Evaluation of the Process Parameters on Subcritical Water Gasification of Sorghum by Response Surface Methodology

Açelya Seçer[*a], **Ertürk Şayan**[a], **Şefika Türker Üzden**[a], **Arif Hasanoğlu**[a]

[a]Department of Chemistry, Çukurova University, 01330, Adana, Turkey

Abstract: In this study response surface methodology (RSM) with Box-Behnken design (BBD) was used to evaluate the effects of process parameters of reaction time, initial water volume, amount of feedstock, and amount of catalyst on total gasification and hydrogen production yield by low temperature hydrothermal gasification of Sorghum biomass at 250 °C. Ruthenium(III) chloride was used as a catalyst in catalytic runs. Significances of the main and interacting effects of independent parameters were determined by ANOVA. Numerical optimization was used to optimize the process parameters for maximum yield hydrogen production. The optimum conditions for maximum hydrogen production were determined as a residence time of 58.6 min, water volume of 24.5 mL, and catalyst amount of 0.02 g.

Keywords: Biomass, hydrothermal gasification, hydrogen, response surface methodology, Box-Behnken Design.

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***Corresponding author. E-mail:** acsecer@cu.edu.tr.

INTRODUCTION

Most of the energy need is still met by conventional fossil fuels and the increase in world energy demands results a decrease in traditional energy resources. Also, carbon emission from fossil fuels is a dramatic environmental problem growing day by day and becoming more dangerous. The threat of global warming associated with the increase in greenhouse gas emissions, such as CO_2, has increased the number of research on this issue, and most of the work is particularly related to the development of technologies to reduce these emissions. These effects, combined with declining reserves of conventional sources, necessitated the use of sustainable new generation energy sources, which would replace the old ones (1). Hydrogen, which has the potential to solve these major problems as it can be utilized without any environmental impacts, is a good alternative among the new generation energy fuels. It is not a primary energy source but can be produced from another source to be transformed for later uses. Therefore, hydrogen production technologies are among the most studied and developed technologies in recent years (2). Among these technologies, hydrogen production from biomass has some advantages over others as biomass is abundant and totally renewable (3). Lignocellulosic biomasses are the most abundant and economical raw materials as they can easily be grown in almost all conditions. Their cellulose and hemicellulose contents can also be modified and enriched (4). Furthermore, since the amount of CO_2 that these plants take from the atmosphere by photosynthesis to grow is the same as the amount of CO_2 released when they processed, the net effect of biomass processing on CO_2 emissions is zero. These advantages make lignocellulosic biomass a very good alternative energy source in environmental and economic terms. However, since there is too much moisture in the biomass structure, it may need to be dried for use in some processes, which leads to an increased cost of the processes. In this process, water is a participant of the system and acts as both the reaction medium and the reactant, and thus does not need to be removed from the medium (5). Properties of water at different temperature and pressures are different than those of water under normal conditions and the water amount directly affects the system pressure. So that, water amount, reaction temperature and system pressure are the key parameters affecting the system performance and the product gas distributions (6). Also different types of catalysts can also be used in hydrothermal gasification for specific purposes at different conditions (7–11). Gasification process is a process in which many factors have some effects at the same time, and the relations of these effects with each other are as important as their individual effects. Therefore, a method in which each of these effects can be examined together with the interacting effects can be very useful for the development of the process. Response surface methodology (RSM) is defined as a method in which statistical and mathematical techniques are used together for development and optimization of processes (12). The relationship between one or more response variables and a set of quantitative parameters can be examined with a response surface method called Box–Behnken design (BBD). It is a variety of rotational designs from incomplete multi–factor designs, which are used in the estimation of second order model parameters. The number of test points for BBD is determined by the “N= 2k(k–1) + nc“ equation where “k” indicates the number of factors and “nc” indicates the number of central attempts (13,14). Because the lower and upper limits for all factors in design are never covered at the same time, unsatisfactory results from extreme values are prevented by BBD. The experimental designs have fewer design points and fewer experiments to be performed. Examples of the use of the method in gasification can be found in the literature (15–19).

In this study, we perform the hydrothermal gasification of sorghum at 250 °C and evaluate the individual and simultaneous effects of residence time, initial water volume, amount of biomass, and amount of catalyst in terms of hydrogen production with RSM combined with BBD. In a previous study, we performed the gasification of kenaf biomass at sub-critical conditions at temperatures from 250 to 325 °C, and obtained a maximum H_2 mole fraction in the gaseous product (44.5%) at 250 °C with $RuCl_3$ catalyst (20). So in this study the temperature was kept constant at 250 °C. In this way the gasification process was performed and evaluated at milder conditions than traditional ones for better energy efficiency. Since the traditional studies can only deal with the individual factor effects, this study also brings novelty to the literature by not only determining the individual effects of independent parameters on gasification performance but also understanding the interacting process parameters. Numerical optimization was used to optimize the process parameters for maximum hydrogen yield. The factors affecting hydrogen production from gasification of sorghum under these conditions were examined together, as well as how the factors could be modified according to each other to achieve the desired result under the desired specific conditions. In addition, the most suitable conditions for hydrogen production could be determined by 95% confidence level with few experiments.

MATERIALS AND METHODS

Materials

Sorghum is used as lignocellulosic biomass which was ground to pass 140 meshes. Moisture, ash and elemental analysis results of sorghum biomass are given in Table 1. Anhydrous Ruthenium(III) chloride (99%, J&K) was used as the catalyst in catalytic runs.

Table 1. Moisture, ash and elemental analysis results of sorghum biomass .

	Sorghum
C (wt %, dry)	39.8
N (wt %, dry)	0.8
H (wt %, dry)	5.2
S (wt %, dry)	N/A
O (wt %, dry)[a]	45.8
Moisture (wt %)	8.1
Ash (wt %, dry)	8.4
Volatile matter (wt %, dry)	nd
Fixed carbon (wt %, dry)	nd

[a]: calculated from difference; nd: not determined

Method

Gasification experiments

Sorghum biomass was gasified at 250 °C. The gasification of biomass was performed in a 100 mL stainless steel high pressure reactor (PARR Model 4590 micro bench type) equipped with magnetic drive stirrer and temperature controller system. The desired amount (dry, ash–free basis) of sorghum biomass and catalyst (in experiments where the catalyst is used) was placed in the reactor with the desired volumes of water which was stated in the experimental plan. Then the reactor was purged with Argon for air removal and sealed. Argon gas was sent to the system with a continuous input and output during purge process. The relevant pressures were monitored to confirm that there was no amount of gas left in the reactor that would affect the gasification results. Reactor temperature was raised to 250 °C starting from the room temperature and gasification was continued for the time specified in the experimental plan by stirring at 1000 rpm continuously via the magnetic–drive. The internal (autogenous) pressure inside the reactor was observed between 100–350 psi depending on the amount of initial water used. At the end of the process the reactor was taken out of the heating system and was immediately cooled down to room temperature using an ice–cold water mixture.

Gas and liquid product analysis

Gaseous products were collected into a gas buret that was filled with water and the total gas volume was measured by water displacement. A dual–channel Varian 450 series GC equipped with two TCD detectors were used for product characterization. Remaining liquid products were transferred into a cellulose thimble with dichloromethane and extraction method was applied using dichloromethane solvent and analyzed with Gas Chromatography–Mass Spectrometry (GC–MS) to obtain detailed chemical compositions. GC–MS analysis was performed by Thermo Finnigan GC–MS using Thermo TR-5MS capillary column (60 m x 0.25 mm ID x 0.25 µm). Detailed information about gas and liquid product analysis were given in previous studies (21).

Experimental design and optimization

A 4–factor and 3–level design was performed by Design Expert 12 software to evaluate the effects of performance parameters of reaction time (min), water volume (mL), amount of feedstock (g), and amount of catalyst (g) and to optimize these parameters for maximum hydrogen production. Total volume, hydrogen and carbon dioxide volumes produced after gasification were used for response factors. The independent variables were coded as follows; “A” for reaction time %, “B” for water volume, “C” for biomass amount and “D” for catalyst amount. The low, center, and high levels of each factor level were donated as –1, 0 and +1, respectively. Experimental range levels of the independent variables were given in Table 2. 15 experiments were performed in a randomized order. A quadratic equation (Eq. 1) was used to establish a mathematical relationship between the variables and the response;

$$Y=\beta_0+\sum_{i=1}^{N}\beta_i\times X_i+\sum_{i=1}^{N}\beta_{ii}\times X_i^{2}+\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\beta_{ij}\times X_{ij}$$

(Eq. 1)

where Y is the predicted response, N is the number of variables, X_i is the independent variable, β_0, β_i, β_{ii}, and β_{ij} are the intercept terms, the linear effect, the squared effect and the interaction effect, respectively (22).

Table 2. Experimental range and levels of the independent variables.

Variables	Factor	Range and Level		
		–1	0	1
Time (min)	A	0	50	100
Water volume (mL)	B	0	35	70
Biomass amount (g)	C	1	4	6
Catalyst amount(g)	D	0.01	0.10	0.20

RESULTS AND DISCUSSION

The effects of four factors, namely reaction time (F1), initial water volume (F2), amount of catalyst (F3), and amount of biomass (F4) on hydrothermal gasification sorghum biomass at 250 °C were evaluated by employing Box-Behnken designed RSM. The experimental points, in coded and actual values, with observed response values were given in Table 3. The l results were determined by using analysis of variance (ANOVA) statistically. The term “A” is coded for reaction residence time (min); “B” is for the volume of water (mL) in the reactor, “C” is for biomass weight used (g), and “D” is for amount of catalyst (g).

Table 3. Experimental plan and the observed response values.

Experimental plan									Observations		
	F1	F2	F3	F4					R1	R2	R3
Run number	Residence time	Water volume	Biomass	Catalyst	A	B	C	D	Total gas	H_2	CO^2
	min	mL	g	g					mL	mL	mL
1	-1	0	-1	0	15	15	1	0.11	126.0	53.5	62.8

2	-1	0	1	0	15	15	6	0.11	558.0	187.5	340.9
3	1	0	-1	0	60	15	1	0.11	166.5	54.0	30.8
4	1	1	0	0	60	30	4	0.11	325.5	115.2	169.9
5	0	0	0	0	38	15	4	0.11	349.0	112.9	196.5
6	0	-1	1	0	38	0	6	0.11	557.0	114.0	312.8
7	0	0	-1	-1	38	15	1	0.01	126.0	57.7	59.8
8	0	0	0	0	38	15	4	0.11	357.0	115.0	204.4
9	1	-1	0	0	60	0	4	0.11	380.0	113.9	224.4
10	0	-1	0	-1	38	0	4	0.01	380.0	128.6	211.6
11	0	0	-1	1	38	15	1	0.20	107.1	38.6	57.1
12	0	-1	0	1	38	0	4	0.20	325.5	43.8	220.5
13	0	0	1	-1	38	15	6	0.01	660.0	226.0	399.0
14	-1	0	0	1	15	15	4	0.20	650.0	134.0	88.0
15	0	0	0	0	38	15	4	0.11	423.3	81.3	246.2
16	0	1	-1	0	38	30	1	0.11	76.0	3.8	66.5
17	0	-1	-1	0	38	0	1	0.11	162.9	59.0	187.2
18	1	0	1	0	60	15	6	0.11	528.1	196.5	263.1
19	0	1	0	-1	38	30	4	0.01	354.0	48.0	191.0
20	0	0	0	0	38	15	4	0.11	380.6	91.0	119.5
21	0	0	0	0	38	15	4	0.11	236.0	82.5	148.9
22	-1	0	0	-1	15	15	4	0.01	308.5	126.0	171.0
23	0	1	1	0	38	30	6	0.11	444.1	122.3	303.7
24	-1	-1	0	0	15	0	4	0.11	465.5	133.0	237.6
25	-1	1	0	0	15	30	4	0.11	199.5	43.0	157.8
26	1	0	0	1	60	15	4	0.20	309.2	56.5	146.7
27	0	0	1	1	38	15	6	0.20	532.5	98.4	216.8
28	1	0	0	-1	60	15	4	0.01	460.0	183.8	251.3
29	0	1	0	1	38	30	4	0.20	253.0	37.1	194.6

Effects of process parameters total gas volume

The significance of the effects of input process variables (reaction residence time, “initial volume of water (mL) in the reactor, biomass weight used and amount of catalyst) and their interactions on total gas volume at 250 °C were determined by ANOVA. The results are given in Table 4. Values of coefficients of determination (R^2) statistically measures how close the data are to the fitted regression line and the strength of the relationship between the model and a variable. The values of R^2 for the responses of pressure were also given in Table 4. The values of R^2 and adjusted R^2 were calculated as 0.9136 and 0.8272. Predicted R-squared is a measure of how well the model predicts a response value. It helps to determine the overfitting a regression model. An over fit model includes an excessive number of terms, and it begins to fit the random noise in the sample. A predicted R-squared that is distinctly smaller than R-squared is a warning sign for overfitting. It is computed as:

$$Pred.R^2 = 1 - \left[\frac{PRESS}{SS_{residual} + SS_{model}}\right] = 1 - \left[\frac{PRESS}{SS_{total} - SS_{curvature} - SS_{block}}\right] \quad \text{(Eq.2)}$$

PRESS is the “predicted residual sum of squares” for the model. A measure of how well a particular model fits each point in the design. The coefficients for a new model are calculated with one point “deleted”. The new model’s prediction is subtracted from the “deleted” observation to find the predicted residual.

This is done for each data point. The predicted residuals are squared and added together to form the PRESS. The Adjusted R-squared and Predicted R-squared should be within approximately 0.20 of each other to be in “reasonable agreement.” If they are not, there may be a problem with either the data or the model (23).

The Predicted R^2 of 0.7133 is in reasonable agreement with the adjusted R^2 of 0.8272; i.e. the difference is less than 0.2. These results indicated that the proposed equation was appropriate to evaluate the relationship of total gas volume with the input variables without overfitting.

Table 4. ANOVA results for total gas volume.

Source	F-value	p-value
Model	10.57	< 0.0001
A-time (min)	0.3525	0.5622
B-water volume (mL)	7.06	0.0188
C-weight of biomass (g)	116.63	< 0.0001
D-weight of catalyst (g)	0.2279	0.6405
AB	2.48	0.1380
AC	0.2745	0.6086
AD	13.41	0.0026
BC	0.0375	0.8492
BD	0.1197	0.7346
CD	0.6529	0.4326
A^2	1.54	0.2356
B^2	1.91	0.1884
C^2	0.6549	0.4319
D^2	1.41	0.2547
Lack of Fit	0.9076	0.5925
R^2	0.9136	
Adjusted R^2	0.8272	
Predicted R^2	0.7133	

The empirical model defining the relative impact of the input variables on total gas volume in terms of coded values is shown below;

$Y_1 = (349.2 – 11.5A – 51.8B + 209.6C – 9.26D + 52.9AB – 17.6AC – 123.1AD – 6.51BC – 11.6BD – 27.2CD + 32.7 A^2 – 36.5B^2 – 21.4C^2 + 31.4) \times D^2$ (Eq. 3)

where Y_1 represents the total gas volume. The factor coefficients give ideas about the relative effects of the factors on the desired response. The negative sign of a coefficient indicates that the increasing levels of the factor cause decreases in the desired response values whereas the positive sign means an increasing effect of the coefficient on the desired response in contrast.

According to ANOVA results, the Model F–value was 10.57 with a very low p value (<0.0001), which implied that the overall model is significant for the response of total gas volume. Hence, the model can be used to express the significance of the model parameters. P-values less than 0.0500 indicate model terms are significant, in this case B, C, AD are significant model terms. The model term “B” represents the initial water volume in the reactor and found to have a significant effect on total gas yield. The direction of the effect was found to be negative in equation 3 which means the increasing initial volumes of water used in the process will cause decreases in total gas volume obtained in the process. The direction of the individual effect of the water volume factor was graphically expressed by the one factor graph of total gas volume as a function of water volume in Figure 1(a). The pressure–temperature behavior of water in closed systems has been studied by Laudise (24). When the vessel was filled initially with water to less than 32% of the vessel capacity, the liquid level drops as the temperature increases because the liquid is lost, i.e. the water boils to dry. If the vessel is filled initially with water to 32%, the liquid level remains unchanged as the temperature rises. In the case of the loss of liquid to the vapor phase is exactly balanced by the liquid volume expansion. In a closed vessel filled more than 32% with water, the liquid will expand to completely fill the vessel at some temperature below the critical temperature. The higher the filling percentage, the lower the temperature at which the phase in the vessel becomes liquid (24). As the volume of water is increased, the volume of vapor decreases and the volume of liquid phase increase in the reactor. All these changes observed in the liquid-vapor phase levels of the system depending on the gasification conditions lead to changes in product distribution and gasification yields (20). Therefore, in a closed system, the vapor and its level In general, gas–gas and gas–solid reactions occur faster than liquid–liquid and liquid–solid reactions. In experiments where lower volumes of water were used, probably the gas–gas and gas–solid reactions are more likely to be more effective and the process becomes more efficient than the experiments in which higher volumes of water were used (20).

The other significant and effective model term “C” represents the weight of biomass to be gasified, and the positive sign of “C” in equation indicates that the direction of the effect is positive. Figure 1(b) also shows that the increased amount of biomass leads to an increase in total gas volume.

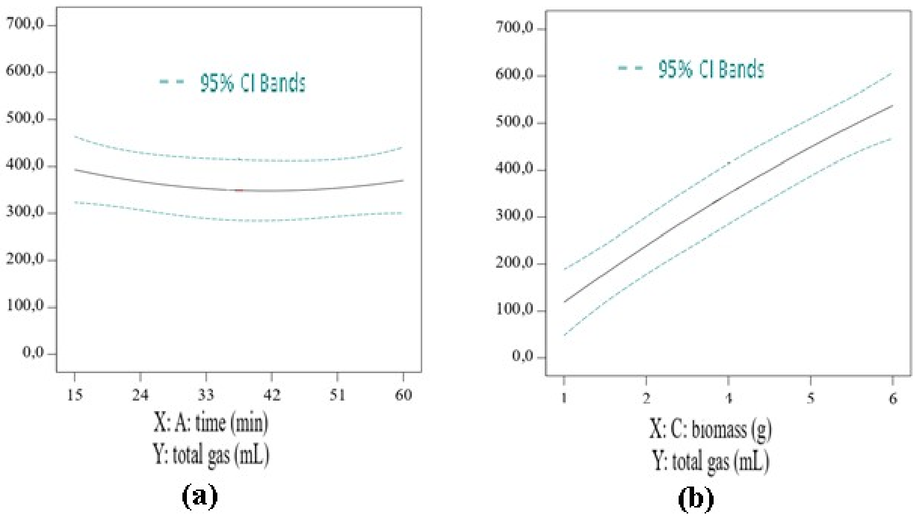


Figure 1. Total gas volumes (mL) as function of a) reaction time (min) b) biomass amount (g).

An interaction effect is the simultaneous effect of two or more independent factors on at least one desired response in which their joint effect is significantly greater (or significantly less) than the sum of the parts. Here, the significant term "AD" expresses the interaction effect between the residence time and amount of catalyst. As the coefficient factor of AD in equation is relatively higher, it can be said that this interaction affects the total gas production more than other factors. Also the direction of the effect is negative. To have more information about the effects of this interaction, the interaction graph (Figure 2(a)) and 3-dimensional (3D) response surface plots of total gas volume against residence time and catalyst amount (Figure 2(b)) can be examined.

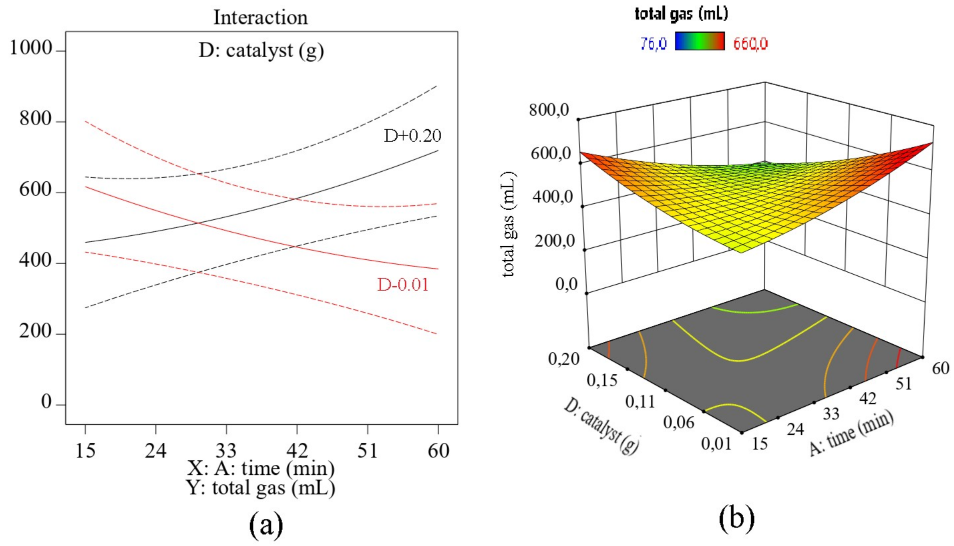


Figure 2. (a) Interaction graph of reaction time and catalyst amount (b) 3D response surface plot of total gas volume as function of catalyst amount and reaction time.

According to the information given by the interaction graphs, while the increase in the reaction times at the low levels of catalyst (D-0.01) caused a decrease in the total volume, the lower the reaction times and the higher the total gas volume production at higher catalyst amount levels (D+0.02). This result shows that the reaction time can be shortened by increasing the amount of catalyst, or the reaction times should be kept longer if a high amount of gas is desired by using lower amounts of catalyst. Since the reaction rate of hydrolysis in subcritical water is slower than that in supercritical water (25), it is difficult to gasify high molecular weight constituents of biomass such as cellulose and lignin. However, it is advantageous to gasify biomass in this temperature region since the input thermal energy would be low even though the gasification rate would be slow. This means that the role of the catalyst in low temperatures becomes important (7). Many catalysts such as nickel, ruthenium, palladium, platinum and rhodium have been examined and reported to be effective to increase the gasification performances at subcritical gasification conditions. (9).

Although the gaseous products formed after experiments are mixtures of H_2, CO_2, CO and CH_4, the major products are hydrogen and carbon dioxide, even CO_2 has the greatest ratio almost in all runs (37-71%). H_2 contents vary from 15% to 55% whereas the CO and CH_4 contents vary between 1% and 10%. No significant correlations between the process parameters and the CO and CH_4 contents of the product gas can be found, so only the effects of process parameters on hydrogen and carbon dioxide production will be evaluated in this study.

Effects of process parameters on H_2 yield and CO_2 production

The ANOVA results showing the significance of the process parameters and on hydrogen production and R^2 values are given in Table 5. The values of R^2 and adjusted R^2 were calculated as 0.9502 and 0.9003. The Predicted R^2 of 0.7681 is in reasonable agreement with the adjusted R^2. These results indicated that the proposed equation was appropriate to evaluate the relationship of hydrogen volume with the input variables.

Table 5. ANOVA results for hydrogen volume and carbon dioxide volume.

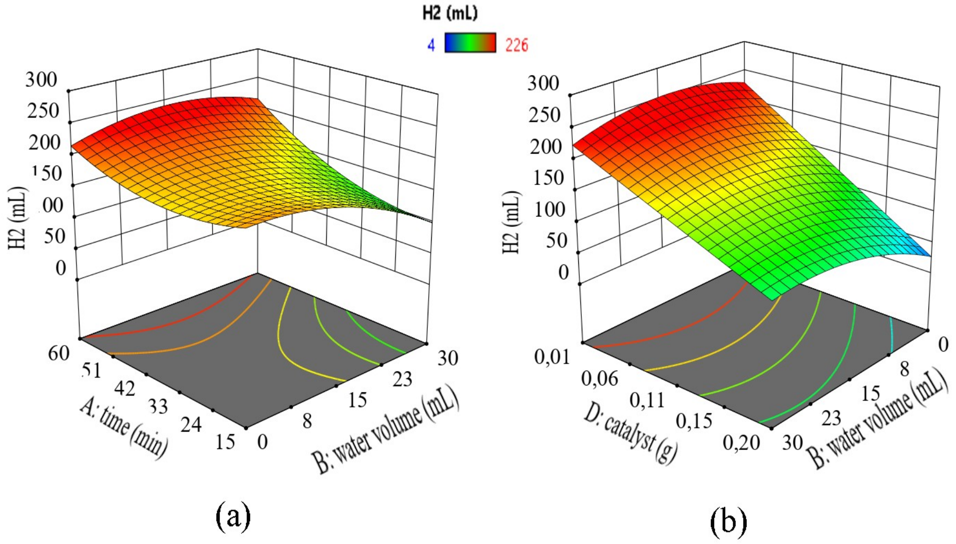
	H_2		CO_2	
Source	F-value	p-value	F-value	p-value
Model	19.06	< 0.0001	7.76	0.0002
A-time (min)	0.5294	0.4789	0.0341	0.8562
B-water volume (mL)	14.26	0.0020	1.93	0.1861
C-weight of biomass (g)	132.03	< 0.0001	94.36	< 0.0001
D-weight of catalyst (g)	37.55	< 0.0001	5.64	0.0324
AB	7.19	0.0179	0.0836	0.7767
AC	0.0617	0.8075	0.2734	0.6092
AD	15.76	0.0014	0.0609	0.8087
BC	3.48	0.0833	0.0176	0.8963
BD	4.70	0.0479	0.0036	0.9527
CD	10.13	0.0067	4.21	0.0593
A^2	16.78	0.0011	0.3073	0.5881
B^2	16.28	0.0012	1.31	0.2724
C^2	0.3967	0.5389	0.0217	0.8850
D^2	0.0002	0.9882	0.0093	0.9244
Lack of Fit	1.12	0.4985	0.6904	0.7116
R^2	0.9502		0.8858	
Adjusted R^2	0.9003		0.7717	
Predicted R^2	0.7681		0.5882	

The empirical model defining the relative impact of the input variables on hydrogen volume in terms of coded values is shown below;

$Y_2 = 96.6 + 3.6A – 18.6B + 56.2C – 30.1D + 22.8 AB + 2.1AC – 33.8AD + 15.9BC + 18.5BD – 27.1CD + 27.4A^2 – 27.0B^2 + 4.2C^2 + 0.1D^2$ (Eq. 4)

where Y_2 represents the hydrogen volume.

According to ANOVA B, C, D, AB, AD, BD, CD, A^2, B^2 are significant model terms on hydrogen production since the p-values are lower than 0.05. Water volume (B) was found to be effective on hydrogen production as water is one of the main actors of the hydrothermal process. The direction of the effect seems negative as the factor coefficient of B is negative in Eq. 3. Besides the main effect, water volume is also an interacting parameter the reaction time and catalyst amount, so the certain effect of the water volume factor should be evaluated in terms of so the effect of water volume on hydrogen production should be evaluated by taking into account these interactions. Figure 3(a) and (b) show the 3D surface plots of hydrogen volume as a function of water volume/reaction time and water volume/catalyst amount.



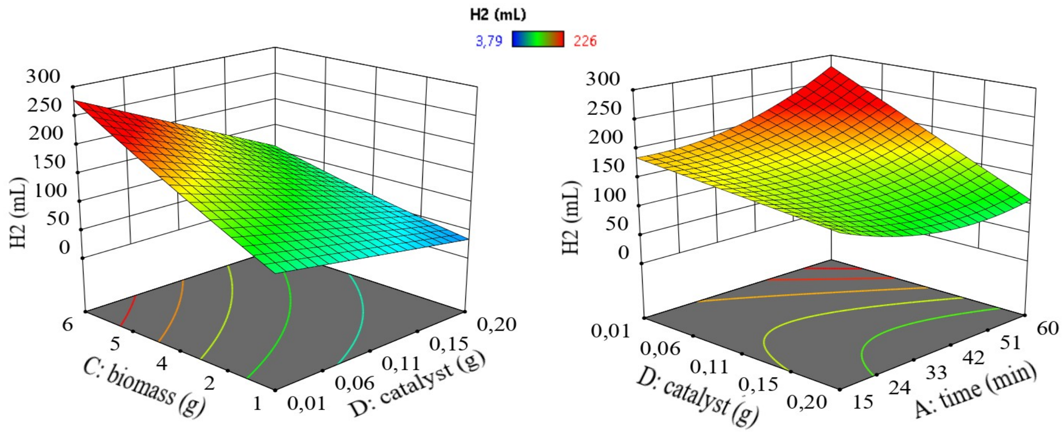
(a) (b)

Figure 3. 3D response surface plots of hydrogen volume as function of (a) reaction time (min)/water volume (mL); (b) catalyst amount (g)/water volume (mL).

The relationship between volume and reaction time from Figure 3(a) shows that the increase in hydrogen volume with the increasing reaction time is higher at the highest levels of water volume and reaction time is an effective parameter to reach higher yields of hydrogen. On the other hand, reaction time becomes less effective and there is no significant difference between the hydrogen volumes produced in any reaction time at the lower levels of water volume. This result may indicate that gasification reactions occur rapidly at low water volumes and the effect of the reaction period becomes insignificant. Thus reaction time for such conditions can be kept less provided that the water volume is reduced in order to achieve higher hydrogen yields.

Figure 3b shows the interactions of the water volume with the catalyst amount. It is seen from the figure that more hydrogen is produced at lower levels of catalyst. While the amount of water at the lower levels does not have a significant effect on the volume of hydrogen gas produced, the volume of hydrogen gas tends to increase slightly up to a level of water volume, but tends to decrease slightly after this level. The increase in the amount of catalyst results in a reduction in hydrogen production. Catalyst amount is a significant process parameter in terms of its main effect and negativity of the direction of this effect can also be seen in the Eq. 4 from the negative sign of the factor coefficient “D”. But the effect of water volume on hydrogen production becomes highly significant at higher amounts of catalyst, and in order to increase the volume of hydrogen gas at high levels of catalyst, the amount of water must also be increased. The $RuCl_3$ catalyst can be active on both the surface and in the interior of the biomass, contributing to the formation of more gaseous products and hydrogen, since it can be diffused into the interior of the biomass along with water via dissolution. The $RuCl_3$ catalyst is also efficiently dispersed in the interior of the biomass with water as more $RuCl_3$ is dissolved with an increasing volume of water at 250 °C. This provides a catalytic effect on both the surface and inside of the biomass leading to an increase in production of hydrogen other gas products.

The interaction effects of catalyst amount/reaction time and catalyst amount/biomass weight are also effective on hydrogen production. These effects can be evaluated from the 3D surface plots of hydrogen volume plotted against catalyst amount/reaction time and catalyst amount/biomass amount, which were shown in Figure 4 (a) and (b).



(a) (b)

Figure 4. 3D response surface plots of hydrogen volume as function of (a) biomass amount (g)/catalyst amount (g); (b) catalyst amount(g)/time.

It can be seen from Figure 4 (a) that at higher levels of catalyst amounts (D+0.20g), it is possible to obtain more hydrogen gas at shorter reaction times, but the volumes of hydrogen gas obtained are not as high as the lower levels of catalyst amounts even if the reaction times are shortened. At low catalyst amount levels (D-0.01g), the reaction time is highly effective on the process and the need to be extended to increase the produced hydrogen volumes. Figure 4 (b) shows an increase in the effect of the amount of catalyst on the process by increasing the amount of biomass in the reactor and higher volumes of hydrogen can be produced with increasing the biomass feed of the reactor at lower levels of catalyst amount. This is due to the fact that longer reaction times are required to complete the interaction of a certain amount of dissolved catalyst with the biomass, due to the lower mass ratio of catalyst/biomass.

The ANOVA results showing the significance of the process parameters and on carbon dioxide production and R^2 values are given in Table 4. The values of R^2 and adjusted R^2 were calculated as 0.8858 and 0.7717. The Predicted R^2 of 0.5882 is in reasonable agreement with the adjusted R^2. These results indicated that the proposed equation was appropriate to evaluate the relationship of hydrogen volume with the input variables. The empirical model defining the relative impact of the input variables on carbon dioxide volume in terms of coded values is shown below;

Y3 ={183.1+2.3A – 17.6B+122.7C – 30.0D + 6.3AB – 11.5AC – 5.4AD + 2.9BC – 1.3BD – 44.9CD - 9.5A}2 +19.62 -2.5 C2 – 1.7 (Eq. 3)

where Y3 represents the carbon dioxide volume. According to ANOVA results, biomass amount (C) and catalyst amount (D) are the significant parameters which are effective on produced CO_2 volume. The value of the factor co-efficient of C, which is relatively higher than the others, indicates that biomass concentration is highly effective on carbon dioxide volume. The direction of the effect is positive which means the increasing levels of biomass concentration will increase the produced carbon dioxide volumes. Biomass concentration has no interaction with the other factors as the model terms AC, BC and CD were found to be insignificant. The other variable, which has a significant effect on carbon dioxide production, is the catalyst amount. The factor coefficient of “D” in equation is negative indicating that the higher levels of catalyst amount will result in a decrease in carbon dioxide production. The carbon dioxide volume as function of amount of catalyst and amount of biomass is given in Figure 5.

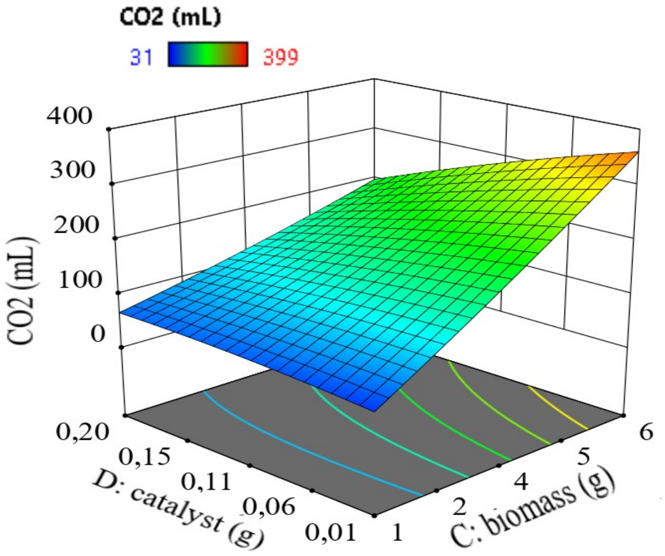


Figure 5. 3D response surface plots of carbon dioxide volume as function of catalyst amount (g)/ biomass amount (g).

Optimization of the process parameters for maximum hydrogen production

The main part of the study was to determine the optimum conditions for high hydrogen production from co–gasification of sorghum biomass and coal by supercritical water gasification under mild conditions. Desirability function and numerical optimization method were used to optimize the variables by targeting the maximum total gas and hydrogen volume. Figure 6 shows the desirability values at the end of the hydrogen volume maximization study, with the desirability value of 1.0 depending on the selected maximum total gas with a maximum hydrogen content goal for the variables. The optimum conditions for maximum hydrogen production were determined as residence time of 59.3 minutes, water volume of 10.5 mL with a catalyst amount of 0.02 g. The optimal parameter values were validated by experiments. The predicted and experimental values are given in Table 6. The 3D response surface plot of desirability as a function of coal percent and water volume is given in Figure 5.

The experimental results were close to those predicted. 985 mL total gas was produced including 253 mL H_2 (1.7 mmol H_2/g feedstock). Hydrogen selectivity is calculated from Eq. (4) as 36.9 %. The total feedstock conversion was found as 76.0 % (w/w). Feedstock conversion was calculated from Eq. (5).

$$Hydrogen\,selectivity=\frac{(moles\ of\ H_2)}{(total\ moles\ of\ H_2+CO_2+CO+CH_4)}\times 100$$

(Eq.4)

$$Conversion=[Total\ material\ loaded\ into\ the\ reactor\,(daf)-char]\times 100$$

(Eq.5)

The remaining liquid was also qualitatively analyzed by GCMS and was found to include mainly furfural (15.4 min) 2, 4-dimethylfuran (28.6 min), and phenol (24.9).

Table 6. The predicted and experimental values of optimized process parameters for maximum hydrogen production.

	Time (min)	Water volume (mL)	Biomass (g)	Catalyst (g)	Total gas (mL)	H_2 (mL)	CO_2 (mL)	CO (mL)	CH_4 (mL)	Desirability
Predicted	59.3	10.5	6.0	0.02	699	265	348	51	35	1
Experimental	59.0	10.5	6.0	0.02	685	253	335	51	46	

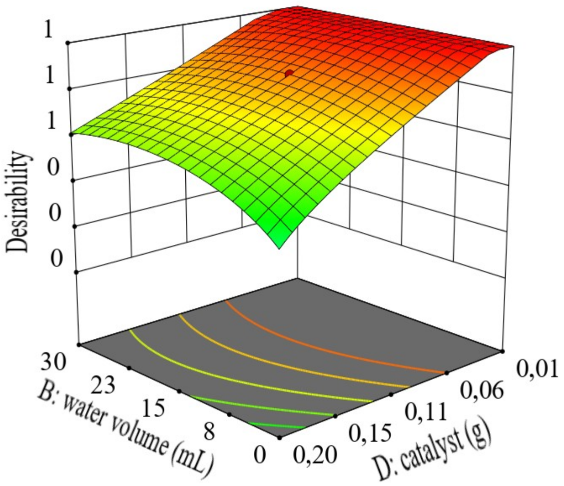


Figure 6. The 3D response surface plot of desirability function for maximum hydrogen volume against water volume (mL) and catalyst amount (g) at constant feedstock mass (6.0 g).

CONCLUSIONS

In this study, hydrothermal co–gasification of sorghum biomass is performed at a constant temperature of 250 °C in a batch type closed stainless-steel reactor. The individual and simultaneous effects of residence time (min), initial water volume (mL), feedstock amount (g) and catalyst amount on the responses of total gas volume, hydrogen yield and carbon dioxide production were evaluated by Box–Behnken design (BBD) combined with response surface modelling (RSM). The significance of the factors and their interactions were determined by Analysis of variance (ANOVA). It has been found that, in order to increase the total gas volume obtained from the process, the water volume should not be increased above a certain value. Also the reaction time can be shortened by increasing the amount of catalyst, or the reaction times should be kept longer if a high amount of gas is desired by using lower amounts of catalyst. The reaction time is to be kept low, the water volume must be reduced in order to achieve higher hydrogen yields. The effect of water volume on hydrogen production becomes highly significant at higher amounts of catalyst, and in order to increase the volume of hydrogen gas at high levels of catalyst, the amount of water must also be increased. The optimum conditions for maximum hydrogen production from 6.0 g of sorghum were determined as residence time of 59.3 minute, water volume of 10.5 mL with a catalyst amount of 0.02 g. At these conditions 76.0 % of biomass is converted to 685 mL total gas with 36.9% hydrogen selectivity.

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