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Parametric studies on catalytic pyrolysis of coal-biomass mixture in a circulating fluidized bed

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Abstract−Pyrolysis is an efficient way of thermally converting biomass into fuel gas, liquid product and char. In this research, pyrolysis experiments were carried out in a circulating fluidized bed reactor with a riser diameter of 25 mm and height 1.65 m. The biomass used was corn cobs. The experiments were conducted systematically using two level factorial design with temperature ranging from 650 to 850 degree Celsius, corn cobs and catalyst contents in feed ranging from 0 to 100%, and from 1 to 5 wt%, respectively, and Ni loaded on catalyst ranging from 5 to 9 wt%. The results showed that when temperature and catalyst contents in feed and Ni loaded on catalyst increased, the percent of hydrogen and carbon monoxide increased. The amount of corn cobs was found to have an effect only on the composition of hydrogen. Carbon dioxide was also observed to increase slightly. On the other hand, the percent of methane was considerably decreased. The optimum conditions were 850 degree Celsius, corn cob content in feed of 100%, catalyst content in feed of 5% and Ni loaded on catalyst of 9%. At this condition the percentages of hydrogen and carbon monoxide were 52.0 and 18.0, respectively.

Key words: Pyrolysis, Biomass, Circulating Fluidized Bed, Corn Cobs, Experimental Design

INTRODUCTION

Biomass can be efficiently used by thermal-chemical conversion, i.e., pyrolysis, gasification or combustion. Biomass may vary significantly in its physical and chemical properties due to its diverse origins and types. However, biomass can structurally be composed of cellulose, hemicellulose and lignin [Antal et al., 1982; Cagler and Demirbas, 2002]. Pyrolysis is a more efficient way to convert biomass into fuel gas, oil and char, and therefore, has been studied extensively [Chen et al., 2003]. The pyrolysis of biomass is a complex process, strongly dependent on the experimental conditions, i.e., pressure, temperature, biomass species, reactor type as well as the addition of catalyst [Yun and Lee, 1999; Demirbas, 2002]. Circulating fluidized bed technology has been used in coal combustion for more than two decades with great success [Chen et al., 2004], but its application in biomass pyrolysis is still lagging. Circulating fluidized bed technology can be effectively applied to catalytic biomass pyrolysis by supplying a unique ability for the wide range variation of solids residence time and online catalyst regeneration [Lappas et al., 2002]. According to the literature [Tomishige et al., 2004], the tar removal from the product gas stream by catalytic cracking is one of the most promising methods and it has been investigated for more than two decades. Some nickel-based catalysts [Lee et al., 2000; Courson et al., 2003], dolomite [Gil et al., 1999] and olivine [Rapagna et al., 2000] catalysts have been found to be active catalysts for tar cracking in the reactor within the temperature range of 800-900 °C for dolomite and olivine, and 700-800 °C for nickel-based catalysts. In this work, we studied the behavior of coal-biomass blends during devolatilization and the effects of operating conditions, i.e., temperatures, composition of coal-biomass mixtures, amount of Ni-loading on Al_2O_3 and concentrations of catalyst on the product gas compositions in a circulating fluidized bed reactor.

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EXPERIMENTAL

1. Coal and Biomass Samples

Coal from Banpu (located in the northern part of Thailand) and corn cobs from Nakornrajsema province (located in the north-east of Thailand) were employed as feedstocks. Table 1 shows the proximate and ultimate analysis of Banpu coal and corn cobs.

2. Catalyst Preparation

The catalyst used in the experiments, Ni/Al_2O_3, was prepared by impregnation method. The impregnated solution consisted of aque-

Table 1. The proximate and ultimate analysis of coal and corn cobs

	Coal	Corn cobs
Proximate analysis (wt%) (as received)		
Fixed carbon	19.24	13.15
Volatile	37.68	75.18
Moisture	17.38	9.61
Ash	25.70	2.06
Ultimate analysis (wt%) (daf)		
C	58.44	45.04
O	33.85	48.53
H	5.16	5.79
N	0.68	0.64
S	1.87	-

ous solutions of nickel nitrate at nickel concentrations of 5, 7 and 9 wt%, respectively. The gamma alumina supported was immersed in the impregnated solution and heated to 70 °C (nickel loading). After loading, it was dried at 120 °C overnight and calcined at 600 °C for 5 h. The final catalyst obtained was reduced in the hydrogen atmosphere at 500 °C for 5 h. The catalyst was then characterized by a Brunauer-Emmett-Taylor (BET) and SEM analyses.

3. Thermal Decomposition of Coal and Corn Cobs

Thermal decomposition of coal and corn cobs was studied by using Thermogravimetric/Differential Thermal Analyzer (TG/DTA Perkin Elmer N535). A sample of approximately 20 mg was loaded and weight loss was recorded continuously as a function of time or temperature, in the range 30-950 °C. All experiments were carried out at atmospheric pressure, under inert nitrogen with a flow rate of 50 ml/min. The effect of heating rate was examined by using two different values of 20 and 100 °C/min. In addition, the synergetic effect between coal and biomass was investigated by using various compositions of coal-biomass blends.

4. Circulating Fluidized Bed (CFB)

Pyrolysis of coal and biomass mixture was further studied in a circulating-type reactor. A pilot-scale CFB was constructed, and the schematic diagram of the experimental unit is shown in Fig. 1. The apparatus mainly consists of a riser, cyclone, downcomer and return-leg as well as an electrical heater and gas sampling system. The riser is 1.65 m in height and 25.4 mm in diameter. To heat the riser to ignition temperature of fuel (about 500 °C), 2 kW electrical heaters were installed around the riser wall, which were insulated with refractory material to prevent heat loss. The temperatures along the riser were measured with K-type (chromel-alumel) thermocouples. When the riser temperature reached the desired temperature, 15 g of sample (coal or coal-corn cobs mixture) was fed to the top of the riser. The temperature inside the riser was controlled by a temperature controller. The gas sampling bag was placed at the outlet of the dehumidifier unit (using silica gel). The gas samples were analyzed by gas chromatography (Thermo Finnigan). The CFB reactor was operated using N_2 as the carrier gas at the flowrate of 1.5 L/min. This gas velocity was confirmed to be in fast fluidization regime in the riser and the bed materials were returned through the downcomer.

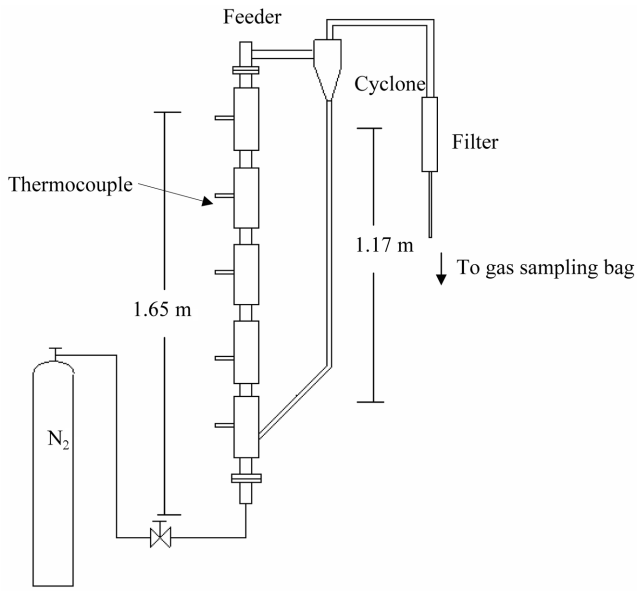


Fig. 1. A schematic diagram of the circulating fluidized bed (CFB) reactor.

Table 2. Two levels factorial design

Factors	Low	High
Temperature, °C	650	850
Percent corn cobs	0	100
Percent catalyst	1	5
Percent Ni loaded	5	9

Table 3. BET area of catalysts

Sample	BET area (m^2/g)
Al_2O_3	325.00
Ni/Al_2O_3-Ni 5%	178.55
Ni/Al_2O_3-Ni 7%	177.19
Ni/Al_2O_3-Ni 9%	175.86

5. Parametric Study

The effects of operating conditions were investigated using a 2^k factorial design. The temperature (A), percentage corn cobs in fuel (B), percentage catalyst (C), and percentage Ni loaded on catalyst (D) are the four factors to be considered (k=4) with the low and high level values shown in Table 2. With these experiments, their effects as well as interactions can be analyzed and determined by using analysis of variance (ANOVA). Analysis of variance is a statistical tool for testing multiple treatments whether they have significant impact on the observed responses.

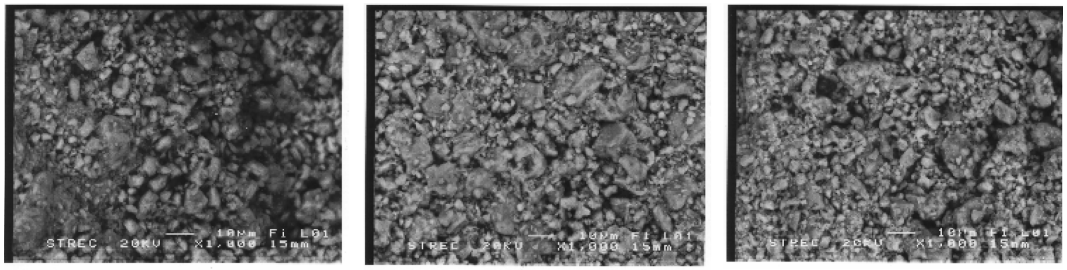
RESULTS AND DISCUSSION

1. Catalysis Characterization

Table 3 shows the BET results of the catalysts obtained. It can be seen that the surface area of the gamma alumina is rather high, but when nickel was loaded (impregnated) from 5 to 9% the surface area was decreased by half. This implies the impregnation of Ni on the surface of alumina. The result can be emphasized by SEM photographs as shown in Fig. 2.

2. Thermal Decomposition of Corn Cobs and Coal Blends

Fig. 3 shows the TG and DTG results of corn cobs at the heating rates of 20 and 100 °C/min. Considering the DTG results, the first peak taking place at 73 °C represented moisture release. Between 200-400 °C, there are two peaks: the first one corresponds to the decomposition of hemicelluloses while the second corresponds to the decomposition of cellulose, whereas lignin decomposes in a broad range of temperatures [Caballero et al., 1997]. This is related to the TG results that give two significant changes in weight loss. The first one is due to moisture release; the second to the hemicellulose decomposition and the third corresponds to the cellulose decomposition. The slow decomposition of lignin was observed at the temperature greater than 400 °C. Significant differences in TG and DTG profiles for different heating rates were not observed. Thus, the heating rate does not have any influence on the thermal decomposition of corn cobs. However, it should be noted that the effect might be



(a) 5% Ni (b) 7% Ni (c) 9% Ni

Fig. 2. SEM images of Ni/Al_2O_3 catalyst.

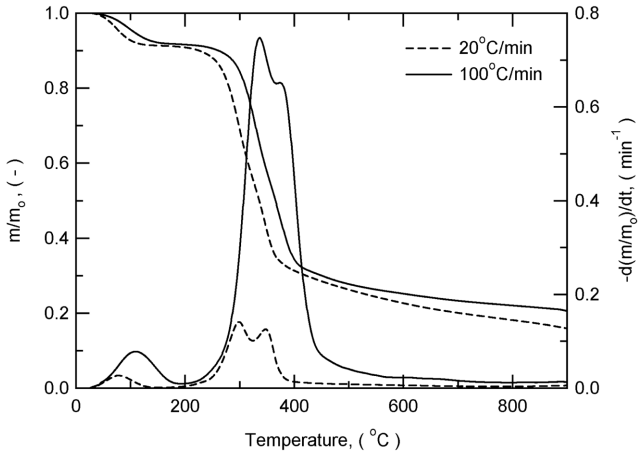


Fig. 3. TG and DTG graphs of corn cobs.

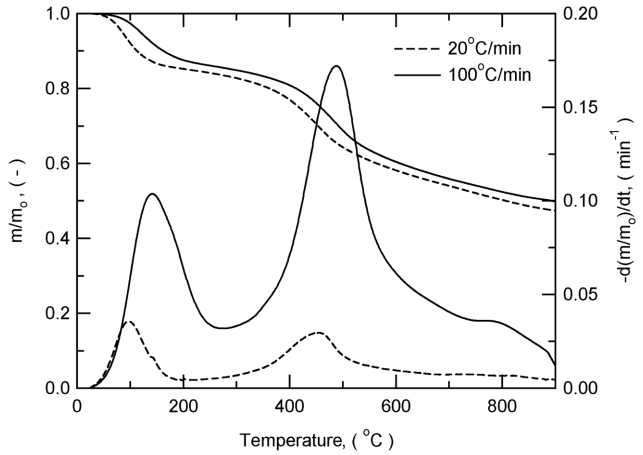


Fig. 4. TG and DTG graphs of coal.

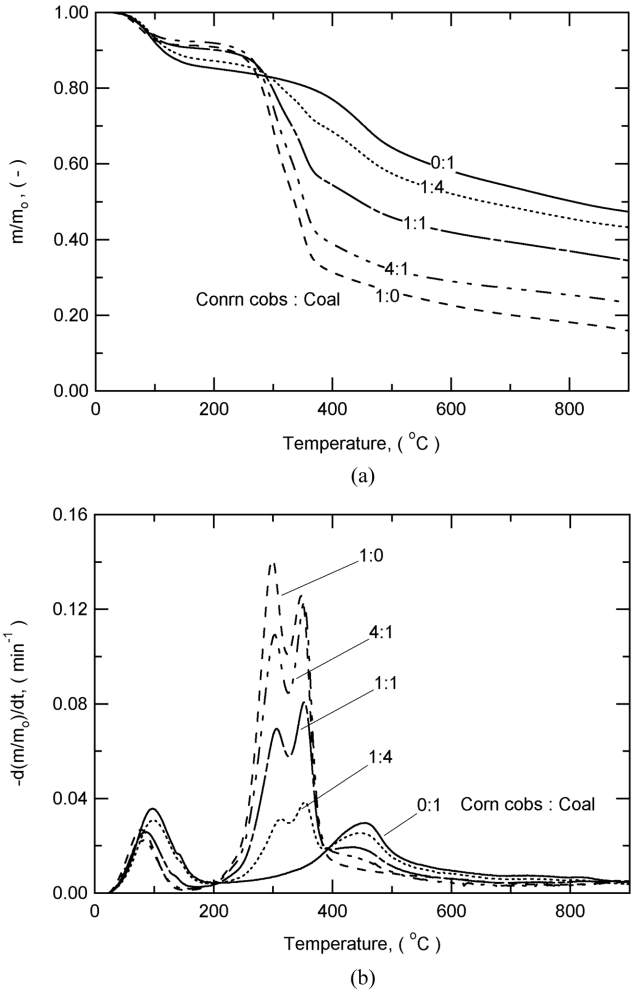


Fig. 5. TG and DTG graphs of corn cobs and coal blends: (a) TG and (b) DTG.

observed if the heating rate is particularly high, e.g., larger than 100 °C/min. Such a high heating is difficult to reach by using the conventional TG employed in this work. The maximum pyrolysis rate occurs at 300 °C at a rate of 74%/min.

Fig. 4 shows the TG-DTG graphs of coal obtained with heating rates of 20° and 100 °C/min. It can be seen from the DTG curve that moisture evolved at 91 °C (compared to 72.9 °C in the case of corn cobs). It can be observed that the decomposition of coal starts at about 250 °C, which is higher than the one corresponding to corn cobs. The maximum pyrolysis rate occurs at 451.5 °C at a rate of 17%/min, which is much lower than that of corn cobs.

Decomposition of coal continues until the end of the experiment. A large portion of volatiles are released in the first step of the pyrolysis process, between 250 and 450 °C, while non-condensable gases are released at a temperature higher than 600 °C resulting from ring condensation [Vamvuka et al., 2000].

The TG and DTG results of corn cobs and coal blends are shown in Fig. 5. As clearly shown, the height of the peaks gradually increases

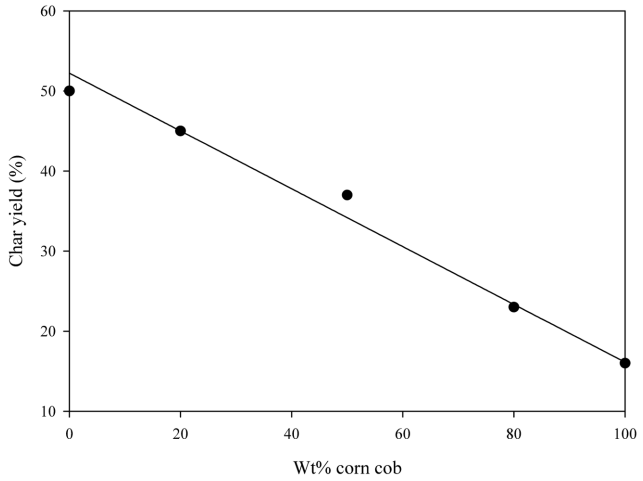


Fig. 6. Relation between wt% corn cobs and char yield.

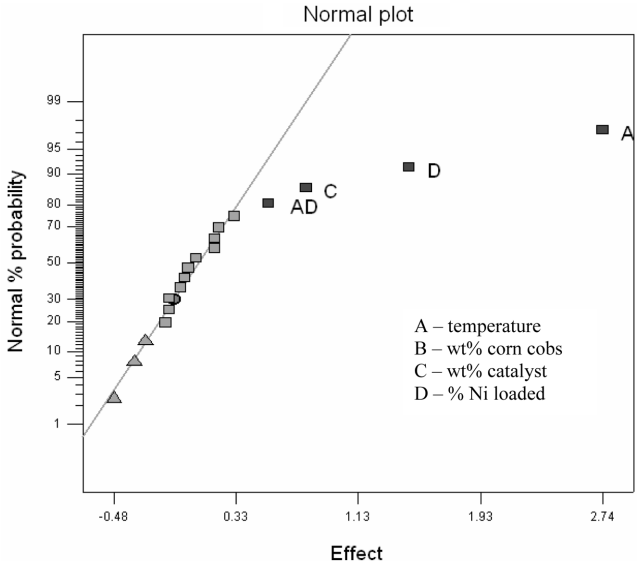


Fig. 7. Normal probability plot for H_2.

with increasing amount of corn cobs in blends, indicating an enhancement of volatile quantities released. It can also be observed that the position of the maximum peak is shifted to lower temperatures, as the ratio of corn cobs in the mixture is increased. The results of blends were observed to become closed to that of corn cobs when the composition of corn cobs in the mixture increased. The amount of char generated during co-pyrolysis decreased with increasing corn cobs content in the blend.

The measured data for char yield (CY) are plotted against wt% corn cobs in Fig. 6. It can be seen that there is a linear relationship between char yield and the amount of corn cobs in the mixture. This finding indicates that there are no synergistic effects between corn cobs and coal in the solid phase during the pyrolysis stage. However, possible gas-solid interactions or interactions in the gas phase cannot be excluded. Similar results have been reported in the literature [Vuthaluru, 2004].

3. Parametric Analysis of Catalytic Pyrolysis of Corn Cobs and Coal Blends in a CFB Reactor

Applying two-level factorial design, the influences of the following factors on gas composition and properties of the remaining char were investigated.

Factor A - temperature (°C)
Factor B - wt% corn cobs
Factor C - % catalyst used
Factor D - % Ni loaded on catalyst

The experiments were carried out based on the conditions shown in Table 2.

3-1. Influence on Gas Composition

The gas products were collected by gas bags after the sample was loaded into the reactor. The gas composition was analyzed by GC. The effects of each factor on components of gas products are discussed as follows.

3-1-1. Hydrogen

Fig. 7 shows the normal probability plot for H_2. This plot shows treatment factors that have significant effects on the observed response. It can be seen that temperature has the highest effect on H_2 production. The second and third factors are % nickel loading, and

Table 4. ANOVA table of H_2

Factor	SS	DF	MS	Fo	P-value
A	269.78	1	269.78	879.94	<0.0001
B	28.36	1	28.36	92.49	<0.0001
C	3.90	1	3.90	12.72	0.0044
D	45.23	1	45.23	147.51	<0.0001
AB	7.16	1	7.16	23.34	0.0005
AD	8.85	1	8.85	28.87	0.0002
ABD	2.64	1	2.64	8.61	0.0136
Curvature	0.67	1	0.67	2.17	0.1685
Error					
Total					

SS=Sum squares, DF=degrees of freedom, MS=Mean Square, Fo=ratio of MS (factor) and MSE, P-value is the probability of obtaining a value for the test statistic that is as extreme or more extreme than the value actually observed.

weight percent of corn cobs. The interaction effects such as temperature-% Ni-loaded, temperature-% corn cobs, and temperature-% corn cobs-%Ni loaded are also important. These results were confirmed by ANOVA results in Table 4. On the contrary, the F-value of 2.17 for curvature in the Table 4 implies that there is no curvature in the design space. In other words, only the linear effect of the factors is important; the higher order term is not. Fig. 8 shows the cube plot for H_2 at 3 wt% catalyst. This plot is useful for representing the effects of three factors at a time. They show the predicted values from the model for a combination of the −1 and +1 levels of any three factors selected. In this case, we obtained the maximum of 50.52 wt% H_2 at temperature of 850 °C, wt% corn cobs equal to 100 and % Ni loaded of 9 (see also Table 4). The reason is that, with the same amount of mass as received, corn cob contains hydrogen about 70% higher than that content in coal. Thus using corn cobs alone as fuel, the amount of hydrogen produced was increased significantly.

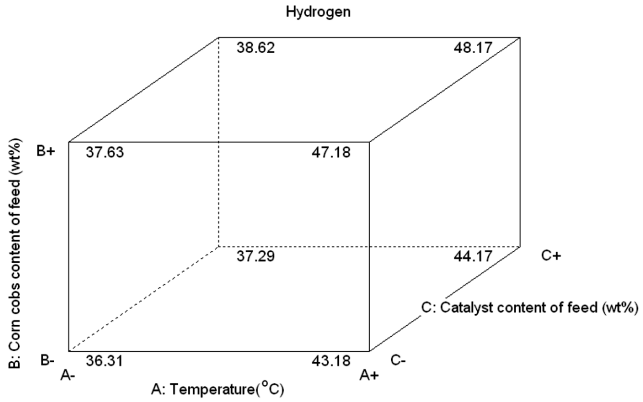


Fig. 8. Cube graph of H_2 at 3 wt% catalyst.

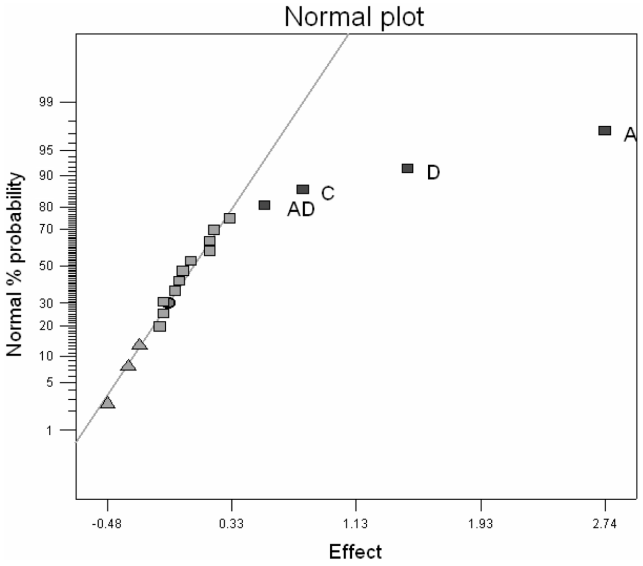


Fig. 9. Normal probability plot for CO.

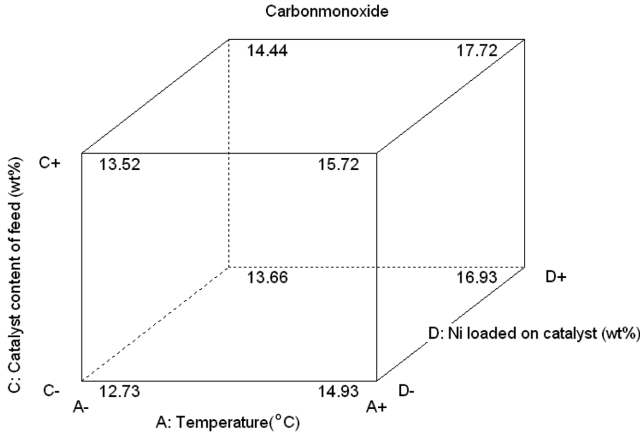


Fig. 10. Cube graph of CO at 50 wt% corn cobs.

3-1-2. Carbon Monoxide

The normal probability plot for CO is shown in Fig. 9. The plot shows that the factors A, C, D and AD are significant. A cube graph for CO is plotted in Fig. 10. It can be observed that the maximum

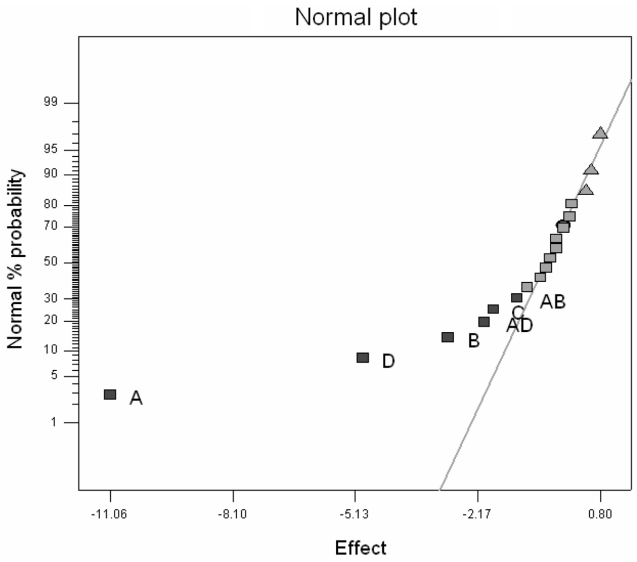


Fig. 11. Normal probability plot for CH_4.

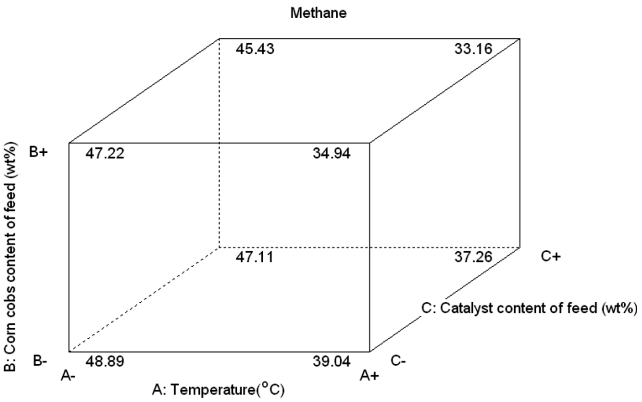


Fig. 12. Cube graph of CH_4 at 7 wt% Ni loaded.

% CO obtained is 17.72 corresponding to temperature of 850 °C, % catalyst of 5 and % Ni-loaded of 9. Here, the content of corn cobs (B) seems to have no significant effect on both % CO and % CO_2 as shown later. This result seems to contradict the fact that the corn cobs have higher carbon content in the volatile matter than coal. An explanation is that it was observed that the amount of carbon released as CO and CO_2 was increased with the increase of gas yield at higher corn cob content in fuels, though their gas compositions in the product gas were not changed, compared with the other gases, such as H_2 and methane. In other words, the compositions of H_2 and CH_4 changes were more pronounced than the oxide of carbon.

3-1-3. Methane

Fig. 11 shows the normal probability plot for methane. In this case, the factors A, B, C, D, AB and AD are significant with negative effect. This implies that in order to decrease CH_4 formation, these factors have to be increased. The reduction of CH_4 with increasing temperature can be explained by equilibrium theory where the lighter compound is preferable at higher temperature. The increasing of the catalyst also promotes the reforming of CH_4. This is relevant to the results of lighter gas products, e.g., H_2 and CO, mentioned above. A cube graph for CH_4 is shown in Fig. 12. The maximum % CH_4

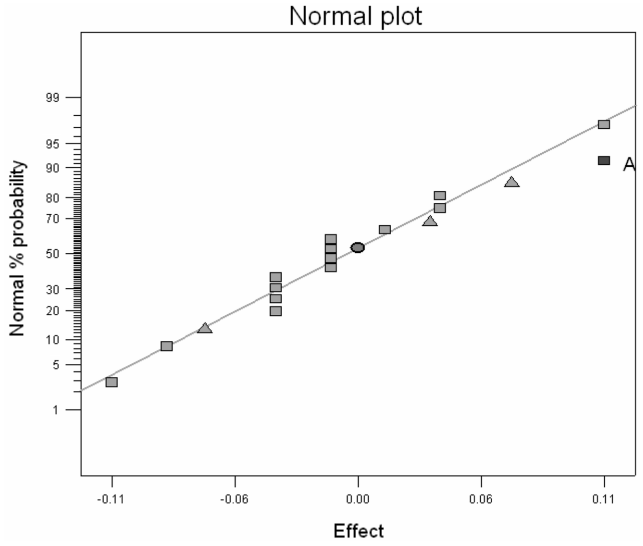


Fig. 13. Normal probability plot for CO_2.

obtained is 48.87 corresponding to temperature of 650 °C, 0% corn cobs, 1% catalyst and 5% Ni loaded.

3-1-4. Carbon Dioxide

Fig. 13 shows the normal probability plot for carbon dioxide. None of the factors above has a significant effect on CO_2 generation. A cube graph for CO_2 is shown in Fig. 14. The composition of % CO_2 obtained was very close among each treatment. The values were between 1.78 and 1.977.

3-2. Influence on Char Properties

The remaining char was collected after the reaction finished. Its properties were represented in terms of proximate analysis results. The effects of each factor on char properties were discussed as follows.

3-2-1. Volatile Matter

Fig. 15 shows the normal probability plot for volatile matter. Factors A, and B are significant with negative effects. On the other hand, the interaction AB gives a positive effect. This implies that a higher value of factor A or B will cause the remaining volatile in char to

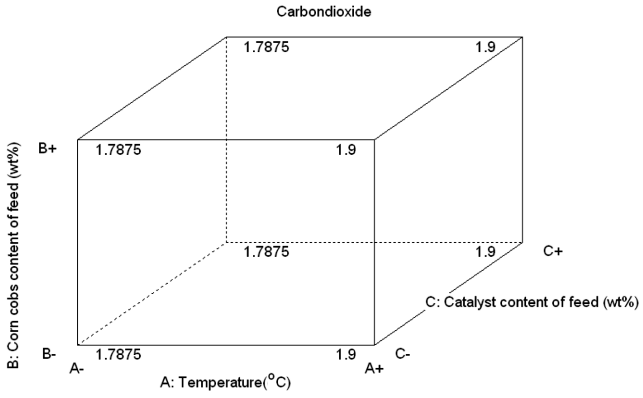


Fig. 14. Cube graph of CO_2 at 3 wt% catalyst.

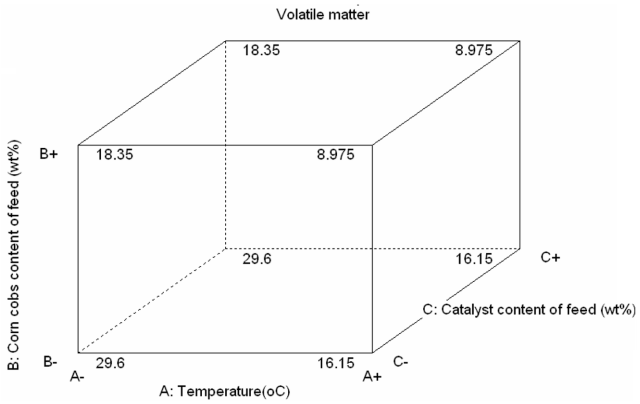


Fig. 16. Cube graph of VM at 7 wt% Ni loaded.

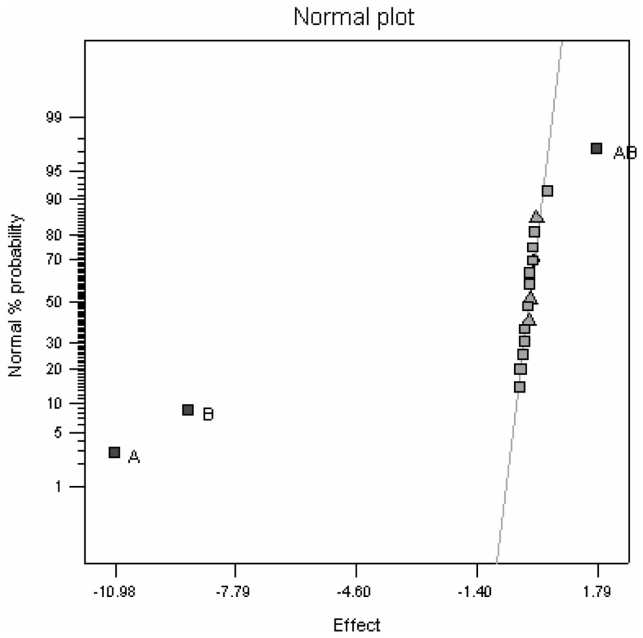


Fig. 15. Normal probability plot for volatile matter (VM).

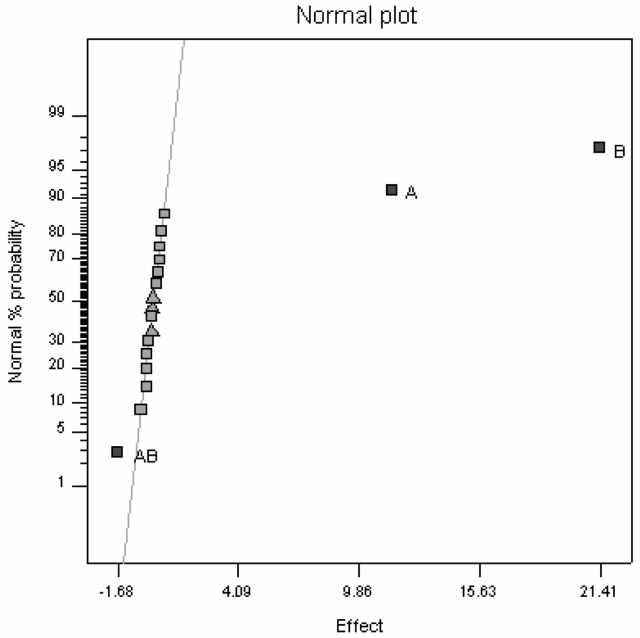


Fig. 17. Normal probability plot for fixed carbon (FC).

be less. The figure also shows that temperature has a stronger effect than corn cobs content in feed. However, when increasing both effects together, the remaining volatile is increased. A cube graph for VM is shown in Fig. 16. One can observe that the factor C has no influence on the response at all. That is, the amount of catalyst does not have any role in the properties of the remaining char.

3-2-2. Fixed Carbon

Fig. 17 shows the normal probability plot for fixed carbon. In this case, the factors A and B are significant with positive effects. However, the factor AB gives slightly a negative effect. CA cube graph for FC is shown in Fig. 18. The same conclusion was obtained as in the case of volatile matter. That is, the amount of catalyst does not have any role in fixed carbon in the remaining char.

3-2-3. Ash

Fig. 19 shows the normal probability plot for ash. In this case, only factor B is significant with a negative effect. This is corresponding with the fact that the more biomass used, the less ash that remained after combustion.

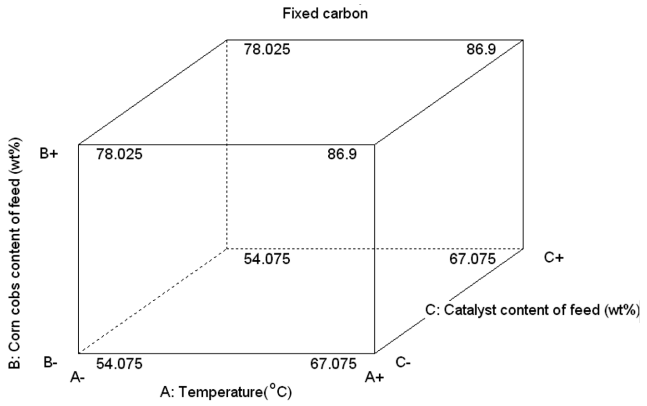


Fig. 18. Cube graph of fixed carbon at 7 wt% Ni loaded.

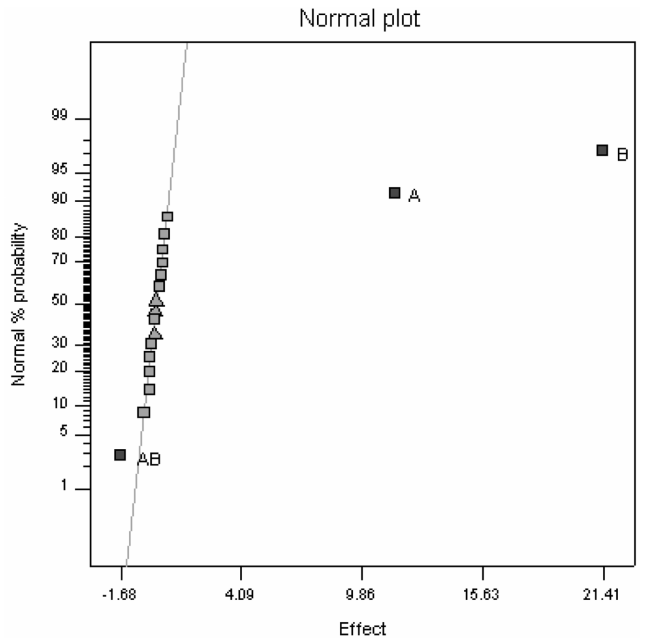


Fig. 19. Normal probability plot for ash.

CONCLUSIONS

Thermogravimetric analysis (TGA) was conducted to investigate the path of coal and biomass decomposition. After the analysis, it was found that there is no synergistic effect among the mixtures in the solid-phase. Parametric studies on catalytic pyrolysis of coal-biomass mixture in a circulating fluidized bed were carried out in order to determine the factors that play important roles in gas synthesis. It was found that temperature, % Ni loading and weight of biomass have high impact on H_2 production, respectively, while the first two factors also have the same effect on CO produced. The third factor in CO production is % catalyst, instead of the biomass. The char was also analyzed and their remaining reported.

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