

Hydrogasification of various carbonaceous sources using pressure change properties

Wang Seog Cha[†], Il Hyun Baek* and Hyun Tae Jang**

Kunsan National University, Kunsan 573-701, Korea

*Korea Institute of Energy Research, Daejeon 305-343, Korea

**Hanseon University, Seosan 356-706, Korea

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Abstract—Hydrogasification experiments were carried out in a batch reactor capable of operating at 800 °C and 8 MPa. Carbonaceous matters used in the experiments were bituminous and anthracite coal and sawdust. It was found that the decreasing rate of hydrogen gas pressure was closely related to the rate of gas production. This result was confirmed by the change of char conversion. The methane content in the gas products and char conversion rose with the increase of temperature and pressure. The addition of water activated the hydrogasification reaction until the proper level of water amount (up to 30 wt%), but an excess level of water inhibited the reaction. The activation energy of bituminous coal and sawdust char obtained by the Arrhenius plot was 187 KJ/mole and 77 KJ/mole, respectively. In case of loading of catalysts, all catalysts loaded to the char did not give a positive effect in hydrogasification, but the catalytic effect depended on type of catalyst metals and char. In the present hydrogasification of bituminous coal and sawdust, the order of activities for the catalysts tested was $K_2CO_3 > Na_2CO_3 > Fe(NO_3)_2 > Ni(NO_3)_2 > FeSO_4$.

Key words: Hydrogasification, Gas Composition, Pressure Decrease, Char Conversion, Catalyst

INTRODUCTION

Among the three important fossil fuels, coal, petroleum, and natural gas, natural gas serves as the cleanest energy source with its less carbon dioxide and other pollutants emitted during utilization. On the other hand, the abundance of natural gas is quite limited and a supply shortage will inevitably occur in the near future. In contrast, coal and/or biomass are in larger abundance, widely distributed in the world. To produce a substitute natural gas (SNG), the hydrogasification of coal and other solid fuel sources such as biomass has been studied and processes have been designed for some cases [1-3].

The results show that the product gas yields are greatly affected by reaction conditions such as residence time, heating rate, temperature, hydrogen pressure, and the type of carbon source [4]. Some scientists have developed a new process called Zero Emission Carbon (ZEC) [5]. The ZEC process consists of four main processes: gasification, carbonation, calcination, and fuel cell. In the gasification process, the hydrogasification reaction would be used to make methane rich gas stream. Hydrogasification processes have been developed in various types and stages for the production of SNG [6-8]. However, the technologies have several disadvantages such as high severities of gasification conditions, low methane production, and unattractive economics [9].

Total conversion of carbon sources from hydrogasification stage requires high temperature and high pressure. A catalytic process to reduce the reaction temperature would advantageous. Transition metals as catalysts for hydrogasification of carbons have shown prom-

ise in recent years [10]. Alkali and alkali earth metals are known to be useful catalysts for water vapor gasification [11]. The kinetics of hydrogasification of carbon has been studied by many authors [12]. Different empirical reaction rate equations have been proposed, but the reported activation energies vary between 50 and 360 KJ/mol. The reason for these differences may be the multiplicity of the carbon materials and the reaction conditions applied [13].

More information is necessary before hydrogasification can be used practically. Therefore, the hydrogasification phenomenon and characteristics of several carbon sources for ZEC process have been investigated. The effects of reaction pressure, reaction temperature, water content on carbon conversion and composition of produced gases have been determined. Also the kinetics of hydrogasification has been studied in a range of pressure and temperatures relevant for probable technical processes.

EXPERIMENTAL

A schematic diagram of the hydrogasification reaction system is shown in Fig. 1. The system consisted of three main parts, namely reactant gas injection, main reaction and product gas analysis. Hydrogen gas was fed to the reactor for the hydrogasification reaction and helium gas was also fed to the reactor for the safety and leakage test. The reactor was made of a heat resistant Inconel tube (0.025 m I.D. × 0.2 m height), which was designed for operation at 1,200 °C and 10 MPa. An electric heater was installed on the hydrogasification reactor to raise the reactor temperature to hydrogasification conditions (500-800 °C). Temperature and pressure distributions measured during the hydrogasification reaction were recorded in a computer through a data acquisition system (PCL812).

The product gas analysis was performed by using gas chromatography (Varian, CP-3800) with a thermal conductivity detector with molecular sieve 13× and Porapak N columns. Approximately

[†]To whom correspondence should be addressed.

E-mail: wscha@kunsan.ac.kr

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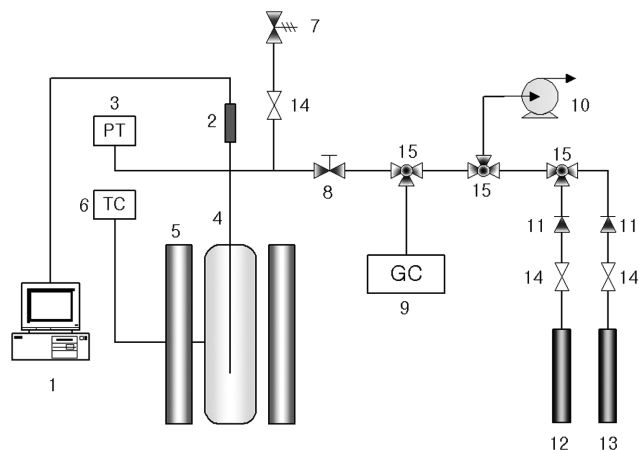


Fig. 1. Schematic diagram of experimental apparatus used in this study.

- | | |
|---------------------------|-----------------------|
| 1. Computer | 9. Gas chromatography |
| 2. Thermocouple | 10. Vacuum pump |
| 3. Pressure transducer | 11. Needle valve |
| 4. Reactor | 12. Hydrogen cylinder |
| 5. Furnace | 13. Helium cylinder |
| 6. Temperature controller | 14. On-off valve |
| 7. Relief valve | 15. Three-way valve |
| 8. Metering valve | |

1 g of char was placed in the reactor and heated to the desired operating temperature. Then hydrogen gas was injected to the reactor. The reaction lasted for 3 hrs. The product gas was collected by a vacuum pump and analyzed by gas chromatography.

Char specimens used in this study were prepared by the devolatilization of several carbon sources at 900 °C for 1 hr in an inert atmosphere. The char specimens were ground to 60-80 mesh.

To investigate the catalytic effect, an amount of char was impregnated with an aqueous solution of K_2CO_3 , Na_2CO_3 , $Ni(NO_3)_2$, $Fe(NO_3)_3$, and $FeSO_4$. The resulting char was dried in a dry oven for 24 hrs and then heated at 350 °C in flowing hydrogen to reduce the catalyst on char prior to hydrogasification. The amount of catalyst added was given in weight percent of metallic elements charged to char at the impregnation. The properties of carbonaceous sources are given in Table 1.

RESULTS AND DISCUSSIONS

Hydrogasification of carbonaceous matter such as coal and biomass is a complex reaction including fast pyrolysis of volatile matter and very slow hydrogen addition reaction of char. Therefore, our experiments were focused upon the hydrogen reaction of char which rate determining step in hydrogasification of carbonaceous

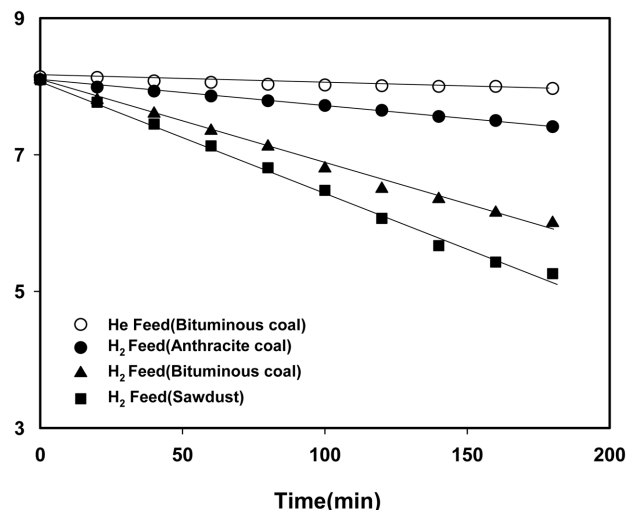
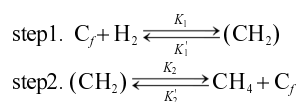


Fig. 2. Pressure profile with reaction time for the carbonaceous matter.

matter.

Fig. 2 presents the curves for the change in reactor pressure of several chars with reaction time at 800 °C and 8 MPa. Whereas the curve for pyrolysis under helium showed no difference, those under hydrogen demonstrated the significant influence of this reactive gas on hydrogasification such as methane formation and reaction.

For the gasification of chars in pure hydrogen, the following fundamental reaction steps are postulated:



Where C_f : active center on carbon surface

$C(H_2)$: surface complex formed by the chemisorption of hydrogen or by decomposition of methane at an active center

In the above reactions, two hydrogen molecules react with one carbon molecule and then convert to one methane molecule. From the stoichiometric relationship of the hydrogasification reaction, the consumption rate of hydrogen is regarded as the formation rate of methane. The change of mole of reactant and product gas under constant reactor temperature and volume correlates to the change of pressure in certain circumstances [14,15]. Thus, reactor pressure was decreased at a specific rate under specific reaction conditions, which was confirmed by Fig. 3 representing pressure change of sawdust char. Each pressure curve had a specific rate, and the decreasing rate of pressure curve increased with the increase of initial reac-

Table 1. Proximate and ultimate analysis of bituminous coal and sawdust

Samples	Proximate analysis				Ultimate analysis					
	Fixed carbon	Volatile matter	Ash	Moisture	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	Ash
Bituminous coal	52.52	32.32	12.78	2.48	72.25	4.7	8.12	1.62	0.53	12.78
Anthracite coal	2.74	58.15	4.23	34.88	59.50	1.33	3.50	0.23	0.56	34.88
Sawdust	16.31	77.19	1.21	5.29	45.62	6.38	46.24	0.52	0.03	1.21

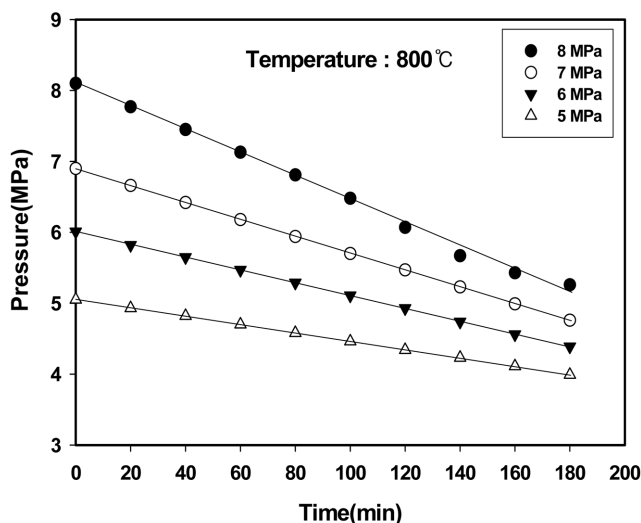


Fig. 3. Change of pressure profile of sawdust char with reaction time for the various initial reaction pressures.

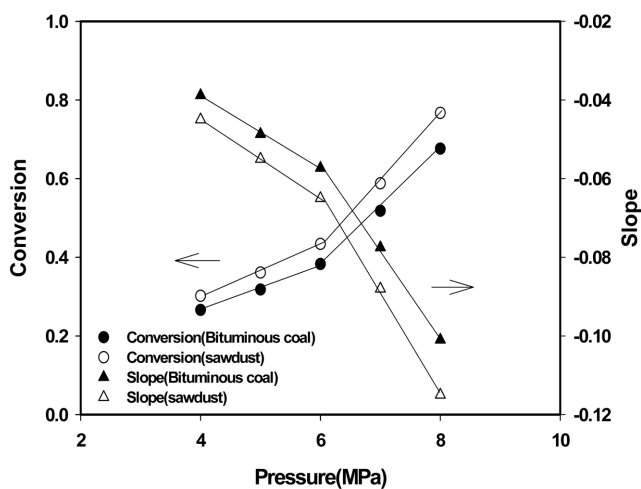


Fig. 4. Conversion and slope of pressure profile with the initial reaction pressure.

tor pressure.

The effect of reaction pressure on conversion and slope of bituminous coal and sawdust char is shown in Fig. 4. Thus, the slope was obtained by the regression of specific pressure curve. Some investigators stated that pressure-dependence of reactivity was a low level of 0.3 below 550 °C, and the pressure-dependence was largely increased above 550 °C [16,17]. Slope was rapidly increased above 6 MPa due to pressure-dependence. Conversion of char was also rapidly increased above 6 MPa similar to that of the slope.

The effect of reaction temperature on conversion and slope of bituminous coal and sawdust char is shown in Fig. 5. The slope was relatively small below 600 °C, but largely increased with operating temperature above 600 °C. Arendt and Heek [17] reported that hydrogen reacts with the volatiles evolved from the decomposing coal around 500 °C, and then proceeds rapid hydrogasification of very reactive carbon atom above 600 °C. The conversion of coal char also sharply increased above 600 °C, similar to that of the slope.

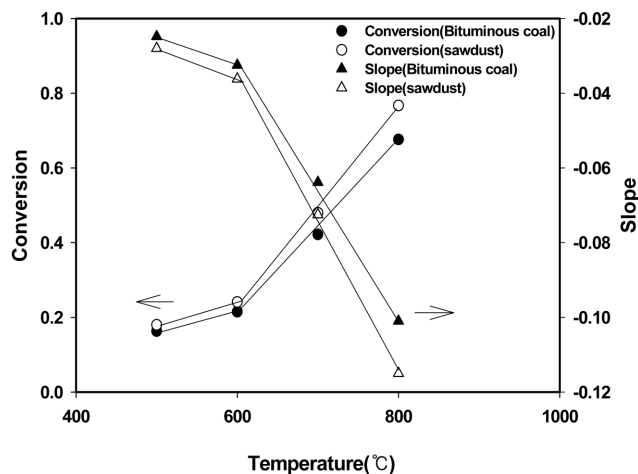


Fig. 5. Conversion and slope of pressure profile with the reaction temperature.

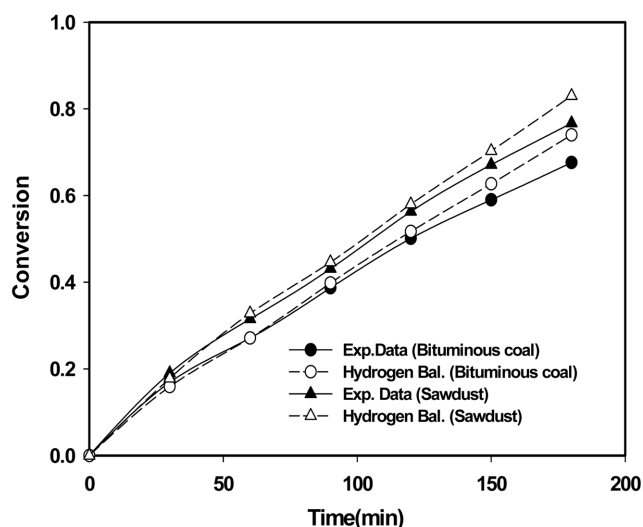


Fig. 6. Comparison of experimental conversion data with the model prediction in hydrogasification of chars.

The experimental and calculated data of conversion are compared in Fig. 6. The calculated data were obtained by a mass balance model of hydrogen gas and experimental data measured every 30 minutes at 800 °C, 8 MPa.

The conversion in hydrogasification of char is defined as

$$X = \frac{W_o - W}{W_o - W_{ash}} \quad (1)$$

Where W_o is the initial mass of char, W_{ash} is the mass of ash in the char, W is the mass of char at a given time.

The following correlation equation about the conversion of char and partial pressure of hydrogen gas is derived by a mass balance of hydrogen gas in the reactor.

$$\frac{N_{C_0} dx}{2 dt} = k P_{H_2} \quad (2)$$

By integrating and rearranging of Eq. (2), Eq. (3) is obtained.

$$X = \frac{2k}{N_{Co}} \int_0^t P_{H_2} dt \quad (3)$$

From Eq. (3), the char conversion is predicted by the hydrogen gas pressure measured. It was shown that the prediction of the hydrogen gas mass balance model was in good agreement with the char conversion measured in both cases of coal and sawdust char. Based on these results, it was found that the reaction degree of hydrogasification was obtained by on-line monitoring of hydrogen gas pressure of the reactor.

The k and k_s in hydrogasification reaction kinetics are defined as follows. Eq. (4) gives the reactivity, the specific reaction rate (rate per unit mass of residual fixed carbon) as:

$$K_s(X) = \frac{1}{1-X} \frac{dX}{dt} \quad (4)$$

As the reactivity, the average reaction rate is defined as,

$$k = \int_0^1 k_s(X) dX \quad (5)$$

The Arrhenius plot calculated by Eq. (5) for both bituminous coal and sawdust char is given in Fig. 7. The apparent activation energy

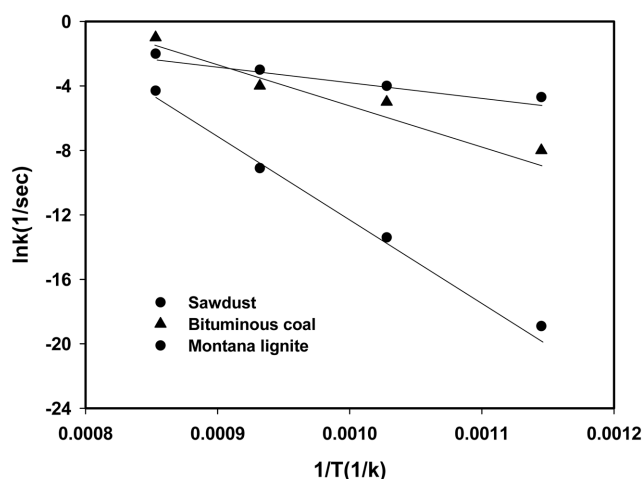


Fig. 7. Arrhenius plot for hydrogasification of chars.

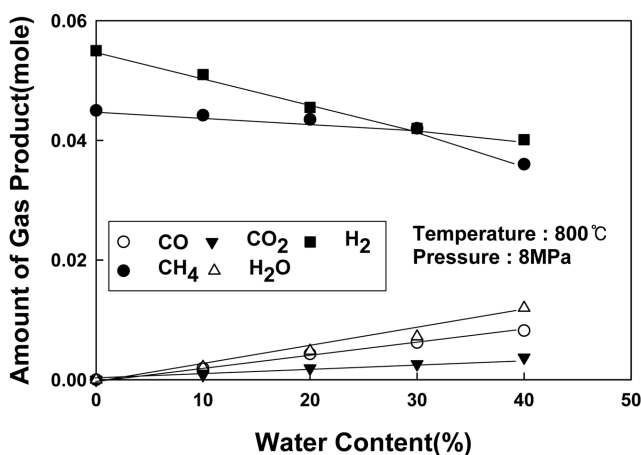


Fig. 8. Mole change of gas products of sawdust char with water content.

could be determined from this plot by linear regression. The activation energy of bituminous coal was 187 KJ/mole and that of sawdust was found to be 77 KJ/mole. The literature gives the activation energy for hydrogasification of coal and sawdust as 150-210 KJ/mole and 66-93 KJ/mole [18,19]. Our results of activation energy were similar to that of other researchers. And, the sawdust char showed much larger reaction rate compared to the coal char.

Mole change of gas products of sawdust char with water content is represented in Fig. 8. There, methane, the main product of hydrogasification, was a sustained level of 0.048 mole until a water content of 30 wt%, after which it largely decreased. Moles of carbon monoxide, carbon dioxide, and water were increased monotonically with the increase of water content due to acceleration of gasification reaction and water gas shift reaction. The composition of gas products was methane of 47.6 vol%, carbon monoxide of 7.9 vol%, carbon dioxide of 3.0 vol%, water of 8.5 vol%, and hydrogen of 33.0 vol% at the condition of 800 °C, 8 MPa and 30 wt% water content in which obtained the maximum yield of methane gas. The above basic data of gas composition and reaction properties under various operating conditions will be used for the design and proper operation of a hydrogasification and carbonation system in the ZEC process.

Different results on catalytic hydrogasification of char have been reported. The reason for these differences may be the multiplicity of carbon material, mineral matter, and the reaction conditions applied. The catalytic activities of alkali, alkaline earth, and transition metal, which are known to be useful catalysts for hydrogasification, are shown in Table 2. The reaction conditions were temperature of 800 °C, pressure of 8 MPa, and catalyst amounts of 5 wt%. It was shown that Na and K of group were more active than other metals, which was due to the greater uniform dispersion of catalysts on the surface of char. As the order of activities in the same group is $K > Na > Li$, K has higher catalytic activity than Na [11]. In the case of K_2CO_3 catalyst, there was a conversion increase of 15-19% in bituminous char and 12-13% in sawdust char compared to the no catalyst. Though Ni catalyst can exist in the elemental form representing higher activity in the reduced condition, the activity of Ni catalyst is somewhat lower than that of other metal due to some sintering of Ni element at the condition of 800 °C and 8 MPa [20]. A conversion decrease of 5% was found due to the nickel sintering in our results. In the case of $FeSO_4$, sulfate form of Fe catalyst significantly inhibited hydrogasification, because of the sulfur poisoning of Fe element as well as mineral matter of char [21]. Large de-

Table 2. Change of CH_4 moles and char conversion depending on catalyst loading

Catalysts	Bituminous coal		Sawdust	
	CH_4 (mole)	Conversion	CH_4 (mole)	Conversion
K_2CO_3	0.053	0.801	0.059	0.910
Na_2CO_3	0.050	0.756	0.056	0.859
$Ni(NO_3)_2$	0.042	0.629	0.046	0.73
$Fe(NO_3)_2$	0.044	0.665	0.049	0.765
$FeSO_4$	0.032	0.481	0.036	0.545
No Catalyst	0.045	0.676	0.050	0.761

crease of 28% occurred in both bituminous and sawdust char in this study. The order of activities for the catalysts tested was $\text{K}_2\text{CO}_3 > \text{Na}_2\text{CO}_3 > \text{Fe}(\text{NO}_3)_2 > \text{Ni}(\text{NO}_3)_2 > \text{FeSO}_4$.

CONCLUSIONS

1. It was observed that the decreasing rate of pressure represented the production rate of gas products in the hydrogasification, which was confirmed by the conversion. From this relation, an estimate could be made of the degree of reaction from the monitoring of hydrogen gas pressure.

2. The moles of gas product and conversion of char were increased with the increase of reaction pressure and temperature. The moles of methane remained nearly constant up to a water content of 30 wt%, after which they largely decreased. Moles of carbon monoxide, carbon dioxide and water increased linearly with the increase of water content.

3. The conversion predicted by mass balance model of hydrogen gas had a good agreement with the conversion measured by experiment. The activation energy of bituminous coal and sawdust char was 187 kJ/mole and 77 kJ/mole, respectively.

4. The order of activities for the catalysts tested was $\text{K}_2\text{CO}_3 > \text{Na}_2\text{CO}_3 > \text{Fe}(\text{NO}_3)_2 > \text{Ni}(\text{NO}_3)_2 > \text{FeSO}_4$.

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NOMENCLATURE

E	: activation energy [kJ/mol]
k	: rate constant [1/sec]
k_s	: specific rate constant [1/sec]
N_{co}	: moles of char [mol]
P_{H_2}	: partial pressure of hydrogen [atm]
T	: time [sec]
W	: mass of char [kg]

W_{ash}	: mass of ash [kg]
W_o	: mass of char at completion of devolatilization [kg]
X	: conversion of solid

REFERENCES

1. G. Chin, G. Liu and Q. Dong, *Fuel*, **66**, 356 (1983).
2. N. C. Nahas, *Fuel*, **62**, 1564 (1983).
3. S. N. Rodjeen, L. S. Mekasut, P. P. Kuchontara and P. P. Piumsomboon, *Korean J. Chem. Eng.*, **23**, 216 (2006).
4. S. H. Lee, K. B. Choi, J. G. Lee and J. H. Kim, *Korean J. Chem. Eng.*, **23**, 576 (2006).
5. J. Ruby, A. Johnson, H. Ziock and K. Lackner, *Proceeding of 21st international technical conference on coal utilization & fuel systems*, Clearwater, Florida, 4-7, March, 767 (2002).
6. T. Kalina, M. Plains and R. E. Moore, US patent, 3,847,567 (1974).
7. D. S. Scott, US patent, 4,822,935 (1989).
8. H. F. Feldman, US patent, 4,152,122 (1979).
9. K. K. Koh, N. C. Nahas, M. Plains, R. E. Pennington and L. W. Vernon, US patent, 4,094,650 (1978).
10. A. Zhang, M. Kaiho, H. Yasuda, M. Zabat, K. Nakano and O. Yamada, *Energy*, **30**, 2243 (2005).
11. D. W. McKee, C. L. Spiro, P. G. Kosky and E. J. Lamby, *Fuel*, **62**, 217 (1983).
12. C. Y. Wen and J. Huebler, *I&EC Process Design Develop.*, **4**(2), 142 (1965).
13. D. B. Anthony and J. B. Howard, *AIChE J.*, **22**(4), 625 (1976).
14. W. S. Cha, I. H. Baek and S. D. Park, *J. Korean Ind. Eng. Chem.*, **15**, 34 (2004).
15. W. S. Cha, I. H. Baek and S. D. Park, *J. Korean Ind. Eng. Chem.*, **15**, 570 (2004).
16. M. Makino and Y. Toda, *Fuel*, **60**, 321 (1981).
17. P. Arendt and K. Heek, *Fuel*, **60**, 779 (1981).
18. A. Tomita, O. P. Mahajan and P. L. Walker Jr., *Fuel*, **56**, 137 (1977).
19. T. Suzuki, M. Funaki, K. Tanaka, N. Okazaki and T. Yamada, *Fuel*, **75**, 627 (1996).
20. T. Yamada, A. Tomita, Y. Tamai and T. Homma, *Fuel*, **62**, 246 (1983).
21. Y. Nishiyama, *Fuel*, **65**, 1403 (1986).