Assesment of Thermochemical Conversion of Glycerol: Pyrolysis vs Steam and CO_2 Moderation

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Abstract— **Glycerol is the byproduct of biodiesel production that has been considered a strong alternative candidate to petro diesel. Stochiometrically, one mole of glycerol is generated for each mole of triglyceride feedstock or per three moles of produced biodiesel. This is translated to over 10% production volume/mass. As the biodiesel market is expanding as renewable and CO_2 neutral, a sound solution for velarizing the glycerol byproduct is necessary and before it becomes a waste burden. Economically, the glycerol market is saturated and substantial production can lead to imbalanced pricing. Therefore, filling the energy needs following thermochemical conversion of glycerol into clean syngas fuel can lead to a dual favorable impact on reducing process waste and leading to clean fuel production. In this work the process metrics in using Glycerol as feedstock for the production of syngas fuel is evaluated under pyrolysis, steam and CO_2 moderators. Process metrics are assessed using the cold gasification efficiency following equilibrium analysis and under sweeping reaction temperatures. Results achieved a maximum of 83% (0.43 CO : 0.57 H_2), 84% (0.20 CO : 0.55 H_2), and 80% (0.40 CO : 0.30 H_2), for the pyrolysis, steam and CO_2 gasification. The conclusion of this work is in line with previous literature that emphasizes the technical feasibility of thermochemical conversion of glycerol into syngas.**

Keywords; Glycerol gasification, Glycerol Pyrolysis, Biodiesel

I. INTRODUCTION

The fear of fossil energy depletion, steep price fluctuation, and adding the recurring negative environmental impact has been driving nations for energy portfolio reform with renewable energy balancing. The transportation sector is heavily dependent on diesel fuel and biodiesel has been considered for offsetting the shortage. In other parts of the word it has been considered as an emerging replacement fuel, triggered by its lower CO_2 emission and numerous renewable resources, i.e. soybean, rapeseed, palm oil, sunflower oil, cotton oil, animal fats and waste streams including waste cooking oil, trapped grease and animal fats, and beef tallow. Research on biodiesel production has been leveraged both technically and economically, promoting its full scale production from plant cultivation, lipid separation and conversion leading to glycerol as byproduct [1].

The conversion efficiency is also tied to the conversion device type and the adopted methodology. A summary of the type of these reactors types, i.e. batch, semi-continuous, and continuous reactors and their pros and cons are listed in table 1. The different methodology with respect to the production scale and economic feasibility is discussed elsewhere by the author which favors large scale sonicated continuous reactor, yet with government incentive [2]. Transesterification is the most common and industrialized technology compared to micro emulsions and thermochemical cracking [3]. In the conversion of lipids, Figure 1 summarizes the transesterification process of the triglycerides leading to production of biodiesel and glycerol byproduct. Accordingly, each mole of lipid feedstock results in 3 moles of biodiesel in addition to one mole of glycerol byproduct. While side and undesirable reactions takes place by the presence of impurities (i.e. water and free fatty acids) soap can also be formed from the transesterification of free fatty acids with a methoxide because of basic catalysis mitigated by acidic catalysts for lipids with high FFA content [4].

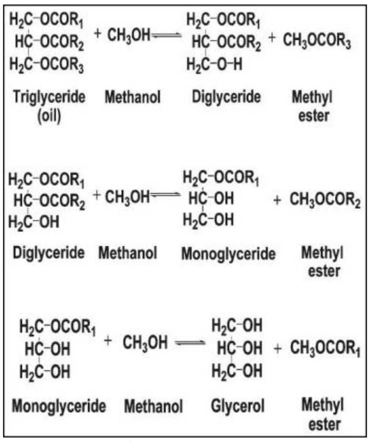

Figure 1: Transesterification reaction mechanism [5]

Crude byproduct glycerol contains various adulterants such as saponified fatty acids, methanol, water, catalysts and ash [6] [7], all of which require purification that renders glycerol a better monetary value. Approaches of glycerol utilization are listed in Table 2. Purification, as the most common method to generate a usable glycerol grade is an energy/cost intensive and low yield process. One of the eye-opening ways would be the production of hydrogen from glycerol, as advocated by the stoichiometry of its pyrolysis as per equation (1).

$$C_3H_8O_3 \xrightarrow{Heat} 3CO + 4H_2 \qquad (1)$$

Table 1: Summary of Biodiesel reactor types [5]

Reactor type	Description	Advantages	Disadvantages
Batch	Reactants are put in a tank which has an agitator. Products are drained out for processing.	Low capital cost, flexibility in feedstock variation	Low yield, Energy intensive
Semi continuous	Alcohol and oil are reacted initially in a smaller tank that feeds a larger one like the case of a batch.	-	More labor requirements
Continuous	Very similar to batch but reactants are continuously added and products removed	Large scale production, consistent product quality	Complex process monitors

Table 2: Methods of glycerol utilization [9] [10]

Method	Advantage	Disadvantage
Purification via distillation	Used in food and pharmaceutical	Highly expensive, low yield
Water treatment	Digestion	Highly expensive, low yield
Direct combustion	Optimization of energy integration	Toxic, safety issues, burner choking
Solid fuel blending	-	Requires binding materials
Hydrogen production	Obtain syngas for energy production	Several ways: steam reforming, gasification, pyrolysis, …
Triacetyl-glycerol production	It is used as a fuel additive for the reduction of engine knocking	Involves several steps
Etherification	Ether of glycerol can be used as diesel fuels	-

Even though purification has evolved through the years (electro-dialysis [11], acidification [12]), it still proves to be an expensive method to properly utilize crude glycerol. Hence it is important to promote this stream to propel biodiesel industry [13]. A potential and efficient way of using glycerol as an energy source is through thermo-chemical conversion (pyrolysis and gasification and fuel synthesis). On the other hand, glycerol combustion, in equation (2), has proven to be an 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 [14].

$$C_3H_8O_3 + 3.5O_2 \rightarrow 3CO_2 + 4H_2O - 1655kJ/mol \qquad (2)$$

Yoon et al. [15] 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 are varied. Experiments suggest that an increase in microwave power increases both gasification efficiency and syngas heating value, while increasing oxygen and steam ratios had the opposite effect; the optimum oxygen:glycerol molar ratio ranged between 0-0.4. Other similar work was performed by Tapah et al. [16] where catalytic supercritical water gasification was used 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. A simple pyrolysis of glycerol in steam was performed by Stein et al. [17]. Product gases at 600°C pyrolysis composed of CO, CO_2, H_2, CH_4 and C_2H_4 [18]. Steam reforming of glycerol has also pursued as an effective method of hydrogen production. This is expressed according to glycerol aqueous phase/steam reforming in equation (3) as:

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 + 128kJ/mol \qquad (3)$$

Temperatures and steam to glycerol ratios are the process tuning parameters. Adhikari et al. [19] 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. Operating temperatures can be decreased to 600°C while using Ru/Y2O3 [20] or 400°C if using Ir/CeO2 catalyst [21]. Several other catalysts (Ni/AL2O3, Ni/TiO2) have different effects on conversion depending on the selectivity and temperature [22].

In addition to thermo-chemical conversion, some studies investigate bio-chemical conversion of glycerol to hydrogen biogas through anaerobic digestion. Mangayil et al. [23] looked into the potential of converting crude glycerol to hydrogen in an enriched microbial environment. A maximum hydrogen yield of 1.1 ± 0.1mol per mol of consumed glycerol is produced. A comparison between results obtained from crude and pure glycerol shows no effect of impurities on H_2 yield. It should be noted that biological conversion is a very slow process and is sensitive to synergy of numerous parameters, i.e. inoculant media, nutrition level, C:N ratio cultivation time and optimal bacterial temperature brining more risk to success of the process for industrialization level.

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 CO_2 agents to generate gaseous fuel. Using CO_2 for gasification is pathways to utilize and reduce CO_2 emissions. The goal of this work is to investigate the process conditions and gasification metric indicated by cold gasification efficiency. The temperature was varied between 500°C and 1,500°C surpassing the optimal CGE to also investigate the composition of the syngas and formation mechanism. This work focuses on the gasifier process with no consideration of any sensible heat recovery, which could change the process metric, and an integrated gasification combined cycle plant (IGCC) is considered. This will be a complementary study of this work.

II. MATERIAL AND METHODS

A. *Calorometry and TGA Glycerol analysis*

Samples of pure glycerol (see figure 2), pharmaceutical grade crude glycerol as a result of optimal conversion of waste cooking oil in our lab using ultrasound transesterification were collected and subjected to bomb calorimeter (Parr 6100 Calorimeter) and TGA/STA (TA 600) analyses.


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Figure 2: Color difference between pure glycerol (left) and unrefined/crude glycerol byproduct (right)

Table 3: HHV for pure and crude glycerol samples

Glycerol	HHV (MJ/kg)
Pure	18.175
WCO crude	22.972

The crude glycerol marked a higher heating value (HHV) than the pure as shown in Table 3. This is due to the presence of other substances with a higher calorific value than glycerol such as methanol (22.884 MJ/kg), FAME (40.168 MJ/kg) [24] and TG (40.212 MJ/kg).

Proximate analysis of the pure and crude glycerol is shown in figure 3. The multiple steps of weight loss correspond to the demoisturaization, devolatilization, and potential combustion of a substance, should oxygen be used in the latter step. In the pure glycerol sample, only one major weight loss took place showing that the only substance is in fact glycerol. However, the crude byproduct sample is a mixture of several sub components that corresponds to district de-moisturaization and volatilization temperatures and char combustion. Nevertheless, 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%.

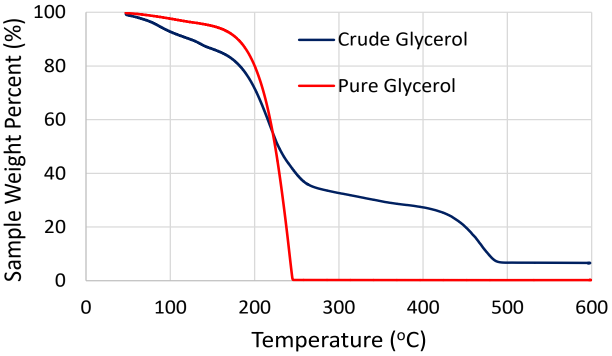

Figure 3: TGA wt% graphs for pure and crude glycerol

Therefore, there are marked differences between pure and crude glycerol and the composition depends on the deployed conversion process. This analysis is to identify this variation in the property and the difficulty in the purification of such a byproduct. 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.

B. *Systematic Analysis and conversion metrics*

A low fidelity systematic analysis of gasification is designated to estimate the product species and energy required. The low fidelity analysis is based on a zero-dimensional analysis using Gibbs free energy minimization. The model in use is developed by Shabbar and Janajreh [25] and assumes an infinite reaction time with no reference to species' spatial distribution nor reactor's geometrical aspects. 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 [27]. It gives the concentration of all the possible products. A detailed description of how the model works and what equations it uses can be found elsewhere [25], [28]. It should be noted that this is an essential modeling step to steer both experimental and reactive high fidelity flow analysis. It should be noted also that commercial software such as Hysys and Aspen are based on the same equilibrium modeling strategy.

$$C_3H_8O_3 \text{ or } +mH_2O \text{ or } + nCO_2 \longleftrightarrow x_1\mathrm{H_2}+ x_2\mathrm{CO}+ x_3\mathrm{CO_2},+ x_4\mathrm{CH_4}+ x_5\mathrm{C_2H_2}+ x_6\mathrm{C_2H_4}+ x_7\mathrm{C_2H_6}+ x_8\mathrm{H_2O}+ x_9\mathrm{C}+ x_{10}\mathrm{O_2} \text{ [25]} \quad (4)$$

This modeling has been validated with the experimental work of Valliyappan et al. [24] 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 a perfect match as depicted in figure 4 for the main gasification species, i.e. H_2, CO, and CH_4.

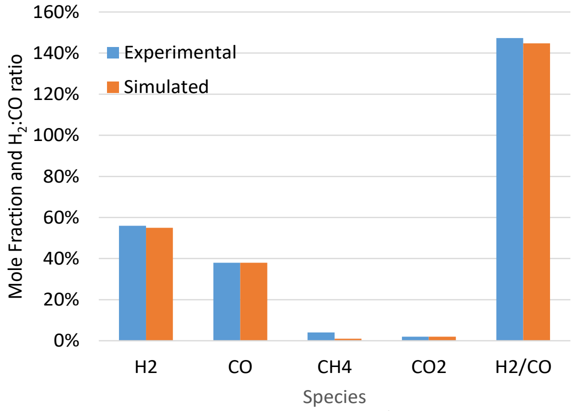

Figure 4: Model and experimental validation of the main species results

In equation (4) *m* and *n* are the steam or CO_2 molar value, respectively, specified at one time. The Cold Gas Efficiency (CGE) of gasification is also obtained from the ratio of the HHV of the product syngas (H_2, CO and CH_4) to the HHV of the feedstock (glycerol) and added and needed process heat. This is described in equation (5) as:

$$CGE = \sum_{i=1}^{H_2,CO,CH_4} HHV_i \, / (HHV_{Gly} + Heat_{added}) \qquad (5)$$

Where HHV_i and HHV_{Gly} is the high heating values for the syngas species, i.e. H_2, CO and CH_4 and Glycerol.

III. RESULTS & DISCUSSION

During the gasification of glycerol, multiple reactions proceeded. At elevated temperatures only dual chain species are also cracked and any released oxygen is consumed immediately. A summary of the main reactions are given in table 4.

Table 4: Summary of the incurring main reaction of glycerol cracking

Reaction	Energy (kJ/mol)
1. $C_3H_8O_3 + 3H_2O \leftrightarrow 7H_2 + 3CO_2$	+128
2. $C_3H_8O_3 \leftrightarrow 4H_2 + 3CO$	+250
3. $CO + H_2O \leftrightarrow CO_2 + H_2$	-41
4. $CO + 3H_2 \leftrightarrow CH_4 + H_2O$	-206
5. $CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	-165
6. $C + H_2O \leftrightarrow CO + H_2$	+131
7. $C + 2H_2 \leftrightarrow CH_4$	-75
8. $C + CO_2 \leftrightarrow 2CO$	+172

A. Glycerol Pyrolysis

In the pyrolysis (absence of an oxidizer O_2) of glycerol, both *n* and *m* in eq. (4) are set to zero and a temperature sensitivity study is applied. The theoretical endothermic glycerol pyrolysis reaction is represented by equation (2) in table 4. Figure 5 presents these results which clearly showed that for higher temperatures, the decomposition is more efficient and higher syngas mole fractions are obtained. Hydrogen has larger values than carbon monoxide which theoretically complies with the pyrolysis reaction of table 4.

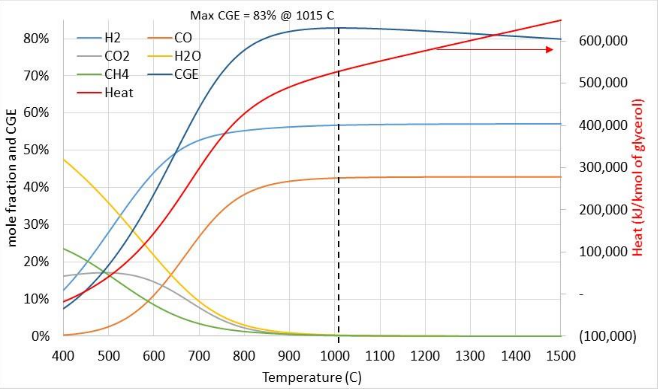

Figure 5: Pyrolysis of glycerol with respect to temperature

Below 600°C, results of equilibrium model ceased to be applied. Beyond this temperature the main species (CO, H_2, H_2O, CO_2, and CH_4) coexist and only the syngas prevails when it reaches at 1015°C. The H_2 and CO mole fraction reach maximum theoretical values of 0.57% and 0.43%. The maximum CGE is achieved marking 83% at this temperature. Beyond this temperature a noticeable drop in the CGE emerges as the additional heat goes into the product as sensible and unaccounted output according to equation (5). These results are also in line with the work of Valliyappan et al. [28] who experimentally carried out glycerol pyrolysis used different packing bed materials and temperature in atmospheric N_2 flow environment in a tubular reactor. The products were mostly gas, essentially consisting of CO, H_2, CO_2, CH_4 and C_2H_4. They observed that the glycerol conversion and product distribution is determined by temperature, carrier flow rates and particle diameter of packing material.

B. Glycerol Steam refoming/gasification

This is less and mildly endothermic compared to pyrolysis reaction as see in equations (1) and (2) in table 4. This reaction has less of a tendency to produce CO as it is inclined to be consumed according to the water-gas shift and methanation reactions of equations (3) and (4) of table 4, respectively. Therefore, low 20% CO and high 50% H_2 mole fractions are reasonable results as shown in figure 6. A 84% highest CGE was achieved at 775°C as the reaction did not strictly followed the stoichiometric equation (1) of table 4 and methane were formed and co-existed with the remaining water at a substantial molar fraction of 10% and 20%, respectively. Literature supports additional water molar than the stoichiometry to achieve higher syngas conversion but that also comes at the cost of higher heat and temperature leading to lower CGE. The influence of temperature in molar ratio of the product syngas appears to be of a secondary effect. The CGE commence to linear decrease beyond the 775°C as unaccounted and lost sensible heat in the product. 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.

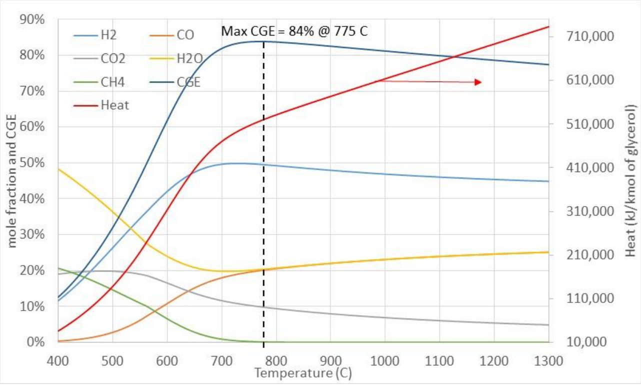

Figure 6: H_2O gasification with respect to temperature

C. *Glycerol CO_2 gasification*

The stoichiometry of the CO_2 glycerol gasification is seen in table 4 by combining the 1st and 3rd equations and is written in equation (6) as:

$$C_3H_8O_3 + 4CO_2 \leftrightarrow 4H_2O + 7CO \qquad +415\ \text{kJ/mol} \qquad (6)$$

It is a highly endothermic reaction but falls far from completion, as these results are depicted in figure 7. The best CO molar fraction swings from 40% at the optimal efficiency to 50% at the very high process temperature. The Methane ceases to exist at the 770°C where the maximum efficiency is attained. The H_2O and H_2 converge to an equal mole fractions at the very high temperature (2,200°C) near 20%, while CO_2 is consumed down to 10% fraction. Near the optimal conversion the distribution of the molar fractions are 40% and 30% is the syngas share (CO and H_2, respectively), and near 10% and 20% for H_2O and CO_2, respectively. The Glycerol CO_2 gasification efficiency is inferior to glycerol pyrolysis steam gasification which each optimally achieved 83% at 1015°C or 84% at 775°C, respectively.

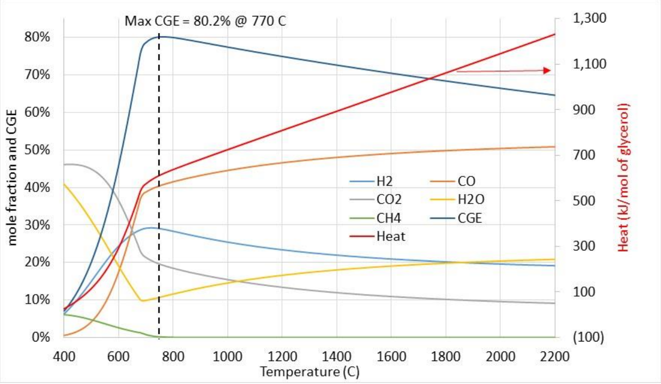

Figure 7: CO_2 gasification with respect to temperature

IV. CONCLUSION

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 comparison study of the gasification analysis of glycerol can be inferred:

- Firstly, Glycerol gasification/pyrolysis optimally achieved 83% CGE at 1015°C and almost theoretical/stoichiometric molar fraction distributions at 57% H_2 and 43% of CO.
- Secondly, systematic Glycerol steam gasification reaches an optimal conversion of 84% at 775°C. The conversion did not strictly follow the theoretical/stoichiometric. The CH_4 was formed and co-existed with steam and syngas (CO and H_2) at molar fraction respectively of 10%, 20%, 20% and 50%.
- Thirdly, systematic CO_2 conversion achieved an efficiency of 80% at syngas molar fractions of 40% CO and 30% H_2 and near 10% and 20% for H_2O and CO_2, respectively.

The Glycerol CO_2 gasification efficiency marked the lowest and the furthest theoretical conversion compared to pyrolysis and steam gasification.

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