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Parametric study via full factorial design for glycerol supercritical gasification

Houcinate Ibtissem^a, Outili Nawel^a, Weiss-Hortala Elsa^b and Meniai Abdeslam-Hassen^a

^aProcess Engineering Faculty, Laboratory of Environmental Process Engineering LIPE, Constantine3 University, Constantine, Algeria;

^bRAPSODEE Center, IMT Mines Albi, Albi, France

ABSTRACT

Supercritical water gasification is a promising technology for pollution treatment and syngas production from biomass. The produced gas is composed of hydrogen, carbon dioxide, methane, carbon monoxide and traces of ethane and other light hydrocarbons. This work aims to give a comprehensive experimental study of the supercritical water gasification of glycerol using a full factorial design of experiments (DOE). The effect of five factors, namely: temperature [458 °C–542 °C], residence time [40–90 min], pressure [23–27 MPa], initial concentration of glycerol [10–19 wt%] and KOH catalyst quantity [0.60–1.475 wt%], were investigated on several responses such as the gasification efficiency (GE), syngas composition and lower calorific value (LCV) of the produced gas. First order mathematical models correlating each considered response in terms of the considered factors were developed and validated. Also, the significance of the factors effect was validated using analysis of variance. The results showed that the produced gas composition and quality were strongly influenced by temperature and initial concentration. The largest gas production was detected at a temperature of 542 °C, a residence time of 40 min, a pressure of 27 MPa, a concentration of 10 wt% glycerol and a KOH catalyst percentage of 1.475 wt%.

KEYWORDS

Full factorial design; gasification efficiency; glycerol; hydrogen production; lower calorific value; supercritical water gasification

Introduction

Biomass is one of the most widely used renewable energy sources in the world. It accounts around 10% of the global energy consumption [1] due to the relatively low cost and reliability of biomass energy, generating much less significant pollution compared to fossils. The term “biomass” refers to any organic matter derived from living or dead plant material available on a renewable basis and any waste biomass such as municipal solid waste (MSW), biosolids municipal (wastewater) and animal waste (fertilizer) [2]. Biomass generally contains cellulose, hemicelluloses, lignin and low percentages of other substances, including minerals and organic molecules [3].

There are several processes for converting biomass to syngas, like anaerobic digestion and fermentation based biochemical processes [4] and thermochemical processes such as combustion, liquefaction, pyrolysis and gasification [5,6].

In supercritical water gasification of biomass, at temperatures and pressure above 374 °C and 22.1 MPa, respectively, a high pressure keeps fluid density close to that of liquids. Increased thermal conductivity and higher temperature promote the endothermic reforming reaction. [7]. The high temperature keeps the viscosity close to that observed in the gases, increasing the diffusion rates [8]. These properties allow the production of a mixture of recoverable gases and energy (CO, H₂, CH₄, etc.) from wet biomass [9]. The composition of the gaseous mixture produced depends not only on the critical operating temperature and pressure, but also on other parameters such as initial biomass concentration, residence time and the presence of a catalyst and several other parameters. For this, different researchers

have experimentally studied the effect of the operating conditions on supercritical water gasification.

R. Cherad et al. [10] studied supercritical water gasification of *Laminaria hyperborea* in a batch reactor for hydrogen, methane production and the carbon gasification efficiencies, under various operating parameters namely: presence of catalyst Ru/Al₂O₃ (5–20%), feed concentration (3.3–13.33%), residence time (0–120 min) and temperature (400 °C–550 °C), their results showed that the carbon gasification efficiencies increased with reaction temperature, reaction hold time and catalyst loading but decreased with increasing feed concentrations. The presence of catalyst (Ru/Al₂O₃) promoted the production of hydrogen. In the same context F. Xia et al. [11] studied the effect of operating parameters on the gasification efficiency of lignin, in the presence of KOH as a catalyst in a batch autoclave at the following operating conditions ranges: (5–30 min) for the residence time, (0.5–10) for mass ratio of H₂O to lignite, (400 °C–600 °C) for temperature and (0%–20%) for mass ratio of KOH to lignite, and they found that 47% of the gasification efficiency was achieved at 30 min, 550 °C and with 10% KOH. The use of higher values of mass ratio of H₂O to lignite, temperature and KOH as catalyst can lead to higher values of gas yield and gasification efficiency GE. Ding et al. [12] did also study the effect of temperature (400 °C–550 °C) and weight ratio water/biomass (3: 1 and 7: 1) for different catalysts (Ni/CeO₂/Al₂O₃, KOH, calcined dolomite and calcined olivine) on cellulose and pinewood for hydrogen production. The results showed that using KOH for the catalytic gasification of cellulose, the H₂ yield increased to 194% at 400 °C and a water/biomass ratio of 3. Qadaryah et al. [13] considered the gasification in sub

Table 1. Intervals of variation of the studied factor in coded and real values.

Variable	Unit	Symbol	Range and level		
			-1	0	1
Temperature	°C	T	458	500	542
Residence time	min	ts	40	65	90
Glycerol concentration	Wt %	Ci	10	14.5	19
Pressure	MPa	P	23	25	27
potassium hydroxide catalyst (KOH)	Wt%	Cat	0.6022	1.0386	1.475

and supercritical water for the degradation of glycerol in a batch reactor investigating the effects of temperature (200 °C–400 °C) and reaction time (20–60 min) on acrolein, acetaldehyde and allyl alcohol productions. Acrolein was formed throughout the reaction (sub- and supercritical medium), whereas the amount of acetaldehyde increased at temperature of 400 °C where it disappeared to produce allyl alcohol which also disappeared, breaking down into other products at long residence time.

Several factors had been studied by researchers and had proven their individual effects on different dependant variables of supercritical gasification process. However the authors claimed that no previous work had yet considered all these factors, motivating the present study where the effects of five operating parameters (temperature, pressure, initial concentration, residence time and KOH catalyst concentration) on several responses or objectives such as the gases (H₂, CO, CH₄, CO₂) production, the gasification efficiency, the lower calorific value and the generated hydrocarbons (C_xH_y), in batch reactors using supercritical water gasification process, and pure glycerol (C₃H₈O₃) as biomass. The choice of this biomass was mainly guided by its natural abundance. Indeed, glycerol is found in all vegetable and animal oils and fats and also it is a by-product of the transesterification of vegetable oils to produce biodiesel and of the saponification reactions [14]. Due to the significant increase of biodiesel production, the value of this by-product had received more attention in recent years [15]. Glycerol as a transesterification by-product has low purity (around 50%–55%) that can be increased by purification treatments to more than 95%, achieving the glycerol commercial purity [16].

The experimental design methodology was applied to study the supercritical gasification of pure glycerol using the 25 full factorial designs of experiments (DOE). The considered factor ranges were [458 °C–542 °C] for the temperature, [23–27 MPa] for the pressure, [10–19 wt%] for the initial concentration of glycerol, [40–90 minutes] for the residence time and [0.60–1.475 wt%] for the potassium hydroxide (KOH) catalyst concentration.

The results analysis was performed statistically and graphically by means of the Minitab 16 software, which was used for regression analysis of the obtained experimental data to estimate the coefficients of the first order models and the analysis of variance.

Materials and methods

Reagents

Glycerol (C₃H₈O₃) with a purity of 99.9% was supplied by SIGMA ALDRICH. Glycerol solutions were prepared with ultrapure water. The experiments were carried out with

Table 2. The used factorial design.

Run order	Coded value					Real value				
	T	ts	Ci	P	Cat	T	ts	Ci	P	Cat
1	-1	-1	-1	-1	-1	458	40	10	23	0.6022
2	1	-1	-1	-1	-1	542	40	10	23	0.6022
3	-1	1	-1	-1	-1	458	90	10	23	0.6022
4	1	1	-1	-1	-1	542	90	10	23	0.6022
5	-1	-1	1	-1	-1	458	40	19	23	0.6022
6	1	-1	1	-1	-1	542	40	19	23	0.6022
7	-1	1	1	-1	-1	458	90	19	23	0.6022
8	1	1	1	-1	-1	542	90	19	23	0.6022
9	-1	-1	-1	1	-1	458	40	10	27	0.6022
10	1	-1	-1	1	-1	542	40	10	27	0.6022
11	-1	1	-1	1	-1	458	90	10	27	0.6022
12	1	1	-1	1	-1	542	90	10	27	0.6022
13	-1	-1	1	1	-1	458	40	19	27	0.6022
14	1	-1	1	1	-1	542	40	19	27	0.6022
15	-1	1	1	1	-1	458	90	19	27	0.6022
16	1	1	1	1	-1	542	90	19	27	0.6022
17	-1	-1	-1	-1	1	458	40	10	23	1.475
18	1	-1	-1	-1	1	542	40	10	23	1.475
19	-1	1	-1	-1	1	458	90	10	23	1.475
20	1	1	-1	-1	1	542	90	10	23	1.475
21	-1	-1	1	-1	1	458	40	19	23	1.475
22	1	-1	1	-1	1	542	40	19	23	1.475
23	-1	1	1	-1	1	458	90	19	23	1.475
24	1	1	1	-1	1	542	90	19	23	1.475
25	-1	-1	-1	1	1	458	40	10	27	1.475
26	1	-1	-1	1	1	542	40	10	27	1.475
27	-1	1	-1	1	1	458	90	10	27	1.475
28	1	1	-1	1	1	542	90	10	27	1.475
29	-1	-1	1	1	1	458	40	19	27	1.475
30	1	-1	1	1	1	542	40	19	27	1.475
31	-1	1	1	1	1	458	90	19	27	1.475
32	1	1	1	1	1	542	90	19	27	1.475

Table 3. Lower calorific value of produced gases [19].

Gas	Lower calorific value (kJ/mol)
H ₂	242.70
CO	283.40
CH ₄	803.30
C ₂ H ₄	1323.97
C ₂ H ₆	1437.11
C ₃ H ₈	2044.13
C ₄ H ₁₀	2653.60

pure glycerol solutions of concentrations ranging in (10%–19% by weight), in the presence of an alkaline potassium hydroxide catalyst (KOH, 0.6%–1.475% by weight).

Experimental protocol

The experiments were carried out in the RAPSODEE laboratory of IMT- Mines of Albi in France, at 458 or 542 °C in batch reactors with allowable maximum temperature and pressure of 600 °C and 30 MPa, respectively. These cylindrical 316 stainless steel mini-autoclaves had inner and outer diameters of 8.5 and 31.4 mm, respectively and an internal volume of 5 ml. The volume of a glycerol solution was calculated using the density (ρ) depending on the desired temperature and pressure conditions, the properties of the water were calculated by the Mathcad Code IAPWS97 program developed by Benmekhlouf et al. [16]. This solution was introduced into the reactors with the appropriate quantity of potassium hydroxide as a catalyst. Then the reactor was sealed and placed in an electric oven (Nabertherm L5/11/320), preheated to the desired temperatures 458 °C and 542 °C (a time of 9 minutes was necessary to achieve the desired temperature). At the end of the desired reaction time (40–90 minutes), the reactor was left

Table 4. Experimental responses of the used DOE.

Run order	H ₂	CH ₄	CO	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₄ H ₁₀	C ₃ H ₈	GE (%)	L.C.V (kJ/mol)
1	0.401	0.015	0.020	0.378	0.0024	0.004	0.00182	0.007	20.410	142.580
2	0.660	0.197	0.001	0.558	0.0059	0.053	0.00139	0.036	34.880	479.706
3	0.572	0.085	0.010	0.679	0.0123	0.029	0.00384	0.029	38.266	337.331
4	0.675	0.238	0.002	0.630	0.0019	0.079	0.00070	0.037	39.740	549.187
5	0.293	0.013	0.029	0.265	0.0022	0.005	0.00227	0.009	15.172	123.056
6	0.477	0.175	0.002	0.500	0.0055	0.059	0.00155	0.042	31.893	439.056
7	0.254	0.035	0.000	0.190	0.0033	0.006	0.00065	0.006	10.804	116.740
8	0.454	0.199	0.002	0.490	0.0023	0.070	0.00230	0.042	32.043	467.130
9	0.221	0.000	0.043	0.194	0.0000	0.001	0.00069	0.002	11.229	72.741
10	0.665	0.182	0.001	0.547	0.0046	0.050	0.00099	0.034	33.862	458.875
11	0.540	0.094	0.000	0.431	0.0068	0.017	0.00179	0.017	24.892	279.106
12	0.530	0.181	0.002	0.442	0.0022	0.056	0.00052	0.024	28.145	407.558
13	0.142	0.004	0.037	0.152	0.0008	0.001	0.00086	0.003	9.024	59.187
14	0.430	0.150	0.003	0.428	0.0038	0.049	0.00287	0.035	27.342	380.393
15	0.313	0.050	0.003	0.374	0.0062	0.017	0.00164	0.012	20.881	179.409
16	0.458	0.189	0.004	0.474	0.0022	0.064	0.00228	0.039	30.774	443.818
17	0.528	0.011	0.001	0.396	0.0024	0.003	0.00062	0.004	20.721	155.261
18	0.719	0.196	0.001	0.511	0.0057	0.049	0.00160	0.028	32.237	472.056
19	0.508	0.039	0.001	0.375	0.0053	0.008	0.00139	0.009	20.603	195.583
20	0.605	0.187	0.001	0.484	0.0032	0.052	0.00144	0.027	30.519	436.067
21	0.305	0.032	0.001	0.319	0.0040	0.010	0.00116	0.008	17.340	139.915
22	0.520	0.145	0.003	0.437	0.0071	0.040	0.00155	0.029	27.351	373.304
23	0.366	0.040	0.001	0.307	0.0044	0.011	0.00134	0.012	17.228	170.811
24	0.494	0.233	0.003	0.496	0.0022	0.073	0.00119	0.039	32.804	497.604
25	0.488	0.025	0.001	0.390	0.0042	0.006	0.00117	0.007	20.850	171.005
26	0.823	0.230	0.001	0.581	0.0047	0.057	0.00108	0.034	36.811	545.917
27	0.687	0.069	0.001	0.584	0.0090	0.016	0.00197	0.017	32.203	297.055
28	0.643	0.224	0.001	0.519	0.0015	0.067	0.00061	0.028	33.280	493.473
29	0.249	0.006	0.017	0.254	0.0014	0.002	0.00094	0.004	13.669	85.244
30	0.536	0.177	0.003	0.481	0.0047	0.054	0.00326	0.037	30.826	441.008
31	0.487	0.079	0.002	0.452	0.0062	0.021	0.00158	0.020	25.876	266.126
32	0.467	0.178	0.002	0.426	0.0021	0.056	0.00202	0.033	27.774	412.634

for 20 min to be cooled down to the ambient temperature (18. 8 ± 2 °C).

A phase separation system containing a manometer was used to open the mini autoclave, the reactor was under N₂ pressure, and the manometer indicated the volume of the produced gas mixture, once the reactor was open. Then, the gaseous and liquid phases were recovered and analyzed.

Product analysis

Gaseous phase

The recovered gases were analyzed by gas micro chromatography (Agilent PGC-3000), identifying and quantifying in few seconds the produced gases: H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₈ and C₄H₁₀, with Helium as the carrier gas.

Liquid phase

The liquid residues recovered after phase separation were analyzed by gas chromatography-mass spectrometry (GCMS-TQ 803, collision-induced dissociation (CID)), with Argon and Helium as the carrier gases and a GC-2010 column to identify and quantify the different intermediates of the solution at the end of the reaction. The major compounds in the final solutions were as follows: butanediol, dimethyl phenol, methyl cyclopentanone, methyl phenol, propylene glycol, glycerin, butene diol, oxime methoxy-phenyl, 2- trimethyl cyclopentanone, ethanone, 1-(1-cyclohexen-1-yl)-, trimethyl cyclopentanone, ethyl phenol.

The total organic carbon (TOC) meter (Schimadzu TOC-5050) was used to measure the amount of carbon organic and inorganic fractions present in the residue of glycerol solutions.

Design of experiments

Full factorial designs may be denoted by the exponential notation 2^k, which simply expresses the number of experiments for the case of k factors, each one has two levels: the maxima and the minima coded (+1) and (−1), respectively. Thus, for the present study 32 experiments were used for the five considered independent variables: Temperature (T), residence time (ts), initial glycerol concentration (Ci), pressure (P) and KOH catalyst concentration (Cat). Table 1 shows the respective ranges and levels of the studied factors whereas Table 2 presents the 32 experiments of the full factorial design 2⁵, both in real and coded values.

In this work, several responses were considered using the factorial design, namely gasification efficiency, gas yield, TOC, lower calorific value and the quantities of all produced gases. The study was thus multiobjective with 10 studied responses.

Gasification efficiency and gas yield

The efficiency of the gasification GE (%) and the gas yield are calculated as follows:

$$GE = \frac{\text{Total masse of gaseous product}}{\text{Total mass of glycerol feed}} \quad (1)$$

$$\text{Gas yield} = \frac{\text{molar amount of gaz } i}{\text{molar amount of glycerol feed}} \quad (2)$$

Lower calorific value (LCV)

The lower calorific value of a fuel is the energy (per unit of mass) released by its combustion at constant pressure and under normal temperature and pressure conditions (0 °C

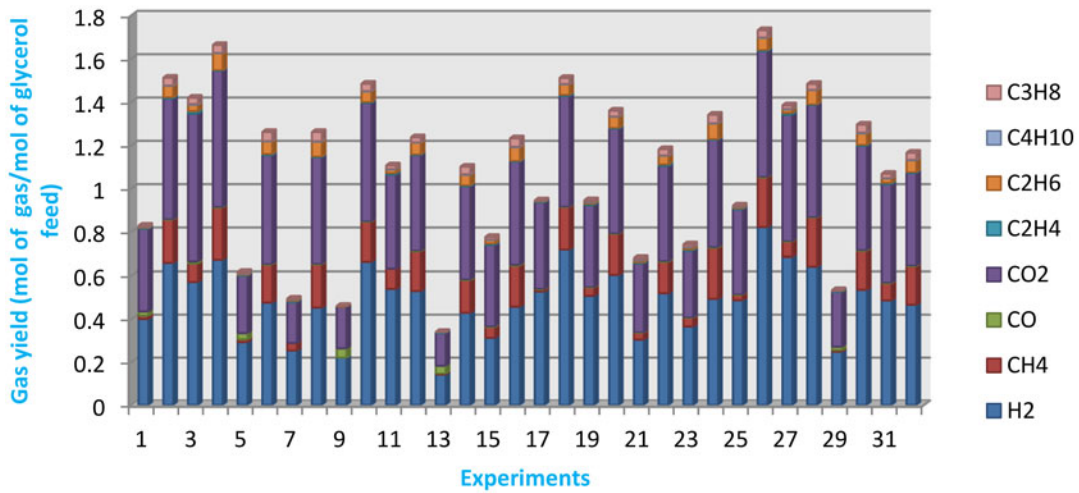


Figure 1. Gas yield composition for the 32 experiments of the factorial design.

Table 5. Regression coefficients and signification tests for H₂ production.

Term	Coef	Coef Ert	t-value	p-value
Constant	0.485	0.00234	206.61	0.003
T	0.088	0.00234	37.33	0.017
ts	0.019	0.00234	7.94	0.080
Ci	-0.094	0.00234	-40.20	0.016
P	-0.005	0.00234	-2.01	0.294
Cat	0.042	0.00234	17.91	0.036
T ts	-0.050	0.00234	-21.36	0.030
T Ci	0.002	0.00234	0.66	0.626
T P	0.002	0.00234	0.66	0.628
T Cat	-0.013	0.00234	-5.67	0.111
ts Ci	0.003	0.00234	1.14	0.459
ts P	0.017	0.00234	7.28	0.087
ts Cat	-0.013	0.00234	-5.57	0.113
Ci P	0.000	0.00234	-0.16	0.900
Ci Cat	-0.004	0.00234	-1.76	0.326
P Cat	0.026	0.00234	10.96	0.058
T ts Ci	0.018	0.00234	7.51	0.084
T ts P	-0.030	0.00234	-12.81	0.050
T ts Cat	-0.004	0.00234	-1.73	0.333
T Ci P	-0.003	0.00234	-1.35	0.406
T Ci Cat	0.000	0.00234	0.13	0.921
T P Cat	-0.006	0.00234	-2.62	0.232
ts Ci P	0.008	0.00234	3.27	0.189
ts Ci Cat	0.017	0.00234	7.37	0.086
ts P Cat	0.001	0.00234	0.38	0.770
Ci P Cat	-0.014	0.00234	-5.91	0.107
T ts Ci P	0.006	0.00234	2.69	0.226
T ts Ci Cat	-0.013	0.00234	-5.39	0.117
T ts P Cat	-0.001	0.00234	-0.61	0.650
T Ci P Cat	-0.002	0.00234	-0.73	0.598
ts Ci P Cat	-0.009	0.00234	-3.79	0.164

Coef=regression coefficients of the model; Coef Ert=standard error for the coefficient; t-value=student test value; p-value=probability value.

and a pressure of 1013mbar), assuming that the fumes contain water vapor [17].

The lower calorific value of a produced gas mixture is calculated as follows [18]:

$$LCV = \frac{\sum LCV_i \text{ mole of gaz } i}{\text{mole of biomass}} \quad (3)$$

The lower calorific values of the various pure gases produced in the supercritical water gasification of glycerol are shown in Table 3.

Mathematical models

Data analysis of the used DOE allowed correlating each considered response in terms of all the considered coded

Table 6. Regression coefficients and significance tests for CO₂ production.

Term	Coef	Coef Ert	t-value	p-value
Constant	0.430	0.001725	249	0.003
T	0.071	0.001725	41.03	0.016
ts	0.030	0.001725	17.43	0.036
Ci	-0.052	0.001725	-29.92	0.021
P	-0.009	0.001725	-5.22	0.120
Cat	0.009	0.001725	5.09	0.124
T ts	-0.035	0.001725	-20.39	0.031
T Ci	0.018	0.001725	10.40	0.061
T P	-0.004	0.001725	-2.42	0.250
T Cat	-0.017	0.001725	-9.91	0.064
ts Ci	-0.007	0.001725	-3.93	0.159
ts P	0.012	0.001725	7.04	0.090
ts Cat	-0.013	0.001725	-7.51	0.084
Ci P	0.011	0.001725	6.58	0.096
Ci Cat	0.010	0.001725	5.76	0.109
P Cat	0.032	0.001725	18.33	0.035
T ts Ci	0.017	0.001725	9.77	0.065
T ts P	-0.029	0.001725	-16.78	0.038
T ts Cat	0.008	0.001725	4.37	0.143
T Ci P	-0.013	0.001725	-7.30	0.087
T Ci Cat	-0.008	0.001725	-4.63	0.135
T P Cat	-0.009	0.001725	-5	0.126
ts Ci P	0.016	0.001725	9.25	0.069
ts Ci Cat	0.013	0.001725	7.76	0.082
ts P Cat	0.005	0.001725	3.02	0.204
Ci P Cat	-0.027	0.001725	-15.72	0.040
T ts Ci P	-0.006	0.001725	-3.70	0.168
T ts Ci Cat	-0.012	0.001725	-6.86	0.092
T ts P Cat	-0.007	0.001725	-3.96	0.158
T Ci P Cat	0.012	0.001725	6.89	0.092
ts Ci P Cat	-0.021	0.001725	-12.31	0.052

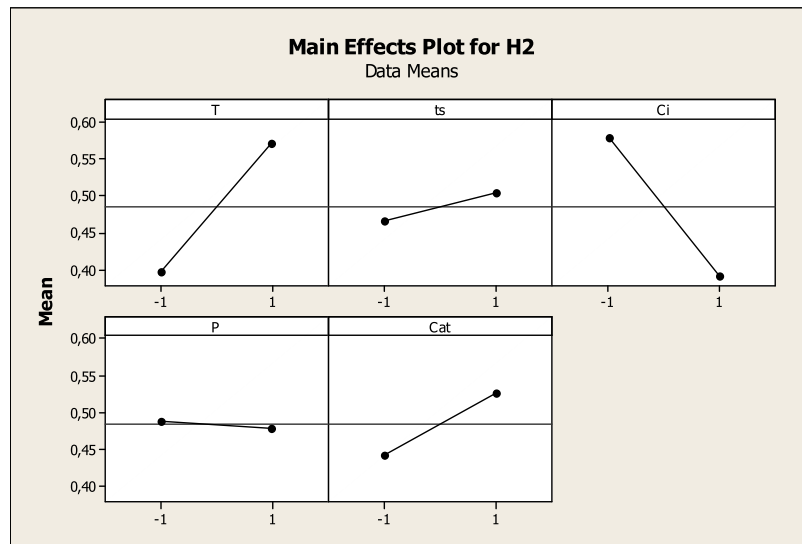
factors X and their interactions, with first order mathematical models of the general form:

$$Y = a_0 + \sum_{i=1}^5 a_i X_i + \sum_{i \neq j}^5 a_{ij} X_i X_j + \sum_{i \neq j, k}^5 a_{ijk} X_i X_j X_k + \sum_{i \neq j, k, l}^5 a_{ijkl} X_i X_j X_k X_l \quad (4)$$

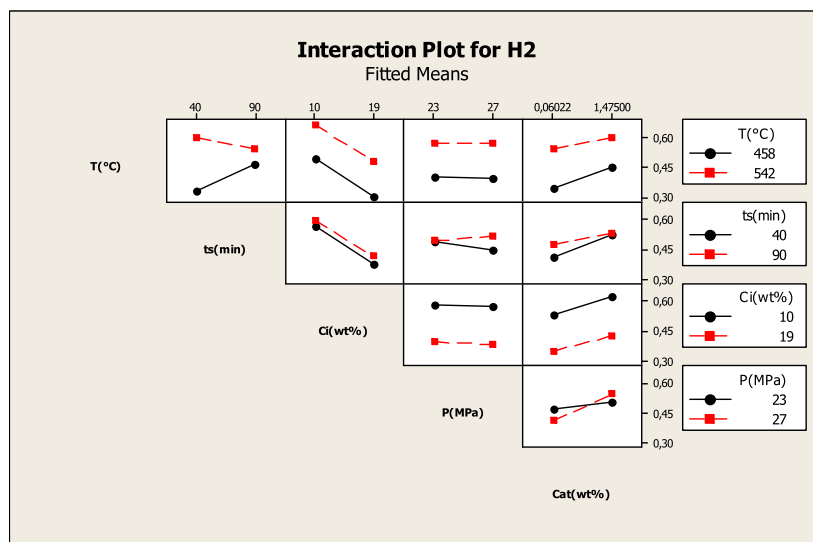
With: Y the considered response, X_i the main factor, X_iX_j the two levels interactions, X_iX_jX_k the three levels interactions and X_iX_jX_kX_l the four levels interactions, the factors are in the coded values. The a's denote the coefficients of the model.

Results and discussions

In order to study and quantify the effect of the five independent variables on the performance of the gasification



(a)



(b)

Figure 2. Effect of the operating parameters on the hydrogen production (a) main effects plots, (b) interactions plots.

of glycerol in supercritical conditions, 10 responses of the factorial design were measured for each experiment.

The experiments suggested by the factorial DOE with the recommended operating conditions of Table 2, were performed and each experiment of the design matrix was carried out three times to obtain the mean responses shown in Table 4.

The results show the wide variations of the produced gases compositions, with the operation conditions, and as illustrated by Figure 1, the major produced gases were H₂, CH₄ and CO₂. The CO and the other hydrocarbons productions were negligible. Also, the H₂ richest syngas was obtained at the maximum temperature, pressure and KOH catalyst concentration values and minimum residence time and initial glycerol concentration values, corresponding to operating conditions of Experiment 26. However Experiment 13 led to the poorest H₂ syngas at operating conditions opposite to those of Experiment 26.

Mathematical models and significance effects

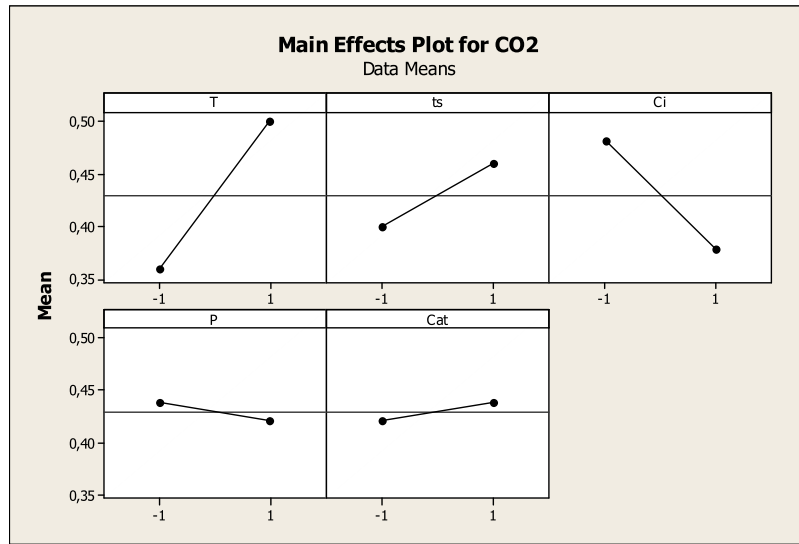
The data processing of the obtained results were carried out using Minitab to get a model that correlates each

response to the main factors and all the interactions. Also, the effects of the factors are studied and the models validated using the regression coefficients and signification tests tables with 95% of significance level.

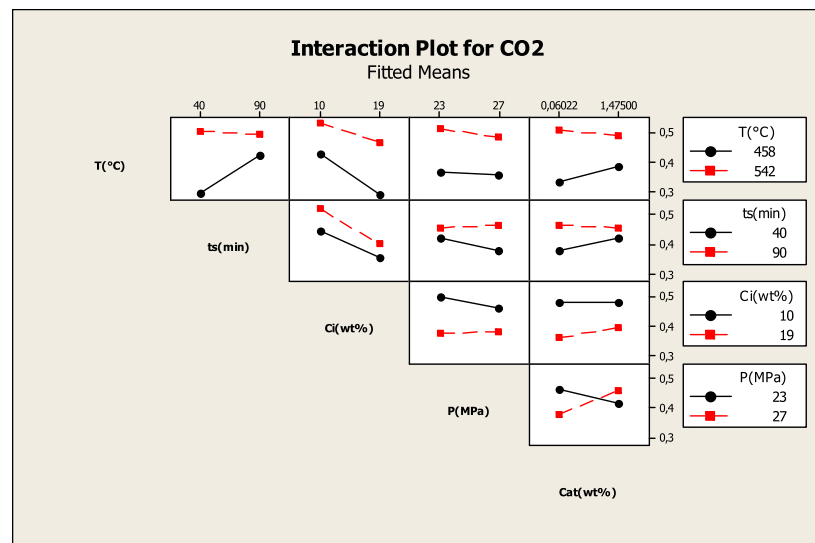
Hydrogen production

Table 5 presents the significance test of the factors and validates the model with a coefficient of determination $R^2=0.9998$ and it also shows the significance of each main factor and all the interactions. The results of Figure 2 show that temperature, residence time and catalyst concentration had positive effects on H₂ production, whereas the initial concentration had a strong negative influence and the effect of pressure was slightly negative but negligible.

The significant negative effect of the initial concentration on hydrogen production (a Student value of -40.20) is confirmed by Dianningrum et al. [20] who showed that a high initial glycerol concentration was not in favor of H₂ production. The adverse effect of increasing the concentration of glycerol on the steam reforming reaction could be



(a)



(b)

Figure 3. Effect of the operating parameters on the carbon dioxide production (a) main effects plots, (b) interaction plots.

very sensitive to the concentration of reactive water and solvent, while it had little effect on the pyrolysis reaction providing a gas production source. Also, a high concentration of biomass led to dehydration or polymerization of liquid intermediates to form chars [21,22]. The presence of catalyst (KOH) had a positive effect on hydrogen production, as confirmed by Kruse et al. [23] who found that the presence of KOH improved the water gas-shift reaction, leading to an increase in the produced hydrogen amount. According to the literature, strong pressure favors the water gas-shift, methanation of CO and CO₂, but reduces the reaction rate of biomass decomposition by radical reaction [24,25]. On the other hand, the results show no significant effect of the pressure; this may be due to the low pressure range studied, in agreement with the results found by Guo et al. [24] during the gasification of sawdust.

Regarding interaction effects, the results in Table 5 show that the most important one was due to the interaction between temperature and residence time (with a t -value of -21.36) which affected negatively the H₂ yield. A short residence time of 40 min was sufficient to obtain a high amount of hydrogen. So, it is not necessary to work

with long residence time when high temperature is prevailing.

In fact Figure 2(b). shows that the most important effect of binary interaction is the interaction between temperature and residence time followed by the interaction pressure and catalyst concentration. All the other binary interactions may be considered to be non significant.

Carbon dioxide production

The mathematical model that describes the production of CO₂ was developed with a correlation factor R^2 of 0.9998. As shown in Table 6, temperature was the most important factor with a positive effect on carbon dioxide production followed by the residence time and a non significant effect of the catalyst concentration with a p -value of 0.124. On the other side, the initial concentration had a negative effect on CO₂ yield with a non significant effect of pressure.

Table 6 shows the positive effect of temperature and residence time alone, which is in favor of the water gas-shift reaction producing CO₂ as a secondary gas [20], while their interaction has a strong negative effect with p and t -value s of 0.031 and -20.39 , respectively.

Table 7. Regression coefficients and signification tests for CO production.

Term	Coef	Coef Ert	t-value	p-value
Constant	0.006	0.001346	4.55	0.138
T	-0.004	0.001346	-3.09	0.200
ts	-0.004	0.001346	-3.05	0.201
Ci	0.001	0.001346	0.58	0.667
P	0.001	0.001346	1.01	0.497
Cat	-0.004	0.001346	-2.80	0.218
T ts	0.004	0.001346	3.07	0.201
T Ci	0.000	0.001346	-0.01	0.993
T P	-0.001	0.001346	-0.89	0.536
T Cat	0.004	0.001346	2.79	0.219
ts Ci	-0.001	0.001346	-0.63	0.641
ts P	-0.002	0.001346	-1.18	0.448
ts Cat	0.003	0.001346	2.21	0.271
Ci P	0.000	0.001346	0.35	0.784
Ci Cat	0.001	0.001346	0.55	0.681
P Cat	0.000	0.001346	-0.22	0.860
T ts Ci	0.001	0.001346	0.53	0.692
T ts P	0.002	0.001346	1.24	0.432
T ts Cat	-0.003	0.001346	-2.45	0.247
T Ci P	0.000	0.001346	-0.31	0.809
T Ci Cat	-0.001	0.001346	-0.42	0.749
T P Cat	0.000	0.001346	0.11	0.931
ts Ci P	0.000	0.001346	0.3	0.817
ts Ci Cat	0.000	0.001346	-0.11	0.932
ts P Cat	0.001	0.001346	0.45	0.731
Ci P Cat	0.001	0.001346	0.45	0.732
T ts Ci P	0.000	0.001346	-0.25	0.844
T ts Ci Cat	0.000	0.001346	0.1	0.935
T ts P Cat	-0.001	0.001346	-0.59	0.661
T Ci P Cat	-0.001	0.001346	-0.53	0.688
ts Ci P Cat	-0.001	0.001346	-1	0.500

Table 8. Regression coefficients and signification tests for CH₄ production.

Term	Coef	Coef Ert	t-value	p-value
Constant	0.115	0.00606	18.96	0.034
T	0.078	0.00606	12.80	0.050
ts	0.018	0.00606	2.89	0.212
Ci	-0.008	0.00606	-1.38	0.393
P	0.000	0.00606	-0.02	0.989
Cat	0.002	0.00606	0.33	0.798
T ts	-0.007	0.00606	-1.08	0.476
T Ci	-0.003	0.00606	-0.56	0.676
T P	-0.004	0.00606	-0.61	0.653
T Cat	0.002	0.00606	0.28	0.825
ts Ci	0.001	0.00606	0.21	0.869
ts P	0.001	0.00606	0.09	0.943
ts Cat	-0.003	0.00606	-0.56	0.677
Ci P	-0.002	0.00606	-0.39	0.762
Ci Cat	0.003	0.00606	0.45	0.733
P Cat	0.007	0.00606	1.08	0.476
T ts Ci	0.007	0.00606	1.09	0.473
T ts P	-0.008	0.00606	-1.24	0.433
T ts Cat	0.002	0.00606	0.26	0.840
T Ci P	-0.001	0.00606	-0.19	0.878
T Ci Cat	-0.004	0.00606	-0.63	0.640
T P Cat	0.003	0.00606	0.5	0.705
ts Ci P	0.000	0.00606	0.07	0.953
ts Ci Cat	0.006	0.00606	0.96	0.514
ts P Cat	-0.001	0.00606	-0.13	0.915
Ci P Cat	-0.005	0.00606	-0.89	0.536
T ts Ci P	-0.003	0.00606	-0.45	0.729
T ts Ci Cat	-0.001	0.00606	-0.14	0.913
T ts P Cat	-0.003	0.00606	-0.46	0.724
T Ci P Cat	-0.003	0.00606	-0.45	0.730
ts Ci P Cat	-0.003	0.00606	-0.50	0.705

Guo et al. [24] showed an increase in CO₂ yields with temperatures above 650 °C during the hydrothermal gasification of glycerol and explained it by a strong water gas-shift activity.

Figure 3(a) illustrates the slight effect of pressure and catalyst amount on carbon dioxide production and outlines the strong positive effect of temperature and the negative one for the initial concentration. On the other side, Figure 3(b) shows that the most important interaction effect was between the temperature and the residence time, similarly to hydrogen production.

Carbon monoxide production

The mathematical model that describes the production of CO was developed with a correlation factor R² of 0.984. Statistically and according to Table 7, no parameter did have a significant effect on the yield of CO produced by supercritical gasification of glycerol under the studied operating conditions domain, with all the p-values of main factors and their interactions greater than 0.05. Statistically no parameter had a significant effect, since the production of carbon monoxide was very low.

Experimentally, the effects of temperature, residence time and the presence of catalyst were slightly negative on CO production, as shown in Figure 4(a), and are considered the most influential factors. These parameters favored water gas-shift and methanation reactions, where CO was better and faster consumed. Changes in pressure led to a positive effect and a two-fold increase of CO level with an increase of 4 MPa (experiments 1 and 9). Under supercritical conditions, high pressure was in favor of the hydrolysis and water gas-shift reaction, but inhibited the pyrolysis reaction [26]. The initial concentration had a positive effect on the production of CO which increased by almost a factor of 2

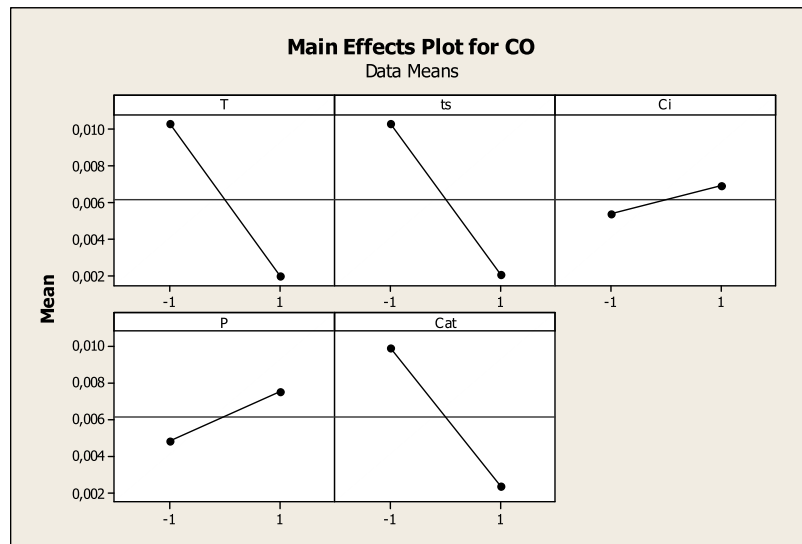
with 9wt% increase in glycerol. S.GUO et al. [27] found that the gases were issued mainly from two types of reactions, a pyrolysis and a steam reforming of glycerol and intermediate products. The steam reforming reaction could be very sensitive to the concentration of water as a reagent and where a higher concentration of glycerol could lead to water acting as the limiting reagent, while the pyrolysis reaction might be insensitive to the concentration of water.

Graphically, Figure.4(b) shows a significant effect of the interactions: T-ts, T-Cat and ts-Cat, but statistically the effect is insignificant (Table 7) because the CO yield was very low as shown on the y-axis.

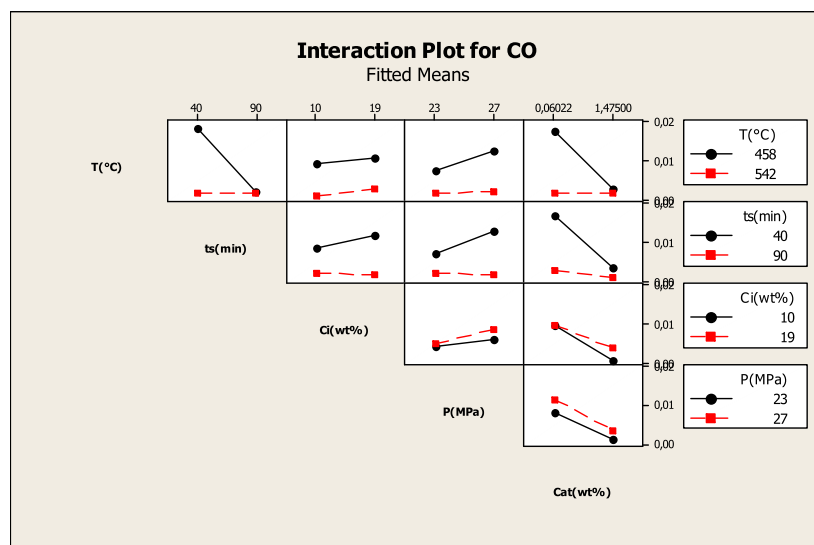
Methane production

The correlation factor R² of the production of methane is equal to 0.9946 and as shown in Table 8, temperature was the only significant effect with p-value of 0.05.

Figure 5(a) shows the effect of the various parameters on the production of methane, the temperature influenced more positively the methane production than the residence time, favoring the reaction of methanation. Both water gas-shift reactions and methanation could be considered as competitive reactions, and that at high temperatures and long residence time methanation was better promoted. The initial concentration and had a small negative effect on the production of methane. On the other side, the catalysts had a small positive effect, whereas the pressure had no effect on the methane production. The produced hydrocarbons were C₂H₄, C₂H₆, C₃H₈ and C₄H₁₀. They were present in very small quantities and the factors had almost similar effects to those on methane production, confirming the results found by GUO et al. [27]. Slight variations of the



(a)



(b)

Figure 4. Effect of the operating parameters on the carbon monoxide production (a) main effects plots, (b) interactions plots.

temperature and the residence time with increasing the concentration, led to increased molar fractions of CH_4 and C_2H_x .

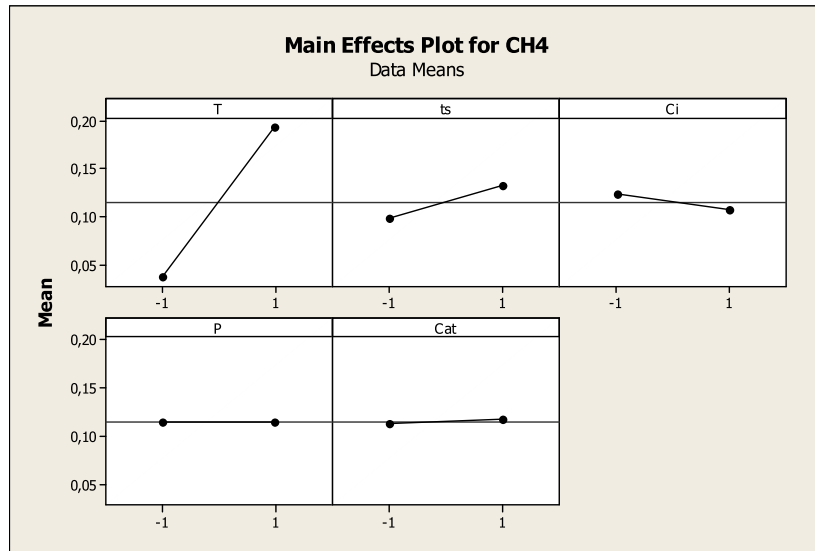
As shown on [Figure 5\(b\)](#), no interaction presented a significant effect.

Gasification efficiency

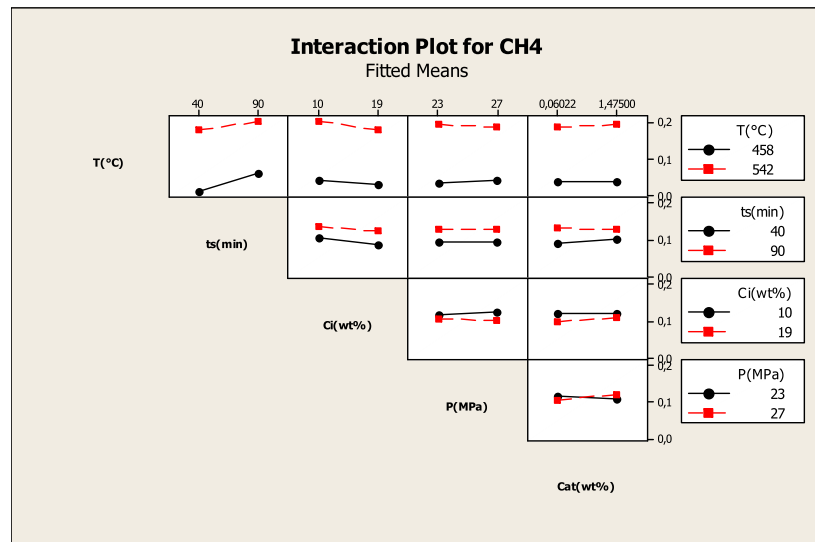
The mathematical model which describes the efficiency of gasification as a function of the operating parameters has a correlation factor R^2 of 0.9883. As can be seen from [Table 9](#) all the main factors are significant with p -value less than 0.05, except the catalyst with a p -value of 0.058 which is very close to a condition of significance. The results show that contrary to the other studied responses, several factors interactions, with level two, three and four factors, are considered statistically significant for the gasification efficiency (see [Table 9](#) and [Figure 6\(b\)](#)). For the binary interactions T-ts, T-Ci, T-Cat, ts-P, ts-Cat, Ci-Cat, P-Cat and Ci-P, it was found that the interaction between

temperature and residence time had the highest t -value of -63.9 . For the ternary interactions T-ts-Ci, T-ts-P, T-Ci-P, T-Ci-Cat, ts-Ci-P, ts-Ci-Cat and Ci-P-Cat, it was found for this case that the interaction between temperature, residence time and pressure had the most important effect with a t -value of -54.67 . The quaternary interactions that had no effects for all the studied responses, had showed significant effects on gasification efficiency and were: T-ts-Ci-P, T-ts-Ci-Cat, T-ts-P-Cat, T-Ci-P-Cat and ts-Ci-P-Cat with a t -value of -41.05 for the interaction between residence time, initial concentration, pressure and catalyst.

According to [Figure 6\(a\)](#) and [Table 9](#), initial concentration and pressure had negative effects but all other factors had positive ones. The temperature and the residence time had positive effects on the gasification efficiency, with the former having the most positive influence. The increase in the gasification efficiency was mainly due to the high rate of gas production, to the various intermediate reactions (steam reforming, water gas shift and methanation) that were favored by these parameters. The initial concentration



(a)



(b)

Figure 5. Effect of the operating parameters on the methane production (a) main effects plots, (b) interactions plots.

of glycerol had a more negative effect on the gasification efficiency compared to the pressure. These results were in agreement with other studies like the one reported in [26].

Low calorific value

The model had a correlation factor R^2 of 0.9976. As shown in Table 10 and Figure 7(a), statistically, the temperature was the only factor with the most significant and important positive effect (p -value = 0.034 and t -value = 18.65).

Residence time had also a positive effect but lesser than that of temperature while initial concentration had a slightly negative effect as shown in Figure 7(a). It is also shown that catalyst and pressure had negligible effects.

The important effect of temperature on the low calorific value of the obtained gas, had also been outlined by the work of Nanda et al. [28] in their study of a gasification of wheat straw, where their results showed about sevenfold increase of the LCV when the temperature passed from 300 °C to 550 °C. The present work results show an increase

of LCV of the produced syngas from 59.184 to 549.184 kJ/mol corresponding to the operating conditions of Experiment 4 (the maxima of temperature and residence time) and Experiment 13 (the minima of temperature and residence time) respectively (see Table 4). From Figure 7(b), it is shown that the interaction T-ts was the only important one.

According to Equation (3), the lower calorific value is a function of the quantities of produced hydrocarbons gases and it indicates the content of combustible gases in the obtained gaseous mixture. Figure 8 shows the composition of the gaseous phase in terms of the energy capacity of the gas produced. From the experimental point of view, the results show that a high temperature favored the production of hydrocarbon-rich energy gas, whereas the heating values of methane and propane had shown a thirteen and fivefold increase, respectively, compared to the twofold power increase for hydrogen (Experiments 1 and 2). The maximum global LCV was identified in Experiment 4, where the temperature and residence time were increased at the same time, hence the positive effect of the interaction of the two parameters. The overall LCV decreased slightly

Table 9. Regression coefficients and signification tests for gasification efficiency.

Term	Coef	Coef Ert	t-value	p-value
Constant	24.862	0.03054	848.65	0.001
T	5.408	0.03054	195.54	0.003
ts	1.836	0.03054	63.66	0.010
Ci	-2.788	0.03054	-89.88	0.007
P	-0.432	0.03054	-14.91	0.043
Cat	0.391	0.03054	10.98	0.058
T ts	-1.826	0.03054	-63.91	0.010
T Ci	0.857	0.03054	31.22	0.020
T P	-0.312	0.03054	-10.98	0.058
T Cat	-0.731	0.03054	-25.46	0.025
ts Ci	-0.346	0.03054	-11.34	0.056
ts P	0.577	0.03054	18.63	0.034
ts Cat	-0.657	0.03054	-21.74	0.029
Ci P	0.535	0.03054	18.04	0.035
Ci Cat	0.562	0.03054	19.58	0.032
P Cat	1.760	0.03054	60.92	0.010
T ts Ci	1.023	0.03054	36.07	0.018
T ts P	-1.596	0.03054	-54.67	0.012
T ts Cat	0.291	0.03054	10.34	0.061
T Ci P	-0.663	0.03054	-22.34	0.028
T Ci Cat	-0.511	0.03054	-18.59	0.034
T P Cat	-0.354	0.03054	-11.38	0.056
ts Ci P	0.838	0.03054	29.09	0.022
ts Ci Cat	0.825	0.03054	28.57	0.022
ts P Cat	0.271	0.03054	8.94	0.071
Ci P Cat	-1.478	0.03054	-50.05	0.013
T ts Ci P	-0.409	0.03054	-14.42	0.044
T ts Ci Cat	-0.622	0.03054	-22.18	0.029
T ts P Cat	-0.425	0.03054	-15.12	0.042
T Ci P Cat	0.524	0.03054	17.96	0.035
ts Ci P Cat	-1.200	0.03054	-41.05	0.016

with the increase in the initial glycerol concentration, the composition of the gaseous mixture changed and the carbon monoxide increased along with some light hydrocarbons (C_2H_6 , C_4H_{10} and C_3H_8). The overall calorific value and minimum hydrogen were obtained with increasing initial glycerol concentration and pressure simultaneously (Experiment 13). The presence of catalyst increased the overall calorific value of the gaseous mixture with a significant increase in the calorific value provided by the hydrogen, which showed the selectivity of the catalyst (KOH) for the production of hydrogen.

Studied factors classification

The previous sections have shown that the studied operating parameters had not the same effect on the DOE responses. To outline the effects of the factors and their interactions on a target response, the Pareto graph was used and it is a vertical bar graph in which values are plotted in decreasing order of relative frequency from left to right. Indeed, Pareto chart is useful for analyzing which variables have the greatest effect on a given response and allows taking a decision according to the objective of the study. Also, it can classify all the factors and their interactions and shows the significant ones using the critical t -value (12.71 for the obtained models) where the factors with absolute t -value greater than this critical one are considered as significant.

Figures 9 and 10 shows an example of Pareto chart generated by Minitab to represent the factors classification for hydrogen production and gasification efficiency as study objectives.

As can be seen from these results, a non significant factor for a given response may be significant for another

Table 10. Regression coefficients and signification tests for LCV.

Term	Coef	Coef Ert	t-value	p-value
Constant	315.28	7.553	41.74	0.015
T	140.83	7.553	18.65	0.034
ts	31.57	7.553	4.18	0.149
Ci	-28.06	7.553	-3.72	0.167
P	-3.18	7.553	-0.42	0.746
Cat	6.79	7.553	0.90	0.534
T ts	-24.25	7.553	-3.21	0.192
T Ci	3.82	7.553	0.51	0.702
T P	-4.97	7.553	-0.66	0.630
T Cat	-3.89	7.553	-0.52	0.697
ts Ci	0.50	7.553	0.07	0.958
ts P	3.73	7.553	0.49	0.708
ts Cat	-7.47	7.553	-0.99	0.504
Ci P	-0.55	7.553	-0.07	0.953
Ci Cat	4.33	7.553	0.57	0.669
P Cat	20.17	7.553	2.67	0.228
T ts Ci	15.61	7.553	2.07	0.287
T ts P	-19.64	7.553	-2.60	0.234
T ts Cat	1.08	7.553	0.14	0.909
T Ci P	-3.70	7.553	-0.49	0.710
T Ci Cat	-7.96	7.553	-1.05	0.483
T P Cat	2.23	7.553	0.30	0.817
ts Ci P	6.22	7.553	0.82	0.561
ts Ci Cat	13.86	7.553	1.84	0.318
ts P Cat	0.43	7.553	0.06	0.963
Ci P Cat	-13.51	7.553	-1.79	0.324
T ts Ci P	-4.98	7.553	-0.66	0.629
T ts Ci Cat	-6.92	7.553	-0.92	0.528
T ts P Cat	-5.66	7.553	-0.75	0.590
T Ci P Cat	-0.80	7.553	-0.11	0.933
ts Ci P Cat	-10.72	7.553	-1.42	0.391

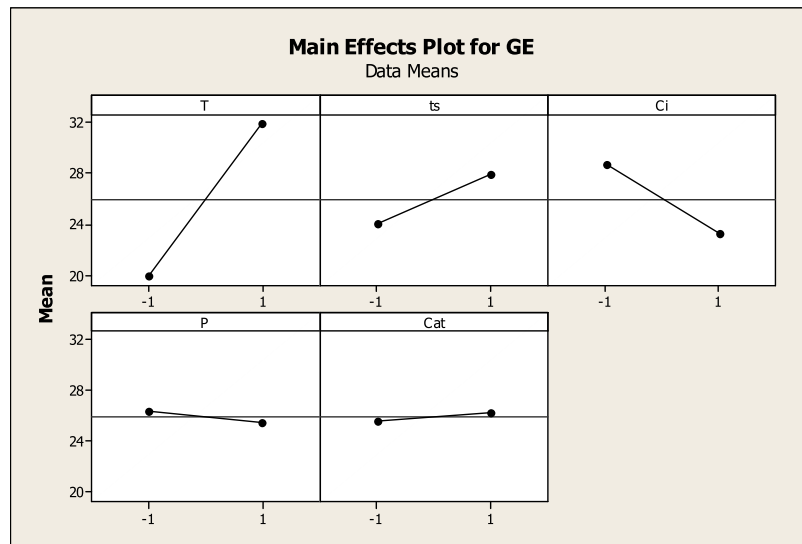
one. Also, the factors effects do not have the same impact on the studied responses. For instance the pressure effect was not significant on the H_2 production but was significant on gasification efficiency. Furthermore, it was clearly shown that the temperature was the most significant factor affecting the GE followed by the initial concentration, contrary to the H_2 production where the effects of these two factors were non significant. As mentioned above, several binary interactions and even ternary and quaternary interactions which are not usually considered, had showed a significant effect. The analysis of the obtained results justified the consideration of all factors and responses and the selection of operating conditions to be applied depends on the main objective for using supercritical gasification.

Comparison with previous results

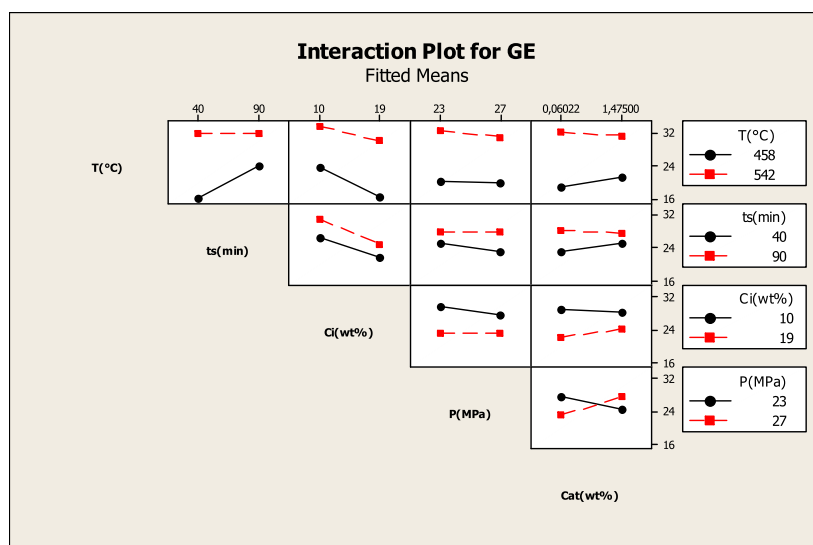
A comparison of supercritical gasification of glycerol with the work of Wu et al. [29] was performed under the same conditions of initial concentration of glycerol, temperature, pressure and residence time (5 wt%, 500 °C, 25 MPa and 60 min, respectively) in a batch reactor. However their work was carried out in absence of catalyst and for a comparison purpose only, an experiment under the same conditions was carried out following the same protocol.

Table 11 shows that the obtained gases production yields are very close to those reported by Wu et al. [29]. In both works, the produced syngas was rich in CO_2 and with no traces of butane, due to the very small amount produced that could not be detected by the analysis apparatus.

A comparison between gas production from supercritical gasification of glycerol and other biomasses in the same conditions was also performed. Table 12 compares the



(a)



(b)

Figure 6. Effect of the operating parameters on the gasification efficiency (a) main effects plots, (b) interactions plots.

obtained results of supercritical gasification of glycerol at 500 °C with those of Cherad et al. [10] at the same temperature, 25 MPa and a residence time of 30 min. They used an initial concentration of 6.66 wt% of Laminaria Hyperbora. It is clear that the yields of CH₄, CO, and CO₂ productions, reported in [10] were much higher than those given by the SCWG of glycerol. However the quantities of hydrogen were very close and L. Hyperbora allowed a greater production due to its composition containing nitrogen and sulfur which acted as a catalyst during the process [10].

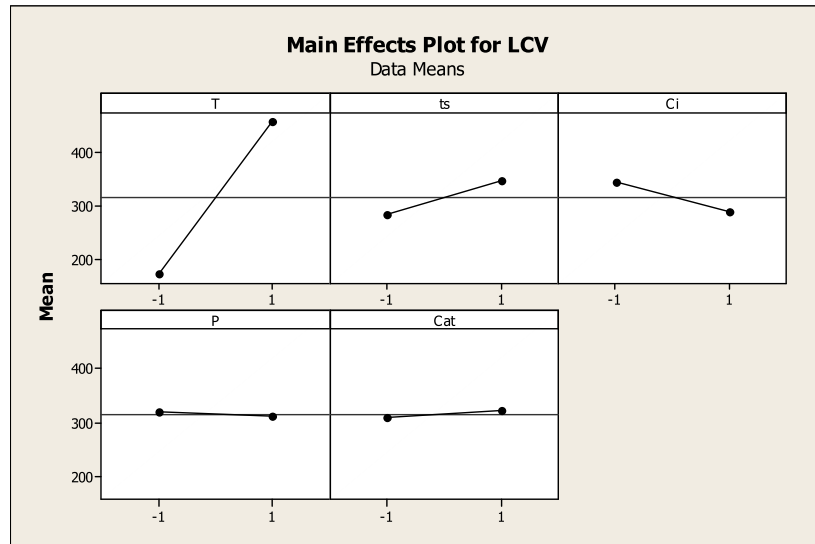
Table 12 shows also the comparison of glycerol supercritical gasification with that of sugarcane bagasse studied by sheikhdavoodi et al. [31]. The operating conditions of the study were: 500 °C, 25 MPa, 9 w% of initial concentration of biomass and 15 min as a residence time. As shown in Table 12, sugarcane bagasse produced the most H₂-rich syngas and CO₂ and CO yields were most important than those produced by glycerol at the same conditions.

Finally, a comparison between glycerol supercritical gasification in batch and tubular reactor was also performed. The results of the work of Guo et al. [27] in a tubular

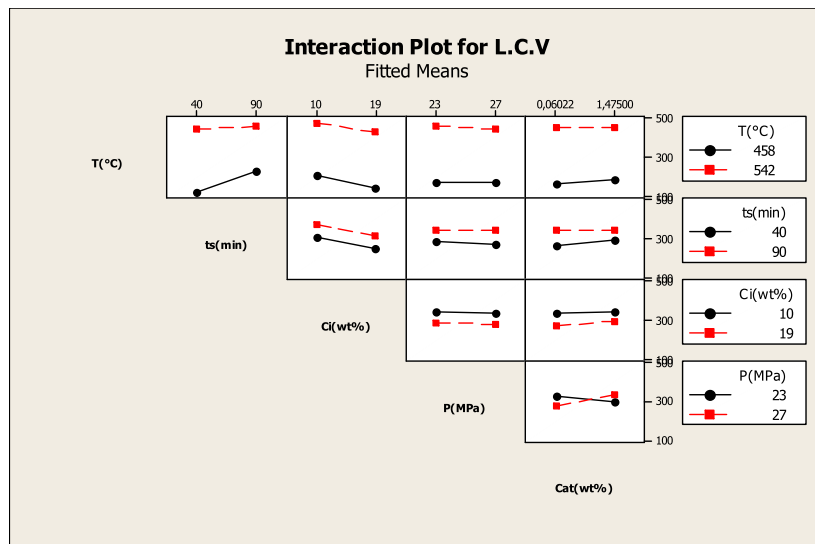
reactor are reported in Table 13 and show that the yields of CH₄, CO₂ and CO are much higher in tubular reactor in only 10 s than in batch reactor in 60 min, for the same conditions of temperature, pressure and initial concentration of glycerol with an important production of H₂. This is explained by the fact that the chemical equilibrium is more quickly reached in a tubular reactor [30].

Conclusion

Supercritical water gasification of glycerol led mainly to syngas such as hydrogen, methane, monoxide and carbon dioxide. The first order mathematical models describing all responses were obtained with satisfactory correlation factors, through an experimental study based on an experimental design using MINITAB 16. This study also showed the effect of different parameters on each gas produced. Temperature was the main factor that had the most positive effect on all responses except on carbon monoxide. In the other side, the initial concentration influenced positively the CO yield and negatively the remaining responses. The temperature, the residence time and the presence of



(a)



(b)

Figure 7. Effect of the operating parameters on the low calorific value (a) main effects plot, (b) interaction plot.

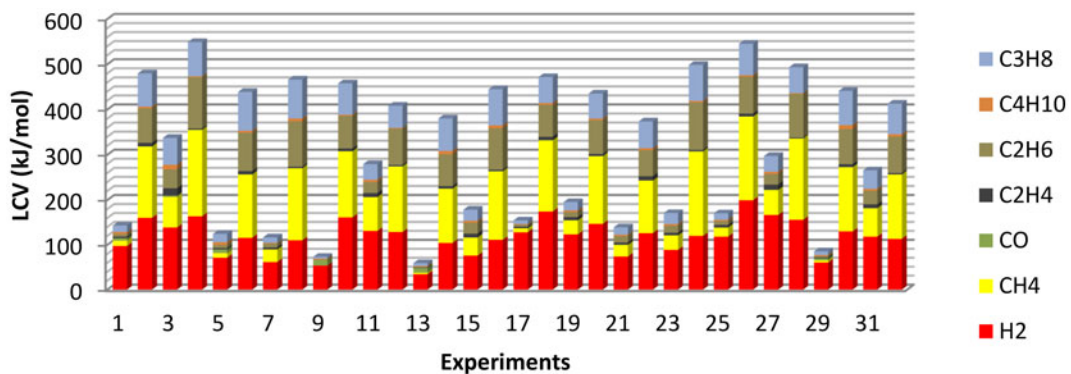


Figure 8. LCV of the produced gas mixture for all the DOE experiments

potassium hydroxide (KOH) as alkali catalyst favored the water gas-shift reaction; hence these factors acted positively on the production of recoverable gases. The pressure had almost no significant effect on all the responses studied except the gasification efficiency. The comparison of the results obtained from this work with previous ones has shown that a greater gas production was obtained in a tubular reactor. The maximum gas produced was identified

in Experiment 26, for an initial glycerol concentration of 1.475 wt%, a temperature of 542 °C, a residence time of 40 min, a concentration of catalyst of 10 wt% and a pressure of 27 MPa.

This study showed the effect of the operating parameters and their interactions on the quantity and quality of the produced gas from hydrothermal gasification of glycerol over the chosen intervals of operating conditions. The

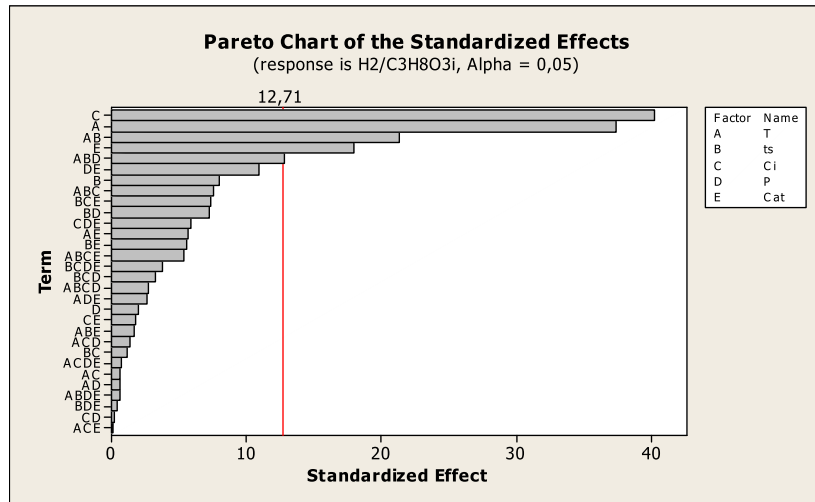


Figure 9. Pareto chart of the standardized effects for hydrogen production.

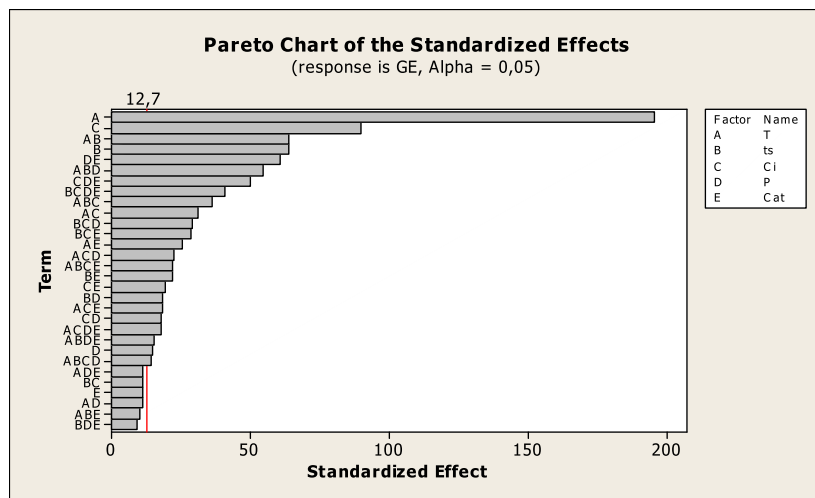


Figure 10. Pareto chart of the standardized effects for gasification efficiency.

Table 11. Gas yields (mol of gas/mol of glycerol) from SCWG of 5 wt% of glyceol without catalyst (500 °C, 25 MPa, 60 min).

	This work	From [29]
H ₂	0.51	0.56
CO ₂	0.65	0.72
CO	0.19	0.12
CH ₄	0.20	0.17
C ₂ H ₄	0.008	0.02
C ₂ H ₆	0.061	0.07
C ₃ H ₈	0.054	0.05

Table 12. Comparison of syngas produced (mol of gas/kg of biomass) by supercritical gasification of glycerol, *Laminaria Hyperbora* and sugarcane baggase).

	This work ^a (glycerol)	From [10] ^a (<i>Laminaria Hyperbora</i>)	This Work ^b (Glycerol)	From [30] ^b (Sugarcane bagase)
H ₂	5.68	5.18	4.62	6.60
CO ₂	6.26	13	5.21	10
CO	1.21	4	1.11	2
CH ₄	0.61	2	–	–

^a6,66 wt% concentration of biomass, 500 °C, 25 MPa and 30 min.

^b9 wt% concentration of biomass, 500 °C, 25 MPa and 15 min.

classification of effects significance of the five studied factors and their interactions according to the fixed objective was performed.

On the basis of the promising results presented in this paper, an optimization study of the operating parameters for different optimization objectives over larger intervals

Table 13. Gas yields (mol of gas/mol of glycerol) from SCWG of 5 wt% of glycerol at 500 °C and 25 MPa in batch and tubular reactor in 60 min and 10 s respectively.

	This work	From [30]
H ₂	0.51	2.59
CO ₂	0.65	0.93
CO	0.19	0.96
CH ₄	0.20	0.52

using quadratic mathematical models and also the use of other types of catalysts will be presented in the future.

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Disclosure statement

No potential conflict of interest was reported by the authors.

References

- [1] Hervé B, Mathis P. La biomasse, énergie d'avenir? Editions Quae. France; 2013.
- [2] Sriram N, Shahidehpour M. Renewable biomass energy. Chicago (IL): Electric Power and Power Electronics Center, Illinois Institute of Technology. IEEE. 2005.

- [3] Pacheco de Resende FL. Supercritical water gasification of biomass. The University of Michigan; 2009. Available from: https://deepblue.lib.umich.edu/bitstream/handle/2027.42/62405/feluis_1.pdf?sequence=1
- [4] Lioret C. FERMENTATIONS. *Encyclopaedia Universalis* [online]. Available from: <http://www.universalis.fr/encyclopedie/fermentations/>
- [5] Craig LC. Biomass energy a glossary of terms. Western Regional BIOMASS Energy Program. Reprinted with permission of: U.S. Government Interagency Program, Principal Funding: Department of Energy. Program Management: Bonneville Power Administration; USA. 1998.
- [6] Bassil Georgio M. Gazéification de la biomasse: élimination des goudrons par lavage, étude expérimentale et modélisation [Biomass gasification: tarring by washing, experimental and modeling study]. Alimentation et Nutrition. Villeurbanne: Université Claude Bernard - Lyon I; 2012. French.
- [7] Boukis N, Diem V, Habicht W, et al. Methanol reforming in supercritical water. *Ind Eng Chem Res.* 2003;42(4):728–735.
- [8] Loppinet-Serani A, Aymonier C, Cansell F. Current and foreseeable applications of supercritical water for energy and the environment. *ChemSusChem.* 2008;1(6):486–503.
- [9] Ruiz JC, Boutin O. Gazeification de biomasse en eau supercritique [Biomass gasification in supercritical water]. Saint Denis: Ed. Techniques de l'ingénieur; 2013. French.
- [10] Cherad R, Onwudili JA, Williams PT, et al. A parametric study on supercritical water gasification of *Laminaria hyperborea*: a carbohydrate-rich macroalga. *Bioresour Technol.* 2014;169: 573–580.
- [11] Xia F, Tian S, Ning P, et al. Catalytic gasification of lignite with KOH in supercritical water. *Can J Chem Eng.* 2013;92:421–425.
- [12] Ding N, Azargohar R, Dalai AK, et al. Catalytic gasification of cellulose and pinewood to H₂ in supercritical water. *Fuel.* 2014; 118:416–425.
- [13] Qadariah L, Machmudah, S, Sasaki, M, et al. Degradation of glycerol using hydrothermal process. *Bioresour Technol.* 2011; 102:9267–9271.
- [14] DI Costanzo G. GLYCÉRINE (glycérol). *Encyclopaedia Universalis* [online]. Available from: <http://www.universalis.fr/encyclopedie/glycerine/>
- [15] Cahn A. 5th world conference on detergents: reinventing the industry: opportunities and challenges. American Oil Chemists; New York. 2003, p. 182.
- [16] Benmakhlof N, Outili N, Meniai AH. Modeling and optimization of phenol hydrothermal oxidation in supercritical water. *Int J Hydrogen Energy.* 2017;42(17):12926–12932.
- [17] Thomas P-F. Précis de Physique-chimie: cours et exercices. Edition Bréal; Paris. 2006.
- [18] Wu M. Etude de procédés de conversion de biomasse en eau supercritique pour l'obtention d'hydrogène. Application au glucose, glycérol et bio-glycérol [Study of process of conversion of biomass to supercritical water to obtain hydrogen. Application to glucose, glycerol and bio-glycerol]. Toulouse: Université de Toulouse, Unité de Recherche RAPSODEE; 2012. French.
- [19] Roy-Auberger M, Marion P, Boudet N. Gazéification du charbon [Coal gasification]. Saint Denis: Ed. Techniques de l'Ingénieur, Réf. J5200 v1; 2009. French.
- [20] Laras B-I, Dianningrum SW, Choi H, Kim Y, et al. Hydrothermal gasification of pure and crude glycerol in supercritical water: a comparative study. *Int. J. Hydrogen Energy.* 2014;39(3): 1262–1273.
- [21] Sinağ A, Kruse, A, Schwarzkopf, V. Key compounds of the hydrolysis of glucose in supercritical water in the presence of K₂CO₃. *Ind Eng Chem Res.* 2003;42:3516–3521.
- [22] Chuntanapum A, Matsumura Y. Char formation mechanism in supercritical water gasification: a study of model compounds. *Ind Eng Chem Res.* 2010;49(9):4055–4062.
- [23] Kruse A, Meier D, Rimbrecht P, et al. Gasification of pyrocatechol in supercritical water in the presence of potassium hydroxide. *Ind Eng Chem Res.* 2000;39(12):4842–4848.
- [24] Guo LJ, Lu YJ, Zhang XM, et al. Hydrogen production by biomass gasification in supercritical water: a systematic experimental and analytical study. *Catal Today.* 2007;129:275–286.
- [25] Gadhe JB, Gupta RB. Hydrogen production by methanol reforming in supercritical water: suppression of methane formation. *Ind Eng Chem Res.* 2005;44(13):4577–4585.
- [26] Akiya N, Savage PE. Roles of water for chemical reactions in high-temperature water. *Chem Rev.* 2002;102(8):2725–2750.
- [27] Guo S, Guo L, Cao C, et al. Hydrogen production from glycerol by supercritical water gasification in a continuous flow tubular reactor. *Int J Hydrogen Energy.* 2012;37(7):5559–5568.
- [28] Nanda S, Reddy SN, Vo D-VN, et al. Catalytic gasification of wheat straw in hot compressed (subcritical and supercritical) water for hydrogen production. *Energy Sci Eng.* 2018;6(5): 448–459.
- [29] Wu Q, Bulza S, Corcoveanu C, et al. Supercritical water conversion of glycerol: comparative parametric study between batch and continuous process. Available from: <https://www.isasf.net/fileadmin/files/Docs/DenHaag/HtmlDir/Papers/CO42.pdf>
- [30] Sheikhdavoodi MJ, Almassi M, Ebrahimi-Nik M, et al. Gasification of sugarcane bagasse in supercritical water; evaluation of alkali catalysts for maximum hydrogen production. *J Inst Energy.* 2015;88(4):450–458.
- [31] Houcinat I, Outili N, Meniai AH. Optimization of gas production and efficiency of supercritical glycerol gasification using response surface methodology. *Biofuels.* 2018;9(5):625–633.