

Green LPG

©Svenskt Gastekniskt Center – December 2010



Christian Hulteberg, Jan Brandin & Andreas Leveau
Biofuel-Solution AB

SGC:s FÖRORD

FUD-projekt inom Svenskt Gastekniskt Center AB avrapporteras normalt i rapporter som är fritt tillgängliga för envar intresserad.

SGC svarar för utgivningen av rapporterna medan uppdragstagarna för respektive projekt eller rapportförfattarna svarar för rapporternas innehåll. Den som utnyttjar eventuella beskrivningar, resultat eller dylikt i rapporterna gör detta helt på eget ansvar. Delar av rapport får återges med angivande av källan.

En förteckning över hittills utgivna SGC-rapporter finns på SGC's hemsida www.sgc.se.

Svenskt Gastekniskt Center AB (SGC) är ett samarbetsorgan för företag verksamma inom energigasområdet. Dess främsta uppgift är att samordna och effektivisera intressenternas insatser inom områdena forskning, utveckling och demonstration (FUD). SGC har följande delägare: Svenska Gasföreningen, E.ON Gas Sverige AB, E.ON Sverige AB, Lunds Energikoncernen AB (publ), Göteborg Energi AB, och Öresundskraft AB.

Följande parter har gjort det möjligt att genomföra detta utvecklingsprojekt:

Energimyndigheten
Biofuel-Solution AB
Göteborg Energi AB
AEGPL European LPG Association

SVENSKT GASTEKNISKT CENTER AB



Jörgen Held

Executive Summary

The use of energy gases with renewable origins will become important with diminishing fossil resources. This as the infrastructure of the gaseous fuels is well built out and the distribution networks already exist. LPG is one of the most versatile fuels around, perfect for rural areas and in many other applications. The fossil origin of the fuel will, in today's climate and environmental debate, however position it as a thing of the past and not part of the future energy supply. The technology and development performed under this and previous programs with the Swedish Gas Centre will however suggest a way to bridge this conception and make LPG a part of the future energy mix.

This report constitutes the results from the development performed under the SGC program 210 and is aimed at verifying the results from the previous SGC program 198, proving the concept for producing propane from renewable glycerol. The process and its intended uses can be viewed in figure ES 1.



Figure ES1 The process at a glance.

Attractive and potentially profitable LPG premium segments that can be reached by producing bio-propane would be the autogas market. Another attractive segment to target is the outdoor and camping segment, where there already exist awareness for nature and the environment. A third interesting segment is in small-scale heat or combined heat and power generation, where a premium price can be reaped for renewable energy as well as the addition of LPG to biogas. Another important aspect of the renewable LPG is that it motivates external stakeholders, such as local, regional, national and international governments as well as environmental and other lobby groups to consider LPG a part of the future energy mix and not a thing of the past.

A good starting point for two and three carbon energy gases is glycerine, with its three carbon backbone. The reason for focusing on glycerine is its benign chemical nature, it is:

- Harmless from a toxic standpoint
- Chemically inert
- Non-corrosive
- Relatively high energy density
- Zero carbon dioxide emissions

It is also readily available as the production of biofuels (from which glycerine is a side-product) in the world has increased markedly over the last 10 year period. This glut in the glycerol production has also lowered worldwide prices of glycerine.

Since the key step in producing energy gases from glycerol is the dehydration of glycerol to acrolein, this step has attracted much attention during the development work. The step has been improved during the performed work and the need for any regeneration of the catalyst has been significantly reduced, if not omitted completely. This improvement allows for a simple fixed bed reactor design and will save cost in reactor construction as well as in operating costs of the plant. The same conclusion can be drawn from the combination of the two functionalities (dehydration and hydrogenation) in designing a catalyst that promote the direct reaction of 1-propanol to propane in one step instead of two.

The experiments with the decarbonylation of acrolein to form ethane show that the catalyst deactivation rates are quite rapid. The addition of noble metal to the catalyst seems to improve the longevity of the catalyst, but the coking is still too severe to provide for a commercially viable process. It is believed that there is a possible way forward for the decarbonylation of acrolein to ethane; it will however require additional time and resources spent in this area.

In this work it has been shown that all of the catalytic steps involved in the production of propane from glycerol have sufficient long-term stability and endurance and it is motivated to recommend that the project continues to pilot plant testing stage. Based on the positive outcome of the project the glycerol-to-LPG technology will be continued into a pilot plant phase. The verification phase, finished with the issue of this report, indicates a pilot plant in operation during 2011 if sufficient funding can be raised. After operation of the pilot, the first commercial plant will be constructed, figure ES 2 show the various stages of development.

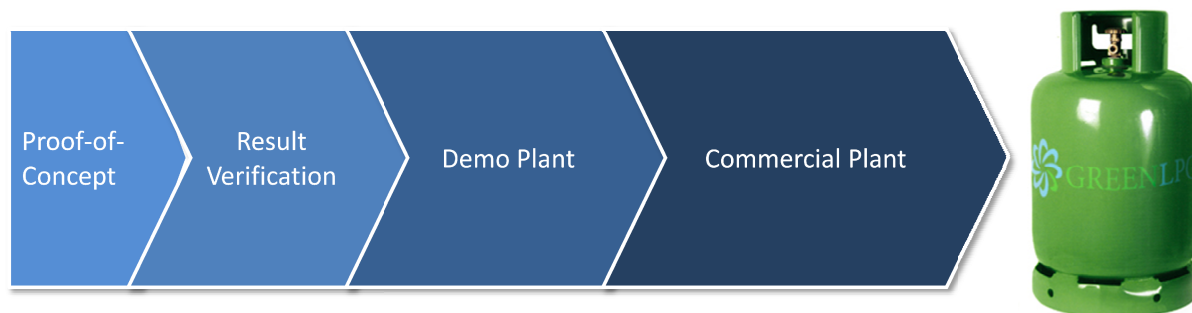


Figure ES 2 Development plan for the glycerol technology.

1	Introduction	1
1.1	Background.....	3
1.2	Disposition.....	3
2	Supply/Demand	4
2.1	Supply.....	5
2.1.1	Present	5
2.1.2	Near Future.....	6
2.1.3	Future	6
2.2	Discussion.....	7
3	Industrial Viability	9
3.1	Experimental.....	9
3.1.1	Experimental Setup 1	9
3.1.2	Experimental Setup 2	11
3.2	Results	13
3.2.1	Phase 1: Improvement of Catalysts and Process Condition.....	13
3.2.2	Phase 2: Long Term Testing	19
3.3	Summary & Conclusions.....	22
4	Production Costs	24
4.1	LPG-Production.....	24
4.2	Gasification.....	26
4.3	Digester Biogas Plant	28
4.4	Production Cost Summary.....	28
5	Conclusions	29
5.1	Future Work.....	29
6	References	31

1 Introduction

The use of energy gases with renewable origins will become important with diminishing fossil resources. This as the infrastructure of the gaseous fuels is well built out and the distribution networks already exist. LPG is one of the most versatile fuels around, perfect for rural areas and in many other applications. The fossil origin of the fuel will, in today's climate and environmental debate, however position it as a thing of the past and not part of the future energy supply. The technology and development performed under this and previous programs with the Swedish gas centre will however suggest a way to bridge this conception and make LPG a part of the future energy mix. Several applications of green LPG can be envisioned, all market niches, where the product can generate significant benefit in the form of additional revenue.

The first application that is suggested as a good niche application would be autogas. Autogas in itself is already a good alternative fuel with environmental benefits such as lower NOx emissions. However, by producing green LPG from a renewable by-product, it will be possible to produce carbon-dioxide-neutral LPG. Using this carbon-dioxide-neutral LPG as a motor vehicle fuel will then qualify the fuel as a 2nd generation vehicle fuel. This will allow for tax benefits in most countries and within the European Union it will be credited with twice the CO₂ removal compared to 1st generation biofuels [1], a bird eyes view to the process is given in figure 1.



Figure 1 The process at a glance.

Another attractive segment to target is the outdoor and camping segment, where there already exist awareness for nature and the environment. This segment would perhaps be willing to pay a premium of 50-100% (calculated on the gas component of an LPG bottle). In the same category, the people buying ecological coffee would purchase green LPG for domestic applications such as for barbeque and other home applications. Another interesting segment is in small-scale heat or combined heat and power generation, where a premium price can be reaped for renewable energy; and in the addition of LPG to biogas.

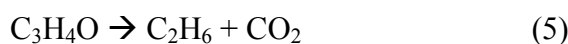
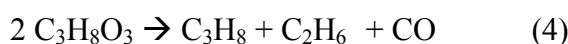
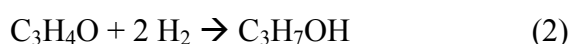
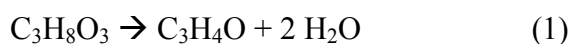
Another important aspect of the renewable LPG is that it motivates external stakeholders, such as local, regional, national and international governments as well as environmental and other lobby groups to consider LPG a part of the future energy mix and not a thing of the past.

A good starting point for two and three carbon energy gases is glycerine, with its three carbon backbone. The reason for focusing on glycerine is its benign chemical nature, it is:

- Harmless from a toxic standpoint
- Chemically inert
- Non-corrosive
- Relatively high energy density
- Zero carbon dioxide emissions

It is also readily available as the production of biofuels (from which glycerine is a side-product) in the world has increased markedly over the last 10 year period. This glut in the glycerol production has also lowered worldwide prices of glycerine.

For preparing energy gases from glycerol there are several pathways, first of all the phase in which the reaction is to be performed will have to be chosen. The reactions performed within this report are all in the gas phase; working in the gas phase allows for low quality glycerol to be used. The reactions that have been used for producing propane and ethane are:



The first reaction describes the formation of acrolein from glycerol. In the second reaction, acrolein is reacted with hydrogen to form propanol and in the third reaction hydrogen reacts with propanol to form propane and water. The fourth reaction describe a general pathway (without correct stoichiometry) for the combined production of ethane and propane directly from glycerol; omitting a number of reaction steps.

1.1 Background

Biofuel-Solution has researched on the use of glycerine for producing fuels and chemicals since 2006 and end-products include:

- Energy gases
- Aldehydes and alcohols
- Monomers

The energy-gas related research has been funded by the Swedish Gas Centre (SGC) since 2008 and resulted in a proof-of-concept report the same year. The report clearly displayed the technical feasibility of producing higher alkanes from glycerol [2]. And, perhaps more importantly, showed that production costs can be reasonable.

The use of glycerine in fuel applications is interesting, and perhaps even more so in automotive fuel applications, as it is classified as a by-product [1]. Meaning that 2nd generation biofuels can be produced using it, as well as being an interesting feedstock for chemical synthesis.

For clarity, the term glycerol refers to the pure chemical compound 1,2,3-propanetriol, the term glycerine applies to the purified commercial products normally containing more than 95% glycerol. Several grades of glycerine are available, such as food-grade glycerine or pharma-grade glycerine. Aside from these qualities there are two types of crude glycerine, separated by their salt content.

1.2 Disposition

In the second chapter of this report, the supply/demand situation of the glycerine market is described and the future supply is discussed as well. In the third chapter of this report, the results from the catalyst testing will be reported. This is divided into two sections; the first section deals with the catalyst improvements and the second with the long-term endurance testing of the best catalyst candidates. Finally production-cost estimates are given and conclusions drawn.

2 Supply/Demand

The traditional demand of glycerine is from a number of products, including toothpaste, drugs, cosmetics, tobacco etc. In tobacco it is used as an additive for casing the tobacco leaves to stop them from crumbling during processing. In cosmetics it is used in creams and lotions as a skin softener. In the food industry it is used e.g. as a heat transfer medium in direct contact with foods in quick freezing and as a lubricant in machinery used for food processing. In figure 2, the market distribution is depicted [3-4].

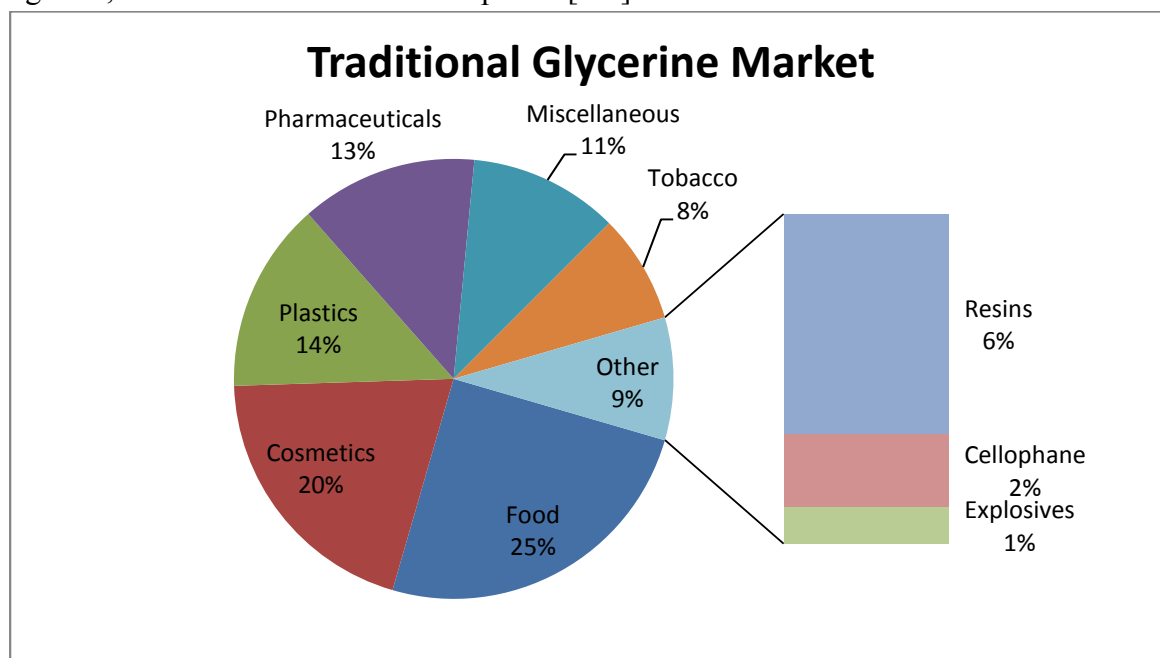


Figure 2 Market distribution of glycerine, total market volume 750 000 tpa (tonnes-per-annum).

The utilization of glycerine is many-fold with over 2000 different applications, arising from the glycerine properties [5]:

- Water solubility
- Odorless
- Colourless
- Sweet
- Absorbs and retain water
- Dissolves flavours and dyes
- Plasticizer properties
- Non-toxic
- Biodegradable

Historically all glycerine has been derived from natural resources (triglycerides), but in 1943 the first synthetic glycerine was produced from allyl chloride. In 1990 this fossil-fuel based production accounted for 30% of the glycerine production, but as of today this capacity has been shut down or converted to other end-products.

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

2.1 Supply

Glycerine-crude can be divided into two major classes, hydrolysis crude glycerine which is derived from triglyceride hydrolysis and contain low amounts of inorganic salts. And what is referred to as spent lye, the residual, salt-containing glycerine from the soap industry and biodiesel industry. Either these qualities (or crudes) can be upgraded to food-grade or pharmaceutical-grade glycerine. In this chapter, the focus will be on sources for crude glycerine and not on the distilled or purified qualities of glycerine.

Currently, the present supply of glycerine is mainly constituted of the production within the biodiesel industry; however, there are several alternative sources that may materialize over the next couple of years. There are also other alternatives that appear likely but on a slightly longer timescale. All of these alternatives will be dealt with in this chapter.

As is the case with crude oil, different sources of crude-glycerine will be cheaper than others. This can be due to the accessibility of the crude, as well as the resulting contamination of the glycerine. Analogue to the crude-oil case, different sources will become attractive given different circumstances. However, when producing fuels and chemicals with significantly higher value than glycerine, the break-even point where backward integration is reasonable becomes significantly lower.

2.1.1 Present

The major present supply in the world is from traditional sources derived from triglycerides. These are used in the food industry for producing fatty acids, fatty acid alcohols etc., however, the majority of the present supply of crude glycerine stems from the biodiesel industry.

The European production of crude glycerine was roughly 800 000 tpa from the biodiesel industry (2008) [6] and the traditional production is about 300 000 tpa [3]. In the US the corresponding figure is 320 000 tpa in the biodiesel industry [7] and 220 000 tpa from the traditional industry [3]. In Latin America the traditional production was 75 000 tpa glycerol [3] and 260 000 tpa crude glycerine from the biodiesel industry [7]. In Asia the biodiesel production is expected to continue to grow, especially in Malaysia and Thailand, accounting to some estimated 400 000 tpa of crude glycerine in 2010 [8, estimated]. The additional traditional rest-of-the-world production of glycerine is estimated to 200 000 tpa of glycerine [3] and another 50 000 tpa to 100 000 tpa crude glycerine is estimated from the Oceania biodiesel pro-

duction. This totals some 1 880 000 tpa of crude glycerine from the biodiesel industry and 800 000 tpa from the traditional industry.

With reservations for small differences in the year of which the statistics was obtained, there is an oversupply of some 4-5 times currently in the glycerine market compared to the traditional supply. This is also reflected in the cost of glycerine where glycerine was traded for 1500 €/ton in 1995 but 200-400 €/ton as of today and the crude-grade glycerine is traded at around 70 €/ton.

2.1.2 Near Future

Another near-future opportunity for readily available crude-glycerine is within the bio-ethanol industry. In the fermentation process some 5-10% glycerine is produced as a side-product with the ethanol produced. In 2008 in the US bioethanol industry alone, an estimated 1 600 000 tpa of glycerine was produced [9]. Several ventures focus on utilizing or extracting this resource from the distillers waste, e.g. Texas based GlycosBio Inc. and Primafuel Inc out of California.

When this figure is extended to account for the rest of the worlds ethanol production an abundance of glycerine become obvious in the ethanol-industry as well as in the biodiesel-industry. Accounting for the 60 billion litres of ethanol produced in total, including the US production, another 3 000 000 tpa of crude-glycerine is available for fuel and chemical synthesis [10].

This gives a total of 2 700 000 tpa of glycerine from the traditional industry and biodiesel industry and another 3 000 000 tpa in potential from the ethanol industry. Including this figure in the demand/supply equation, the production is 7 times higher than the traditional demand.

2.1.3 Future

With the advent of new processes for fuel production, particularly production of triglycerides from algae, glycerine will continue to be a side-product. This type of production has gained further credibility after ExxonMobil invested \$600 000 000 in this kind of development [11]. This large-scale fuel production will give rise to large amounts of glycerine, even though how much is difficult to estimate at the time of writing.

There is also less conventional means of production by which the glycerine supply side can be further improved. The first means of such production would be through fermentation using particular types of yeast. Analogue to ethanol, glycerine can be produced from a variety of substrates including:

- Sugar
- Starch
- Cellulose

One advantage with this process is that higher glycerol-in-water concentrations can be achieved compared to ethanol-in-water concentrations in traditional fermentation. According to literature [12] it would be possible to reach 20% glycerine in water before inhibition occurs, compared to 12% in ethanol fermentation. The 20% solution would be suitable for direct handling in gas-phase processes for glycerine conversion.

Another method would be to use algae to produce the desired glycerine directly, without the triglyceride addition. This can, and has been done, be performed using an algae from the *Dunaliella* group [13], figure 3.



Figure 3 Example of algae production (courtesy of Primafuel Inc.)

These algae have the advantage of not only producing glycerine in high yields and quantities, but also surviving in very high saline concentrations. The use of these high saline concentrations effectively avoids contamination from other living organisms. As mentioned above, the contribution to the supply of this kind of production is difficult to estimate. However, it is plausible that in conjunction with fuel or chemical production from the glycerine, it may be economically feasible to perform.

2.2 Discussion

To conclude, there is already a vast production of glycerine in the world today. The production in the traditional industry and the biodiesel industry amount to some 2 700 000 tpa as of today. This figure outstrips the demand by 3-4 times. Additional to that supply, there is another 3 000 000 tpa already produced, but not utilised, in the bioethanol industry, that can be utilised in a near future. Adding this number to the production side, the supply is exceeded at least 7 times.

On top of this there is the advent of future process such as fuel production from algae, which will result in another side-product stream of glycerine. To this, dedicated alternative methods of production, such as fermentation and dedicated glycerol-algae production can be added.

This indicates that the present overproduction of glycerine will persist over both the foreseeable future as well as in a more distant future. With this feedstock potential in mind, the use of glycerine as a starting point for fuels and chemicals synthesis seems to be a logic decision, realised by many organisations and governmental bodies [14].

3 Industrial Viability

In this section, the experimental work performed under the previous SGC contract, disseminated in SGC report 198 [1], will be verified and continued. Previously the concept of producing ethane and propane from glycerol was demonstrated. In the following section, the catalyst improvements made and long term testing of the same will be presented.

3.1 Experimental

In this section the experimental procedure will be reported, describing the performed experiments and the experimental set-up used. Two experimental set-ups are used in the project, the first one described is the one used for catalyst screening and the second one described is the long-term testing equipment. In the first part of the experimental work, improvements of the catalyst formulation and reaction conditions was done to increase the yield of energy gases, in comparison to the work reported in [1]. In the second part, long term experiments were performed on the selected catalysts to investigate their stability and endurance.

3.1.1 Experimental Setup 1

In the experimental setup, the carrier gas (or the reactant gas) and the liquid are mixed and passed through a pre-heater. Second, the gas mixture is passed through the reactor and then on to a condensation and gas separation step (Figure 4). The gas and liquid are mixed before entering the hot-zone of the pre-heater, where the liquid is evaporated to steam almost instantaneous. The flow of the gas is controlled by a MFC (Mass Flow Controller) and the liquid flow by a Cori-Flow (Coriolis-type mass flow controller). The liquid is fed from a pressure vessel to a manifold where it is mixed with the gas component before entering the pre-heater.

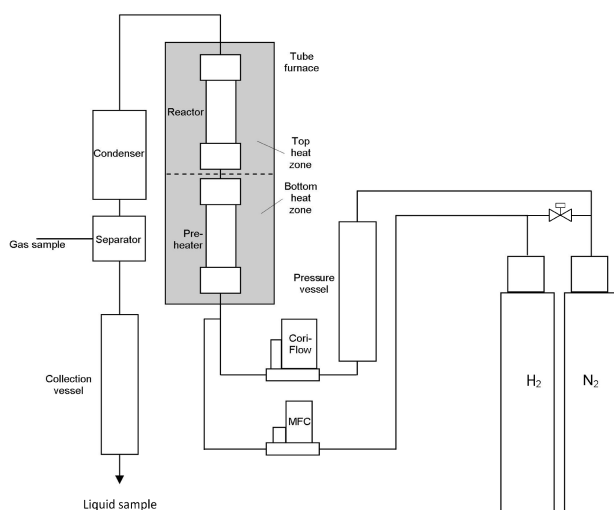


Figure 4 Schematics of the experimental setup

The pre-heater/reactor (Figure 5) is situated in a vertically divisible two-zone tube furnace (Figure 6). The two temperature-zones in the oven are regulated independently of each other and the temperatures are set so that the inlet temperature of the catalyst bed is as close as possible to the wanted temperature.

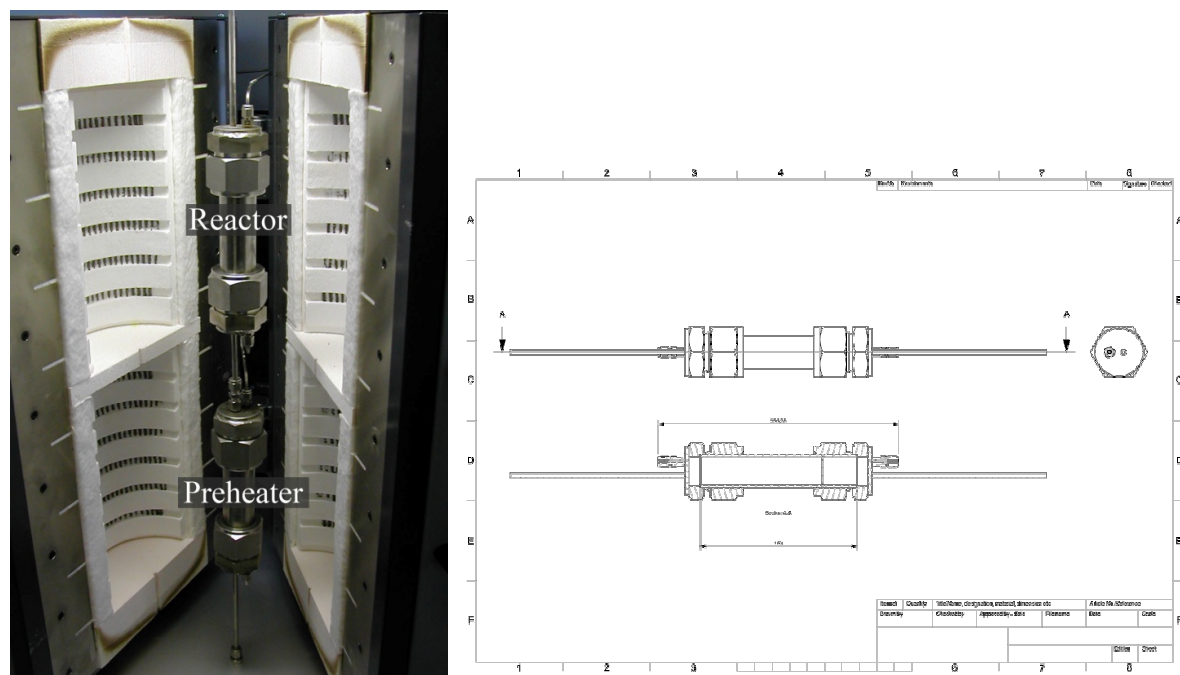


Figure 5, Figure 6 Pre-heater and reactor inside the tube furnace and the pre-heater/reactor blue-print.

The temperatures are monitored by four thermocouples, two in the pre-heater and two in the reactor. The inlet temperature is measured where the catalyst bed starts and the outlet temperature is measured inside the bed, approximately 1 cm before the top of the bed.

One gas and one liquid sample are taken at a fixed interval during the whole of the test time. The gas analysis is then 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 sample is analysed on a Varian CP-3800 gas chromatograph equipped with a 1177 split/split-less injector, a CP-wax 58/FFAP column and a flame ionisation detector. Figure 7 show the two GCs used for the experiments.

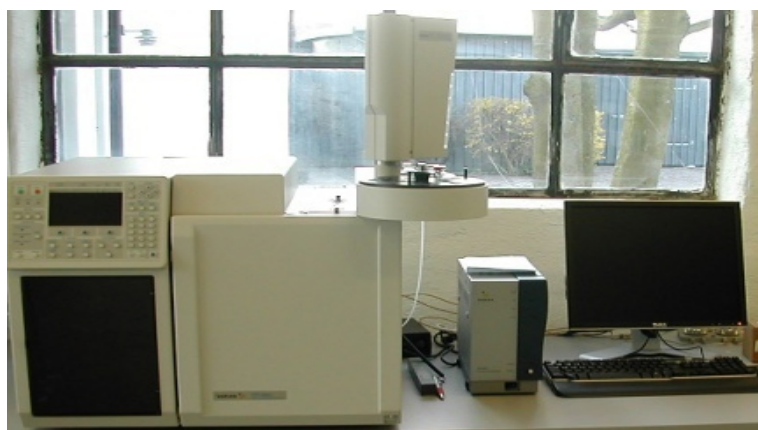


Figure 7 The two gas chromatographs used for performing the analysis with the liquid analyzer to the left and the gas analyser centred.

3.1.2 Experimental Setup 2

The second experimental setup is for long-term testing. The setup is built with an automated control and safety system, making it suitable for continuous around the clock testing. In the setup (figure 8), carrier gas (or reactant gas) is mixed with the liquid before being vaporised in a pre-heater. The vaporised liquid/gas mix are then passed through the reactor, on to a condenser and gas separation step and finally collected in a vessel. The gas is controlled by a MFC and the liquid by an HPLC-pump (High Pressure Liquid Chromatography). The gas and liquid are mixed in a manifold before entering the pre-heater.

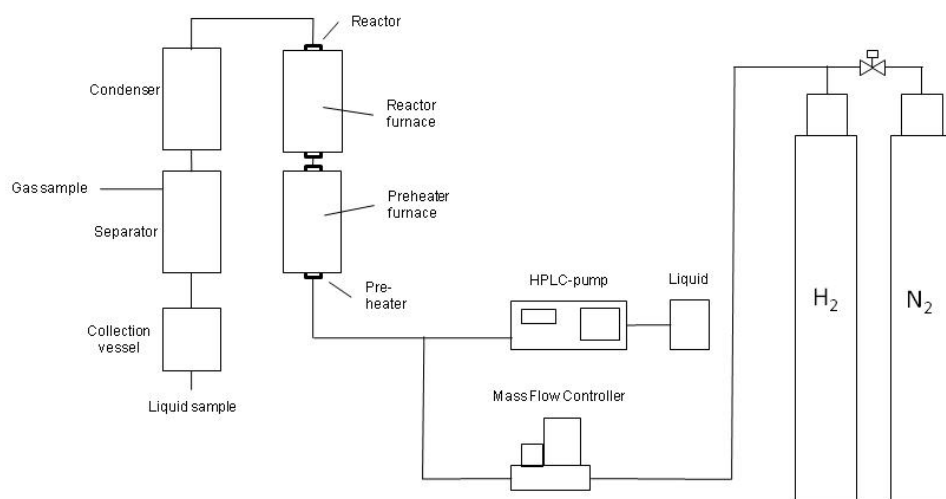


Figure 8 The second experimental setup.

The reactor and pre-heater is situated in two tube furnaces, they are set individually so that the inlet temperature of the catalyst bed is the preferred one. The temperature of the catalyst bed is monitored by two thermocouples, situated at the start of the bed and approximately 1 cm before the top of the bed.

A gas and a liquid sample are taken every day for the whole of the test period. These samples are then analysed in the CP-4900 and a CP-3800 gas chromatograph, as depicted in the “Experimental Setup 1” section.

For the long-term catalyst testing a new test rig was constructed as already mentioned. The test rig was fitted with around the clock monitoring by a PLC system. Initially a “Hazards and Operability Studies” (HazOp) was made to determine all the different safety and construction concerns. Construction wise there were added extra solenoid valves, pressure relief valves, thermocouples, pressure sensors, two level gauges, a differential pressure gauge, a humidity sensor (figure 9) and many other additional small components required for safe operation.

The liquid level gauges were put in the liquid input vessel as well as in the liquid sampling vessel. These gauges send a signal to the PLC control system shutting it down in case of too low or too high a level. The thermocouples, the differential pressure gauge, the pressure sensors and the humidity sensor all work after the same principle as the level gauges i.e. by sending a signal to the PLC control system shutting the system down. The thermocouples on the furnaces by having a high and low set point, where if the temperature goes above or below these set points a signal is sent. The thermocouples in the reactor bed, in case the reaction gets out of hand, and the pressure gauges by having a high set point which would shut the system down; the humidity sensor by sending a signal if the moisture sensitive tape is wetted.

The PLC programming was done by Eurotherm and for every potential failure mode as described above, the rig would automatically shut down in a controlled manner. The shutdown procedure is as follows:

- The solenoid valves closes, prohibiting gas and liquid to enter
- Any pressure in the system is released
- The two furnaces are turned off
- Nitrogen is flushed to suppress a possible fire



3.2 Results

3.2.1 Phase 1: Improvement of Catalysts and Process Condition

3.2.1.1 Glycerol to Acrolein

13

In the figure 10, below, the results of modified process condition are shown. In this case the nitrogen carrier gas has been exchanged, keeping the partial pressure of acrolein constant. As a result the coking is suppressed and it is now possible to run for more than 100 h with 30 w% glycerol; there was no severe coking even at 105 h. This means that the time-on-stream for the 30 w% glycerol solution have been increased with at least a factor 5. Further evaluation of the impact of changing the operating conditions is presented in the long-term evaluation section.

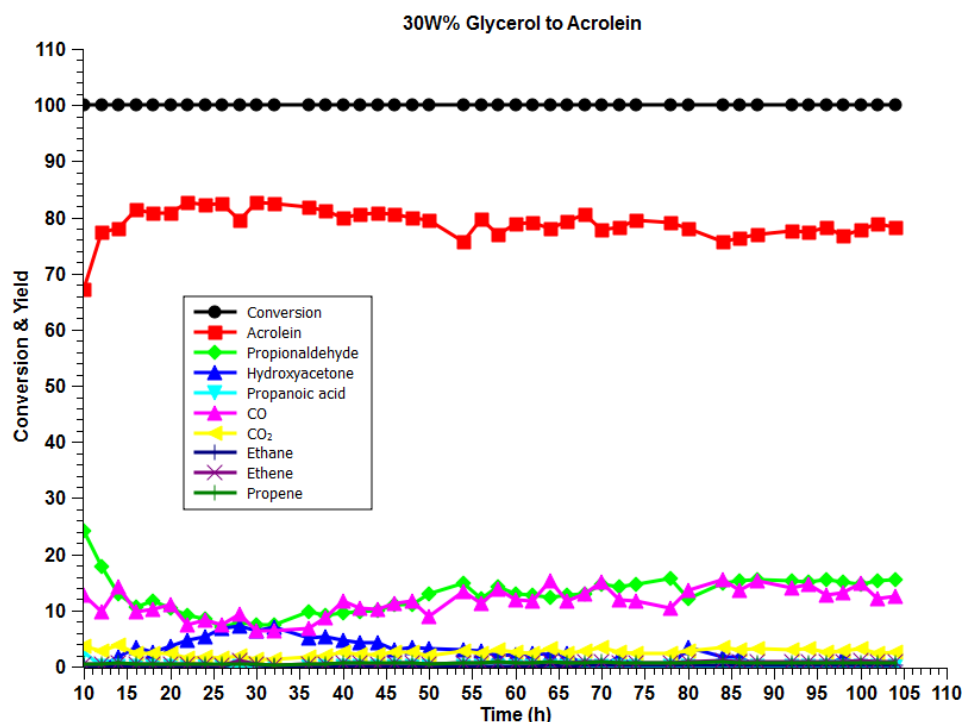


Figure 10 Glycerol to acrolein (experimental setup 1).

3.2.1.2 Acrolein to 1-Propanol

In the reduction of acrolein to 1-propanol (2) a commercial catalyst was used. This catalyst showed very good activity and selectivity and no further improvement was considered at this point.

3.2.1.3 1-Propanol to Propane

In the earlier work [1] the 1-propanol to propane step consisted of two reactions performed on two different catalysts according to:



In this work the two functions have been integrated into one catalyst; a dual-function catalyst. In figure 11 the result of this rather successful merge is shown. The selectivity towards propane is in the range of 95 % while the by-products are mainly low combustible hydrocarbons, like methane, ethane and CO.

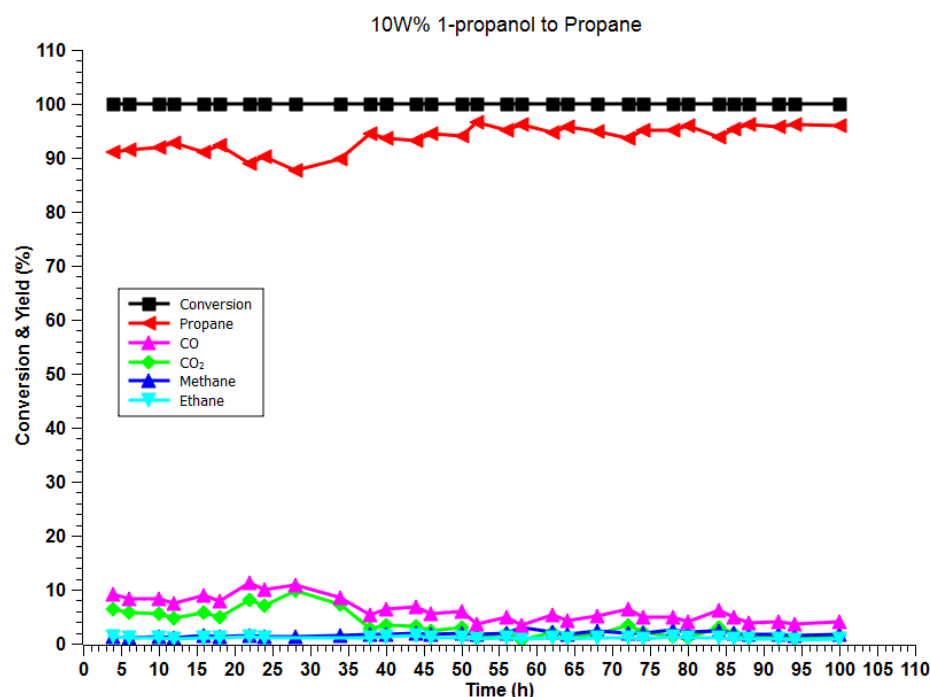


Figure 11 1-propanol to propane (experimental setup 1).

The 10 w% of 1-propanol in water feed, corresponds to approximately 80% yield of a 20 w% feed of glycerol due to the difference in molecular weight between glycerol (92 g/mole) and 1-propanol (60 g/mole). The run was made at temperatures ranging from 285°C to 330°C and 5 bars.

3.2.1.4 Glycerol to Ethane

The above described reactions are consecutive steps in an overall reaction, for instance to propane. In this project, there has also been some initial work regarding a one step process for converting glycerol directly into energy gases.

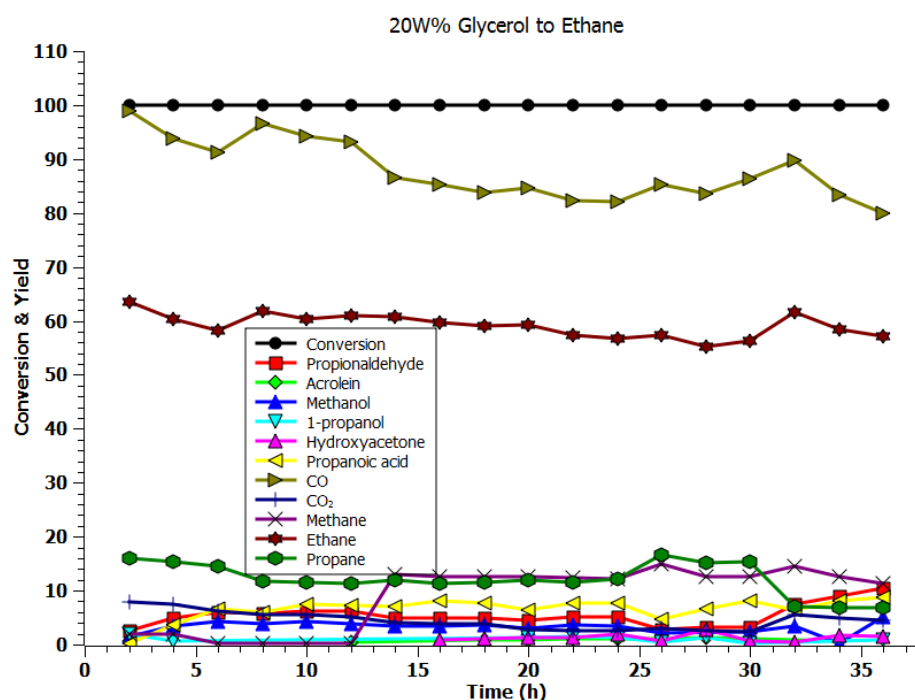


Figure 12 Glycerol to ethane (experimental setup 1).

In figure 12, a newly formulated catalyst have been tested for the direct conversion of glycerol to ethane in the presence of hydrogen at space velocity of 600 h^{-1} . The reaction is run at 300°C and 5 bar. The gas composition is 71vol% H_2O , 25 vol% H_2 and 4vol% glycerol. In this run there is a yield of 60% ethane and about 15 % propane. The yield of CO and methane are based on the total conversion of glycerol and 300% corresponds to a total conversion of the glycerol. In this run there is a conversion of 10-20 % of the glycerol into condensable compounds, like propanoic acid and hydroxyacetone.

The outcome is thus rather good for such a simple process and could probably be further improved. The formed CO could be used to generate the hydrogen needed in the process by the water gas reaction. Thus the drawback of needing hydrogen may be counteracted by internal production.

3.2.1.5 Acrolein to Ethane

In the previous study, the potential for decarbonylating acrolein and producing ethane in one single step was shown. As for the other catalyst system for producing propane, the catalytic system for producing ethane showed promising results in the first report [2]. However, under this research program it was concluded that the first alternative catalyst was less promising than initially believed. Initially the catalyst showed good results, but the deactivation rate was significant, figure 13

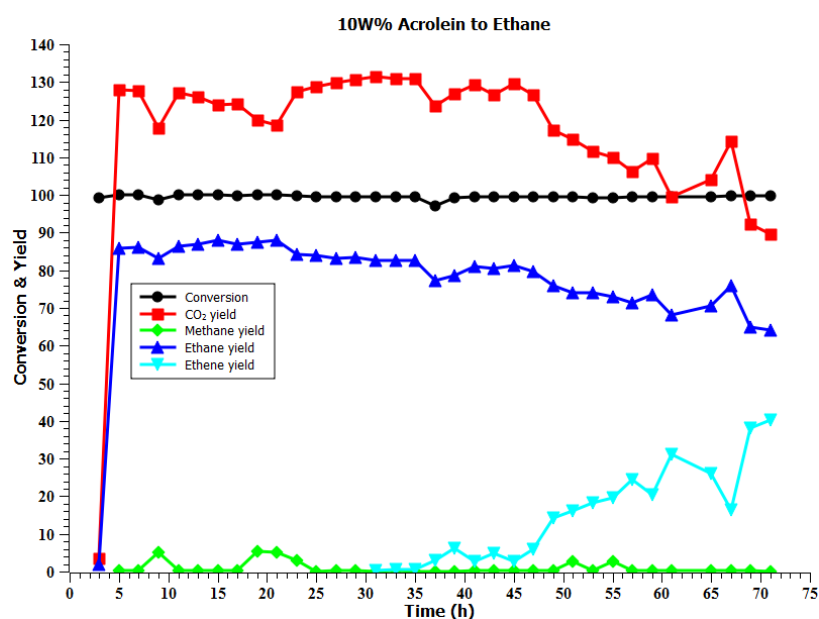


Figure 13 Acrolein to ethane over the BFS1011 catalyst (experimental setup 1).

As can be viewed in the figure the initial production rates of ethane are high, but with time the production rates tails off. In fact, after 70 h of operation the yield is a mere 65%. For counter-act the deactivation, a series of alternative operating conditions were investigated, figure 14.

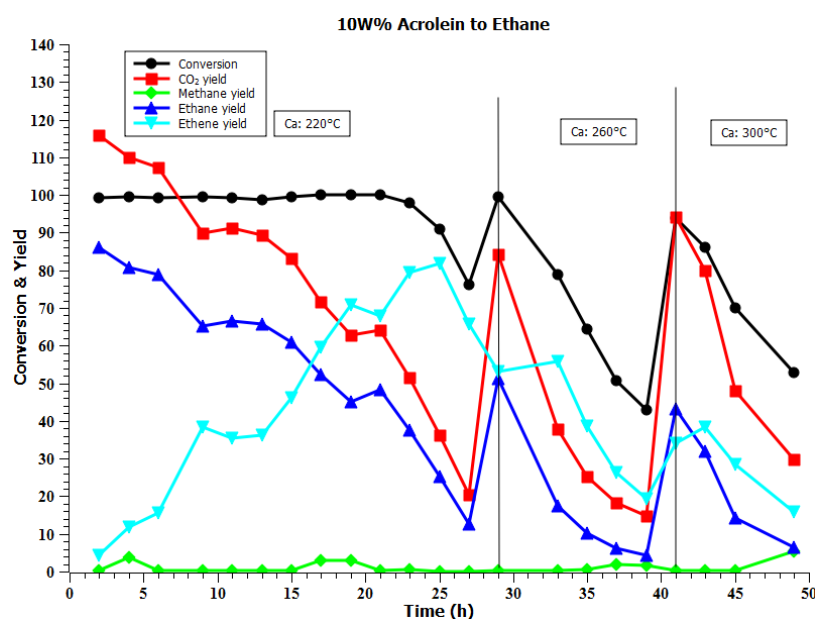


Figure 14 Acrolein to ethane over the BFS1011 catalyst (experimental setup 1).

As can be viewed in the figure, part of the deactivation can be counteracted by increasing the reaction temperature from 220°C to 260°C and finally to 300°C. However, the deactivation cannot be stopped. Additional experimental work was performed with changing the catalyst composition including other active materials and carriers. In figure 15, a figure with Pd supported on Ce/ZrO₂ is demonstrated.

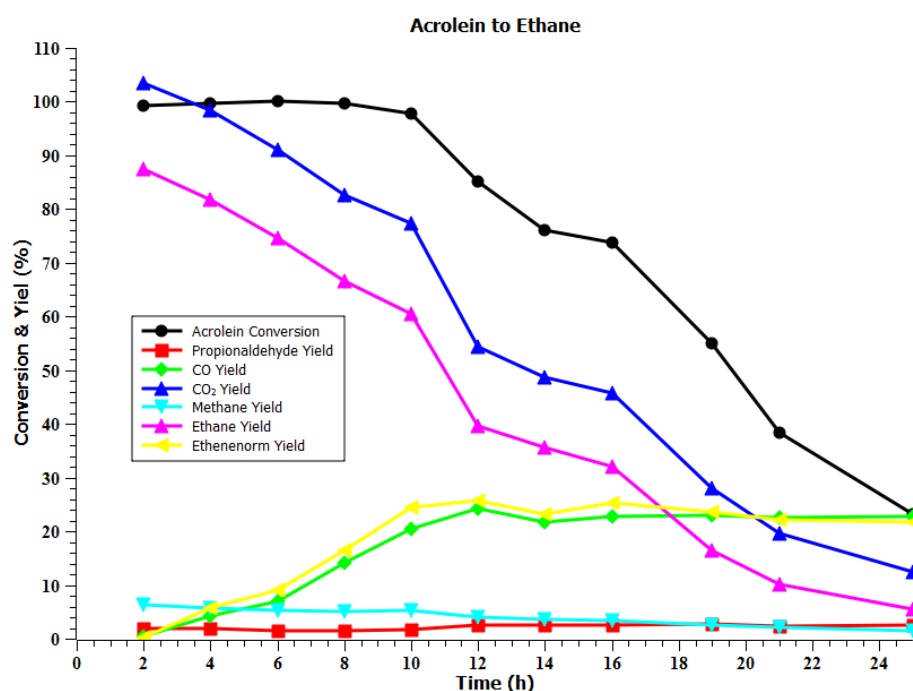


Figure 15 Acrolein to ethane over the Pd/CeZrO₂ catalyst (experimental setup 1).

The same behaviour is true for this catalyst with initial production of ethane, but the catalyst soon switches over and starts to produce ethylene instead. This continues until the conversion of the acrolein starts to tail off. The same behaviour has been shown for similar catalysts in the ethylene application [15], figure 16.

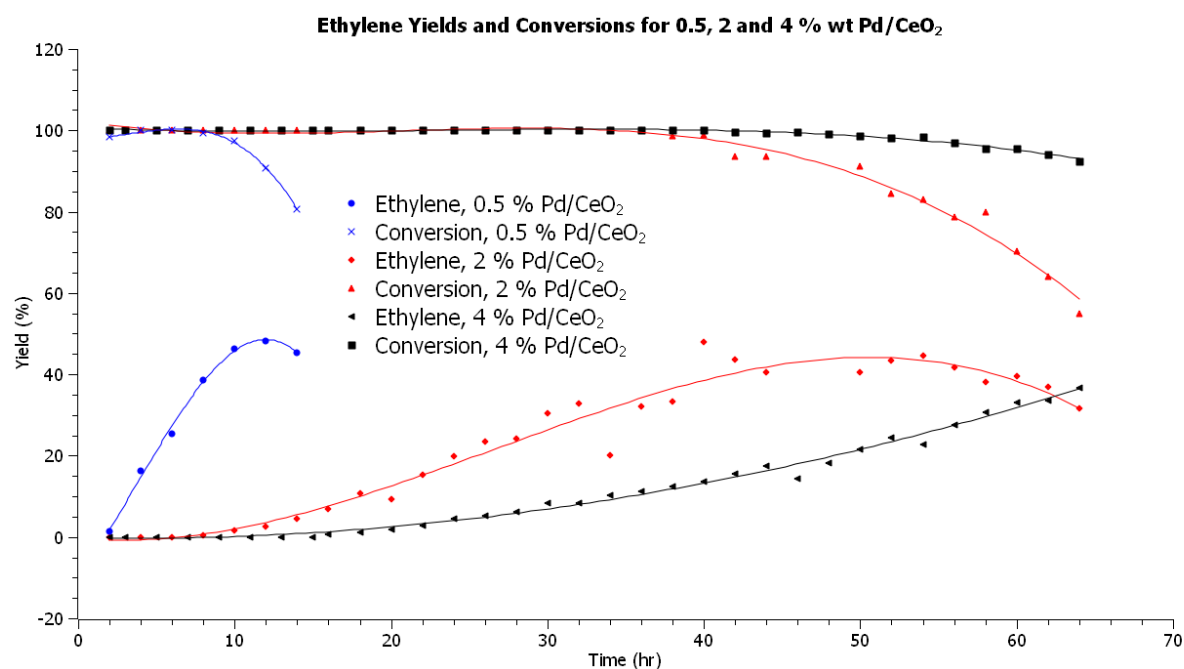


Figure 16 Ethylene yields and conversions for 0.5, 2 and 4% wt Pd/CeO₂, normalised flow [15].

As can be viewed in the figure, the weight percent of noble metal on the catalyst is crucial for the longevity of the catalyst. With 0.5% noble metal the reaction can be sustained for 10 h or so, with 2% noble metal the corresponding time is 50 h and with 4% approximately 100 h. It is obvious that the reaction can be prolonged, but it is believed that the rate of deactivation is still very much too high to be a commercially viable reaction, which is why no long-term endurance tests were performed beyond these experiments.

3.2.2 Phase 2: Long Term Testing

The long term tests were conducted to evaluate the durability of the selected catalysts and conditions. For a successful industrial process the catalyst must show stable operation during at least 500 h.

3.2.2.1 Glycerol to Acrolein

This is the key process in the production of energy gases from glycerol and it is essential that it works on a long term basis. The reaction is a dehydration of glycerol over an acidic catalyst. The problem with acidic catalysts is that they usually cause coking, as a side reaction, when converting hydrocarbons. Also in the case of converting glycerol into acrolein, it is a known problem with coking. This problem is usually solved by stopping the process and burning off the deposited coke with air; a regeneration [16]. In the figures below a novel method to suppress the coke formation is demonstrated, using the same catalyst and otherwise same conditions.

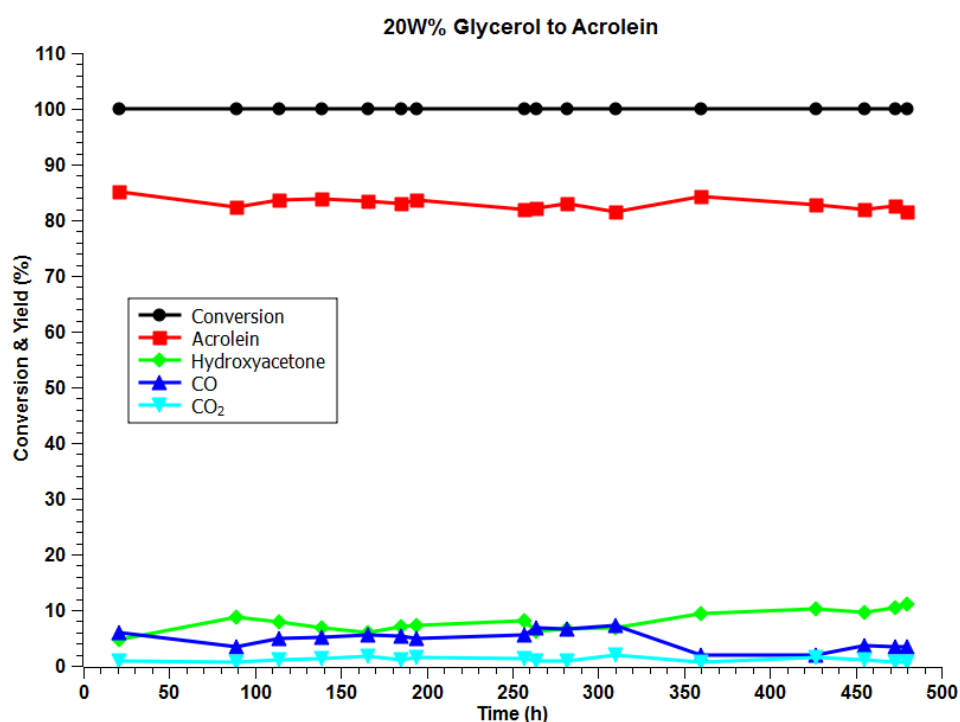


Figure 17 Glycerol to Acrolein, long-term testing with N₂ as carrier gas (experimental setup 2).

In figure 17 a “normal” run over 480 h is shown. In this case nitrogen is used as a carrier gas. The run was performed at 300°C and 5 bar with nitrogen (25 vol%) as carrier gas and a space velocity of 500 h⁻¹. In the run a stable production of acrolein with 85 % selectivity, is shown. However, the experiment was auto-stopped several times during the run due to too high pressure drop in the catalytic bed. The first stop occurred after 200 h (figure 17). After such a stop, the pressure drop decreased. This was probably due to movements in the catalytic bed, caused by the thermal expansion/retraction of the bed/reactor on heating/cooling. This made it possible to restart and continue the run. After 480 h the experiment come to a definite halt and the pressure drop was permanent. When the reactor was opened, the catalytic bed was completely filled with coke, the catalyst grains was embedded in a matrix of coal. Apparently, the formed coke does not block the active surface of the catalyst since the conversion of glycerol remains high and constant (figure 17) but fills the void of the reactor and the catalytic bed so the reactor finally becomes completely clogged.

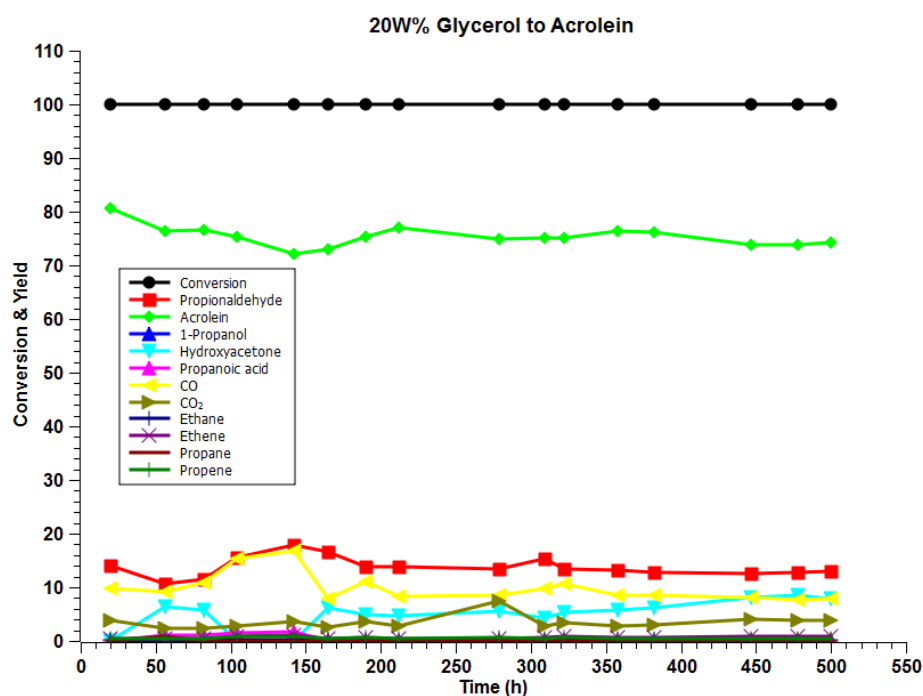


Figure 18 Glycerol to acrolein, long-term testing with alternative operating conditions (experimental setup 2).

In figure 18, the same experiment was repeated with a small difference in operating conditions. The most striking difference between the two runs can be seen in figure 19. During the first 200 h of run little or no pressure drop can be registered. After 200 h there is a, initial slow but exponential, increase of the pressure drop over the catalytic bed. Extrapolation of this increase shows that 1 bar of pressure drop will be reached in 800 h. However, after 500 h, when the run was stopped, the pressure drop over the bed had reached 0.3 bar. The catalytic bed still consisted of individual grains and could be poured out of the reactor with ease. Apparently, the alternative operating conditions suppresses the coking in the catalytic bed. However, not fully explored, one can keep the reactor on stream at least 5 times longer by the use of the alternative operating conditions; indicating one to two regenerations per year of operation in a well designed reactor set-up.

In the product spectra, there is a decrease in the acrolein formation but the missing amount forms propionaldehyde instead. This is the first step in the subsequent hydrogenation/reduction step. So the yield of acrolein equivalents for propane production is the same or slightly higher than in the case before changing the operating conditions.

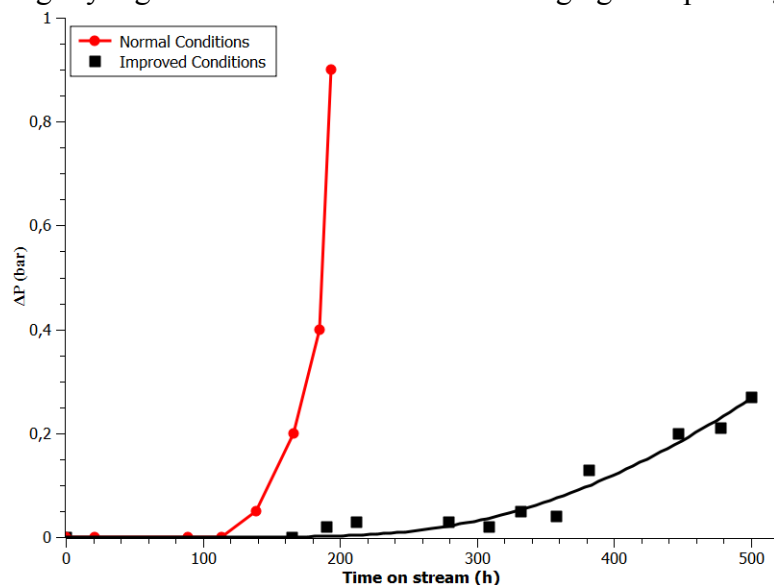


Figure 19 Pressure drop for the glycerol to acrolein long term testing with alternative operating conditions (experimental setup 2).

The improvement of operating conditions have enabled the design of an on-stream fixed catalytic bed, avoiding the requirement for more advanced reactor concepts such as fluidised or moving bed reactors.

3.2.2.2 Acrolein to 1-propanol

The commercial hydrogenation/reduction catalyst (R120) for 1-propanol production from acrolein has been evaluated on stream over a period of 500 h, figure 20.

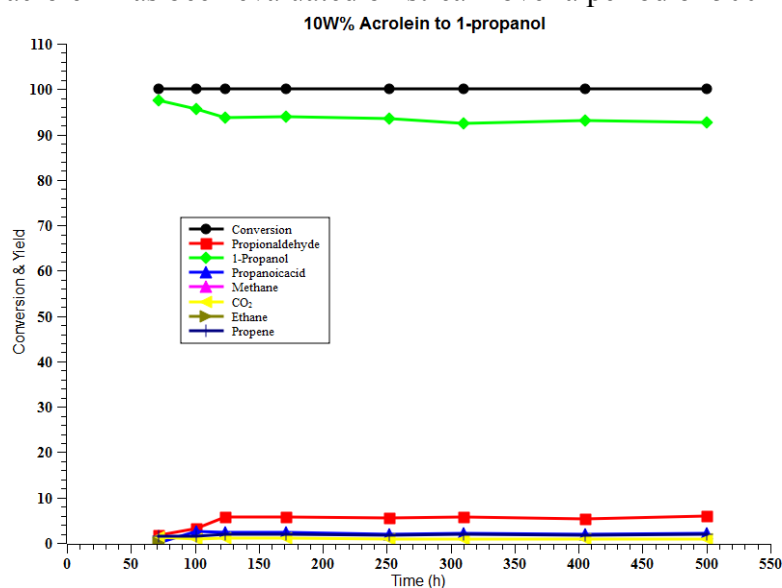


Figure 20 Acrolein to 1-propanol (experimental setup 2)

The experiment was conducted at 250°C and 5 bars and a space velocity of 700 h⁻¹. As carrier gas and reducing agent, hydrogen was used (25 vol%, 4 times the stoichiometric amount). There is >80% yield of 1-propanol and 10% of propionaldehyde. The propionaldehyde could be reduced into 1-propanol in a second step. This means that the reaction would benefit of higher pressure, higher hydrogen ratio or perhaps higher temperature. The operation, over the run, is smooth and stable though, and no coking occur.

3.2.2.3 1-Propanol to Propane

This is the last leg in the reaction scheme from glycerol to propane. The new multi-function catalyst that has been developed within this project was tested for long term stability. The catalyst enables the direct reaction of 1-propanol to propane in one step instead of two.

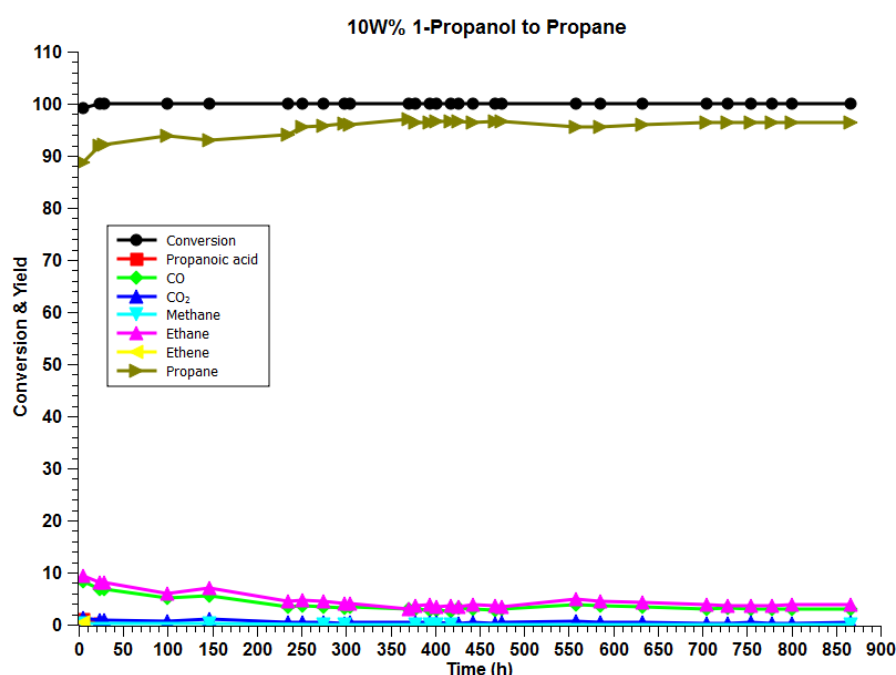


Figure 21 1-propanol to propane, long term testing (experimental setup 2)

In this experiment, the reactor temperature was kept at 300°C and 5 bars and the results are displayed in figure 21. Hydrogen, necessary for the hydrogenation was used as carrier gas (25 vol%, 8 times the stoichiometric amount) and the space velocity was 600 h⁻¹. The operation during the 870 hour on stream is very stable and the yield of propane (95%) is high. The major by-product is ethane (5%) with a corresponding production of CO.

3.3 Summary & Conclusions

The key step in producing energy gases from glycerol is the dehydration of glycerol to acrolein. This step has been significantly improved during the performed work and the need for regeneration of the catalyst has been significantly reduced. This allows for a simple fixed bed reactor design and will save cost in reactor construction. The same conclusion can be drawn from the combination of two functionalities in designing a catalyst that promote the direct reaction of 1-propanol to propane in one step instead of two.

As can be viewed from the experiments with the decarbonylation of acrolein, the catalyst deactivation rates are quite rapid. The addition of noble metal to the catalyst seems to improve the longevity of the catalyst, but the coking is still too severe to provide for a commercially viable process.

It is very important to perform long term testing of the catalysts in the laboratory. This is the step where the stability and endurance of the catalysts is proven. Most of the used catalysts in the multi step processes have been improved or better operating conditions for the catalysts have been found. There is also a promising subtask to formulate new multifunctional catalysts in order to reduce the total number of steps needed for the process. Results from a single step process have been presented; promising although much more work is needed on this issue.

In this work it has been shown that all of the catalytic steps involved in the production of propane from glycerol have sufficient long stability and endurance that it is motivated to recommend that the project continues to pilot plant testing stage.

4 Production Costs

In estimating the production costs, three sizes of plants have been considered. The first plant size is intended for the production of propane for the LPG-market and has been set at 50 000 tonnes of propane per year. The second sized plant is for the production of propane for addition to substitute natural gas produced from woody biomass and has been estimated at 10 MW or 1 700 tonnes of propane per year; this unit would also work well as an on-site propane production unit at a biodiesel plant. The third size considered is for the addition of propane to upgraded fermentor gas, approximately 50 tonnes per annum. For this last size, it is not economically viable with on-site production with the multi-step, hydrogen requiring process developed within the project. However, the single-step, internally hydrogen generated version may be considered for this applications but additional work will have to be carried out in this case for allowing for any kind of production cost estimate.

4.1 LPG-Production

For producing LPG on this scale, the production plant will be more like a chemical or petrochemical plant than anything else. In the estimates the following utilities have been assumed to be present at the site at competitive pricing:

- High pressure steam
- Hydrogen

Aside from that, it has been assumed that low pressure steam can be exported and get credited for. For estimating the investment cost, budget quotes have been received for all major equipment such as heat exchanges, reactor vessels, separation equipment, pumps, compressors etc. These base module costs has been added up and been multiplied with installation factors (5) and factors for unforeseen costs (30%). This brings the investment cost estimate total to 17.5 M€; this value should however be considered an estimate and engineering cost should be added. The investment and financial considerations are summarized in table 1.

Table 1 the financial considerations on the propane production plant.

Plant Investment Cost	17.5	Meur
Loan Financed	50%	of investment
Working Capital	10%	of Investment
Capital cost	10%	
Interest rate debt	5%	
Depreciation	15	years
Operating Hours	8 020	h/year

Out of the overall investment, 50% has been considered from loan financing with an interest rate of 5% on the loan. The working capital required by the plant has been set to 10% of the investment. The capital cost or internal rate of return has been fixed at 10% and the depreciation 15 years. The overall production costs are of course depending on the cost of the feedstock, table 2.

Table 2 the input costs for the production of propane.

Hydrogen	2 000	Eur/ton
HP Steam Import	200 000	Eur/MW/year
LP Steam Export	150 000	Eur/MW/year
Electricity	0.1	Euro/kWh

The cost of glycerol has been constant in the 70 to 150 €/ton range over the last five years. To illustrate the difference in production costs with changing glycerol price, the two extremes of the interval has been plotted with a higher price of 250 €/ton. Hydrogen costs are based on production from natural gas. With this input, the production costs can thus be broken down according to figure 22.

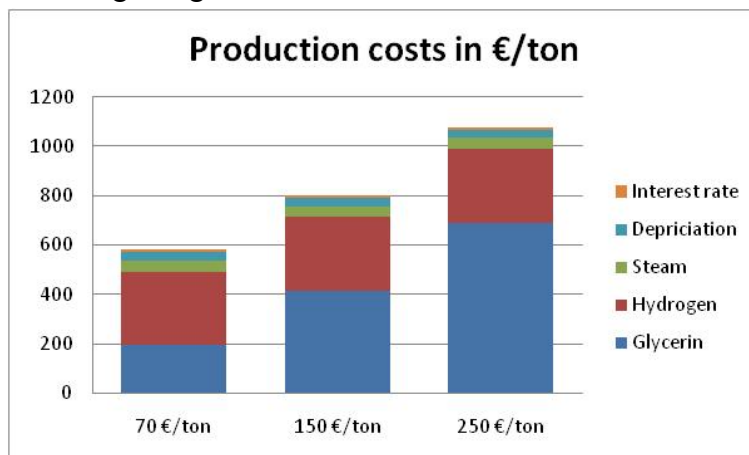


Figure 22 the broken down costs for the production of propane for three different glycerol costs.

As can be viewed from the figure, the production cost is dependent on the glycerol cost to a high degree. The cost of production range from 600 €/ton to 1050 €/ton with the assumptions presented here. It is however believed that by choosing the right site for the integration of this kind of unit, lower cost hydrogen can be used. This is true in the case of e.g. electrolysis plants where hydrogen costs are half compared to that produced from natural gas. In figure 23 this is illustrated.

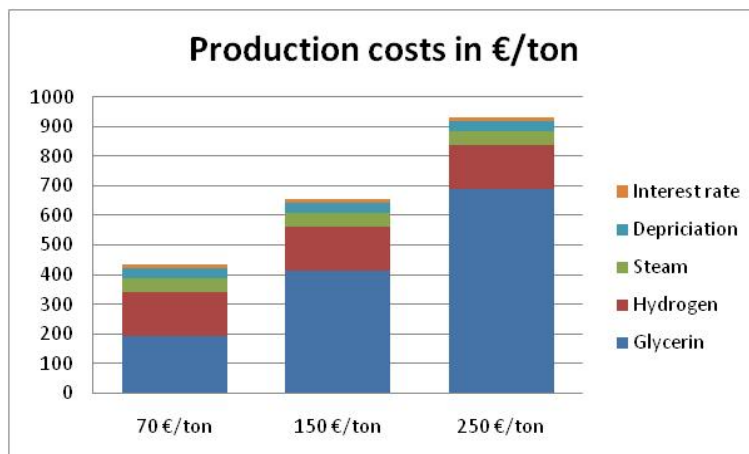


Figure 23 the broken down costs for the production of propane for three different glycerol costs with low cost hydrogen.

As can be seen in the figure, the costs are reduced by about 150 €/ton and making the production costs even more attractive for the propane product. It is however believed that there is a requirement for much higher propane prices for the product to be competitive with bulk LPG. Instead the tax incentives create a good mark-up for the product in consumer applications such as for barbequing or camping segments.

4.2 Gasification

In the case of substitute natural gas produced through upgrading of gasified biomass there is a requirement of additives of higher energy gases to the substitute natural gas (being mainly methane) for the matching of the required Wobbe index. The preferable gas is perhaps ethane if the gas is to be directly used as a vehicle fuel [17], but also propane works fine.

A decent size of substitute natural gas production is 100 MW, in-line with the expansion plans in the Swedish context. The required addition to this is about 10% of propane, 10 MW or approximately 2 000 tonnes of propane per year. The estimated cost of this kind of plant is in the 7 M€ range, including equipment for extracting additional hydrogen from the methane production process; additional information can be viewed in table 3.

Table 3 the financial considerations on the propane production plant.

Plant Investment Cost	7	Meur
Loan Financed	50%	of investment
Working Capital	5%	of Investment
Capital cost	10%	
Interest rate debt	5%	
Depreciation	15	years
Operating Hours	8 020	h/year
Hydrogen	3 500	Eur/ton
HP Steam Import	200 000	Eur/MW/year
LP Steam Export	150 000	Eur/MW/year
Electricity	0.1	Euro/kWh

The working capital is lower in this case, since lower inventory is required. The other investment considerations are equal to the LPG-case. The hydrogen cost is higher due to its biomass based origin, it is however arguable how this should be priced; one suggestion would be to set it to zero since there is no additional cost for the production only a slightly lower overall methane yield. The results can be viewed in figure 24.

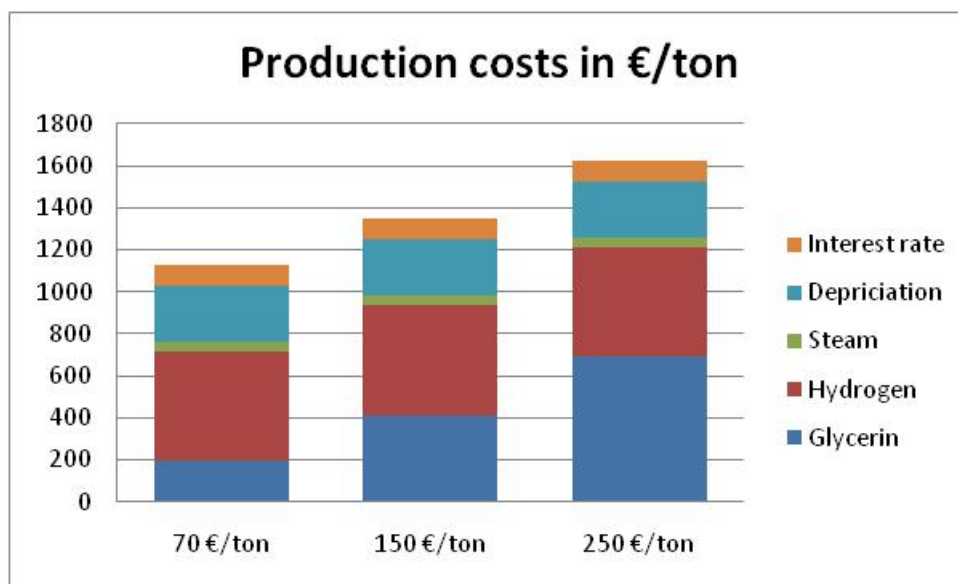


Figure 24 the broken down costs for the production of propane for three different glycerol costs.

As can be viewed in the figure, the cost of production is rather high and the reason for that is twofold. First of all, the hydrogen cost is significantly increased due to the biomass origin of the hydrogen. Secondly, the cost of depreciation is also significantly higher as the investment cost is shared by less production volume. In figure 25, the situation with no hydrogen cost is illustrated.

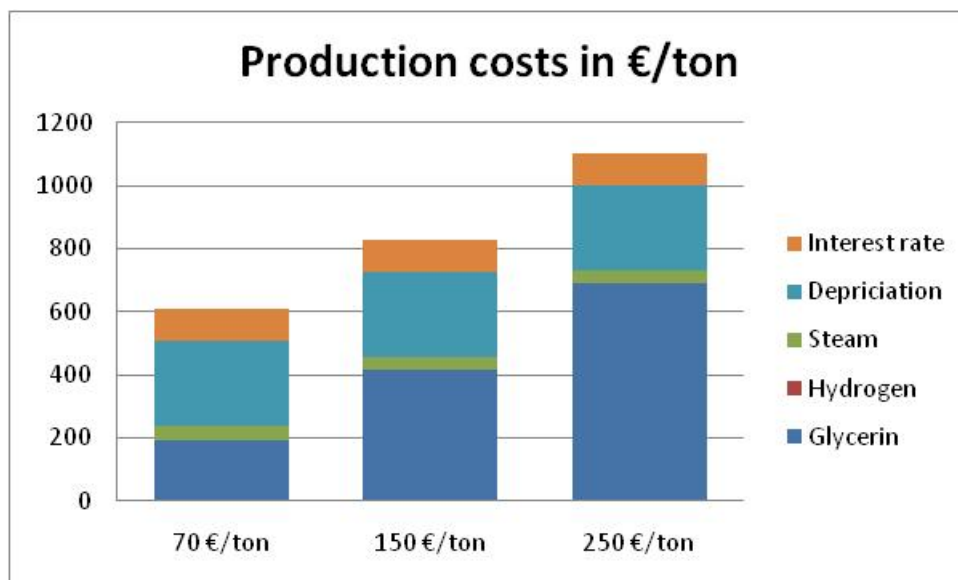


Figure 25 the broken down costs for the production of propane for three different glycerol costs at zero hydrogen cost.

As can be viewed the costs are significantly lowered but the depreciation is still a major cost in the context. The conclusion from this is that a production unit in this size range has to be reengineered to be less like a full-scale chemical plant to lower the investment cost. Targets for the investment cost should be in the 4 to 5 M€ range for this size plant.

4.3 Digester Biogas Plant

As mentioned in the introduction to this chapter, the on-site production for a biogas plant is not suited for a multi-step propane production plant. In fact the proposed ethane process may be better suited. The small production volume of 50 tonnes per annum also put very strict requirements on the investment tolerated. However, there is a requirement for more development and testing of catalysts and operating conditions before this type of plant can be estimated with respect to cost.

4.4 Production Cost Summary

It can be concluded from the production cost estimates that the size of the production plant has a significant impact on the cost of production. The other two major influencing factors are the cost of glycerol and hydrogen. The latter can be dealt with through smart localisation of the production plant and the second by long term supply contracts for the feedstock.

Another conclusion that can be drawn is that the product is not competitive in the bulk segment. The product has to get a premium price, either through tax reduction and/or in special consumer segments. Another possibility for the introduction of the product is a mandate for a renewable component in the LPG.

5 Conclusions

Since the key step in producing energy gases from glycerol is the dehydration of glycerol to acrolein, this step has attracted much attention during the development work. The step has been improved during the performed work and the need for any regeneration of the catalyst has been significantly reduced, if not omitted completely. This improvement allows for a simple fixed bed reactor design and will save cost in reactor construction as well as in operating costs of the plant. The same conclusion can be drawn from the combination of the two functionalities (dehydration and hydrogenation) in designing a catalyst that promote the direct reaction of 1-propanol to propane in one step instead of two.

The experiments with the decarbonylation of acrolein to form ethane show that the catalyst deactivation rates are quite rapid. The addition of noble metal to the catalyst seems to improve the longevity of the catalyst, but the coking is still too severe to provide for a commercially viable process. It is believed that there is a possible way forward for the decarbonylation of acrolein to ethane; it will however require additional time and resources spent in this area.

It is essential to perform long term testing of the catalysts in the laboratory. This is the step where the stability and endurance of the catalysts is proven once and for all. Most of the used catalysts in the multi-step processes have been improved or better operating conditions for the catalysts have been discovered. Another promising result is the formulation of a new multi-functional catalyst in order to reduce the total number of steps needed for the process. Results from this single step process have been presented and it is promising, although much more work is needed on this issue.

In this work it have been shown that all of the catalytic steps involved in the production of propane from glycerol have sufficient long-term stability and endurance and it is motivated to recommend that the project continues to pilot plant testing stage.

5.1 Future Work

Based on the positive outcome of the project the glycerol-to-LPG technology will be continued into a pilot plant phase. The verification phase, finished with the issue of this report, indicates a pilot plant in operation during 2011 if sufficient funding can be raised. After operation of the pilot, the first commercial plant will be constructed, figure 26 show the various stages of development.

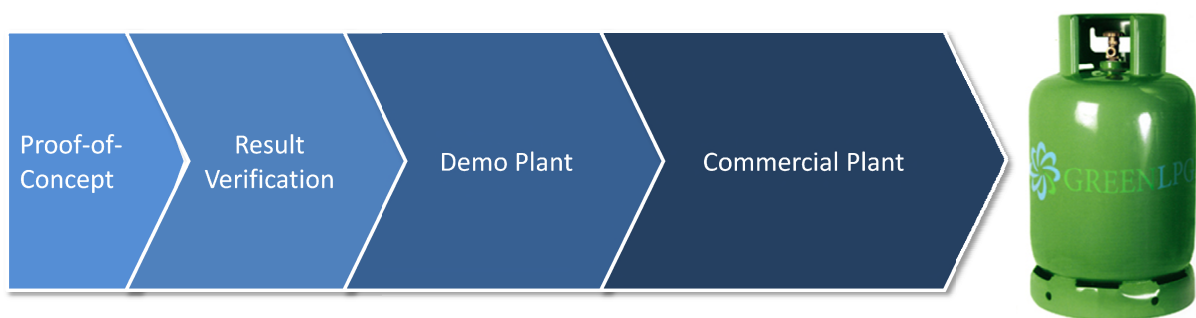


Figure 26 Development plan for the glycerol technology.

Another interesting pathway to further investigate is the direct reaction of glycerol to propane or ethane over one catalyst in one reaction step. This could potentially simplify the operation of a plant and lower the overall investment cost of such a plant and perhaps allow for economic operation even at smaller scales such as for digester biogas production.

6 References

- [1] DIRECTIVE 2009/28/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL, of 23 April 2009, on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC
- [2] Brandin, J.G.M., Hulteberg, P.C., Liljegren-Nilsson, A. SGC rapport 198, "Bio-Propane from glycerol for biogas addition"
- [3] Christoph, R., Schmidt, B., Steinberger, U., Dilla, W., Karinen, R. "Glycerol" Chapter in Ullmann's Encyclopedia of Industrial Chemical p1-16.
- [4] Morrison, L.R. "Glycerol" Chapter in Kirk-Othmer Encyclopedia of Chemical Technology, p1-13.
- [5] "75 years Henkel Glycerine", Henkel KGaA, Düsseldorf 1986, Company brochure
- [6] <http://www.ebb-eu.org/stats.php> 2010-02-22
- [7] <http://cleantech.com/news/5029/us-biodiesel-industry-drowning-surpl> 2010-02-22
- [8] <http://www.britannica.com/bps/additionalcontent/18/24310897/Southeast-Asia-Invests-Big-In-Palm-OilBased-Biodiesel> 2010-02-22
- [9] Gaskin, D.J., "Industrial Biotech's Accelerate Drive to Leverage Glycine" Ethanol Producer Magazine, October, 2009, p78-79
- [10] <http://www.meti.go.jp/report/downloadfiles/g30819b40j.pdf> 2010-02-23
- [11] <http://www.guardian.co.uk/environment/2009/jul/14/green-algae-exxon-mobil> 2010-02-23
- [12] Taherzadeh, M.J., Adler, L., Liden, G., "Strategies for enhancing fermentative production of glycerol-a review", Microbial Technology 31 (2002) 53
- [13] Ben-Amotz, A., Tornabene, T.G., Thomas, W.H., "Chemical Profile of Selected Species of Microalgae with Emphasis on Lipids", J. Phycol 21 (1985) 72-81
- [14] Werpy, T., Petersen, G., "Top value added chemicals from biomass vol. 1, results of screening for potential candidates from sugars and synthesis gas", US DOE Report, 2004

- [15] Väänänen, J., Nilsson, F., “Decarboxylation of Acrolein – a catalytic study”, Masters Thesis, Lund University Faculty of Engineering Technology, chemical Engineering, 2009
- [16] Dubois, J-L., Duquenne, C., Hölderlich, W., Kervennal, J. “Process for the dehydrating glycerol to acrolein”, PCT/EP2006/000736
- [17] Bengtsson, O., Svensson, L., “Beräkning av daggpunkten för uppgraderad biogas”, SGC report 153, 2005



Scheelegatan 3, 212 28 Malmö • Tel 040-680 07 60 • Fax 040-680 07 69
www.sgc.se • info@sgc.se
