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STATISTICAL DESIGN AND MODELING OF THE PROCESS OF SUGARCANE BAGASSE GASIFICATION IN SUPERCRITICAL WATER AND PREDICTION OF HYDROGEN YIELD

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Abstract

To optimize the hydrogen production from sugar cane bagasse gasification in supercritical water, this paper illustrates the application of statistical multivariate analysis and prediction through a multi-regression model, as well as the optimization of the processing parameters in the complex reaction process. This approach is advantageous, especially when experimental evaluation and optimization of a process is time consuming and expensive. By carrying out a finite number of experiments, statistical modeling in this work shows reasonable good prediction ability in terms of the hydrogen, methane, carbon monoxide and carbon dioxide yield. Moreover, not only the synergistic effects between reaction parameters are revealed, but also a comprehensive understanding of the whole production process over variation of all reaction parameters are allowed.

Keyword: Design of experiment; Multiple regression model; Supercritical water; Hydrogen production; sugar cane bagasse.

1. Introduction

Production of fuels from renewable resources has gained considerable attention during the past few years. Biomass is considered a future energy source because it is renewable, abundant, outside of the human food chain, and carbon neutral. Hydrogen from biomass is a fairly good source of energy due to high energy density by weight, inexpensive, clean and efficient properties of hydrogen [1-8].

Meanwhile variety of gasification process of biomass like pyrolysis, thermal gasification, and partial oxidation can produce hydrogen from biomass but their disadvantage such as intensive cost of dewatering or drying pretreatment steps and production of significant quantities of char made these processes less profitable for hydrogen production. However supercritical water gasification (SCWG) is a proper gasification method which can solve these problems because high-moisture-content biomass can be directly processed in supercritical water without additional drying steps [9-11]. In addition, sugarcane bagasse (SB) is among the principal agri-cultural crops cultivated in tropical countries. The annual world production of sugarcane is ~1.6 billion tons, and it generates ~279 million metric tons (MMT) of biomass residues (bagasse and leaves) [12]. SB and sugarcane leaves/trash (SL or ST) contain significant amount of cellulose and hemicellulose, which can be de-polymerized through chemical or enzyme cocktails into simple sugar monomers (glucose, xylose, arabinose, mannose, galactose, etc.) [13].

One of the important goal of chemical reaction engineering is to improve performance (res-ponse), varying the parameters (factors) that affect a chemical process. One factor at time method is the process that varies one factor while keep the other factors constant, consequently the response will improve with the respect to varied factor. For further improvement of response one should adjust the other factors. One factor at time method has some disadvantages. First in processes where many factors exist, it can be very challenging to thoroughly adjust total factors to arrive near global optimum. Second in this method it is important to assume that the interaction of factors would be the same at other setting for the fixed factors and

finally adjusting a given factor, the former optimal setting of another factor might not remain optimal under new conditions. Due to disadvantages of this model a more sufficient and scientific method is necessary to asses all the factors. Design of experiment (DOE) is a proper statistical method to solve this problem and achieve breakthrough improvements [14-16]. Investigation on entire range of each factor is unnecessary time consuming, prohibitively expensive and can be impossible in particular experiment manipulating just a fraction of experimental point that allow estimation with the maximum statistical confidence is the best way to simplify this process.

Statistical methods have been applied in the field of gasification process for hydrogen production, as can be found in quite a few studies [17-21]. The statistical design of experiment allows the investigation of the effects of several preparation variables and their synergetic effects possible though only a small number of experiments. However, the statistical method has not often been used to optimize the performance of a chemical process. Although a few studies [17-21] have used the approach of statistical design of experiment to optimize the reaction process there is a lot of study which have investigate the effect of parameters that affect hydrogen production with traditional method of one factor at time.

In this work, our intention is to build a statistical model to study hydrogen-enriched gas production from SB gasification in supercritical water by using the design of experiment method. The laboratory controllable factors are reaction temperature, SB-loading, reaction time, and water density. These factors were previously observed to significantly affect the hydrogen, methane, carbon monoxide and carbon dioxide yield [21]. However, it was difficult to determine from the experimental data how different parameters interact. Here, we propose to investigate the different effects of reaction parameters and reveal their interaction with emphases on the detailed description of the process of the statistical design and modeling, and to use the obtained statistical model to predict hydrogen production from SB gasification in supercritical water.

2. Experimental

2.1. Materials

SB was used as a source for biomass material. The biomass particles consumed for the experiments were achieved as shavings from Haft-Tappe Manufacturing placed at Haft -Tappe, Khuzestan province, Iran. Plants were dried, and all parts were used in the study. Dried biomass was ground to a particle size<150 micro meter in diameter. The relevant analytical data for SB biomass is given below. The CHNSO elemental analysis results showed that the carbon, hydrogen, oxygen, sulfur and nitrogen content of dry biomass were 58.1%; 6.45%; 34.57%, 0.19% and 0.69%, respectively.

2.2. Gasification of SB

The gasification reaction occurred inside a 316 stainless steel batch reactor with an internal volume of 6 ml (Fig. 1). Deionized water was loaded into the reactor before the bagasse, so its extension for the period of heating would promote mixing. No catalysts were used.

The amounts of SB and water loaded modified with the reaction environments to be used. As an initial point, the desired biomass concentration (gr) was used to determine the mass of bagasse that must be loaded into the reactor. The water loadings consumed in these experiments ranged from 6.5mL to 9.5mL, and the bagasse loadings ranged from 0.05 to 0.25 mg. Setting the reaction temperature caused to pressurized system.

Once being loaded, the reactor was sealed. SCWG was subsequently performed by submersing the sealed reactor in a preheated, isothermal molten salt bath that contains a mixture of potassium nitrate, sodium nitrate and sodium nitrite. The molten salt bath temperature was controlled using an electrical heater and a PID temperature controller. Temperature and pressure were measured using a K-type thermocouple and a pressure gauge after a given reaction time. The heat up time for the reactors is about 5 s. Reactions were performed for times ranging from 5 to 30 min.

After being detached from the molten salt bath, when the desired reaction time had passed, the reactors were placed in cool water bath. This step is planned to inhibit the water and other liquid products from entering the gas chromatographic column during gas sample collection.

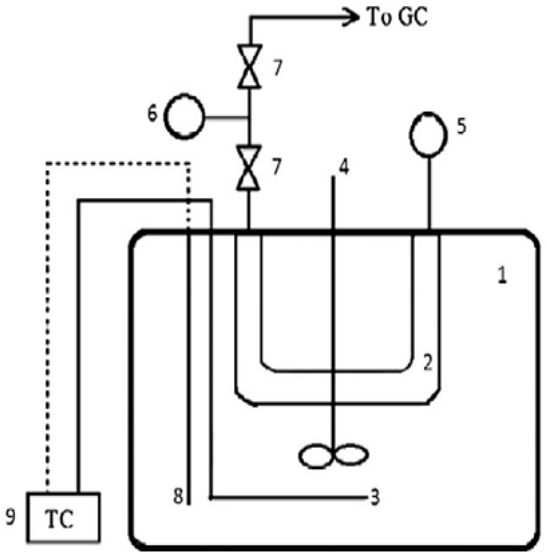

Fig. 1 Scheme of the homemade tube batch micro reactor: 1) molten salt bath, 2) batch tube reactor, 3) electrical heater, 4) mixer, 5) high pressure gauge, 6) low-pressure gauge, 7) high-pressure valve, 8) k-type thermocouple, and 9) PID temperature controller.

2.3. Gas analysis

To collect gas species formed during SCWG, The metal reactor was then connected to a gas sampling valve on a gas chromatograph (GC) equipped with TCD and FID detectors. We used helium as the carrier gas. Prior to the analysis of reaction products, the GC was calibrated with 10 commercial gas standards containing the components of interest in the range of concentrations observed during experiments.

2.4. Statistical design

From a previous study of Hydrogen rich gas production via non-catalytic gasification of SB in supercritical water media [21], four main factors, i.e., reaction temperature, SB-loading, water density, and reaction time, were quantitatively shown to strongly influence the gasification of SB in supercritical water in term of H_2, CO, CO_2 and CH_4. These main variables (reaction parameters) are all continuous (or quantitative) variables because they can be changed continuously in the laboratory. The inherent continuity of the reaction variables benefits model building and allows the resulting model to predict the responses in a coherent manner. The productivity of a chemical process may depend not only on the continuous variables but also on such categorical (or qualitative) variables as the type of reactors. However, these variables are out of the range of our current interest. The factors and their design ranges, as well as the responses of interest for this study, are listed in Table 1. Each individual variable is investigated over a wide range within laboratory experimental limit. Among the four responses H_2 production must be maximized however the production of CO, CO_2 and CH_4 are to be minimized. Between the last three responses that are to be minimized, the CO production is the most important for process design. This is because the production of hydrogen will increase when carbon monoxide undergoes in water gas shift reaction. In order to thoroughly reveal all of the effects and make a linear multiple regression model of the target process, all the linear and quadratic terms are used for each main effect, and all the two and three-factors interaction are also taken into account to incorporate the joint effects of two or three main variables on a dependent variable over and above their separate effects. The terms higher than order two are included for preciseness of the model. For some terms to be considered there may be no evidence that their effects are significant; however, those non-significant terms can be removed using backward elimination (the procedure of removing the least significant term from the maximum model successively to improve the model), resulting in an effective model comprising only the terms with statistical significant effects on the response. In order to build this model with four main variables, a set of experimental points with different factor settings were generated using a custom experimental design

with a commercial statistical software package JMP Version 10 (SAS Institute). The designed factor settings include a fraction of the combinations of the axial point and the end points of each variable, as shown for the *X* factors in Table 2. During the experiments, there may be some minor inconsistencies between the designed values and the actual measured experimental values of the variables. However, the correlation and model regression performed based on the actual values herein is not influenced by the experimental error (this might be called a "setting" error, i.e., it is not the error that results from measurement uncertainty) since the variables are all continuous. It is important to confirm that the variables have been subjected to a proper normalization by the JMP program in the form of

$$\frac{xi-(x\max+x\min)/2}{(x\max-x\min)/2}$$

where X_i is the actual variable value and the subscripts max and min stand for the maximum and minimum value of the variable range.

Table1 The process factors and responses

Process factor	Range
Temperature, X_1 (K)	400-520
SB-loading, X_2 (g)	0.05-0.25
Water density, X_3 (ml)	0.18-0.27
Time, X_4 (min)	10-30
Response	Goal
H_2 (Y_1) (mmol)	Maximize
CO_2 (Y_2) (mmol)	Minimize
CO (Y_3) (mmol)	Minimize
CH_4 (Y_4) (mmol)	Minimize

Table2.Custom design of experiment, including the main factors and the responses

run	X1	X2	X3	X4	Y1	Y2	Y3	Y4
1	400	0.05	0.18	5	0.58	0.83	0.42	0.19
2	400	0.05	0.18	30	0.62	1.23	0.17	0.4484
3	400	0.05	0.27	10	0.8	0.97	0.22	0.16
4	400	0.05	0.27	20	0.95	1.27	0.17	0.274
5	400	0.10	0.25	5	0.623	0.685	0.236	0.122
6	400	0.10	0.22	20	0.6977	1.014	0.118	0.232
7	400	0.20	0.22	30	0.587	0.766	0.1	0.131
8	400	0.25	0.18	5	0.4	0.614	0.188	0.048
9	400	0.25	0.18	30	0.428	0.9	0.078	0.112
10	400	0.25	0.27	5	0.54	1.027	0.129	0.036
11	400	0.25	0.27	30	0.57	1.52	0.054	0.085
12	440	0.05	0.22	5	0.766	1.166	0.45	0.224
13	440	0.10	0.27	30	0.786	1.2	0.102	0.19
14	440	0.20	0.18	20	0.68	0.98	0.085	0.14
15	440	0.25	0.25	15	0.51	0.89	0.122	0.11
16	480	0.05	0.25	20	1.2	1.4	0.06	0.199
17	480	0.10	0.18	10	0.847	1.1	0.095	0.123
18	480	0.20	0.27	5	0.57	0.87	0.11	0.056
19	480	0.25	0.22	30	0.46	0.76	0.098	0.068
20	520	0.05	0.18	5	0.858	1.54	0.58	0.28
21	520	0.05	0.18	30	0.91	1.95	0.24	0.778
22	520	0.05	0.27	5	1.14	1.75	0.398	0.27
23	520	0.05	0.27	20	1.45	2.1	0.23	0.479
24	520	0.20	0.22	20	0.9	1.7	0.128	0.42
25	520	0.25	0.18	5	0.85	0.962	0.26	0.07
26	520	0.25	0.18	30	0.95	1.26	0.11	0.11
27	520	0.25	0.27	20	1.05	2.1	0.06	0.475
28	520	0.25	0.27	30	0.99	2.3	0.0745	0.148

2.5. Response collection

After performing the 28 individual experiments with different factor settings, the yields of H_2, CO, CO_2, and CH_4 are collected, respectively, as listed for the *Y* responses in Table 2. The productions of these gases are defined as the amount of mmol gas produced in reactor.

3. Results and discussion

3.1. Statistical modeling

The data set is chosen with an even distribution across multiple variables; in other words, the level of the main variables chosen in the statistical design data set covers the whole range of possible scenarios in a well-proportioned manner. The broad distribution indicates that no factor setting in the experimental design is duplicated. Each of the experimental data is, therefore, considered to be significant to the modeling, i.e., each point equally contributes to the model on its own.

Multiple regression models may contain some variables whose *t* statistics shows non-significant *p*-value, which is the smallest level of significance that would lead to rejection of the null hypothesis, i.e., the significance level for testing the hypothesis that a parameter equals zero. It is reasonable to consider these variables as the ones that have not displayed statistically significant predictive capability when the other variables are present. Removing those variables simplifies or improves the regression. One approach for simplifying multiple regression equations is the stepwise procedure, including forward inclusion, backward elimination, and stepwise regression. In contrast to the forward inclusion or stepwise regression, backward elimination starts with all the possible predictor variables (effects) in the model and successively eliminates the least significant one based on the value of the *t*-ratio and/or the *p*-value. If the smallest absolute value of the *t*-ratio, which is the ratio of the estimate to its standard error, is less than a cut off value t_{out}, and/or the largest *p*-value is greater than a predetermined level such as 0.05 or 0.10, the variable associated with this *t*-ratio and/or *p*-value is eliminated and the model is refitted. Each subsequent step removes the least significant predictor variable until an unsatisfactory fit is encountered. As an alternative option to forward inclusion or stepwise regression, backward elimination has a distinct advantage, because the former two options will possibly miss some predictor variables due to suppressor effects-the predictor variable shows significant effect on the dependence only in the presence of other variables. When suppression is suspected, forward inclusion and stepwise regression will not be sufficient to identify those variables, since they have to be put into the model together in order to significantly show their joint predictive capability.

Fitting the maximum model with the combination of all the predictor variables was first performed to correlate the dependent variables (responses). The correlation of H_2 yield (Y_1 response) was first carried out, as it is the most important response and is considered as a superior measurement of the desirability of the reaction conditions. Initially, the complete fourth-order model was built by applying the common method of standard least squares using the JMP software. We tentatively assess the general view of how the variables, including all the main variables, and their quadratic terms, as well as their cross terms, affect the hydrogen yield (model 1). As described in our previous work [21], for example, the H_2 profile in terms of reaction temperature shows a quadratic (parabola) pattern, with the maximum H_2 yield shifting from low to high temperature. This phenomenon indicates that under the conditions studied in the SB gasification, certain main variables, i.e., temperature might be most likely to affect the H_2 yield in linear and forth-order manner. Thus, it is reasonable to initially include all of the fourth degree terms of the main variables while constructing the fourth-order model, and then eliminate the least significant ones. (The back elimination regression procedure is demonstrated in detail in Appendix A, for those who are not familiar with this statistical method) The restricted model (model 1 in Appendix A) with all the linear variables and only the significant nonlinear variables are generated by the back elimination procedure. Moreover, further approach to improve the model is performed by considering the whole effect, i.e., eliminating all the least significant variables with *p*-value larger than 0.1, resulting in a more uniform and reliable model (model 2 in Appendix A).

Some diagnostic statistics of model 3 are summarized in terms of actual H_2 yield (Y_1) versus predicted H_2 yield in Table 3. The predicted model covers a wide range of predictions from

0.4 to 1.45 for H_2 yield. The size of the random noise, as measured by the root mean square error (RMSE), is only 0.0955, which is more than an order of magnitude, smaller than the range of predictions. This is strong evidence that the model has good predictive capability. The *R*-square indicates that 94% of the variation in the response can be absorbed by fitting the model

Table3 R-square & RMSE of backward eliminated models

Response	R-square	RMSE(root square error)
Y_1 (H_2 yield)	0.936021	0.095493
Y_2 (CO2 yield)	0.957713	0.156775
Y_3 (CO yield)	0.969044	0.035168
Y_4 (CH_4 yield)	0.919815	0.111654

By applying the same backward elimination method to the CO production (Y_2), CO_2 yield (Y_3), CH_4 yield as used in the regression of H_2 yield (Y_1), only variables that are significant to the dependent variables remain in the model (refer to Table A.3, Table A.4, and Table A.5 of Appendix A). The *R*-square of the regression of $Y_{2,3,4}$ are 0.96, 0.97, and 0.92, representing a model with high quality. The simplified prediction formula derived from model 2 for H_2 yield (Y_1), CO yield (Y_2), CO_2 yield (Y_3), CH_4 yield (Y_4) are listed as follows, where the *X*, *Y* variables are defined in Table 1. Since the main variables are subjected to a standard scaling process, the final form of each variable is in the form of $a(X_i - b)/c$ (where $b = (X_{max} + X_{min})/2$; $c = (X_{max} - X_{min})/2$), where "a" represents the coefficient having a physical meaning. However, in the prediction formula, only the overall coefficients are shown for simplification. Note that some of the main variables, e.g., X_2 and X_3 in the regression of Y_1, which are eliminated from the stepwise process, are derived from the interaction terms and/or quadratic terms with *X* variables in their standardized forms.

$$Y_1=0.7568+0.1835X_1-0.129X_2+0.0708X_3-0.2033X_3-0.0157X_1X_2+0.0387X_4X_1-0.1032X_4X_3+0.0145X_2X_4+0.0145X_2X_4-0.0546X_3X_4-1.2633X_4^3+0.0399X_1X_4X_3-0.0546X_1X_2X_3-0.0156X_4^3+0.0816X_1^4+0.0736X_3^4-0.1359X_4^4 \quad (1)$$

$$Y_2=1.5212+4.26X_1+0.416X_3+0.416X_4+0.7828X_2+0.2176X_1X_3+0.2171X_4X_3+0.0664X_1X_2+0.1211X_2X_3+0.1887X_4X_1+0.3351X_4^2-0.443X_3^2+0.136X_2^2+3.89X_1^3-1.24X_2^3-0.6589X_2^3 \quad (2)$$

$$Y_3=4.3066+1.8529X_1-0.6561X_3+1.9927X_2-0.4483X_2X_3-0.9542X_4X_2+0.7136X_4X_1+1.8882X_4^2-0.7814X_3^2-3.0047X_2^2-1.4402X_2^2-0.3819X_1X_4X_2-0.5182X_2X_4X_3-0.4459X_1X_2X_3 \quad (3)$$

$$Y_4=1.7869+0.4818X_1+0.1431X_3+0.3289X2+0.8011X_1X_3+0.079X_4X_3+0.0326X_4X_2+0.045X_2X_3-0.3846X_4X_1+0.2912X_1^2-0.3351X_4^2+0.443X_3^2+3.89X_1^3-1.24X_4^2+0.0807X_2^3-0.0925X_2^3+0.0457X_1X_4X_2+0.0434X_2X_4X_3+0.0807X_1X_2X_3+0.09X_1X_4X_2X_3 \quad (4)$$

By using the prediction formulas above, the yield value of the H_2, CO, CO_2 and CH_4 can be quantitatively determined at any combination of factor settings in the range shown in Table 1. The prediction profiler of H_2 yield generated by the JMP software shows that high temperature, water density, and low SB-loading favors H_2 yield. The predictions further indicate that by using a high reaction time, a high yield of H_2 is expected to be achieved with high efficiency. By the model prediction, similar levels of optimal H_2 production could be obtained by either high water density which was confirmed by our previous study [21].

As opposed to the prediction for H_2 yield, CO production is favored by low temperature, high SB, and low water density. The desirable setting of temperature, SB loading and water density are opposite to the optimal setting for H_2 yield, which corroborate water gas shift reaction for the gasification of bagasse. Hence, in order to increase the hydrogen production, one has to choose the factor settings that are unfavorable to high CO yield.

3.2. Evaluation experimental parameters effect on hydrogen yield

Based on these modeling functions, for a given factor setting, the hydrogen yield response can be predicted qualitatively and quantitatively. In order to evaluate the predictability of the statistical model 2, direct comparison was performed between the experimental data and the predicted values.

The prediction profiler generated by the JMP software shows that at different setting of temperature, water density, reaction time, and SB-loading, the hydrogen yield exhibits a maximum in the temperature range studied, and the temperature of the maximum hydrogen yield is observed to shift from high to low temperature with increase of the SB-loading. This phenomenon was previously observed from experimental results [21]. The comparison of the hydrogen yield as a function of temperature between predicted value and the experimental results under the same reaction conditions are shown with a contour graph in Fig. 2. The hydrogen yield predicted by the model shows a similar density with the experimental results. The difference of the absolute value of hydrogen yield is very small therefore this observation suggests that the model built with the 28 design factor settings can not only predict the hydrogen yield qualitatively but also quantitatively.

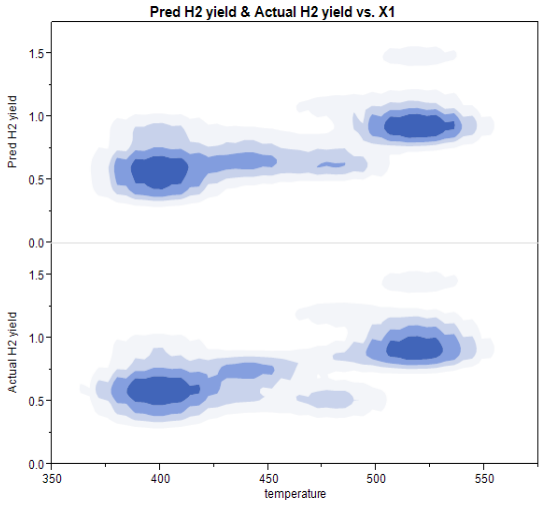

Fig. 2 Comparison of the actual and model predicted hydrogen yield vs. temperature

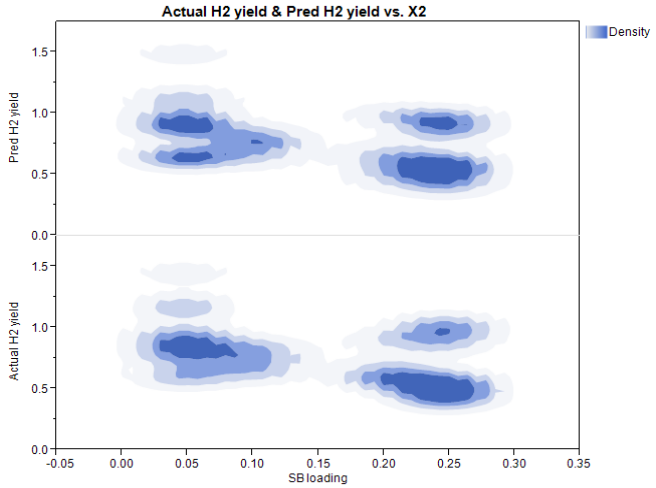

Fig. 3 Comparison of the actual and model predicted hydrogen yield vs. SB-loading

The hydrogen yield with different reaction time, water and SB-loading are also compared between predicted and actual results. As shown in Fig 3, 4, 5 the density and even the values of the predicted hydrogen yield are in good accord with the experimental data. This result further demonstrates that our model is reasonably good at predicting the hydrogen yield qualitatively and quantitatively.

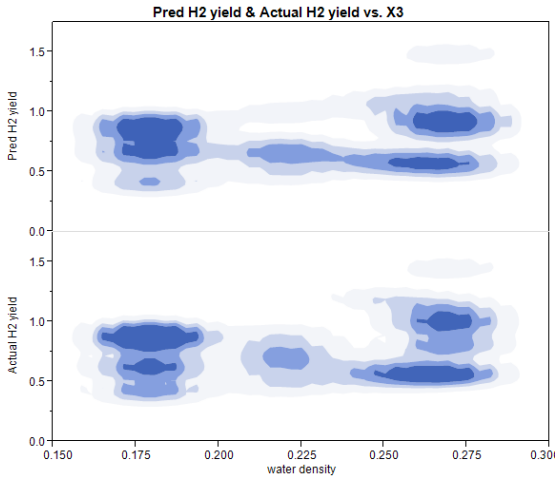

Fig. 4 Comparison of the actual and model predicted hydrogen yield vs. water density

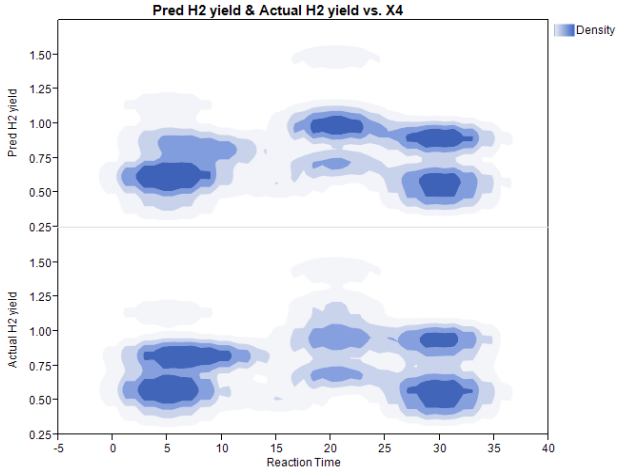

Fig. 5: Comparison of the actual and model predicted hydrogen yield vs. Reaction time

3.3. Evaluation experimental parameters effect on other gaseous products (CO_2, CH_4, etc.) yield

CO_2 was the second main gas product formed at different operating factors of SCWG of SB. The predicted profiler created by JMP software illustrated positive t-Ratio for temperature and SB loading which means high temperature and SB loading will increase amount of CO_2 yield however the t-Ratio of water density in predicted profiler for CO_2 yield was negative as a result high water density will minimize the amount of CO_2 yield.

Fig. 6 displays the CO_2 content and predicted CO_2 yield as a function of SB loading, temperature, and water density. As shown in Fig. 6 actual CO_2 yield and predicted CO_2 yield have similar area of density therefore the model is properly good for predicting CO_2 yield quantitatively.

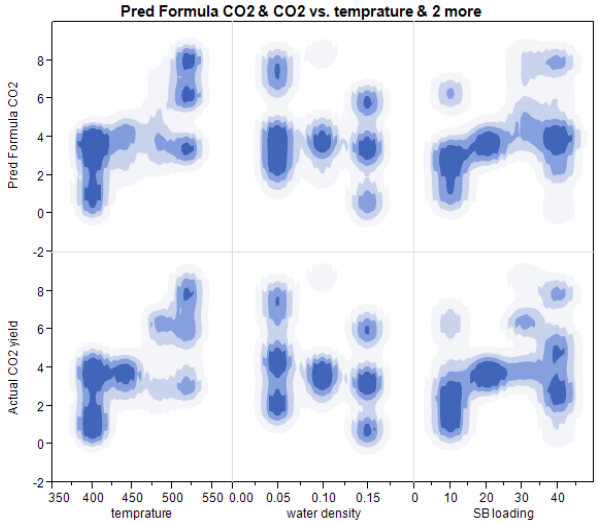

Fig. 6 Comparison of the actual and model predicted CO_2 yield vs. temperature, water density, SB-loading.

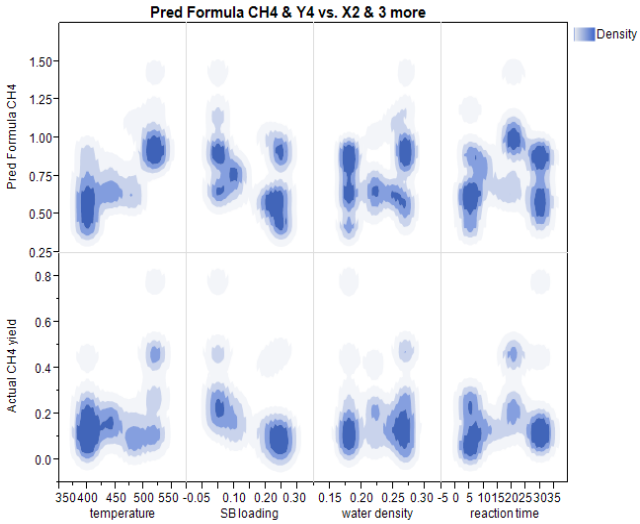

Fig. 7 Comparison of the actual and model predicted CH_4 yield vs. temperature, water density, SB-loading.

It was also observed that the CH_4 yield was lower than the other gaseous products in all SCWG of SB [21]. The experimental results revealed that CH_4 yield increases by increasing temperature. High operating temperature (520°C) led to a high amount of methane formation. CH_4 formation occurs via reaction of H_2 and CO through the following reactions:

$$\text{Methanation:}\quad CO + 3H_2 \rightarrow CH_4 + H_2O$$

$$\text{Hydrogenation:}\quad CO + 2H_2 \rightarrow CH_4 + 1/2O_2$$

The prediction profiler produced by the JMP software showed that at different setting of temperature, water density, and SB-loading, the methane yield exhibits variety response in the factors range studied. Hence, in order to increase the hydrogen production, one has to choose the factor settings that are unfavorable to high CH_4 yield. The comparison of the CH_4 yield as a function of temperature, water density, and SB loading between predicted value and the experimental results are shown with a contour graph in Fig 7. As demonstrated in Fig. 7 the model is fairly good for predicting CH_4 yield quantitatively.

The other important gas species produced through SCWG of SB was CO. Predicted profiler produced by the JMP software introduces temperature (t-Ratio=-8.83) and water density (t-Ratio=-4.63) as important factor for CO yield. The t-Ratio for these two factors is negative which means high temperature and water density can decrease CO yield with water gas shift reaction as illustrated in previous work [21]. Hence manipulating water density and temperature is extremely important to minimize CO yield with water gas shift reaction. The comparison of the CO yield as a function of time, temperature, water density, and SB loading between predicted value and the experimental results are shown with a contour graph in Fig. 8. As demonstrated in Fig. 8 the model is fairly good for predicting CO yield quantitatively.

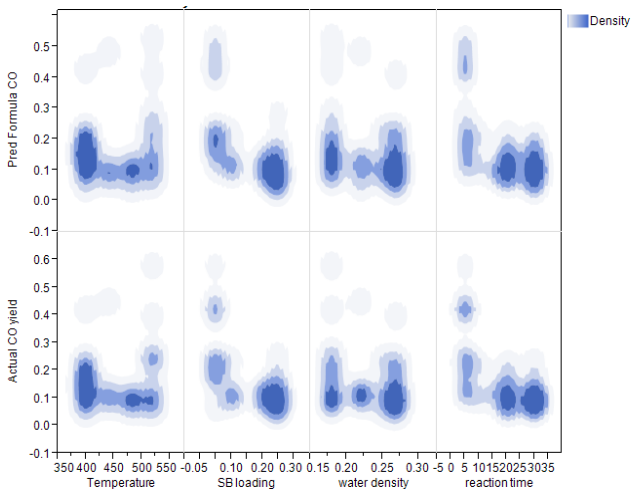

Fig. 8 Comparison of the actual and model predicted CO yield vs. temperature, water density, SB-loading and reaction time.

4. Conclusion

Quantitative models based on four independent variables that significantly influence the hydrogen yield, were developed and improved by a backward elimination method. The results of the modeling of hydrogen yield (Y_1) demonstrated that temperature, water density, and SB-loading are the three most significant factors affecting the hydrogen yield. The relative values and the signs of the *t*-ratio estimate the degree and direction of the effects. The models for the methane yield, carbon dioxide and carbon monoxide yield were built in a similar way. The predictability of the model was tested by comparison of the experimental results and the predicted results using the model. Fairly good agreement was obtained for the hydrogen, carbon dioxide, carbon monoxide and methane yield. The outstanding prediction of the model based on only 28 experimental runs proves that it is practicable to achieve a statistical model through design of experiment approach. By doing this, one can possibly avoid the time-consuming procedure of data collection, especially when a large number of reaction parameters are considered in a chemical process, and scientifically predict the optimal conditions and best results. Furthermore, the global understanding of the whole scenario by variation of the processing parameters allows the generation of new ideas which may facilitate the commercialization process.

5. Appendix A. Backward elimination of statistically insignificant factors

The regression results include the estimated coefficient, standard error, t-ratio, and p-value of each variable of model 1 for hydrogen yield (Y1) as shown in Table A.1. In this model, we get a first impression by considering the parameter estimates, their t-ratios and p-values. The relative value of the estimated coefficient of each variable estimates the average amount of the dependent variable changes when the independent variable changes by one unit with all the other variables constant. The sign of the coefficient represents, on average, the direction of the change while fixing the other variables, e.g., an increase in temperature, reaction time, and water density improves the hydrogen yield, among which temperature and reaction time has the most significant effect; while an increase of the SB-loading decreases the hydrogen yield.

The standard error is the standard deviation of its sampling distribution. It gives some idea of the precision of estimation. Generally, the value of a coefficient or a standard error has little practical use; however, it becomes meaningful when it is used to calculate the *t*-ratio, which is the ratio of the estimate to its standard error. The estimated coefficient of any variable with a larger *t*-ratio (positive or negative) thus infers which variables are more relatively and statistically significant in the regression.

In model 1, it was observed that not all the variables are significant to the regression. Only the variables of temperature, reaction time, SB loading, water density, temperature× temperature× temperature× temperature, time× time× time, temperature × water density

× reaction time, temperature× SB loading × water density, SB loading × reaction time and water density× water density× water density associate with relatively large *t*-ratios (|*t*-ratio|>0.5|). A *t*-ratio is usually small if there is no influence of the corresponding variables. Alternatively, this is also reflected in the *p*-value, e.g., the smaller the *p*-value is, the more convincing the evidence is that the null hypothesis is false, and the more significant the effect of the independent variable to the dependent variable is

Table A.1 The parameter estimates of the regression of Hydrogen production (Y1) for model 1.

Term	Estimate	Standard error	t-Ratio	p-Value
Intercept	0.750675	0.089223	8.41	0.0011
X1(400,520)	0.184094	0.197779	0.93	0.4046
X2(0.05,0.25)	-0.11895	0.185074	-0.64	0.5554
X3(0.18,0.27)	0.156866	0.282251	0.56	0.608
X4(5,30)	0.218732	0.292538	0.75	0.4962
X1*X2	-0.01468	0.044007	-0.33	0.7554
X1*X3	0.000378	0.047495	0.01	0.994
X1*X4	0.037018	0.054196	0.68	0.5321
X2*X3	-0.05953	0.041141	-1.45	0.2214
X2*X4	0.02102	0.056264	0.37	0.7277
X3*X4	0.037319	0.050308	0.74	0.4994
X1*X2*X3	-0.05496	0.045317	-1.21	0.2919
X1*X2*X4	0.004732	0.057258	0.08	0.9381
X1*X3*X4	0.039067	0.056972	0.69	0.5306
X2*X3*X4	0.011832	0.059592	0.2	0.8523
X1*X2*X3*X4	0.007461	0.058101	0.13	0.904
X1*X1*X1	-0.00399	0.206906	-0.02	0.9855
X2*X2*X2	-0.01025	0.198287	-0.05	0.9612
X3*X3*X3	-0.09097	0.286381	-0.32	0.7666
X4*X4*X4	-0.17087	0.3033	-0.56	0.6033
X1*X1*X1*X1	0.0793	0.091221	0.87	0.4337
X2*X2*X2*X2	-0.00065	0.086476	-0.01	0.9943
X3*X3*X3*X3	0.080379	0.091536	0.88	0.4295
X4*X4*X4*X4	-0.1369	0.079728	-1.72	0.1611

In the following backward elimination procedure, we remove the least significant variable for the second-order terms, i.e., the one with the largest *p*-value accompanying small *t*-ratio, in a two-at-a-time manner and refit the model. This process takes five steps (Table A.2), which eliminates the variables temperature × water density, temperature × temperature × temperature, SB loading × SB loading × SB loading, temperature × reaction time × water density× SB loading, reaction time × water density × SB loading, temperature ×reaction time × SB loading, resulting in an improved model (model 2) with all the main variables and only the significant second-order variables.

Among the main variables in model 2 as shown in Table A.2, the *t*-ratios of temperature, water density, SB loading and reaction time are fairly large, which indicates that these main factors are heavily weighted in affecting the hydrogen yield. Generally, as confirmed by previous work [21], the increase of both the temperature and water density improves the hydrogen yield, in which, temperature appears to have more significant effect; the increase of SB loading will decrease the hydrogen yield because of the negative value of t-Ratio also it seems the increase of water density will increase hydrogen yield which can be related to water gas shift reaction.

Table A.2. Backward elimination to build model 2

	1 (model 1)		2		3		4		5 (model 2)	
Term	t-ratio	p-Value	t-ratio	p-Value	T-ratio	p-Value	T-ratio	p-Value	T-ratio	p-Value
Intercept	8.41	0.0011	10.81	<.0001	12.56	<.0001	14.06	<.0001	16.38	<.0001
X1(400,520)	0.93	0.4046	1.15	0.2954	6.30	0.0002	7.40	<.0001	8.28	<.0001
X2(0.05,0.25)	-0.64	0.5554	-0.80	0.4549	-4.92	0.0012	-5.49	0.0003	-5.95	<.0001
X3(0.18,0.27)	0.56	0.608	0.70	0.5130	0.82	0.4384	0.89	0.3934	3.27	0.0068
X4(5,30)	0.75	0.4962	0.98	0.3669	1.21	0.2600	1.41	0.1877	1.42	0.1800
X1*X2	-0.33	0.7554	-0.41	0.6945	-0.48	0.6444	-0.55	0.5945	-0.63	0.5375
X1*X3	0.01	0.994								
X1*X4	0.68	0.5321	0.85	0.4260	0.98	0.3543	1.18	0.2662	1.36	0.2001
X2*X3	-1.45	0.2214	-1.77	0.1264	-2.06	0.0734	-2.29	0.0448	-2.51	0.0275
X2*X4	0.37	0.7277	0.50	0.6372	0.58	0.5769	0.64	0.5356	0.53	0.6028
X3*X4	0.74	0.4994	0.91	0.3966	1.12	0.5	1.24	0.2437	1.41	0.1826
X1*X2*X3	-1.21	0.2919	-1.51	0.1818	-1.74	0.1197	-1.95	0.0795	-2.12	0.0557
X1*X2*X4	0.08	0.9381	0.11	0.9167	0.11	0.9143				
X1*X3*X4	0.69	0.5306	0.85	0.4299	0.97	0.3584	1.18	0.2640	1.31	0.2138
X2*X3*X4	0.2	0.8523	0.26	0.8016	0.31	0.7641	0.34	0.7382		
X1*X2*X3*X4	0.13	0.904	0.17	0.8717	0.18	0.8592				
X1*X1*X1	-0.02	0.9855	-0.03	0.9806						
X2*X2*X2	-0.05	0.9612	-0.06	0.9508						
X3*X3*X3	-0.32	0.7666	-0.40	0.7050	-0.46	0.6608	-0.48	0.6395		
X4*X4*X4	-0.56	0.6033	-0.73	0.4912	-0.93	0.3815	-1.10	0.2989	-1.07	0.3062
X1*X1*X1*X1	0.87	0.4337	1.10	0.3122	1.28	0.2365	1.42	0.1867	1.77	0.1015
X2*X2*X2*X2	-0.01	0.9943								
X3*X3*X3*X3	0.88	0.4295	1.14	0.2977	1.33	0.2216	1.52	0.1597	1.53	0.1526
X4*X4*X4*X4	-1.72	0.1611	-2.13	0.0774	-2.48	0.0384	-2.77	0.0199	-3.03	0.0104
r-square	0.9387109795		0.9387090281		0.9386621367		0.9383952016		0.9360155578	
r-square adjusted	0.5862991115		0.7241906264		0.7929847114		0.8336670443		0.8560350051	

However, the main variables may not affect the response alone in a linear manner, their influence may also be reflected in a quadratic manner, as shown for the large *t*-ratios of the quadratic variables, e.g., *temperature* × *temperature*× *temperature*× *temperature*, and *reaction time* × *reaction time*× *reaction time*× *reaction time*. Especially for the case of water density, which is not as significant as the other main variables in the regression due to the relatively large *p*-value (>0.1) and small *t*-ratio, but which can affect the response negatively and significantly in the form of water density × water density × water density× water density

In most cases, two main variables might interact with each other at levels that affect the response, i.e., the response to one variable varies at different levels of another variable. These interaction effects are reflected in the cross terms in model 2 (see column 5 of Table A.2). SB loading related interaction terms, e.g., SB loading ×water density× temperature, SB loading ×water density, have the most significant effect on the dependent variable, hydrogen yield, which indicates that the effect of temperature on this dependent variable is also dependent on the value of SB-loading, reaction time, and water density, and vice versa.

The interaction terms act as moderator variables which moderate the original relationship of the main variables. In other words, the effect of one variable on the response will differ at different levels of the other variables which interact with the first variable. All the *T-ratio* of the forth-order variables in model 2 are more than |>1.5|, which means they are all significant. Among these independent variables, *forth order of reaction time* has the smallest *p*-value (0.0104), which indicates the most significant variable to the response.

As an indicator of how well the model fits the data, the value of *R*-square estimates the proportion of the variation in the response around the mean that can be attributed to terms in the model rather than to random error [27]. *R*-square equals one when there is a perfect fit (the errors are all zero). Backward elimination of the variables with large *p*-value step by step slightly decreases *R*-square as shown in table A.2. However, the decrease of *R*-square value does not mean the decline of the goodness of fit, for the reason that *R*-square tends to overestimate the predictability of a model, especially for the case with more than one independent variable. The value of *R*-square usually increases as additional variables are incorporated into a regression, even though the new variables have no additional predictive capability. As another version of *R*-square that is adjusted by the degree of freedom in its computation, the adjusted *R*-square is more comparable over models with different numbers of predictors [27], and is generally considered to be a more accurate measure than *R*-square. In Table A.2, adjusted *R*-square is only slightly smaller than *R*-square, especially after the elimination of several insignificant variables, which likely means that no explanatory variables are missing for the fit of the model.

Table A.3. The parameter estimates of the regression of CO_2 yield (Y2) for model 2**.**

Term	Estimate	Standard error	t-Ratio	p-Value
Intercept	1.0343280615	0.0846991867	12.21	<.0001
X1(400,520)	-0.044103352	0.1886643143	-0.23	0.8199
X2(0.05,0.25)	-0.122449541	0.0354047498	-3.46	0.0061
X3(0.18,0.27)	-0.077171469	0.2557174223	-0.30	0.7690
X4(5,30)	0.7029958376	0.2492102373	2.82	0.0181
X1*X2	-0.091478009	0.0415236055	-2.20	0.0522
X1*X4	0.0691637395	0.0478970416	1.44	0.1793
X2*X3	0.1531183323	0.0387404376	3.95	0.0027
X2*X4	0.0974416881	0.0494222807	1.97	0.0769
X1*X3*X4	0.0661453829	0.0506294341	1.31	0.2206
X2*X3*X4	0.1264854486	0.0525346547	2.41	0.0368
X1*X1*X1	0.3584439264	0.1947785792	1.84	0.0956
X3*X3*X3	0.2168943185	0.2592386125	0.84	0.4223
X4*X4*X4	-0.556806995	0.2550412632	-2.18	0.0540
X1*X1*X1*X1	0.1731574959	0.083814952	2.07	0.0657
X2*X2*X2*X2	0.0649107494	0.0814069863	0.80	0.4438
X3*X3*X3*X3	0.2243651155	0.0844806439	2.66	0.0241
X4*X4*X4*X4	-0.195952179	0.0733915513	-2.67	0.0235

The back elimination method has also been used for CO_2 yield (Y_2) CH_4 yield (Y_3), CO yield (Y_4), by considering the overall effect without restriction. The parameter estimates are shown in Table A.3, Table A.4, and Table A.5.

Table A.4. The parameter estimates of the regression of CO yield (Y3) for model 2.

Term	Estimate	Standard error	t-Ratio	p-Value
Intercept	0.0792306861	0.0187479631	4.23	0.0012
X1(400,520)	-0.185757721	0.0423619518	-4.39	0.0009
X2(0.05,0.25)	-0.02711135	0.0367969483	-0.74	0.4754
X3(0.18,0.27)	-0.099154315	0.0589200996	-1.68	0.1182
X4(5,30)	-0.083425498	0.0087570339	-9.53	<.0001
X1*X4	-0.014732722	0.0096404408	-1.53	0.1524
X2*X4	0.0229618715	0.0102914601	2.23	0.0455
X3*X4	0.017285338	0.0099729069	1.73	0.1086
X2*X3*X4	-0.018562893	0.0109827226	-1.69	0.1168
X1*X1*X1	0.2207496688	0.0434962624	5.08	0.0003
X2*X2*X2	-0.053006191	0.0389263123	-1.36	0.1983
X3*X3*X3	0.0766793654	0.0595308438	1.29	0.2220
X1*X1*X1*X1	0.046393059	0.0172680232	2.69	0.0198
X2*X2*X2*X2	0.0689993978	0.0181848608	3.79	0.0026
X3*X3*X3*X3	-0.048670909	0.0178723769	-2.72	0.0185
X4*X4*X4*X4	0.0863242423	0.0161386802	5.35	0.0002

Table A.5.The parameter estimates of the regression of CH_4 yield (Y4) for model 2.

Term	Estimate	Standard error	t-Ratio	p-Value
Intercept	0.7698205072	0.0547894663	14.05	<.0001
X1(400,520)	0.1636639187	0.1347425218	1.21	0.2499
X2(0.05,0.25)	-0.125567898	0.025106766	-5.00	0.0004
X3(0.18,0.27)	0.1500410767	0.176102168	0.85	0.4124
X4(5,30)	0.0451761265	0.0273989476	1.65	0.1274
X1*X3	0.0130262914	0.0279316934	0.47	0.6501
X2*X3	-0.057353375	0.027596878	-2.08	0.0619
X2*X4	-0.004327255	0.0301769153	-0.14	0.8886
X3*X4	0.0371489708	0.0301698934	1.23	0.2439
X1*X2*X3	-0.042915876	0.02883721	-1.49	0.1648
X1*X2*X4	0.0063863181	0.0329354032	0.19	0.8498
X1*X3*X4	0.0161114336	0.0325279281	0.50	0.6301
X1*X1*X1	0.0300397041	0.1380863694	0.22	0.8318
X3*X3*X3	-0.077653176	0.1787918015	-0.43	0.6725
X1*X1*X1*X1	0.1149504324	0.0524925886	2.19	0.0510
X2*X2*X2*X2	0.0248030601	0.0552303115	0.45	0.6621
X4*X4*X4*X4	-0.130657229	0.0516879666	-2.53	0.0281

References

[1] Ghosh, D., Hallenbeck, P.C., 2010. Response surface methodology for process parameter optimization of hydrogen yield by the metabolically engineered strain Escherichia coli DJT135. Bioresour. Technol. 101, 1820–5.

[2] Li, L., Xu, Z.R., Zhang, C., Bao, J., Dai, X., 2012. Quantitative evaluation of heavy metals in solid residues from sub- and super-critical water gasification of sewage sludge. Bioresour. Technol. 121, 169–75.

[3] Azadi, P., Farnood, R., 2011. Review of heterogeneous catalysts for sub- and super-critical water gasification of biomass and wastes. Int. J. Hydrogen Energy 36, 9529–9541.

[4] Guo, Y., Wang, S.Z., Xu, D.H., Gong, Y.M., Ma, H.H., Tang, X.Y., 2010. Review of catalytic supercritical water gasification for hydrogen production from biomass. Renew. Sustain. Energy Rev. 14, 334–343.

[5] Tanksale, A., Beltramini, J.N., Lu, G.M., 2010. A review of catalytic hydrogen production processes from biomass. Renew. Sustain. Energy Rev. 14, 166–182.

[6] Kalinci, Y., Hepbasli, A., Dincer, I., 2009. Biomass-based hydrogen production: A review and analysis. Int. J. Hydrogen Energy 34, 8799–8817.
[7] Dou, B., Song, Y., Wang, C., Chen, H., Xu, Y., 2014. Hydrogen production from catalytic steam reforming of biodiesel byproduct glycerol: Issues and challenges. Renew. Sustain. Energy Rev. 14, 334–343.
[8] Avasthi, K.S., Reddy, R.N., Patel, S., 2013. Challenges in the Production of Hydrogen from Glycerol – A Biodiesel Byproduct Via Steam Reforming Process. Procedia Eng. 51, 423–429.
[9] Hojjat Ansari, M., Jafarian, S., Tavasoli, A., Karimi, A., Rashidi, M., 2014. Hydrogen rich gas production via nano-catalytic pyrolysis of bagasse in a dual bed reactor. J. Nat. Gas Sci. Eng. 19, 279–286.
[10] Chandel, A.K., da Silva, S.S., Carvalho, W., Singh, O. V., 2012. Sugarcane bagasse and leaves: foreseeable biomass of biofuel and bio-products. J. Chem. Technol. Biotechnol. 87, 11–20.
[11] Singh, P., Suman, A., Tiwari, P., Arya, N., Gaur, A., Shrivastava, A.K., 2007. Biological pretreatment of sugarcane trash for its conversion to fermentable sugars. World J. Microbiol. Biotechnol. 24, 667–673.
[12] Davies, O.L., Goldsmith, P.., n.d. Statistical Methods in Research and Production With Special Reference to the Chemical Industry, 3rd Ed.
[13] Hou, T., Yuan, L., Ye, T., Gong, L., Tu, J., Yamamoto, M., Torimoto, Y., Li, Q., 2009. Hydrogen production by low-temperature reforming of organic compounds in bio-oil over a CNT-promoting Ni catalyst. Int. J. Hydrogen Energy 34, 9095–9107.
[14] Kalinci, Y., Hepbasli, A., Dincer, I., 2009. Biomass-based hydrogen production: A review and analysis. Int. J. Hydrogen Energy 34, 8799–8817.
[15] Fermoso, J., Gil, M.V., Arias, B., Plaza, M.G., Pevida, C., Pis, J.J., Rubiera, F., 2010. Application of response surface methodology to assess the combined effect of operating variables on high-pressure coal gasification for H2-rich gas production. Int. J. Hydrogen Energy 35, 1191–1204.
[16] Yusup, S., Khan, Z., Ahmad, M.M., Rashidi, N.A., 2014. Optimization of hydrogen production in in-situ catalytic adsorption (ICA) steam gasification based on Response Surface Methodology. Biomass and Bioenergy 60, 98–107.
[17] Meryemoğlu, B., Hasanoğlu, A., Kaya, B., Irmak, S., Erbatur, O., 2014. Hydrogen production from aqueous-phase reforming of sorghum biomass: An application of the response surface methodology. Renew. Energy 62, 535–541.
[18] Coetzer, R.L.J., Keyser, M.J., 2003. Experimental design and statistical evaluation of a full-scale gasification project. Fuel Process. Technol. 80, 263–278.
[19] Pavón-Orozco, P., Santiago-Hernández, A., Rosengren, A., Hidalgo-Lara, M.E., Stålbrand, H., 2012. The family II carbohydrate-binding module of xylanase CflXyn11A from Cellulomonas flavigena increases the synergy with cellulase TrCel7B from Trichoderma reesei during the hydrolysis of sugar cane bagasse. Bioresour. Technol. 104, 622–30.
[20] Abnisa, F., Wan Daud, W.M.A., 2014. A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil. Energy Convers. Manag. 87, 71–85.
[21] Rashidi, M., Tavasoli, A., 2014. Hydrogen rich gas production via noncatalytic gasification of sugar cane bagasse in supercritical water media. Pet. Coal 56, 324–331.
[22] Ounas, A., Aboulkas, A., El Harfi, K., Bacaoui, A., Yaacoubi, A., 2011. Pyrolysis of olive residue and sugar cane bagasse: non-isothermal thermogravimetric kinetic analysis.
[23] Kumar, R., Verma, D., Singh, B.L., Kumar, U., Shweta, 2010. Composting of sugarcane waste by-products through treatment with microorganisms and subsequent vermicomposting. Bioresour. Technol. 101, 6707–11.
[24] Limtong, S., Sringiew, C., Yongmanitchai, W., 2007. Production of fuel ethanol at high temperature from sugar cane juice by a newly isolated Kluyveromyces marxianus. Bioresour. Technol. 98, 3367–74.
[25] Laser, M., Schulman, D., Allen, S.G., Lichwa, J., Antal, M.J., Lynd, L.R., 2002. A comparison of liquid hot water and steam pretreatments of sugar cane bagasse for bioconversion to ethanol. Bioresour. Technol. 81, 33–44.

[26] Kallioinen, A., Hakola, M., Riekkola, T., Repo, T., Leskelä, M., von Weymarn, N., Siika-aho, M., 2013. A novel alkaline oxidation pretreatment for spruce, birch and sugar cane bagasse. Bioresour. Technol. 140, 414–20.
[27] Walch, E., Zemann, A., Schinner, F., Bonn, G., Bobleter, O., 1992. Enzymatic saccharification of hemicellulose obtained from hydrothermally pretreated sugar cane bagasse and beech bark. Bioresour. Technol. 39, 173–177.
[28] Griffin, G.J., 2011. The effect of fire retardants on combustion and pyrolysis of sugar-cane bagasse. Bioresour. Technol. 102, 8199–204.

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