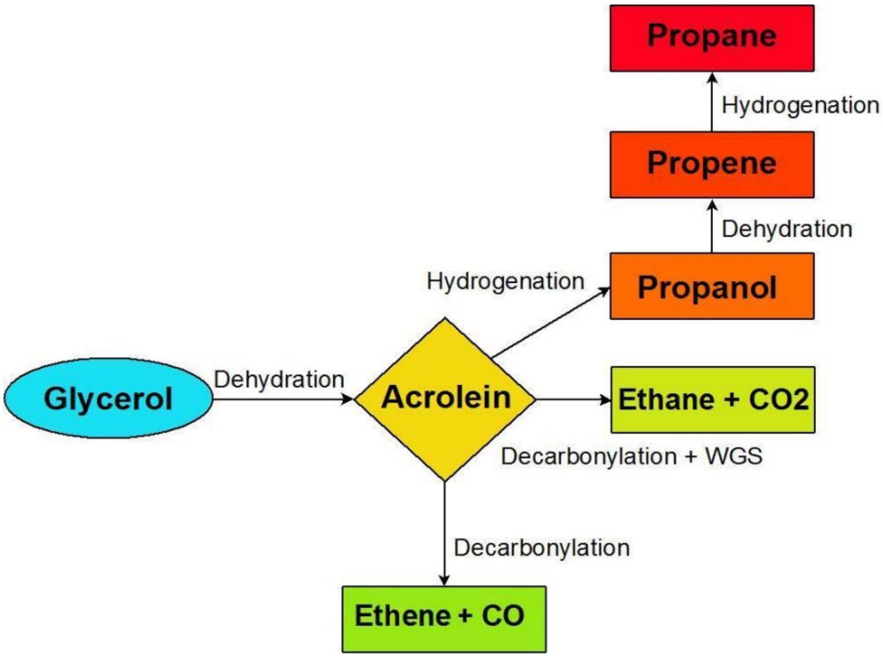
Rapport SGC 198

Bio-Propane from glycerol for biogas addition



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Rapport SGC 198•1102-7371 • ISRN SGC-R-198-SE

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Executive Summary

In this report, the technical and economical feasibility to produce higher alkanes from bioglycerol has been investigated. The main purpose of producing this kind of chemicals would be to replace the fossil LPG used in upgraded biogas production. When producing biogas and exporting it to the natural gas grid, the Wobbe index and heating value does not match the existing natural gas. Therefore, the upgraded biogas that is put into the natural gas grid in Sweden today contains 8-10 vol-% of LPG.

The experimental work performed in association to this report has shown that it is possible to produce propane from glycerol. However, the production of ethane from glycerol may be even more advantageous. The experimental work has included developing and testing catalysts for several intermediate reactions. The work was performed using different micro-scale reactors with a liquid feed rate of 18 g/h.

The first reaction, independent on if propane or ethane is to be produced, is dehydration of glycerol to acrolein. This was showed during 60 h on an acidic catalyst with a yield of 90%. The production of propanol, the second intermediate to producing propane, was shown as well. Propanol was produced both using acrolein as the starting material as well as glycerol (combining the first and second step) with yields of 70-80% in the first case and 65-70% in the second case. The propanol produced was investigated for its dehydration to propene, with a yield of 70-75%. By using a proprietary, purposely developed catalyst the propene was hydrogenated to propane, with a yield of 85% from propanol. The formation of propane from glycerol was finally investigated, with an overall yield of 55%.

The second part of the experimental work performed investigated the possibilities of decarbonylating acrolein to form ethane. This was made possible by the development of a proprietary catalyst which combines decarbonylation and water-gas shift functionality. By combining these two functionalities, no hydrogen have to be externally produced which is the case of the propane produced. The production of ethane from acrolein was shown with a yield of 75%, while starting from glycerol yielded 65-70% ethane using the purposely developed catalyst. However, in light of this there are still work to be performed with optimizing catalyst compositions and process conditions to further improve the process yield.

The economic feasibility and the glycerol supply side of the proposed process have been investigated as well within the scope of the report. After an initial overview of the glycerol supply, it is apparent that at least the addition of alkanes to biogas can be saturated by glycerol for the Swedish market situation at the moment and for a foreseeable future. The current domestic glycerol production would sustain the upgraded biogas industry for quite some time, if necessary. However, from a cost standpoint a lower grade glycerol should perhaps be considered.

In the cost aspect, three different configurations have been compared. The three alternatives are ethane production, propane production with internal hydrogen supply and propane production with external hydrogen supply. The results from the base case calculations can be viewed in table ES1.

Table ES1 Result of the base case cost estimates.

	Propane Intern. H_2	**Propane Ext. H_2**	**Ethane Production**
Glycerol (kg/h)	32	21	36
Water (kg/h)	126	83	144
Hydrogen (kg/h)	N/A	1.3	N/A
Operating Cost			
Glycerol (kr/y)	231 570	152 924	265 137
Electricity (kr/y)	23 157	15 292	26 514
Water (kr/y)	20 165	13 316	23 088
H_2 (kr/y)	N/A	347 347	N/A
Total (kr/y)	274 892	528 879	314 739
Equipment cost (kr/y)	512 170	365 836	219 502
Annual cost (kr/y)	**787 063**	**894 715**	**534 240**
kWh Cost (kr/kWh)	1.60	1.82	0.78

The base case calculations are based on carburating the upgraded biogas, before introducing it to the natural gas grid, from a 24 GWh biogas production facility. This means that the production units supply an acceptable Wobbe index of the final upgraded biogas. The annual cost in table ES1 is the yearly cost of carburating the gas at a 24 GWh biogas site. From the base case, it is obvious that there are differences in glycerol consumption depending on what alternative is chosen. There are also investment cost differences. To further investigate the volatility of the prices, a blend of Monte Carlo techniques were used to generate multiple data sets.

The conclusions from the simulations were that the ethane producing facility has a stronger dependence on the feedstock; it is hence more sensitive to changes in the feedstock cost. It is however not as sensitive to changes in investment cost. If the production cost is compared to the cost of fossil LPG used today, the cost of the LPG is 0.43 kr/kWh. This does however not include the taxation and transporting the fuel. Adding the taxation alone will put an additional 0.25 kr/kWh on the cost, totalling 0.68 kr/kWh. This compares well with the calculated production cost of 0.78 kr/kWh for ethane and with the 50% percentile acquired from the Monte Carlo simulations of 0.94 kr/kWh.

1 Introduction

In Sweden today there are large quantities of bio-methane produced via fermentation of different waste products e.g. manure, municipal waste, stover, etc. In Sweden 330 GWh was used for heating purposes and 40 GWh for electricity production in 2005 (1), while 0.23 TWh was used in the transport sector in 2006 (2). The produced bio-methane is in many cases cleaned, upgraded and transferred to the natural gas grid. However, the bio-methane produced does not, even after upgrading, have the same heating value and wobbe index as the natural gas. The first causes problems concerning metering and billing and the latter is a potential problem to certain groups of equipment. To circumvent this problem in the Swedish context, where Danish gas from the North Sea is mainly used, propane is added to the biogas before it enters the natural gas grid. Currently the added propane is of fossil origin (3) and should therefore be replaced by propane or another gaseous, higher hydrocarbon from a renewable source.

As an alternative source of propane this report aims at investigating the possibilities of producing bio-propane from bio-glycerol. During the production of biodiesel via transestrification from triglycerides, large quantities of glycerol are produced as by-product. For every 10 kg of biodiesel produced, 1 kg of glycerol is formed. The significant worldwide increase in biodiesel production has resulted in a glut on the glycerol market, with decreasing glycerol prices as a result. Glycerol has traditionally been a high-value chemical used in the food and cosmetic industry, but has over the last few years decreased in price from about 7 SEK/kg to less than 0.3 SEK/kg (4). This, in combination with increased feedstock cost, has basically undermined the profitability of any biodiesel operation. It has however created an entirely new research area, glycerol upgrading to high value chemicals.

Besides biogas the produced propane, or propane equivalent, can be envisioned to fulfil other purposes than the biogas application intended. One such alternative use would be as a “green” component in LPG, making it possible to substitute parts of the LPG used to a low carbon footprint LPG.

BioFuel-Solution i Malmö AB have since the beginning of 2007 performed research within the field of glycerol conversion, mainly focused towards other alcohols. This research has to date resulted in 2 US patent applications, in association with an American biodiesel producer, and another 2 patent drafts within the field.

1.1 Background

The area of glycerol research has dramatically developed over the last 5-10 years, from the synthesis of glycerol to the use of glycerol as a starting point for different synthesis. It is generally accepted that the primary source of renewable organic fuels, chemicals and materials will be plant derived biomass (5) (6) (7) (8). But only 3% of the chemicals produced in the US was biomass derived in 2004 (9). However, the US department of Energy (US DoE) aim at increasing the fraction of renewable chemicals to 17% by 2020 and 47% by 2050. To achieve this, the US DoE has identified 12 chemicals to be used as building blocks for high value chemicals (10); glycerol is one of these and is readily available due to its production within the biodiesel industry (11).

The end-products most often mentioned in the glycerol context are ethylene- and 1,2-propylene glycol and lactic acid. The first two chemicals are industrially important for the manufacturing of polymers, cooling fluids, food and cosmetics. Lactic acid is an important food industry chemical and the basis for producing poly-lactic acid (PLA). The demand of these chemicals is 500 ktons per annum (tpa) for lactic acid (12), 1 500 ktpa for propylene glycol (13) and 2 500 ktpa for ethylene glycol (14). The commercialization of production of these products from glycerol using catalytic methods is projected to the very near future.

Another interesting area of research is the utilization of glycerol as a substrate for microbial fermentation of different chemicals (15) (16) (17). However, in the case of fermentation the resulting products end up in a dilute aqueous solution and need some form of separation, usually energy intense, before sale or use. But the selectivity of these processes is generally exceptionally good. The product spectra found in the literature is larger for microbial conversion of glycerol than for catalytic and includes: 1,3-propylene glycol, butanol, ethanol, methanol, hydrogen, propionic acid etc. (18).

Reacting glycerol to useful chemicals can be performed either in the gas phase or in the liquid phase, with both methods having advantages. In the gas phase the glycerol has to be vaporized and then reacted, which potentially lead to heat losses. In the liquid phase, the selectivity is usually lower and more advanced catalysts have to be used to achieve a reasonable product distribution.

1.2 Project Outline

Within the scope of the performed project, the possibility to produce fuel additives to biogas from bio-glycerol has been investigated. The investigated fuel additives have been propane, which is normally used in biogas carburetion, and ethane as an alternative. The need for an additive is determined by the high Wobbe-index of the natural gas used in Sweden, requiring any biogas entering the natural gas grid to have the same Wobbe-index. Biogas (containing mainly methane) is situated in the outskirts of the allowed area for natural gas, figure 1; however the biogas produced and entered into the gas grid, also have to match more specific criterias. In that the exported, upgraded biogas has to match the existing natural gas for metering purposes as well.

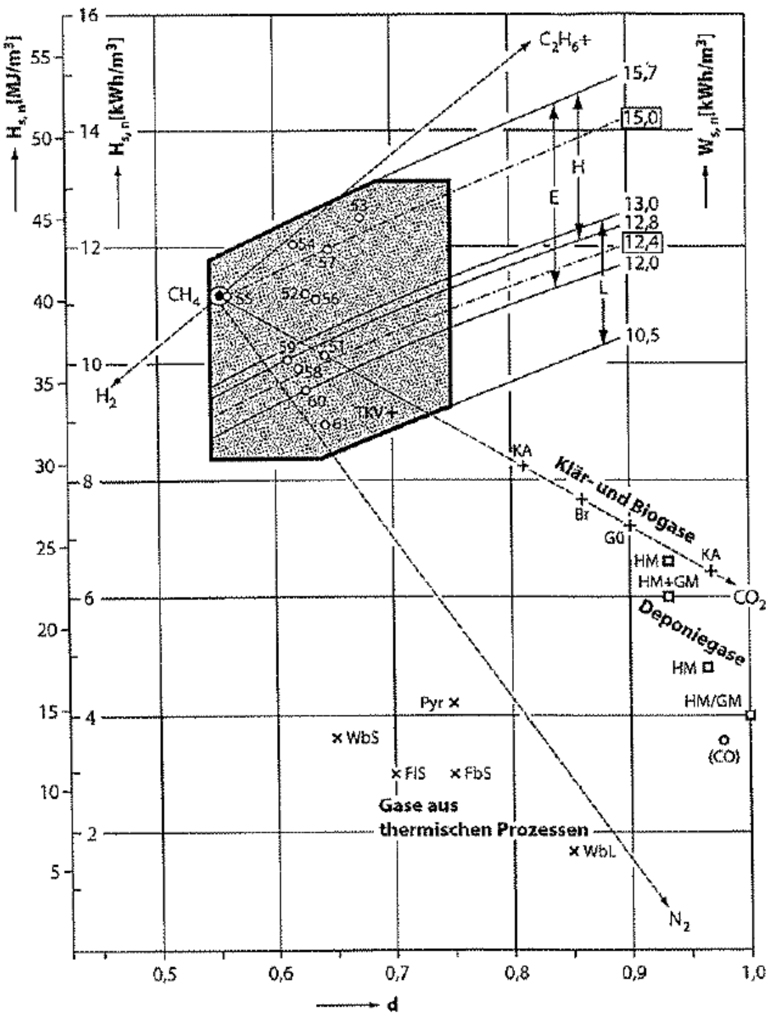


Figure 1 The allowed area for natural gas concerning specific density and natural gas, according to DVGW (19).

The addition of higher hydrocarbons increases both the Wobbe-index and the specific density, while carbon dioxide (formed during the biogas production) lower the Wobbe-index but increase the specific density, according to the information in figure 1. The higher hydrocarbon used today is propane, with a Wobbe-index of 17.8. Using a renewable base for the propane e.g. glycerol from the biodiesel industry, would enable the production of bio-propane or some other gas additive like ethane.

In this study, the possibility of replacing the fossil propane used with bio-propane has been evaluated. From a technical stand-point investigating the possibilities to produce bio-propane from glycerol and from a market perspective, where supply and cost is investigated. The production of bio-propane has been performed using mild chemical methods, without carbon-carbon bond breakage i.e. avoiding syngas production.

2 Experimental Work

Converting glycerol into propane or ethene involves several chemical steps, including dehydrations, hydrogenation and decarbonylation. In figure 2 a scheme over the reaction paths is given.

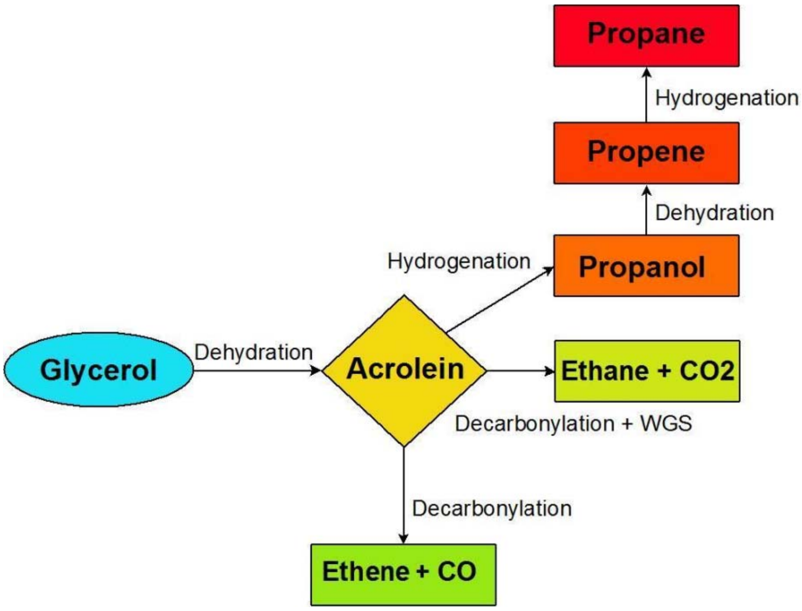


Figure 2 The reaction pathways from glycerol to propane and ethane.

In the experimental work performed within the scope of this study, the individual reactions have first been investigated separately. These reactions have then been combined to include several reactions resulting in a full, but in no way optimized, reaction pathway to propane and ethane. In figure 3 the experimental set-up is depicted for a case where several reactions have been run sequentially.

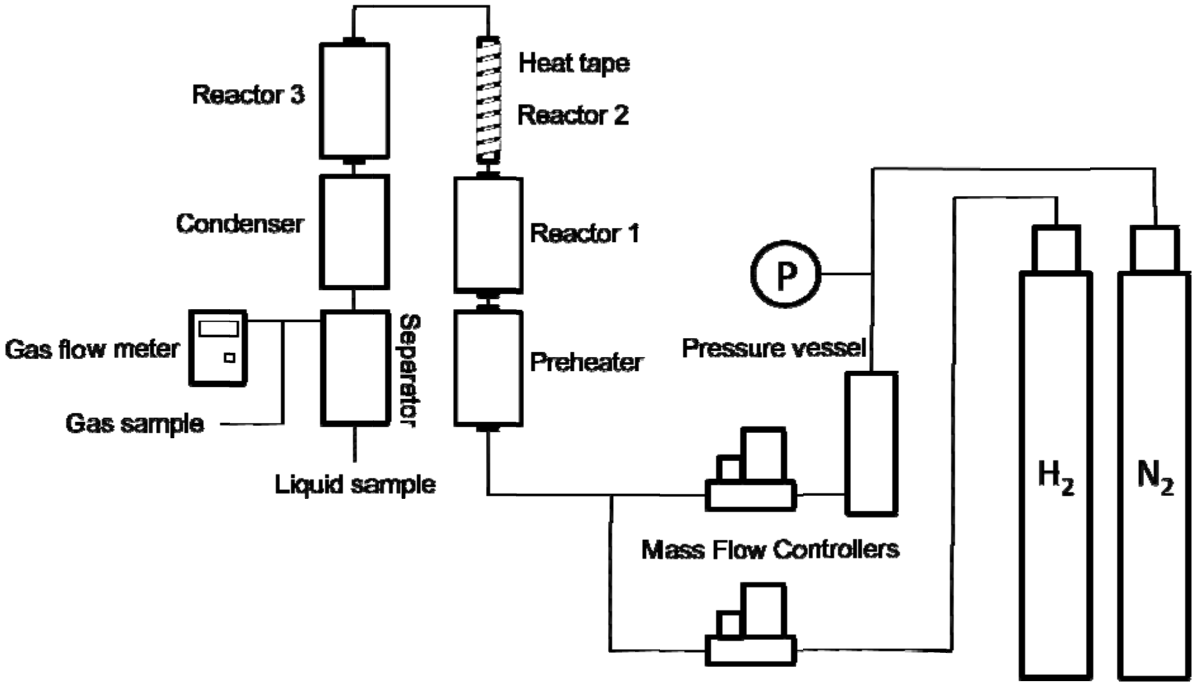
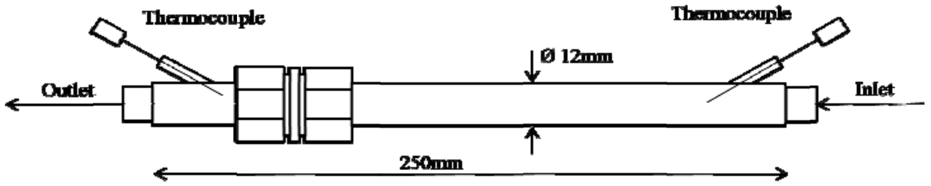


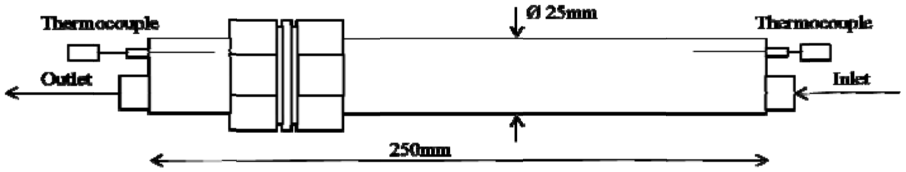
Figure 3 Schematics of experimental setup for running combined, sequential experiments.

The feed usually consists of a water solution with either 10-20 w% of glycerol, acrolein or propanol. The solution is stored in a pressurized vessel and the inlet flow rate is controlled by a mass-flow controller. The inlet liquid flow is heated and vaporized in the pre-heater. At this point, nitrogen or hydrogen gas could be introduced into the stream to facilitate the vaporization. Depending on the actual experiment, one (1) or more of the three reactors in series was used, normally with different catalysts and space velocities. After leaving the final reactor, the gas was cooled down and condensed in a water-cooled condenser. The individual reactors are depicted in figure 4.

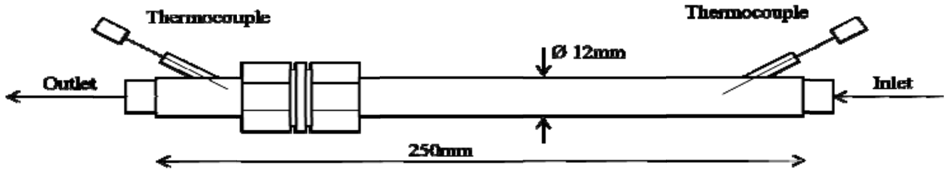
Pre-Heater



Reactor 1



Reactor 2



Reactor 3

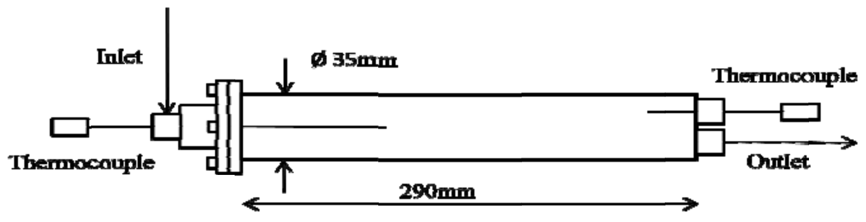


Figure 4 Individual drawings of the pre-heater and the three reactors used.

At this point a liquid sample was collected for analysis. The un-condensable gas was measured by a digital gas flow meter and a gas sample was collected in a sample bag. The liquid analysis were performed using a Varian CP-3800 gas chromatograph equipped with a 1177 split/split-less injector, a CP-wax 58/FFAP column and a flame ionization detector. The permanent gas analysis was performed using a CP-4900 gas chromatograph, using both a molsieve 5A PLOT column and a PoraPlot column with two TCD detectors.

2.1 Results

In this section the results from the various experiments performed will be reviewed, starting with the individual reactions and advancing towards more complex reaction systems.

2.1.1 Glycerol to Acrolein

The first reaction, independent of desired end-product is to convert the glycerol feedstock into acrolein. Acrolein is an unsaturated aldehyde, meaning that it is an activated molecule that can be further processed:

$$HOCH_2\text{-}CH_2OH\text{-}CH_2OH \rightarrow CH_2{=}CH\text{-}CHO + 2\ H_2O$$

Two water molecules are removed from the glycerol molecule (dehydration) on an acidic catalyst. In this case the reaction is performed in the gas phase, at a temperature of approximately 250-300°C. Glycerol solution (20 w% in water) at a rate of 18 g/h was used in this experiment. In the pre-heater the liquid is heated and gasified before entering the dehydrogenation reactor, with 25 g of catalyst (Z-1152 10-20 mesh). A small carrier-gas stream of 50 ml/min of N_2 was added to the gas stream before entering the reactor. The reactor 1 inlet temperature was 265°C and the run was performed atmospheric. The result of a 60 h run is shown in figure 5.

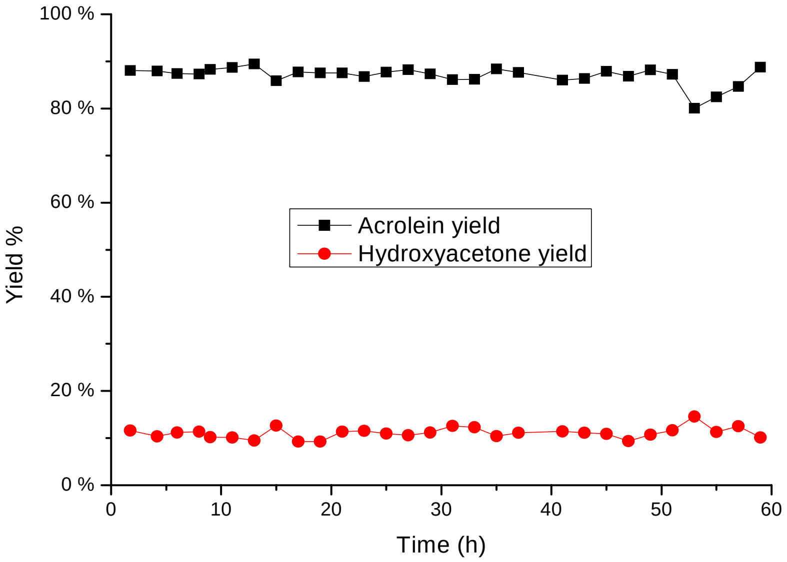


Figure 5 Conversion of glycerol to acrolein, normalized carbon balance.

The experiment was performed over a range of 7 days, operated approximately 8h per day. Full conversion of the glycerol was obtained and the yield of acrolein was high, in the range of 90%. The only condensable by-product obtained was hydroxyacetone, in the range of 10% yield.

2.1.2 Acrolein to Propanol

The next step in obtaining propane from glycerol, is the reaction of the acrolein formed to propanol. In this experiment, the production of 1-propanol is demonstrated using acrolein as a starting point. In reactor 1, 14 g of hydrogenation catalyst was used (BF-1015). A feed of 18 g/h of 10 w% of acrolein in water was used. 400 ml/min of hydrogen was added to the inlet stream in the pre-heater. Inlet temperature to the reactor was 230°C and a total pressure of 5 bar(a) was used, figure 6.

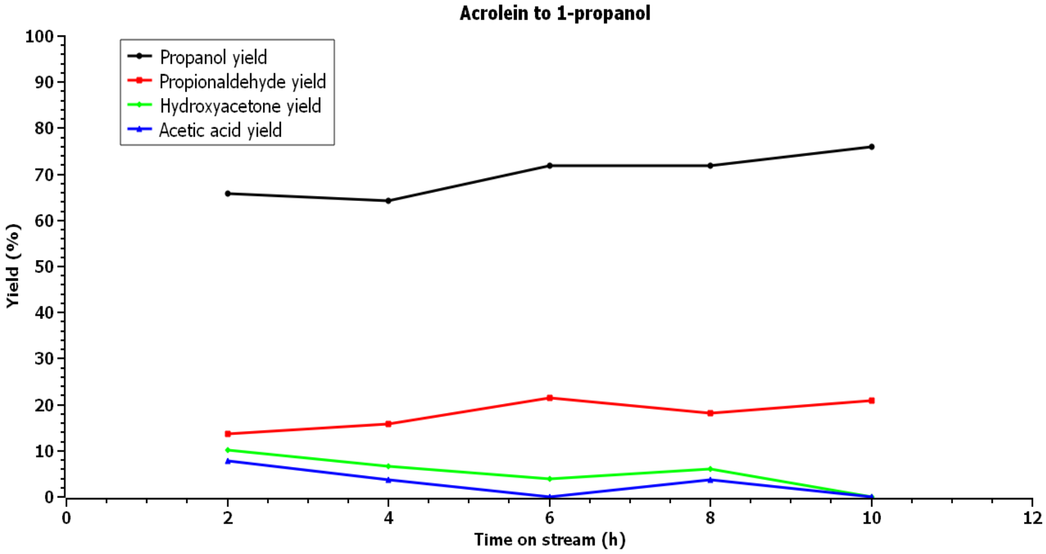


Figure 6 Conversion of acrolein to 1-propanol, normalized carbon balance.

Full conversion of the acrolein was obtained and in figure 6 it can be seen that a yield of 70-80% was obtained. As a by-product, a 20% yield of propionaldehyde was obtained at the specific reaction conditions.

2.1.3 Glycerol to Propanol

In this experimental section the process from glycerol to propanol was demonstrated, that means that the dehydration and hydrogenation steps demonstrated above was integrated. In the experimental setup, in figure 5 above, reactor 1 was loaded with 30 g dehydrogenation catalyst (Z-1152 10-20 mesh) and reactor 2 was loaded with 12 g of a commercial hydrogenation catalyst. The inlet feed rate was 18 g/h of 20 w% glycerol solved in water. Inlet temperatures were 290°C for reactor 1 and 260°C for reactor 2 and the reaction was performed at 5 bar(a) pressure. The results are shown in figure 7.

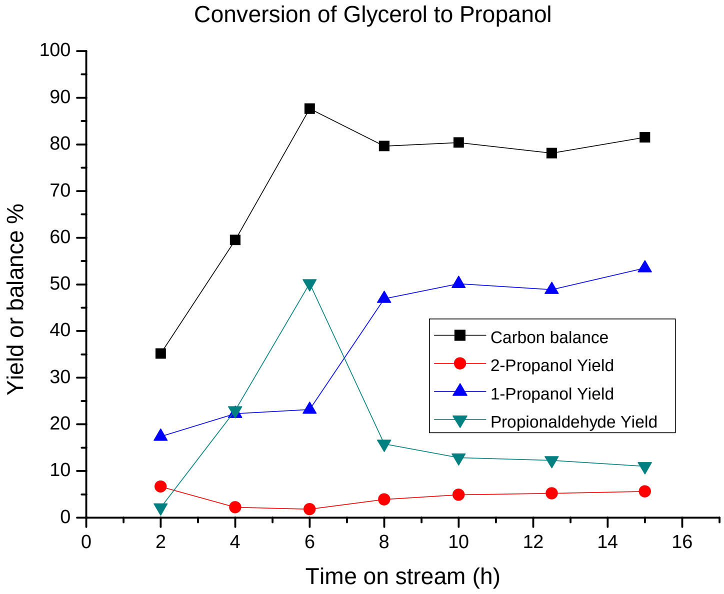


Figure 7 Conversion of glycerol to propanol using two reactors.

The reaction was initialized during a period of 6 hours and then reached a more stable state. The main products are 1-propanol (50% yield) and 2-propanol (5% yield). Both propanols can be dehydrated into propene. The major by-product is propionaldehyde with a yield of 10%. The propionaldehyde is an intermediate in the hydrogenation of acrolein into propanol and can be fully hydrogenated with longer residence time in the reactor, higher temperature or a more active catalyst. In figure 7, it can be seen that a decrease of the propionaldehyde content causes an increase in the propanol content. This means that there is an overall yield in this experiment of 65-70%, with a carbon balance of 80%.

2.1.4 Propanol to Propene

In this experiment the dehydration of propanol into propene was demonstrated. In this case, only reactor 1 in the experimental set-up in figure 3 was loaded with 30 g catalyst (Z-1104 10-20 mesh). The inlet feed to the system was 18 g/h consisting of 10 w% propanol in water. A carrier-gas flow of 50 ml/min of N_2 was added before the pre-heater and used to transport the formed gas-phase components, since the major system component (water) was condensed after the reaction. The inlet temperature of reactor 1 was 255°C and the reaction was performed at atmospheric pressure. The results are shown in figure 8.

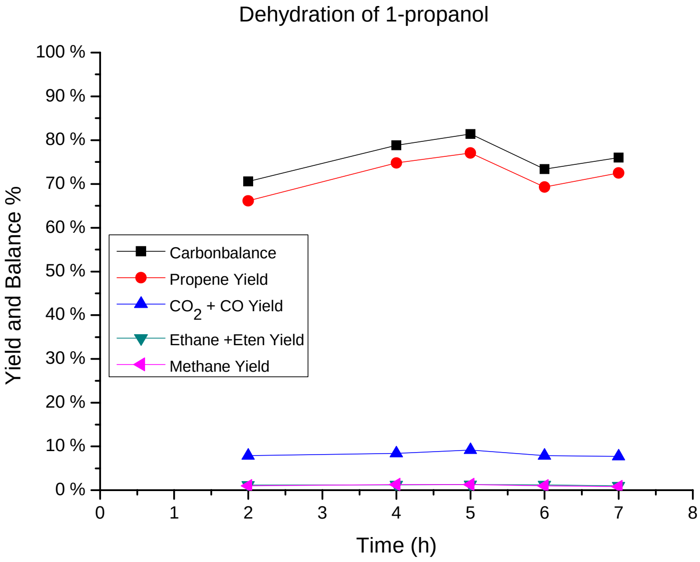


Figure 8 Conversion of propanol to propene.

In figure 8 the major product is propene with a yield of 70-75%. The major by-products are carbon dioxide and carbon monoxide. A small amount of methane is formed (1-2% yield) and traces of ethene and ethane.

2.1.5 Propanol to Propane

In this experiment, the conversion of propanol to propane was demonstrated. Reactor 1 was loaded with 30 g of the dehydration catalyst (Z-1152 10-20 mesh) and reactor 2 was loaded with 14 g of the purposely developed Biofuel #1014 catalyst (10-20 mesh). 18 g/h of 10 w% propanol in water solution was fed to the unit and 400 ml/min of hydrogen was added in the pre-heater. The inlet temperature was 280°C in reactor 1 and 270°C in reactor 2 and the experiment was run at 5 bar(a) pressure. In figure 9 the result of a 30 h run is shown. The yield of propane increases during the first 6-8 hours and is then stabilized around 85%. After 14 hours the inlet temperature of reactor 1 (dehydration) is decreased from 280°C to 230°C. This results in a sharp decrease in the propane production.

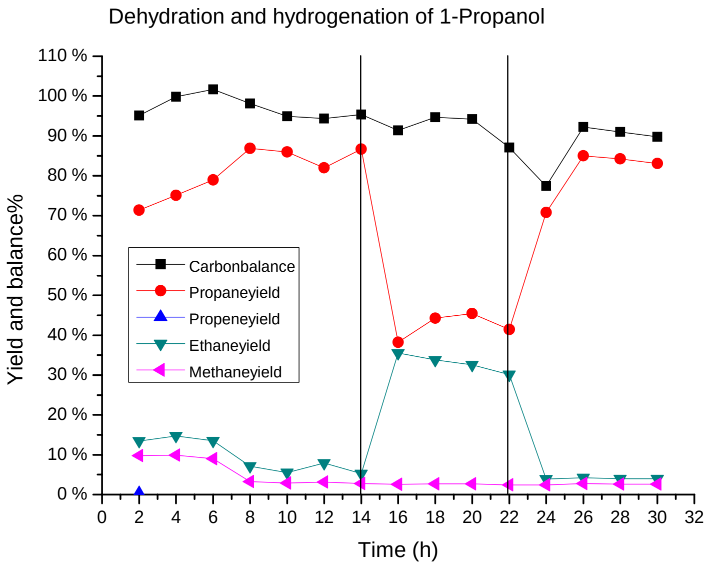


Figure 9 Conversion of propanol to propane.

As the temperature of the dehydration reactor (reactor 1) is decreased the dehydration of propanol decreases and the yield tales off However, after 22 hours the inlet temperature of reactor 1 is returned to 280°C and the propane yield returns to approximately 85%.

2.1.6 Glycerol to Propene

In this experiment the integrated process for production of propene from glycerol is demonstrated. This means that it includes the glycerol to acrolein step, acrolein to propanol step and the propanol to propene step. In the experimental set-up (figure 3) reactor 1 was loaded with 30 g of dehydrogenation catalyst (Z-1152 10-20 mesh), reactor 2 with 12 g of commercial hydrogenation catalyst and reactor 3 with 30 g of dehydrogenation catalyst (Z-1104 10-20 mesh). The inlet temperature was 280°C, 270°C and 280°C for reactor 1, 2 and 3 respectively. The feed was 18 g/h of 20 w% glycerol in water and the operation pressure was 5 bar(a). 400 ml of hydrogen was added to the inlet stream in the pre-heater. In figure 10, the result of a 30 h run is shown.

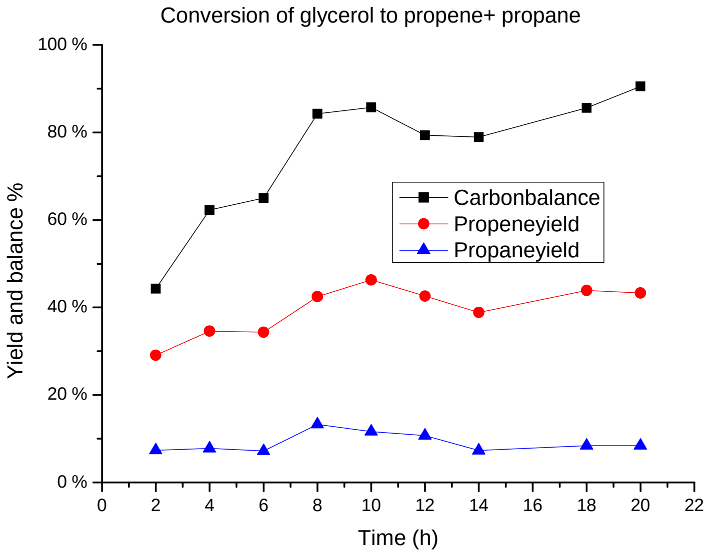


Figure 10 Conversion of glycerol to propene with H_2 present.

In this run, a propene yield of 40% is obtained. There is also a small production of propane, approx. 10% yield. The major by-product, not shown in the figure, is carbon monoxide and carbon dioxide. The propane present is probably a result of the hydrocarbon braking down into CO and CO_2 by reaction with water, releasing hydrogen. This free hydrogen then causes the hydrogenation of the formed propene into propane.

2.1.7 Glycerol to Propane

In this experiment, the production of predominately propane was demonstrated. The same set-up was used as in the experiment described above (Glycerol to Propene) but one further hydrogenation step with 14 g Biofuel #1014 catalyst was added. The inlet temperature was 280°C, 270°C and 280°C for reactor 1, 2 and 3 respectively. The feed was 18 g/h of 20% glycerol in water and the operation pressure was 5 bar(a). 400 ml of hydrogen was added to the inlet stream in the pre-heater. The result of an 8 h run is shown in figure 11.

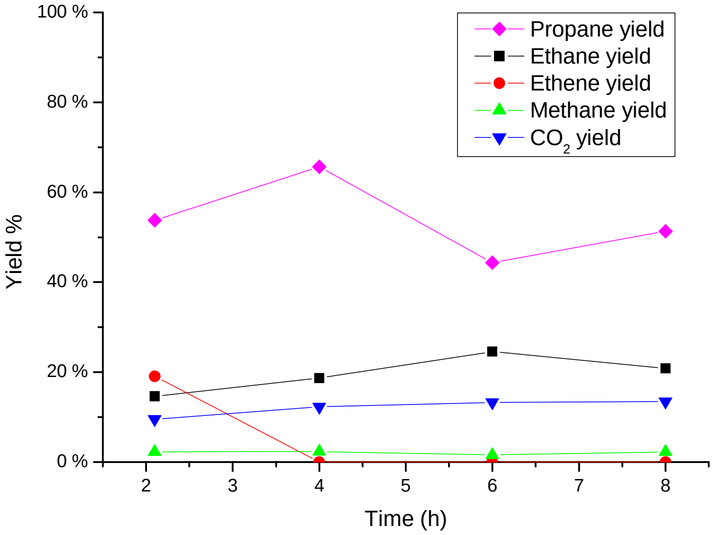


Figure 11 Conversion of glycerol to propane with H_2 present in the reaction mix; the results are shown using a normalized carbon balance.

The yield of propane is approximately 55% but there is also a 20% yield of ethane. This is however a sub-optimized experiment and by tweaking operation parameters and catalyst compositions, the yield of propane is expected to be significantly increased.

2.1.8 Acrolein to Ethene

Another possible way to produce a saturated alkane from glycerol is by decarbonylation of the terminal aldehyde group. In this experiment the production of ethene from acrolein was demonstrated, the unsaturated hydrocarbon is formed since there is a lack of hydrogen production functionality of the catalyst. 14 g of the Biofuel #1013 catalyst was loaded in reactor 1. A 10 w% of acrolein in water solution was fed into the reactor at a rate of 18 g/h. A carrier-gas flow of 100 ml/min of N_2 was added to the stream in the pre-heater. The reactor 1 inlet temperature was close to 300°C and the total pressure was 5 bar(a). In figure 12 the result of a 10 h run is shown.

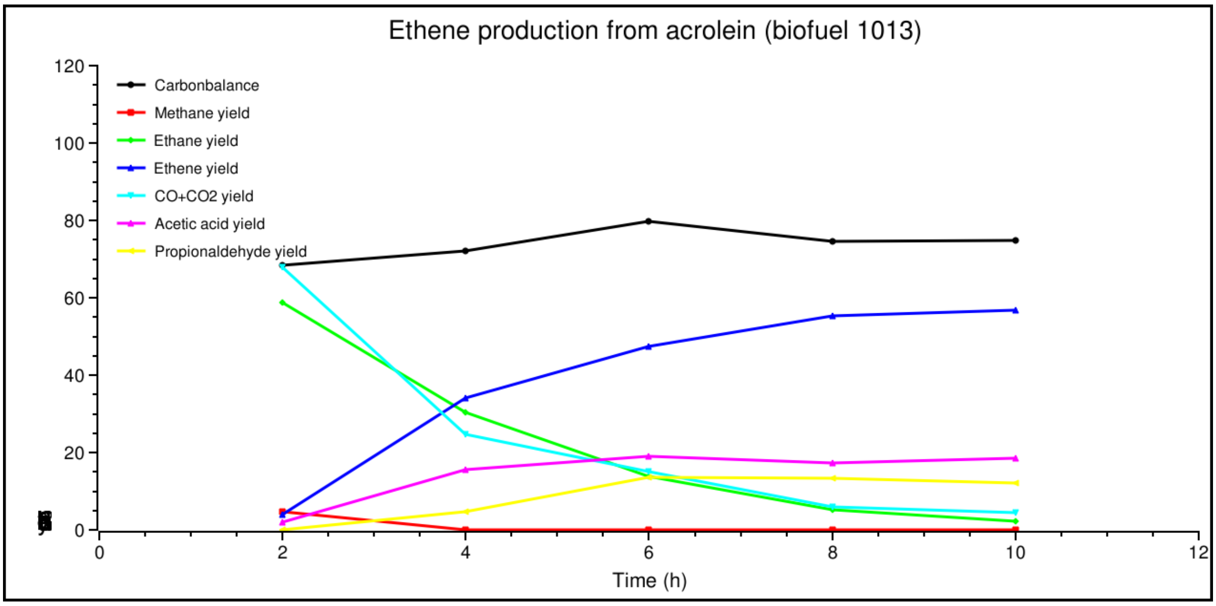


Figure 12 Conversion of acrolein to ethene.

In figure 12 it is possible to see that ethane is formed on a fresh non-reduced catalyst, but the formation decreases and ethene is formed instead. This catalyst is however not optimal for the production of ethane. For this purpose a catalyst with improved hydrogen production functionality have to be developed.

2.1.9 Acrolein to Ethane

In this experiment the production of ethane from acrolein by decarbonylation followed by the water-gas shift reaction was demonstrated. 14 g of the Biofuel #1011 catalyst was loaded in reactor 1. A 20 w% of acrolein in water solution was fed into the reactor at a rate of 18 g/h. 100 ml/min of hydrogen was added to the stream in the pre-heater. The reactor 1 inlet temperature was 270°C and the total pressure was 5 bar(a). In figure 13, the result of a 4 h run is shown.

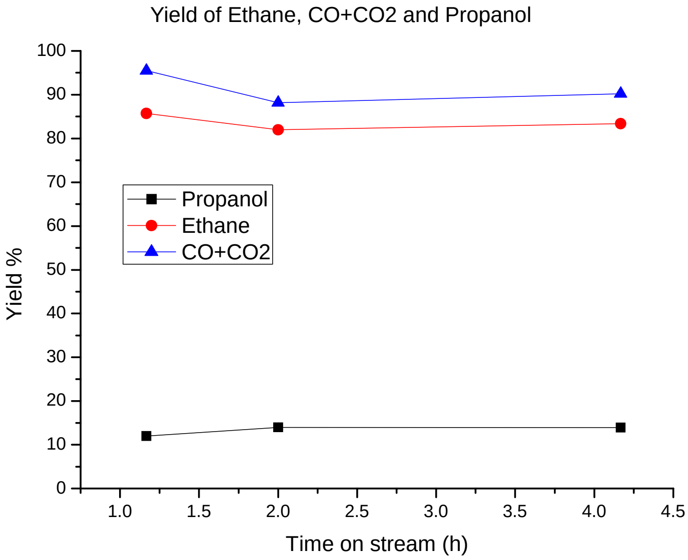


Figure 13 Conversion of acrolein to ethane with H_2 present.

In the reaction either a CO or a CO_2 is formed for each decarbonylated acrolein molecule. This means that the formed amount $CO+CO_2$ and ethane should be equal, if no other by-reaction occurs. The slight surplus of $CO+CO_2$ shows that a minor part of the acrolein is re-formed over the catalyst. Another by-product is 1-propanol formed by hydrogenation of the acrolein, due to the high hydrogen pressure.

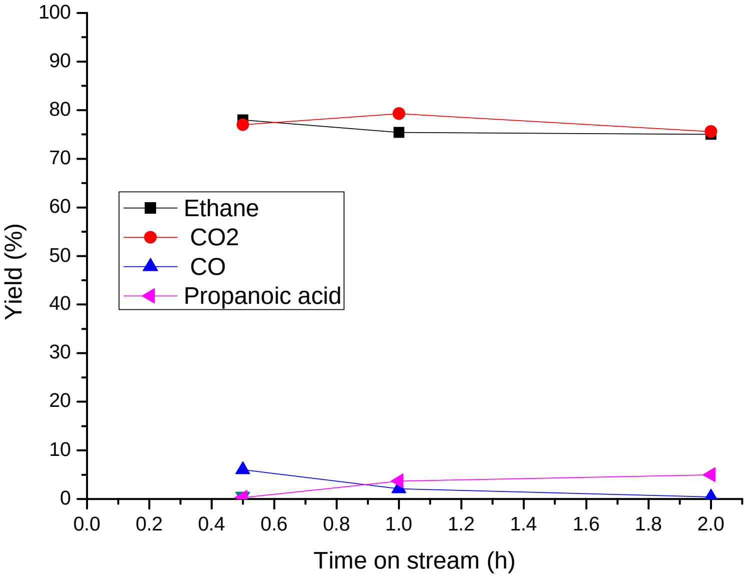


Figure 14 Conversion of acrolein to ethane without H_2 present.

In figure 14, a result is shown of a run with the same conditions but without hydrogen present. Expected products were ethene and carbon dioxide:

$$CH_2{=}CH\text{-}CHO \rightarrow CH_2{=}CH_2 + CO$$

However, rather unexpectedly, the products were ethane and carbon dioxide. This means that the catalyst shifts the formed carbon monoxide to carbon dioxide and hydrogen by reaction with water:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

The formed hydrogen is then consumed by hydrogenation of the formed ethene:

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3\text{-}CH_3$$

This means that the ethane production from acrolein (and the total pathway from glycerol) does not require any external hydrogen supply. The gas mixture with ethane, carbon dioxide, water and a small amount of propanoic acid should be rather simple to separate. This means that the Biofuel #1011 catalyst not only decarbonylates, it also has water-gas shift functionality.

2.1.10 Glycerol to Ethane

In this experiment the complete route from glycerol to ethane was demonstrated using several reactors. Reactor 1 contained 30 g of Z-1152 dehydration catalyst and reactor 2 contained 14g Biofuel #1011. The feed consisted of 18 g/h of 20 w% glycerol in water and 50 ml/min of N_2 was used as a carrier gas. The inlet temperature of reactor 1 was 270°C and for reactor 2 the inlet temperature was 230°C, the total pressure was 5 bar(a). In figure 15, the result from a 20 h run is shown.

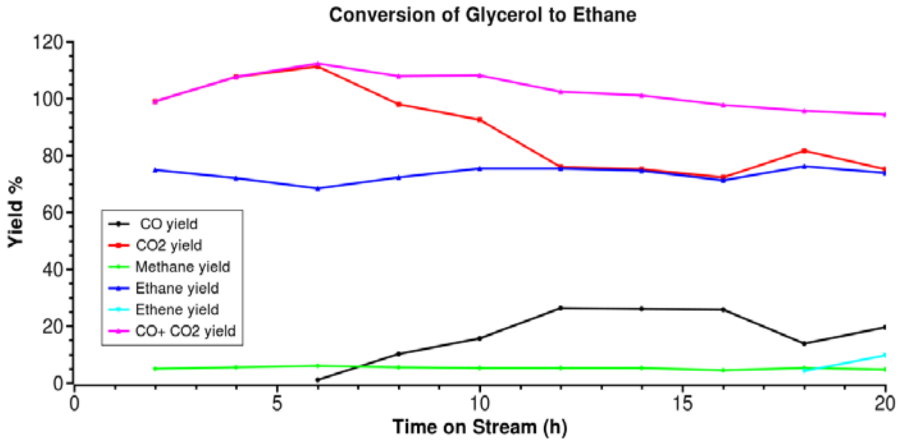


Figure 15 Conversion of glycerol to ethane without hydrogen, normalized carbon balance.

In figure 15 it can be seen that at least two parallel reaction paths takes place. The first one is the expected:

$$\text{Glycerol} \rightarrow \text{Acrolein} \rightarrow \text{Ethane} + CO_2$$

The second one produces carbon monoxide from either glycerol or acrolein, for instance:

$$\text{glycerol} \rightarrow 3\ CO$$

However, during the first 6 hours this carbon monoxide is oxidized into carbon dioxide, maybe during reduction of the catalyst. After 6 hours the amount of carbon dioxide starts to fall down to the same yield as the ethane, indicating an equimolar reaction (one mole acrolein forms one mole ethane and one mole carbon dioxide). While the carbon dioxide starts to decrease, carbon monoxide appears and displays a mirror image. This indicates that the carbon monoxide is formed from a side reaction, competing with the main reaction.

2.2 *Conclusions of Experimental Work*

It have been shown that glycerol in water solutions (10-20 w%) can be converted to various gas phase components. Intermediate steps, as well as total integrated processes have been demonstrated in the performed experiments for both the production of propane and ethane. Conversions to useful products in the range of 55% and above have been achieved in the laboratory scale, without any particular efforts to optimizing the processes. It is expected that there can be significant improvements in the yield by optimization of catalyst compositions, operating conditions etc.

The durability of the catalytic processes has also been demonstrated in medium term runs (10-60 h). This means there is a substantial chance to success with a pilot unit, even though there is a need for additional catalyst and process optimization as well as catalyst life time investigations.

Production of propene or propane can be done in three and four steps respectively with supply of external hydrogen. However, ethane and ethene can be produced in two steps without any supply of hydrogen, a simpler and more cost effective pathway for glycerol utilization than the propane path.

3 Cost Estimate

The production volumes of biodiesel has increased the production of bio-glycerol, as the relation between produced diesel and by-product glycerol is 10:1 on a mass basis. During 2007, the production of biodiesel in the EU 27 was 5 713 000 ton (20). The majority of this production was done in Germany (2 890 000 ton), France (872 000 ton) and Italy (363 000 ton). The Swedish production in the same year was 63 000 ton. The capacity in Europe in 2008 (calculated based on 330 working days per year and plant) is 16 000 000 ton of maximum biodiesel production. This indicates that during 2007, 571 300 ton of glycerol was produced. During the same time frame (2006) the biogas production was 1.3 TWh and at present there are 227 production facilities in Sweden, of which 34 facilities upgrade the biogas to transport fuel quality (21). Out of the 1.3 TWh produced some 0.23 TWh was upgraded and used for transportation purposes in 2006 (2).

In the economic evaluation, three alternatives have been compared. The alternatives are:

1. Propane production from glycerol with internal hydrogen supply.
2. Propane production from glycerol with external hydrogen supply.
3. Ethane production from glycerol.

Each of these units has been sized to match a biogas production capacity of 24 GWh biogas/year, comparable to the biogas facility in Vrams Gunnarstorp. The reaction set-ups are still preliminary and only to be viewed as a basis for the economic evaluation. However, initial calculations have shown that the heat balance closes, to some extent, in most cases depending on the possible inlet glycerol mixture concentration.

3.1 Unit Configurations

In the first process suggestion the hydrogen to support the hydrogenation of the double bonds, the result of the dehydration, is produced by steam reforming of glycerol. The hydrogen is recycled to improve the overall hydrogen balance using an internal PSA (pressure swing adsorption) technology, figure 16. Glycerol and water are pumped from two vessels and mixed. The mixed stream is sent to the glycerol conversion process (stream 6), where it is mixed with hydrogen (stream 14), and to the hydrogen generation process (stream 15). The mixture of glycerol/water and hydrogen is vaporized and passed through a first dehydration/hydrogenation step. The temperature is then adjusted and the gases are past through a second dehydration/hydrogenation reactor where the product propane is produced. The gases are condensed, heating the feed, and is mixed with the product from the hydrogen production. The gases are separated in the PSA, where the product propane and a small amount of CO_2 and hydrogen are rejected as PSA off-gas (stream 23). The hydrogen content of the off-gas is burnt selectively using a catalyst and air (stream 24) and the heat is used to preheat the steam reformer feed. The resulting mixture of CO_2 and propane is sent into the biogas plant (stream 27), where the CO_2 is removed with the CO_2 produced in the biogas fermentation.

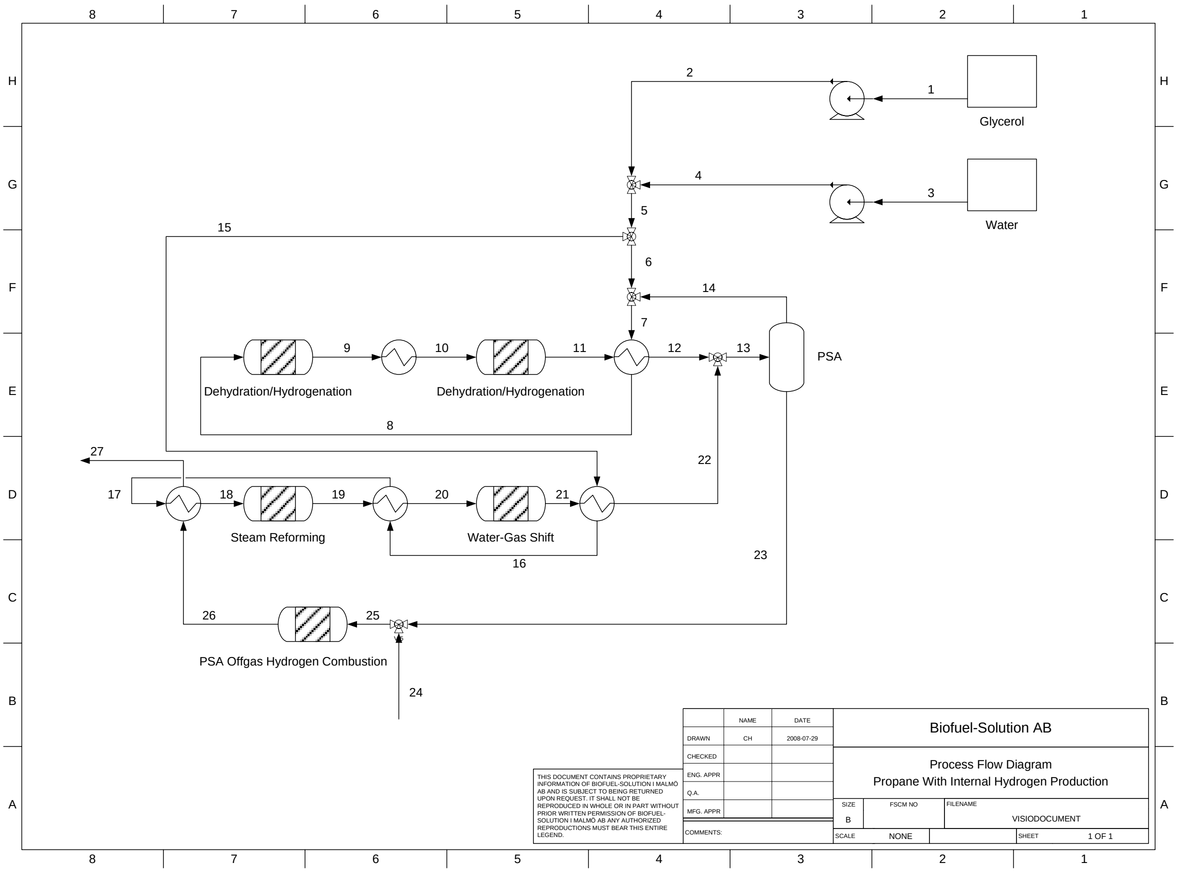


Figure 16 The Process Flow Diagram of the propane process with internal hydrogen production.

To avoid the cost of the hydrogen generation, an alternative set-up with external hydrogen supply has been considered, figure 17. In this case, the hydrogen production via steam reforming has been replaced by an external hydrogen supply (stream 13). The basic process remains the same as in the first case, with internal hydrogen recycle and clean-up.

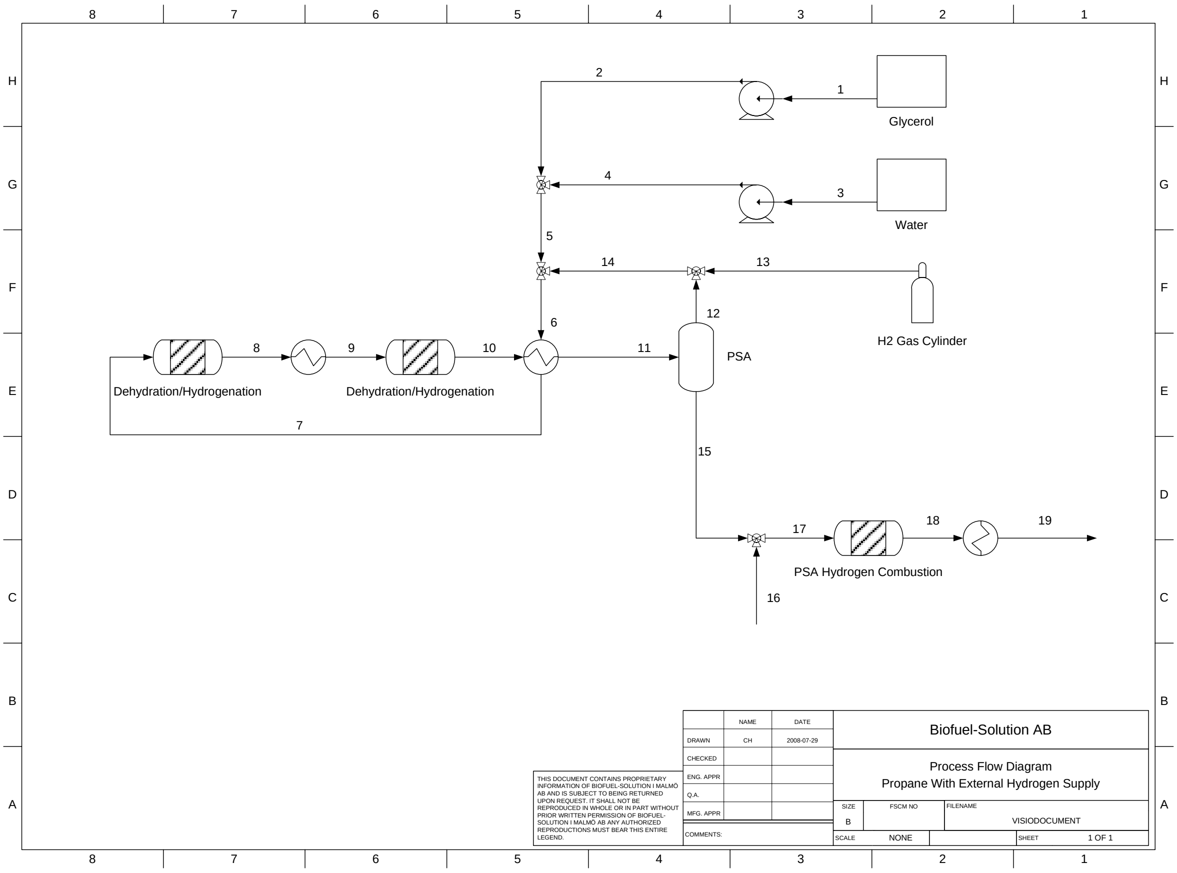


Figure 17 The Process Flow Diagram of the propane process with external hydrogen supply.

In the third case considered, the final product is ethane, figure 18. The glycerol (stream 1) is mixed with water (stream 3) and is vaporized and heated. The mixture is passed through a reactor and the resulting product, ethane and CO_2 (stream 8), is sent to the biogas process gas upgrading for CO_2 removal. The process is simpler than the ones suggested above, but a larger amount (40% excess) is needed to get the correct Wobbe-index of the biogas.

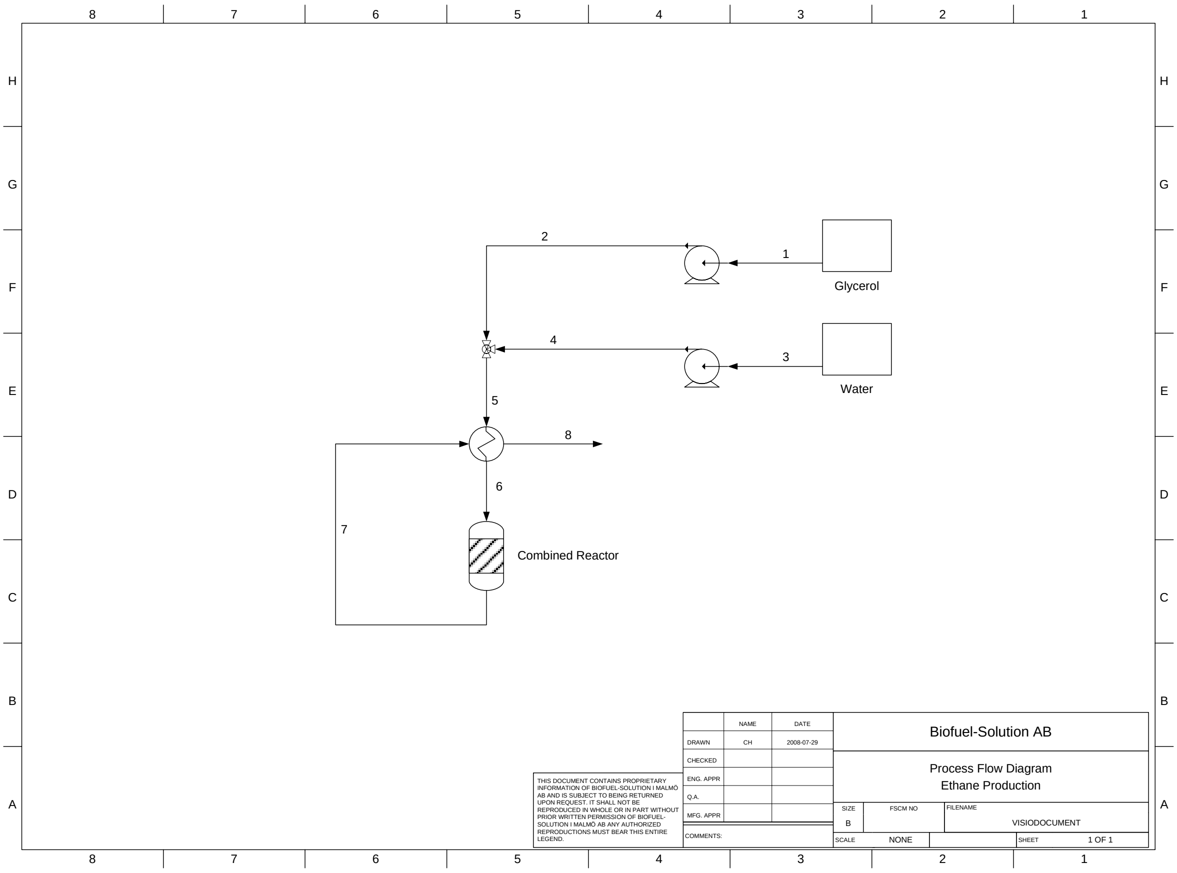


Figure 18 The Process Flow Diagram of the ethane production process.

3.2 Production Cost Estimates

To give a first approximation on the cost of production with the three different alternatives, the production costs have been estimated. In all cases the operating costs has been taken into account. The largest expense is the bio-glycerol used as feedstock, but also cost of electricity and water has been taken into account. The parameters of the three processes used in the cost estimates are summarized in table 1.

Table 1 Parameters used for the production cost estimates.

	Propane Internal H_2	**Propane External H_2**	**Ethane Production**
Glycerol (kr/kg)	0.9	0.9	0.9
Water (kr/ton)	20	20	20
Hydrogen (kr/kg)	0	33	0
Electricity	10% of glycerol cost	10% of glycerol cost	10% of glycerol cost
Investment cost	2 100 000	1 500 000	900 000
Interest rate	7%	7%	7%
Depreciation time	5 years	5 years	5 years
Time On-Line	8 000	8 000	8 000
Process efficiency	60%	60%	70%

The cost of the feedstock has been derived using actual crude glycerol costs, with a cost penalty for the actual clean-up of the glycerol. The investment cost has been decided by estimates on the type of equipment needed and the complexity of each system. The process efficiencies are based on the experimental investigation but the estimate should be considered preliminary, due to the exploratory nature and limited time and scope of the study.

Using the parameters in table 1 the production cost per kWh is 1.82 kr in the case of external hydrogen supply, 1.6 kr/kWh in the case of internal hydrogen production and 0.78 kr/kWh in the ethane case. The production cost of the two first cases doesn't differ very much, but in the case of ethane the production cost is significantly lower.

However, if the annual cost of adding propane to a 24 GWh biogas plant is taken into account, the costs are more level. In the case of internal hydrogen supply, the annual cost would be ~787 000 kr. Which should be compared to ~895 000 kr for the externally supplied hydrogen process and ~534 000 kr for the ethane process. The reason for the relatively high annual cost for the ethane process (compared to the differences in kWh cost) is due to the higher ethane required compared to propane (40% surplus). A cost breakdown for the base case can be viewed in table 2.

Table 2 Result of the base case cost estimates.

	Propane Intern. H_2	**Propane Ext. H_2**	**Ethane Production**
Glycerol (kg/h)	32	21	36
Water (kg/h)	126	83	144
Hydrogen (kg/h)	N/A	1.3	N/A
Operating Cost			
Glycerol (kr/y)	231 570	152 924	265 137
Electricity (kr/y)	23 157	15 292	26 514
Water (kr/y)	20 165	13 316	23 088
H_2 (kr/y)	N/A	347 347	N/A
Total (kr/y)	274 892	528 879	314 739
Equipment cost (kr/y)	512 170	365 836	219 502
Annual cost (kr/y)	**787 063**	**894 715**	**534 240**
kWh Cost (kr/kWh)	1.60	1.82	0.78

Using the base cases to investigate the supply of the feedstock, approximately 10 times the amounts processed in this fictive plant, is required for all the upgraded biogas in Sweden. This indicates that 2 560 tpa, 1 680 tpa and 2 880 tpa of glycerol (for the propane Int. H_2, the Propane Ext. H_2 and the Ethane case respectively) would be enough to supply the Swedish upgraded biogas production with higher alkanes. This indicates that the glycerol produced as a by-product from the biodiesel industry would be feasible as feedstock for this application.

To investigate how the production cost varies with the feedstock cost, a Monte Carlo simulation was performed. The feedstock was set at a lowest available value of 0.6 kr/kg, a maximum value of 2.4 kr/kg and a most likely value of 1.2 kr/kg. Within this range 10 000 values were generated using a normal distribution based on the minimum, maximum and most likely value; a triangulation simulation. In figure 19 the distribution of production costs are shown.

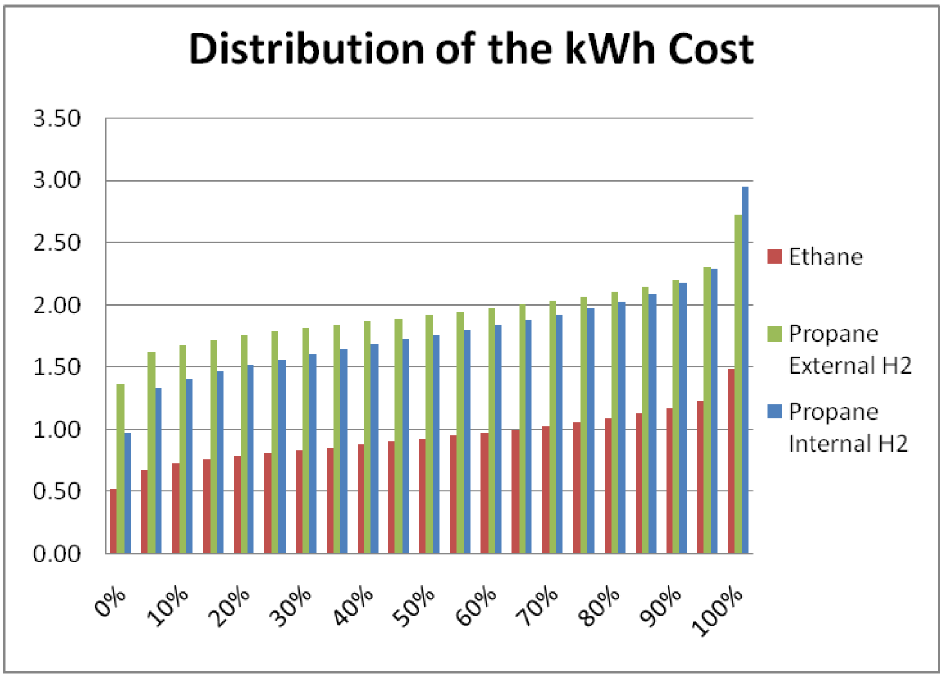


Figure 20 The distribution of the cost of production (kr/kWh) for the three different cases.

It is obvious that the cost of the feedstock does influence the cost of production; the costs vary from 1.43 to 2.40 kr/kWh in the propane case with internal hydrogen generation, 1.71 to 2.35 in the external hydrogen case and 0.64 to 1.43 in the ethane case. It is however apparent that the ethane configuration will give a lower cost independent of feedstock cost with a 50% percentile of 0.92 kr/kWh (50% of the 10 000 cases are below 0.92 kr/kWh). In the case of the annual cases, the difference is somewhat narrower and the ethane case is less favorable at higher glycerol feedstock cost due to the higher consumption, figure 21.

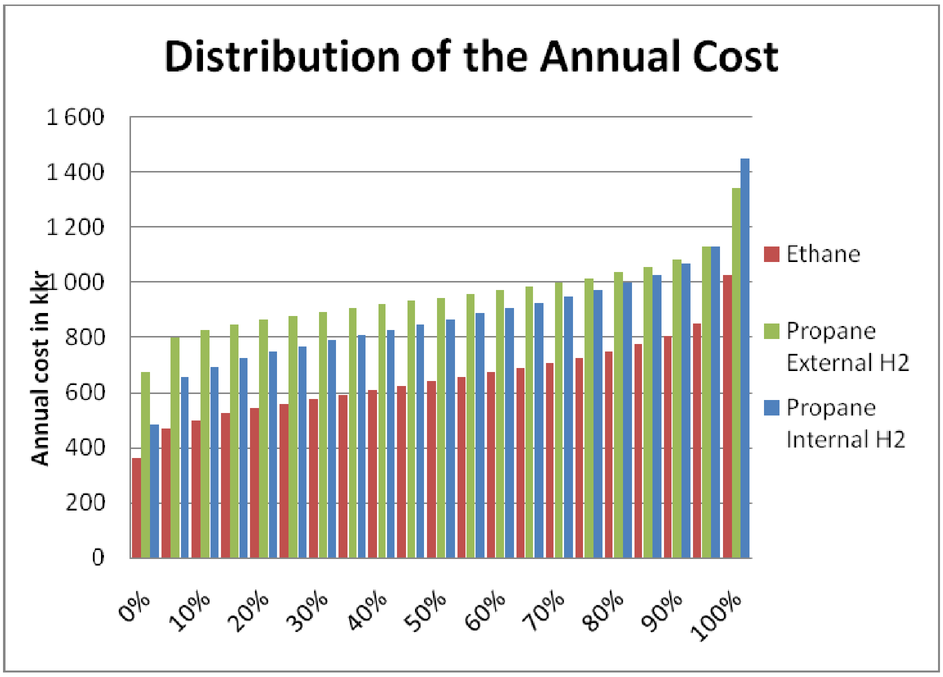


Figure 21 The annual production costs in kkr at different feedstock costs.

When annual cost is investigated, the unit using the least glycerol feedstock (the propane with external supply) is the one with the smallest standard deviation of the three units, ~60 000 kr. In the case of the propane with internal generation the standard deviation is ~90 000 kr and in the ethane case 104 000 kr. The ethane case is hence the most sensitive process to feedstock cost variations but the simulation show that it is also the lowest cost option, 50% of the simulations are below ~650 000 kr in annual cost.

To investigate the effect of the depreciation time, a similar Monte Carlo Simulation was performed. Using the base case parameters from table 1 with the exception of the depreciation time which was set to a minimum of 3 years, a most likely 5 years and maximum of 10 years and 10 000 values were generated using triangulation, figure 22.

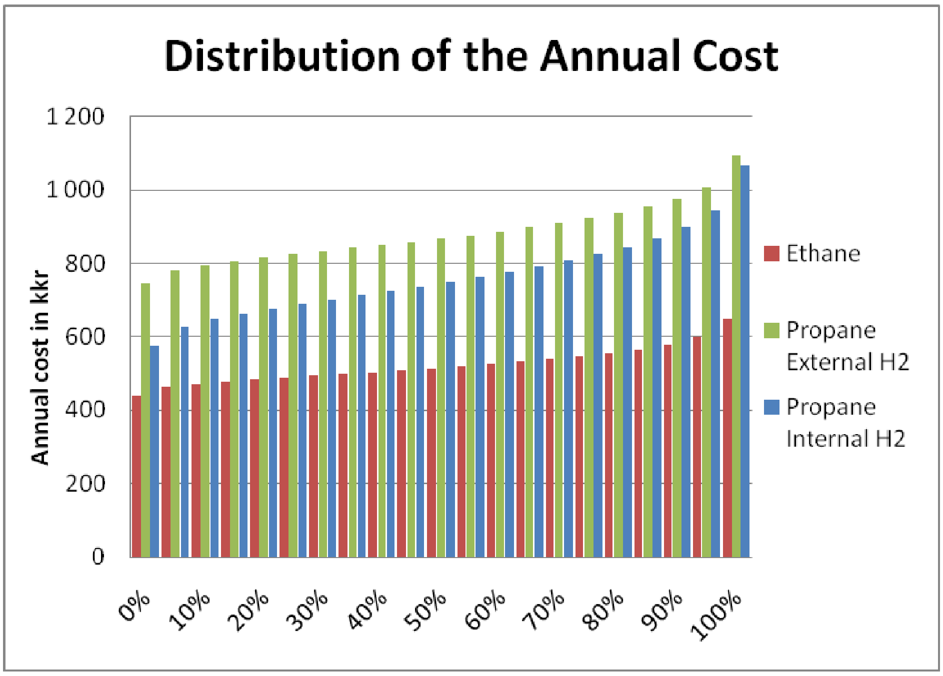


Figure 22 The annual cost distribution of the three processes incurred by a variation of the depreciation time.

The variation of the depreciation time will in general have a big influence on a process with low operation costs and high capital costs. In this case this is true for the two processes producing propane, where the investment cost is higher than for the ethane process. The standard deviation of the ethane process is ~42 000 kr, to be compared to ~69 000 kr (external H_2) and ~97 000 kr (internal H_2).

Another parameter influencing the production and annual costs is the investment cost. To investigate the impact of the investment cost, the estimated investment costs where triangulated using ±30% of the estimate as minimum and maximum values and the original estimate as the most likely value. The other parameters used the settings of the base case, Figure 23.

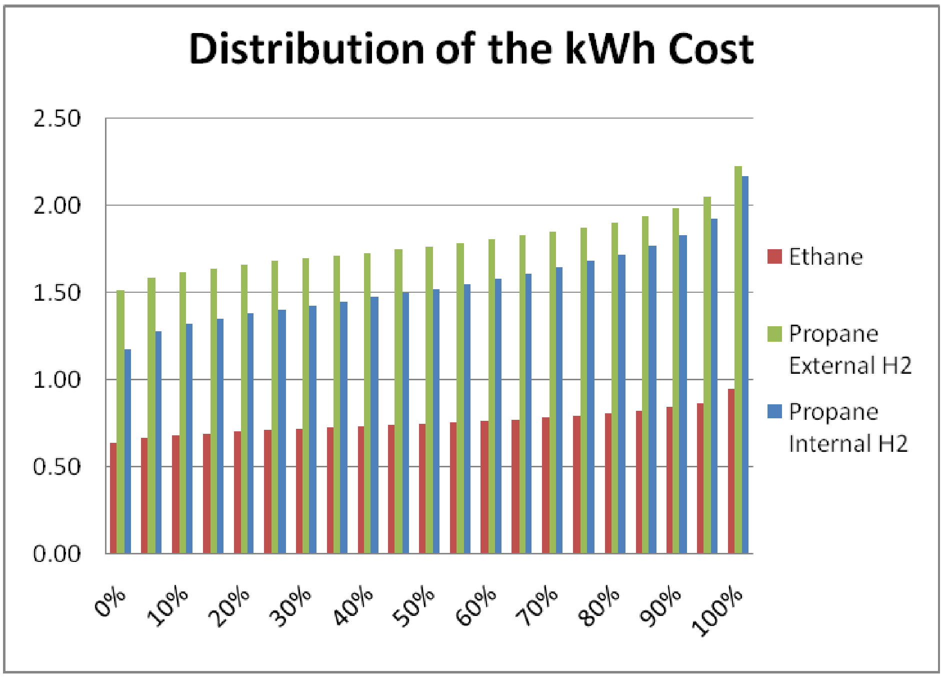


Figure 23 The effect of variations in investment cost.

As can be seen from figure 23 there are no major effects of the investment cost variation in the ethane case. The standard deviation is 0.04 kr/kWh, but in the propane cases the variations are higher. In the propane production case with internal H_2 production the standard deviation is 0.12 kr/kWh and in the external H_2 case it is 0.08 kr/kWh. To get an understanding of the overall variance of the processes, all of the parameters varied individually above have been varied simultaneously between the same levels as before, figure 24.

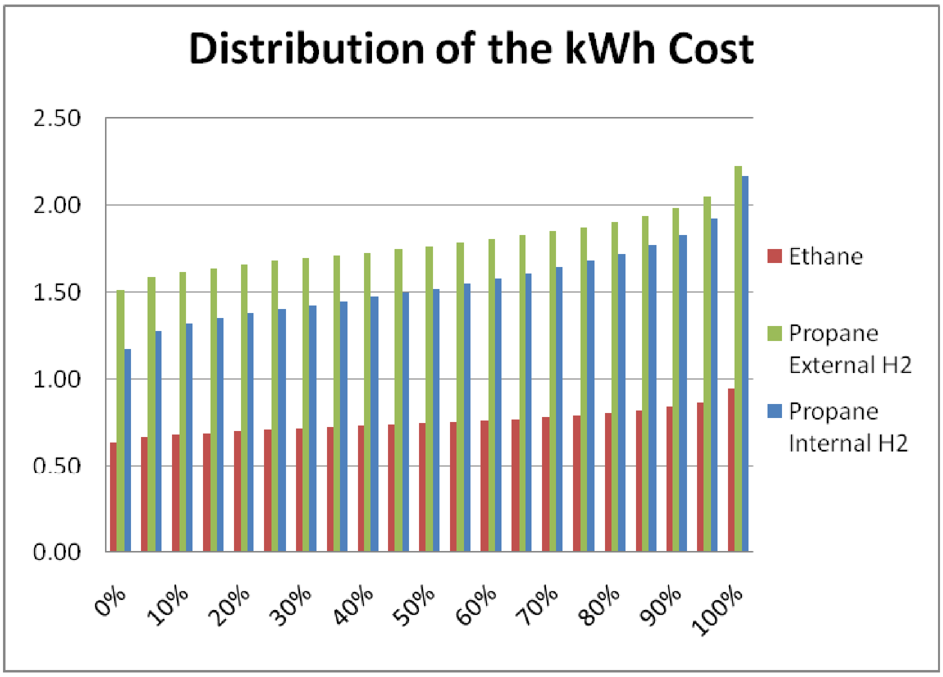


Figure 24 The variations in kWh cost when varying multiple parameters simultaneously.

The variation in production cost per kWh is small for the ethane process compared to the other processes. The mean value is 0.94 kr/kWh and 65% of the 10 000 cases are below 1 kr/kWh. For the other two processes the corresponding numbers are 1.78 kr/kWh (internal H_2) and 1.94 kr/kWh (external H_2) mean values and 65% of the 10 000 simulations are below

1.89 kr/kWh (internal H_2) and 2.01kr/kWh (external H_2). Again, the ethane production cost is substantially lower than the other two alternatives. If the annual cost is considered, there are larger variations, figure 25.

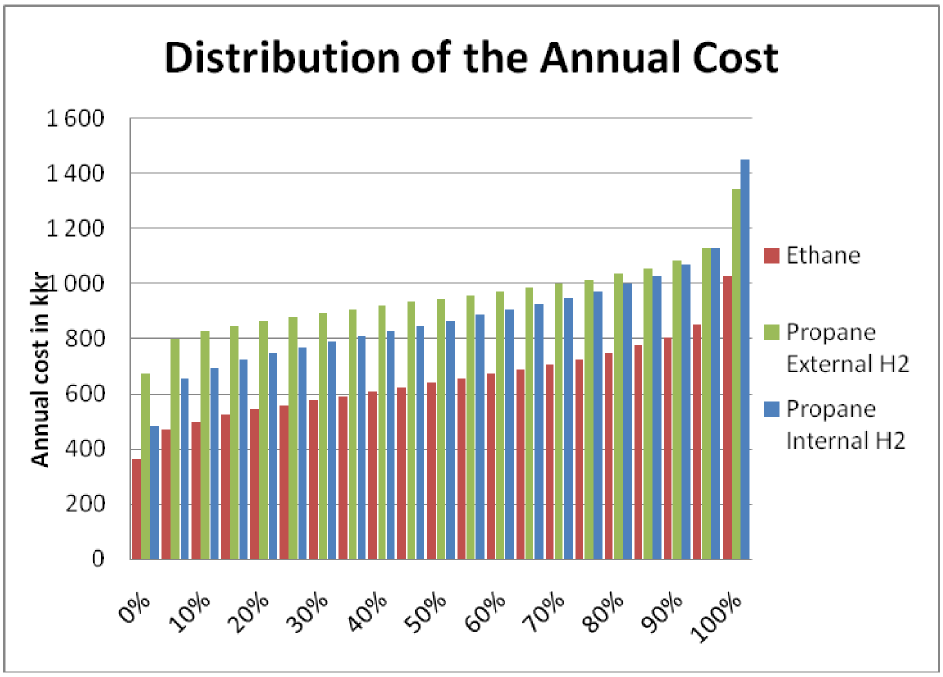


Figure 25 The variations in annual cost when varying multiple parameters simultaneously.

Especially the ethane process display larger variations than the other processes. The mean annual cost of the ethane process is ~647 000 kr, to be compared to ~876 000 kr (internal H_2) and ~952 000 kr (external H_2). The ranges however varies from 364 kkr to 1 030 kkr (ethane), 483 kkr to 1 453 kkr (internal H_2) and 675 kkr to 1 342 kr (external H_2).

However, if the cost per kWh is compared to that of fossil propane (LPG), there are some cost advantages to the fossil fuel. The US Midcontinent spot-price average over the last year (July 07 to July 08) was 149.5 cents/gallon, to be compared to the Mont Belvieu spot-price average over the same time period 151.6 cents/gallon (22). With these spot prices and a dollar rate of 7 kr/USD the kWh cost is 0.42-0.43 kr/kWh, which is lower than that of the produced propane by a factor of 3 to 5. However, the actual spot price in the time of writing is 187.6 cents/gallon, corresponding to 0.54 kr/kWh (23). This cost is not that far of the cost per kWh of the ethane production process (mean of 0.94 kr/kWh in the Monte Carlo simulation varying all parameters), which is promising. Compared to biogas produced by fermentation and upgraded, costing between 0.64 to 0.74 kr/kWh in large scale (24), the ethane process could possibly be competitive in a low to medium feedstock-cost situation.

In Sweden the LPG is traded at 0.43 kr/kWh at the time of writing (25), to that price there is an additional cost for transport and taxes. At the moment the CO_2 tax is 0.24 kr/kWh and the energy tax is 0.01 kr/kWh in the LPG case. With this taken into account, the cost of LPG in the Swedish context would be 0.68 kr/kWh. As the glycerol can be considered a renewable fuel, it is exempt of taxation. This exemption will make the suggested technology even more attractive from a cost angle. In the case of the Swedish market, glycerol can be used to produce an LPG alternative with a small cost premium. If this is combined with green electricity production, the cost difference is even smaller due to the green certificate revenue.

4 Conclusions

The aim of this study was to confirm the technical feasibility of producing bio-propane from a renewable glycerol feedstock. In the experimental work, it has been shown that production of propane with 55-60% yield from glycerol and ethane with 65-75% yield is possible. It should however be noted that the experiments have been performed without extensive optimization; it is therefore expected that there are possibilities of improvements in the yields of both products by optimizing the catalyst compositions and process conditions.

From a technical aspect, both end-products considered are feasible to produce. There are however additional benefits to producing ethane from a simplicity standpoint. This route would omit the need for external or internal hydrogen supply. There is also a possibility to make the process run auto-thermally, by managing to increase the inlet glycerol concentration from 20% to 30% in water. Due to the simplicity and promise of higher yields in the ethane process, it is believed that the glycerol consumption can be approximately the same producing ethane and propane. Even though the produced, end-product kWh is higher in the ethane case.

From an economical standpoint, the production of ethane is more favorable than the production of propane, albeit just as feasible. The production cost of the ethane produced is in the same order of magnitude as the fossil propane used in the biogas industry today. Using ethane as a component in LPG will however be limited by the allowed maximum of 2% ethane. This limitation can however be disregarded at the moment, as the 2% is still a very large market in Sweden and abroad.

The supply side of the glycerol does not seem to be a limiting factor at the moment. The production of upgraded biogas in Sweden today will require about 20% of the byproduct glycerol produced by Perstorp bio-chemicals in Stenungsund. This indicates that the purpose of using glycerol for supplying additional heating value to upgraded biogas is feasible not only today, but for a foreseeable future. However, the economic feasibility is limited by the feedstock cost. Therefore it would be suitable to use a lower grade, crude glycerol, than the one generated in Stenungsund. Another advantage of using glycerol is that a non-poisonous, non-volatile liquid could be transported and converted on-site, instead of the liquefied gas used today.

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