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Supercritical water gasification of glycerol for Hydrogen production using response surface methodology

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Abstract— Supercritical water gasification is a promising technology for the treatment of wet biomass and hydrogen. In this work, supercritical water gasification of glycerol was carried out in mini autoclaves to conduct a hydrogen production optimization study, using the central composite design of experiments. The effect of five operating conditions on the production of syngas by supercritical gasification has been studied namely, temperature (400-600 °C), residence time (5min30s-124min30s), initial concentration of glycerol (3,79-25,21% weight), pressure (20.21 MPa-29.76 MPa) and KOH catalyst quantity (0-2% weight). The results revealed that a high temperature and a long residence time are desirable for hydrogen production and gasification efficiency, the temperature is the most positive effect on both responses, and the presence of potassium hydroxide as a catalyst has a considerable effect on hydrogen production. However, a long residence time is not necessary when handling at high temperature. Also, the increase in the initial glycerol concentration has a negative effect, while the pressure change has no significant effect. According to the models, a maximum of hydrogen produced and gasification efficiency are obtained when the operating conditions are temperature = 599.89 °C, residence time of 60.7957 min, a pressure of 21.3 MPa for an initial glycerol concentration of 3.79 wt% and in the presence of 0.102 wt% KOH.

Keywords— *supercritical water gasification; glycerol; H₂ production; gasification efficiency*

I. INTRODUCTION

Hydrogen is a clean and renewable energy vector [1], it is the cleanest fuel with zero carbon emission [2], its combustion leads only to the production of water H₂O [3]. Hydrogen is often used for the treatment of heavy crude oil, the production of hydrocarbons from the hydrogenation process, the valorization of bio-oils, the manufacture of ammonia and methanol by chemical synthesis [4].

Due to the depletion of fossil energy, biomass as a source of renewable and environmentally friendly energy is a feedstock of hydrogen production [5], by biochemical or thermo chemical conversion [6], the production of hydrogen biochemically is sufficient for practical application, while thermo chemical conversion allows high hydrogen production with better energy efficiency [7]. Thermo chemical methods of hydrogen production are: pyrolysis, conventional gasification, and supercritical water gasification. Pyrolysis is a process of decomposition of carbonaceous materials, by the action of heat (up to 1000 °C) in the absence of oxygen producing a solid (charcoal), condensable vapors (organic oils and water) and combustible permanent gases (CO, H₂, CH₄ and other light hydrocarbons C₂-C₃) and incombustible (CO₂) [8]. Conventional gasification aims at the conversion of an organic charge into combustible gas, the reaction product is therefore a combustible gas (CO, H₂, CH₄, H₂O, N₂) generated at high temperature (800 to 900 °C), under pressure or not, and an inert residue [9]. In the case of wet biomass, these processes are difficult to handle and have low energy efficiency [10]. To solve this problem, a process using the properties of water has been started, this process is supercritical water gasification,

which consists of carrying a wet biomass under conditions above the critical temperature and pressure of water (T_c ≥ 374 °C, P_c ≥ 22.1 MPa), thus producing a mixture of recoverable gases composed mainly of (H₂, CH₄, CO₂, CO and some light hydrocarbons) [11]. This process doesn't require a drying step which makes it less expensive compared to conventional gasification and pyrolysis [12]. In addition, supercritical water gasification of biomass has a high hydrogen yield with sufficient pressure for storage and transport [13]. Therefore, gasification in supercritical water treated different real biomasses such as fruit pulp [14], wheat straw [15], sawdust [7], sugar cane bagasse [16] and olive oil waste [17]. Also, it was applied for model biomass such as cellulose [7],

glucose [18], lignin [19], and glycerol [20], in tubular reactors [15, 21], or batch reactors [16, 22].

The literature on experimental studies shows a variety of operating parameters whose effect has been tested on the rate of hydrogen production such as temperature [20], initial concentration [22, 23], residence time [24] and pressure [22], as well as the presence of catalyst [25].

In order to control the selectivity of hydrogen production, an assembly of operating conditions and the presence of alkaline catalyst is essential. For this fact, an optimization study is required and many researchers have used the surface response methodology as an optimization tool.

The response surface methodology (RSM) using central composite design (CCD) was investigated on the hydrothermal gasification of lignin for the first time by K. Kang et al. [26], in a batch reactor, whose main objective was the optimization of the hydrogen yield by the effect of three parameters, the temperature, the pressure and the water / biomass ratio. A. Raheem et al. [27] have studied the influence of temperature, ZnO-Ni-CaO catalyst load and residence time for the hydrothermal gasification of algae studying several design responses (fractions of H₂, CO, CO₂ and CH₄).

However, in the last few years there has been a growing interest in glycerol as a biomass source of renewable energy, because of its growing generation, and availability at low cost, as a byproduct of biodiesel production by transesterification of vegetable oils [28, 29]. For these reasons, and in order to produce hydrogen, several researchers have studied gasification in supercritical water glycerol experimentally [20-24], but very few researchers have carried out optimization studies on this biomass. From our bibliographic research only F. Yan et al. [30] studied the supercritical water gasification of crude glycerol, using the central composite experimental design to optimize hydrogen production from crude glycerol, and to study the effect of glycerol concentration, temperature and KOH concentration.

So, usually, optimization studies of supercritical gasification considered three parameters in their used experimental design. The present work focuses on a modeling study of the glycerol supercritical water gasification process, and the influence of five operating parameters, temperature, residence time, pressure, initial concentration and presence of potassium hydroxide as catalyst, on hydrogen production, using a central composite design, leading to quadratic correlations between the response and the studied factors.

II. MATERIALS AND METHODS

A. Reagents

The glycerol (C₃H₈O₃) used in this study was purchased from SIGMA ALDRICH, with a purity of 99.9% and glycerol solutions were prepared with ultrapure water. The experiments were conducted with solutions containing pure glycerol of concentrations in the range [3,8-25,21% weight], in the

presence of an alkaline catalyst, potassium hydroxide KOH with concentrations in the range [0-2%weight].

B. Experimental protocol

The experiments were carried out in the RAPSODEE laboratory of IMT- Mines of Albi in France, in mini autoclaves of internal volume of 5 ml. The volume of glycerol solutions were calculated using the density (ρ) depending on the desired temperature and pressure conditions. This solution was introduced to the reactors with the appropriate quantity of potassium hydroxide as catalyst.

The reactor was in stainless steel 316, with inner and outer diameters of 8.5 and 31.4 mm, respectively. The copper seal ensured tightness between the two parts of the autoclave [31]. When the solution was introduced into the reactor, and after closure, the reactor was installed in the oven (Nabertherm L5 / 11 / P320) previously heated to the desired temperature. A time of 9 minutes was necessary to the oven to achieve the desired temperature. Once the residence time of the reaction was reached, the reactor was installed under a hood for 20 minutes to be cooled to ambient temperature. Once the reactor was open, the manometer measured the overpressure (used to calculate the volume of total gas produced). Then, the gaseous and liquid phases were recovered and analyzed.

The recovered gases were analyzed by gaseous micro chromatography (Agilent PGC-3000), identifying and quantifying in few seconds the produced gases: H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₈ and C₄H₁₀. Gas yield was defined as concentration of gas divided by initial concentration of glycerol.

C. Design of experiments

The central composite design was chosen because of its efficient estimation of the quadratic terms in the second degree model, by studying the effect of 5 operating parameters Temperature (T), residence time (ts), initial glycerol concentration (Ci), pressure (P), and potassium hydroxide as catalyst (Cat), with five levels for each factor as presented in table 1. The studied responses of the design were: hydrogen production, gasification efficiency and gas yield. 52 experiments were carried out as suggested by the used CCD. The real factors variation according to the experiments as well as the experimental responses measurements are shown in tables I and II.

The H₂ yield is calculated as follows:

$$H_2 \text{ yield} = \frac{(\text{molar amount of } H_2 \text{ products})}{(\text{molar amount of glycerol feed})} \quad (1)$$

TABLE I. INTERVALS OF VARIATION OF THE STUDIED REAL-CODED FACTORS.

Variable	Units	Symbols	Ranges and Levels				
			-2,38	-1	0	+1	+2,38
Temperature	°C	T	400	458	500	542	600
Residence time	min	ts	5.5	40	65	90	124.5
Glycerol concentration	Wt %	Ci	3.8	10	14.5	19	25.21
Pressure	MPa	P	20.2	23	25	27	29.76
Potassium hydroxide catalyst (KOH)	Wt%	Cat	0	0.6	1.0375	1.475	2.078

In order to determine the optimal condition for a target objective, the H₂ yield is related to the responses using a second order models expressed as follows:

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{ii} x_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} x_i x_j \quad (2)$$

Where Y is the studied response, a_i are the model coefficients and x_i the i factor

III. RESULTS AND DISCUSSIONS

First we carried out the 52 experiments as presented in table2 and the ai models coefficients are estimated for each studied response, using Minitab16 for data treatment of CDD experimental design.

The experimental results of the H₂ yield are shown in Table II:

TABLE II. CENTRAL COMPOSITE MATRIX DESIGN WITH REAL VALUES OF FACTORS AND EXPERIMENTAL H₂ YIELD.

Run	T	ts	Ci	P	Cat	Y _{H2} (experimental)
1	458	40	10	23	0,6	0,40060
2	542	40	10	23	0,6	0,65959
3	458	90	10	23	0,6	0,57200
4	542	90	10	23	0,6	0,67492
5	458	40	19	23	0,6	0,29346
6	542	40	19	23	0,6	0,47693
7	458	90	19	23	0,6	0,25373
8	542	90	19	23	0,6	0,45387
9	458	40	10	27	0,6	0,22064
10	542	40	10	27	0,6	0,66533
11	458	90	10	27	0,6	0,53968
12	542	90	10	27	0,6	0,53005
13	458	40	19	27	0,6	0,14161
14	542	40	19	27	0,6	0,42988
15	458	90	19	27	0,6	0,31280
16	542	90	19	27	0,6	0,45814
17	458	40	10	23	1,475	0,52780
18	542	40	10	23	1,475	0,71939
19	458	90	10	23	1,475	0,50800
20	542	90	10	23	1,475	0,60490
21	458	40	19	23	1,475	0,30548
22	542	40	19	23	1,475	0,52000

23	458	90	19	23	1,475	0,36633
24	542	90	19	23	1,475	0,49413
25	458	40	10	27	1,475	0,48838
26	542	40	10	27	1,475	0,82298
27	458	90	10	27	1,475	0,68719
28	542	90	10	27	1,475	0,64337
29	458	40	19	27	1,475	0,24939
30	542	40	19	27	1,475	0,53612
31	458	90	19	27	1,475	0,48735
32	542	90	19	27	1,475	0,46723
33	400,107	65	14,5	25	1,0375	0,29718
34	599,893	65	14,5	25	1,0375	0,58585
35	500	5,54	14,5	25	1,0375	0,12527
36	500	124,46	14,5	25	1,0375	0,51314
37	500	65	3,7971	25	1,0375	1,29991
38	500	65	25,2029	25	1,0375	0,41237
39	500	65	14,5	20,2432	1,0375	0,16676
40	500	65	14,5	29,7568	1,0375	0,32425
41	500	65	14,5	25	0	0,42929
42	500	65	14,5	25	2,07806	0,70090
43	500	65	14,5	25	1,0375	0,34295
44	500	65	14,5	25	1,0375	0,38951
45	500	65	14,5	25	1,0375	0,31733
46	500	65	14,5	25	1,0375	0,36428
47	500	65	14,5	25	1,0375	0,37327
48	500	65	14,5	25	1,0375	0,38562
49	500	65	14,5	25	1,0375	0,39709
50	500	65	14,5	25	1,0375	0,36428
51	500	65	14,5	25	1,0375	0,31733
52	500	65	14,5	25	1,0375	0,37327

A. Models

The complete quadratic model of the second degree describing the hydrogen production according to the operating parameters (in real value) is as follows:

$$H_2 = -0.565501 - 0.00366908T + 0.0188601ts - 0.156100Ci + 0.179015P - 0.565318Cat + 8.88827.10^{-06}T^2 - 9.59277.10^{-06}ts^2 + 0.00439120Ci^2 - 0.00475588P^2 + 0.195770Cat^2 - 4.77183.10^{-05}T \times ts + 3.25355.10^{-05}T \times Ci + 1.84928.10^{-05}T \times P - 7.24437.10^{-04}T \times Cat + 2.36946.10^{-05}ts \times Ci + 0.000241782ts \times P - 0.00119476ts \times Cat - 4.11065.10^{-05}Ci \times P - 0.00212067Ci \times Cat + 0.0293912P \times Cat \quad (3)$$

The coefficients of determination (R²) of the mathematical models describing hydrogen production is 0.896. Table III presents the regression coefficients and the significance tests for all the parameters studied and their interactions with a statistical risk of 5%.

TABLE III. REGRESSION COEFFICIENTS AND SIGNIFICATION TESTS FOR HYDROGEN PRODUCTION AND GASIFICATION EFFICIENCY.

Source	H ₂		
	Coef	t	P
Constant	0,363912	14,390	0
T	0,080551	6,588	0
Ts	0,035061	2,868	0,007
Ci	-	-9,686	0

	0,118422		
P	0,005162	0,422	0,676
Cat	0,045963	3,759	0,001
T ²	0,015626	1,486	0,147
Ts ²	-	-0,570	0,573
Ci ²	0,088922	8,454	0
P ²	-	-1,809	0,080
Cat ²	0,019024	3,563	0,001
T ts	-	-3,522	0,001
T Ci	0,001560	0,110	0,913
TP	0,001553	0,109	0,914
TCat	-	-0,936	0,357
Ts Ci	0,002666	0,187	0,853
Ts P	0,017089	1,201	0,239
Ts Cat	-	-0,919	0,365
Ci P	-	-0,026	0,979
Ci Cat	-	-0,294	0,771
P Cat	0,025717	1,808	0,080

Coef=regression coefficients of the model, t-value=Student test value, P-value= probability value

According to Table III, all the main factors have a significant effect on the production of hydrogen except the pressure (p-value >0.050). As reported in [32, 33], a strong pressure is in favor of the water gas-shift reaction, methanation of the CO and CO₂, but reduces the rate of decomposition reaction of the biomass by radical reaction. This explains why the pressure has no significant effect on hydrogen production and gasification efficiency.

The initial concentration of glycerol has the most significant but negative effect $t = -9.686$, p-value = 0 and $t = -3.451$, p-value = 0.002, respectively, an increase in the initial concentration causes a decrease in the hydrogen produced. If we compare experiments 37 and 38, when initial concentration of glycerol rises from 3.79wt% to 25.21wt% the hydrogen production decreases from 1.29 to 0.41 mol of H₂ / mol of glycerol and gasification efficiency decreases from 52.4658 to 26.7958%.

For hydrogen production, the remaining significant parameters having a positive effect on hydrogen production can be classified as follows: Temperature > presence of catalyst (KOH) > residence time.

The residence time has a positive effect on H₂ production, with a P_{H2}-value = 0.007 and the interaction between temperature and residence time is the only interaction which has an effect on the production of hydrogen, an increase in temperature and residence time together affects negatively the production of hydrogen. So, in the case of high temperatures, it is not necessary to take a long residence time [34].

B. Optimisation

First, we illustrate the surface plots and contours for the H₂ production in terms of the most important factors affecting them as presented in fig. 1 to 4.

Fig.1 is the three-dimensional graphical representation of the surface area of the hydrogen produced which shows the effect of the temperature and the initial concentration of glycerol, when the residence time is at 65 minutes, the pressure is held at 25 MPa, the catalyst at 1.038 wt%. The graph indicates that the decomposition of glycerol into supercritical water is an overall endothermic process as there is a general trend that as the temperature increases, hydrogen production and gasification efficiency has increased.

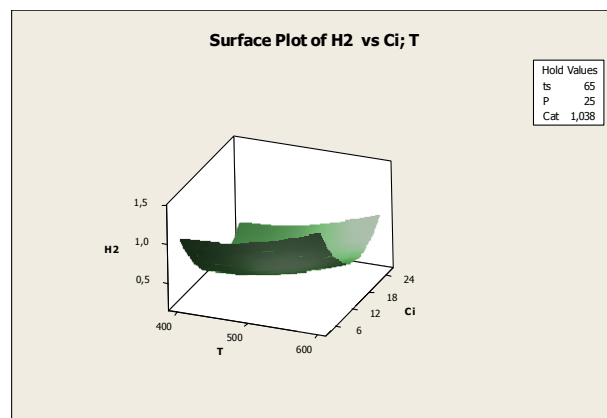


Fig. 1. Surface plot of H₂ yield

More detailed information about the effect of glycerol initial concentration and temperature on the hydrogen production, are in the contour plot. Fig. 2 allows to determine approximately the best combination of operating parameters allowing a maximum of hydrogen produced. The graph shows when a residence time is equal to 40 minutes, a pressure of 23 MPa and 0.6 wt% of KOH, the temperature is greater than 570 °C, allow a maximum hydrogen production higher than 1.4 mol of H₂ / mol of glycerol, using an initial concentration of less than 5wt%.

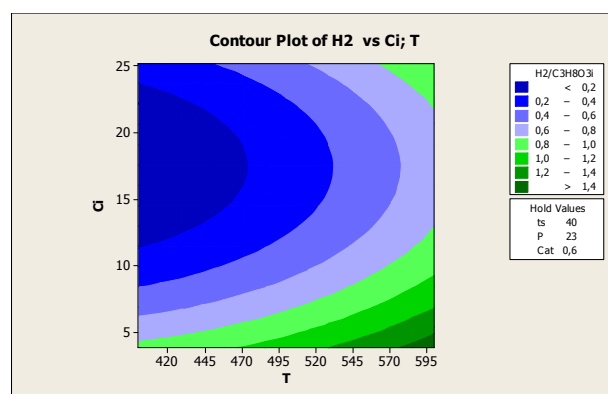


Fig. 2. Contour plot for H₂ production (residence time= 40 min, Pressure= 23MPa, 0,6 wt% of KOH as catalyst).

Then, the optimizer of Minitab was used to obtain the exact optimal operating conditions for a maximum desired response. Figure 5 enables a comparison of the two cases: operating conditions obtained from the optimization of the hydrogen yield.

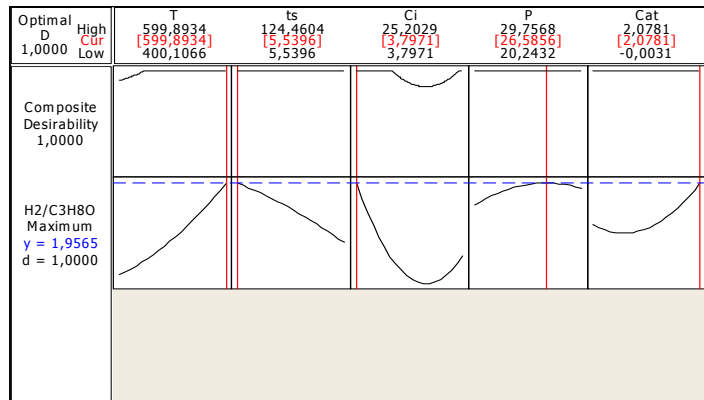


Fig. 3. Minitab results from the optimizer for the hydrogen production.

The optimum factors for the maximum hydrogen yield are presented in Table III, 3.7971 wt% of glycerol concentration and 2.0781 wt% of KOH catalyst, make it possible to obtain 1.9565 mol of hydrogen / mol of glycerol, at optimal conditions of a temperature of 599.8934 ° C, a residence time of 5.5396 minutes and a pressure of 26.5856 MPa.

TABLEIV. OPTIMAL CONDITIONS AND CORRESPONDING OPTIMAL RESPONSES FOR A MAXIMUM OF HYDROGEN PRODUCTION.

Optimal conditions					
Valu es	Temperatur e	Residenc e time	Initial concentration of glycerol	Pressur e	Presence of catalyst(KOH)
Real	599.8934 ° C	5.5396 minutes	3.79 wt%	26.585 6 MPa	2.0781 wt%
H₂ (mol of hydrogen / mol of glycerol)					
1.9565					

TABLEV. OPTIMAL CONDITIONS AND CORRESPONDING OPTIMAL RESPONSES FOR A MAXIMUM OF GASIFICATION EFFICIENCY AND HYDROGEN PRODUCTION.

Optimal conditions					
Values	Temperature	Residence time	Initial concentration of glycerol	Pressure	Presence of catalyst(KOH)
Real	599.8934 ° C	60.7957 minutes	3.79 wt%	21.3MPa	0.102 wt%
Optimal responses					

The composition of the produced syngas changes according to the operating conditions of the reaction. For the optimized conditions, fig. 7 presents the detailed composition of the synthesis gas obtained with the optimal conditions allowing a maximum production of hydrogen only, and a maximum of hydrogen yield and gasification efficiency, respectively.

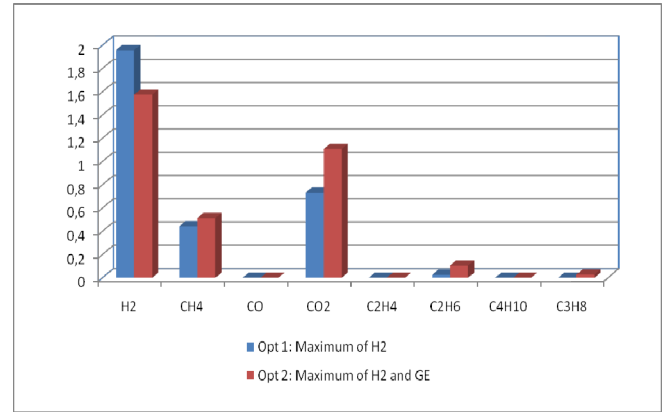


Fig. 4. Composition of the synthesis gas mixture product obtained according to the objective of optimization.

IV. CONCLUSION

In this research, the supercritical water gasification of pure glycerol was studied in the presence of alkaline catalyst (KOH) in mini autoclaves, using the surface response methodology (RSM) and the central composite design (CCD), this allowed to obtain a mathematical model of the second degree describing the production of hydrogen and gasification efficiency according to five operating parameters: temperature, residence time, initial glycerol concentration, pressure and presence of catalyst (KOH), and to study the effect of these parameters on the response studied. The significance tests showed that the initial concentration of glycerol had the most significant negative effect, while the pressure had no significant effect. However, temperature and residence time have a positive effect, and the presence of catalyst has a positive effect on hydrogen production. The interaction between temperature and residence time has a negative effect on the production of hydrogen, this is explained by the fact that a long residence time is not necessary when handling at high temperatures.

The operating conditions obtained for an optimization aimed at a maximum of hydrogen produced of 1.95 mol of H₂ / mol of glycerol, are of temperature = 599.8934 ° C, residence time = 5.5396 min, a pressure of 26.5856 MPa for an initial glycerol concentration of 3.7971 wt% and in the presence of 2 wt% of KOH.

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