Assessment of Thermochemical Conversion of Glycerol: Pyrolysis vs Steam and CO2 Moderation

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1. In many parts of the world biodiesel is fast emerging as a strong replacement fuel due to low CO₂ emission and numerous renewable resources as feedstock.

2. Transesterification is the most common and industrialized technology for biodiesel which leads to production of biodiesel and glycerol byproduct.

3. According to stoichiometry, each mole of lipid feedstock results in 3 moles of biodiesel in addition to one mole of glycerol byproduct.

4. Crude byproduct glycerol contains various adulterants such as saponified fatty acids, methanol, water, catalysts and ash, all of which require purification to have a better monetary value for glycerol.

5. Purification is the most common method to generate a usable glycerol grade but low yield process.

6. Another option would be the production of hydrogen from glycerol through pyrolysis.

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<th>Disadvantage</th>
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<td>Purification via distillation</td>
<td>Used in food and pharmaceutical</td>
<td>Highly expensive, low yield</td>
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<td>Water treatment</td>
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Introduction

1. Direct glycerol combustion causes inefficient burning due to the low calorific value, higher ignition temperature (370 °C compared to 280 °C), high viscosity and salt content, which leads to corrosion and the formation of acrolein.

2. A potential and efficient way of using glycerol as an energy source is through thermo-chemical conversion (pyrolysis, steam reforming and gasification and fuel synthesis).

3. Yoon et al. [1] worked on the production of syngas from crude glycerol through gasification (partial combustion at sub-stoichiometric ratio) using microwave plasma torch; the effect of microwave power as well as oxygen and steam supply were varied. the optimum oxygen : glycerol molar ratio ranged between 0-0.4.

4. Tapah et al. [2] carried out catalytic supercritical water gasification at a temperature range of 400-550°C and a pressure range of 170-270 bar. High yields of syngas and volatile hydrocarbons (methane and ethylene) were reached.

5. A simple pyrolysis of glycerol in steam was performed by Stein et al. [17]. Product gases at 600°C pyrolysis composed of CO, CO2, H2, CH4 and C2H4 [18].

6. Adhikari et al. [3] found that steam reforming at temperatures greater than 627°C, 1 atm and H2O:GL molar ratio of 9:1 produce optimal hydrogen at minimal methane. Several other catalysts (Ni/Al2O3, Ni/TiO2) have different effects on conversion depending on the selectivity and temperature.

7. Literature indicates that limited systematic studies have been done to study the thermochemical conversion of glycerol under different temperature and gasifying agent. It also lacks the comparison of metrics of baseline pyrolysis and using steam or CO2 agents to generate gaseous fuel. Using CO2 for gasification is pathways to utilize and reduce CO2 emissions.

Objectives

1. The goal of this work is to investigate the process conditions and gasification metric indicated by cold gasification efficiency for glycerol gasification.

2. To vary the temperature (500 °C to 1,500 °C) and check the CGE.

3. To investigate the composition of the syngas and formation mechanism.

4. This work focuses on the gasifier process with no consideration of any sensible heat recovery, which could change the process metric should an integrated gasification combined cycle plant (IGCC) is considered.
Methodology

A. Calorimetry and TGA Glycerol analysis
1. Samples of pure glycerol and pharmaceutical grade crude glycerol (from lab experiments) were collected and subjected to bomb calorimeter (Parr 6100 Calorimeter) and TGA/STA (TA 600) analyses.
2. In the pure glycerol sample, only one major weight loss took place showing that the only substance is in fact glycerol.
3. However, the crude byproduct sample is a mixture of several sub components that corresponds to district de-moisturaization and volatilization temperatures and char combustion.
4. The composition of the crude glycerol of the WCO transesterification consists of 2.9% methanol, 5.6 moisture%, 59% pure glycerol, unreacted mono-dia and tri-glycerides of 26.5% and soot of 6%.
5. In the subsequent analysis pure glycerol are employed as process feedstock. This assumption is supported by the percentage of pure glycerol present in the byproduct which takes up to 60%. Hence, the density, boiling point, molecular and chemical formulas, etc. that are an input to the models belong to pure glycerol.
Methodology

B. **Systematic Analysis and conversion metrics**

1. A low fidelity systematic analysis based on a zero-dimensional analysis using Gibbs free energy minimization of gasification is designated to estimate the product species and energy required.

2. The model assumes an infinite reaction time with no reference to species’ spatial distribution nor reactor’s geometrical aspects.

3. The model also presumes chemical/thermodynamic equilibrium and does not take reaction chemical kinetics into consideration. The basis of the system depends on the Equilibrium Constant Method (ECM) which is used for the determination of species concentration at equilibrium as well as product temperature and pressure. This gives the concentration of all the possible products.

4. All modelling has been carried out in Aspen Plus.

\[ C_3H_8O_3 \text{ or } +mH_2O \text{ or } +nCO_2 \rightleftharpoons \ x_1H_2 + x_2CO + x_3CO_2 + x_4CH_4 + x_5C_2H_2 + x_6C_2H_4 + x_7C_2H_6 + x_8H_2O + x_9C + x_{10}O_2 \]

m and n are the steam and CO2 molar value, respectively, specified at one time.
Methodology

1. This modeling has been validated with the experimental work of Valliyappan et al. [4] who used quartz as packing material in a cylindrical reactor of 100cm long and 6cm dia. at the corresponding working temperature and pressure and results show an almost perfect match as depicted in figure 4 for the main gasification species, i.e. H2, CO, and CH4.

![Graph showing mole fraction and H2/CO ratio for species H2, CO, CH4, CO2, and H2/CO ratio.]

The Cold Gas Efficiency (CGE) of gasification is also obtained from the ratio of the HHV of the product syngas (H2, CO and CH4) to the HHV of the feedstock (glycerol) and added and needed process heat

\[
CGE = \frac{H_2, CO, CH_4}{\sum_{i=1}^{n} HHV_i/(HHV_{Gly} + Heat_{added})}
\]

Where \(HHV_i\) and \(HHV_{Gly}\) is the high heating values for the syngas species, i.e. H2, CO and CH4 and Glycerol.

Results

A. Glycerol Pyrolysis

1. Results showed that for higher temperatures, the decomposition is more efficient and higher syngas mole fractions are obtained.

2. Hydrogen has larger values than carbon monoxide which theoretically complies with the pyrolysis reaction.

3. Below 600 °C, results of equilibrium model ceased to be applied. Beyond this temperature the main species (CO, H2, H2O, CO2, and CH4) coexist and only the syngas prevails when it reaches at 1015 °C.

4. The H2 and CO mole fraction reach maximum theoretical values of 0.57% and 0.43%.

5. The maximum CGE is achieved marking 83% at this temperature.
Results

A. Glycerol Pyrolysis

1. Beyond 1015 °C a noticeable drop in the CGE emerges as the additional heat goes into the product as sensible and unaccounted output.

2. These results are also in line with the work of Valliyappan et al. [4] who experimentally carried out glycerol pyrolysis used different packing bed materials and temperature in atmospheric N2 flow environment in a tubular reactor.

3. The products were mostly gas, essentially consisting of CO, H2, CO2, CH4 and C2H4. They observed that the glycerol conversion and product distribution is determined by temperature, carrier flow rates and particle diameter of packing material.

Results

B. Glycerol Steam reforming/gasification

1. Low 20% CO and high 50% H₂ mole fractions are achieved.

2. A 84% highest CGE was achieved at 775 °C as the reaction did not strictly followed the stoichiometry.

3. Methane formation was seen with water at a substantial molar fraction of 10% and 20%, respectively.

4. The influence of temperature in molar ratio of the product syngas appears to be of a secondary effect. The CGE commences to linear decrease beyond the 775 °C as unaccounted and lost sensible heat in the product.

5. The development of a conditioned reactor for glycerol conversion requires a settlement between the obtained results from the low fidelity systematic analysis, considering the most effective and feasible implementation.
Results

c. Glycerol CO₂ gasification

\[ C_3H_8O_3 + 4CO_2 \leftrightarrow 4H_2O + 7CO + 415KJ / Mol \]

1. It is a highly endothermic reaction but falls far from completion. The best CO molar fraction swings from 40% at the optimal efficiency to 50% at the very high process temperature.

2. The Methane ceases to exist at the 770°C where the maximum efficiency is attained.

3. The H₂O and H₂ converge to an equal mole fractions at the very high temperature (2,200°C) near 20%, while CO₂ is consumed down to 10% fraction.

4. Near the optimal conversion the distribution of the molar fractions are 40% and 30% of the syngas share (CO and H₂, respectively), and near 10% and 20% for H₂O and CO₂, respectively.

5. The Glycerol CO₂ gasification efficiency is inferior to glycerol pyrolysis steam gasification which each optimally achieved 83% at 1015°C or 84% at 775°C, respectively.
Conclusion

1. This work focuses on the systematic analysis of thermochemical conversion of glycerol. This product emerges in a large quantity as biodiesel is pushing itself as a good contender to offset a substantial portion of the petro diesel. Crude glycerol is the byproduct of the well established transesterification process and to purify it and dump it in the food or pharmaceutical markets may negatively reduces the value of this saturated market. Using glycerol as commodity feedstock for syngas production is another viably opportunity for this byproduct to blaze.

   A. Firstly, Glycerol gasification/pyrolysis optimally achieved 83% CGE at 1015°C and almost theoretical/stoichiometric molar fraction distributions at 57% H₂ and 43% of CO.

   B. Secondly, systematic Glycerol steam gasification reaches an optimal conversion of 84% at 775°C. The conversion did not strictly follow the theoretical/stoichiometric. The CH₄ was formed and co-existed with steam and syngas (CO and H₂) at molar fraction respectively of 10%, 20%, 20% and 50%.

   C. Thirdly, systematic CO₂ conversion achieved an efficiency of 80% at syngas molar fractions of 40% CO and 30% H₂ and near 10% and 20% for H₂O and CO₂, respectively.

2. The Glycerol CO₂ gasification efficiency marked the lowest and the furthest theoretical conversion compared to pyrolysis and steam gasification.
Thank You