

# Gas Phase Conversion of Waste Glycerol to Synthesis Gas: Equilibrium Product Distribution

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**Abstract**— Glycerol is a major by-product of vegetable oil *trans*-esterification with an alcohol. It is usually partially refined and sold to improve the economics of a biodiesel production plant. Unfortunately, the price of glycerol is expected to decrease as many biodiesel production plants come on stream. For this reason, more attention is focused on various processes that can add value to the waste glycerol. In this study the gas phase glycerol conversion to synthesis gas has been simulated using ChemCad 6.4. The effects of glycerol purity (20 - 80 wt.%) and reaction temperature (300 – 1000°C) on synthesis gas production have been predicted at equilibrium conditions. The data suggest that the higher the glycerol purity, the lower the required temperature to produce synthesis gas with a H<sub>2</sub>/CO ratio of 2/1, suitable for Fischer-Tropsch (FT) process.

**Index Terms**— Equilibrium, glycerol, synthesis gas

## I. INTRODUCTION

GLYCEROL is a major by-product of the biodiesel production process from vegetable oils and alcohols. It is often cost effective for small and moderate sized biodiesel production plants to partially purify the glycerol and sell the product (80 wt.%) to industrial glycerol refiners. Biodiesel production increases around the globe as more biodiesel production facilities come on stream and more facilities are still in construction. This means that more glycerol will be produced and this will affect glycerol market value. Haas *et al.* [1] have shown that the decreases in the value of glycerol are linearly correlated with an increase in biodiesel production costs, with each US\$0.01 reduction in glycerol value causing an approximate US\$ 0.008 rise in production cost. More research has recently focused on possible routes of adding value to the glycerol from the biodiesel production process to improve the economics of the process. For example Sankar *et al.* [2] investigated the possibility of producing glycolate from the oxidation of glycerol over supported gold and palladium nanoparticles. Glycolic acid is an important chemical that has uses as a cleaning agent as well as a chemical intermediate. Wang *et al.* [3] used carbon nano-tubes supported ruthenium nano-particles for selective hydrogenolysis of glycerol to glycols. Simonetti *et al.* [4]

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have studied the gas-phase conversion of glycerol to synthesis gas over carbon-supported platinum and platinum-rhenium catalysts. Synthesis gas is generally referred to a mixture of H<sub>2</sub> and CO. This mixture is generally used as feed to various significant processes such as synthetic fuel production (Fischer-Tropsch process), methanol production, and gas turbines for electricity generation in integrated gasification combined cycle (IGCC) etc. Although glycerol catalytic conversion processes have gained more attention, very little is known on the thermodynamics limitations for these processes. Hence, this study aims at determining the equilibrium limitations for the gas phase conversion of waste glycerol to synthesis gas. In particular the effects of glycerol purity and reaction equilibrium temperatures on the product composition, the produced synthesis gas H<sub>2</sub>/CO ratio and the carbon selectivity to CO will be established.

## II. METHODOLOGY

To maintain a common basis for calculations, the amount of glycerol in the feed was kept constant at 800 kg/h but the amount of water was varied to represent various degrees of glycerol purity. Feed streams consisting of 80, 70, 60, 50, 40 and 20 wt.% glycerol were considered in this study. The glycerol conversion was modeled by Gibbs free energy minimization in ChemCad. The Gibbs reactor model is based on the principal that at chemical equilibrium the total Gibbs energy of the system has its minimum value. By attempting to minimize the total energy of the system, individual equilibrium constants are not considered. Rather, the possible reaction species are noted, and the distribution of these species is established using a general mathematical technique to give a minimum free energy for the system [5]. The glycerol conversion process was carried by heating up the glycerol feed to various reaction temperatures (300 – 1000°C) at constant pressure (1 bar) and determining the equilibrium composition of the product. CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, ethane, propane, methanol, ethylene glycol, acetol and solid carbon were considered as possible reaction species. Solid carbon was not available in ChemCad and was added to the components database. It was modeled as graphite and the heat capacity polynomial coefficients determined by Butland and Maddison [6] were used for the simulation. The

enthalpy and Gibbs energy of formation for the solid carbon were entered as 0 kJ/mol. All the other components with their physical and chemical properties were available in ChemCad components database.

### III. RESULTS AND DISCUSSION

Simulation results predicted complete conversion for glycerol and no solid carbon formation for the whole temperature range considered. The system Gibbs energy minimization calculations only predicted the formation of CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and traces of CH<sub>3</sub>OH under the conditions used. Fig. 1 shows the molar compositions for CO (Fig. 1a), H<sub>2</sub> (Fig. 1b), CO<sub>2</sub> (Fig. 1c) and CH<sub>4</sub> (Fig. 1d). It can be observed from the data that for the same glycerol purity, for example 80%, as the equilibrium temperature

increases, CO composition is insignificant below 400°C above which it starts increasing with temperature up to ca. 700°C where the increase in CO composition with the increases in temperature becomes less significant (Fig. 1a). The H<sub>2</sub> composition increases with the equilibrium temperature but passes through a maximum at ca. 800°C (for 80% glycerol purity, Fig. 1b). The CO<sub>2</sub> also increases with the temperature and goes through a maximum at ca. 410 (80% glycerol purity, Fig. 1c) after which it decreases with the increase in temperature. The CH<sub>4</sub> monotonically decreases with the temperature increase and is ca. 0% above 800°C.

A combination of the following major reactions can explain these results:

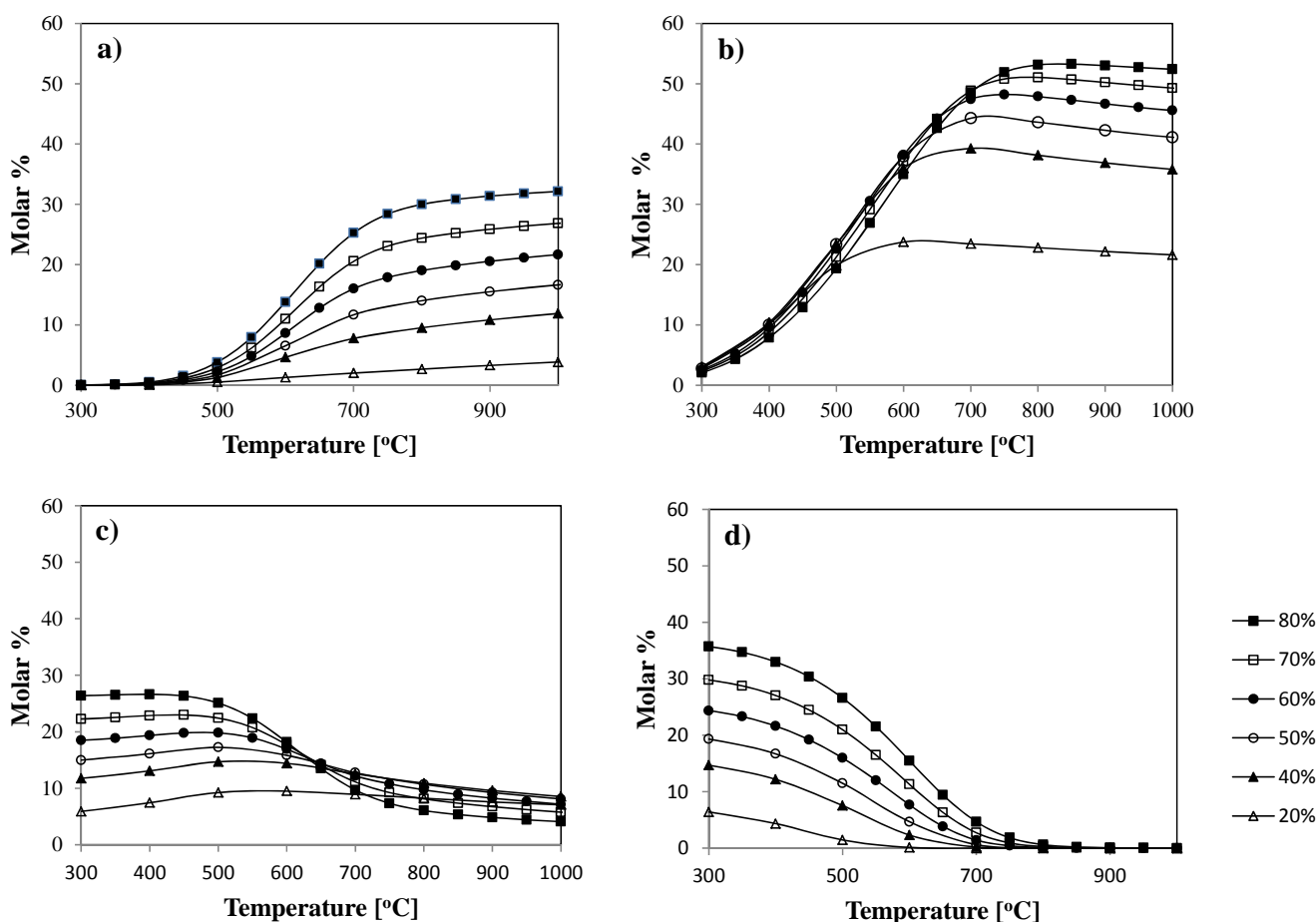
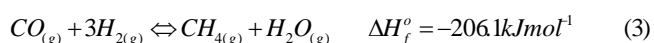
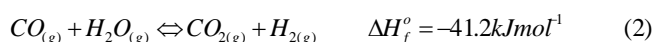


Fig. 1. Equilibrium compositions of gas phase glycerol conversion reaction species as function of glycerol purity and reaction temperature: a) CO, b) H<sub>2</sub>, c) CO<sub>2</sub> and d) CH<sub>4</sub>.



CO is first produced by an endothermic reaction (reaction 1) and subsequently consumed in the water-gas-shift (WGS) (reaction 2) and methanation (reaction 3) reactions to respectively produce CO<sub>2</sub> and CH<sub>4</sub>. At temperatures below 400°C, these two exothermic reactions (2 and 3) are favored and almost all the CO produced by reaction 1 is consumed by reactions 2 and 3. As the temperature increases above 400°C, the increase in CO production by the favored endothermic reaction 1 becomes more significant than the CO consumption by methanation and WGS reactions. As methanation and WGS reactions are exothermic, their extents are decreased when the temperature increases. At the same time the increased CO production by reaction 1 would favor these two reactions. The monotone decrease in CH<sub>4</sub> composition suggests that the effect of temperature on the methanation reaction equilibrium is more significant than the effect of CO composition via reaction 1. However, the CO<sub>2</sub> composition first increases before decreasing with temperature. This can be explained by the fact that the effect of CO increase on the WGS equilibrium via reaction 1 is first more significant than that of temperature. As the temperature increases more H<sub>2</sub> is formed by reaction 1 and less is consumed by reaction 3. This decreases the extent of reaction 2 and thus explains the maximum observed in H<sub>2</sub> composition as the temperature increases. The H<sub>2</sub> is produced by two reactions: i) the endothermic reaction 1 that favors H<sub>2</sub> production with the increase in temperature and ii) the exothermic WGS reaction 2. It is consumed by reaction 3. At higher temperatures, the methanation reaction shuts off (Fig. 1d), the WGS reaction extent decreases and the H<sub>2</sub> composition tends to the stoichiometric composition of reaction 1 (H<sub>2</sub> / CO ratio = 1.33) as shown in table 1

where H<sub>2</sub>/CO ratios are presented as function of temperature and glycerol purity. To achieve an H<sub>2</sub>/CO of 2/1 required for processes such as FT or methanol synthesis, appropriate equilibrium temperatures as function of glycerol purity must be determined. Fig. 2 shows the required temperatures to achieve an H<sub>2</sub>/CO ratio of 2/1 for various glycerol purities.

These data suggest that the higher the glycerol purity, the lower the temperature required to achieve an H<sub>2</sub>/CO ratio of 2/1. Very low glycerol qualities will require very high temperatures, sometimes unpractical, to meet these H<sub>2</sub>/CO ratio requirements. For example with 80% glycerol, a temperature of ca. 650°C is needed to achieve an H<sub>2</sub>/CO ratio of 2/1 compared to the unpractical 3200°C required for 20% glycerol mixture.

Table 2 presents the carbon selectivity to CO as function of temperature and glycerol quality. For the same glycerol quality, the carbon selectivity to CO increases with the reaction temperature. For example with 80% glycerol, the highest carbon selectivity for CO is 88.7% at 1000°C. At 650°C, the temperature required to achieve H<sub>2</sub>/CO ratio of 2/1 for 80% glycerol, the carbon selectivity to CO is only ca. 50%, meaning that the remaining 50% of carbon in glycerol is lost as CH<sub>4</sub> or CO<sub>2</sub>. To minimize the loss of carbon from glycerol, high temperatures leading to H<sub>2</sub>/CO ratios of less than 2/1 will be required. This could be useful if the obtained synthesis gas can be blended with an H<sub>2</sub> rich synthesis gas to reach just the H<sub>2</sub>/CO ratio.

#### IV. CONCLUSION

The effects of glycerol purity and equilibrium temperatures for the glycerol to synthesis gas reaction on product composition, produced synthesis gas H<sub>2</sub>/CO ratio and carbon selectivity to CO have been predicted by Gibbs energy minimization using ChemCad 6.4. The data suggest that the higher the glycerol purity, the lower the temperature required to produce synthesis gas with an H<sub>2</sub>/CO ratio of 2/1, suitable for Fischer-Tropsch (FT) process.

TABLE I  
H<sub>2</sub>/CO RATIO AS FUNCTION OF TEMPERATURE AND WATER CONTENTS

Glycerol purity	Temperature [°C]							
	300	400	500	600	700	800	900	1000
80%	55.1	14.6	5.1	2.5	1.9	1.8	1.7	1.6
70%	83.1	21.7	7.3	3.4	2.4	2.1	1.9	1.8
60%	120.1	30.9	10.0	4.4	3.0	2.5	2.3	2.1
50%	170.8	42.9	13.5	5.8	3.8	3.1	2.7	2.5
40%	245.2	59.6	18.2	7.7	5.0	4.0	3.4	3.0
20%	583.9	127.0	37.6	18.0	11.6	8.5	6.7	5.6

TABLE II  
CO SELECTIVITY (% , CARBON BASED) AS A FUNCTION OF TEMPERATURE AND GLYCEROL PURITY

Glycerol purity	Temperature [°C]							
	300	400	500	600	700	800	900	1000
80%	0.1	0.9	6.9	29.1	63.8	81.7	86.5	88.7
70%	0.1	0.8	6.3	27.5	59.8	74.3	79.2	82.3
60%	0.1	0.7	5.9	26.0	54.1	65.9	71.3	75.2
50%	0.0	0.7	5.7	24.2	46.6	56.6	62.6	67.3
40%	0.0	0.7	5.5	21.7	37.9	46.6	53.1	58.2
20%	0.0	0.7	4.7	12.1	18.5	24.6	30.3	35.3

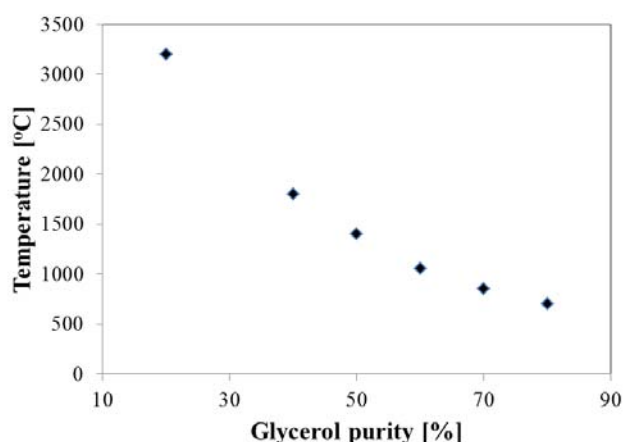


Fig. 2. Reaction temperature leading to synthesis gas with an equilibrium H<sub>2</sub>/CO ratio of 2/1 as a function of glycerol purity

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