

Syngas production and optimization from glycerol pyrolysis

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Glycerol is a by-product from the biodiesel production which represents 10% of product total mass. Due to the present-day high demand for biodiesel, the glycerol availability has increased, while its market price decreased substantially. Glycerol pyrolysis is carried out in a fixed bed reactor filled with alumina oxide. The packing material diameter was varied between 0.5-0.85 millimeters. The reaction temperature was varied in the range of 750-850°C, the reaction time from 20 to 40 min, glycerol quantity from 1 to 3 mL and flow rate of carrier gas from 10 to 50 ml/min.

The process parameters listed above (factors) were used to evaluate the syngas production yield. The best results, on average, were over 80 % v/v of glycerol for gas products and among them the highest amount of gas were of H₂ e CO. Besides these gases, CO₂, CH₄, C₂H₄ and C₃H₈ were also obtained in smaller proportions.

1. Introduction

Biodiesel (alkyls esters) is a clean burning fuel derived from renewable lipid feedstock such as vegetable oil or animal fat. It is biodegradable, non-inflammable, non-toxic and produces lesser CO₂, sulfur dioxide and unburned hydrocarbons than petroleum-based fuel. Glycerol is a by-product from the biodiesel production which represents 10% of product total mass (Silva et al, 2008). Due to the present-day high demand for biodiesel the glycerol availability has increased while its market price decreased substantially. Glycerol is a very important industrial feedstock. Its applications are found in medical and pharmaceutical, cosmetic, chemistry (glyceraldehyde), food and many other industries. However, the crude glycerol derived from biodiesel production cannot be used directly like industrial feedstock because of the impurities. Consequently, novel techniques must be developed in accordance with the final use and value can be added to crude glycerol. Moreover, the utilization of glycerol to produce biofuels and value-added secondary products would make biodiesel more economically feasible (Fernández et al, 2009). The crude glycerol pyrolysis is a promising way to produce biofuels such as hydrogen and syngas (feedstock used in synthetic fuels production via Fisher-Tropsch reaction) and avoid its accumulation in the environment (Valliyappan, 2004). As other pyrolysis processes, syngas production from glycerol pyrolysis depends on different process conditions and process technologies adopted. Products of high

value-added such as hydrogen or syngas can be produced from the pyrolysis of glycerin using a fixed bed reactor. Syngas is mainly produced by gasification of natural gas, coal, and occasionally from heavy oil residues. Hydrogen is mostly used in refinery hydrotreating operations, for ammonia production and in fuel cells. And syngas can be used to produce fuels and chemicals. The objective of this work is to investigate the process conditions in a fixed bed reactor that would give the maximum yield of product gas and H₂/CO (syngas). The experiments were carried out according to a 2⁴ factorial design plus three central points (Box and Hunter, 1978).

2. Materials and Method

2.1. Materials

The experiments carried out with commercial glycerol, with a purity of 99%, were supplied by Labsynth LTDA. Alumina oxide (fixed-bed material) was supplied by Sigma-Aldrich Chemical Company. Sodium chloride (Labsynth) was used in the ice bath. Argon (supplied by White Martins) was used as carried gas.

2.2. Equipments

Glycerol pyrolysis was designed to be carried out continuously. The equipments are listed in Figure 1. The stainless steel reactor was 200 mm long by 10.75 mm of internal diameter filled with alumina oxide. A liquid chromatograph pump (model Waters 515 HPLC Pump) was used to deliver glycerol to the reactor. The pyrolysis system was equipped with electric furnace (100mm x 100mm x 163mm), ice bath, argon cylinder, flow meter, valves and temperature controller. The gas and liquid products were collected in Tedlar® bags of 5 L (with a polypropylene fitting for sampling) and the liquid tank (500 mL) of steel.

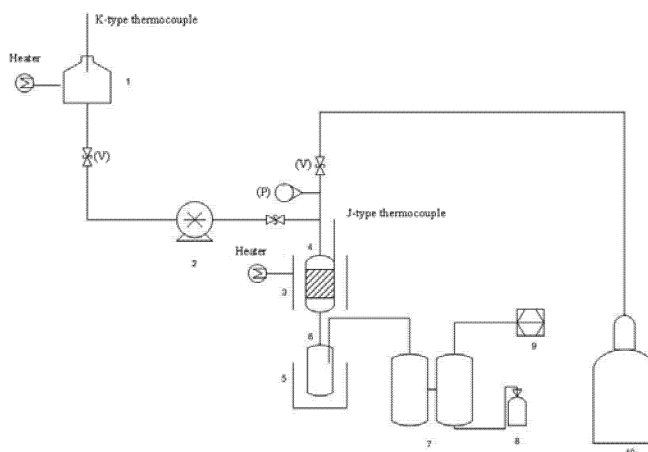


Fig. 1. Experimental set up for pyrolysis of glycerol.

1. Reactant beaker 2. LDC Analytical pump 3. Electric furnace 4. Fixed bed reactor 5. Ice bath 6. Liquid collector 7. Gas collector 8. Bags of 5L, 9. Computer 10. Argon cylinder, V – Valve, P – Flow meter

2.3. Method of analysis

The products obtained from the glycerol pyrolysis were analysed by gas chromatograph (GC). The determination of the permanent gas (hydrogen, carbon monoxide) were realized by thermal conductivity detector (TCD) with a molecular sieve column (50m x 0.53mm x 50 μ m) supplied by Agilent, while carbon dioxide and light hydrocarbons were analysed by flame ionization detector (FID) equipped with a plot column RT-QSPLOT (3 m x 0,32 mm) supplied by Restek U.S. The liquid products were analysed in a chromatograph HP 5970 equipped with a mass-spectrometer detector (GC-MS) and capilar column Cwax 20M (30 m x 0,25 mm x 0,25 μ m).

3. Results an Discussion

The best glycerol conversion to gas products was 80 % v/v of glycerol. The main gas products were H₂ and CO. Besides these gases, CO₂, CH₄, C₂H₄ and C₃H₈ were also obtained in smaller proportions. The liquid product compositions were methanol, ethanol, acetone and acetaldehyde.

In the experiments, it was used a commercial catalyst (alumina) with a diameter between 0.50-0.85 millimeters. Through the experimental design, it was studied the influence of the process variables: temperature (T), reaction time (t), glycerol quantity (G) and flow rate of carrier gas (Ar). The responses analyzed were the conversion of glycerol into hydrogen (H₂) and carbon monoxide (CO). Table 1 shows the experimental design level and results.

Table 1: Factorial design of the glycerol pyrolysis.

Run	T (°C)	t (min)	G (ml)	Ar (ml/min)	% H ₂	% CO
1	750	20	1.0	10	25.634	45.343
2	850	20	1.0	50	37.556	39.408
3	750	40	1.0	50	34.613	42.682
4	850	40	1.0	10	33.437	38.124
5	750	20	3.0	50	29.405	45.673
6	850	20	3.0	10	31.493	43.853
7	750	40	3.0	10	25.539	47.115
8	850	40	3.0	50	40.365	32.142
9	800	30	2.0	30	32.832	42.839
10	800	30	2.0	30	31.235	42.502
11	800	30	2.0	30	28.303	44.805

Two codified models that describe H₂ and CO concentration as function of the glycerol quantity (G), reaction time (t), reaction temperature (T) and flow rate of carrier gas (Ar) were obtained through Statistica software. The results of the model fitted in the form of an ANOVA (analysis of variance) are shown in Tables 2 and 3. The analysis of the H₂ concentration (% mol) shows that the model (equation 1) is significant, as evidenced from the Ftest. The Fcalculated and the Flisted were 20.68 and 3.11, respectively. According to the Ftest, the model had statistical significance when the Fcalculated was larger than the Flisted value. Then, a satisfactory adjustment of the experimental results was done. Table 2 shows the ANOVA of the H₂ concentration.

Table 2: Variance analysis of the model obtained for the H₂.

Source of Variation	SS	DF	MS	F calcul	*F listed
Regress	179.066	2	89.533	20.68	3.11
Residual	34.641	8	4.330		
Lack of fit	24.091	6	4.015	0.76	9.33
Pure Error	10.550	2	5.273		
Total SS	213.707	10			

$$\%H_2(mol) = 31.856 + 3.457T + 3.230Ar \quad (1)$$

Table 3 shows the ANOVA of the CO concentration. The result demonstrates that the model (equation 2) is significant, as evidenced from the Ftest. The Fcalculated and the Flisted were 12.23 and 3.18, respectively. According to the Ftest, the model had statistical significance when the Fcalculated was larger than the Flisted value. Then, a satisfactory adjustment of the experimental results was done.

Table 3: Variance analysis of the model obtained for the CO.

Source of Variation	SS	D F	MS	F calcul	*F listed
Regress	162.049	4	42.26	12.23	3.18
Residual	19.873	6	3.312		
Lack of fit	16.779	4	4.194	2.71	9.24
Pure Error	3.094	2	1.547		
Total SS	181.922	10			

$$\%CO(mol) = 42.226 - 3.411T - 1.777t - 1.816Ar - 1.472Txt \quad (2)$$

The influence of the effects of each variable on the H₂ concentration was shown in Figure 3(a) and the carbon monoxide concentration in Figure 3(b).

Figure 3(a) (Pareto graphic) presents the influence of the variables effect on H₂ concentration from glycerol pyrolysis. The Pareto for the H₂, the vertical line P = 0.1 indicates the magnitude of statistically significant effects in this analysis, and makes clear that the reaction temperature (T) and flow rate of the carrier gas (Ar) are significant for the confidence level of 90%. Figure 3(b) (Pareto graphic) presents the influence of the variables effect on CO concentration from glycerol pyrolysis. The Pareto for the CO, the vertical line P = 0.1 indicates the magnitude of statistically significant effects on this analysis, and makes clear that the reaction temperature (T),

reaction time (t) and flow rate of the carrier gas (Ar) are significant for the confidence level of 90%.

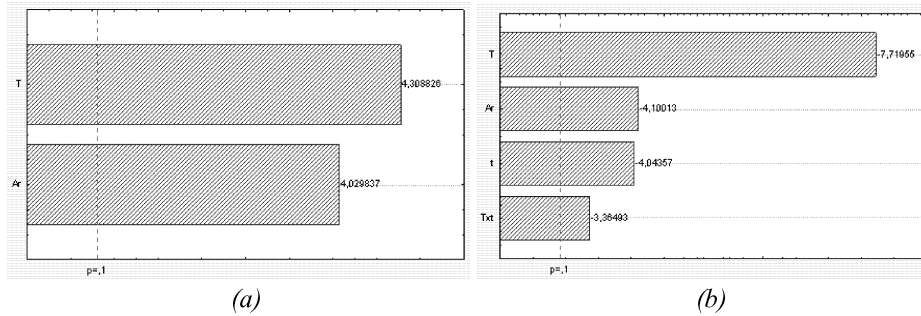


Fig. 3(a) Main effects of variables in the hydrogen concentration. (b) Main effects of variables in the carbon monoxide concentration.

Figures 5, 6 and 7 were obtained from the linear model (equation 1) and indicate which are the points that give higher glycerol conversion into hydrogen concentration (% mol). Figure 5 shows how the reaction temperature (T) and flow rate of the carrier gas (Ar) influence the hydrogen concentration. Concentrations above 40% mol can be obtained using reaction temperatures superior to 850 °C and flow rate of the carrier gas superior to 50 mL/min (dark red area of the figure).

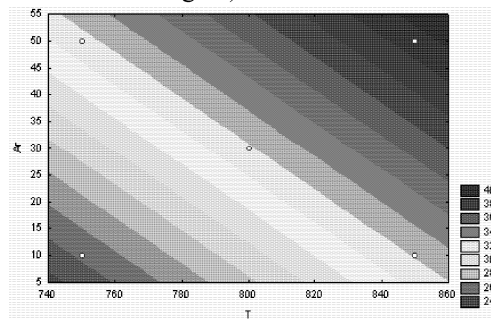


Fig. 5. Contour surface for the glycerol conversion into hydrogen volume as function of the reaction temperature (T) and flow rate of the carrier gas (Ar).

Figures 8, 9, 10 and 11 were obtained from the linear model (equation 2) and indicate which are the points which give higher carbon monoxide concentration.

Figure 8 shows how the reaction temperature (T) and reaction time (t) influence the glycerol conversion into carbon monoxide. Concentrations above 46% mol can be obtained using reaction times lesser than 30 minutes and are independent of the reaction temperature (the orange area of the figure). Figure 9 shows how the reaction temperature (T) and the flow rate of carrier gas (G) influence the carbon monoxide concentration. Concentrations above 48 mol% can be obtained using flow rate of carrier

gas and reaction temperature lesser than 10 ml / min and 750 °C, respectively (dark red area of the figure).

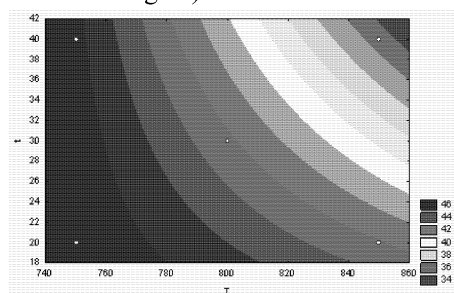


Fig. 8. Contour surface for the glycerol conversion into carbon monoxide as function of the reaction temperature (T) and reaction time (t).

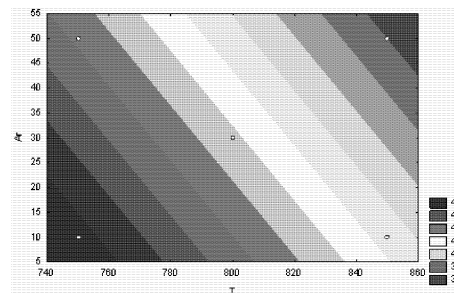


Fig.9. Contour surface for the glycerol conversion into carbon monoxide as function of the reaction temperature (T) and flow rate of the carrier gas (Ar).

4. Conclusion

This work presents a preliminary study of glycerol pyrolysis to syngas. The best hydrogen concentration obtained was 40% mol and the best CO concentration was 48% mol. The best glycerol conversion in gas products was 80% wt. In future works of this research group, the influence of the flow rate of carrier gas and the process variable optimization will be studied. A comparative study of the glycerol from biodiesel process will be carried out. The literature reports about syngas production from glycerol, but the variables that influence this production have not been optimized. With the development of this work, by optimizing the variables expected to obtain high conversion of glycerol into syngas. Moreover, other catalysts and other variables in the experimental design would be tested, such as flow rate of the carrier gas. In future works, the pyrolysis study of the glycerol from biodiesel production will be performed and the results of the commercial glycerol pyrolysis will be compared with biodiesel by-product pyrolysis.

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