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GLYCEROL-BASED ISOBUTANOL

Report from an f3 project

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THE SWEDISH KNOWLEDGE CENTRE
FOR RENEWABLE TRANSPORTATION FUELS

PREFACE

This report is written with financial support from the Swedish Knowledge Centre for Renewable Transportation Fuels (f3 – fossil free fuels). It is the final report from a research project entitled "Glycerol-based isobutanol", focusing on the production of isobutanol from crude glycerol. Lund University, Preem and Biofuel-Solution have been active partners in this project, with the main part of the work being performed by the research team at Lund University. A reference group has reviewed the material presented in this report and provided valuable feedback to the authors. The members of the project group and the reference group are listed below.

The research on glycerol supply which is presented in the second chapter is the basis for the article "Is there a future in glycerol as a feedstock in the production of biofuels and biochemicals?" published in the peer reviewed journal *Biofuels, Bioproducts and Biorefining* [1]. The material presented in chapters three to seven is the basis for an article manuscript in preparation.

Project group

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SAMMANFATTNING

I jakten på förnybara bränslen diskuteras flera olika substitut och additiv för bensin. Det vanligaste idag är etanol, men isobutanol har visat sig vara en god kandidat eftersom ämnet har utmärkta bränsleegenskaper med avseende på energitäthet, syreinnehåll och ångtryck. I projektet har möjligheten för termokemisk framställning av isobutanol från glycerol undersökts, med avseende på tillgång på råvara, processekonomi och växthusgasutsläpp. I projektet har ett fall med en fristående produktionsprocess studerats, samt ett fall där processen integreras i ett traditionellt petroleumraffinaderi.

Huvudråvaran för processen är glycerol, en biprodukt från framställningen av första generationens biobränslen. Glycerol är en viktig biprodukt vid produktionen av biodiesel, där glycerol motsvarar cirka 10 % av den totala bränsleproduktionen. Den stora biproduktionen av glycerol från biodiesel har lett till att marknaden för glycerol i stort har kollapsat, vilket har lett till att glycerol blivit en attraktiv grund för nya processer för produkter och kemikalier från förnybara källor. Även vid produktionen av bioetanol bildas glycerol som en biprodukt, som dock inte används i dagsläget. I framtida scenarier, där glycerol motsvarande upp till 10 % av etanolproduktionen kan frigöra stora mängder glycerol. Prognoser av IEA och OECD-FAO visar att produktionen av flytande biobränslen, framförallt första generationens biodiesel och bioetanol, kommer att fortsätta öka under överskådlig framtid vilket talar för att det kommer vara möjligt att producera nya produkter med glycerol som råvara.

Processen från glycerol sker i tre steg. I det första steget omvandlas glycerolen till propanal via akrolin; i det andra, parallella steget produceras formalin från metanol; i det tredje steget reagerar formalin med propanal och bildar metakrolin som hydreras till isobutanol. Förutom glycerol är metanol och vätgas, som produceras från naturgas via ångreformering, viktiga strömmar som går in i processen. Processens integrationsmöjligheter har studerats och värmebehovet har optimerats med pinch-analys. Möjligheterna att integrera processen med ett befintligt petroleumraffinaderi har studerats i en fallstudie som utgått ifrån Preemraff Lysekil. Tekno-ekonomiska kalkyler har gjorts för att beräkna en investeringskostnad för processutrustningen, samt för att beräkna produktionskostnaden för isobutanol från glycerol. Koldioxidutsläppen från produktionen har beräknats för att undersöka hur mycket lägre utsläpp glycerolbaserad isobutanol ger jämfört med fossil bensin.

Rapporten visar att det är tekniskt möjligt att producera glycerolbaserad isobutanol. Processen har ett stort värmebehov, men det finns goda möjligheter att täcka värmebehovet genom intern processintegration. Den största vinsten med att integrera processen med ett befintligt petroleumraffinaderi är att kunna utnyttja befintlig kapacitet för vätgasproduktion och andra stödsystem. Produktionskostnaden för isobutanol från en fristående anläggning (1 140 $/m^3) visar sig bli 22 % högre än vid produktion i en anläggning integrerad med ett befintligt raffinaderi (935 $/m^3). Den största delen av produktionskostnaden beror på kostnaden för processens råvaror, såväl för det fristående som för det integrerade fallet. Produktionskostnaden är också betydligt högre än för bioetanol som ses som den starkaste konkurrenten av biobaserade drivmedelsadditiv.

Beräkningarna på processens utsläpp av växthusgaser visar att glycerolbaserade isobutanol ger betydliga besparingar jämfört med fossil bensin, ungefär 55 %. Då glycerol från biodieselpro-

duktion inte belastas med några klimatutsläpp enligt EUs direktiv om förnybar energi härleds huvuddelen av växthusgasutsläppen från den metanol och vätgas som används i processen, då båda dessa produceras från naturgas.

Denna rapport visar att det är tekniskt möjligt att producera glycerolbaserad isobutanol för inblandning i bensin, både med avseende på produktionsteknik och också produktens användbarhet, till ett pris som gör ämnet intressant för vidare utredning av möjligheter för kommersiell implementering.

SUMMARY

In the search for renewable vehicle fuels several different gasoline additives have been discussed and reviewed. Today bioethanol is the most commonly used option, but isobutanol is being proposed as a better alternative by many stakeholders, due to its superior fuel characteristics, e.g. energy density, oxygen content and vapor pressure. The research project “Glycerol-based isobutanol” has investigated the possibility to produce isobutanol from glycerol with respect to feedstock availability, process economics and savings in GHG emissions. The process has been studied both as a stand-alone fuel production process and integrated with an existing petroleum refinery, a case study together with Preemraff Lysekil.

The starting point for the process is glycerol, a waste product from the production of first generation biofuels. Glycerol is a significant byproduct from biodiesel production, in which glycerol corresponds to about 10% (w/w) of the total fuel production. The rapidly increasing production of biodiesel, and thus also glycerol, has led to a market collapse for glycerol in the last decade. This has led to an increasing interest in glycerol as a feedstock for renewable fuels and chemicals. Glycerol is also formed as a byproduct in the production of bioethanol, this quantity is however not utilized today, but in future scenarios glycerol volumes corresponding up to 10% (w/w) of the bioethanol production may become available. Projections from IEA and OECD.FAO show that the production of first generation biofuels will continue to increase, indicating that glycerol will continue to be available as a suitable feedstock for renewable fuels and chemicals.

The production of glycerol-based isobutanol is divided into three parts. In the first, glycerol is converted to propanal via acrolein; in the second parallel part, methanol is converted to methanal; in the final part methanal and propanal are condensed to methacrolein which is hydrogenated to isobutanol. Methanol and hydrogen are, besides glycerol, important feedstocks for the process. By using process integration methodology, i.e. pinch analysis, the energy demand of the process has been optimized. The possibility to integrate the production process into an existing petroleum refinery, Preemraff Lysekil, has also been studied. A techno-economic assessment of the process has been performed to calculate the capital investment costs and operation costs of the process. Finally, the greenhouse gas emissions from glycerol-based isobutanol have been calculated and compared with fossil gasoline.

The results show that the proposed production process is technically viable. The process has a large heat demand, which to a significant degree can be supplied by internal heat exchanging, according to the results from the process integration studies. Integrating the process with an existing petroleum refinery enables the use of existing utilities and hydrogen production capacity which is an important benefit. The techno-economic assessment shows that the cost for production of glycerol-based isobutanol from a stand-alone plant (1 140 $/m^3$) is 22% higher than from a plant integrated with a refinery (935 $/m^3$). The largest share of the production cost is due to the cost for raw materials, both for the stand-alone and integrated case. The calculated production cost is significantly higher than for bioethanol, which is considered to be the main competitor among biobased gasoline blendstocks.

The calculations on GHG emissions show that glycerol-based isobutanol is a fuel which yields significant reductions – about 55 %% – in emissions when compared to fossil gasoline. As glycerol from biodiesel production is not loaded with any CO2 emissions according to the EU directive on renewable energy the main contributions are due to the methanol and hydrogen consumed in the process, as both are produced from natural gas.

Glycerol-based isobutanol is viable from a technical viewpoint, considering both the proposed production process and the suitability of isobutanol as a gasoline blendstock, and the calculated production cost is in a ranger which could make the process also economically feasible

CONTENT

1 INTRODUCTION

The use of liquid vehicle fuels based on renewable feedstocks will increase with diminishing fossil resources. Ethanol has, to date, been the renewable fuel of choice to substitute fossil gasoline, but isobutanol may well be a better option due to its higher carbon-to-oxygen ratio, high energy density and low Reid vapour pressure. A possible starting point for producing isobutanol is glycerol, which through a series of reactions can be converted to isobutanol. Glycerol is readily available as the production of biofuels (from which glycerol is a side-product) in the world has increased markedly over the last 10 year period. This glut in the glycerol production has also lowered worldwide prices of glycerol. This research project has investigated the supply and demand of glycerol, the technical viability of a glycerol-based isobutanol production process, and the possibility to integrate process into existing petroleum refinery capacity.

1.1 BACKGROUND

The use of glycerol in fuel applications is interesting, and perhaps even more so in automotive fuel applications, as it is classified as a waste with zero carbon dioxide emissions in the European Union [2]. As a waste product from the growing biodiesel industry, glycerol production has increased and prices have decreased rapidly over the last decade. This has generated interest in using glycerol as a feedstock for new applications, such as liquid fuels and renewable chemicals. Several grades of glycerol are available, such as food-grade glycerol or pharmaceutical-grade glycerol. Aside from these qualities there are two types of crude glycerol, separated by their salt content.

Isobutanol has received an increasing interest over the last years as it is a suitable gasoline additive which can be made from renewable sources. Isobutanol can be produced via fermentation in a process similar to ethanol production, in fact it has been proposed that ethanol production plants should be retrofitted to produce isobutanol instead. This project has focused on the thermochemical conversion of glycerol to isobutanol which is a process much more similar to those that petrorefineries are accustomed to today. Integrating the production at an existing refinery site instead of setting up a stand-alone isobutanol production facility adds to the possibilities of producing the isobutanol to a market competitive price as utilities, infrastructure and other costs can be shared with existing processes.

1.2 DISPOSITION

The second chapter of this report describes the initial study on the present and future viability of glycerol as a feedstock for renewable fuels and chemical. The third chapter presents the effects on petrol quality and characteristics when adding isobutanol to the mix. The fourth chapter presents the developed production process and results from the process modelling. Chapter five presents the aspects considered for integrating the process into an existing petrorefinery, a case study based on the refinery Preemraff Lysekil. In the sixth chapter the techno-economic assessment is described. Chapter seven presents the calculated GHG emissions from the process. Finally some general conclusions are presented in chapter eight.

2 VIABILITY OF GLYCEROL AS FEEDSTOCK

After the boom for liquid biofuels in general, and biodiesel in particular, glycerol has become abundant on the world market. This is due to the fact that glycerol is an inevitable byproduct from the biodiesel production process, in which vegetable oils are reacted with an alcohol to produce fatty acid methyl esters, biodiesel. Historically, the production of glycerol followed the production of soap, a process in which glycerol is also formed as a byproduct. Later, glycerol was also produced through synthesis from petroleum based feedstocks. Glycerol is used in more than 2000 applications, which range from pharmaceuticals to foodstuffs and explosives [3], [4]. However, over the last decade the production has come to outnumber the demand several times and the price has crashed. In the wake of the rapidly changing market, the interest to develop new applications for the versatile chemical has increased. Simultaneously glycerol synthesis facilities have seen their profit margins shrink and some of the facilities have shut down or converted the production train into other end products [5].

2.1 TRADITIONAL DEMAND

The traditional demand for glycerol spans a large number of industries. In the tobacco industry glycerol is used as an additive to stop the tobacco leaves from crumbling; in cosmetics and pharmaceuticals it is used as a moisturizer and skin softener; in the food industry it is used as a lubricant in machinery used for food processing and for sweetening. The utilization of glycerol is thus many-fold, arising from the many favourable properties of the compound; it is water soluble, odourless, colourless, absorbs and retains water, dissolves flavours and dyes, has placticizing properties, is non-toxic and biodegradable [3]. Figure 1 shows the distribution of the traditional market demand for glycerol [3], [4].

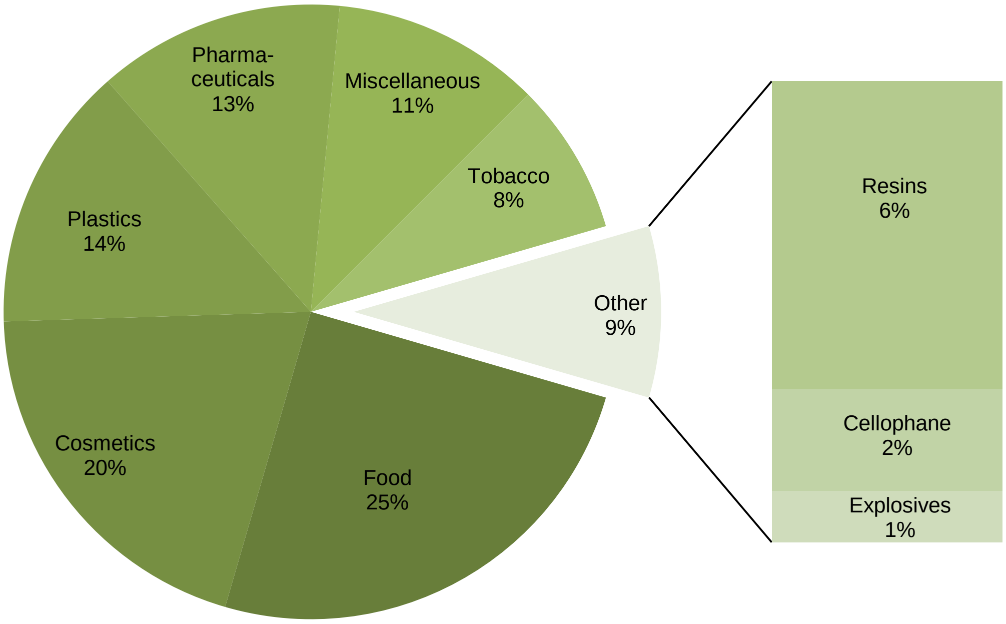

Figure 1 Traditional market distribution of glycerol, total market volume 750 000 tpa (tonnes-per-annum).

The traditional uses of glycerol have had a small growth over the last 30 years, corresponding to 2% per year or from 550 000 tpa (tonnes-per-annum) to 750 000 tpa, from 1986 to 1998. About 65% of the production is in the US and Europe. Since 1995 there has been an overproduction of glycerol in the world and the increasing production of biodiesel increases the oversupply further. It has been estimated that in 2020 the production from the traditional industry and the biodiesel industry will be six times the demand, unless significant changes in demand develop [3].

2.2 EMERGING DEMAND

The increasing production and decreasing prices have drawn attention to glycerol and potential new uses for the chemical. Several research reviews on new possible for glycerol show a large interest in finding new applications. A first review was published in 2007 [6] and since several other publications have presented possibilities for thermochemical and biological conversion of glycerol to valuable fuels and chemicals. The long list of products that can be produced from glycerol includes, according to these reviews, 1,3-propanediol, different butyl ethers, β-carotene, propionic acid, epichlorohydrin, ethanol, methane, syngas and hydrogen. Proposed production paths for these compounds span fermentation with yeast or bacteria, gas phase reforming, liquid phase reforming, pyrolysis and gasification [6–11].

Glycerol in its pure form has been tested as fuel, both as a liquid fuel and as biomass pellet additive. Burning liquid glycerol is problematic as the crude glycerol contains a large share of water, which lowers the heating value, and impurities such as potassium salts, which can cause severe corrosion on the equipment [12]. Adding glycerol to biomass pellets decreased the pellet quality and increased the emission of particles from the combustion [13]. Further, combustion of glycerol at too low temperature leads to the formation of acrolein, which is very toxic. Thus, glycerol does not seem to be a very promising fuel or fuel additive.

Glycerol has been used as an additive to anaerobic digesters producing biogas, with good results. The addition of glycerol boosts methane production and can be used to substitute as well energy crops as manure and sewage sludge [10], [14]. This has been proposed as an energy efficient way to treat the waste glycerol from biodiesel production, as the energy can be utilized as bio-SNG in a variety of applications.

Using glycerol as feedstock for renewable chemicals has also been researched and the chemicals which have been proposed to be produced from glycerol are, among others, 1,3-propanediol, acrolein, epichlorohydrin and lactic acid [10], [11]. In fact, both acrolein and epichlorohydrin were formerly used to produce glycerol, but the reversed reaction has now become the more interesting due to the low prices for glycerol.

The European Union has in the 7th Framework Programme funded three large projects trying to utilize waste glycerol as feedstock for chemicals and fuels. The PROPANERGY project focused on producing 1,3-propanediol and biogas from glycerol, thus producing both a chemical and a fuel. The SUPERMETHANOL project focused on reforming glycerol to methanol in supercritical water with the goal to return the methanol to the biodiesel production [10]. These two projects have yet not published any results in scientific journals. The GLYFINERY project focused on bioconversion of glycerol to ethanol and recently published results claiming the highest conversion rate of glycerol to ethanol reported to date, however with low productivity [15].

Using glycerol as a feedstock to produce ethanol has gained interest from several researchers, mainly on *E. coli* as the microbial agent for ethanol production [16–18]. High productivity for ethanol production from glycerol has also been reported when using strands of *Klebsiella pneumoniae* [19]. Glycerol is interesting for ethanol production as it is available at a low cost, but the carbon is also easily available for the microbial agents, making the production cheaper than using ordinary sugars. This research is still ongoing and the application seems not to be ready for industrial scale-up, but the ethanol industry may well show a large interest in glycerol in the future.

2.3 TRADITIONAL AND PRESENT SUPPLY

Glycerol production in industrial scale has completed a circle with respect to feedstock technology. Historically all glycerol has been derived from natural resources (triglycerides), but in the middle of the 20th century, production of synthetic glycerol increased quickly and accounted for about half the market in the 1960s and 1970s. Synthesis of glycerol from propene follows three main paths. In 1990 this fossil-fuel based production accounted for 30% of the glycerol production, but as of today this capacity has been shut down or converted to other end-products. In fact, the process has now been reversed and glycerol is used to produce the former intermediary epichlorohydrin in some plants.[7] Turning from synthesized product to feedstock shows just how drastic the change has been on the glycerol market in recent years. With the large-scale introduction of liquid biofuels to the market, glycerol is now available at a level exceeding demand by several times. This is mainly due to the fact, that glycerol is an inevitable by-product in the production of first generation biodiesel, which has increased from almost nothing to 20 billion liters per annum in just over a decade [20].

Glycerol-crude can be divided into two major classes, the first being hydrolysis crude glycerol which is derived from triglyceride hydrolysis and contain low amounts of inorganic salts and the second being spent lye, the residual, salt-containing glycerol from the soap and biodiesel industry. Either of these two crude qualities can be upgraded to food-grade or pharma-grade glycerol. In this project the focus has been on sources for crude glycerol and not on the distilled or purified qualities of glycerol. As is the case with crude oil, different sources of crude-glycerol will be cheaper than others. This can be due to the accessibility of the crude, as well as the resulting contamination of the glycerol. Analogue to the crude-oil case, different sources will become attractive given different technical and economic circumstances.

The European production of crude glycerol was roughly 950 000 tpa from the biodiesel industry in 2010 [21] and the traditional production is about 300 000 tpa [3]. In the US the biodiesel industry produced about 340 000 tpa in 2011 [22] and 220 000 tpa from the traditional industry [3]. In Latin America the traditional production was 75 000 tpa glycerol [3] and 260 000 tpa crude glycerol from the biodiesel industry. In Asia, which has been a major glycerol importer, the biodiesel production is expected to continue to grow, especially in Malaysia and Thailand. The additional traditional rest-of-the-world production of glycerol is estimated to 200 000 tpa of glycerol [3] and another 50 000 tpa to 100 000 tpa crude glycerol is estimated from the Oceania biodiesel production. This totals some 1 880 000 tpa of crude glycerol from the biodiesel industry and 800 000 tpa from the traditional industry.

With reservations for small differences in the year of which the statistics was obtained, there is an oversupply of some 4-5 times currently in the glycerol market compared to the traditional supply. This is also reflected in the cost of glycerol where glycerol was traded for 1500 €/ton in 1995 but 200-400 €/ton as of today and the crude-grade glycerol is traded at around 100 €/ton, depending on crude quality and freight options.

2.4 GLYCEROL AND BIOFUELS

As described above, the major supply of glycerol comes from the biodiesel industry. Another near-future opportunity for readily available crude-glycerol is within another part of the liquid biofuels industry, from bio-ethanol production. The connection between glycerol and liquid biofuels is thus likely to remain strong in the foreseeable future.

In **Figure 2**, two different projections for the global production of liquid biofuels are shown. The OECD-FAO projection is based on data from the *OECD-FAO Agricultural Outlook 2011-2020* [20] which, among many other products, projects the future for agricultural production of liquid biofuels. The IEA projection is based on data from the *Medium-term Oil & Gas Markets 2010* [23]. Although the IEA forecast is slightly lower than that by OECD-FAO, a drastic increase in fuel ethanol production and a somewhat slower increase in biodiesel production is forecasted by both organizations. It is obvious that liquid biofuels will be important in the coming decade, and thus by-products from the production will increase.

Biodiesel production has peaked globally in the last years, according to statistics. Europe was the first large market for production and consumption of biodiesel, but recently the Americas have started and expanded production, and Asia is following. Projections from OECD-FAO [20] and IEA [23] both show an increase in biodiesel production over the coming years.

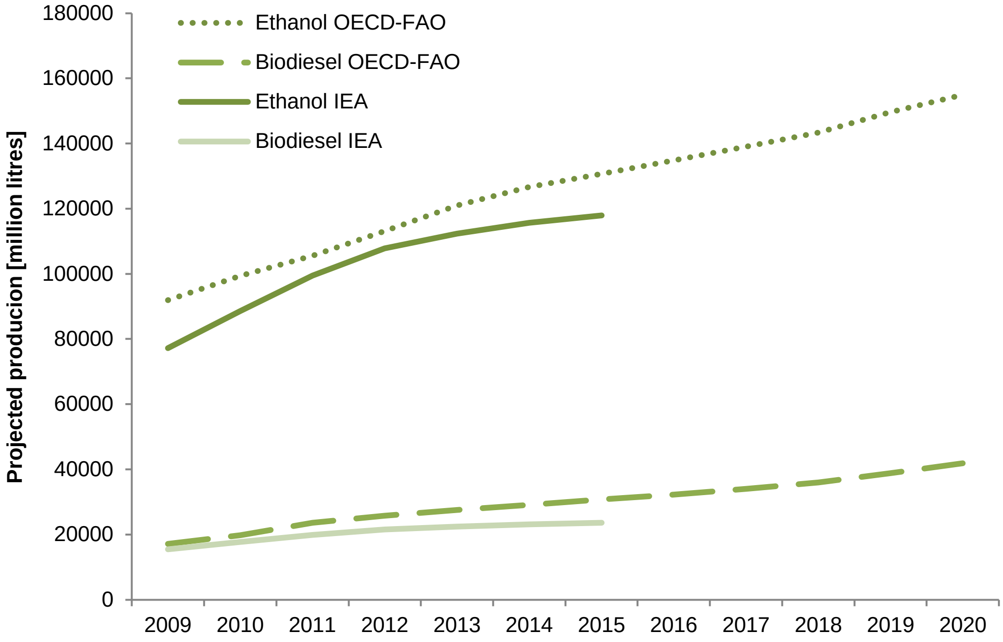

Figure 2 Forecast of global production of liquid biofuels by OECD-FAO [20] and IEA [23] in millions of litres.

In the biodiesel production process vegetable oils such as palm oil or rapeseed oil, are reacted with an alcohol to form fatty acid esters. Commonly, the process is performed with methanol, producing fatty acid methyl esters (FAME). Glycerol is produced in the process when splitting the triglyceride molecules. The glycerol is separated from the biodiesel product by splitting the product stream into two phases, one organic phase containing the biodiesel and one aqueous phase containing glycerol (50-60 %), methanol (10-30 %), catalyst salts (8-20 %) and water (<5 %) together with a small share of other compounds such as soap and free fatty acids. The methanol is recovered from the aqueous phase and recirculated to the transesterification and by adding an acid, e.g. sulfuric acid, the catalyst salts are neutralized [5]. After processing the crude glycerol stream contains about 80 % glycerol, 10 % water, 7 % ash and less than 1 % methanol [15]. The glycerol amounts to approximately 10 % (w/w) of the biodiesel produced [7].

To reduce the contamination of the glycerol produced in the process, using heterogeneous catalysts instead of the traditional homogeneous NaOH and KOH catalysts is an important improvement. Heterogeneously catalyzed processes for biodiesel production are developing and has been reviewed recently [24], [25]. However, although complete process designs using this type of process are available [26] and several plants are operating with heterogeneous catalysts, the traditional approach is still the most common.

When fermenting sugars to ethanol, glycerol is produced as an unwanted by-product by the yeast, a way to produce glycerol that has been known since 1858 and was used during World War I when demand peaked [27]. Earlier research shows that production levels of glycerol compared to ethanol can vary in the range of 5-15 % (w/w), depending on feedstock and process conditions [28]. This glycerol is however not as easily recovered as the glycerol from biodiesel production as it is but one component in the residual stream from the fermentation process. This stream also contains other chemical compounds, which possibly could be of interest in a future integrated ethanol and biorefinery process such as acetic acid, succinic acid and other organic acids and higher alcohols [29]. Using a conservative estimate of 3%, the glycerol produced by the bio-ethanol industry turns out to be a very large quantity globally. Today, this resource is not utilized in the chemical industry, as the recovery of the resource has been difficult. However, it is also questionable if this resource will become available, as current research shows that it is a suitable feedstock for ethanol production as described earlier in this chapter. Turning in-house waste streams to feedstock will of course be very interesting for ethanol producers if researchers present a process viable also at industrial scale.

Estimates of how much glycerol can be extracted from bioethanol production processes are in the interval 3-10% of the ethanol. Using these estimates and a glycerol production corresponding to 10% of biodiesel production, the production of glycerol from liquid biofuels can be projected based on these forecasts. **Figure 3** shows the global production of glycerol based on the OECD-FAO forecast for liquid biofuels. Although the glycerol fraction in biodiesel production is higher than in ethanol production, ethanol production accounts for a very large potential supply if these glycerol streams would be made available. When switching substrate for ethanol production from sugar, maize and wheat to wood, straw and bagasse in the production of second generation bio-ethanol, by-production of glycerol may decrease due to changing production characteristics and new yeasts optimized for ethanol production from these new feedstocks. However, following the development of production of liquid biofuels and its by-products will be important as it is the most important source of glycerol already today and the production of biofuels is growing rapidly.

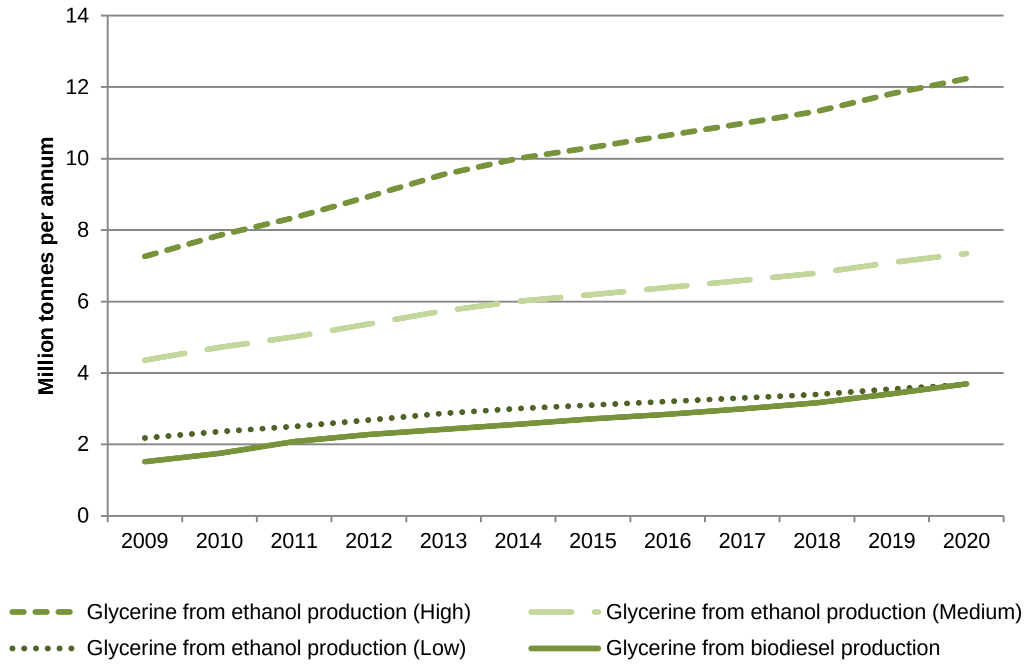

Figure 3 Forecast of global production of glycerol as by-product of liquid biofuels production in ktonnes per annum. Forecast based on OECD-FAO data [20].

2.5 LONG-TERM FUTURE

With the advent of new processes for fuel production, particularly production of triglycerides from algae, glycerol will most probably continue to be a significant by-product. This type of production has gained further credibility over the years as investments and research increase, i.e. ExxonMobil made its first biofuel investment in microalgae and invested $600 000 000 such development in 2009 [30]. Although microalgae have received much attention the last years as they have a high productivity and can be grown without competing with food crops for arable land, the market is still awaiting large-scale introduction of algal oils. The US Navy and the shipping company Maersk are two other important stakeholders that are investing in fuels from algal oils [31]. Large-scale production of biodiesel from algal oils will give rise to large amounts of glycerol, albeit the quantities that will become available are difficult to estimate.

Another method would be to use algae to produce the desired glycerol directly, without the triglyceride addition. This can, and has been done, be performed using an algae from the Dunaliella group [32]. These algae have the advantage of not only producing glycerin in high yields and quantities, but also surviving in very high saline concentrations. The use of these high saline concentrations effectively avoids contamination from other living organisms. As mentioned above, the contribution to the supply of this kind of production is difficult to estimate. However, it is plausible that in conjunction with fuel or chemical production from the glycerol, it may be economically feasible to perform.

There are also less conventional means of production by which the glycerol supply side can be further improved. The first means of such production would be through fermentation using particular types of yeast. Analogue to ethanol, glycerol can be produced from a variety of substrates including sugars, starch and cellulose. One advantage with this process is that higher glycerol-in-water concentrations can be achieved compared to ethanol-in-water concentrations in traditional fermentation. According to literature [33] it would be possible to reach 20% glycerol in water before inhibition occurs, compared to 12% in ethanol fermentation. The 20% solution would probably be suitable for direct handling in gas-phase processes for glycerol conversion.

This indicates that the present overproduction of glycerol will persist over both the foreseeable future as well as in a more distant future. With this feedstock potential in mind, the use of glycerol as a starting point for fuels and chemicals synthesis seems to be a good decision, realized by researchers, companies and governmental bodies. The competition for using glycerol to produce iso-butanol will probably be toughest from the already large other industries for liquid biofuels, such as the bio-ethanol and biodiesel industries.

3 ISOBUTANOL AS A GASOLINE ADDITIVE

This chapter presents some important aspects of isobutanol to common petroleum based gasoline. A comparison to the performance of ethanol is presented in most cases, as the isobutanol is likely to in many cases substitute the ethanol that is added to gasoline today, according to policies such as the European Renewable Energy Directive. This is by no means an exhaustive comparison between the two alcohols, a task which was not included in this R&D project, and the use of them as fuels, the chapter is merely intended to point to some important characteristics of fuel additives. Apart from the thermochemical production route described in this report, isobutanol production via fermentation of sugars with an integrated separation has been proposed, a process similar to ethanol production [34]. It would also be able to retrofit ethanol production facilities to isobutanol production, which could mean a fast increase in global production volumes if there is a breakthrough for the utilization of isobutanol instead of ethanol as fuel additive.

Table 1 Characteristics of important gasoline compounds.

Compound	Molar weight [g/mol]	Oxygen content [wt%]	Density [kg/m^3]	C	H	O
Methanol	32.04	49.93	791.0	1	4	1
Ethanol	46.07	34.73	789.0	2	6	1
Isopropanol	60.10	26.62	785.0	3	8	1
Isobutanol	74.12	21.58	803.0	4	10	1
MTBE	88.15	18.15	740.4	5	12	1
ETBE	102.18	15.66	736.4	6	14	1

MTBE = Methyl tert-butyl ether; ETBE = Ethyl tert-butyl ether

3.1 REID VAPOUR PRESSURE

The vapour pressure is an important physical property of volatile liquids, such as gasoline components. The vapour pressure affects many characteristics of the fuel, such as engine start-up and warming. There are also commonly limits to the vapour pressure of gasoline as a measure of air pollution control. The vapour pressure of gasoline is usually determined using the standardized Reid method (SS-EN 13016-1) in which the vapour pressure of petroleum products is determined at 37.8°C (100°F), it is thus called the Reid vapour pressure (RVP). The blend RVP of isobutanol (~0.3 bar) is significantly lower than that of ethanol (~1.3) which is a benefit as it is thus easier to run engines on gasoline with additives also in colder climates, e.g. Sweden.

3.2 ENERGY AND OXYGEN CONTENT

The energy content of isobutanol (28 MJ/L) is slightly below that of ordinary gasoline (32 MJ/L), but closer than ethanol (21 MJ/L) [35]. In fact, it is not necessary to perform any modifications to a gasoline fired engine to enable it to run on a fuel with a high content of isobutanol.

The total content of oxygen in gasoline is limited by international standards. As isobutanol has four carbon atoms per oxygen atom, compared to two in the ethanol molecule, and a higher energy content, it would be possible to add 16 vol% isobutanol to the gasoline compared to max 10 vol% for ethanol, without breaking the barrier set by the max 3,7 wt% oxygen content. Thus, more of the fossil gasoline could be replaced by a renewable fuel by switching from ethanol to isobutanol as blendstock.

Further, the corrosion problems that are associated with ethanol blends in gasoline may be significantly reduced by using isobutanol as additive instead. Pipelines, tanks and engines suffer from faster corrosion not only to the corrosiveness of dry ethanol, but also from the fact that ethanol absorbs water from the surroundings increases the corrosion [36]. Although the available data is less complete on the isobutanol case, studies indicate that the use of isobutanol may significantly reduce the corrosion problems associated with the bioalcohol gasoline additives.

Some important characteristics of isobutanol compared to ethanol as a gasoline additive is summarized in **Table 2**.

Table 2 Comparison between ethanol and isobutanol as gasoline blendstock.

Fuel characteristic	Ethanol	Isobutanol
Blend octane number [(RON+MON)/2]	112	102
Blend RVP [bar]	1.2 - 1.5	0.30 - 0.35
O_2 content by weight	34.7 %	21.6 %
Net energy of gasoline	65 %	82 %

Within the project, experiments have also been performed to study the blending characteristics of isobutanol in different gasoline compositions. The results are shown below in **Table 3**.

Table 3 Maximum content by volume of some gasoline components in 95 octane gasoline, restricted by the total oxygen content (<3.7%) in the fuel.

Density of gasoline	740.0 kg/m^3	750.0 kg/m^3
Methanol	6.95 %	7.04 %
Ethanol	**10.02 %**	**10.15 %**
Isopropanol	13.13 %	13.30 %
Isobutanol	**15.84 %**	**16.05 %**
MTBE	20.38 %	20.64 %
ETBE	23.74 %	24.05 %

4 THE ISOBUTANOL PRODUCTION PROCESS

4.1 PROCESS CHEMISTRY

The proposed production process which has been modelled using Aspen PLUS is a process in which glycerol in several steps is converted to propanal, to which methanal is added in a condensation reaction to form methacrolein. Thereafter, a final hydrogenation process gives isobutanol as the main products. **Figure 4** shows the main products formed in the reactions in the process. This section presents the three main parts of the production process, the production of propanal from glycerol, production of formalin from methanol, and the condensation of the two compounds and subsequent hydrogenation to give the final product isobutanol. The process has been developed by Biofuel-Solution, a company active within the field of developing new process for the chemical engineering industry. Results from the experimental work performed in the laboratories of Biofuel-Solution have been the basis for modeling the glycerol-to-propanal and the methacrolein-to-isobutanol processes. The model has been developed for a production of 80 000 tonnes per annum (tpa) which is equal to a glycerol inflow of 110 000 tpa, This production volume has been chosen as it corresponds to approximately 10 % of the annual gasoline production at Preemraff Lysekil, which is the refinery chosen for the case study, and thus the volume could be utilized on the site without need for further transportation of the product.

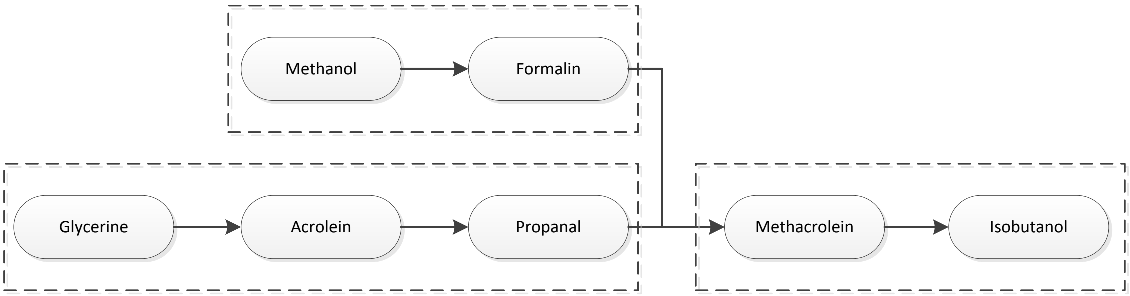

Figure 4 The main conversion steps in the three parts of the proposed production process.

4.1.1 Glycerol to propanal

The first step in the process is the gas phase dehydration of glycerol to form acrolein in a steam and hydrogen rich environment to limit the formation of carbon depositions on the catalyst. Thus, the first process step is the vaporization of a mix of glycerol and water, whereafter the gas is mixed with hydrogen before entering the reactor. The reactor (Reactor 1) is operated at a temperature about 250-300ºC and at an elevated pressure of 5-10 bar(g). The main product formed is acrolein according to the reaction described in Eq. 1 but some propanal is formed according to Eq. 2 already in this first reactor together with some unwanted byproducts such as hydroxyacetone, carbon dioxide and carbon monoxide.

$C_3H_8O_3 \rightarrow C_3H_4O + 2\,H_2O$ Eq 1

$C_3H_8O_3 \rightarrow C_3H_6O + 2\,H_2O$ Eq 2

The stream leaving the reactor is then fed directly to the next reactor (Reactor 2) in which all of the acrolein is hydrogenated to propanal, according to Eq. 3, at a slightly lower temperature, 150-200ºC.

$C_3H_4O\ + H_2 \rightarrow C_3H_6O$ Eq 3

The stream leaving the second reactor contains approximately 75% water and 15% propanal (by weight) with the rest mainly being carbon dioxide, carbon monoxide and hydroxyacetone. The stream is condensed and in a flash column the pressure is decreased and the light gases are separated from the rest of the stream to recycle the hydrogen. In the bottom of a first distillation column the hydroxyacetone is then removed together with some water to produce a stream with a higher concentration of propanal before the condensation reaction.

4.1.2 Methanol to formalin

Parallell to the production of propanal from glycerol is production of formalin in a separate reactor (Reactor 3), which is modeled based on the Perstorp Formox process. The thermal oxidation of methanol is a known process, according to the reaction in Eq. 4.

$CH_4 + ½\, O_2 \rightarrow CH_2O + H_2O$ Eq 4

The reaction takes place in the gas phase at 400-450ºC and 4-8 bar(g). The inlet stream containing air and methanol is heated by the exiting stream in a heat exchanger. The oxidation is highly exothermic which supports the reactor with the heat needed to keep it at the elevated temperature. Some of the product is also recirculated to stabilize the reactor temperature. The formalin is then cooled to ambient temperature and mixed with the propanal stream.

4.1.3 Propanal and formalin to isobutanol

After mixing the propanal and the formalin stream at ambient temperature, the stream is then again heated to enable the condensation reaction which forms methacrolein according to equation 5. The process is operated at a high pressure of 100-150 bar(g) and a temperature of 250-300ºC for an efficient conversion (Reactor 4).

$CH_2O +\ C_3H_6O \rightarrow C_4H_6O + H_2O$ Eq 5

Hydrogen is then added to the methacrolein stream, and the hydrogenation reaction, equation 6, is performed in the final reactor of the process (Reactor 5), which is operated at a slightly lower temperature of 200-250ºC but still at a high pressure.

$C_4H_6O + 2\ H_2 \rightarrow C_4H_{10}O$ Eq 6

The product stream is cooled down to ambient temperature and in a flash column the hydrogen, together with some carbon dioxide is separated from the product stream which mainly contains isobutanol and water. These two are separated using well-known heterogeneous azeotropic distillation technology [37]. The product stream is fed into a decanter which separates it into one organic and one aqueous phase. The organic phase is fed to a stripper which gives an azeotropic mix of water and isobutanol from the top stage and pure isobutanol from the bottom. The aqueous phase is fed to another stripper which gives the azeotropic mix in the top and water from the bottom. The two top streams are then mixed, condensed and fed to the decanter again.

4.2 PROCESS FLOW

The process flow diagram of the glycerol based isobutanol process is shown below in **Figure 5**. The main inlet and outlet streams of the process are shown in **Table 4** and **Table 5**.

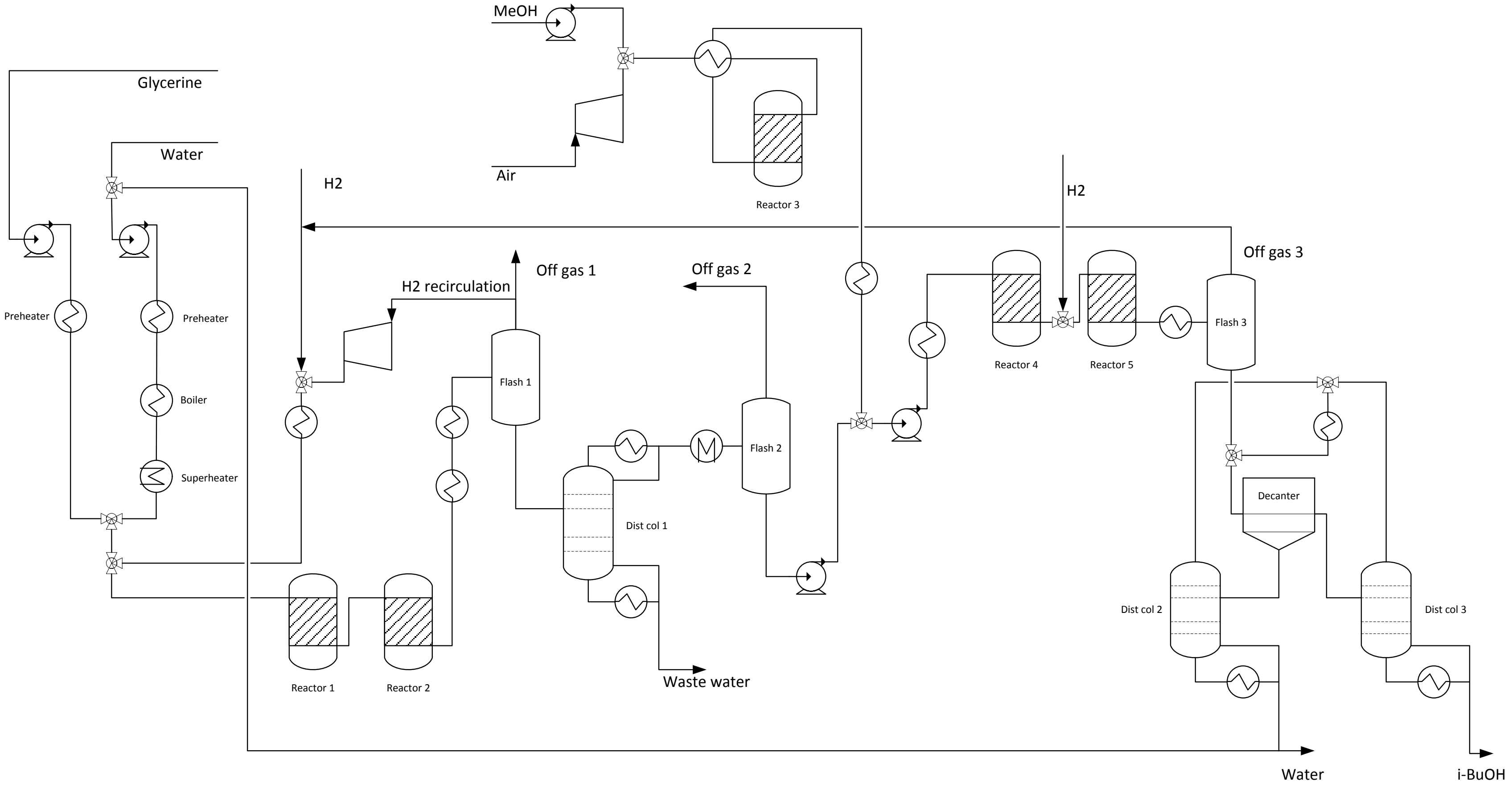

Figure 5 Process flow diagram showing the production of isobutanol from glycerol, after complete process design and integration.

Table 4 Inlet streams to the process.

Component	Mass flow (tonnes per hour)	Flow (tonnes per annum)
Water	41.0	329 000
Glycerol	13.7	110 000
Hydrogen	0.82	6 600
Methanol	4.45	356 000
Air	9.54	76 300

Table 5 Outlet streams from the process.

Component	Mass flow (tonnes per hour)	Flow (tonnes per annum)
Isobutanol	10.2	81 900
Waste water	46.9	375 000
Off-gas	7.70	61 600

5 PROCESS INTEGRATION

Process integration is interesting for several reasons, for example the use of existing locations and equipment can lower the investment cost and increase the energy efficiency of the process and increase the use of existing processes and utilities. The meaning of the concept process integration is double in this context. Firstly, it relates to the use of methodologies studying the possibilities to minimize the energy demand of a process by exchanging heat between different parts of the process, i.e. integrating the process with itself. Secondly, the concept relates to trying to place and combine the new process with existing processes at an operating petro-refinery, i.e. integrating the process with others. This chapter deals with both aspects. First, some general aspects of process integration are presented then the work with integrating the process in the first meaning of the concept, then finally a case study of integrating the isobutanol production process with Preemraff Lysekil is presented.

5.1 THE PROCESS INTEGRATION TOOLBOX

Process integration is the name for a collection of methodologies which deal with enhancing the efficiency of industrial processes by identifying demands in different parts of the processes and trying to meet these demands by supply from another part of the process. The most common way of studying process integration relates to the study of heat demands and trying to supply as much of the needed heat as possible from internal processes. What started mainly as an ambition to minimize heating costs in process industries in the wake of the energy crisis of the 1970s has today evolved into a set of methodologies all aiming to increase the efficiency in the use of natural resources and energy. As the aims of process integration have evolved from only looking at possible exchanges, so has the scope of the subject. Today, most commonly the scope of process integration encompasses the whole process site and includes utility functions such as heat and power generation, energy and water demand, the raw materials used in the process, the products and byproducts produced and the emissions and wastes generated within the process. **Figure 6** shows the system under study in modern process integration.

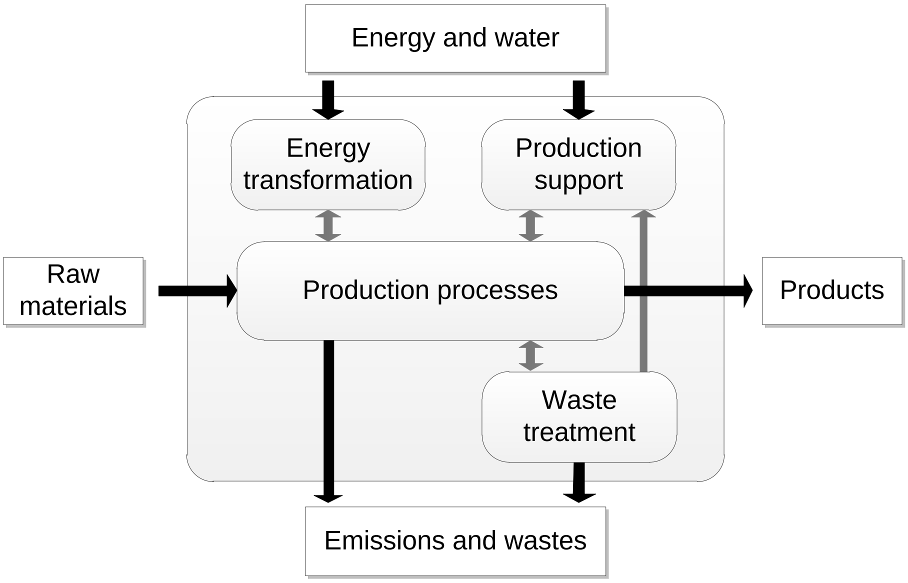

Figure 6 The system under study in process integration. Figure adapted from [38].

One of the most used tools in the process integration methodology toolbox is pinch analysis which was originally developed in the late 1970s by Linnhoff and Flower. The method has since been further developed and is today extensively used to design optimized heat exchanger networks at process sites. The basic idea behind the method has also been transferred from energy exchange to mass exchange, enabling networks for important materials such as fresh water or hydrogen to be designed using a similar approach [39]. In later years, the pinch analysis methodology has also been expanded to include phase changes, the different characteristics when handling liquid or gaseous streams and the special characteristics of pressurized streams [40]. A thorough guide to pinch analysis and many other of the methods from the process integration toolbox is available in [41]. Several, but not all of these new developments have been used within the process integration part of this project.

5.2 STUDIED ASPECTS OF PROCESS INTEGRATION

5.2.1 Heat demand

The isobutanol production process requires a lot of energy in the form of heat. The highest heat demand is located in the beginning of the process where water and glycerol is vaporized. This is needed as the first reaction is a gas phase process. Covering this demand will need external heat sources at high temperatures. However, as several of the reactions taking place in the production process are exothermal, the process produces a significant amount of heat at reasonable temperature levels, between 250 and 420ºC. There are thus significant possibilities for supplying the heat needed in the processes from internal heat sources. Further, the process may also be able to export some low-pressure steam, which may be interesting for other simultaneous processes taking place at the refinery. It is thus beneficial to be able to connect the process to a steam system with consistent heat and pressure levels instead of supplying the heat needed at each demand site with an individual boiler.

Visualizing the process heat demand is done using composite curves – one for the cold streams (in need of heating) and one for the hot streams (with need for cooling) – or a so called grand composite curve which combines all streams and heat demands into one graph. The composite curves of the process are shown below in **Figure 7** and the grand composite curve (GCC) is shown in **Figure 8**. As can be seen in the figure, the shifted pinch temperature is 175ºC. The single largest heating demand is at 170ºC and comes from the need to boil water at 10 bar(g) in the beginning of the process. As can be seen in the figure, there is a gap between the hot and cold composite curves, symbolizing the need for external hot and cold utility. The calculated minimum energy demand and other key data from the pinch are shown in **Table 6**.

Table 6 Key results from the pinch analysis.

Parameter	Value
Total heat demand	55.0 MW
Total cooling demand	73.7 MW
Used ΔT	10 ºC
Shifted pinch temperature	175 ºC
Minimum hot utility	5.47 MW
Minimum cold utility	24.1 MW
Used hot utility	6.71 MW
Used cold utility	25.4 MW

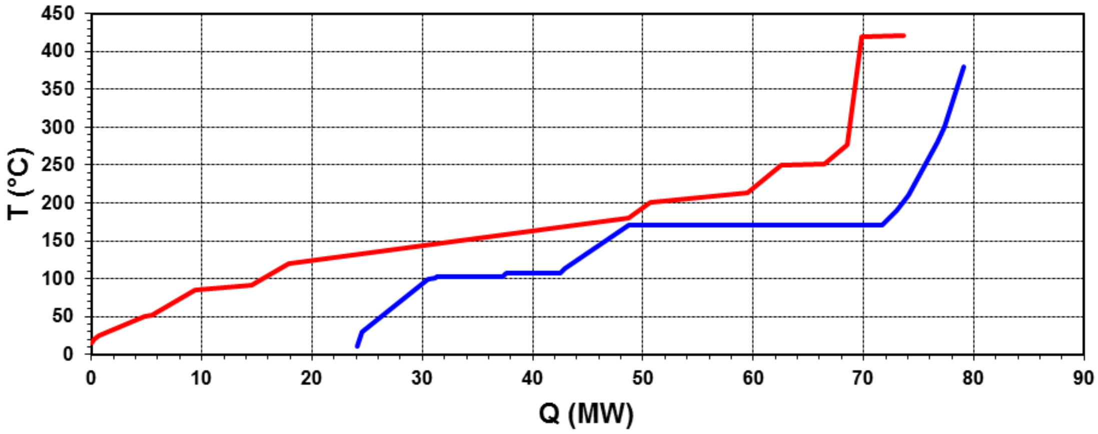

Figure 7 Composite curves of the process showing the demand for heating and cooling. Hot streams, which have a cooling demand, are shown in red and cold streams, which have a heating demand, are shown in blue.

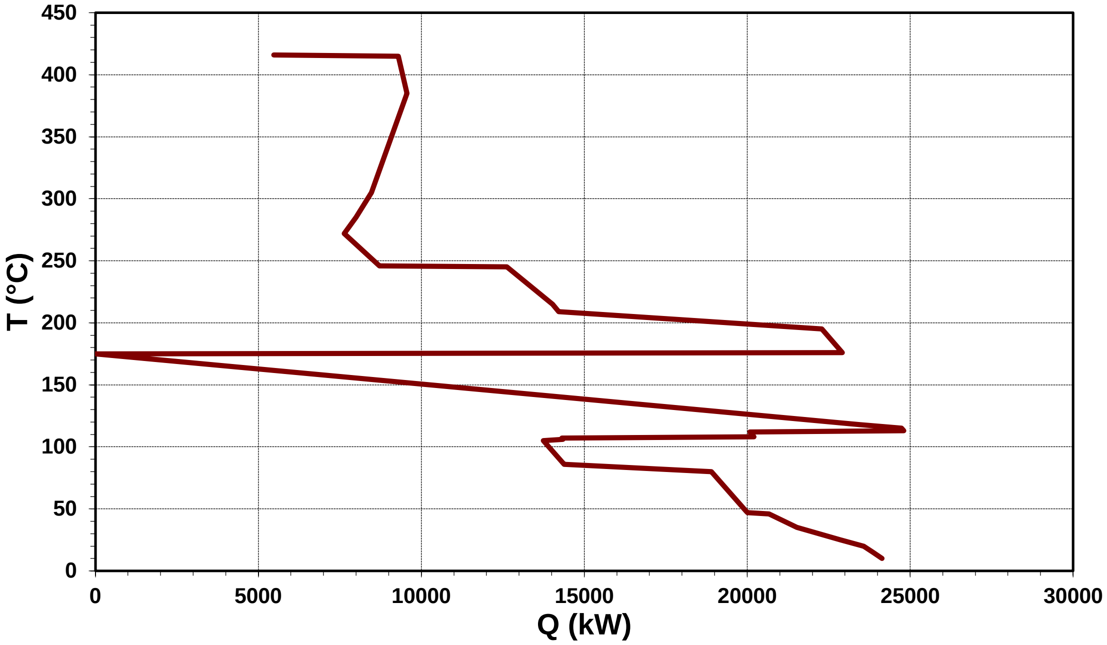

Figure 8 Grand composite curve of the production process after heat integration.

5.2.2 Hydrogen demand

A major reason for integrating the glycerol-based isobutanol production process into an existing petrorefinery structure is the need for hydrogen in the process. Hydrogen is needed in several of the reactions in the production process, as was shown in section 4.1. In total, the hydrogen demand for an isobutanol production of 80 000 tpa is approximately 3 200 tpa, which is a significant amount. On a petro refinery, hydrogen is produced as a byproduct when converting naphtha to gasoline components. If the hydrogen produced from this operation is insufficient to provide the refinery with enough hydrogen, a separate reformer is used for hydrogen production. Commercial stand-alone hydrogen production at a scale equal to the one needed for the isobutanol production process is today from natural gas in a steam reformer. Hydrogen production is however already an important operation at petro refineries as the hydrogen is needed to saturate aromatic compounds in many products. Further, the hydrogen in the isobutanol process is needed at a very high pressure, about 150 bars. The high compression of hydrogen requires expensive high pressure compressors and thus it is highly interesting to use existing compressors, if there is enough capacity. Thus, not only the flow of hydrogen is interesting when studying process integration opportunities, but also the quality of the streams, i.e. the purity and pressure.

No proper hydrogen pinch analysis has been performed within the scope of this project; instead a simplified method has been used in which minimum quality levels for hydrogen export have been established. The hydrogen rich streams leaving the process have been compared to these minimum requirements. If the streams have been deemed to be of good enough quality they are exported to the hydrogen system, whereas otherwise the gas stream is injected into a tail gas system which is used in a boiler where the gas is combusted to generate necessary heat. The hydrogen content and total flow of the three off gas streams is shown in **Table 7**. Of these streams the only one deemed to have a high enough quality to be recycled into the process is the one named Off gas 3, leaving the process after the final flash column (Flash 3).

Table 7 Total mass flow and hydrogen content of off gas streams.

Gas stream	Total mass flow	H_2 mass frac	H_2 molar frac
Off gas 1	307 kg/h	7.7 %	60.5 %
Off gas 2	33.3 kg/h	0.3 %	6.2 %
Off gas 3	44.3 kg/h	31.2 %	89.5 %

5.2.3 Process utilities

At a large chemical process industry site such as a petroleum refinery, there is commonly a large number of utilities available that are shared between the different processes at the site. These utilities include compressed air, cooling water, deionized water, steam and nitrogen. All of these resources must be used efficiently to ensure a sustainable use of resources and energy in the process. In this project, the process integration of these utilities into the new process is studied on a rather superficial level. Obviously, it is more economically efficient to share the investments in expensive utility plants between several processes and therefore it is highly interesting to utilize existing utilities in the process instead of investing in new.

5.2.4 Risks of process integration

When integrating a new process into an existing infrastructure, such as that of a petro refinery, it is important to balance the possibilities to save energy and equipment costs with the risks of integration. An important aspect to consider is the downtime integration. Integrating a new process into an existing utility system, e.g. steam supply, is most often beneficial. However, it may be possible to further integrate the process by using streams from other production processes on the site, e.g. sharing compressors or using heat from another process. The risk with integrating two separate production processes is, of course the risks for unintended downtime. When two processes which are not subsequent in the production are integrated, it may force the one process to shut down should there be problems with the other. Managing these risks is a crucial aspect when considering process integration and investments in new technology and must always be done using site specific information.

5.3 CASE STUDY – PREEM RAFF LYSEKIL

5.3.1 About the refinery

The refinery chosen to be the object for the case study in this research project is Preemraff Lysekil. The refinery was constructed in 1975 and is the largest petrorefinery in Scandinavia with the capacity to refine more than 11 million tonnes of crude oil per annum. Since its construction the refinery has been further developed in several steps, integrating new processes into the existing refinery configuration. The Lysekil refinery was chosen for the case study as it has a surplus of hydrogen during normal operation, a surplus which can be efficiently utilized by the glycerol-based isobutanol production process.

Figure 9 Satellite image of Preemraff Lysekil situated by Brofjorden on the Swedish west coast. On the left hand side is the crude oil import harbour and in the upper right corner is the product export harbour. Image from Google Earth (Lantmäteriet/Metria).

The refinery is situated on the west coast of Sweden, outside the city of Lysekil, with oil tanker access to the refinery from Brofjorden for crude imports and product exports. **Figure 9** shows an aerial view of the refinery.

5.3.2 Process integration aspects

Preemraff Lysekil today produces hydrogen from naphtha reforming in a unit operating below full capacity. There is thus existing capacity available that could be used to produce the hydrogen needed for the isobutanol production process. However, the refinery is today investing in technology for importing and utilizing LNG (liquid natural gas), which will replace naphtha as feedstock to the steam reformer in which hydrogen is produced. In this project, LNG and natural gas prices have therefore been the basis for the techno-economic calculations. Further, the pressure and temperature levels of the steam used for heating in the process are the same as those used at Preemraff Lysekil.

6 TECHNO-ECONOMIC ASSESSMENT

The techno-economic assessment will be performed on two cases, a standalone case and a case where the suggested process for isobutanol production is integrated at Preemraff Lysekil. The cost estimates will be based on open-literature data for the individual unit operation and factorial methods will be used for calculating the overall investment cost. The underlying data for dimensioning the components included in the investment cost is derived from the heat and mass balance. The production cost will be based on estimated cost-of-goods and consumables derived from the heat and mass balances described above, as well as other operating costs. In this pre-FEED phase of cost estimation, a precision of ±30% is reasonable to aim at with respect to capital investment.

6.1 INVESTMENT COSTS

As mentioned in the introduction to this chapter, the overall investment cost is based on the unit operations that constitute the process. Each unit operation has been estimated with respect to equipment cost based on information in existing open-literature databases [42], [43]. These equipment costs are corrected with a material factor and a pressure factor to match the requirements in the process at hand. The equipment costs are corrected for inflation and will be reported in US dollars for 2011. These adapted equipment cost are then multiplied with a Hand factor for the equipment type, to take into account piping, installation, warranties, insurance etc. The Hand factors for each equipment type is reported in **Table 8**. To the final investment cost there is also working capital and start-up cost added.

Table 8 The Hand factors of selected equipment

Equipment type	Hand factor
Fractionation column	4
Pressure vessels/tanks	4
Heat exchangers	3.5
Fired heaters	2
Pumps	4
Compressors	2.5
Reactors	4

Two separate estimates have been made with respect to investment costs, for a standalone plant and for a plant integrated with the Preemraff Lysekil refinery. The investment cost estimates are presented in **Table 9**. In general, the major difference between the two is the need for investing in a hydrogen plant or if existing infrastructure may be used. Other differences include a minimum requirement of buildings and that it has been assumed that existing storage vessels are available for glycerol and isobutanol storage; the cost of wastewater treatment has also been adjusted for existing or non-existing infrastructure. The cost of the entire formaldehyde and hydrogen plants have been estimated based on literature references as single units, and has not been componentized [44], [45]. The side-production of steam from the hydrogen plant is sufficient for meeting the overall steam demand of the site in the standalone configuration, why no boiler is required on the site [46]. Most estimates have been based on a CEPI of 460 (2005), but in the case of the formalin factory this is estimated 2010 and the hydrogen plant in 1994; this is normally outside the time limit of what is recommended with respect to using CEPI [43] but has been the only publically available data identified. Start-up costs have been assumed to be 10% of investment cost [43].

Table 9 The major equipment and auxiliary equipment costs presented (including the Hand factor) in MUSD.

Equipment type	**Cost**	
	Standalone	**Integrated**
Reactors	8.64	8.64
Heat Exchangers	3.71	3.71
Pumps	3.12	3.12
Compressors	3.66	0.58
Columns	0.99	0.98
Storage Vessels	1.21	-
Equipment Cost	*21.33*	*17.01*
Instrumentation	11.73	9.35
Buildings	9.60	-
Formaldehyde Plant	6.71	6.71
Hydrogen Plant	43.07	-
Investment Cost	*92.45*	*26.36*
Working Capital	13.3	13.3
Start-Up	9.25	2.64
Overall Initial Cost	***115.03***	***42.33***

There is quite some difference between the two investigated cases from an investment point of view. The standalone case with respect to the equipment cost (excluding formaldehyde and hydrogen) differ approximately 4 MUSD. However, including the buildings and instrumentation as well the difference amounts to about 16 MUSD. With that said, the major difference in the investment cost between the cases is due to the hydrogen plant investment. The overall difference in initial costs (investment cost, working capital and start-up costs) is more than 73 MUSD in the favour of the integrated case. Assuming an economic life of 15 years and 10 % discount rate, the annuity becomes 15.1 and 5.6 MUSD for the two cases respectively.

6.2 PRODUCTION COSTS

Investment cost aside, there are operating costs in addition to producing the desired isobutanol. The production costs are divided into raw materials, utilities and other operating costs such as labour. The raw materials in the standalone case are glycerol, methanol and methane while in the integrated case methane is exchanged for hydrogen; it is assumed that the natural gas is supplied from the transmission grid, making compression unnecessary. There is however a fine line dividing the raw materials and the utilities in that the hydrogen production in the standalone case also supports the steam production needed in the plant [46]; the costs of raw materials and utilities are summarised in **Table 10**.

Table 10 Base-case input costs for the glycerol-based isobutanol production.

Inputs	**Cost**	
	Standalone	**Integrated**
Glycerol ($/tonne)	350	350
Methanol ($/tonne)	411	411
Natural Gas ($/MWh)	59	-
Hydrogen ($/tonne)	-	1500
Electricity ($/MWh)	100	100
HP steam ($/tonne)	-	100
MP steam ($/tonne)	-	50
Water ($/tonne)	0.2	0.2
Waste water ($/tonne)	20	10

The cost of the raw materials is highly interesting. In particular the cost of glycerol is difficult to assess. The glycerol cost has varied significantly over the last couple of years and is due much to the biodiesel industry. The quality used in the plant is crude grade containing significant amounts of salts. The cost used here is considered to be a conservative average cost when purchasing the volumes considered here. Methanol costs are easier to access, the volumes are large and the chemical is bulk traded. The 411 $/tonne used here is the 2011 yearly average for Europe [47]. The raw material and utilities aside, there is also a need for labour at the plants. The required amount of personnel has been estimated using guidelines in which ascribe the fraction of persons required per unit operation type [43]. These fractions are multiplied with the number of unit operations of each type and summarized. In the standalone case here considered there are 3 compressors (0.09 persons/shift/unit), 5 reactors (0.25 persons/shift /unit), 6 towers (0.25 persons/shift /unit), 11 heat exchangers (0.05 persons/shift /unit), 3 evaporators (0.15 persons/shift /unit), 1 demineralisation unit (0.25persons/shift /unit) and one waste water treatment plant (0.9 persons/shift /unit). Summing this up, 6 persons are required per shift and with 5 shifts this totals 30 operators. Assigning 71 500 $/person/year in overall cost this gives the overall labour cost. In the integrated case, it has been assumed that an additional 2 persons per shift are required. The isobutanol production cost in the base case is reported in **Table 11**.

Table 11 Base-case production costs per m3 of isobutanol.

Inputs	**Cost ($/m^3 isobutanol)**	
	Standalone	**Integrated**
Raw material		
Glycerol	514	514
Methanol	157	157
Natural Gas	217	-
Hydrogen	-	109
Sub-total	*888*	*779*
Utilities		
Electricity	10	6
HP steam	-	69
MP steam	-	-
LP steam	-	-
Water	0.6	.6
Waste water treatment	73	18
Sub-total	*84*	*94*
Labour	21	7
Capital cost	148	54
Total cost	***1 140***	***935***

As may be seen in the table, the raw materials constitute a significant share of the production costs (76% in the standalone case and 81% in the integrated case). Comparing the production cost for glycerol-based isobutanol with ordinary gasoline, it is higher. The production cost for ordinary gasoline today is approximately 850 $/m^3, with crude oil price being the most important variable [48]. Comparing the production cost of glycerol-based isobutanol with the cost for bioethanol may however be more relevant. Earlier studies show a production cost for bioethanol as low as 250-300 $/m^3 for South American sugar cane ethanol, but in the range of 500-900 $/m^3 for ethanol produced from starchy feedstocks, e.g. corn or wheat, in USA or Europe [49]. As the heating value of isobutanol is about 30 % higher than that of ethanol, a production cost of 700$/m^3 for bioethanol equals the production cost for isobutanol in the integrated case, when comparing the costs on an energy basis (33.3 $/GJ). The stand-alone production cost of 1 140 $/m^3 corresponds to an ethanol production cost of about 850$/m^3 (40.7 $/GJ).

The utility costs for the two production routes are almost equal when comparing absolute numbers, this bers, this despite the fact that the integrated plant show its heat requirement here, while the standalone standalone case show its heat requirement in the natural gas column. It should be noted that the standalone case has 6 tonnes/h of HP steam which could be exported and sold should there be a heat sink heat sink in the vicinity. This has however not been considered in the calculations. The base-case cost case cost distribution for the two cases are displayed in

Figure 10.

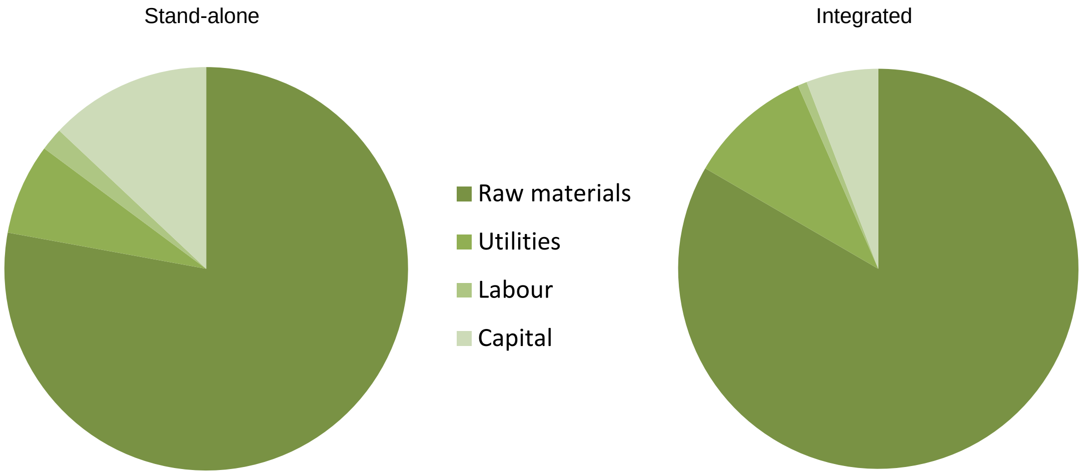

Figure 10 The production-cost distribution of the standalone (left) and integrated (right) case respectively.

6.3 SENSITIVITY ANALYSIS

There are several parameters that influence the production costs of the isobutanol. The first parameter to rameter to be investigated is the glycerol cost. The cost of glycerol assumed is on the high side looking at looking at the past 10 years of cost history. The effect of varying the cost of glycerol by ±50% has been has been investigated both in the standalone and the integrated cases,

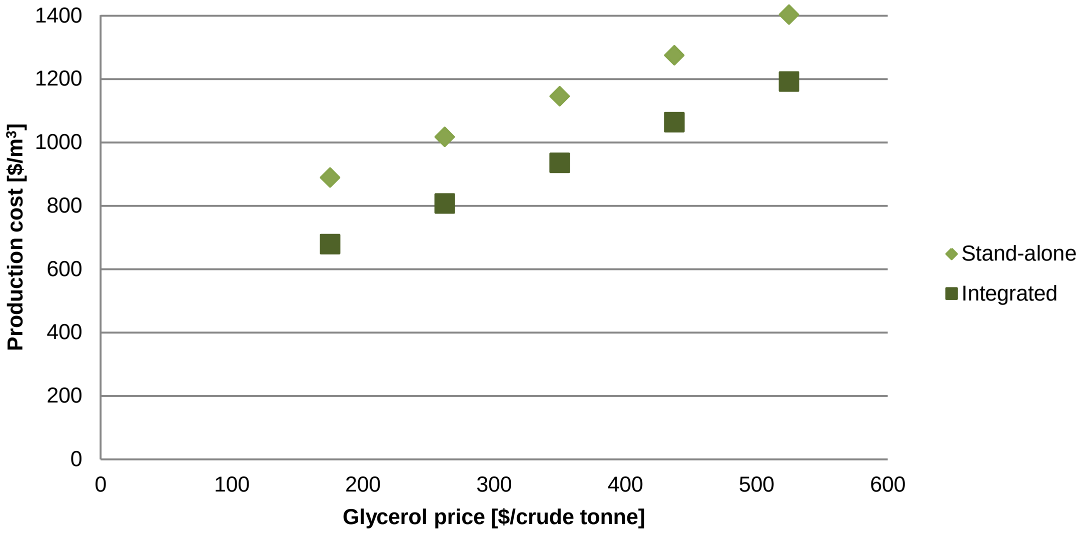

Figure 11.

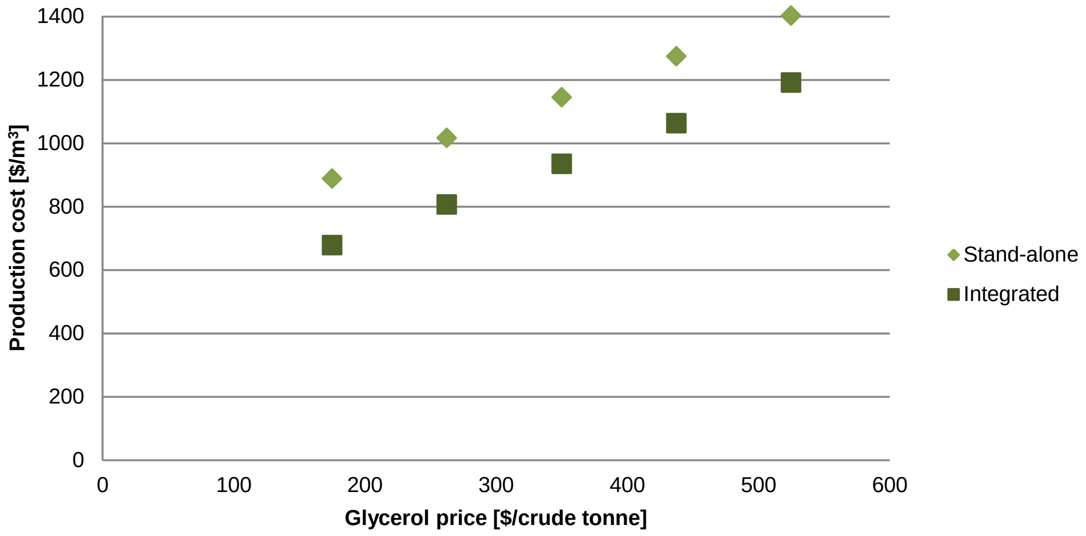

Figure 11 The sensitivity of the production cost with respect to the crude glycerol cost for the standalone (left) and integrated (right) cases.

As can be viewed in the figures, there is a very significant effect of changing the cost of the glycerol. Indeed a 50% change in the cost will lower the cost of production by 23% or a factor of 0.46, calculated for the standalone case. As mentioned above the cost of glycerol has historically been quite low and there are still quantities that may be purchased at below 100$/ton. However the requirements with respect to volume in this will probably give a glycerol input price in the 300-400 $/ton region at present. A deeper analysis of the glycerol price and its relation to requested volumes would be important to evaluate the impact on production cost for significantly smaller production volumes. That was however outside the scope of this research project. The methanol price does also influence the production cost,

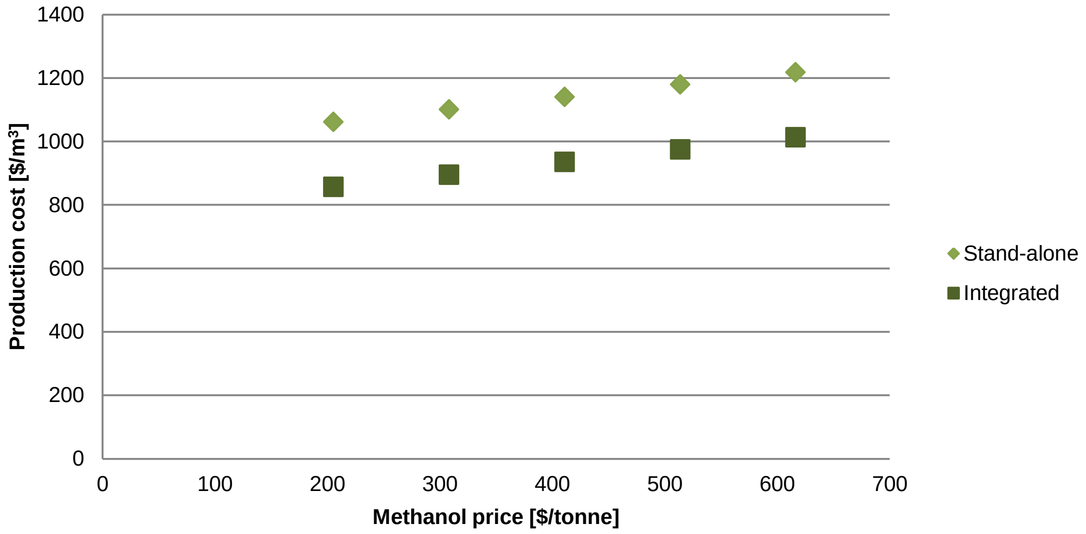

Figure 12.

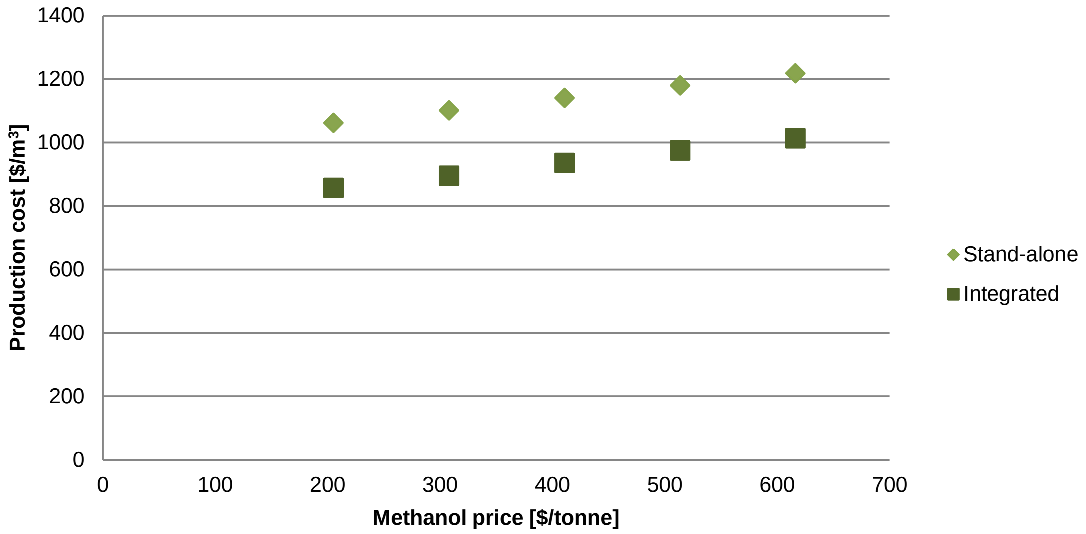

Figure 12 The influence of the methanol cost on the cost of isobutanol, standalone (left) and integrated (right) case respectively.

The corresponding 50% cost change leads to an overall production cost change of 7% or a factor of 0.14, calculated for the stand-alone case. This factor has been determined for the other costs as well and they are all summarized in **Table 12**.

Table 12 The sensitivity of the isobutanol production cost for a 50% change in parameter cost.

Parameter	Stand-alone	Integrated
Glycerol	23 %	27 %
Methanol	7 %	8 %
Natural Gas	10 %	-
Hydrogen	-	6 %
Electricity	0.4 %	0.3 %
HP steam	-	4 %
Water	0.1 %	0.1 %
Waste water	3 %	1 %

From this table it is clear that the cost of glycerol has the highest impact and that this is higher in the integrated case, indeed all factors are higher in this case since the operating cost is a larger share of the production cost. The second most influential factor is the natural gas cost in the standalone case followed by the methanol. In the integrated case, the hydrogen and methanol costs have similar impact. The only other factor with measurable impact on the production cost is the waste water treatment cost and the HP steam cost (in the integrated case).

These data are valid now, but what prices will be in ten years is of course difficult to say. Investments are always uncertain, but today it seems rather probable that the price for natural gas used in these calculations is very conservative. Due to the increasing production of shale gas in

North America, the prices for natural gas and products produced from natural gas are likely to decrease. This is especially the case for plants with the possibility to use LNG, as the LNG market can respond more quickly to changes in supply and demand than traditional natural gas markets which are supplied by single pipe-lines. A decreasing price for natural gas would affect also the price for methanol and hydrogen in this process, as they are both produced directly from natural gas.

7 REDUCTIONS IN CO_2 EMISSIONS

As glycerol is considered a waste from the biodiesel production, it carries no GHG emissions, according to the European Fuel Quality Directive [50]. The possibilities to reach a significant reduction in CO_2 emissions compared to fossil gasoline thus seem positive. However, as the process requires significant amounts of methanol and hydrogen, which is produced from LNG, there are significant CO2 emissions from the process. To quantify the savings in greenhouse gas emissions from using glycerol based isobutanol instead of fossil gasoline, calculations according to the EU RED Annex V [50] have been performed. The calculations do not aspire to present a complete life-cycle analysis of the CO2 emissions as a real LCA has not been possible to perform within the scope of this project. Important data for the calculations are however collected from earlier LCAs, and from Biograce which is a project aiming to harmonize the calculations on GHG emissions from biofuels within the EU. The emissions from the glycerol-based isobutanol are compared to the average GHG emissions from gasoline, which according to RED are 83.8 g CO_2/MJ [2].

These calculations include production emissions, i.e. arising from the production and use of methanol [51], the production of hydrogen from natural gas steam reforming [52] and the generation of steam in a natural gas fired boiler with 90% efficiency [51]. Further, the calculations also include emissions from production of the electricity needed in the process. The power generation is credited with CO_2 emissions equal to the Nordic average [53]. The results from the CO2 emissions calculations are shown below in **Table 13**.

Table 13 CO2 emissions from the glycerol-based isobutanol production process.

Input	Quantity	Unit	Reference
Feedstocks			
Methanol			
- specific CO_2 emissions	1981	g CO_2-eq/kg MeOH	[51]
- demand	0.43	kg MeOH/kg iBuOH	
- CO_2 contribution	860.4	g CO_2-eq /kg iBuOH	
Hydrogen			
- specific CO_2 emissions	11888	g CO_2-eq /kg H2	[52]
- demand	0.03	kg H_2/kg iBuOH	
- CO_2 contribution	315.7	g CO_2-eq /kg iBuOH	
Glycerol			
- specific CO_2 emissions	0.00	g CO_2-eq /kg GlyOH	[2]
- demand	1.34	kg GlyOH/kg iBuOH	
- CO_2 contribution	0.00	g CO_2-eq /kg iBuOH	
Utilities			
Steam			
- specific CO_2 emissions	77.03	g CO_2-eq /MJ steam	[51]
- demand	2.35	MJ steam/kg iBuOH	
- CO_2 contribution	181.4	g CO_2-eq /kg iBuOH	
Electricity			
- specific CO_2 emissions	100	g CO_2-eq / kWh_{el}	[53]
- demand (integrated)	0.08	kWh_{el} /kg iBuOH	
- CO_2 contribution (integrated)	7.51	g CO_2-eq /kg iBuOH	
- demand (stand alone)	0.13	kWh_{el}/kg iBuOH	
- CO_2 contribution (stand alone)	12.52	g CO_2-eq /kg iBuOH	
Total			
Total CO_2 emissions (integrated)	1185	g CO_2-eq /kg iBuOH	
	33.93	g CO_2-eq /MJ iBuOH	
Total CO_2 emissions (stand- alone)	1190	g CO_2-eq /kg iBuOH	
	34.07	g CO_2-eq /MJ iBuOH	
GHG emission savings			
Reference emissions	83.80	g CO_2-eq /MJ gasoline	
GHG emissions savings (integrated)	53.3%		
GHG emissions savings (stand alone)	53.2%		

As seen in the table above, the major share of the GHG emissions are due to the use of methanol produced from natural gas (63%). Because of these emissions, the isobutanol does not reach the 60% GHG emissions savings that will be requested of biofuels in the EU in the future. Should methanol with lower associated CO_2 emissions be used, i.e. renewable methanol, the savings in GHG emissions would be increased significantly. If methanol in the future would be produced from grown trees the CO_2 emissions associated with this methanol could decrease to 139.3 g CO_2/kg MeOH according to the scenarios which are published in RED [2]. Should such methanol be used in the glycerol-based isobutanol production process the relative reductions in CO_2 emissions would increase from 53.3% (53.2%) to 80.7% (80.5%). On the other hand, if glycerol would be credited with a share of the emissions associated with producing feedstock to the biodiesel industry, the savings would decrease significantly. Should the emissions associated with glycerol increase from 0 to 600 g CO_2/kg GlyOH, the relative reduction in CO_2 emissions compared to gasoline would decrease with half.

As has been shown in these calculations, which are not complete carbon footprint calculations but give important insights, the impact of the glycerol-based isobutanol is strongly correlated with the emissions associated with the production of the important feedstocks methanol and glycerol. Large scale production of methanol from renewable resources is not yet economically feasible, which hinders the introduction of such bio-methanol in the process, whereas the question of CO_2 emissions associated with glycerol production is connected to European policy development.

8 CONCLUSIONS

This project has investigated the possibility of using glycerol as feedstock in a new process for production of isobutanol, for use as a biobased blendstock in gasoline. As a new thermochemical production process is a very large investment, the process must seem to be viable over many years. Therefore, the project was initiated with a study of the present and future glycerol market to determine the viability and future availability of glycerol. The total available glycerol volume is mainly due to the production of biodiesel from vegetable oils, a process in which glycerol is an inevitable by-product. The production of biodiesel is increasing, and is likely to continue to increase according to several projections and forecasts, and thus the production of glycerol is also increasing. Further, the production of bioethanol via fermentation of sugars also produces several by-products such as carboxylic acids and glycerol. Should the ethanol production plants be converted into biorefineries extracting several products from the fermentation slurry, new large volumes of glycerol could be made available.

Isobutanol is very well suited to be gasoline blendstock, it is actually a better blendstock than ethanol which is commonly used today. This is due to the fact that isobutanol has a lower reid vapour pressure, higher energy content and a lower oxygen content which makes it possible to substitute more fossil gasoline products with biobased blendstock while maintaining the quality of the gasoline, as stipulated by national and international standards.

The isobutanol production process consists of three parts, one in which glycerol is converted to propanal via acrolein, one in which methanol is converted to formalin, and one in which formalin and propanal is condensed to methacrolein which is hydrogenated to isobutanol. The process has been optimized using pinch analysis to make use of as much heat as possible, and to limit the cooling demand. However, as the process contains several highly exothermic reactions, a significant cooling demand remains, as does a demand for heating at high temperatures.

As the process requires rather large volumes of hydrogen for the hydrogenation steps, it is very interesting to integrate this process into a refinery which already has access to hydrogen production. There are also other aspects of the process which makes integration into existing refinery infrastructure a suitable choice, compared to a stand-alone plant, e.g. the demand for high pressure steam for heating in some of the process steps, the need for harbor facilities for feedstock import and the need for treatment of large volumes of waste water. The techno-economic investigation showed that there are indeed large benefits from integrating the process into existing refinery infrastructure. Expanding the use of existing facilities and personnel, sharing costs for utilities and equipment makes the production cost for isobutanol significantly lower than if a new production site designated for the isobutanol process is to be built. The production cost for isobutanol in the stand-alone case (1 140 $/m^3) is approximately 22% higher than for the integrated case (935 $/m^3), according to the cost estimates presented in this report. The production cost is in the same range as the production cost for bioethanol from wheat. Thus, it could be crucial if fuel policies in the near future will demand the use of ethanol as blendstock for gasoline, or if any biobased blendstock will be allowed.

With regard to the feedstock being biobased, and thus promising major reductions in carbon dioxide emissions, this report shows that the isobutanol saves about 55% of GHG emissions compared to ordinary fossil gasoline. The GHG emissions associated with the process exist due to the use of natural gas in the production of hydrogen needed in the process, and due to the methanol used for production of formalin. If methanol produced from renewable feedstocks were to be used, a very high reduction in CO_2 emissions would be reached. Methanol and hydrogen are important in many chemical engineering processes and thus the interest in producing them from renewable sources is increasing. Renewable methanol is available today but at a significantly higher price than traditional methanol. Using renewable methanol would increase the isobutanol production cost to levels significantly higher than market price. With optimized technology and increased production of renewable methanol and new technologies for renewable hydrogen production, it may become possible to produce glycerol-based isobutanol in the proposed process in the future yielding higher savings in GHG emissions.

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