Glycerol Gasification In Supercritical Water: Effects Of Operating Parameters

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Glycerol Gasification in Supercritical Water: Effects of Operating Parameters.

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Abstract

Supercritical water gasification (temperature and pressure greater than or equal to 374 ° C and 22.1MPa, respectively) is a promising technology to produce non-fossil energy, producing a valuable gas mixture mainly composed of hydrogen, monoxide and carbon dioxide, methane and other light hydrocarbons such as ethylene, ethane, propane and butane, with no trace of gaseous pollutants. The wet biomass used in supercritical gasification makes the process less expensive compared to other processes that require drying. Also, the aqueous medium allows a reduction in the production of tars and chars thanks to the physicochemical properties of water. In this study, the gasification of glycerol in supercritical water was studied in the presence of potassium hydroxide as a catalyst. **The effect of the three operating parameters on gas production was studied (temperature, initial glycerol concentration and residence time), in the presence of catalyst (0.6 wt% of KOH).** ***The experiments were carried out in discontinuous mini autoclave at the RAPSODEE center (Albi). The results show that increasing the temperature from 458 to 542 °C has a positive effect on the supercritical water gasification of glycerol. A longer residence time of 50 minutes can increase the quantity of methane. Unlike the initial concentration of glycerol has a negative effect on gas production. When the glycerol concentration increases by 9 wt%,*** **The quantities of gas produced have decreased considerably, hydrogen and carbon dioxide have been reduced by half, while carbon monoxide has increased proportionally with increasing initial concentration..** ***Analysis of the remaining glycerol solutions after the completion of the reaction for different temperatures by GC-MS showed that they mainly contained aldehydes, phenols and its isomers.***

Keywords: *supercritical water gasification, glycerol, gas yield.*

I. Introduction

Recently, a considerable effort has been made to find clean and renewable resources for sustainable development [1], almost 10% of energy is provided by biomass [2]. Biomass is one of the most abundant renewable resources and can be converted into liquid and gaseous fuels by thermal processes [3]. One of the procedures used is hydrothermal gasification, which consists of carrying a biomass in the supercritical conditions of water (temperatures above 374 ° C and pressures above 22.1 MPa). At the supercritical region, the high pressure keeps the density of the fluid close to those of liquids, increasing thermal conductivity [4]. The high temperature keeps viscosity close to those observed in gases, increasing diffusion rates [5]. These properties make supercritical water a good solvent for many reactions [6]. The gases produced by gasification in supercritical water are mainly H_2, CH_4, CO and CO_2. The efficiency of these processes and the quantities of gas produced are influenced by various parameters such as the type of biomass (real [7] or model biomasses [8]), the operating parameters (temperature [9], initial concentration of the biomass [7], pressure [10], residence time [11], presence of catalyst [9], and

the type of reactor (tubular reactors [7] or batch reactors [8]).

The glycerol is one of the most studied biomasses in the SCWG, abundant and inexpensive; it is a co-product of the saponification reaction [12] and a by-product of the transesterification reaction of vegetable oils to produce biodiesel [13].

Q.M. Yu-wu et al. [8] studied the gasification of bioglycerol and pure glycerol in supercritical water with and without catalyst (K_2CO_3). The experiments were carried out in batch autoclaves. Organic and inorganic compounds and the structure of bioglycerol have favored the production of light hydrocarbons, while pure glycerol favors the production of H_2 and makes it possible to simultaneously obtain energetic gases and valuable platform molecules.

S.Guo et al. [14], used glycerol for hydrogen production by gasification in supercritical water. The experiments were conducted in a continuous flow tubular reactor at 445~600°C and 25 MPa. The study of the effect of the various parameters has been studied, the temperature of the reaction, the residence time, the concentration of glycerol and the alkaline catalysts NaOH, Na_2C0_3, KOH and K_2CO_3. The efficiency of gasification increases with increasing temperature at the initial glycerol concentration.
In this work, the influence of three parameters on the quantities of gas produced (temperature, initial concentration of glycerol and the residence time) was studied, the experiments were carried out in 5 mL batch reactors, Analysis of the liquids by GC-MS was carried out to identify the various components of the liquid phase after completion of the reaction.

II. Experimental

A. Raw materials and reactants

The glycerol ($C_3H_8O_3$) used in this study is purchased by SIGMA ALDRICH, with a molar mass of 92 g.mol^{-1}. Glycerol is a colorless and very dense liquid substance, and glycerol solutions have been prepared with ultrapure water.

The catalyst used in these experiments is potassium hydroxide (KOH) in the form of white colored pellets, with a molar mass of 56.11 g. mol^{-1}.

B. Reactor system and experimental procedure

The experimental study of the supercritical water gasification of glycerol was carried out in the RAPSODEE laboratory of IMT- Mines d'Albi, in mini-autoclaves of 5 ml, reaching a temperature of 600 ° C and 30 MPa.

The masses of water, glycerol (10 and 19 wt %) and catalyst (KOH = 0.6 wt %) filled in the reactors are depending on the desired temperatures and pressure (458-542 ° C, 23MPa). With a residence time that ranges from 40 to 90 minutes.
Once prepared, the mini-autoclaves are placed in a oven Nabertherm L5 / 11 / P320, a heating time of 9 minutes is necessary to reach the temperature of handling.

Final phase, once the reaction is complete, the reactors will be placed under the hood for 20 minutes to cool. Once the reactor is open, the two gaseous liquid phases will be recovered.

Gas yields (mol of gas mol^{-1} of glycerol) are defined by the following equations:

$$\text{Gas Yield} = \frac{\text{mol of gas produced}}{\text{mol of glycerol feed}} \quad (1)$$

C. Products analyses

- *Gas analysis*

After opening the mini autoclave, the gases produced were analyzed by gas chromatography to quantify and identify the various gases produced, such as H_2, CO_2, CO, N_2, CH_4 and other hydrocarbons. The volume of each gas was estimated with a calibration curve.

- *Liquid analysis*

The recovered liquid was analyzed by gas chromatography-mass spectrometry, GCMS-TQ 8030, collision-induced dissociation (CID), the CID gas is argon and the carrier gas is helium. With GC-2010 column, injection initial temperature 25°C and that of the interface temperature 230°C, column inlet pressure 100kPa and column flox 1.7mL/min. This device allows quantifying and identifying the following liquid compounds: glycerol, various phenol isomers, and aldehydes.

III. Results and discussion

A. Effect of temperature

Temperature is one of the parameters which is expected to have a positive influence on the gas production from the glycerol gasification. Figure 1 shows the gas yield from the gasification of 10 wt% of glycerol in supercritical water at two temperatures of 458°C and 542°C, and a concentration of catalyst (KOH) of 0.6wt%, for 90 min reaction time.

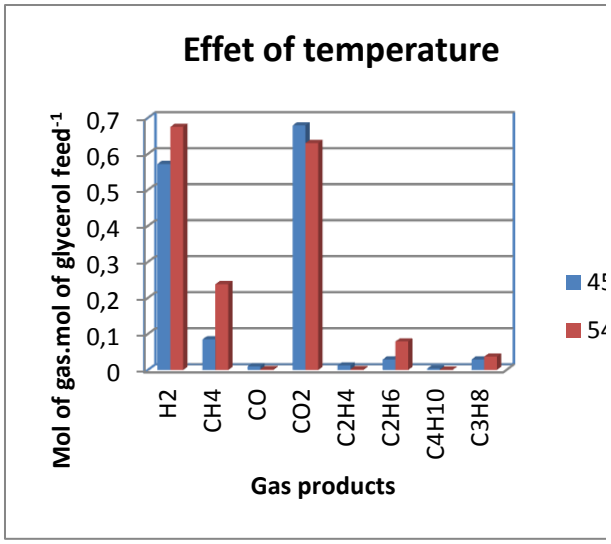

Figure 1. Effect of temperature on gas yield (23MPa, an initial glycerol concentration of 10wt%, 0.6% of KOH catalyst for 90 min residence time).

The gases produced were H_2, CO_2, CO, CH_4 and small amounts of C_2H_4, C_2H_6, C_3H_8 and C_4H_{10}. Figure 1 shows that the largest amount of gas is that of hydrogen and with the increase in temperature, it increases even more than 0.4 to 0.66 mol of H_2.mol of glycerol feed^{-1}. A temperature also promotes the production of carbon dioxide, methane and little hydrocarbons, while the amount of carbon monoxide decreases by 0.02 to 0.0009 mol of CO.mol of glycerol feed^{-1}, confirming that high temperature promotes the reaction of "water gas-shift" ($CO+H_2O \rightarrow H_2+ CO_2$) and "methanation" ($CO+ 3H_2 \rightarrow CH_4 + H_2O$), which leads to higher production of hydrogen, carbon dioxide and methane.

Analysis of the remaining glycerol solutions after recovery of the gases at 458°C and 542°C by GCMS showed the presence of the various organic materials mainly phenol and these monomers and aldehydes as shown in the table below.

Table1. GCMS analysis of glycerol solutions after gasification in supercritical water at 458°C and 542°C.

Components	$\frac{Mass\ of\ component}{Total\ mass\ of\ liquid}$	
	458°C	542°C
2-methyl-Phenol	0	27.96
2,6-dimethyl-Phenol	0	0.86
3, 5-dimethyl-Phenol	0	15.36
3-ethyl-Phenol	0	5.84
2,3-dimethyl-Phenol	0	2.23
2-ethyl-4-methyl-Phenol	0	1.54
4-(2-propenyl)-Phenol	0	0.96
methoxy-phenyl	0	2.98
3, 5-dimethyl-Phenol	4.63	3.03
2, 3-dihydro-1H-Inden-5-ol	0	0.94
2-methyl-3-Pentanol	2.84	0
2,3-Butanediol	2.69	0
2-methyl-Cyclopentanone	5.79	0
4-Hydroxy-3-hexanone	5.19	0
6-Hepten-3-ol	16.25	0
1-(1-methylethyl)-Cyclopentene	4.15	0
Glycine	1.96	0
2, 3-dimethyl-2-Cyclopenten-1-one	8.77	0
3, 4, 4-trimethyl 2-Cyclopenten-1-one	3	0
1-(1-cycloohexen-1-yl)-Ethanone	2.8	0
2-Phenylindolizine	0	0.73
P-cresol	0	19.53

B. Effect of initial concentration

The effect of the initial concentration was studied at a temperature of 458 ° C. for two values of initial concentration of glycerol of 10 and 19 wt% and a concentration of catalyst (KOH) 0,6%, for 90 min residence time.

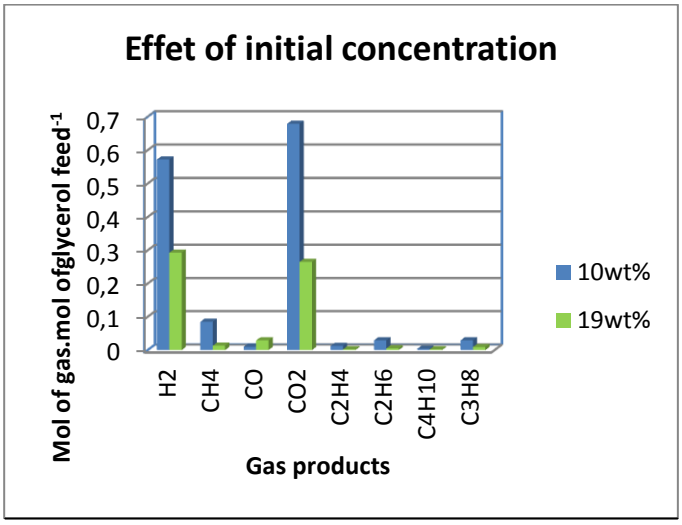

Figure 2. Effect of initial concentration of glycerol on gas yield (458°C, 23MPa, 0.6% of KOH catalyst for 90 min residence time).

As shown in figure 2 the increase in the initial concentration of glycerol affects negatively the hydrogen produced; it decreases from 0.572 to 0.293 mol of H_2 .mol of glycerol feed^{-1}, and acts in the same way on all other gases except carbon monoxide which increases from 0.01 to 0.029 mol of CO. mol of glycerol feed^{-1}.

Concentration is an important parameter for gas production selectivity. A higher concentration of glycerol (means less water) this reduces the water gas-shift reaction rate, increasing the amount of CO and decreasing CO_2 and H_2. The decrease in the amount of hydrogen leads to a decrease in the rate of methanation, which occurs at a small amount of CH_4 mainly from the pyrolysis reaction of the

intermediate products (Int → CO + CH_4 [15]). Also, a higher concentration of glycerol generates an increase in the percentage of the char formation, which reduces the efficiency of the gasification and the quantities of gas produced.

C. *Effect of residence time*

The experiments were carried out on residence times of 40 and 90 minutes, a temperature of 458 ° C, 23 MPa, 10 wt% of initial glycerol concentration, 0.6% of catalyst. Figure3 shows that the hydrogen yield increases from 0.4 to 0.57mol of H_2/mol of glycerol feed for an increase from 40 to 90min of residence time, indicating that hydrogen production is favored with low residence time. The methane has increased by 6 more times, which can be explained by the fact that the "methanation reaction" is favored with a long residence time. CO decreases from 0.02 to 0.01 mol of CO. mol of glycerol $feed^{-1}$, it indicates that a long residence time favors the reaction of CO with water (water gas-shift reaction) and with hydrogen (reaction of methanation).

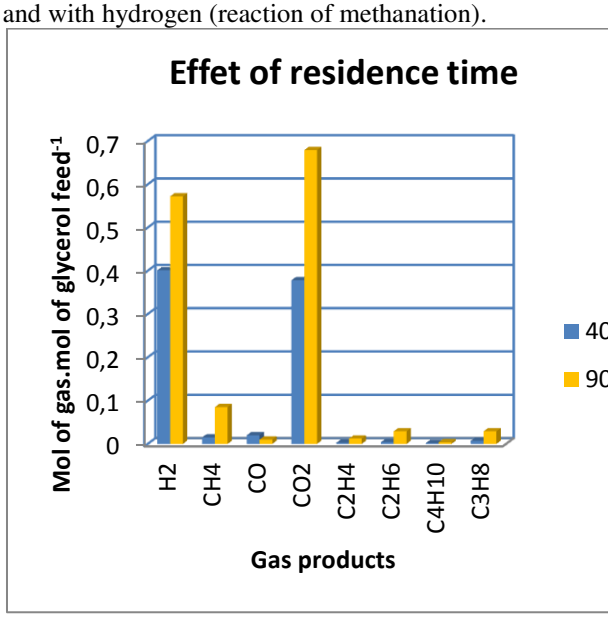

Figure 3. Effect of residence time on gas yield (458°C, 23MPa, 0.6% of KOH catalyst for 90 min residence time).

These results are similar to those of Q.M.Yu-wu [16], who found that hydrogen is produced during the first moments of the reaction and then stabilizes, while methane appears. The methanation reaction is obviously not favored in the first moments of the reaction. Under these conditions, carbon monoxide is not quantifiable. This may be due to its consumption in the methanation reaction, but only from 10 minutes of reaction, or the production of CO is extremely low.

IV. Conclusion

The various operating parameters studied in this study all have an effect on the gasification of glycerol in supercritical water. The quantities of gas produced increase with the temperature rise from 458 °C to 542°C. A long residence time favors the production of methane, while hydrogen production is favored with a low residence time. The initial concentration had a negative effect on the gasification of glycerol in supercritical water, except for carbon monoxide which increases with increasing initial concentration. The addition of the catalyst promotes gasification in supercritical water, analysis of the remaining glycerol solutions after completion of the gasification reaction in supercritical water at different temperature, by GC-MS showed that the products remaining in the solution are phenols and these monomers, as well as aldehydes.

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