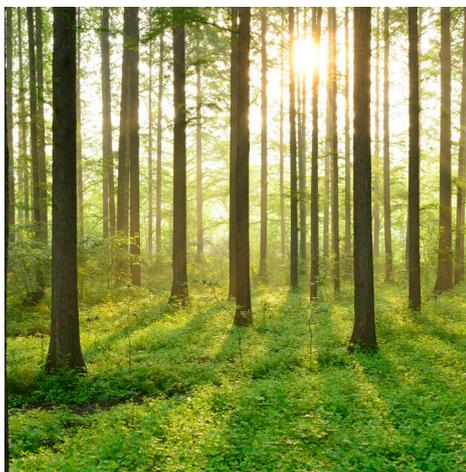


# DEMONSTRATING RENEWABLE PROPANE

REPORT 2018:538



ENERGIGASTEKNIK



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# Demonstrating Renewable Propane

Upscaling and alternative feedstocks

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## Foreword

**This project evaluated the production of LPG from renewable sources. The report has been produced by BioFuel-Solution AB and the authors Christian Hulteberg, Andreas Leveau and Øyvind Nørregård.**

The authors would like to acknowledge the Swedish Energy Agency, Energiforsk - Swedish Energy Research Center, for its financial contribution to the project within the scope of the program "Samverkansprogram Energigasteknik" – The cooperation research program Energy gas technology.

These are the results and conclusions of a project, which is part of a research program run by Energiforsk. The author/authors are responsible for the content.

This work was also made possible by financial support from Calor Gas and SHV Energy.

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## Sammanfattning

**Det finns en betydande infrastruktur på plats för användning av gasol. Gasolen används i allt från uppvärmning till kemiska processer och som fordonsbränsle. För att kunna använda denna infrastruktur även efter energisystemet ställts om till förnybara råvaror utvecklas teknik för att producera gasol från just sådana råvaror, t.ex. glycerol och cellulosa.**

Denna rapport sammanfattar konstruktionen av en pilotanläggning för just produktion av gasol från glycerol, men även framsteg gjorda inom omvandling av cellulosa till gasolråvara.

Projektmålen var att syntetisera gasol från glycerol med minst 85% energibehållning. Producera gasol som uppfyller kraven att fyllas på bilar eller i flaskor. Kontinuerlig drift av anläggningen under 2000 h och syntetisera minst 50 kg gasol inom specifikation. Samt att verifiera experimentellt en ny rutt till gasol från alternativ råvara.

Arbetet har delats in i två delar där den första delen har fokuserat kring design, konstruktion och användning av en pilotanläggning för att producera förnybar gasol. Denna gasol produceras från glycerol som är en biprodukt från produktion av främst biodiesel, men som även erhålls i andra sammanhang. Piloten, med syfte att producera 100 g/h gasol, har designats genom att först ta fram en processbeskrivning. Därefter har denna beskrivning använts för att göra, i tur och ordning, processflödesdiagram, mass- och energibalanser, rör- och instrumenteringsdiagram samt detaljdimensionering av de i piloten ingående komponenterna. Efter design har piloten konstruerats, driftsatts och körts under ett antal tusen timmar.

Under arbetet med piloten har ett antal lärdomar kunnat dras. Dessa är inte enbart av hög vetenskaplig/teknisk karaktär, utan även av rent praktisk natur. Till exempel är det svårt att hitta roterande, t.ex. kompressorer, utrustning i liten skala.

Baserat på de resultat som presenteras går det nog att säga att piloteringen varit relativt framgångsrikt, trots många oväntade händelser under vägen. Händelser som tvingat fram en förlängning av projektet i förhållande till den ursprungliga tidplanen. Målet om kontinuerlig drift under lång tid har passerats med råge. Gaskvaliteten är inte helt i enlighet med specifikationerna, men det skulle med största sannolikhet gå att lösa med ytterligare ett reningssteg. Detta gjordes dock inte på grund av tidsbrist. Vad gäller det kvantitativa målet att producera 50 kg propan har detta mötts, men gasens kvalitet har inte varit av rätt kvalitet. Vad gäller utvecklingen av en process för alternativ råvara till processen från cellulosa så har signifikanta framsteg gjorts. Dock återstår arbete med både katalysatorer och processen innan den kan anses vara kommersiell.

## Summary

**There is a significant infrastructure in the world for using liquefied petroleum gas (LPG). The fuel is used in many applications, spanning from heating to chemical processes as well as a vehicle fuel. To be able to use this infrastructure also after a transition from fossil to renewable sources, a technology for producing LPG from such resources (glycerol, cellulose etc.) is being developed. This report summarize the construction and operation of a pilot plant converting glycerol into LPG. But also report the progress made in turning cellulose into a LPG feedstock.**

The project aimed at synthesizing LPG from glycerol with at least 85% energy conservation, fulfilling specifications for transport fuel or bottling. It also aimed at operating the pilot plant for more than 2,000 h and synthesizing at least 50 kg of LPG within specification. Another specific project aim was to verify experimentally a new route to LPG starting from an alternative, renewable source.

The work has been divided into two parts, where the first part has been focused on the design, construction and operation of a pilot plant for synthesizing renewable LPG in the 100 g/h scale. The LPG is produced from glycerol, a side-product from the production of biodiesel and other renewable fuels. The pilot design started by defining the process description. Based on this design document, process flow diagrams, heat and mass balances, piping and instrumentation diagrams as well as detailed dimensioning of pilot components have been performed. After the design-phase, the pilot was constructed, commissioned and operated for several thousands of hours.

Working with the pilot, a number of conclusions have been possible to draw. Conclusion not only of scientific nature, but also of practical, operational aspects. E.g. how difficult it is to find rotating equipment (compressors mainly) suitable in small scale.

Based on the results presented, it is clear that the pilot has been rather successfully designed and operated, albeit there have been many unexpected snags during the course of the project. Also resulting in a delay in finalizing the project as compared to the original time plan. The goal of long-term operation of the plant has been surpassed with comfortable margin. The gas quality is perhaps not perfectly matching that of commercial gas, but it is believed that this may be solved with an additional purification step, which was not included in the pilot operation due to time constraints. Also, the quantitative goal of 50 kg of propane produced has been met, however, as previously discussed, this propane has not been on-specification. With respect to the production of an alternative feedstock for the process from renewable sources, significant progress has been made. However, there is still a requirement of more development with respect to the catalysts used and the process before this may be commercialized.

Both of the processes investigated hold promise for a future commercialization. The process for turning glycerol into renewable propane has been significantly advanced during the project. However, there are still steps required in moving the process into full scale. The final gas separation will have to be solved, as well as the liquefaction of the gas. This should be a rather straight forward engineering feat. Thereafter, it is suggested that a commercial demo is constructed, preferably one collocated with existing infrastructure for hydrogen generation and potentially also gas purification/liquefaction. A suitable scale for this plant would be on the order of 10,000 tonnes per annum of propane. Thereafter plants in the size of 50,000 to 100,000 tonnes per annum should be perfectly feasible.

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# 1 Introduction

**LPG is an existing, well-adapted energy carrier that is very well suited for use in rural areas with no natural gas grid. It is also a very clean-burning fuel that when used in, e.g. internal combustion engines, produce very little soot and NO<sub>x</sub>-emissions. Further lowering the environmental impact, producing a renewable and sustainable LPG, is highly desirable.**

This report documents the progress in a project for implementing and commercializing a process for producing renewable propane, which is the main constituent in liquefied petroleum gas (LPG) in Sweden. The project is a continuation of a development that was initiated in 2006 by Swedish company Biofuel-Solution AB, turning glycerol into renewable chemicals and fuels [1-5]. The technology has been covered by three patents granted and enforced in 34 European countries as well as the US and India. The project has been performed as a joint development project with British Calor gas Ltd. as well as their parent company SHV Energy BV. In this particular project, two different parts have been investigated. The first part is the construction of a demonstration unit in the 100 g propane/h scale, with the purpose of showing the technology developed in an integrated and up-scaled fashion. The second part of the project involves the development of new technology for utilizing cellulose as an alternative feedstock to the process.

## 1.1 PROJECT GOALS

The overall goals of the project as stated in the application was as follow:

1. Synthesize LPG from glycerol with at least 85% energy conservation
2. Produce LPG fulfilling the autogas and bottle specifications
3. Continuous operation (2,000 h)
4. The synthesis of min. 50 kg of on specification LPG
5. Experimental verification of an alternative process pathway for feedstock

The first four goals are related to the design, construction and operation of a pilot plant, while the last goal is related to a research and development part of the project.

## 1.2 REPORT STRUCTURE

The report will start by giving a background to the technology developed as well as some insights into the current market situation for various feedstocks potentially useful for the conversion to LPG. The next part will report the design, construction and operation of the pilot unit, including operational experience and result data. The second to last section will report the development performed within the conversion of cellulose to renewable LPG and the final section will give the conclusions of the project and references to literature cited in the report.

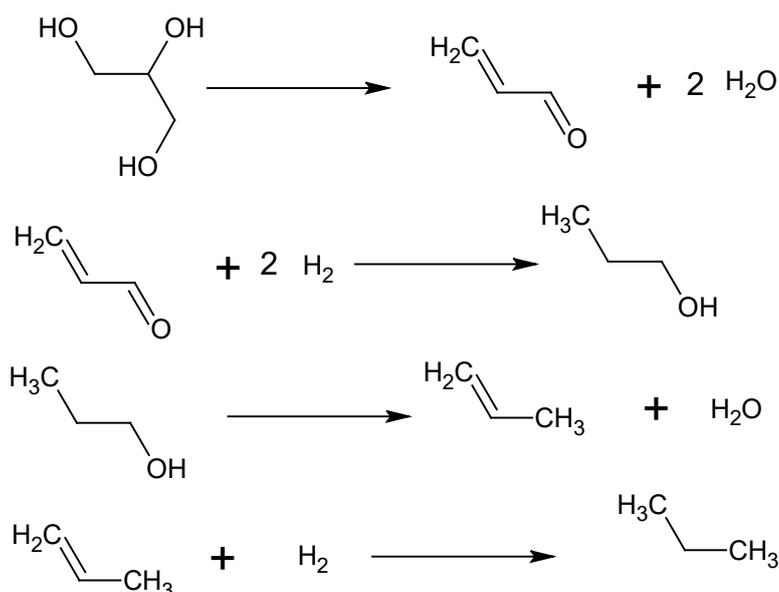
## 2 Background

The background section aim at giving a top-level overview of the current development in renewable LPG, including the process further investigated in this report. But also, the background to using alternative feedstocks for producing propane is introduced here.

### 2.1 CURRENT DEVELOPMENT IN RENEWABLE LPG

The process converting glycerol into LPG has been developed over the last 10 years and has resulted in a number of publications [1-4] and one patent covering this particular area [5]. The process is performed in the gas phase and the intention is to operate it on the crude glycerol grade coming from the production of biodiesel. The production of biodiesel in the EU in 2016 amounted to 10.7 million tonnes of oil equivalents [6], which would give a corresponding production to some 1 million tonnes of glycerol, on-top of the glycerol stemming from the traditional processing of oils and fats, e.g. for production of fatty acids and fatty acid alcohols. This will put the amount of glycerol available for valorization in Europe alone in the range of 1.2-1.3 million tonnes per year, which the corresponding number for the globe is a factor 2-3 of this [7].

There are many attempts in the literature on how to transform glycerol into value-added products, too many to report in this context. However, the book by Pagliaro and Rossi is a good starting point [8] and here are also some other references given for the reader to look into more details if interested [9-50]. The pathway followed in this particular case is an initial dehydration of glycerol forming acrolein, followed by a hydrogenation of acrolein to propanol, dehydration of propanol to propylene and finally a hydrogenation of propylene forming propane. Please find a reaction scheme below.



Scheme 1 The reactions from glycerol to propane.

There is quite a lot of research directed to finding a solution to renewable LPG production. The reason for this is from a technical perspective most likely the flexibility, low sulfur content and low tendency of soot formation of LPG as a product as well as decoupling the cost of LPG from fossil energy costs. There are methods being developed for using genetically modified *E. coli* bacteria [51]. The organism can, after genetic modification synthesize propane instead of triglycerides from a sugar substrate. Another method is the use of renewable dimethyl ether [52], which is a viable pathway at least up to a certain blend (10-15% [53]) after certain modifications to the current LPG infrastructure. Finally, there is one commercial output of renewable LPG based on hydrogenated vegetable oils from the Neste Rotterdam refinery. The capacity is 40 ktonnes per year and the product is marketed by SHV energy [54].

## 2.2 ALTERNATIVE FEEDSTOCKS

In this section, a background is given to the work with alternative cellulose-based and alcohol-based feedstocks. As a basis for the continued experimental work, an initial economic assessment has been performed for the two pathways outlined.

### 2.2.1 Cellulose-based feedstock

The process presented above implies that the glycerol needed is provided from the large surplus coming from the production of bio-diesel. With a sudden increase in demand of glycerol, a cellulose based feedstock would fit in well as another green alternative. By finding a reaction pathway to glycerol starting from glucose, a process is made possible and even promising for taking cellulose, e.g. fibers that the paper and pulp industry has deemed too short for using in paper, in account for production of propane.

By using cellulose as feedstock several process steps are necessary prior to be able to extract the glucose needed for further reaction to glycerol. The steps as shown in Figure 1 can be concentrated down to the following; pre-treatment, enzymatic hydrolysis, hydrogenation and hydrogenolysis, followed by the same multiple steps as mentioned above to reach the final product, Propane/LPG.

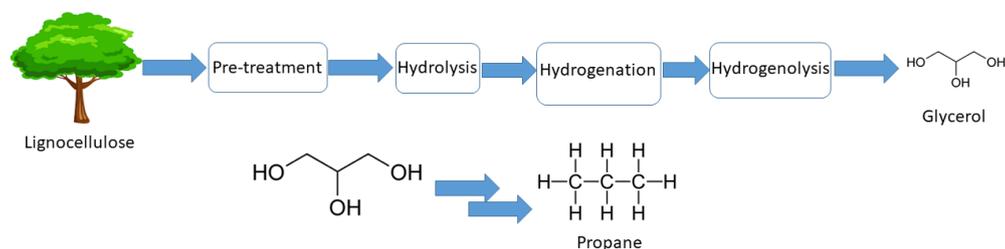


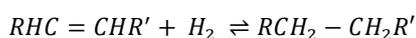
Figure 1 The full chain from wood to glycerol.

Starting from the beginning with pre-treating the wood, this process step can be performed in several ways. The different ways can be divided into; mechanical, combined chemical and mechanical and finally biological [55]. Mechanical methods of pre-treatment, such as milling are often considered as non-sustainable

due to the high demand of energy required for the process. One commercially available method, suitable for wood types such as pine or willow, is treating the wood with acids. The acids separate the hemicellulose from lignin by extracting the lignin into the liquid acid phase. This pre-treatment also breaks down the structure of all constituents in the lignocellulosic material; cellulose, hemicellulose and lignin, into smaller molecular chains [56]. A downside regarding pre-treating with acids is that parts of the product is lost, with the degradation of the polymeric structure in both hemicellulose and cellulose, turning into other by-products e. g. furanes, fenols and weak acids. Among furanes the most common by-products are furfural and 5-hydroxymethyl-5-furfural (HMF). The concentration of by-products are highly depending on choice of execution of the pre-treatment. Concentrations will as an example differ between a one step proceeedure compared to a two step proceeedure. Three weak acids are formed during the pretreatment: acetic, leuvlinic and formic acid.

After the lignin is separated the partly degraded cellulose and hemicellulose is available for hydrolysis. The purpose of the hydrolysis is to break down polysaccharides into monosaccharides. This conversion is mainly performed enzymatically wherein a mix is needed to be able to degrade both hexoses and pentoses [57].

Hydrogenation is defined as the addition of hydrogen gas,  $H_2$ , to a molecule as shown as an example in reaction 1, wherein a double bond is saturated.



*Reaction 1*

As the reaction shows saturation is more commonly performed at unsaturated carbon-carbon bonds rather than at carbonyl-carbons, carbon-oxide bonds. It is however shown by hydrogenation of acrolein to 1-propenol that the selective hydrogenation of carbonyl group is possible [58]. This reaction pathway is performed through a catalyst, usually a metal surface, of which the most common metals are transition metals such as platinum, palladium and nickel.

The reaction is most commonly considered to take place only at the metal surface and thus it is of importance to able to create an as dispersed metal surface as possible. This is performed by adding the active metal onto a porous material consisting of an agglomeration of crystallites, in most cases a metal oxide, in different sizes. When the catalytic material is in place, the metal surface is activated through reduction with hydrogen gas at elevated temperatures, characteristic for the combination of the metal and the metal support. After the reduction of the metal surface it is possible for the substrate to adsorb onto the metal surface where to reaction can take place. For the hydrogenation of D-glucose to D-sorbitol, which is one of the proposed process steps in the route from glucose to glycerol, the reaction can be considered to resemble the pattern shown in Figure 2.

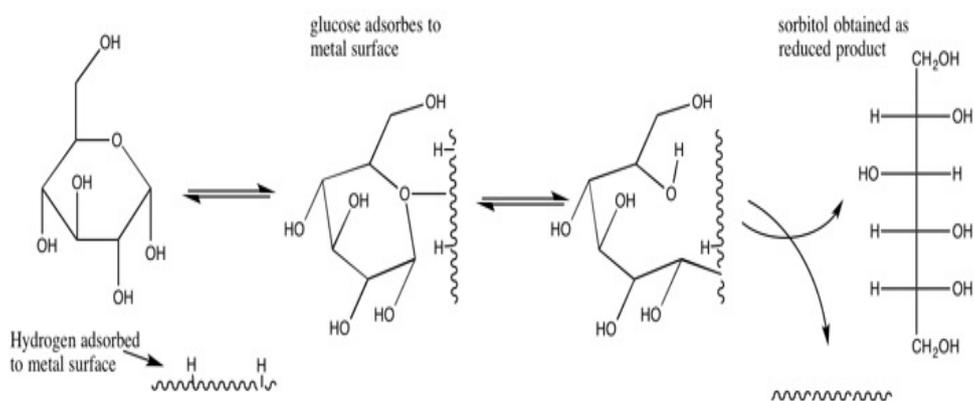


Figure 2 The ring-opening of glucose.

Catalysts intended for hydrogenation are usually consisting of transition metals dispersed on a support material, which in turn consists of an agglomeration of different sizes of one or many types of metal oxides. Earlier attempts of hydrogenation of glucose has shown that catalysts including metals such as ruthenium or nickel are suitable for this specific reaction [59-63].

In experiments performed by Kusserow et al. [59], ruthenium dispersed on an alumina/carbon-support converted glucose, in a glucose-water solution, up to 70% with a sorbitol selectivity of 90%. Tests were performed in a 300 mL autoclave reactor, with a temperature of 120 °C and a pressure of 120 bar. Same conditions over a commercial Ni/SiO<sub>2</sub> catalyst also showed a selectivity towards sorbitol of 90% but only a conversion of 30% of the glucose. Analyses also showed leaching of nickel from the catalyst ending up as ions in the product solution. When dispersing ruthenium on activated carbon Crezee et al. stated that the reaction is of first order except initially when it is of a zero order when initial glucose concentrations of 50% or higher are used [60]. These reaction parameters were found when performing tests at 100-130 °C and pressures of 40-75 bar.

According to B.J. Arena, it is well worth taking precautions to preserve the catalyst life in a continuous process [64]. When using reactors in stainless steel (SS316), the release of small amounts of iron from the reactor wall could be correlated to catalyst deactivation of the Ru-based catalysts used. This deactivation could be avoided using a coating of some kind on the reactor wall, e.g. PTFE. Another contaminant to be considered is oxygen. Oxygen dissolved in the reaction mixture may oxidize the glucose forming gluconic acid. This acid may in turn react with iron from the reactor to form iron gluconate, which acts as a very strong catalyst poison [64]. Sulfur may in addition be mentioned as a strong catalyst poison, which may be easily adsorbed on the catalyst surface. To avoid sulfur poisoning, a guard bed should be used to stop these components before they reach the actual catalyst bed.

The process for producing sorbitol on an industrial scale is well known in industry and is performed on a scale of about 800 000 tonnes per annum [65]. Amongst the largest producers are Roquette Frères, Cargill and SPI Polyols. The production is based on Raney nickel, due to the low cost of the catalyst. The catalyst is used in a pressurized batch or continuous reactor [66]. Due to the leaching of Ni to the

product, studies for replacing the Raney nickel catalysts have been done extensively. The best alternative to date seems to be Ru-based catalysts [59]. Based on this and the large number of patents on Ru-catalysts for this application, this is believed to be the industrial standard [67, 68].

The production of sorbitol is today based on a multi-step process starting from sugar in a continuous process [69]. The process starts by an enzymatic hydrolysis of the sugar to form glucose and fructose. By passing the mixed sugar intermediate solution through an ion exchanger, two separate fractions may be produced. The glucose solution is then further processed [70]; when processing starch there is no need for ion exchanging as glucose is the only resulting product. The glucose is then hydrogenated in a trickle-flow reactor with hydrogen, figure 3 [59].

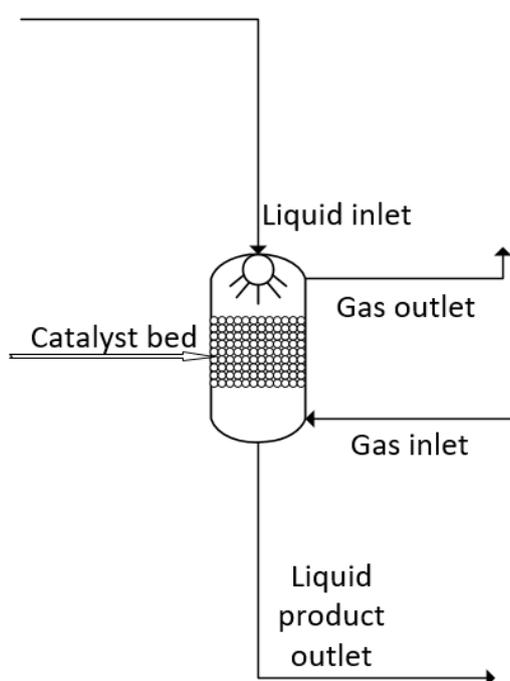


Figure 3 Schematic reactor overview for a trickle-flow reactor.

If the process is performed batch-wise, the glucose solution and the hydrogen is added in a closed vessel and the reaction is performed during vigorous stirring. Regardless of whether the process is performed continuously or in batch mode, the reaction occurs at 70-120 °C and 40-120 bar [60-63, 71, 72].

The final step in producing glycerol from cellulose is the hydrogenolysis of sorbitol. Hydrogenolysis is the cleaving of a molecule using hydrogen, in this case breaking a carbon-carbon bond. The reaction pathways may be different, depending on catalyst and molecule and may be selective to different bond types. The common factor is that one atom is usually carbon. When performing a hydrogenolysis of sorbitol, the expected reaction mechanism is that sorbitol is dehydrated, and the cleaving of the resulting product is performed via a retro-

aldol reaction. The resulting product is a ketone and an aldehyde. Polyols may be achieved by rehydration of the carbonyl carbon [73]. A possible reaction pathway can also be a dehydrogenation where two hydrogen molecules are split off, followed by a retro-michaelis reaction, splitting the molecule yielding a molecule with a double bond and a keton [74]. A simplified reaction scheme may be viewed below, figure 4.

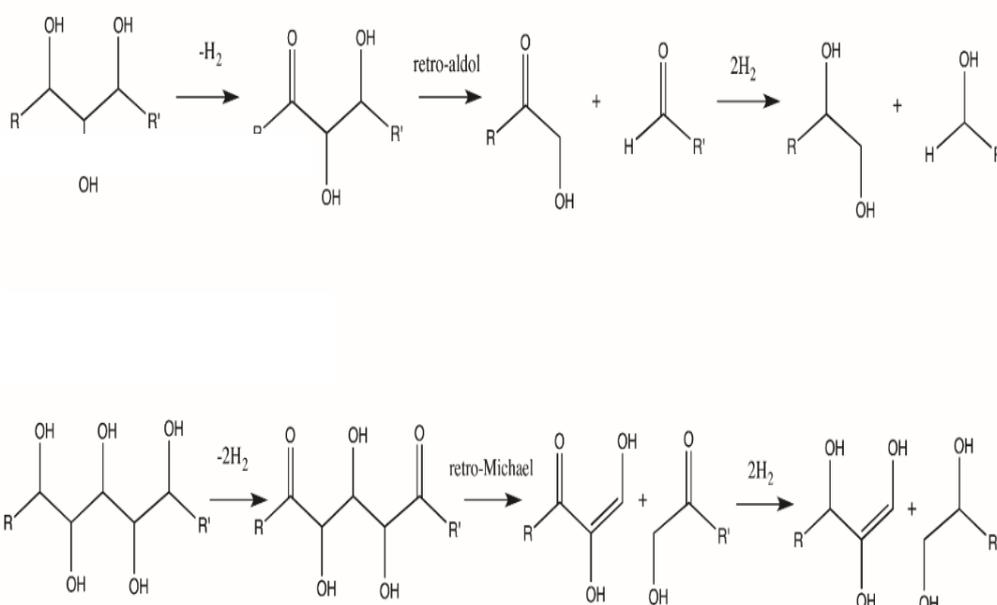
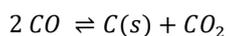


Figure 4 The suggested reaction mechanisms.

Hydrogenolysis has previously been performed using sorbitol as a reactant, but oftentimes with the purpose of producing ethylene glycol or propylene glycol and not glycerol [73, 75]. The production of glycerol has been considered an undesired side-product. Given the less common process pathway chosen here, with the intention of producing glycerol, the catalyst choice is another one than the one traditionally chosen. Hydrogenolysis of sorbitol has been shown to proceed well over basic catalysts [76]. The hydrogenation of glucose is very selective, the carbonyl group is readily available for reaction. Unfortunately, it is more difficult performing the hydrogenolysis of sorbitol selectively due to the required carbonyl group transition. These transitions may occur at all six OH-groups, two primary and four secondary, making it difficult to selectively address only one OH-group. The retro-aldol reaction can be performed from both directions in relation to the carbonyl; except for primary carbonyls, lowering the likelihood of selectivity. The reaction with hydrogen proceeds according to first order kinetics for the interval 200-230 °C and 200-380 bar [77]. Due to the presence of  $\text{Ca}^{2+}$  on the surface, also other reaction mechanisms may be envisioned that could increase the yield and selectivity of the most commonly desired products ethylene glycol, propylene glycol and glycerol [75, 78, 79].

During hydrogenolysis of sorbitol, products such as xylitol and ribitol have been obtained [77, 80]. This makes it possible to predict that products that contain one single carbon atom, e.g. CO and CH<sub>4</sub>, may have been formed. CO is not a desired product as it may undergo subsequent polymerization reactions forming large carbon fragments after adsorption to the catalyst surface. This will inevitably block the pore structure and render parts of the catalyst inaccessible to the reactants; the polymerization is believed to occur according to:



*Reaction 2*

The carbon formation is counteracted by the high presence of water during reaction as well as the hydrogen partial pressure in the reactor, why it is believed that carbon formation should not be a highly deactivating factor if low sorbitol (or glucose) concentrations are employed [81]. However, the formation of CO may contribute to a secondary reaction resulting in more methane production. Several types of deactivation due to the solubility of the support in the liquid has been reported [80]. When using MgO as the basis for the catalyst formulation, this completely dissolves, indicating substantial deactivation. To counter act this, the solution may, e.g. be fully saturated with MgO, resulting in a basic solution. This will however result in downstream purification issues.

To assess the potential of the technology, a brief assessment was made. The major assumptions of this assessments are listed in table 1.

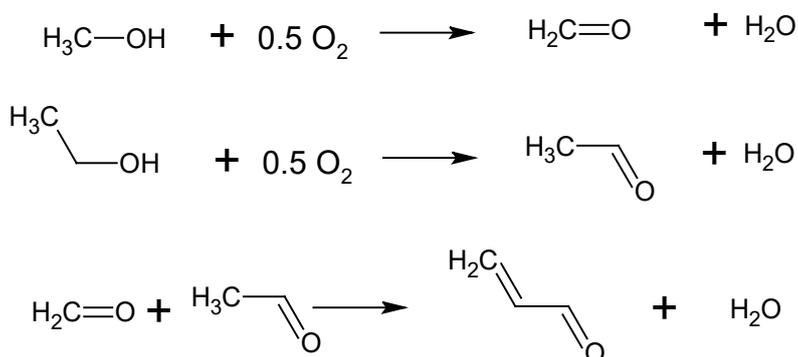
**Table 1 Economic assessment parameters cellulose-based feedstock.**

Parameter	Value
Stem wood	115 €/tonne
Hydrogen cost	2,500 €/tonne
Yield of glycerol and propylene glycol	85%

Using these assumptions, an indicative price range for the glycerol and propylene glycol produced is 350-400 €/tonne, which is not that much higher than the current cost of glycerol. Based on this, the main focus on developing an alternative, renewable feedstock was placed on the cellulose pathway.

### 2.2.2 Alcohol-based feedstock

There is also a possibility to convert a mixture of ethanol and methanol to an intermediate product in the process. This approach is based on the production of the two aldehydes, formaldehyde and acetaldehyde. These are then reacted in the gas phase to form the intermediate acrolein [82, 83]. It is also possible to use a bifunctional catalyst first forming the acetaldehyde from ethanol and then condensing the acetaldehyde with formaldehyde [84].



**Scheme 2** The reactions involved in producing propane from alcohols.

As depicted above, the condensation reaction yields, in theory, 100% acrolein. However, there are certain side-products also produced such as CO<sub>2</sub> and CO. For performing an overview of the economic assessment, certain assumptions have been made; these are presented in table 2.

**Table 2** Economic assessment parameters.

Parameter	Value
Acetaldehyde yield from ethanol	75%
Acrolein yield from acetaldehyde and formalin	85%
Cost of renewable ethanol	700 €/tonne
Cost of renewable methanol	500 €/tonne

It has been assumed that the cost of renewable methanol is about twice the market price of ordinary, natural gas-based methanol. Using these figures, the operating expenditure for producing renewable acrolein is more than 1,200 €/tonne. Based on this figure and the current cost of LPG, it was decided to focus on the cellulose-based feedstocks from an experimental point of view.

## 3 Pilot design and operation

For demonstrating the process in larger scale, a pilot plant has been designed. The purpose of the plant is to produce renewable propane at about 100 g/h scale and to assess not only the single pass option, but also the effects of recycling gas over the reactor system to investigate potential deactivation of catalysts. In this section, the system design will first be given, followed by the results from operating the plant.

### 3.1 PILOT DESIGN

The pilot plant has been designed by first defining the process description, the final version of this read:

To evaluate the production of propane from glycerol, a micro-pilot is constructed. The aim of the pilot is to have a relatively flexible set-up which allows for testing of all six steps from glycerol to LPG:

1. Vaporization of pre-mixed crude glycerol
2. Dehydration of glycerol to acrolein
3. Hydrogenation of acrolein to propanol
4. Dehydration of propanol to propylene
5. Hydrogenation of propylene to propane
6. Condensation and separation/purification of propane

The specified outlet flow rate is 0.1 kg of propane per h in the condensed state. Samples will have to be collected and sent away for external analysis. The unit will include two dehydration reactors, two hydrogenation reactors and a separator, as well as necessary feed and collection vessels. The hydrogen supplied will originate from bottles and recycle will be attempted. The hydrogen should be variable from 1-5 times the stoichiometric. The system will be electrically heated, and no heat integration will be performed.

The unit will be able to operate continuously without supervision, for at least 100 h, but with local controllers and alarms. The unit will be supplied with enough control and supervision equipment, to enable safe and meaningful operation and data collection. During off-spec production or during commissioning, the propane will be vented.

Based on this description, the process flow diagram was drawn up, the piping and instrumentation diagram was made, and the heat and mass balance solved. Finally, the detailed design was performed using the information from these design elements. These parts of the design process will be described in the next few sub-sections.

#### 3.1.1 Process flow diagram

In figure 5, the process flow diagram is reported. The process starts with the glycerol and the water in two different containers. These liquids are moved from these containers (streams 1 and 2) into an electric heater for vaporization. There after they are mixed with the hydrogen recycle (stream 17) and passed through a

dehydration reactor forming mainly acrolein and propionaldehyde (stream 8). After the dehydration reaction, the gas is cooled using natural convection and then hydrogenated into propanol (stream 9). The gases are re-heated and further dehydrogenation to propylene (stream 11), cooled using natural convection and finally hydrogenated to propane (stream 12). The gases are cooled (heat exchangers are denoted HX) and passed through a flash vessel where hydrogen and other, mainly non-condensable gases are separated from the propane product (stream 14). This stream is re-compressed and passed through the reactor system again (stream 17); make-up hydrogen is added to this stream (stream 16). The propane stream is further separated from the inlet and formed water in the separation section (streams 20 and 21).

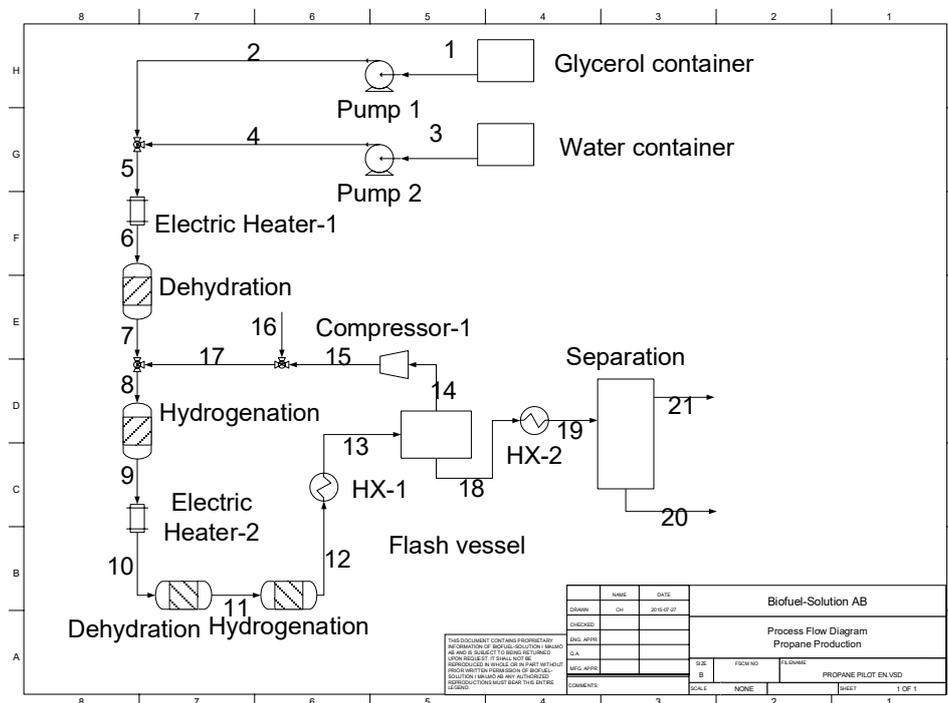


Figure 5 Process flow diagram.

### 3.1.2 Piping and Instrumentation diagram

Based on the process flow diagram, the process has been interpreted into a piping and instrumentation diagram, figure 6 a and b. This differs from the process flow diagram in that the level of detail is greater and includes the sensors needed for operating and measuring the process. The streams are numbered using the following syntax: first the stream number, followed by the material of the pipe (SS for stainless steel, TF for Teflon), followed by the outer diameter in mm. The sensors are noted TT for temperature transmitter, LS for level sensor, PT for pressure transducer.

Finally, the following abbreviations are used:

- MFC is mass flow controller
- PCV is pressure control valve
- PRV is pressure relief valve
- VS is vessel
- EMV is electro-magnetic valve
- HX is heat exchanger
- CHV is check-valve

There are quite a few differences compared to the process flow diagram. The first main difference is in the feeding system, where a pre-mixed glycerol-water solution is used instead of two separate tanks (VS-1). This has been done to overcome the high viscosity of the glycerol, which resulted in feeding difficulties. In addition, the compression section is much more complex compared to the process flow diagram, as will be further discussed below in section 3.2.1. The final compressor (depicted in figure 6b) is quite a lot more complex than was initially thought necessary.

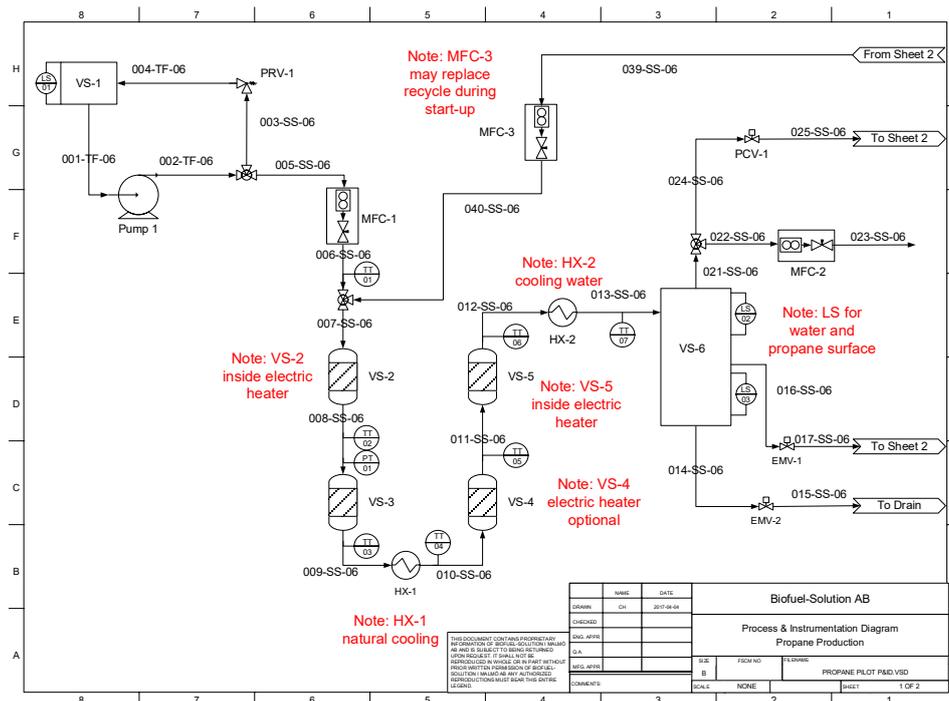


Figure 6a First sheet of the piping and instrumentation diagram.

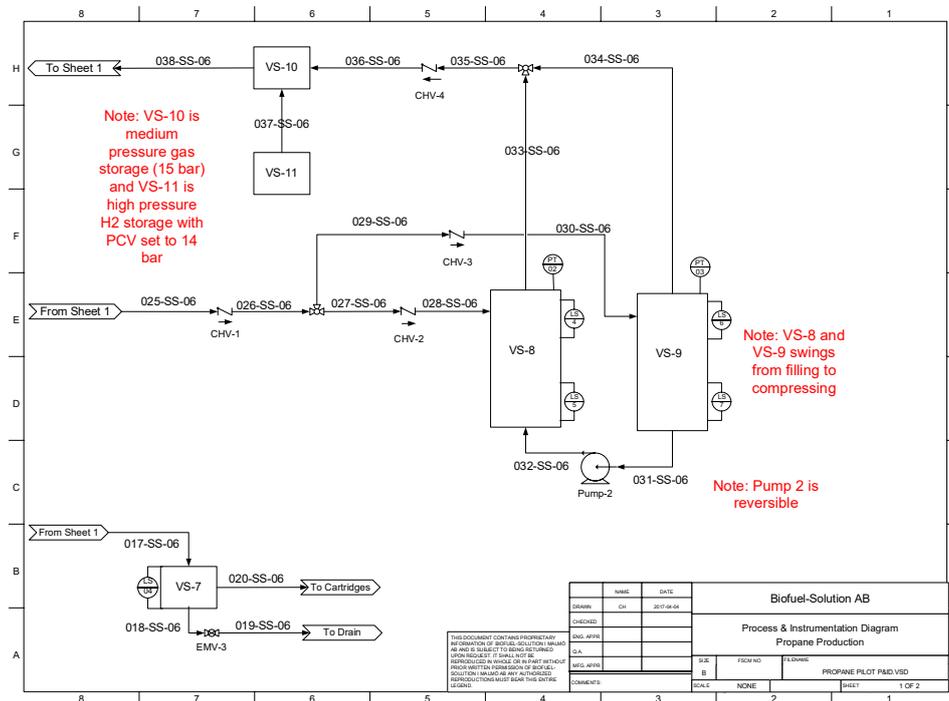


Figure 6b Second sheet of the piping and instrumentation diagram.

### 3.1.3 Heat and mass balance

It is quite difficult presenting heat and mass balance data in a comprehensive way. Table 3 below contains a majority of the streams needed to understand the ins and outs of the process flow diagram. The numbers refer to the process flow diagram in figure 5. To make the table more readable, some of the streams have been omitted. These are the ones that has been deemed to have little relevance in that they are repetitions or simple mixing of other streams.

Table 3 Heat and mass balance.

	2	4	6	7	8	9	10	12	15	16	17	19	20	21
<b>Temperature (°C)</b>	18.7	18.7	19	276.7	266.5	180	250	250	36.1	20	32.4	25	182.2	90.3
<b>Pressure (bar)</b>	13	12	11.9	11.9	11.7	11.5	11.4	11.2	12	13	12	10.9	10.5	10.5
<b>Vapor Frac</b>	0	0	0.91	1	1	1	1	1	1	1	1	0	0	1
<b>Mole Flow (mol/h)</b>	3	63	111	111	117	111	111	111	34	11	44	75	72	3
<b>Mass Flow (g/h)</b>	285	1426	1565	1565	1565	1565	1565	1565	117	21	139	1441	1311	130
<b>Volume Flow (l/h)</b>	1	1	426	426	448	364	424	431	72	22	94	2	2	9
<b>Flow (NI/h)</b>	1	1	997	2483	2618	2487	2487	2487	758	237	995	2	2	69
<b>Mass Flow (g/h)</b>														
<b>GLYCEROL</b>	285	285	285	285	0	0	0	0	0	0	0	0	0	0
<b>WATER</b>	1141	1141	1142	1142	1251	1251	1251	1304	2	0	2	1302	1300	3
<b>ACROLEIN</b>	0	0	t	t	165	t	t	t	t	0	T	t	t	t
<b>HYDROGEN</b>	0	0	87	87	87	75	75	69	66	21	87	t	0	t
<b>PROPANE</b>	0	0	50	50	50	50	50	180	50	0	50	127	0	127
<b>PROPANOL</b>	0	0	t	t	0	177	177	t	t	0	t	t	t	t
<b>HYDROXAC</b>	0	0	0	0	11	11	11	11	0	0	0	11	11	0

Stream	2	4	6	7	8	9	10	12	15	16	17	19	20	21
<b>Mass Frac</b>														
<b>GLYCEROL</b>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<b>WATER</b>	1	1	1	1	1	1	1	1	0	0	0	1	1	0
<b>ACROLEIN</b>	0	0	t	t	0	t	t	t	t	0	t	t	t	2
<b>HYDROGEN</b>	0	0	0	0	0	0	0	0	1	1	1	77 PPM	t	851 PPM
<b>PROPANE</b>	0	0	0	0	0	0	0	0	0	0	0	0	9 PPM	1
<b>PROPANOL</b>	0	0	t	t	0	0	0	t	t	0	t	t	t	0
<b>HYDROXAC (PPM)</b>	0	0	1	1	0	0	0	0	19	0	16	0	0	0
<b>Mole Flow (mol/h)</b>														
<b>GLYCEROL</b>	3	0	0	3	0	0	0	0	0	0	0	0	0	0
<b>WATER</b>	0	63	63	63	69	69	69	72	0	0	0	72	72	0
<b>ACROLEIN</b>	0	0	t	t	3	t	t	t	t	0	t	t	T	t
<b>HYDROGEN</b>	0	0	43	43	43	37	37	34	33	11	43	0	T	0
<b>PROPANE</b>	0	0	1	1	1	1	1	4	1	0	1	3	T	3
<b>PROPANOL</b>	0	0	t	t	0	3	3	t	t	0	t	t	T	t
<b>HYDROXAC</b>	0	0	t	t	0	0	0	0	t	0	t	0	0	t

Stream	2	4	6	7	8	9	10	12	15	16	17	19	20	21
<b>Mole Frac</b>														
<b>GLYCEROL</b>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<b>WATER</b>	1	1	1	1	1	1	1	1	0	0	0	1	1	0
<b>ACROLEIN</b>	0	0	t	t	0	t	t	t	t	0	t	t	t	1
<b>HYDROGEN</b>	0	0	0	0	0	0	0	0	1	1	1	728 PPM	t	0
<b>PROPANE</b>	0	0	0	0	0	0	0	0	0	4	1	1	1	
<b>PROPANOL</b>	0	0	0	t	t	0	0	0	0	t	1	1 PPB	0	
<b>HYDROXAC (PPB)</b>	0	0	0	274	274	0	0	0	0	0	1	1 PPM	0	

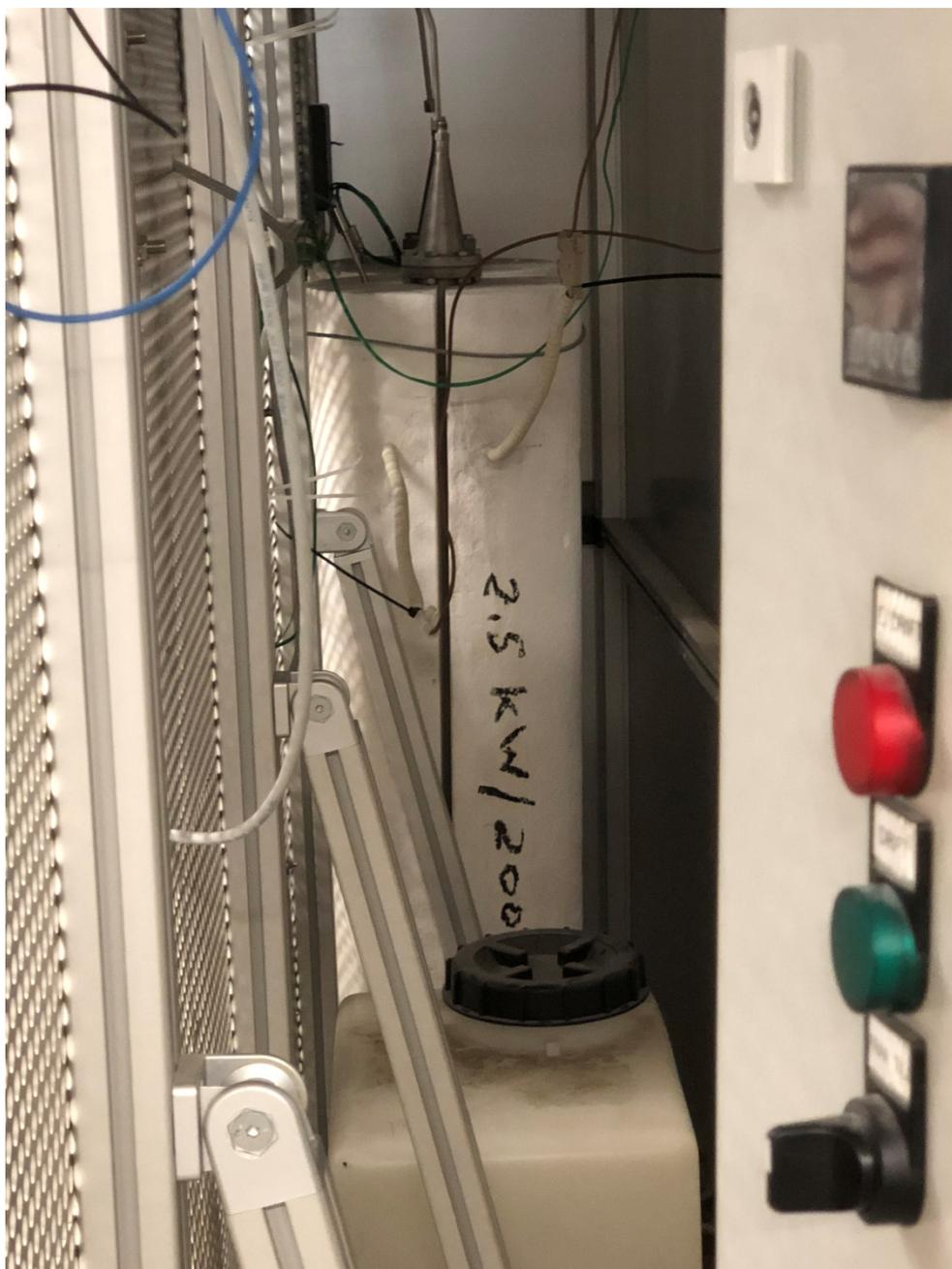
### 3.1.4 Detailed design

The above schematics, heat and mass balances has been used in detail dimensioning of the actual equipment used in the demonstration of renewable propane production. The first figure in this section, figure 7, show the pilot in its entirety. The reactors and heaters have all been skid-mounted to be accessible from both front and back. In addition, the entire skid may be rolled out of the test bay using the wheels in the bottom. Starting from the left in the picture, the first thing to be seen is the electrical cabinet and the control computer.



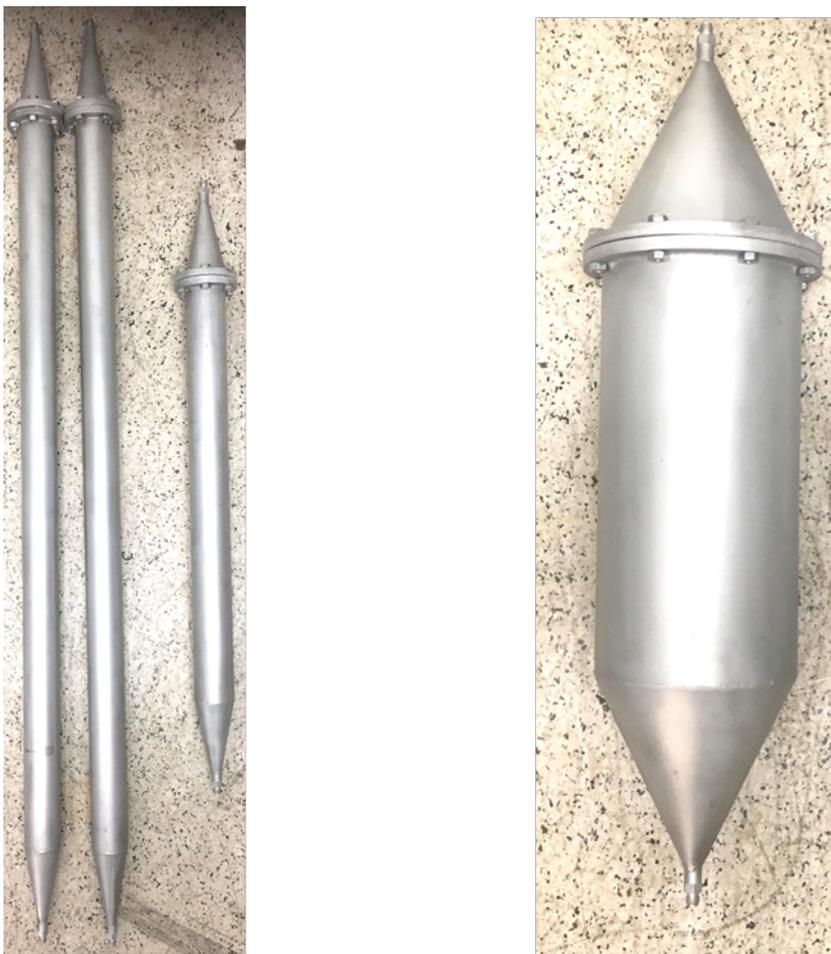
Figure 7 The pilot set-up.

The next part of the pilot, moving to the right in the figure is the first vaporizer used and the reactor, visible as a vertical part starting with gray insulation, followed by a black heating mantle. After the in-between insulation, it is repeated with gray insulation and a black heating mantle. Underneath the reactor and vaporizer is the compression pump. Next to the first set of reactors, moving to the right in the figure, are the second set of reactors. Again, starting from the top with a gray insulation part and a black heating mantle; the final hydrogenation reactor is just an insulated tube reactor. The final part of the set-up, to the far right is the compression and separation vessels. As alluded to earlier in the text, there was a second vaporizer added after some time. The reason for adding this will be explained later in the text, but it is clearly visible in figure 8, with the glycerol/water tank in the foreground.



**Figure 8** The second vaporizer and the glycerol/water vessel.

The vaporizer and the reactor vessels look quite different depending on the type of reaction performed. Figure 9 contain the new vaporizer type to the left and the dehydration reactor to the right. The vaporization and the hydrogenation type reactors are designed to have a high heat exchange-to-volume ratio, while the dehydration reactor type is designed for handling pressure drop build-up. The catalysts in the reactor are of proprietary type and similar to the ones described schematically in several publications [1-4].



**Figure 9** The second vaporizer type to the left (2 vessels), a hydrogenation reactor next to them and the dehydration reactor type.

There has been a large effort spent in re-compressing the recycle gas. The current set-up is depicted in figure 10. The gas enters into one of the two equally sized vessels situated on top of each other. When the pressure in the vessel reaches a certain set-point, the system switches and starts filling the other vessel. At the same time a pump moves water from the recently switched-to vessel to the vessel with high gas pressure. This increases the pressure of the gas further and it can be moved to an interim storage from where the gas can be returned.



**Figure 10** The compressor vessels and propane/water separator.

The key component in the design of the compression is a reversible pump, figure 11. This pump has been selected from the hose pump family and can handle pressures up to 16 bars. The key component here is that it can be used in both directions without any valve movements required and that it does not allow for backflow in-between the two vessels.



Figure 11 The pump used for creating the recompression pressure in the system.

In addition, to control the system, a control program was generated using the software labview. The system handled the control off all pumps, heaters and valves. The only thing done off-line was the analysis of the samples. The control computer and electric cabinet, with slave temperature controllers on the side, are depicted in figure 12.



Figure 12 The control computer and electrical cabinet with slave controllers.

Finally, before venting the product gas, any oxygenated hydrocarbons were collected in an activated carbon filter, which can be found in figure 13.



**Figure 13** Activated carbon filter.

The gas analysis was performed using a Varian CP-4900 2-Channel Micro Gas Chromatograph (one mol-sieve 5A PLOT column and one PoraPlot column, with double TCD detectors). The liquid analysis was performed using a Scion 456-GC Gas Chromatograph equipped with a 500  $\mu$ l inert steel sample loop 1/16" for Valco injection valve, a Rtx-DHA-50 Cap. Column 50m, 0.20mm ID 0.5 $\mu$ m equipped with a FID detector, figure 14.

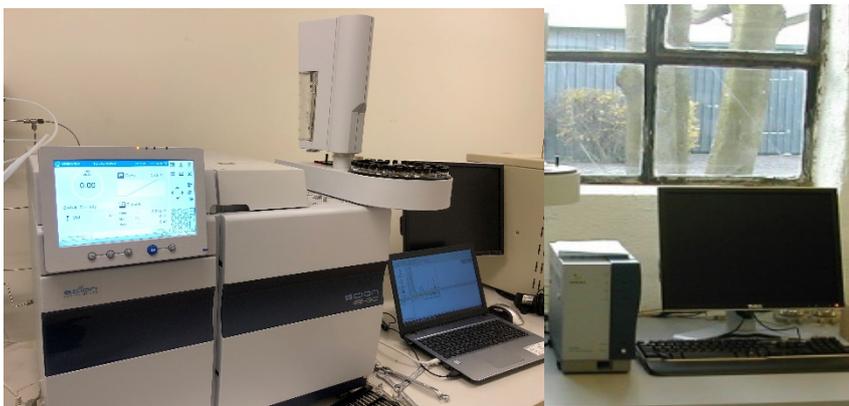


Figure 14 Analysis equipment used in the project.

## 3.2 RESULTS

This section will report on the results from operating the pilot. The pilot has in total been operated for more than 3,000 h. In this includes star-up and shakedown testing, as well as operation in several *modus operandi*. This section starts with summing the operational experience gathered during the project duration, mainly focusing on non-function items and the solutions to these with the intention to ensure that other investigators avoid making the same mistakes. This is followed by a section reporting the performance of the vaporization, the synthesis of the intermediate acrolein and finally the production of propane.

### 3.2.1 Operational experience

In this section, a few particular questions will be brought to the attention of the research and development community. The first is the initial idea of using a pump with an overflow (via a pressure relief valve) to feed liquid to the system. This did not work well due to pulsations in the flow due to the pumping action. There are two possible solutions to this problem: either install a pulsation dampener or use an interim storage solution.

The first approach is probably the most elegant one, if it can be made to work, this was however not possible during the current project. The second solution was the one finally employed in the pilot. In this solution, a vessel was equipped with two level sensors and the pump was set to fill the vessel rather quickly (approximately 60 seconds). The vessel was pressurized using nitrogen and the pressure in the vessel was enough for pushing the liquid very stably into the mass flow controller (Coriolis type), resulting in a very stable flow at the expense of a few liters of nitrogen every few hours. During pumping, a pressure relief valve ensured nitrogen vacation. This problem may of course be avoided if another combination of pump and mass flow controller is chosen; more expensive factory produced units exist solving the problem.

Another important lesson learned is that it is difficult to find rotating equipment suitable for miniaturized applications. It was realized already at the onset of the project that it would be difficult finding a compressor that would be suitable for compressing the recycle gas. However, it was not believed to be this difficult. No

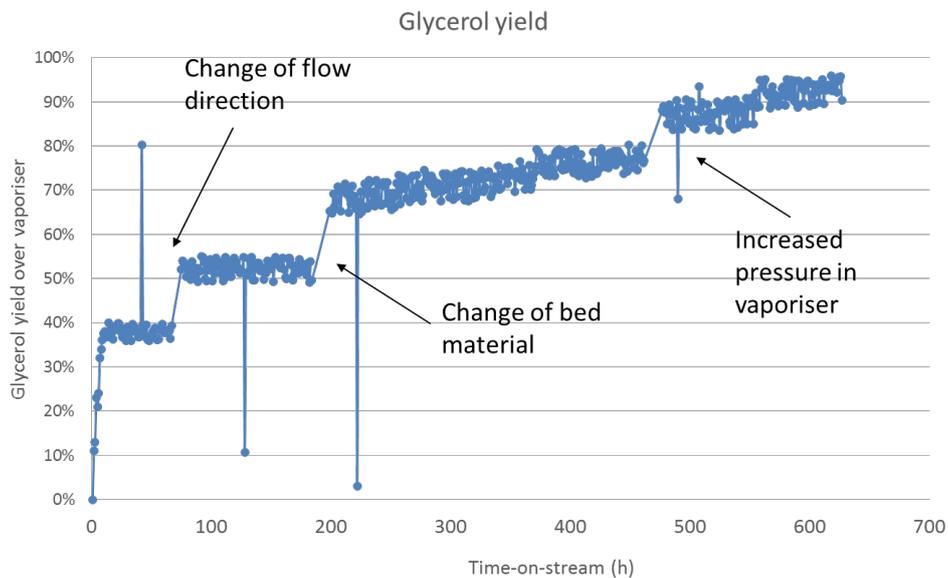
compressor was found that was designed for this low flowrate and the design pressure that was useful with combustible gases. A larger, electrical compressor was tried, but the mismatch in flow rate made the operation impossible in the end. Therefore, the already described hydraulic compressor was designed and constructed to solve this issue. This however cost a lot of time and effort in finalizing.

Also, the vaporization was found to be important. The loss of material over this first section was found initially to be high and a reconstruction was required. The most important lessons learned from this redesign is that the bed material is important, but also factors such as flow direction and surface-to-volume ratio play a significant role in the productivity of this type of equipment. It also goes to prove the notion that it does not matter how good the downstream equipment is if the input feedstock fails to reach it.

Finally, the last lesson learned is that a complex process requires a complex control system. It was believed that localized control could be possible, using for instance local PID-controllers for temperature. This worked rather well initially, before the testing with a recycle loop was initiated. However, the hydraulic compressor with a number of additional sensors and feedback to the system made this control strategy unsustainable. This was solved by developing a LabVIEW-based program for controlling the entire process. The local PID-controllers were still used but made to work as slaves using a computer-controlled set-point. This also allowed for better logging opportunities for temperature and pressure data, making post-run evaluations more transparent.

### 3.2.2 Vaporisation

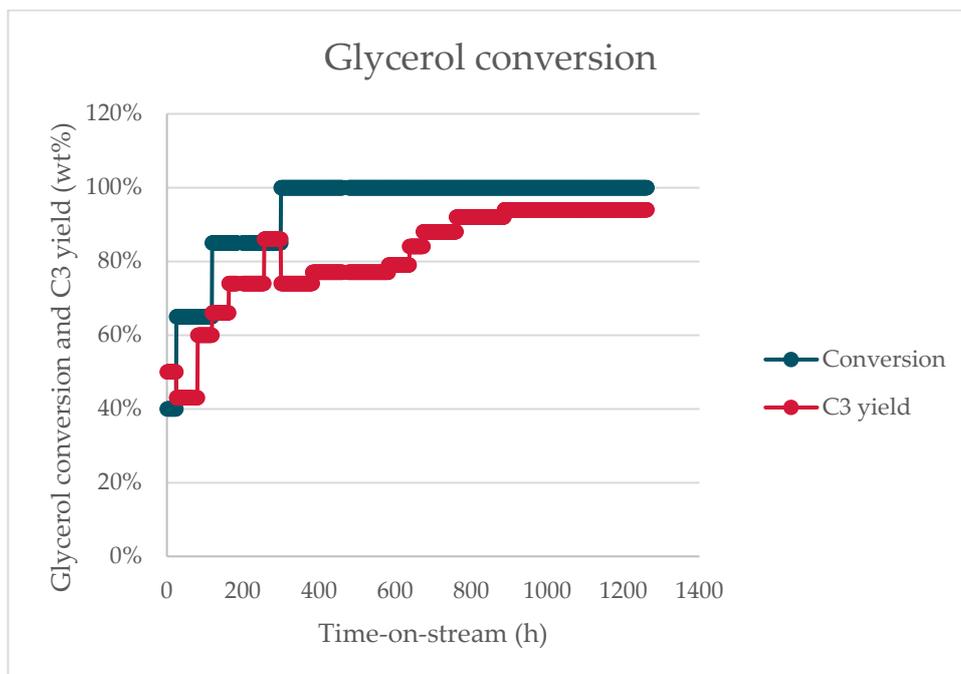
As alluded to in the text above, the vaporization of the glycerol/water mixture was unexpectedly difficult. Initially, the first vaporizer did not perform well at all. It was conceived after some time that the vaporization system has to be redesigned. The results of the first 600-650 h of operation with the new vaporizer is reported in figure 15. The initial yield is not very impressive and therefore some additional modifications have been made. First, the flow direction was bottom up, which resulted in too high agglomeration of glycerol in the lower part of the vaporization vessel. By reversing the flow, top-down, the yield could be increased from about 40% to a little more than 50%. The next step was to change the bed material to a finer particle material with no solid acid sites. This increased the yield from 50% to about 65%, which in combination with fine-tuning the temperature increased the yield to just about 80%. Finally, by increasing the pressure in the vaporizer, the final vaporization recovery was in the 90-95% range on a weight basis.



**Figure 15** The results of the vaporization of glycerol over the second vaporizer configuration, flowrate equivalent to 100 g/h of propane.

### 3.2.3 Acrolein synthesis

The intermediate synthesis of acrolein is a key in producing high yielding propane. If there are side-products formed in the system, they will most likely form in the first reactor. The production of acrolein is dependent on the conversion, but also the yield of acrolein over the reactor. The results of the testing are depicted in figure 16.



**Figure 16** The conversion and yield of C3 (acrolein and propionaldehyde).

As can be seen in the figure, the reaction also required quite a lot of trimming before reaching acceptable conversion and yields. About 10% of the acrolein formed is hydrogenated to propionaldehyde in this step, the reported yield is the sum of these two hydrocarbons.

### 3.2.4 Propane

The production of propane was commenced after the yield to C<sub>3</sub>-carbon chains were increased to a reasonable degree, i.e. more than ca 90%. The production of propane was continued for quite some time and the results may be viewed in figure 17.

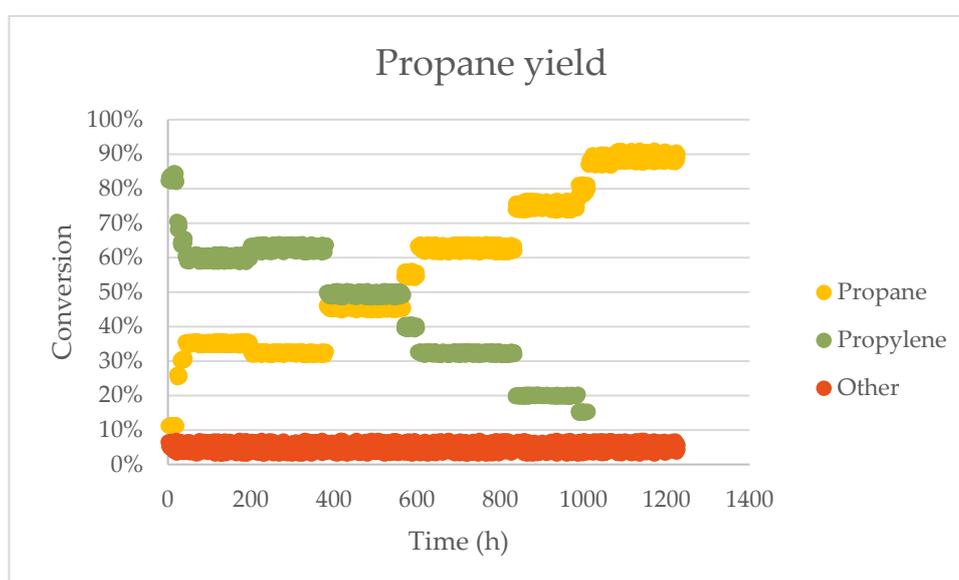


Figure 17 The conversion of glycerol to propane, recycle initiated at ca 200 h.

As can be viewed from the figure, the yield of propane was increased over time and there is no trend in decreasing production. It should be noted that the production was performed initially without recycle (ca 200 h) and then with recycle of hydrogen.

### 3.2.5 Gas quality

The content of propylene should not be a problem in the case of producing LPG. The main challenge to purity is in the 3-5% of others formed. Most of these components are formed already in the vaporization of glycerol and in the first stage of reaction. The main contaminant formed is hydroxy acetone (acetol), which make up some 80-90% of the overall (carbon containing) contamination. This contaminant is separated very easily as it has a very high boiling point and will be separated with the water used and formed in the process. The other contaminants are unconverted propanol, carbon monoxide and hydrogen. In the operation of the pilot, with recycle under the best conditions, the composition of the gas is according to table 4.

**Table 4 Gas composition under best operating conditions.**

Component	Amount	Unit
Propane	94	% by volume
Propylene	6	% by volume
Hydrogen	328	ppm
Carbon monoxide	24	ppm
Propanol	7	ppm

As may be viewed in the table, the main contaminant is hydrogen, followed by CO and propanol. This quality is in itself not good enough to match commercial quality propane, but it is believed that commercial quality may be accomplished by one stage of liquefaction of the gas. Alternatively, in a transition stage, the gas may be blended with fossil-based gas and thus meet the requirements.

### 3.3 CONCLUSIONS

Based on the results presented, it is clear that the pilot has been rather successfully designed and operated, albeit there have been many unexpected snags during the course of the project. Also resulting in a delay in finalizing the project as compared to the original time plan. The goal of long-term operation of the plant has been surpassed with comfortable margin. The gas quality is perhaps not perfectly matching that of commercial gas, but it is believed that this may be solved with an additional purification step, which was not included in the pilot operation due to time constraints. Also, the quantitative goal of 50 kg of propane produced has been met, however, as previously discussed, this propane has not been on-specification.

## 4 Alternative feedstocks

In this section, the work performed with finding alternative routes for producing glycerol or other feedstocks to the process from cellulose is reported.

### 4.1 EXPERIMENTAL

When performing both hydrogenation and hydrogenolysis experiments a 4575B, 500 mL stainless steel autoclave batch reactor, shown in Figure 18, with associated impeller and oven was used. Hydrogen gas, from *Strandmöllen AB*, was added directly from the gas bottle and the control valve to the reactor via the internal dip tube of the reactor. For smooth operations when adding the gas and when flushing the system additional needle valves was placed on both inlet and outlet of the reactor. After start-up was completed the inlet of the hydrogen gas was changed from de dip tube to the head space of the reactor to be able to extract samples at different run times. Operating pressure was monitored digitally through associated measuring equipment, Parr 4848 reactor controller.

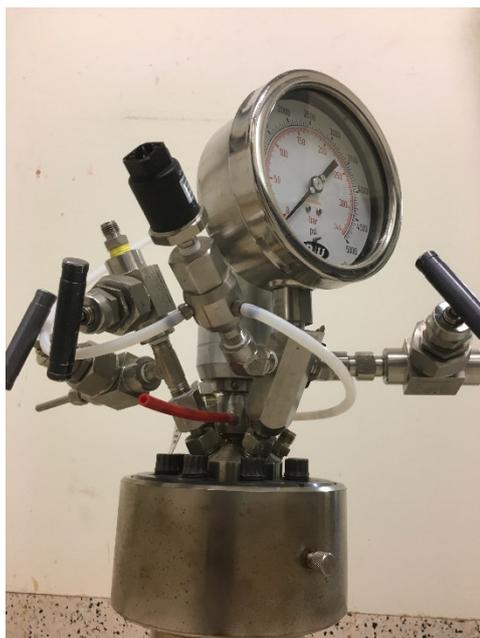


Figure 18 The reactor used for experimental work.

Catalysts using nickel and ruthenium were prepared on aluminium oxide, with or without the addition of magnesium oxide. The catalysts were prepared using starting materials from Sigma Aldrich. When producing the Ru-based catalysts, ruthenium acetyl acetonate is dissolved in toluene. Thereafter, the aluminium oxide (Sasol, Puralox 100/150) was added and the temperature was increased to just below the toluene boiling point and the solvent is vaporized. The Ru catalyst were calcined in air at a temperature of 350 °C for 4h. The temperature ramp used during calcination was 120 °C/h. Thereafter the catalyst was reduced using 10,000

ppm of hydrogen in nitrogen at 270 °C for 4 hours. The difference before and after calcination of the Ru-catalyst is visible in figure 19.



**Figure 19** The Ru-catalyst before and after calcination.

When preparing the Ni-based catalyst, nickel nitrate was dissolved in water and the pores within the catalyst-support was allowed to fill with the solution, so called incipient wetness impregnation. The catalyst was then dried at 120 °C for 90 minutes in a hot air oven. Thereafter it was calcined at 450 °C for 4 hours and finally reduced at 400 °C for 4 hours in 10,000 ppm hydrogen in nitrogen, figure 20.



**Figure 20** the Ni-based catalyst before and after calcination and reduction.

To minimize the effects of outer mass transport of hydrogen to the reaction, the catalyst support was ground to 120-250 mesh before impregnation. The catalysts were characterized before and after use using nitrogen physisorption and evaluated using the BET and the BJH method for surface area and pore volume and area distributions [85, 86]. The reduction properties of the catalysts have been determined using a Micromeritics TPD/TPR 2900. The TPR results are reported in figure 21 and show that the reduction of Ni is in the 400 °C range, which is in-line with previous reports [61, 87].

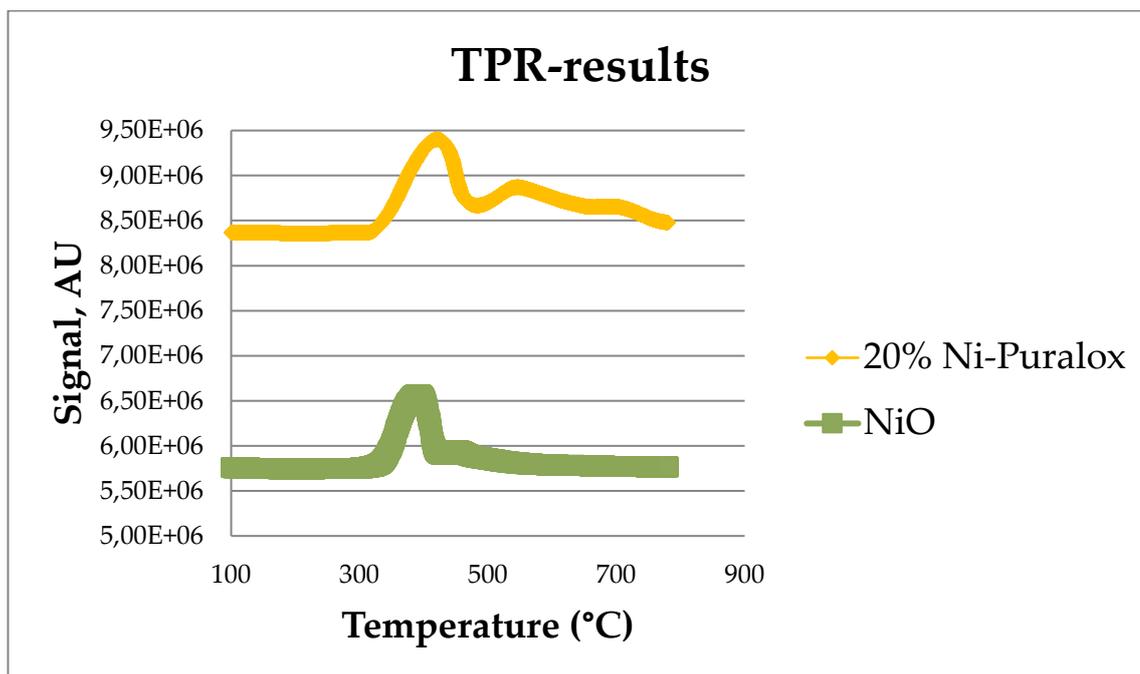


Figure 21 temperature programmed reduction of the Ni-catalyst compared to pure NiO.

The hydrogenation experiments were initially performed by adding 100 ml of reaction solution, containing 20% glucose in deionized water. There after about 1g of catalyst was added to the reactor. The reactor was sealed and mounted in an apparatus for stirring. The procedure was later modified such that 200 ml of solution was used to make sampling and analysis simpler. He reactor was flushed to remove oxygen using nitrogen and after the flush, the temperature was increased to the reaction temperature, which varied from 80 to 120 °C. After reaching the operating temperature, the pressure was increased to 50 bar with hydrogen and stirring (800-1,200 rpm) was started.

A similar methodology was used for the hydrogenolysis experiments, with the difference that only 10% of sorbitol was used. Also, the operating temperature was higher with the literature indicating 215 °C as a sweet spot. Samples were collected periodically during the operating time (4 hours) and were frozen for later analysis. Before analysing, the samples were diluted to keep the concentration of the resulting products below 10 g/l. Before analysis the samples were also filtered using 0.2 µm filters from Scantex. The analysis was performed using a UPLC with both RI and UV-detectors. The column used for separation was an Aminex HPX-87H coloum with 0.005 M sulphuric acid as the mobile phase. A result from the initial analysis work and calibration can be viewed in figure 22.

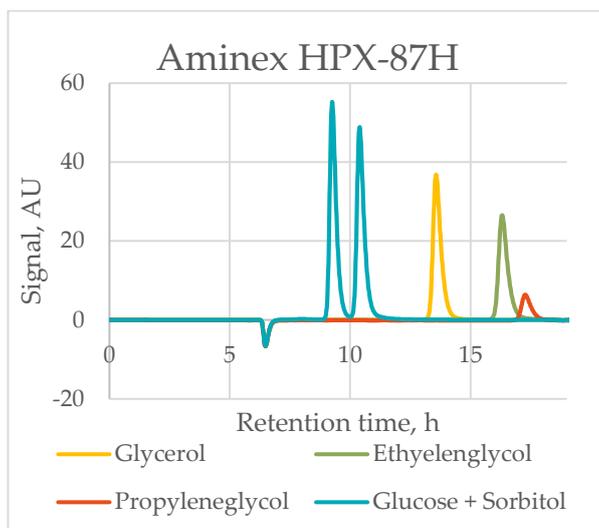


Figure 22 The eluation of components using the best column tested.

The gas phase in the reactor was also analyzed using the Scion 456 already reported on above. As the hydrogenation of glucose to sorbitol is already commercial, only a few experiments in this regard was performed and only a limited amount of catalysts were tested.

#### 4.1.1 Results and discussion

In the table below, a summary has been made of the experiments performed in the batch reactor. The table contain both experiments from the hydrolysis of glucose and from hydrogenolysis of sorbitol.

Table 5 Summary of experiments performed.

Experiment	Catalyst	Pressure at operating temperature (bar)	Temp. (°C)	Conve rsion	Selectivity (sorb*/Glyc.**)	Selectivity to 3 carbon molecules
Glucose hydrogenation	1 % Ru/Puralox	50	90	24 %	57 %*	N/A
Glucose hydrogenation	20 % Ni/Puralox	50	90	26 %	79 %*	N/A
Glucose hydrogenation	20 % Ni Puralox Reducerad in situ	50	90	0 %	0 %*	N/A
Sorbitol hydrogenolysis	2 % Ru/Puralox Reducerad in situ	50	215	54 %	35 %**	54 %
Sorbitol hydrogenolysis	20 % Ni/Puralox	50	215	36 %	44 %**	83 %
Sorbitol hydrogenolysis	20 % Ni/Puralox + 2 g CaO	50	215	18 %	25 %**	44 %
Sorbitol hydrogenolysis	2 % Ru/Spinell	50	215	7 %	17 %**	86 %
Sorbitol hydrogenolysis	2 % Ru/Spinell + 1 g CaO	50	215	44 %	29 %**	39 %

As can be seen from the data, the production of sorbitol from glucose was quite low. The conversion seems to be leveling out at about 24-26%, which is believed to be due to equilibrium constraints. The selectivity is on the contrary quite good for the Ni-based catalyst with 79% and it is believed that this can be improved further should no commercial catalyst be sourceable. However, at this point in time, there was no point in spending more resources on the experimental work.

When looking at the sorbitol hydrogenolysis, it is obvious that high selectivity towards 3-carbon species can be achieved. The highest selectivity is reported over the two catalysts without CaO present in the experiments (83 and 86% respectively). However, a higher conversion would have been desirable. There are quite a few interesting observations when looking at the hydrogenolysis of sorbitol, figure 23. For instance, most of the catalyst show a trend where the conversion goes to a certain value and then stabilize with time; except for Ni/Puralox showing an increase in conversion.

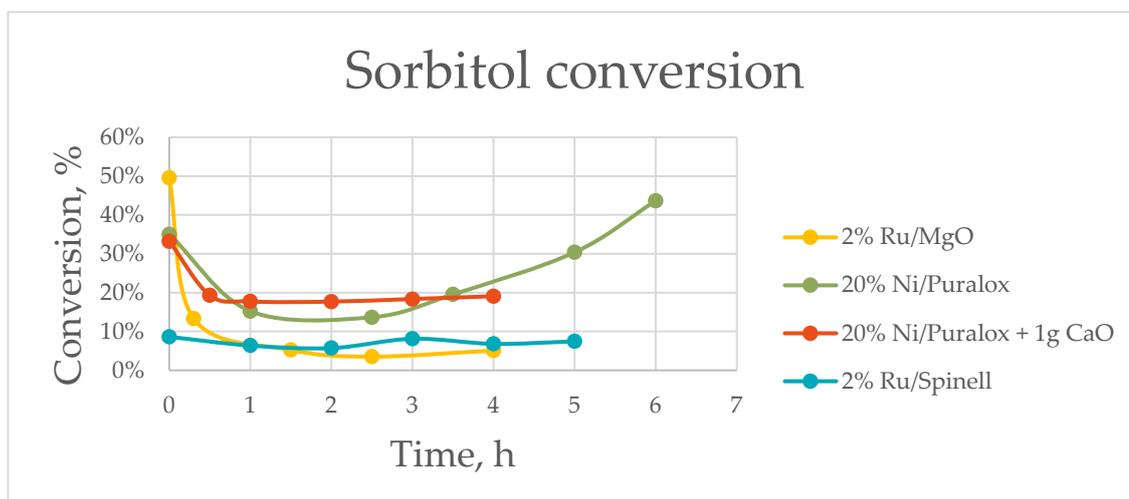


Figure 23 Conversion of sorbitol using various catalysts as a function of time.

As for the selectivity, the trends are similar as most catalysts show a trend leveling out with respect to selectivity to the three most desired compounds Figure 24-26.

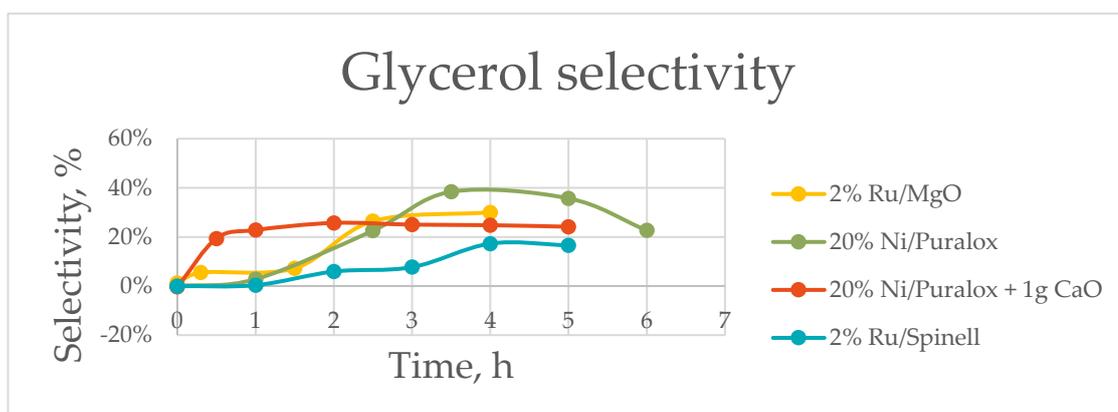


Figure 24 Glycerol selectivity for the four catalysts investigated.

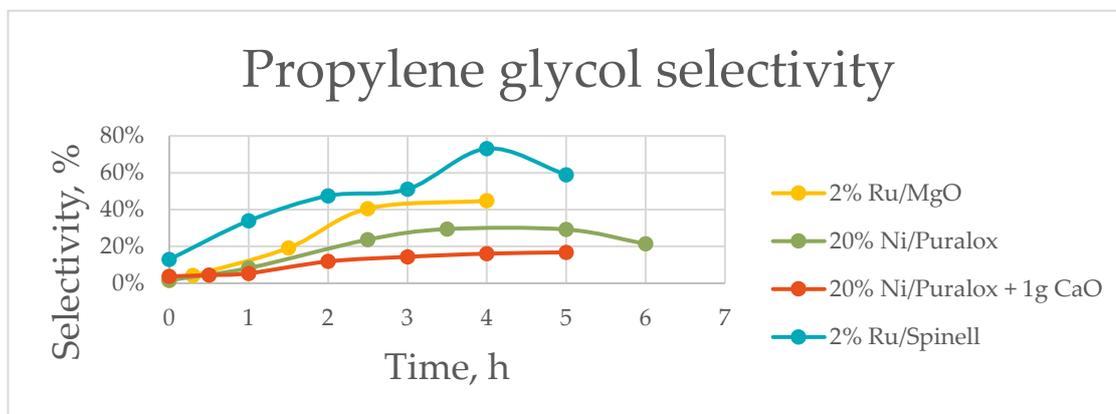


Figure 25 Propylene glycol selectivity for the four investigated catalysts.

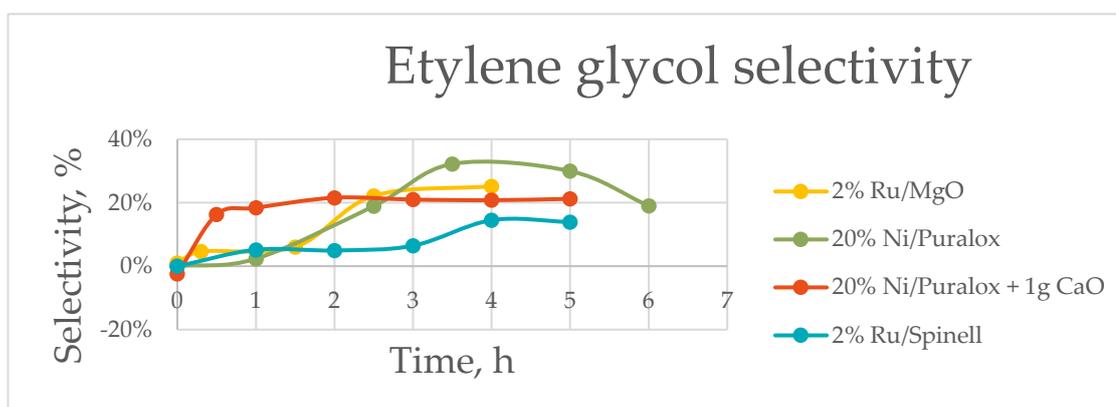


Figure 26 Etylene glycol selectivity for the four investigated catalysts.

The most active catalyst (20% Ni on Puralox) was further investigated and the side-products further reviewed, figure 27. As can be seen, there are traces of several other compounds such as fructose, ribitol and mannose, as well as some unknown compounds. These compounds are in-line with what has been reported previously in the literature [88].

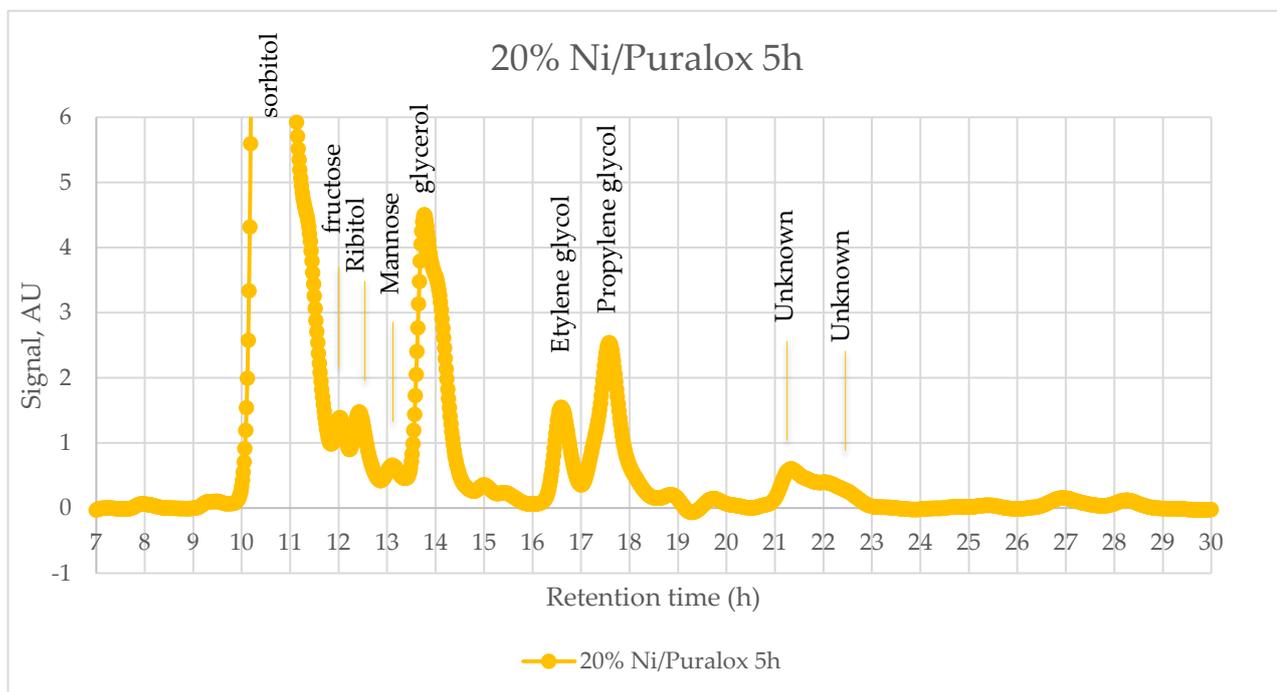


Figure 27 Analysis of side-products for 20% Ni-catalyst, sample after 5h.

With respect to the gas phase, both methane and carbon dioxide can be identified, figure 28. Interestingly, also traces of propane can be identified in the gas phase.

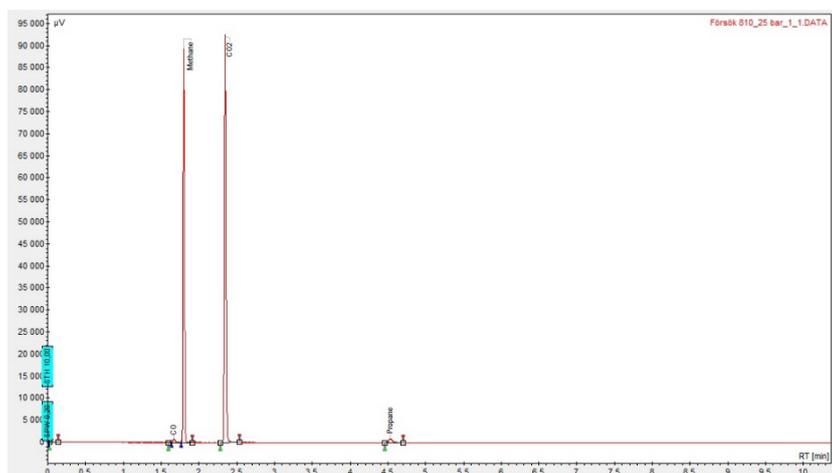


Figure 28 Gas-phase analysis of the headspace gas of the reactor after operating with the Ni-catalyst for 5h at 215 °C.

After operation, the catalysts were investigated using nitrogen physisorption and the results are summarized in table 6.

**Table 6 results from physisorption of nitrogen on select catalysts before and after use.**

Material	BET-surface (m <sup>2</sup> /g)	Pore-volume (cm <sup>3</sup> /g)	Micropore-volume (cm <sup>3</sup> /g)	Average pore diameter(Å)
20% Ni/Puralox ored (färsk)	69.2	0.19	$9 \cdot 10^{-4}$	110
20% Ni/Puralox (använd)	132.6	0.36	$7 \cdot 10^{-4}$	109
2 % Ru/Puralox reducerad in situ (använd)	142.6	0.48	$9 \cdot 10^{-5}$	135

Only the most promising catalysts were chosen for post-mortem analysis. From the BET analysis, it is clear that there is a change in the surface area before and after use of the catalyst. The main change is in the creation of larger surface area. This creation may be caused by two different phenomena, the formation of carbon and the laking of alumina from the support. The fist one is the most likely one and will also provide for an avenue with catalyst recycle.

In general, the catalyst activity is on the low side, in general lower than the one normally presented in literature. This may be due to the lower level of active metal used, e.g. for the Ru-based catalysts containing 50% of the active material compared to other researchers [75, 76, 89]. It was also surprising to find a negative effect of the MgO promoter as both Ni/MgO as well as Ru on activated carbon with basic promoters have shown positive results [76, 78].

#### 4.1.2 Conclusion

The most active catalysts are the ones based on an acidic support ( $\gamma$ -alumina), which is surprising based on the literature. The glucose hydrogenation is performed with rather high selectivity of 79% and the sorbitol hydrogenolysis with a selectivity of about 83-85%. The conversions are however on the low side, ranging from single digit to just below 50% depending on case.

This will pose a problem unless the activity of the catalyst can be improved, or a process solution can be found in which the feedstock can be separated and recycled. Due to the difference in reaction temperature between the two stages, the most likely solution will be one where the hydrogenation and the hydrogenolysis are performed in different reactors and at different conditions to optimize each reaction step on their own right.

## 5 Discussion and conclusions

Based on the results presented, it is clear that the pilot has been rather successfully designed and operated, albeit there have been many unexpected snags during the course of the project. Also resulting in a delay in finalizing the project as compared to the original time plan. The goal of long-term operation of the plant has been surpassed with comfortable margin. The gas quality is perhaps not perfectly matching that of commercial gas, but it is believed that this may be solved with an additional purification step, which was not included in the pilot operation due to time constraints. Also, the quantitative goal of 50 kg of propane produced has been met, however, as previously discussed, this propane has not been on-specification. The most active catalysts are the ones based on an acidic support ( $\gamma$ -alumina), which is surprising based on the literature. The glucose hydrogenation is performed with rather high selectivity of 79% and the sorbitol hydrogenolysis with a selectivity of about 83-85%. The conversions are however on the low side, ranging from single digit to just below 50% depending on case.

This will pose a problem unless the activity of the catalyst can be improved, or a process solution can be found in which the feedstock can be separated and recycled. Due to the difference in reaction temperature between the two stages, the most likely solution will be one where the hydrogenation and the hydrogenolysis are performed in different reactors and at different conditions to optimize each reaction step on their own right.

Both of the processes investigated hold promise for a future commercialization. The process for turning glycerol into renewable propane has been significantly advanced during the project. However, there are still steps required in moving the process into full scale. The final gas separation will have to be solved, as well as the liquefaction of the gas. This should be a rather straight forward engineering feat. Thereafter, it is suggested that a commercial demo is constructed, preferably one collocated with existing infrastructure for hydrogen generation and potentially also gas purification/liquefaction. A suitable scale for this plant would be on the order of 10,000 tonnes per annum of propane. Thereafter plants in the size of 50,000 to 100,000 tonnes per annum should be perfectly feasible.

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# DEMONSTRATING RENEWABLE PROPANE

Liquefied petroleum gases, LPG is an interesting fuel with multiple application areas, e.g. as a vehicle fuel, for barbequing and for heating. The major source of LPG today is fossil based and a renewable source of LPG is desired.

Here a pilot demonstrator plant for producing renewable liquefied petroleum gases has been designed, constructed and operated for more than 3,000 h. The product, propane that is a major constituent in LPG, produced was rather close to the specifications of bottled LPG, but still need at least one more purification step before meeting the requirements. In addition, an alternative feedstock source was investigated.

The main process uses glycerol, a side-product from the biofuels industry, and the prospect of using cellulose as a starting point for LPG production was demonstrated. It is however clear that additional work is required to make this process commercial.

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