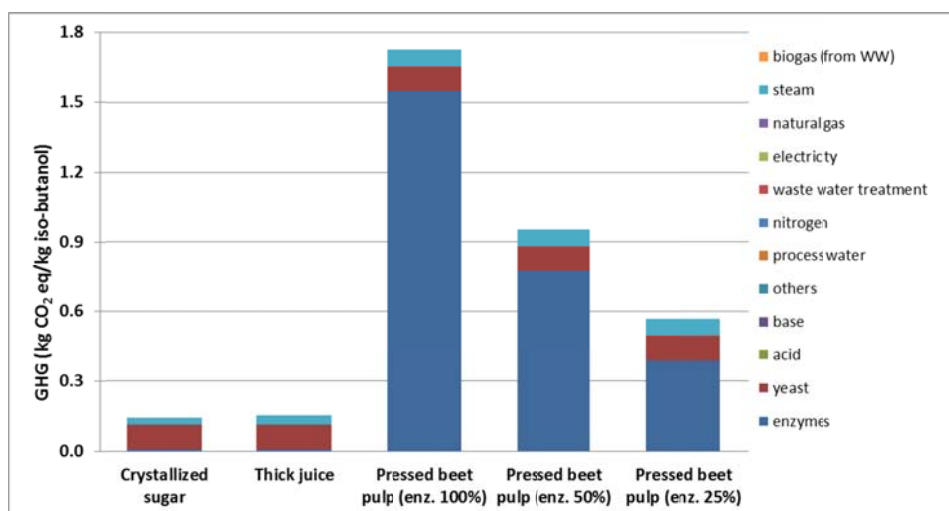


Figure 12-7. GHG for isobutanol production, system factory gate-to-factory gate

12.3.3 isobutanol conversion

Similarly to the isobutanol production, the total environmental impacts for isobutanol conversion were calculated for each processing unit based on Table A- 9 and Table A- 10. The NREU and GHG emissions associated to each processing step of isobutanol conversion are shown in Figure 12-8 and Figure 12-9, respectively. Environmental impacts for fossil-based isobutanol were included for comparison purposes. In this case, there are not credits for energy or material by products. Although four final products are obtained from the isobutanol platform, economic allocation is not applied at this point (but it is done later). This implies that the impacts of the entire process chain are allocated to the main product, here isobutanol.

12.3.4 Integrated process

The environmental impacts of the three processing stages were integrated taking into account the use of each raw material per kg of isobutanol produced (see bold numbers in Table A- 7). The NREU and GHG emissions for each section/step are shown in Figure 12-10 and Figure 12-11 for the three raw materials includes the two cases for environmental impacts reduction associated to enzymes production.

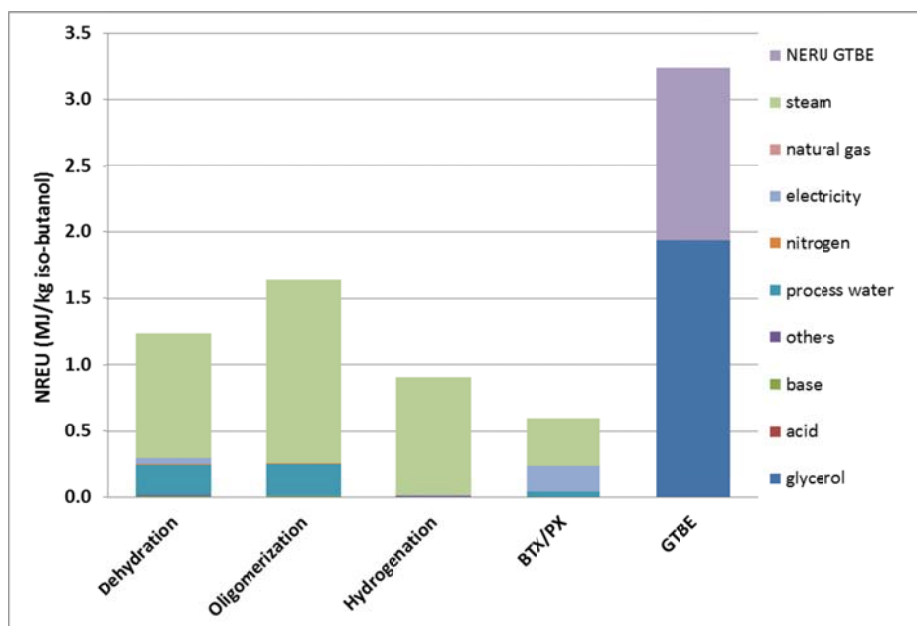


Figure 12-8. NREU for isobutanol conversion, system factory gate-to-factory gate

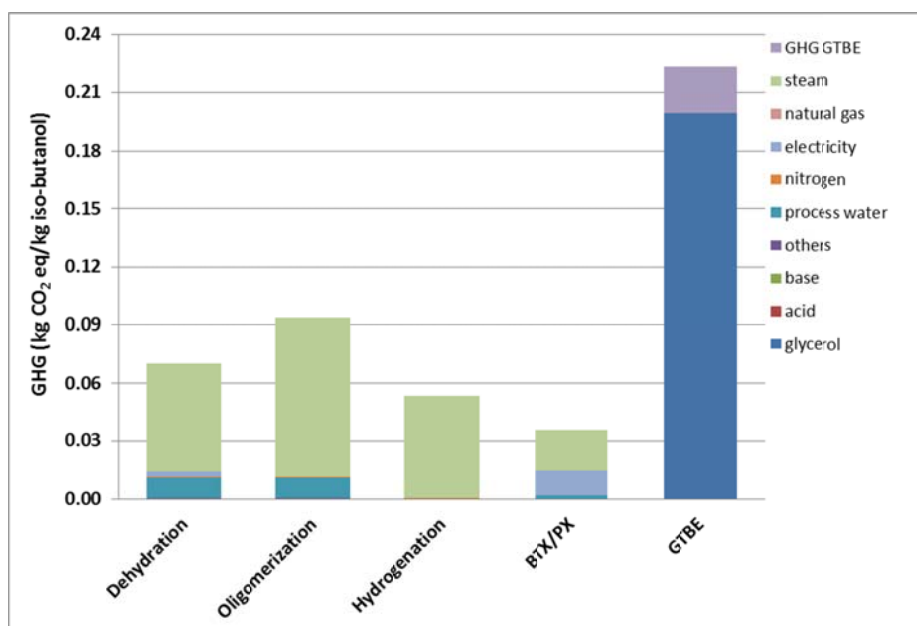


Figure 12-9. GHG for isobutanol conversion, system factory gate-to-factory gate

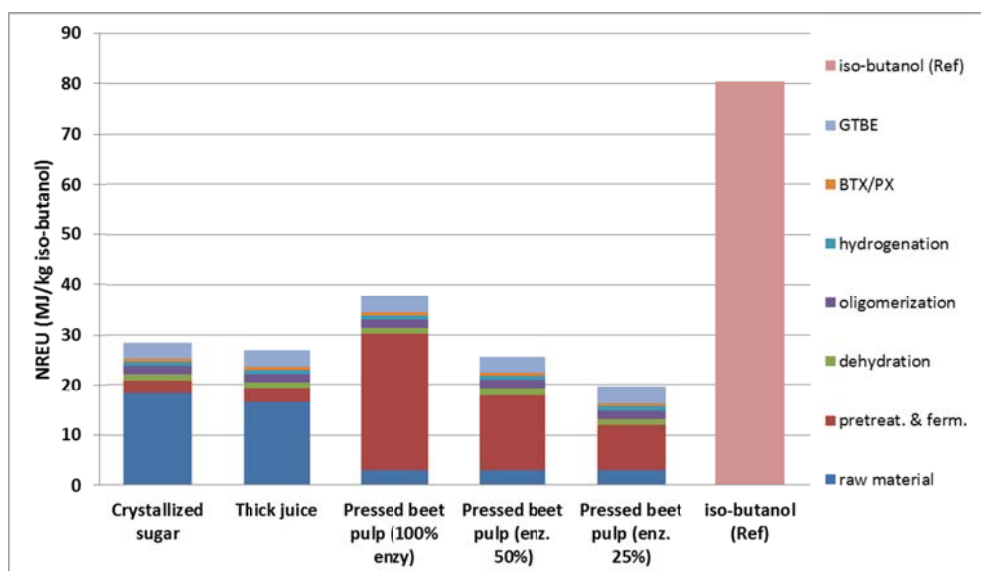


Figure 12-10. NREU for isobutanol platform, system cradle-to-grave

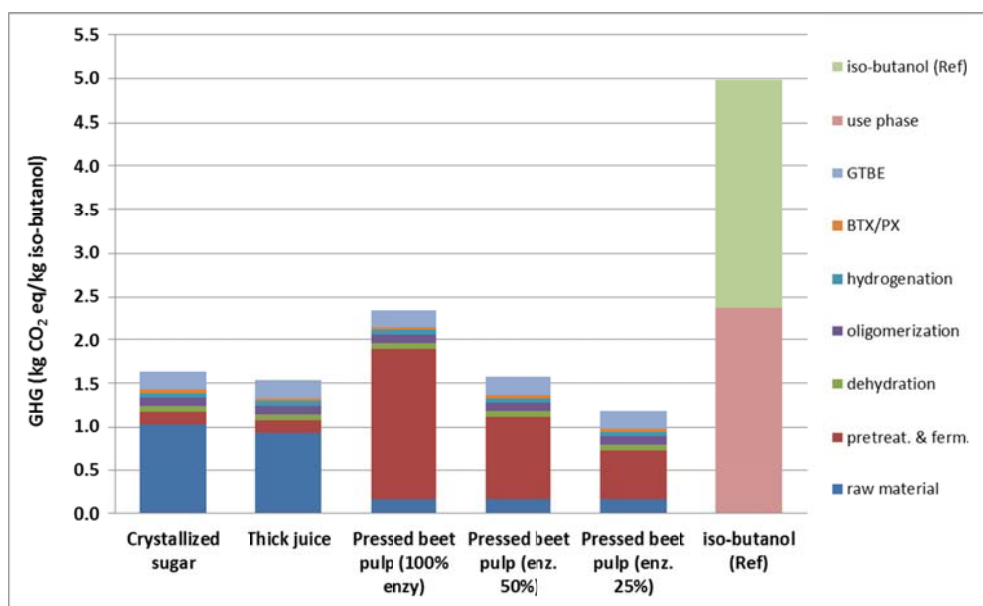


Figure 12-11. GHG for isobutanol platform, system cradle-to-grave

The environmental impacts of the integrated systems were distributed among all products by using the economic allocation factors (see Table A- 11) which were in turn calculated from their commercial prices (see Table A- 11) and mass flows (see Table A- 9). The NREU and GHG emissions of each product per 1 kg of raw isobutanol used are shown in Figure 12-12 and Figure 12-13, respectively. The impacts were further calculated per 1 kg of each final product using the respective production ratios. These results are shown in Figure 12-14 and Figure 12-15 for NREU and GHG respectively. The environmental impacts for the oil-based counterparts were also included; but due to lack of data, MTBE was used as reference of GTBE.

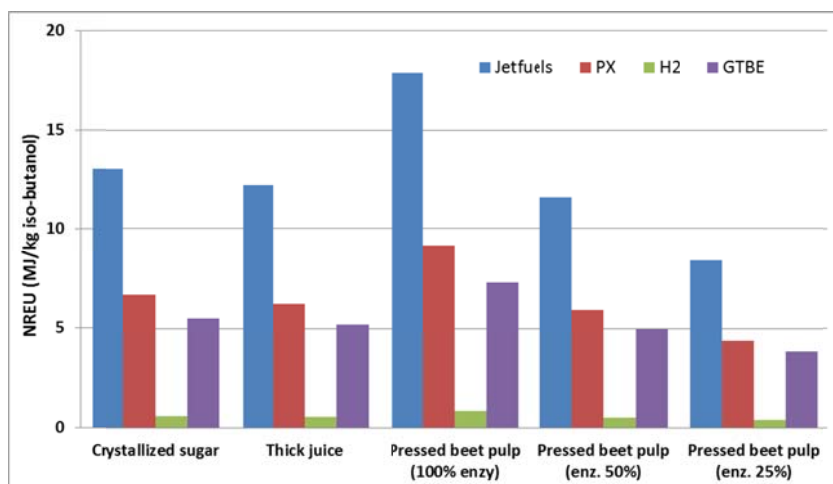


Figure 12-12. NREU for the integrated isobutanol platform per kg of isobutanol (economic allocation), system cradle-to-grave

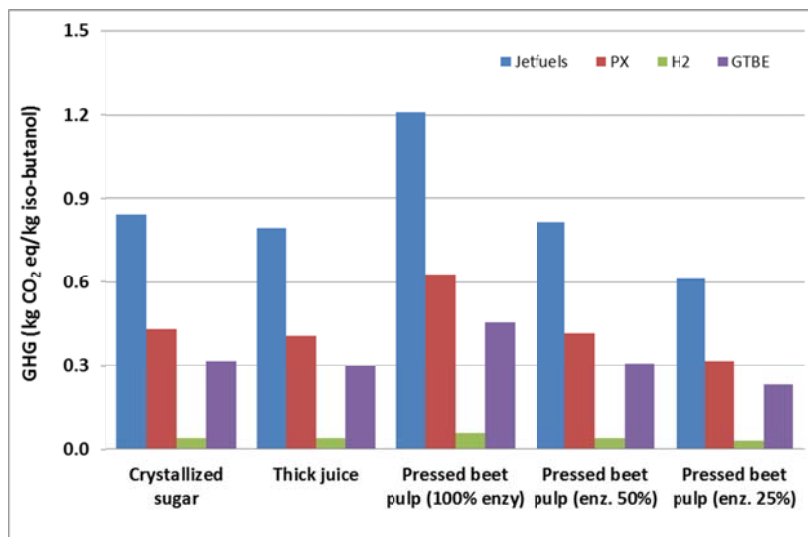


Figure 12-13. GHG for the integrated isobutanol platform per kg of isobutanol (economic allocation), cradle-to-grave

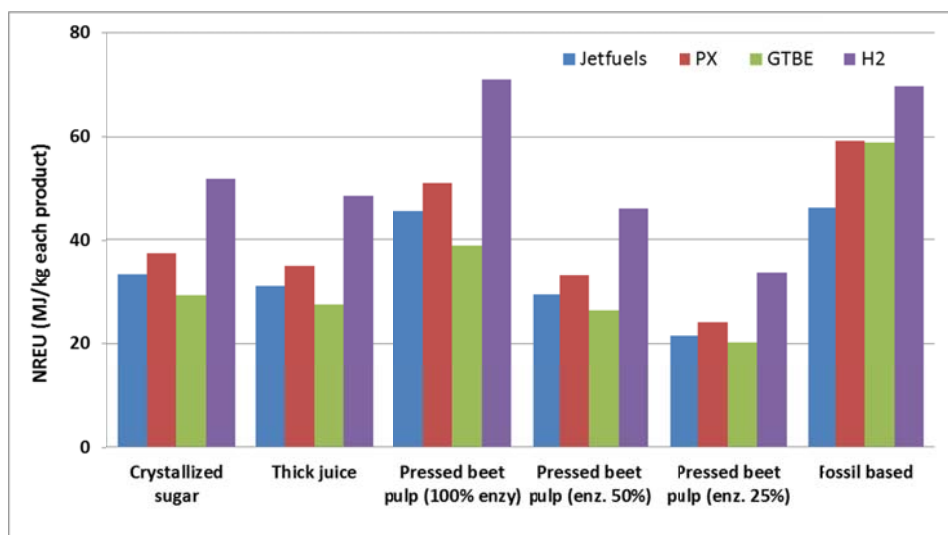


Figure 12-14. NREU of the integrated platform per kg of each final product (economic allocation)

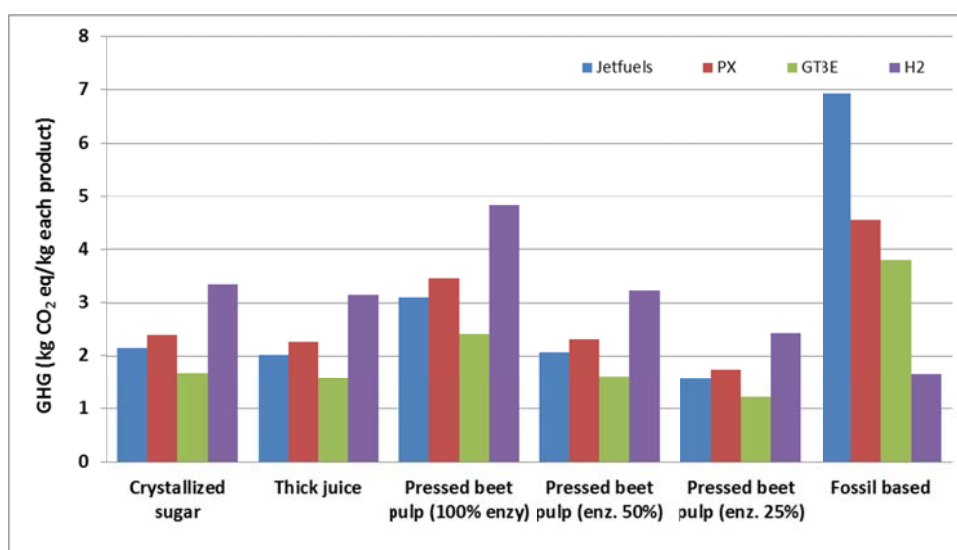


Figure 12-15. GHG NREU of the integrated platform per kg of each final product (economic allocation)

12.4 Interpretation

The total environmental impacts for pressed pulp beet production are in essence the same as those for crystallized sugar, the only difference between these two is the choice of the functional unit, *i.e.* 1 kg of pressed pulp beet vs. 1 kg of crystallized sugar (see Figure 12-1 and Figure 12-2). This is evident when the economic allocation factors are compared for both raw materials (see Figure 12-3). The total environmental impacts for thick juice production are the lowest (see Figure 12-1 and Figure 12-2) because the consumption of natural gas and electricity is assumed to be reduced by 30% and 10% respectively compared to crystallized sugar.

The allocated environmental impacts per kg of raw material are 1.4 times higher for crystallized sugar than those for thick juice and 14.3 times higher than those for pressed pulp beet (Figure 12-4 and Figure 12-5).

The advantageous environmental impacts associated to the pressed beet pulp as raw material disappears in the isobutanol production stage (Figure 12-6 and Figure 12-7). In this case, the environmental impacts for pressed beet pulp processing (per kg of isobutanol produced) are around 10.6-11.3 times higher than those for crystallized sugar and thick juice but these ratios can further be lowered to around 3.5-3.8 if the impacts associated to enzymes production/usage are reduced by 75%.

Once isobutanol is produced and purified², its conversion process is common to the three raw materials and the distinction among the three alternatives is not anymore possible. In this case, steam and glycerol are the main contributors³ (see Figure 12-8 and Figure 12-9). The integrated environmental impacts of the whole isobutanol platform are much lower in almost all cases compared to the fossil-based isobutanol production (see Figure 12-10 and Figure 12-11). For instance, if isobutanol is considered as the final product, the NREU would be reduced by 74%, 76% and 62% by using crystallized sugar, thick juice and pressed pulp beet respectively. In the latter case, a total reduction of 85% could be possible if the emissions associated to the enzymes production/usage are reduced by 75%. For the GHG emissions, these reductions would be 76%, 78% and 62% for crystallized sugar, thick juice and pressed pulp beet respectively. In the latter case, a total reduction of 85% could be possible if the emissions associated to the enzymes production/usage are reduced by 75%.

The total environmental impacts of the isobutanol platform were allocated accordingly to the value flow of the products (Table A- 11) in respective decreasing order: jet fuel, p-xylene, GTBE and H₂ (Figure 12-12 and Figure 12-13).

The NREU for almost every final product is lower than its respective fossil-based counterpart when either crystallized sugar or thick juice is used as raw material as shown in Figure 12-14⁴. This is also the case for pressed pulp beet but only when the impacts associated to enzymes production/usage are reduced to 50% or 25%. Similarly, the GHG emissions (including emissions from the use phase of fuels and end-of-life waste incineration for materials) are in general lower than those from the fossil-based products when crystallized sugar, thick juice or pressed pulp beet (only with the reduced impacts for enzymes production/usage) are used as shown in Figure 12-15. Thus, significant NREU reductions are obtained for jet fuel, p-xylene and GTBE in four of the five analyzed scenarios. On the other hand, considerable GHG emissions reductions are only possible for jet-fuel in the same four

² Purification of iso-butanol is assumed to happen in *PS.//* giving that the waste water stream has already been considered in this processing section.

³ Utilities consumption in the GTBE unit have not been considered due to lack of data.

⁴ The environmental impacts for conventional jet fuel (CJF) and for ultra-low sulfur jet fuel (ULSJF) were taken from Stratton, R. W., H. M. Wong and J. I. Hileman (2010). Life cycle greenhouse gas emissions from alternative jet fuels. Partner project 28 report. Version 1.2. 2010. P. 133. (<http://web.mit.edu/aeroastro/partner/reports/proj28/partner-proj28-2010-001.Pdf>) for three levels of impacts: low (US oil and Straight Run Jet Fuel process), average (weighted average of all crude oil fed into US refineries and weighted average processes) and high (Nigerian crude and Hydroprocessed Jet Fuel). These results are in line with those values provided by the project partners.

SkyNRG provided three values of CO₂ emission for jet fuel production: 82.9 g CO₂/MJ (IPCC), 90.0 g CO₂/MJ (RSB en RED) and 88.1 g CO₂/MJ (EPA). Assuming a LHV of 43.2 MJ/kg, those numbers would be: 3.58 kg CO₂ eq/kg (IPCC), 3.89 kg CO₂ eq/kg (RSB en RED) and 3. 81 kg CO₂ eq/kg (EPA).

cases; however these reductions have major influence on the global performance of the isobutanol platform because jet-fuel has the highest economic weighting factor on the platform. On the contrary, the higher emissions for hydrogen are nearly irrelevant because its weighting factor is around 2%. In the case of p-xylene and GTBE they might compensate the GHG benefits achieved with jet-fuel production. A comparison for each final product has been included in the Annex.

Based on the economic allocation factors of the isobutanol platform, the environmental impacts of an oil-based equivalent platform were calculated. In other words, a theoretical fossil-based system with the same products distribution was assumed and its environmental impacts were calculated as shown in Figure 12-16 and Figure 12-17.

All in all, the isobutanol platform offers significant environmental advantages when crystallized sugar or thick juice is used as raw material. In addition, pressed beet pulp would be an interesting alternative only if the environmental impacts of enzymes production/usage are reduced by more than 50%. The NREU of the whole platform can be reduced by 36%, 40% and 58% with respect to its fossil-based equivalent if crystallized sugar, thick juice and pressed pulp beet (with 25% of the environmental impacts from enzymes) respectively. In the case of GHG emissions these reductions would be 62%, 64% and 72%, respectively.

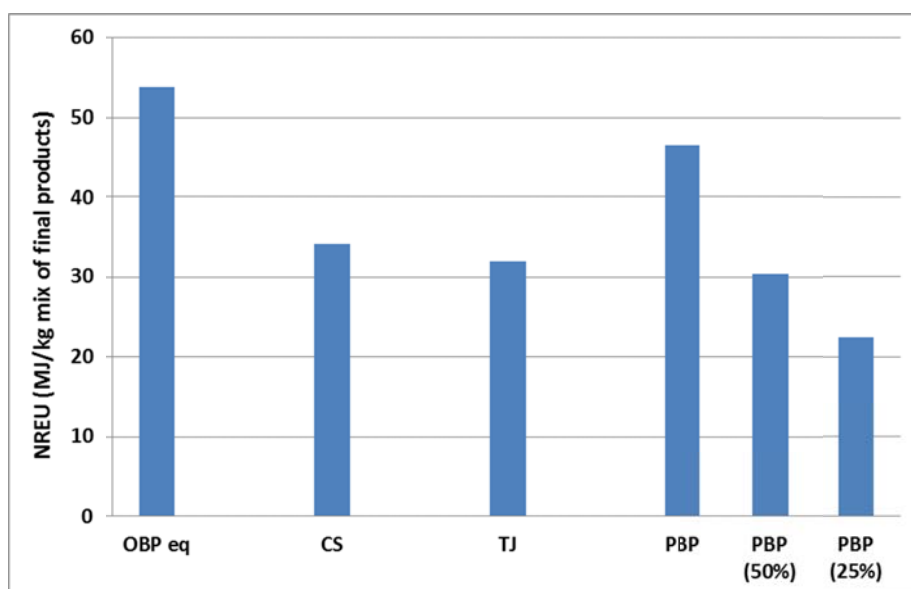


Figure 12-16. Comparison of NREU for isobutanol platform with its oil-based equivalent. **eq**: Oil-based equivalent platform (same products distribution as isobutanol platform); **CS**: Crystallized sugar; **TJ**: Thick juice; **PBP**: Pressed beet pulp; **PBP (50 %)**: Pressed beet pulp with 50% use of enzyme; **PBP (10 %)**: Pressed beet pulp with 10% use of enzyme.

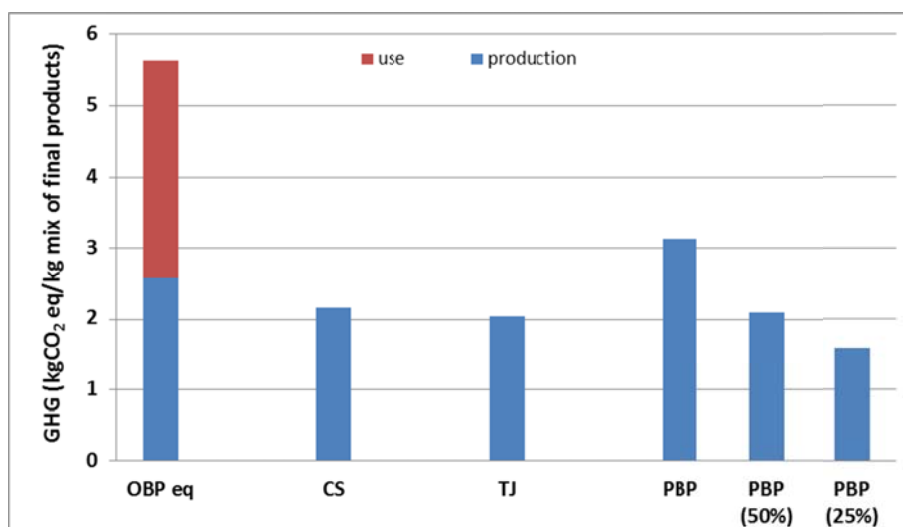


Figure 12-17. Comparison of GHG emissions for isobutanol platform with its oil-based equivalent

13 Conclusions and recommendations

13.1 Conclusions

Based on our literature review, we do not foresee major technical hurdles for the isobutanol platform for most of the steps. However, using current prices, the proposed value chains around isobutanol are not profitable. Thick juice seems too expensive as raw material. Beet pulp is not too expensive, but the enzymes required to hydrolyze beet pulp are estimated to be too expensive.

The environmental impacts associated to enzymes showed to have significant effects on the environmental performance of the isobutanol platform, therefore achievable reductions on its environmental impacts were included as sensitivity analyses scenarios. Integrated results showed that the use of crystallized sugar and thick juice offer environmental benefits for the isobutanol platform with respect to their oil-based counterparts. In addition, pressed pulp beet could also be a suitable raw material if the environmental impacts associated to enzymes are reduced by more than 50%. The NREU of the whole platform can be reduced by approximately 35%, 40% and 60% with respect to its fossil -based equivalent if crystallized sugar, thick juice and pressed pulp beet (with 25% of the environmental impacts from enzymes) respectively. In the case of GHG emissions this reduction would be 60%, 65% and 70% respectively.

13.2 General recommendations

As processes are generally sensitive to minor changes, we recommend that all steps are experimentally verified and catalysts and processes are qualified with products produced from the intended raw material(s).

We also recommend to further refine the economic model with input from technology licensors and the obtained experimental data. The current estimations are not sufficiently accurate. The next stage of the program should aim for -30/+50 % (generally a complete Aspen or similar model based on actual conversions and product distributions).

A third recommendation is to extend the biomass scope with lignocellulose biomass, next to the beet pulp. Lignocellulosic biomass with a combined glucose and xylose content of approximately 50% may provide a sufficiently high isobutanol yield. The “non-fermentable part” contains a significant amount of lignin, which may undergo a cascading process, i.e. initially co-firing it in a power plant, and later upgrading this stream to (marine/jet) fuel components and chemicals. The combination of such a product portfolio may prove to be more economical in the future.

13.3 Recommended upstream work

- To try to avoid the high costs of enzymatic hydrolysis, all existing methods used for lignocellulose pretreatment should be conceptually checked for their suitability for beet pulp hydrolysis.
- Batch enzymatic hydrolysis is the default configuration, but the absence of lignin might enable continuous enzymatic hydrolysis and recycle/retention of the enzymes, and this should be studied. Immobilization on particles seems unsuitable, though, considering the polymeric substrate and the associated danger of diffusion limitation.
- In continuous enzymatic hydrolysis, good enzyme stability can compensate for high a price for a certain enzyme activity. Thus, enzyme stabilization should be focused on.
- Options such as simultaneous enzymatic hydrolysis and fermentation, and consolidated bioprocessing should still be explored. A proof of principle was recently obtained for isobutanol production by consolidated bioprocessing (Minty et al. 2013).
- Maybe microbial cells can be developed that can convert incompletely hydrolyzed beet pulp. It should be estimated if that could lead to savings on enzymes.
- More ideas should be developed considering the valorization of the proteins. Recovery of the proteins or their products should be taken into account.
- Last but not least, the enzymatic hydrolysis of lignocellulosic feedstocks and fermentation to isobutanol from should be explored next to the beet pulp case.

13.4 Recommended downstream experimental work

The conversions of isooctane (or other C8 precursors) need to be further developed. This is expected to require a catalyst and process development program.

The largest downstream expense in the platform is the production of p-xylene.

Typical classes of fermentation impurities investigated in the literature did not negatively impact isobutanol dehydration. However, further experimental work is required in order to determine:

- a) long-term effects of impurities or water content on dehydration catalyst life;
- b) how the impurities affect isobutanol conversion;
- c) how the impurities affect isobutylene selectivity;
- d) the fate of by-products from these impurities on the different downstream processes (depending on the product – p-xylene, jet fuel, GTBE).

13.5 Recommendations from the LCA

The isobutanol platform is conceptually similar to the production process of poly-ethylene from bio-ethanol. In both cases the first step is related to agricultural activities and production of fermentable sugars. In a second step, the alcohols are produced by fermentation and converted to the monoolefin precursor. And in the last step, the added value products are synthesized.

Publically available processing data and internal calculations of UU (for advanced development stage) for bio-poly-ethylene production are used to put into perspective the results here obtained.

The NREU and GHG emissions associated to: fermentation and purification (of ethanol and isobutanol), dehydration (to ethylene and isobutene) and final conversion (to polyethylene and i-C8/i-C12+) of the ethanol-based and isobutanol-based processes were compared (confidential information).

The environmental impacts for the ethanol-based process are in all cases higher than those for the isobutanol-based process. From this perspective, it is recommended to do a more detailed and deeper analysis of the processing data because there are a series of reasons that might lead to higher environmental impacts for the isobutanol-based respect to the ethanol-based process:

1. The alcohol concentration and its production rate are usually lower for the isobutanol process than for the ethanol process due to the higher toxicity of isobutanol, i.e. LD50 ethanol: 6200 mg/kg (rat, oral) and LD50 isobutanol: 2460 mg/kg (rat, oral). In consequence, higher volume of water and higher operation time are expected for the isobutanol process.

2. Both alcohols have a minimum boiling point azeotrope with water but the boiling temperature is higher for the azeotrope isobutanol/water. In addition, the isobutanol concentration in the azeotrope is lower, indicating that more water must be evaporated in the case of isobutanol.

3. The dehydration enthalpy is twice higher for the ethanol process than for isobutanol process. However, the environmental impacts are around four times higher for the ethanol-based process. Assuming that the dehydration reaction is possible using the azeotropic mix alcohol/water (which is the case for ethanol dehydration and no further purification is required), the ratio between both the heats of reaction and the environmental impacts should be nearly equivalent.

4. The ratio between the environmental impacts for both processes may be influenced by the ratio between the molecular weights which is the case for the dehydration reaction. However, this ratio is lower than 1, meaning that if the environmental impacts are compared in a molar basis, the differences will even be higher.

Based on the aforementioned points, it is expected that the environmental impacts of the isobutanol platform increase when more detailed data are available. However, the new impacts could further be reduced by process optimization and heat integration. Thus, one could expect that the final environmental impacts might increase by 10-20% (max.).

13.6 Recommended technology providers

We have identified the following potential technology providers for the different steps:

- Enzymatic hydrolysis: **Dyadic**, Dupont, **DSM**
- Fermentation: **GEVO**, **BUTAMAX**, Global Bioenergies
- Isobutanol dehydration: CBI (formerly ABB-Lummus), Axens, CD-Tech (part of Lummus), Uhde
- Oligomerisation UOP, Axens, Dupont, CBI, KBR, CD-Tech, Snamprogetti (SAIPEM), Uhde, Huls
- Aromatization UOP, Chevron, SABIC, Exxon, GTC
- Hydrogenation UOP, Chevron, CBI, Axens, refining hydrocarbon technologies, KBR, CD-Tech, Snamprogetti

The ones in boldface are proposed to be contacted for follow-up work.

13.7 Proposed project plan 2nd phase

Based on the aforementioned recommendations that originate from different sections within the IBPR, overall recommendations have been formulated which are implicitly included in the subsequent research plan for the next phase (18 months). If agreed upon, the plan will need to be detailed with respect to timing and use of financial resources.

13.7.1 Pilot production of GTBE from beet sugar.

On the basis of the results, there is already sufficient incentive to try to obtain several hundred liters of GTBE from thick juice by pilot production. This amount should suffice for motor tests such as those that are mandatory for selling fuels. The required amount corresponds to fermentations to obtain ~500 kg isobutanol. Pilot facilities that can provide this within a reasonable time are available in the Netherlands, but might also be provided by the aforementioned fermentation technology providers.

Partner responsible for a detailed plan: GTBE Company / Procede.

13.7.2 Conceptual evaluation of lignocellulose as feedstock for an isobutanol platform

For jet fuels and p-xylene, the current economic calculations indicate that other feedstocks or routes should be explored. It is proposed to explore lignocellulose, which may allow valorization of lignin as co-product. By analogy to the current study, the economic feasibility should be calculated.

Partner responsible for a detailed plan: Zirk-tech.

13.7.3 Lab-scale testing of production of jet fuels and p-xylene

In case the previous step has an economically favourable outcome (according to an intermediate go/no-go decision), the conversion of fermentative isobutanol to jet fuels and p-xylene should be tested on lab scale to obtain up to a few kg product.

Partners responsible for a detailed plan: Zirk-tech and ECN.

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Appendix 1. Notation used

Abbreviations

IBPR Isobutanol Platform Rotterdam

RCI Rotterdam Climate Initiative

Symbols

t metric tonne

\$ US dollars

Appendix 2. Patents related to isobutanol production

All the patents found related to isobutanol production and recovery from the main technology providers discussed in Section 5.2 are gathered in Table A- 1.

Butamax Advanced Biofuels

Table A- 1: Granted US patents of Butamax Advanced Biofuels related to production and recovery of isobutene

Patent #	Title
8,373,009	Recovery of butanol from a mixture of butanol, water, and an organic extractant
8,373,008	Recovery of butanol from a mixture of butanol, water, and an organic extractant
8,372,612	Production of four carbon alcohols using improved strain
8,283,144	Fermentative production of four carbon alcohols
8,273,558	Fermentative production of four carbon alcohols
8,241,878	Recombinant yeast host cell with Fe-S cluster proteins and methods of using thereof
8,222,017	Ketol-acid reductoisomerase using NADH
8,206,970	Production of 2-butanol and 2-butanone employing aminobutanol phosphate phospholyase
8,188,250	Butanol dehydrogenase enzyme from the bacterium <i>Achromobacter xylosoxidans</i>
8,178,328	Fermentative production of four carbon alcohols
8,129,162	Ketol-acid reductoisomerase using NADH
8,017,364	Solvent tolerant microorganisms
7,993,889	Fermentative production of four carbon alcohols
7,910,342	Fermentative production of isobutanol using highly active ketol-acid reductoisomerase enzymes
7,851,188	Fermentative production of four carbon alcohols

Table A- 2: Patent applications of Butamax Advanced Biofuels related to production and recovery of isobutene

Patent #	Title
20130001061	Recovery of butanol from a mixture of butanol, water, and an organic extractant
20120323047	Use of thiamine and nicotine adenine dinucleotide for butanol production
20120322117	Enzymatic production of alcohol esters for recovery of diols produced by fermentation
20120258873	Reduction of 2,3-dihydroxy-2-methyl butyrate (dhmb) in butanol production
20120237988	Butanol strain improvement with integration of a polynucleotide encoding a polypeptide that catalyzes pyruvate to acetolactate conversion
20120231515	Butanol dehydrogenase enzyme from the bacterium <i>achromobacter xylosoxidans</i>
20120208246	Production of alcohol esters and in situ product removal during alcohol fermentation
20120196341	Fermentive production of four carbon alcohols
20120164302	Methods and systems for removing undissolved solids prior to extractive fermentation in the production of butanol
20120156738	Production of alcohol esters and in situ product removal during alcohol fermentation
20120156735	Recombinant host cells comprising phosphoketolases
20120151996	Oxygenated butanol gasoline composition having good driveability performance
20120149080	Yeast production culture for the production of butanol
20120144902	Oxygenated butanol gasoline composition having good driveability performance
20120064561	Activity of fe-s cluster requiring proteins
20120058541	Engineering resistance to aliphatic alcohols
20120035398	Process to remove product alcohol from a fermentation by vaporization under vacuum
20120015416	Expression of hexose kinase in recombinant host cells
20110315541	Systems and methods for alcohol recovery and concentration of stillage by-products
20110313206	Fermentive production of four carbon alcohols
20110312053	Supplementation of fatty acids for improving alcohol productivity
20110312044	Extraction solvents derived from oil for alcohol removal in extractive fermentation
20110312043	Extraction solvents derived from oil for alcohol removal in extractive fermentation
20110301388	Fermentive production of four carbon alcohols
20110294179	Method for producing butanol using two-phase extractive fermentation

20110288345	Recovery of butanol from a mixture of butanol, water, and an organic extractant
20110288344	Recovery of butanol from a mixture of butanol, water, and an organic extractant
20110283604	Biodegradation of renewable hydrocarbon fuel blends
20110269199	Alcohol dehydrogenases (adh) useful for fermentive production of lower alkyl alcohols
20110250610	Fermentive production of isobutanol using highly active ketol-acid reductoisomerase enzymes
20110244536	Fermentive production of isobutanol using highly effective ketol-acid reductoisomerase enzymes
20110195505	Bacterial strains for butanol production
20110162953	Recovery of butanol from a mixture of butanol, water, and an organic extractant
20110159558	Method for producing butanol using extractive fermentation with electrolyte addition
20110136193	Method for producing butanol using extractive fermentation with osmolyte addition
20110136192	Flux to acetolactate-derived products in lactic acid bacteria
20110124060	Yeast production host cells
20110112334	Fermentive production of four carbon alcohols
20110111472	Fermentive production of four carbon alcohols
20110097773	Method for producing butanol using extractive fermentation
20110023354	Reduced rvp oxygenated gasoline composition and method
20100221802	Method for producing butanol using two-phase extractive fermentation
20100221801	Yeast with increased butanol tolerance involving a multidrug efflux pump gene
20100167365	Yeast with increased butanol tolerance involving high osmolarity/glycerol response pathway
20100167364	Yeast with increased butanol tolerance involving cell wall integrity pathway
20100167363	Yeast with increased butanol tolerance involving filamentous growth response
20100136641	Strain for butanol production with increased membrane unsaturated trans fatty acids
20100129887	Increased production of isobutanol in yeast with reduced mitochondrial amino acid biosynthesis
20100129886	Production of isobutanol in yeast mitochondria
20100120105	Carbon pathway optimized production hosts for the production of isobutanol
20100112655	Enhanced pyruvate to 2,3-butanediol conversion in lactic acid bacteria
20100093020	Solvent tolerant microorganisms and methods of isolation
20100081183	Enhanced dihydroxy-acid dehydratase activity in lactic acid bacteria
20100081182	Enhanced iron-sulfur cluster formation for increased dihydroxy-acid dehydratase activity in lactic acid bacteria
20100081179	Increased heterologous fe-s enzyme activity in yeast
20100081154	Identification and use of bacterial [2fe-2s] dihydroxy-acid dehydratases

Gevo Inc.

Table A- 3: Granted US patents of Gevo Inc. related to production and recovery of isobutene

Patent #	Title
8,373,012	Renewable jet fuel blendstock from isobutanol
8,304,588	Recovery of higher alcohols from dilute aqueous solutions
8,283,505	Recovery of higher alcohols from dilute aqueous solutions
8,273,565	Methods of increasing dihydroxy acid dehydratase activity to improve production of fuels, chemicals, and amino acids
8,232,089	Cytosolic isobutanol pathway localization for the production of isobutanol
8,193,402	Renewable compositions
8,158,404	Reduced by-product accumulation for improved production of isobutanol
8,153,415	Reduced by-product accumulation for improved production of isobutanol
8,133,715	Reduced by-product accumulation for improved production of isobutanol
8,101,808	Recovery of higher alcohols from dilute aqueous solutions
8,097,440	Engineered microorganisms capable of producing target compounds under anaerobic conditions
8,071,358	Methods of increasing dihydroxy acid dehydratase activity to improve production of fuels, chemicals, and amino acids

8,017,376	Methods of increasing dihydroxy acid dehydratase activity to improve production of fuels, chemicals, and amino acids
8,017,375	Yeast organism producing isobutanol at a high yield

Table A- 4: Patent applications of Gevo Inc. related to production and recovery of isobutene

Patent #	Title
20120323055	Renewable compositions
20120288910	Methods of increasing dihydroxy acid dehydratase activity to improve production of fuels, chemicals, and amino acids
20120271082	Variations on prins-like chemistry to produce 2,5-dimethylhexadiene from isobutanol
20120190089	Engineered microorganisms capable of producing target compounds under anaerobic conditions
20120171741	Renewable Xylenes Produced from Biological C4 and C5 Molecules
20120107891	Recovery of higher alcohols from dilute aqueous solutions
20120107890	Recovery of higher alcohols from dilute aqueous solutions
20120058532	Engineered microorganisms capable of producing target compounds under anaerobic conditions
20120045809	Engineered Microorganisms for the Production of One or More Target Compounds
20120040080	Methods for the economical production of biofuel precursor that is also a biofuel from biomass
20120034666	Methods of increasing dihydroxy acid dehydratase activity to improve production of fuels, chemicals, and amino acids
20120028324	Engineered microorganisms capable of producing target compounds under anaerobic conditions
20120028323	Yeast organism producing isobutanol at a high yield
20120028322	Methods of increasing dihydroxy acid dehydratase activity to improve production of fuels, chemicals, and amino acids
20120015417	Methods of increasing dihydroxy acid dehydratase activity to improve production of fuels, chemicals, and amino acids
20110318799	Yeast organism producing isobutanol at a high yield
20110288352	Renewable jet fuel blendstock from isobutanol
20110287500	Cytosolic isobutanol pathway localization for the production of isobutanol
20110275129	Reduced by-product accumulation for improved production of isobutanol
20110236942	Reduced by-product accumulation for improved production of isobutanol
20110201090	Yeast microorganisms with reduced by-product accumulation for improved production of fuels, chemicals, and amino acids
20110201073	Reduced by-product accumulation for improved production of isobutanol
20110201072	Modified alcohol dehydrogenases for the production of fuels and chemicals
20110183393	Methods of increasing dihydroxy acid dehydratase activity to improve production of fuels, chemicals, and amino acids
20110183392	Yeast organism producing isobutanol at a high yield
20110172475	Integrated methods of preparing renewable chemicals
20110087000	Integrated Process to Selectively Convert Renewable Isobutanol to P-Xylene
20110076733	Cytosolic isobutanol pathway localization for the production of isobutanol
20100062505	Butanol production by metabolically engineered yeast
20090246842	Engineered microorganisms for producing propanol
20090226991	Yeast organism producing isobutanol at a high yield
20090226990	Methods for the economical production of biofuel from biomass
20090215137	Methods for the economical production of biofuel precursor that is also a biofuel from biomass
20090171129	Recovery of higher alcohols from dilute aqueous solutions
20090155869	Engineered microorganisms for producing n-butanol and related methods
20080293125	Engineered microorganisms for producing isopropanol

Appendix 3. Isobutanol dehydration

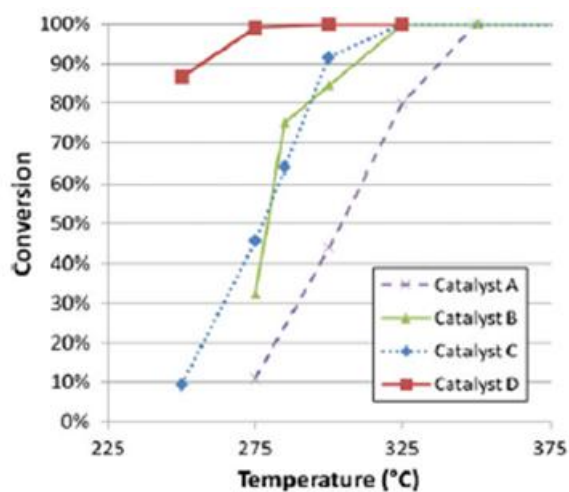


Figure A- 1. Conversion of isobutanol versus temperature over four catalysts (Taylor et al. 2010).

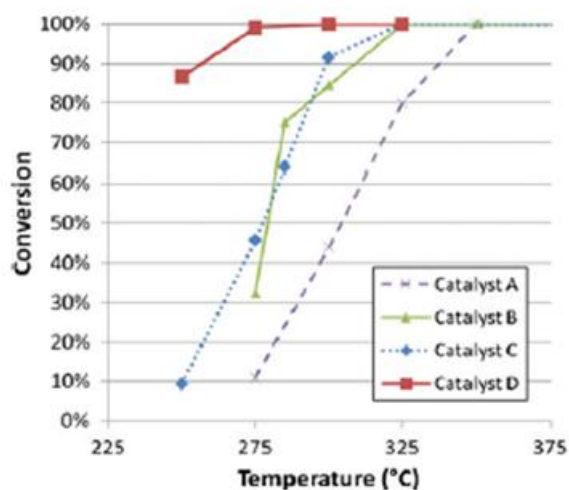
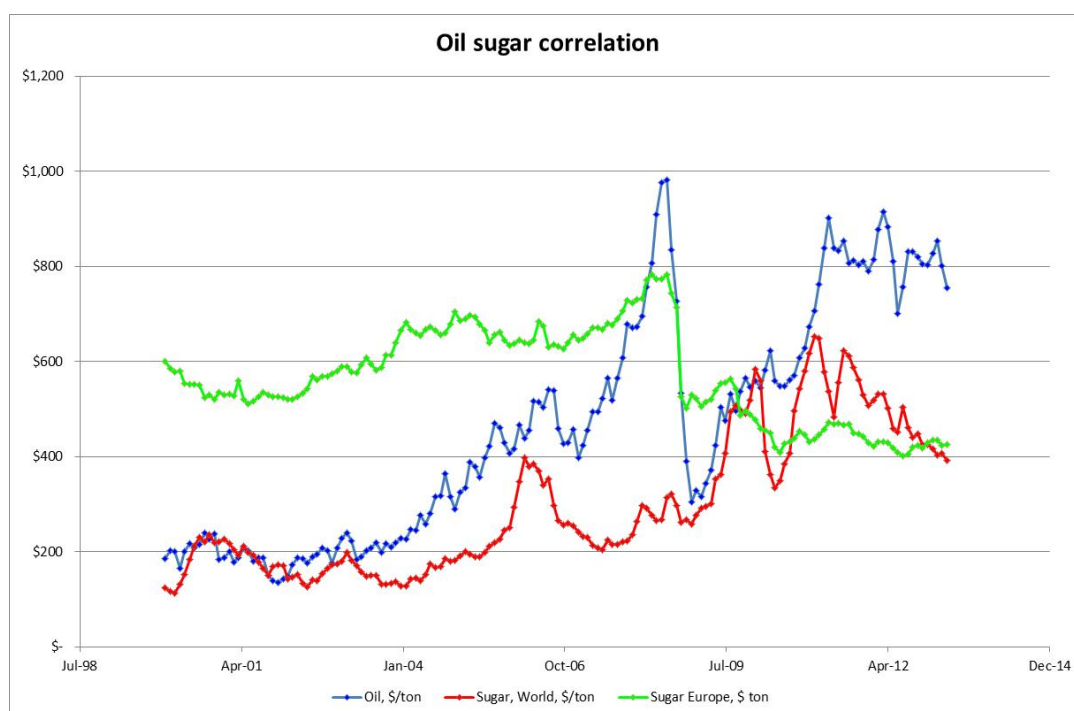
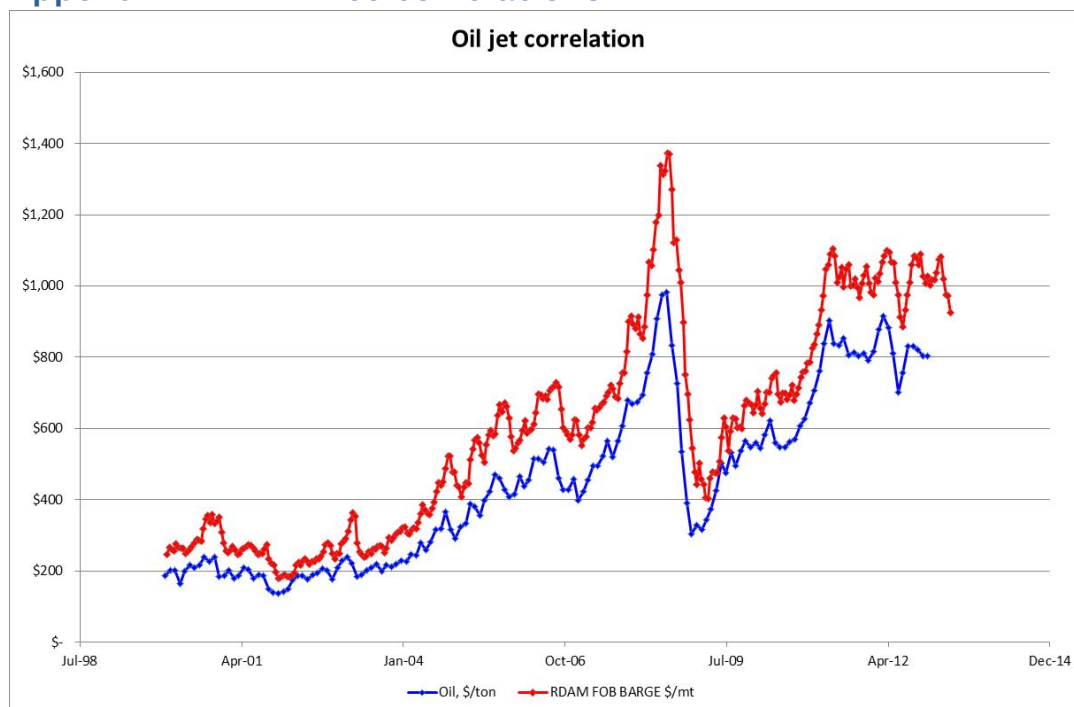
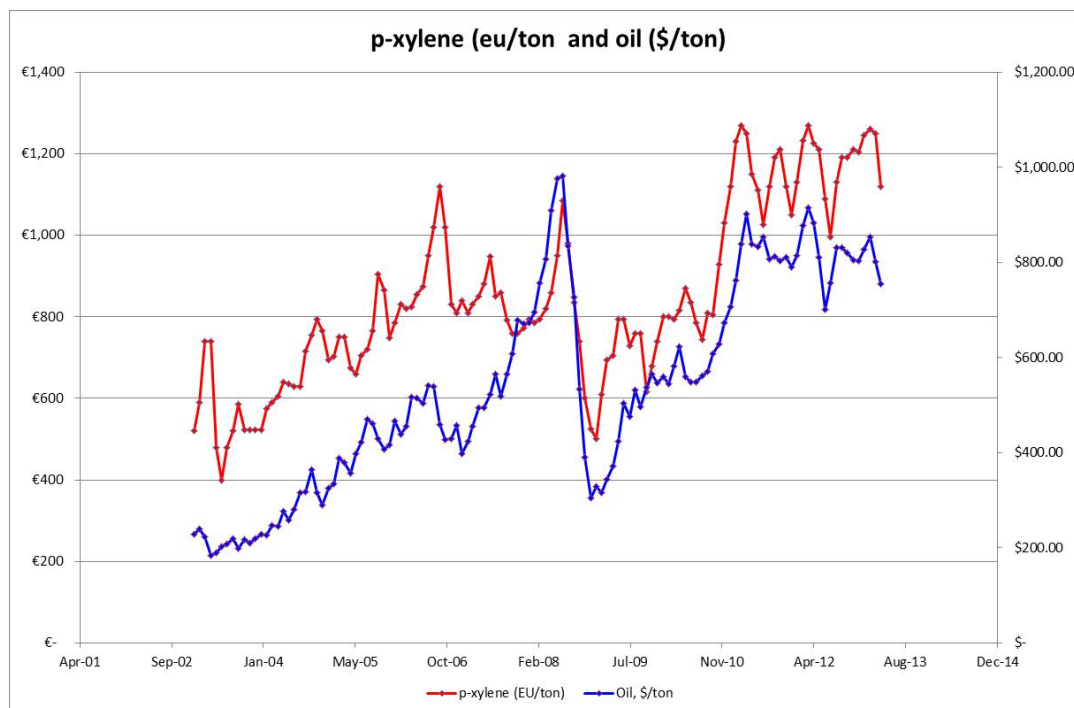


Figure A- 2. Selectivity to isobutylene versus temperature (Taylor et al. 2010).

Appendix 4. Price correlations





Sugar (WORLD) and oil	78.4%
Oil and Jet	99.1%
SUAGR (EU) and oil	-22.5%
p-xylene to oil	85.0%

Ratios

Jet over sugar low	1.05
Jet over sugar high	4.93
Jet over sugar median	1.97
p-xylene over sugar low	1.23
p-xylene over sugar high	4.63
p-xylene over sugar median	2.83
p-xylene over sugar average	2.89

Appendix 5. LCA

The life cycle and process description

The isobutanol platform can be divided in three key processing sections and 11 modules:

S.I. (Section I) Production of feedstocks

M.A. Growing and harvesting of sugar beet

M.B. Processing of sugar beet

S.II. (Section II) Production of isobutanol

M.C. Pretreatment of feedstocks

M.D. Fermentation of sugars to isobutanol

S.III. (Section III) Production of fuels/chemicals

M.E. Dehydration of isobutanol to isobutene

M.F. Etherification of isobutene to tri glycerol tertiary butyl ether (GTBE)

M.G. Oligomerization of isobutene to i-C8 and i-C12/i-C16 fractions

M.H. Separation of i-C8 and i-C12/i-C16 fractions

M.I. Hydrogenization of i-C12/i-C16 fraction to Jet-fuel

M.J. Reforming of i-C8 fraction to BTX/PX

The first section involves all agricultural activities for sugar beet production (*i.e.* seeding, farming and harvesting) including transportation from the cultivation farms to the milling facilities of *Suiker Unie*. In a second step, sugar beet are processed into either crystalized sugar or thick juice, generating significant amounts of by-products and wastes (*i.e.* molasses, sugar factory lime, wet beet pulp, pressed beet pulp and dry beet pulp). Some of these by-products can be recycled to the initial agricultural stages or can alternatively be used as raw materials for further conversion processes.

The milling process produces three potential raw materials that can be used for isobutanol production in the second processing section, they are: *i)* crystalized sugar, *ii)* thick juice and *iii)* pressed beet pulp.

The simplified flow diagram of the isobutanol platform is shown in Figure A- 3.

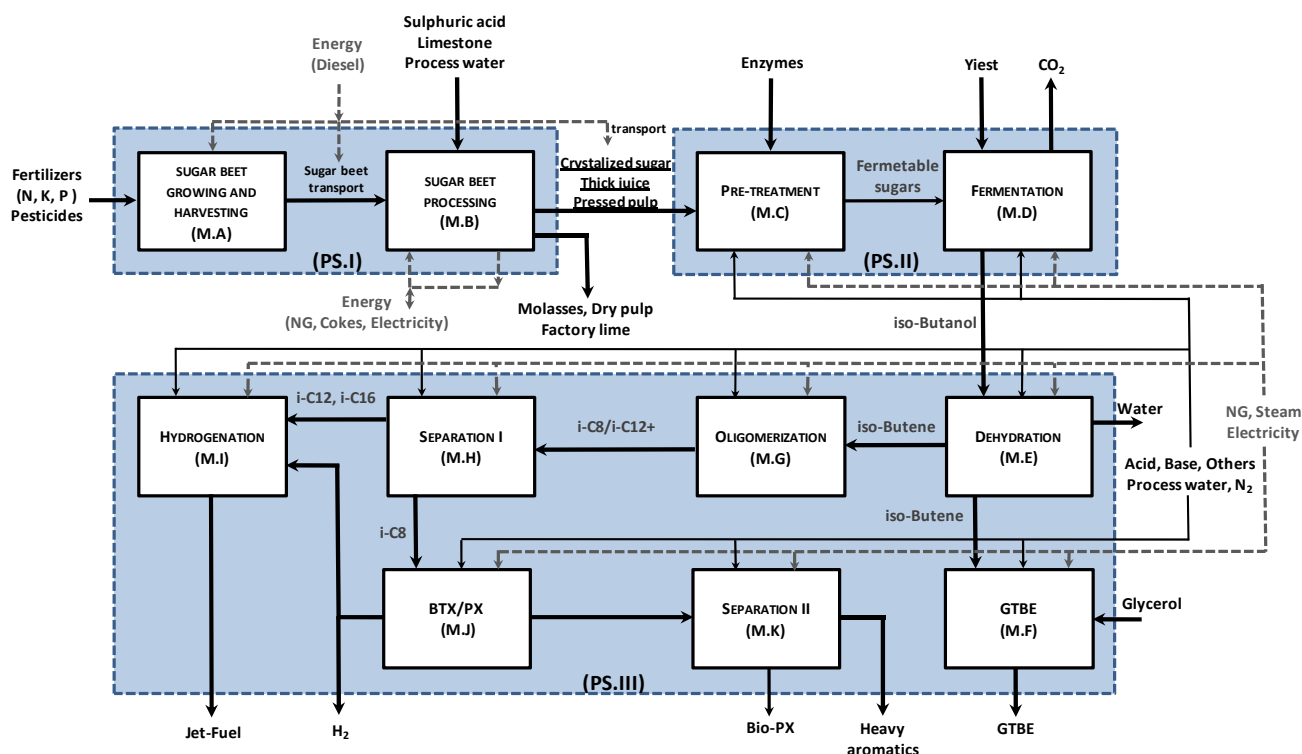


Figure A- 3: Flow diagram of the isobutanol platform. (PS: Processing Section, M: Module).

The mass and energy balances for Section I and Section II differ for each raw material since different quantities and processing units are required; while for Section III the mass and energy balances are identical per kg of isobutanol for the three raw materials (*i.e.*, the processing units and services requirements are the same per kg of isobutanol and consequently per kg of the final mix of products). The mass and energy balances are presented in Appendix 5.

Life cycle inventory data

Two sources are used for the mass and energy balances:

- the inputs and outputs data file provided by Suiker Unie for the Campaign 2012.
- the excel document “bijlage 4 - IBPR process economics_Finconcept” distributed to the all project partners.

Material and energy inputs/outputs

For sugar beet production and processing (*i.e.* PS.I. and PS.II.), data for the 2012 campaign was used.

The mass and energy inputs/outputs for sugar beet production and processing are shown in Table A- 5 and Table A- 6, respectively, per 1 kg of raw material produced.

The material and energy inputs/outputs for isobutanol production are shown in Table A- 7 and Table A- 8, respectively, per 1 kg of isobutanol produced.

The material and energy inputs/outputs for isobutanol conversion to fuels/chemicals are shown in Table A- 9 and

Table A- 10, respectively, per 1 kg of isobutanol utilized.

Prices of products and by-products used are shown in Table A- 11.

Inventory assumptions

To complete the mass and energy inputs/outputs tables, the following assumptions were made:

1. di- and tri-glycerol tert-butyl ether (GTBE) are produced in a ratio product 85% and 15 % respectively⁵.
2. Thick juice is assumed to be the mix of molasses + crystallized sugar, for mass balance effects (70-80% dm.).
3. For thick juice production, the consumption of heating and electricity is reduced by 30% and 10% respectively compared to the crystallized sugar production.
4. Biogas and electricity production in *PS.I* were included based on the mass and energy balances provided by Suiker Unie.
5. For economic allocation the prices provided by Suiker Unie were used (they provided prices for almost all by-products).
6. A price of 1.0 euro/ton for wet beet pulp was used for allocation purposes.
7. The environmental impacts of enzymes production were calculated based on the NREL report (mass and energy balances).(Humbird et al. 2011) However, the use of enzymes and (consequently) their impacts might be reduced in the short term.(Nielsen et al. 2007; Zhu and Zhuang 2012) The effect of this input is analyzed throughout the paper.
8. LHV Cokes: 29.5 MJ/kg; LHV NG: 47.14 MJ/kg; LHV Conventional Jet Fuel: 43.1 MJ/kg; LHV Ultra-Low Sulfur Jet Fuel: 43.1 MJ/kg. NG density: 0.777 kg/m³. Carbon content of Conventional Jet Fuel: 85.9%; Carbon content of Ultra-Low Sulfur Jet Fuel: 86.2% (GREET 2010; Stratton et al. 2010).
9. Prices for H₂: 2000 €/ton and GTBE: 750 €/ton (30% higher than MTBE: 750 USD/ton, exchange rate of 0.77 euro/USD). These values were used for the economic allocation.
10. Energy process for the GTBE unit was assumed to be equal to this for MTBE.
11. The use of acid, base and other (as provided in the mass balances of the economic analysis) were assumed to correspond to: hydrochloric acid, sodium hydroxide, and oil-based isobutanol⁶.
12. For waste water: 50.0 kg COD/m³ (Patel et al. 2006), and 0.3 Nm³ biogas/kg COD.⁷
13. For the fuels studied (jet fuel and GTBE), their production and combustion for propulsion was assumed. By analogy, for materials (para-xylene), all steps of production and end-of-life waste management by incineration are considered. We therefore refer to the system boundaries as cradle-to-grave LCA.

⁵ Communication with Sjaak van Loo

⁶ The assumption of iso-butanol usage as "other components" is intended to reduce the effect of these unknown materials (*i.e.*, "other components") on the final environmental analysis. To that end the most standard compound is selected.

⁷ Data shared by M.Sc. Mehboob Nawas (from UU) from communication with Henk Dijkman from PAQUES.

Table A- 5. Material inputs and outputs for sugar beet production and processing

Material:	Units	Crystallized sugar	Thick juice	Pressed beet pulp
Inputs				
N fertilizer	kg N/ton RM	8.92	7.54	8.71
P fertilizer	kg P ₂ O ₅ /ton RM	3.15	2.67	3.08
K fertilizer	kg K ₂ O/ton RM	6.52	5.51	6.36
lime fertilizer	kg CaCO ₃ /ton RM	12.48	10.56	12.19
pesticides	kg/ton RM	0.38	0.32	0.37
sowing seeds	kg/ton RM	0.19	0.16	0.19
sulfuric acid	liter/ton RM	1.81	1.53	1.77
limestone	kg/ton RM	8.84	7.47	8.63
process water	m ³ /ton RM	0.26	0.22	0.25
Outputs				
crystallized sugar	kg/ton RM	1000	0	976
molasses	kg/ton RM	182	0	178
sugar factory lime	kg/ton RM	191	162	187
thick juice	kg/ton RM	0	1000	0
wet beet pulp	kg/ton RM	0	0	0
pressed beet pulp	kg/ton RM	1024	866	1000
dry beet pulp	kg/ton RM	52	44	51

* RM: specific raw material: crystallized sugar, thick juice or pressed beet pulp

Table A- 6. Energy inputs and outputs for sugar beet production and processing

Energy:	Units	Crystallized sugar	Thick juice	Pressed beet pulp
Inputs				
diesel	liter/ton RM	8.85	7.48	8.64
cokes	kg/ton RM	1.18	1.00	1.15
NG for sugar production	m ³ /ton RM	116.70	69.11	113.96
NG for drying of beet pulp	m ³ /ton RM	9.46	8.00	9.24
NG for pressing dry beet pulp	m ³ /ton RM	0.86	0.73	0.84
electricity from the grid	kWh/ton RM	18.21	13.87	17.79
Outputs				
biogas (own production)	m ³ CH ₄ /ton RM	15.89	13.45	15.52
electricity to the grid)	kWh/ton RM	31.06	26.27	30.33

Table A- 7. Material inputs and outputs for isobutanol production

Material:	Units	Crystallized sugar	Thick juice	Pressed beet pulp
Inputs				
crystallized sugar	kg/ton isobutanol	2701	0	0
thick juice	kg/ton isobutanol	0	3376	0
pressed beet pulp	kg/ton isobutanol	0	0	6242
enzymes	kg/ton isobutanol	1.0	1.0	220.0
yeast	kg/ton isobutanol	100	100	100
acid	kg/ton isobutanol	0.10	0.10	0.10
base	kg/ton isobutanol	0.10	0.10	0.10
others	kg/ton isobutanol	0.10	0.10	0.10
process water	kg/ton isobutanol	45	60	120
nitrogen	kg/ton isobutanol	0.75	1.00	1.00
Output	Units	Crystallized sugar	Thick juice	Pressed beet pulp
waste water	kg/ton isobutanol	75	100	160
isobutanol	kg/ton isobutanol	1000	1000	1000

Table A- 8. Energy inputs for isobutanol production

Energy:	Units	Crystallized sugar	Thick juice	Pressed beet pulp
Inputs				
electricity	kWh/ton isobutanol	0.038	0.050	0.100
natural gas	m ³ /ton isobutanol	7.50E-07	1.00E-06	1.00E-06
steam	kg/ton isobutanol	113	150	300

Table A- 9. Material inputs and outputs for isobutanol conversion to fuel/chemicals

Material	Units	Dehyd.	Oligom.	Hydrog.	BTX/PX	GTBE
Inputs						
glycerol	kg/ton isobutanol	0	0	0	0	56.1
acid	kg/ton isobutanol	0.072	0.061	0.039	0.018	X
base	kg/ton isobutanol	0.072	0.061	0.039	0.018	X
others	kg/ton isobutanol	0.072	0.061	0.039	0.018	X
process water	kg/ton isobutanol	13641	13834	63.0	2168	X
nitrogen	kg/ton isobutanol	0.72	0.61	0.39	0.18	X
Output						
PX	kg/ton isobutanol	0	0	0	181	0
H ₂	kg/ton isobutanol	0	0	0	9	0
Jetfuel	kg/ton isobutanol	0	0	394	0	0
GTBE	kg/ton isobutanol	0	0	0	0	190
Intermediate						
isobutene to oligom	kg/ton isobutanol	719	0	0	0	X
isobutene to GTBE	kg/ton isobutanol	72	0	0	0	X
i-C8	kg/ton isobutanol	0	205	0	0	X
i-C12, i-C16	kg/ton isobutanol	0	410	0	0	X

Table A- 10. Energy inputs and outputs for isobutanol conversion to fuel/chemicals

Energy	Units	Dehyd.	Oligom.	Hydrog.	BTX/PX	GTBE*
Inputs						
electricity	kWh/ton isobutanol	3.90	0.25	0.25	18.43	X
natural gas	m ³ /ton isobutanol	7.19E-07	6.15E-07	3.94E-07	1.81E-07	X
steam	kg/ton isobutanol	237.3	350.5	225	90	X

* see assumption 10.

Table A- 11. Sale prices of raw materials, by-products, intermediates and final products

Product	euro/ton	Product	euro/ton	Economic allocation factors for products**
granulated sugar	400	isobutanol	616	
molasses	130	isobutene	731.5	
sugar factory lime	4.1	Jet-fuel	962.5	0.5198
thick juice	375	PX	1078	0.2670
wet beet pulp	1.0	H ₂	1500	0.0177
pressed beet pulp	28.0	GTBE	750.8	0.1954
dry beet pulp	170.0			

** relative to the total of all outputs

Individual comparison of environmental impacts for each product

Notation in the figures:

CJF, high: Conventional Jet Fuel, High (hydroprocessing);

CJF, baseline: Conventional Jet Fuel, Baseline (Average);

CJF, low: Conventional Jet Fuel, Low (Straight Run Process);

ULSJF, high: Ultra-Low Sulfur Jet Fuel from Conventional Crude, High (hydroprocessing);

ULSJF, baseline: Ultra-Low Sulfur Jet Fuel from Conventional Crude, Baseline (Average);

ULSJF, low: Ultra-Low Sulfur Jet Fuel from Conventional Crude, Low (Straight Run Process) (all previous impacts were taken from (Zhu and Zhuang 2012));

PX (SP): p-xylene (simapro);

H₂ (SP): hydrogen (simapro);

MTBE (SP): Methyl tert-butyl ether (simapro);

MeOH (SP): Methanol (simapro); **Gly (SP):** Glycerol (simapro);

CS: Crystallized sugar;

TJ: Thick juice;

PBP: Pressed beet pulp;

PBP (50 %): Pressed beet pulp with 50% use of enzyme;

PBP (25 %): Pressed beet pulp with 25% use of enzyme.

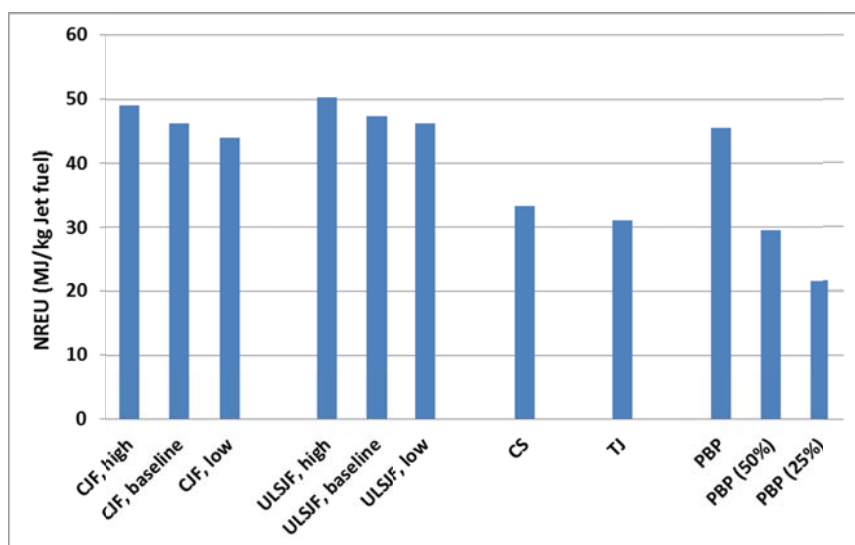


Figure A- 4. Comparison of NREU for jet fuel.

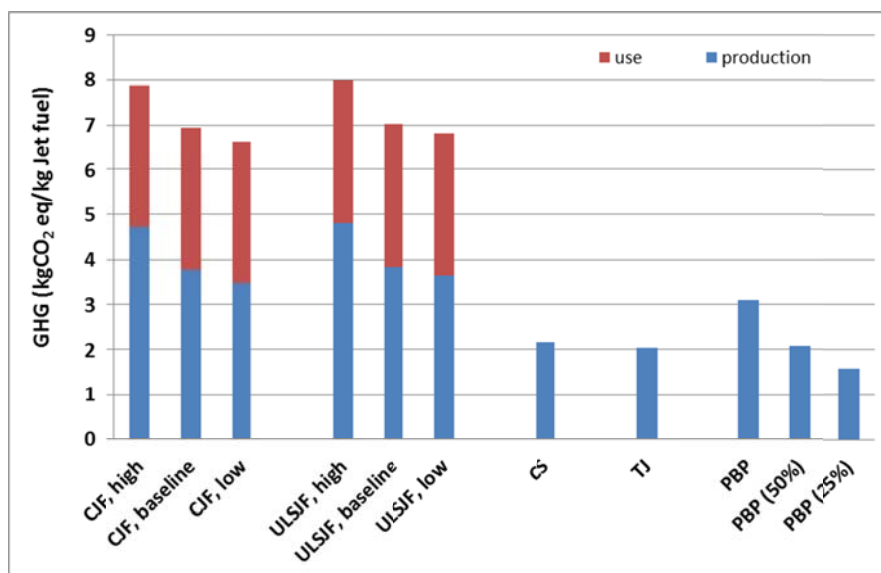


Figure A- 5. Comparison of GHG for jet fuel.

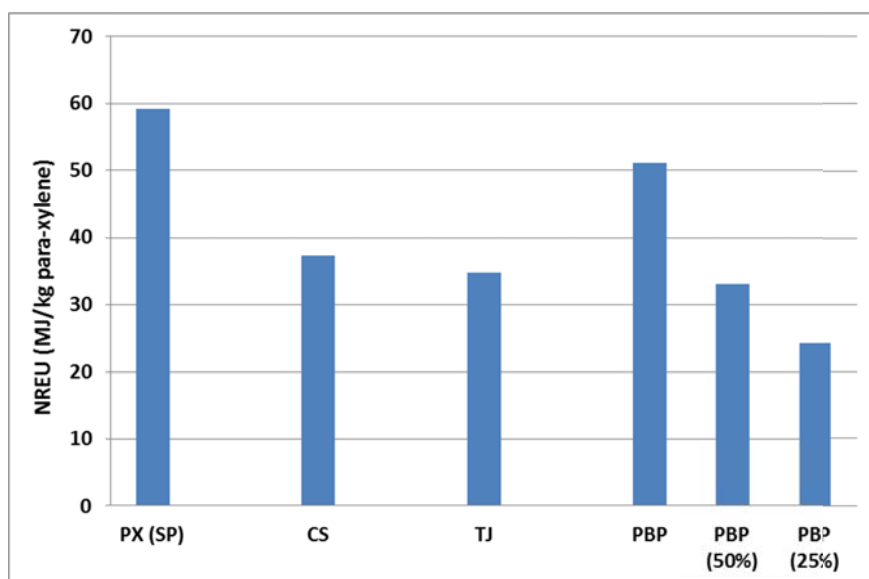


Figure A- 6. Comparison of NREU for p-xylene.

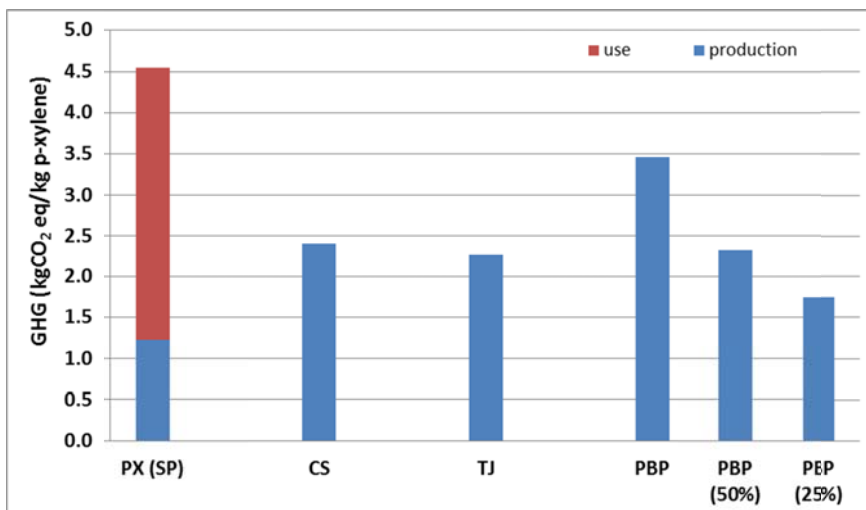


Figure A- 7. Comparison of GHG emissions for p-xylene.

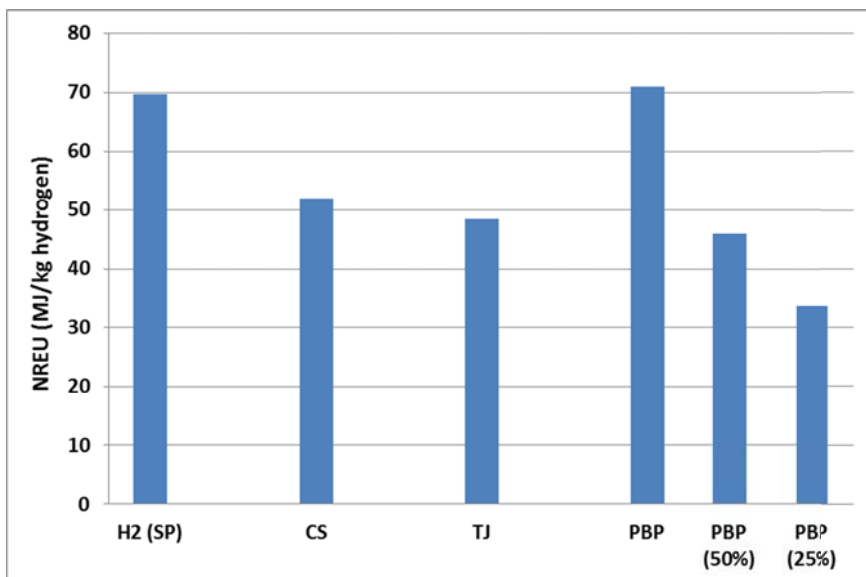


Figure A- 8. Comparison of NREU for hydrogen.

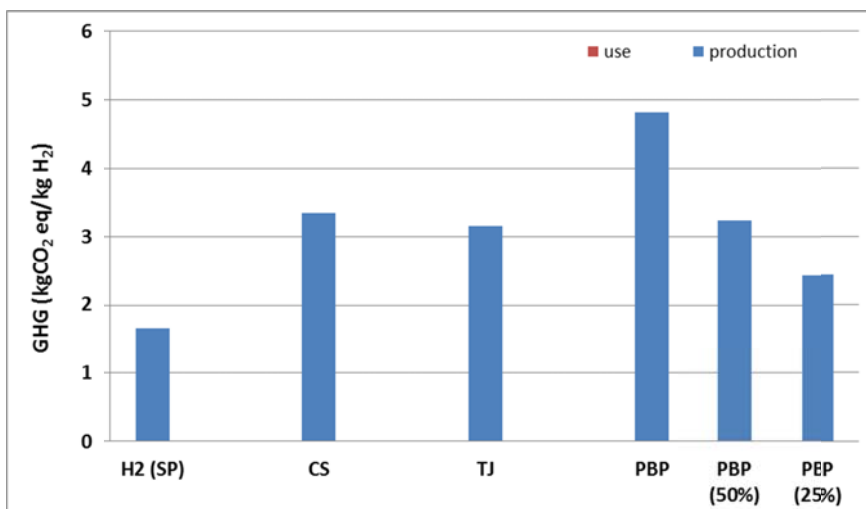


Figure A- 9. Comparison of GHG emissions for hydrogen.

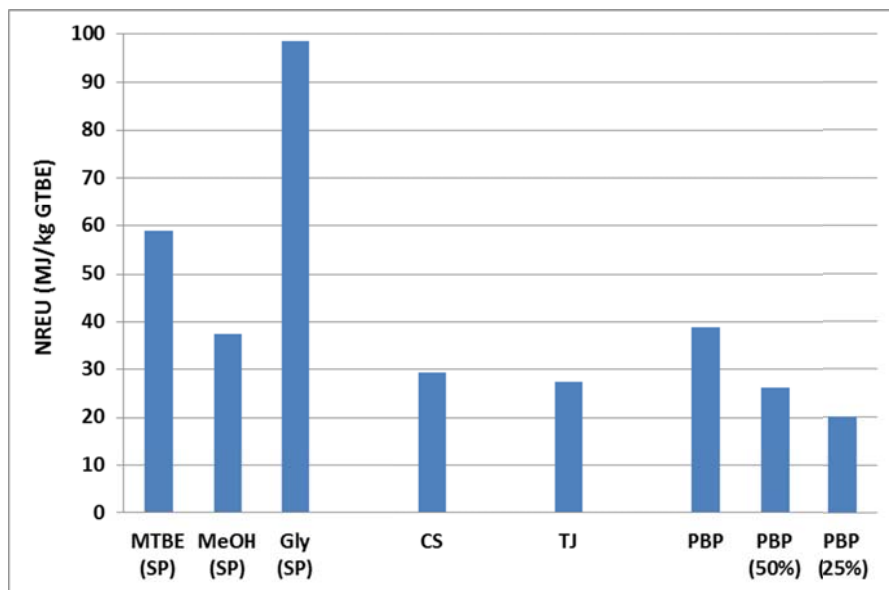


Figure A- 10. Comparison of NREU for GTBE.

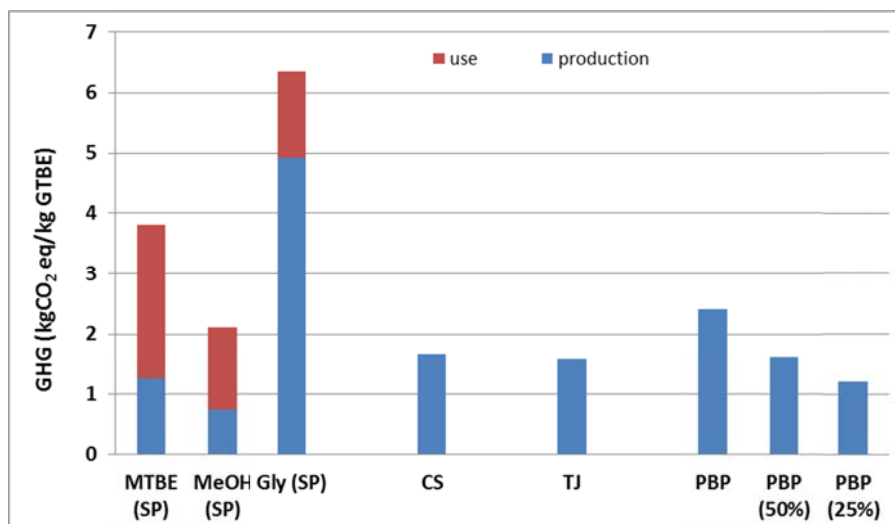


Figure A- 11. Comparison of GHG emissions for GTBE

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