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SIMULATION OF AIR-STEAM GASIFICATION OF GLYCEROL USING ASPEN HYSYS

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Abstract. *In the current energy context, efforts are being made to eliminate the dependence on fossil fuels, so several researches have been developed to find substitutes for these fuels. Biodiesel is a fuel of renewable origin that has gained relevance because it seems to be the most suitable fuel to replace fossil diesel. Alternately to the production of biodiesel, 10% of glycerol is produced, this compound has become a worldwide problem since its applications in the conditions in which it is obtained are very restricted, which has led to the accumulation or incineration of this by-product. The increase in biodiesel production worldwide has led to an accelerated decrease in the price of glycerol, which directly affects the price of biodiesel; therefore, alternatives have been developed to give added value to this by-product, among them gasification. This work evaluates, by means of a simulation model developed in Aspen HYSYS, the energetic valorization of crude glycerol obtained from biodiesel production, by means of gasification by partial oxidation, using air-steam mixture as gasifying agent. The added air helps to reduce the process costs, since it decreases the steam requirements and the heat demand of the process. The properties of the substances involved in this process will be estimated using the Peng-Robinson thermodynamic model modified by Strijek and Verak (PRSV). With the developed model, a parametric analysis will be carried out to optimize the gasification process, defining parameters such as optimum temperature and pressure and the steam/glycerol and air/glycerol ratios, which make the gas produced have the highest heating value.*

Keywords: *Glycerol, gasification, energy, simulation*

1. INTRODUCTION

In recent decades, the world has experienced an increase in energy demand, depletion of oil reserves and increased emissions of greenhouse gases (GHG), especially carbon dioxide (CO_2), this has stimulated research on alternative fuels (Coronado et al., 2014). Among these alternative renewable fuels is biodiesel, which has great potential for reducing CO_2. However, its production generates the formation of a by-product known as glycerol, which cannot be discarded in nature, thus tending to become a major environmental and economic problem as production and world reserves expand, making the search for new uses (Coronado et al., 2014; Quispe et al., 2013). The world production of biodiesel has increased rapidly in recent years, reaching 46 billion liters (OECD-FAO, 2017). It is estimated that the glycerol market is expected to surpass the $5 billion mark in 2024, due to fueling the cleanest energy demand in the world (Ahuja et al., 2018).

Glycerol is obtained through the production of biodiesel and has characteristics that prevent it from being used in the main current applications, due to the presence of impurities resulting from the catalysts used in transesterification (Paz, 2013). In this process, it always generates 10% glycerol on biodiesel production (Crnkovic et al., 2012; Quispe et al., 2013). Even though pure glycerol has applications in the food, cosmetics and pharmaceutical industries, glycerol refining becomes expensive for biodiesel producers. Therefore, the glycerol generated during the biodiesel process is often considered a waste by-product (Jiang e Agrawal 2014; Leoneti et al., 2012).

The literature presents several technologies for the use of glycerol, one of which is gasification (He et al. 2017). Due to its environmental benefits and economic advantages, gasification is one of the primary processes for producing a valuable fuel gas known as syngas (Mohammed et al. 2011). As appointed by He et al. (2017) crude glycerol has been used frequently as an additive in the gasification of biomass to improve gas yields and the hydrogen fraction of the produced gas, however, there are some studies about gasification of crude glycerol.

Valliyappan (2004) studied crude and technical glycerol steam reforming in a fixed bed reactor. The influence of glycerol/water ratio was analyzed at a bed temperature of 800 ºC and concluded that temperature increase as well as moisture content increase in steam gasification significantly affected hydrogen and syngas production promoting steam reforming reactions. Yoon et al. (2010) gasified crude glycerin using a bench-scale entrained flow gasifier under pure oxygen or air supply conditions as a gasification agent. Gasification was performed in a temperature range of 950–1500 °C and at a excess air ratio of 0.17–0.7 for oxygen or air blown gasification. From the results, syngas heating value, carbon conversion and cold gas efficiency of more than 2500 kcal/N m^3, 92% and 65% were achieved, respectively. Dou et al. (2010) compared the effect of temperature on crude and technical glycerol steam gasification, using a fixed-bed reactor with and without dolomite as catalyst. Sabio et al. (2017) and Suero et al. (2015) has studied the influence of bed temperature, water/glycerol ratio, and feed flow rate, on the performance of non-catalyzed crude glycerol steam gasification. Almeida et al. (2018) studied the gasification of glycerol in a fixed bed reactor using steam as a gasifying agent. The authors evaluated the effect of temperature on the gas composition plus the gasification performance parameters were taken.

According to Almeida et al. (2020) although there are some studies, either simulation or experimental, on technical glycerol gasification, crude glycerol gasification is not yet sufficiently studied, especially regarding non-catalyzed fixed bed gasification using steam as a gasification agent. Air-steam gasification of glycerol is an alternative to produce syngas. The added air helps to reduce the process costs, since it decreases the steam requirements and the heat demand of the process, however, there are few works in the literature on air-steam gasification of glycerol.

2. MATERIALS AND METHODS

The simulation of the glycerol gasification process with air and steam was developed using Aspen HYSYS® software, which has multiple unit operations for process simulation, a large set of thermodynamic packages for property estimation and adequately simulates gas phase processes (Lee et al., 2019).

2.1 Simulation model

For the development of the simulation model in the Aspen HSYSY® software, the Peng-Robinson thermodynamic package was selected, which is suitable for simulating processes where liquids and gases interact. The following considerations were assumed in the model developed:

- Glycerol was considered as a pure component.
- The process air is only composed of oxygen and nitrogen.
- The chemical reactions reach equilibrium.
- Air and glycerol enter the system at ambient conditions.
- Steam enters the reactor at 150 °C temperature and 100 kPa pressure.

Table 1 shows the reactions involved in the process, which are considered in the simulation model.

Table 1. Reactions of the air-steam gasification process (Moreira et al., 2021).

N°	Reactions	
R1	Partial oxidation	$C_3H_8O_3 + 1.5O_2 \rightarrow 3CO_2 + 4H_2$
R2	Steam reforming	$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2$
R3	Glycerol cracking	$C_3H_8O_3 \rightarrow 3CO + 4H_2$
R4	Oxidation of CO:	$CO + 0.5O_2 \rightarrow CO_2$
R5	Water-gas-shift:	$CO + H_2O \rightarrow CO_2 + H_2$
R6	Oxidation of H_2:	$H_2 + 0.5O_2 \rightarrow H_2O$
R7	Oxidation of CH_4:	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
R8	Reforming of CH_4:	$CH_4 + H_2O \rightarrow CO + 3H_2$

Figure 1 shows the flow diagram of the simulation model developed, which consists of a Gibbs reactor (GR) which simulates partial combustion, cracking and steam reforming of glycerol (R1-R3), an equilibrium reactor (ER) which simulates gas phase reactions (R4-R8) and a phase separator (PS), which removes excess moisture in the product gas.

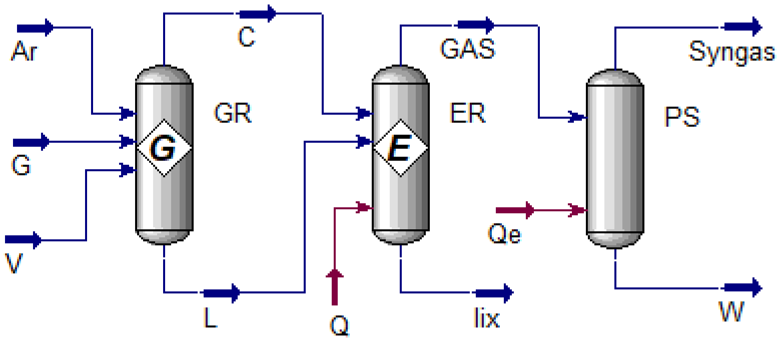

Figure 1. Aspen HYSYS simulation model flowchart

2.2 Validation of simulation model

The model was validated by means of a calibration test, (Mendoza et al., 2021) which assumes a linear correlation between the values predicted by the model and those taken from reference studies (See equation (1)).

$$y = m \cdot x + b \tag{1}$$

Then the two hypothesis tests shown in equations (2) and (3) must be performed.

$$\begin{cases} H_0: b = 0 \\ H_1: b \neq 0 \end{cases} \tag{2}$$

$$\begin{cases} H_0: m = 1 \\ H_1: m \neq 1 \end{cases} \tag{3}$$

Where, H_0 is the null hypothesis and H_1 is the alternative hypothesis.
For both tests the objective is not to reject H_0 and thus it is concluded that there is a statistical correspondence between the experimental values and those obtained from the model.
Table 2 shows the data and reference studies used to validate the model.

Table 2. Reference data for model validation

T(°C)	S/G	Simulation	Literature	Reference
500	9	0,6723	0,6800	Zhang et al., 2007
700	9	0,6694	0,6590	Dou et al., 2014
650	9	0,6703	0,6500	Nichele et al., 2012
800	8	0,6660	0,7000	Byrd et al., 2008
350	4	0,4660	0,4500	Chen et al., 2011
727	1	0,4300	0,4500	Jimmy et al., 2017
700	2	0,5397	0,5400	Kotnala et al., 2021

Where S/G is the ratio of the molar fluxes of steam and glycerol.

2.3 Parametric analysis of the process

The parametric analysis was carried out with the intention of determining the behavior of the heating value and hydrogen mole fraction in the product, against variations in the gasification temperature and the air and steam flows entering the reactor. In addition, ranges in the model parameters that improve the characteristics of the gas produced were determined. Table x shows the ranges of temperature variation and the steam-to-glycerol (S/G) and air-to-glycerol (A/G) ratios.

Table 3. Parameter variation range.

Parameter	Minimum value	Maximum value
Temperature (°C)	400	800
S/G	1	10
A/G	0,5	3

2.4 Optimization of the gasification process

The gasification system was optimized using the optimizer analysis tool included in the aspen HYSYS environment. For this purpose, the efficiency of the gasification system(η), calculated by means of equation (*4*), was defined as the objective function.

$$\eta = \frac{\dot{m}_{syngas} LHV_{syngas}}{\dot{m}_{glycerol} LHV_{glycerol} + \dot{m}_{steam} h_{steam} + Q} \tag{4}$$

Where $\dot{m}_{syngas}$, $\dot{m}_{glycerol}$, $\dot{m}_{steam}$, are the mass flow rates of product gas, glycerol, and steam, respectively.
While LHV_{syngas} and $LHV_{glycerol}$ are the lower heating powers of gas and glycerol. On the other hand, h_{steam}, represents the enthalpy of the vapor at inlet conditions and Q the heat required in the glycerol gasification process.
The optimization problem was programmed in the software, indicating the objective function and the requirement, as shown in equation (5) and the constraints presented from equation (6) to equation (8).

$$max\{\eta\} \tag{5}$$

Subject to:

$$350\ °C \leq T \leq 900\ °C \tag{6}$$

$$1 \leq S/G \leq 9 \tag{7}$$

$$0{,}5 \leq A/G \leq 3 \tag{8}$$

Where T is the gasification temperature.

In the optimizer settings panel, the successive quadratic programming method was selected for the optimization. It finds the optimal values of the problem by solving the Karush-Kuhn-Tucker optimality conditions by means of Newton's or approximate Newton's method (Rodríguez & Granda, 2005).

3. RESULTS AND DISCUSSIONS

3.1 Simulation model

The model developed considered as initial conditions a temperature of 650 °C, a S/G = 2 and A/G = 1, obtaining a gas with a lower heating value of 11,94 MJ/kg and the composition shown in Table 4.

Table 4. Composition of product gas.

Substance	Mole fractions
H_2O	0,0327
CO_2	0,1499
CO	0,1904
CH_4	0,0343
H_2	0,4941
N_2	0,0986

Figure 2 shows the comparison of the percentage of hydrogen obtained in the simulation and that reported in the literature. The validation of the model showed that with a significance level of 0.05 there is no statistical difference between the results obtained from the simulation and those obtained from the literature. Since the p-value for the null intercept test (equation (2)) was estimated at 0.7847, while for the unit slope (equation (3)) test it turned out to be 0.7490. Therefore, the null hypotheses are not rejected.

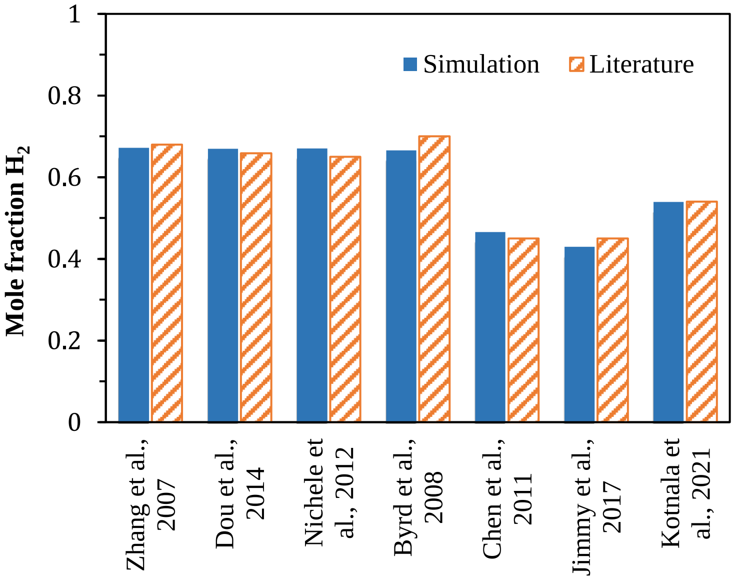

Figure 2. Compilation of model results

3.2 Parametric analysis of the process

Figure 2 shows the composition behavior of syngas considering (S/G = 2) and (A/G = 1) in different temperatures. A concentração de hidrogênio atinge o platô aproximadamente em uma temperatura de 650°C. No caso do metano apresenta uma redução considerável na composição molar do syngas, essa redução está explicada pela elevada proporção de vapor, o qual fomenta a reação de reforma de metano (R8) promovendo a maior formação de hidrogênio. Finalmente, o monóxido de carbono aumenta proporcionalmente com a temperatura, de forma semelhante ao hidrogênio atinge uma ligeira estabilidade na sua concentração aproximadamente a partir dos 650°C. O comportamento obtido na simulação é muito semelhante ao resultado obtido por Ismaila et al. (2021).

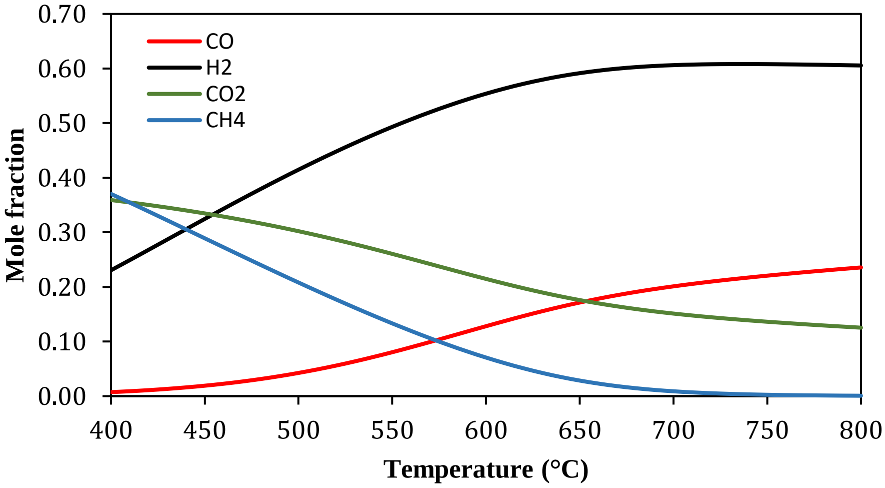

Figure 3. Product distribution as a functions of reaction temperatures.

In Figure 4 the behavior of the hydrogen fraction is observed, before the variations of the S/G and A/G ratios, where we note that the molar fraction of hydrogen increases as the S/G ratio increases, this behavior is due to that excess steam favors reforming reactions and the water-gas-shift reaction (R2, R5 and R8). For its part, the A/G ratio encourages oxidation reactions, so the molar fraction of hydrogen decreases with its increase. This same behavior was observed by Díaz-Alvarado & Gracia (2012).

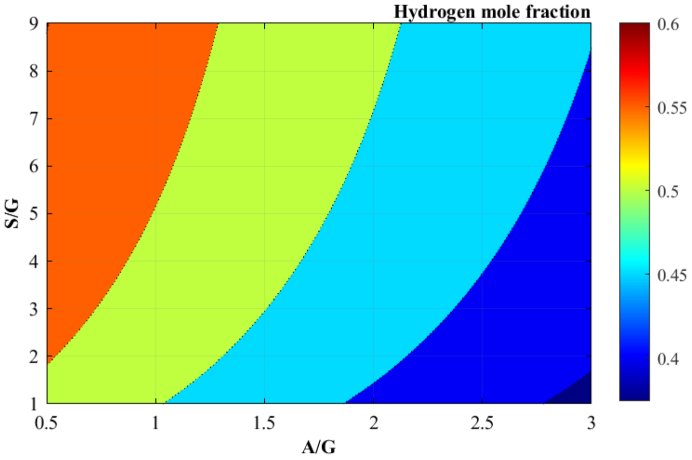

Figure 4. Effects of SG and A/G ratios on hydrogen content.

The effects of the S/G and A/G variations on the calorific value of the gas are shown in Figure 5, where it is observed that the calorific value decreases as the S/G ratio increases, this is due to the fact that the conversion of methane and carbon monoxide in hydrogen and carbon dioxide, and hydrogen has little mass contribution to calorific value since its low molecular weight makes the effect of its high calorific value dissolve when mixed with gases of higher molecular weight. This same behavior was observed by Tamošiūnas et al. (2019) in gasification with arc plasma. On the other hand, the increase in the A/G ratio also decreases the caloric power because it favors the oxidation of the fuel species.

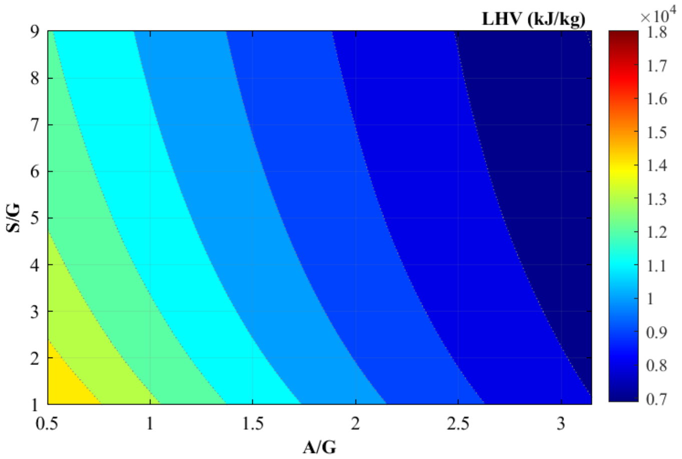

Figure 5. Effects of SG and A/G ratios on LHV.

3.3 Process optimization results

The optimization of the thermal efficiency of the glycerol gasification process was carried out by setting a maximum number of 300 iterations, an allowable tolerance of 1e-4 and a maximum step between iterations of 0.1. Table 5 shows the values of the parameters that maximize the energy efficiency of the process.

Table 5. Composition of product gas.

Parameter	Optimum value
Temperature (°C)	617,5
S/G	1
A/G	0,5

At the optimum point, an efficiency of 86.78% was obtained, a calorific value of the syngas of 14.06 MJ/kg and a heat requirement in the process of 83.43 kWh per kmol of glycerol entering the process. Figure 6 shows the optimum point of the energy efficiency of the process in terms of the S/G and A/G relationships. The results for temperature and the impact of the S/G ratio and efficiency are consistent with what was found by Hajjaji et al. (2014) in steam reforming, who reports an optimal efficiency of 85%, for temperature values between 600 and 700 °C, additionally finds that the efficiency of the process decreases with increasing the S/G ratio.

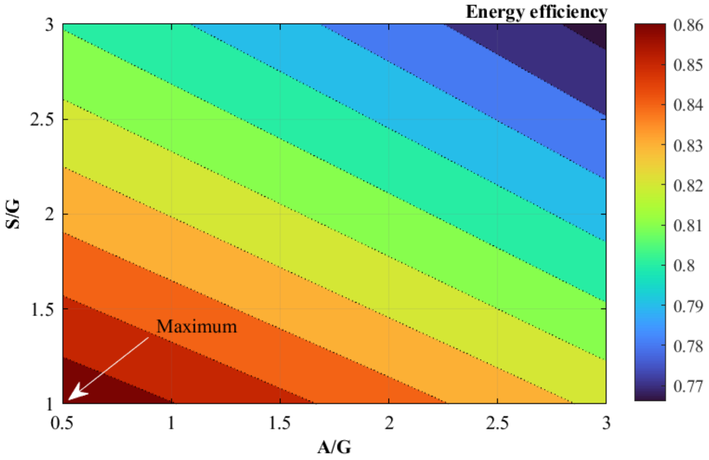

Figure 6. Optimal process point

The composition of the syngas in the optimal state is presented in Table 6, where it is observed that the optimal efficiency is obtained by having relatively high proportions of hydrogen, conserving considerable amounts of methane and CO that also contribute energy to the process, while they must be kept low fractions of CO_2 and N_2, which do not provide energy to the process and favor the dilution of gases, reducing their calorific value.

Table 6. Composition of syngas in optimum state

Substance	Mole fractions
H_2O	0,0327
CO_2	0,1593
CO	0,2048
CH_4	0,1058
H_2	0,4351
N_2	0,0623

4. CONCLUSIONS

The modeling and optimization of the glycerol gasification process with water-air as gasifying agents was carried out, concluding that the model used in this work can predict the composition of the synthesis gas. Additionally, it was found that, to produce a hydrogen-rich synthesis gas, the S/G ratio must be at least 2, however, the A/G ratio must be at least 0.5; this condition guarantees a high value of LHV. In this work, an energy efficiency analysis was presented where the optimum point is reached when the S/G ratio is equal to 1 and the A/G ratio is equal to 0.5. Finally, it was shown that the final composition of the synthesis gas was rich in H_2, CO and CH_4.

5. ACKNOWLEDGEMENTS

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