Scaling up a Gas-Phase Process for Converting Glycerol to Propane

Christian Hulteberg 1,∗ and Andreas Leveau 2

1 Department of Chemical Engineering, Faculty of Engineering, Lund University, P.O. Box 124, 221 00 Lund, Sweden
2 Biofuel-Solution AB, Rödklintsgatan 2b, 218 73 Tygelsjö, Sweden; andreas.leveau@biofuel-solution.com
∗ Correspondence: Christian.Hulteberg@chemeng.lth.se; Tel.: +46-733969420

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Abstract: It is of interest to study not only the fundamental behavior of catalysts and reactors but also to ensure that they can be scaled up in size. This paper investigates the scale-up of a glycerol-to-propane process starting from fundamental laboratory data from micro-reactor testing to the kilogram scale. The process is described in detail and consist of the use of design documents and computer simulations for determining the sizes of the unit operations involved. The final design included a vaporizer section for a glycerol/water mixture, four reactors in tandem with subsequent dehydration and hydrogenation reactions, a flash vessel to separate the excess hydrogen used, and a compressor for recycling the excess hydrogen with additional light components. The system was commissioned in a linear fashion, which is described, and operated for more than 3000 h and more than 1000 h in the final operating mode including recycle. The major results were that no catalyst deactivation was apparent aside from the slow build-up of carbonaceous material in the first dehydration reactor. That the system design calculations proved to be quite close to the results achieved and that the data generated is believed to be sufficient for up-scaling the process into the 1000 to 10,000 tonnes-per-annum range.

Keywords: glycerol; scale-up; chemical engineering; catalysis; LPG; liquefied petroleum gas (LPG)

1. Introduction

There are several aspects to consider when it comes to scaling up processes. There is a clear distinction between the scientists advocating the approach where every process should stem from the investigation of said process in small-scale studies. On the other hand, others believe that the only effective method is to construct a large plant and work out the errors by empirical trial and error [1]. This is not distinct, but a sliding scale. The first step in scaling up is normally moving from a small test set-up to a pilot plant, even though the piloting step may be skipped. There are, however, several distinctions between a normal test set-up and a pilot plant. The pilot plant is operated to study critical process features; it should be large enough to be relevant with respect to results, small enough to keep cost reasonable, it should be concerned with engineering and economic problems and involve several unit operations.

In the case of scaling up a catalytic process, there are several things that need to be considered aside from the process vessels and separation issues. Also, the catalyst formulation must be transferred to a suitable form, normally a pellet, an extrudate, or (in cases where pressure drop is an issue) a monolith shape [2]. There are indeed other situations that further complicate the design, e.g., are recycle-streams to be considered or not. Recycles are oftentimes omitted to simplify the pilot operation. However, there may be a lack of results as trace compounds that are potential catalyst poisons will not accumulate in the system to the degree they will in the final process.
When it comes to converting glycerol, a low-value side product of the biodiesel industry, to higher-value compounds, there have been many suggestions [3,4]. The conversion methods vary from liquid to gaseous state, and the state of aggregation will pose different problems on full-scale processing. In the liquid state, for instance, any contaminants in the glycerol will have to be removed upstream of the process or end up in the reactor. In contrast, in the processing in the gas phase, contaminants of inorganic nature may be removed during vaporization of the feedstock. On the contrary, the energy required for vaporizing the glycerol may be substantial and will be a large heat sink in the process.

The process that will be subject for scale-up in this paper is based on the gas-phase conversion of glycerol into propane, acting as a renewable liquefied petroleum gas (LPG). The reactions for transforming the glycerol into propane may be viewed in Figure 1.

**Main reactions**

\[
\text{HO-CH}_2-\text{CHOH} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + 2 \text{H}_2\text{O}
\]

\[
\text{H}_2\text{C}=\text{CH}_2 + 2 \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH}
\]

\[
\text{H}_2\text{C}=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_3
\]

**Possible side-products**

\[
\text{HO-CH}_2-\text{CHOH}, \text{HO-CH}_2-\text{COOH}, \text{O}=\text{C}
\]

*Figure 1. Reactions involved in transforming glycerol to propane and the side products acetol, propylene glycol, carbon monoxide, and carbon dioxide.*

The first reaction is much investigated, and several catalysts for this reaction have been studied, e.g., heteropoly-acids and other supported inorganic acids [5–16], zeolites [17–21], mixed oxides [22–28], and sulphated zirconia [29,30]. In general, the reaction is catalyzed by acid sites. Earlier work has shown that the effect of pore condensation in this stage may cause catalyst deactivation [31,32]. For the following catalyst steps, there is less material published, which is to be expected as they are less frequently investigated. There are some examples in the literature, and the hydrogenation of acrolein to propanol may be performed using nickel or noble metal-based catalysts [33–36]. The dehydration of the propanol uses the same type of acid sites as the first dehydration reaction, and the final hydrogenation reaction from propylene to propane may be performed on supported nickel or noble
metal catalysts [33–36]. The process includes not only catalytic unit operations but also separation and recycling of excess hydrogen needed to get reasonable conversions in the hydrogenation stages as per the equilibrium constraints. The pilot plant constructed includes most of the unit operations needed in the full scale, but heat integration has been omitted.

2. Results and Discussion

This section presents the results of designing and operating the pilot plant and the first section deals with the system design, including the heat and mass balance. The second part describes the experimental results.

2.1. System Design

The first document to be generated based on the process description, as previously described, is the process flow diagram. The diagram contains the main unit operations of the system but omits sensors, drain valves, safety equipment, etc. The process flow diagram has been used as a basis for the heat and mass balance, Figure 2.

As can be seen in the figure, the glycerol/water pre-mixed solution is pumped to the pressure needed to keep a 10 bar(g) exit pressure and the pressure drop over the system. The feed pressure is 14 bar(g), and the flow rate is controlled by a mass flow controller. The feedstock (stream 3) is then first mixed with hydrogen recycle (stream 18) and vaporized in the vaporizer section. The up-stream mixing of hydrogen before the vaporizer improves the vaporization as it lowers the partial pressure of glycerol in the gas and helps in avoiding polymerization of the glycerol. The polymerization of glycerol in the vaporizer section lowers the overall yield in the process. There is also an added benefit from adding the hydrogen upstream of the dehydration section [31] as it lowers the side-product formation and build-up of pressure drop. In the dehydration reactor, the main product is acrolein, but also propionaldehyde and hydroxyacetone are formed. The formation of propionaldehyde is not a problem; it is an intermediate compound on the way to propane. The formation of hydroxyacetone represents a loss of material, and it will be removed with the water leaving the process (stream 12). The hydroxyacetone (or its hydrogenation product propylene glycol) cannot be recycled in the system as it causes severe carbon formation in the dehydration reactor [32]. Exiting the dehydration reactor
(stream 6), the gases are cooled by natural convection, and the acrolein and the propionaldehyde are reacted to form propanol. The stream exiting the first hydrogenation reactor (stream 7) is reheated and then passed through the second dehydration reactor forming propylene. This gas stream (stream 10) is cooled, condensed, and allowed to flash in a flash vessel. The gas exiting the flash vessel (stream 13) contain the excess hydrogen as well as propane as the major constituents according to the heat and mass balance, also the formation of CO, CO\textsubscript{2}, and CH\textsubscript{4} will lead to accumulation in the recycle loop. The introduction of traces of inert gases such as He and N\textsubscript{2}, e.g., as contaminants in the hydrogen inlet, will have the same cumulative effect. Therefore, about 5% of the recycle stream is bled off (stream 14). To compensate for the loss of hydrogen via reaction and bleed-off, make-up hydrogen is added to the system (stream 17). Also, using the process flow diagram, the heat and mass balance could be calculated, Table 1.

**Table 1.** Results from the heat and mass balance calculations, normal operation, t indicates traces

|        | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  | 13  | 14  | 15  | 16  | 17  | 18  |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| **Temperature (°C)** | 12.7 | 14.7 | 226.7 | 226.7 | 181 | 251 | 251 | 251 | 251 | 251 | 251 | 251 | 251 | 251 | 251 | 251 | 251 |
| **Pressure (bar)** | 1.0  | 1.0  | 1.0  | 1.0  | 0.91 | 2.0  | 2.0  | 2.0  | 2.0  | 2.0  | 2.0  | 2.0  | 2.0  | 2.0  | 2.0  | 2.0  | 2.0  |
| **Mole Flow (mol/h)** | 66  | 111 | 111 | 111 | 111 | 111 | 111 | 111 | 111 | 111 | 111 | 111 | 111 | 111 | 111 | 111 | 111 |
| **Mass Flow (g/h)** | 1426 | 1562 | 1562 | 1562 | 1562 | 1562 | 1562 | 1562 | 1562 | 1562 | 1562 | 1562 | 1562 | 1562 | 1562 | 1562 | 1562 |

| **Mole Flow (mol/h)** | 3   | 3   | 3   | 3   | 3   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |
| **Water** | 63  | 63  | 63  | 69  | 69  | 69  | 69  | 69  | 69  | 69  | 69  | 69  | 69  | 69  | 69  | 69  | 69  |
| **Acrolein** | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 3   | 3   | 3   | 3   | 3   | 3   | 3   | 3   | 3   | 3   |
| **Hydrogen** | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |
| **Propane** | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |
| **Propanol** | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   | 0   |

Based on the heat and mass balance, the various components could be designed. From previous small-scale experiments to some part published elsewhere [31,32,35,36], the suitable space velocities for the reactors have been determined and are reported in Table 2 along with other important parameters for reactor design. In summary, the lower space velocity for the dehydration reaction is in part due to the slower reaction kinetics of this reaction compared to the hydrogenation reaction. However, it is also due to the fact that there is expected fouling of the catalyst due to the formation of carbon on the catalyst and the catalyst amount chosen is to sustain a minimum of 4000 h of operation.

**Table 2.** Parameters used for reactor design

| Reactor     | Space Velocity (h\textsuperscript{-1}) | Length/Diameter | Reactor Volume (L) |
|-------------|----------------------------------------|-----------------|--------------------|
| Dehydration 1 | 1000                                   | 2               | 1.3                |
| Hydrogenation 1 | 5000                                  | 10              | 1.2                |
| Dehydration 2 | 1000                                   | 2               | 1.3                |
| Hydrogenation 2 | 5000                                  | 10              | 1.2                |

As may be viewed in the table, there are two types of reactors designed for the two different types of reactions. The first reactor, the dehydration reactor type, is dominated by a slow, mildly endothermic reaction that is chemically controlled. In addition, there are side-reactions in the first reactor that gives rise to an increased pressure drop over time. Therefore, the reactor design was chosen to result in a
rather wide and short reactor. By employing a low length-to-diameter ratio, the reactor can be operated for quite a long time before having a too high pressure drop. In addition, the wider reactor required a larger inlet section to avoid maldistribution of the gas. The target inlet temperature to this reactor is 280 °C. The second dehydration reactor used the same reactor design for practical purposes; the low length-to-diameter ratio is not required in this case. The second reactor type is widely different from the first in that it has a much higher length-to-diameter ratio. This has been chosen based on the highly exothermic nature of the hydrogenation reaction to allow for cooling of the generated heat. Ideally, this reactor should be operated as an isothermal tube reactor to get as high conversion as possible given the equilibrium of the reaction. The optimal operating temperature has been found to be 180 °C for the catalyst used. The reactors are schematically reproduced in Figure 3.

![Figure 3. Reactors designed for the process.](image)

Both the compression and the vaporization sections posed many challenges during the implementation of the pilot, and most of the operation downtime was due to these two unit operations. The operational problems will be discussed in more detail in the next paragraph. The initial design for the compressor was to use a mechanical compressor. However, after working through a couple of these, with no success, it was decided to construct a hydraulic compression system. The system used two vessels that were used intermittently such that one vessel was filling with the gaseous exit from the flash vessel (stream 15). The filling continued until the vessel pressure reached 8 bar(g). Thereafter, a pump was started and filled the vessel with water and at the same time evacuating the second vessel. The compression ratio of the gas was 1:50, and the gas was moved to an intermediate buffer vessel, from which the gas was fed to the system. The second vessel, once empty from water started filling up with gas.

The vaporizer section was also reconstructed during the pilot operation. The first vaporizer was similar to the dehydration reactor in that it had a rather low surface-to-volume ratio. This proved unsuccessful as the shell temperature of the vaporizer vessel had to be kept to high, leading to polymerization of the glycerol. The second vaporizer contained two parallel vessels with a much higher surface-to-volume ratio. In Figure 4, there is a picture illustrating the shape of the vaporizers as compared to the shape of the hydrogenation reactors.
2.2. System Operation

In this section, the results from the actual operation of the pilot will be reported. The pilot was operated for more than 3000 h and the first heading report some of the lessons learnt operating the plant. Thereafter, the results from the vaporization, the dehydration and, finally, the overall process will be reported.

Figure 4. The final vaporizer vessels compared to the hydrogenation reactor.
2.2.1. Operating Experience

As mentioned previously, the major problems with operating the plant arose from the vaporization and the compression part. The compression part has been discussed above, and the use of a hydraulic compressor is proven to be an option for systems of this size. However, this is nothing that is recommended when moving to a larger scale, only a solution to a problem arising from the miniaturization of the plant. The vaporizer section and the solutions employed there will be further discussed under the next heading. However, aside from these two major issues, there are some other operating experiences that can be further detailed.

The first one pertains to the use of a pump for supplying the mixed glycerol and water. The original design contained a piston pump with rather good pressure capacity, feeding a loop where a majority of the liquid flow was circulated back to the storage tank, and a small flow was taken to the pilot plant using a Coriolis mass flow controller. This proved to be impossible to stably operate due to the pulsations caused by the pump, not allowing the mass flow controller to operate properly. This was solved by installing a buffer vessel kept at pressure using nitrogen. The vessel was filled up rapidly (about 1 min) using the pump, and the mass flow controller was fed a constant pressure liquid from the vessel for several hours of operation. Two level-controllers on the vessel ensured the vessel filled up when needed and did not overflow during pumping. It is believed that this problem could also have been solved by using a pulsation dampener on the pressure side of the pump.

Another lesson learned is that a complicated process with multiple reactors and feedback loops requires an advanced control system. It was thought that localized control could be possible, using for local PID-controllers for temperature. This functioned rather well at first, before running with the recycle loop. However, the hydraulic compressor that added a number of additional sensors and the feedback loop to the system made this control strategy unmanageable. This was solved by developing a LabVIEW-based program for regulating the process. It also permitted better logging of temperature and pressure data, making post-run assessments more rewarding.

2.2.2. Vaporization

The loss of material over this first section was initially too high due to the low surface-to-volume ratio, leading to a too high shell temperature of the vaporizer and polymerization of the glycerol. The redesign into a longer and narrower vaporizer tube was a step forward. However, it is also apparent that the bed material is important, as is the flow direction. It also goes to prove that it does not matter how good the downstream equipment is if the input feedstock fails to reach it.

As already mentioned, the vaporization of the glycerol/water mixture was hard to achieve, more so than initially believed. The first vaporizer did not function at all, and the vaporization system was redesigned. The operation of the new vaporizer was done for some 600–650 h before the operation was good enough for adding reaction steps, Figure 5. The initial operating results of the new system were quite poor however, and additional modifications were required. The first change was a switch of flow direction from bottom-up to top-down. It was apparent after the initial analysis that the initial flow direction resulted in too much glycerol accumulating in the bottom part of the vaporization vessel. The flow-reversal increased the yield from about 40% to slightly above 50%. This was, however, not enough for a high yielding operation; thus, the next step was to change the filling material in the vaporizers added to promote heat transfer. By choosing a material with finer particles, 1–2 mm instead of 4–6 mm, and without acidic sites (sintered α-alumina), the yield was further increased from 50% to about 65%. By fine-tuning the temperature of the vaporizer and finally increasing the pressure in the vaporizer section, the final recovery in the vaporizer section surpassed 90%. In addition to the glycerol analysis, the permanent gas analysis showed an initially high formation of CO and some CO$_2$ during the vaporization. This is associated with the formation of solid carbon on the packed bed of the vaporizer. At the final operating conditions, the yield of CO was 1.4 wt % and CO$_2$ 0.3 wt % respectively. This, together with the glycerol analyzed, represent 99.2 wt % of the carbon entered into the system, indicating a minor loss of carbon still, likely due to solid carbon formation.
2.2.3. Dehydration

Producing acrolein with high yield is really a requisite for producing propane with a high degree of recovery. Any side-products formed during operation of the system is most likely to be formed in this reaction step. This is due to the polymerizing ability of the acrolein and the potential pore condensation of glycerol in the catalyst. As can be seen from Figure 6 there was much work needed in getting the overall yield of acrolein to a reasonable level. As the reactor is operated with hydrogen present, there will be some propionaldehyde formed, about 1:10 with respect to acrolein, and the results are referring to the combined acrolein and propionaldehyde yield. There is a strong relationship between the operating conditions of the reactor and the resulting products. Too low a temperature and there will be unconverted glycerol breaking through, and too high a temperature there will be too much side-products formed. The results in Figure 6 show that initially, the temperature was too low for allowing for complete glycerol conversion, but after some operating experience was gained, the yield crept up towards and above the 90% line. The analysis of the side-products showed that during operation at the final conditions, between 2.4 wt % and 2.6 wt% of the inlet glycerol is converted into acetol. There is also a yield of CO of about 1.9 wt % and CO2 0.4 wt % respectively, indicating a slight increase in the formation of carbon oxides in the conversion step.

Figure 5. Results of the vaporization of glycerol over the second vaporizer configuration reproduced with permission [37].

Figure 6. Conversion of glycerol and yield of C3 (acrolein and propionaldehyde) during some 1200 h of operation. Reproduced with permission [37].
2.2.4. Combined Process

After getting the vaporization section working to some reasonable degree and getting yields of acrolein and propionaldehyde over the first reactor that were reasonable, the full process was considered, Figure 7. The system was first operated as a once-through system with a much higher hydrogen flow rate. Initially, the yield of propane was low, in favor of propylene. This was, however, helped by increasing the temperature in the final hydrogenation reactor. The yield of propane was increased to about 35% before recycling was commenced. During the next 1100 h of operation, the yield of propane was increased to about 85–89% and the last 250 h the overall yield of propane was close to 90%. The remaining material shows up as 2.5–2.6 wt % propanediol and 2.2 wt % CH₂ and 0.3 wt % CO₂.

There was a worry that there were compounds formed in the first dehydrogenation reactor—e.g., carbon monoxide, or aerosol formation of the Na₂SO₄ salts in the crude glycerol—which would act as a catalyst poison for the hydrogenation catalyst. It was also believed that the accumulation of these, or other catalyst poisons due to recycling, would lead to catalyst deactivation. This might still be the case, but during the time-on-stream illustrated here, there is nothing indicating a deactivation in the later reaction stages. One explanation may be that the catalyst proved to be active in the hydrogenation of CO and CO₂ into CH₄ and most of the carbon oxides were converted into methane. There is, however, a problem with pressure-drop build-up in the vaporizer section and the first dehydration reactor. The first problem is due to the salt formation, and due to the high solubility of the salt, this can be washed out using city water. The second problem is more challenging than the first. After about 1000 h on-stream, the pressure drop is too high, despite operating the system with hydrogen excess and water to dilute the glycerol. The catalyst can be regenerated using a combination of oxygen and steam [32], but this will have to be performed in-situ in the reactor for a full-size unit. This was not tried in the system presented here.

When comparing the performance to the heat and mass balance results summarized Table 1, there are some differences that are interesting to note. The most striking difference is the residual concentration of propylene. In the simulations, the conversion has been very close to unity in the final hydrogenation stage. This proved to be more difficult in real life, and there is still some 3–5% propylene in the exiting mixture. This is not believed to be a problem as propylene is an accepted impurity in LPG. Indeed, the European standard for autogas allows for up to 30% olefins [38]. This is also an
advantage as this lowers the hydrogen consumption in the process. Another difference compared to the original research is that the hydroxyacetone is fully hydrogenated to propylene glycol. This opens up for potential recycling of the water with propylene glycol [39], which was not possible when hydroxyacetone was the reagent due to heavy residue formation. This will significantly lower the operating cost of the final process, as water treatment is associated with significant cost.

3. Materials and Methods

In this section, the system design procedure will be described; this is followed by a section pertaining to information regarding the actual operation of the pilot plant.

3.1. System Design

The basis for any design is a process description, and this design has not been an exception. The process description for this process has been to evaluate the production of propane from glycerol in pilot scale. The aim of the pilot is to have a flexible set-up which allows for testing five steps from glycerol to LPG. The first step is the vaporization of a pre-mixed water and crude glycerol solution, allowing for simultaneous removal of inorganic materials (sodium sulfate). The second step is the dehydration of glycerol to acrolein, followed by cooling and after that the third step, namely hydrogenation of acrolein to propanol. The propanol is further dehydrated to propylene, and the propylene is finally hydrogenated to propane. The specified outlet flow rate is 0.1 kg of propane per hour, and the hydrogen will be supplied from bottles and recycled over the reactor system. The system will be electrically heated; thus, no heat integration will have to be performed. The unit should be able to operate without supervision for a minimum of 100 h at a time. With this specification, along with available data from micro-reactor tests, a process flow diagram could be drawn, the heat and mass balance is calculated, and a piping and instrumentation diagram is drawn. Using the information in the heat and mass balance, the detailed design of the equipment could be performed. The design process is depicted in Figure 8.

Figure 8. Design process.
3.2. Heat and Mass Balance

The heat and mass balance was solved using Aspen plus [40] (Version 8.6, Aspentech, Bedford, MA, USA, 2018). The model uses NRTL as the global property method, and the dehydration reactors are simulated as stoichiometric reactors based on available data. The hydrogenation reactions are simulated as equilibrium reactors and based on experimental data from micro-reactor testing, and this is reasonable. Heat exchangers are short-cut simulated, and flash vessels are simulated using zero energy input. A number of compounds were included in the simulations, and a summary table of the calculations are given in Table 1.

3.3. Experimental Details

The glycerol used for the experiments were from a commercial biodiesel operation (Energigårdsarna, Karlshamn, Sweden) and had a general composition of 80% glycerol, 10% inorganic salts (Na$_2$SO$_4$) and 10% water. The matter organic non-glycerol was lower than 1%, and the glycerol was used as received. The glycerol was mixed with city water to an equivalent of 20% glycerol by weight before being fed to the system using a Bronkhorst CoriFlow meter, and the hydrogen make-up was fed using a Bronkhurst EL-Flow Prestige meter (Bronkhurst High-Tech B.V., AK Ruurlo, The Netherlands). A similar meter was used for bleeding out gas from the recycle loop. The pressure in the process was controlled by using a Bronkhorst EL-Press pressure control device (Bronkhurst High-Tech B.V., AK Ruurlo, The Netherlands). The vaporizer and the two dehydration reactor-furnaces were electrically heated and controlled by type K-thermocouples. The same thermocouple type was used throughout the system. Two vaporizer sections were considered, one with two parallel vessels measuring 800 mm in length and 40 mm in diameter and one with a single vessel measuring 200 mm in length and with a 100 mm diameter. The filling material of the vaporizers sintered α-alumina that was crushed to a suitable size fraction. Two different size-fractions were tried, 4–6 mesh (2.3–4.6 mm) and 10–20 mesh (0.8–1.7 mm). The first vaporizer was heated using a thermal jacket of 1.8 kW and the second vaporizer was heated using ceramic half-shell type heaters of 5 kW. The system was skid mounted and placed within a vented cabinet, the pilot with the single vessel vaporizer is depicted in Figure 9.

![Figure 9. Skid-mounted finished process with a single vaporizer vessel.](image-url)
As can be seen in the figure, there is an electrical cabinet to the left, and then the vaporizer and reactors are mounted on a perforated plate. All wiring is run from the back and easily disconnect such that the entire skid may be rolled out of the vented cabinet for easy maintenance. To the right in the figure, the gas cooler and gas–liquid separation devices are found. The system was operated at 10 bar(g) pressure at the outlet. The vaporizer was filled with an inert material sieved to 10–20 mesh for enhanced heat transfer and for avoiding voids in the vaporizer section. The inorganic salt deposited in the vaporizer section was periodically washed out with city water. The catalyst used for the first and third reactors were based on a pre-treated commercial 10 wt % WO$_3$ by weight supported on ZrO$_2$ in the form of beads 1–2 mm in diameter (Daiichi KKK). This catalyst was chosen based on the micro-reactor experiments reported in [31,32]. The catalyst in the second and fourth reactor was a commercial supported nickel-based hydrogenation catalyst in an extruded form (1.6 mm extrudates, Clariant NISAT). The reactor designs will be further commented in Section 2.1. The flow rates used in the experiments were 1426 g per hour of the pre-mixed glycerol solution, 24 g per hour of hydrogen make-up, and 12 g per hour was purged from the system. An activated carbon filter was employed for removing the oxygenated hydrocarbons before venting to the atmosphere.

A gas and a liquid sample were taken daily over the test period when the pilot was in operation. 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) (Palo Alto, CA, USA). The liquid analysis was performed using a Scion 456-GC Gas Chromatograph equipped with a 500 µL inert steel sample loop 1/16 for a Valco injection valve, a Rtx-DHA-50 capillary column 50 m, 0.20 mm ID 0.5µm equipped with an FID detector (Scion Instruments Inc., Livingston, West Lothian, Scotland, UK). The calibration was performed for the components reported in Table 1 as well as for CO, CO$_2$, and CH$_4$, using a three-point calibration.

### 4. Conclusions

Given the information reported in this paper, it is believed that, at least, in this case, there is some merit to the second approach of up-scaling claimed by [1]. There was no possibility to foresee all the issues that arose during the commissioning and operation of this pilot plant. It was obvious that the complexity of the system, with multiple reactors, requiring different temperatures and operating conditions, and feedback loops required a structured commissioning approach. The linear approach adopted here, verifying one unit-operation, and optimizing it before adding the next and finally adding the recycle, was an effective one. It would require a very experienced design and operations team to do this in a non-linear way.

The pilot operated fairly well at the end of the 3000 h of operation and produced a good quality mixture out of the system. There were several issues and mishaps during the start-up and shakedown testing, with the vaporizer section and the compression being the largest ones, both arising mainly due to the small scale of the operation and not from fundamental mistakes. There was a surprisingly good correspondence between the initial heat and mass balance and the operating results, albeit some discrepancies were found. This indicates that the methodology of performing micro-reactor tests and using the results as a basis for up-scaling via computerized models is sound. The most promising feature of the demonstration is that no catalyst deactivation of the catalysts was apparent aside from the carbon-rich residue build-up in the first dehydration reactor, warranting several thousands of hours of operation should the plant be scaled up further. It is believed that the data would be sufficient to make a scale-up to a commercial demo scale in the 1000 to 10,000 tonnes per annum scale from a technical perspective.

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