

Efficient *in situ* drying of low rank coal in a pressurized down-flow flash dryer

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Abstract—Flash drying of low rank coal with synthesis gas was addressed by using a pressurized down-flow dryer. The proposed method is a potential approach to secure gaseous water that is required in coal processing by utilizing moisture in the low rank coal. The drying process was promoted by increasing the initial temperature of the synthesis gas as a drying medium and decreasing the particle size of the coal. The moisture removal rate of the coal using synthesis gas at 9 bars and 500 °C reached up to 97% within ten seconds. Although it is a higher temperature than that of fixed bed or moving bed dryer, outlet moisture laden synthesis gas had the low level of tar enough to be a feedstock of downstream catalytic process due to the short residence time in the dryer. The chemical composition changes of the coal during the drying resulted in reducing oxygen content to the atomic ratio of oxygen to carbon as 0.1 and enhancing its calorific value. Disappearance of hydroxyl functional group from the surface and physical reduction of the surface area of the coal decreased the moisture re-adsorption capacity, which could prevent the spontaneous combustion of the low rank coal.

Keywords: Low Rank Coal, Flash Drying, Down-flow, Synthesis Gas, Moisture Re-adsorption, Physico-chemical Properties

INTRODUCTION

Low rank coals, occupying nearly half of the reserved coals in the world, are abundant, easily accessible and mineable with low costs [1,2]. They have been considered as a potential primary source of energy and chemicals due to additional advantages of high reactivity, significant amount of volatile matters, and low amount of pollution-generating impurities, such as sulfur, nitrogen, and heavy metals [3,4]. However, high moisture levels in low rank coals result in low thermal efficiency and can increase fire risks and costs of transportation, operation and maintenance [2,5-7].

Drying is an essential step for the efficient utilization of low rank coals prior to a conversion process such as pyrolysis, gasification, liquefaction and combustion. Among various drying technologies, evaporative drying with hot air or flue gas or steam has been the principal approach for the large scale compared to non-evaporative methods such as solvent extraction, mechanical compression and microwave radiation [2,5].

Until now, upon most of dryer designs, moisture in the coal has been discarded without its further utilization. The coal industry has an issue of water shortage [8], hence utilizing moisture in the low rank coal can be a promising option to resolve the issue. This study utilizes synthesis gas for drying the low rank coal and also induces the moisture laden synthesis gas to have more mass and energy, which can also be turned into hydrogen rich synthesis gas through water gas shift reaction. Furthermore, synthesis gas is sig-

nificantly low in oxygen content so that it could reduce fire or explosion by igniting dust [9] and lead to safe operations.

In spite of its benefits, utilizing synthesis gas as a drying medium has been less studied, and furthermore pressurized atmosphere has been rarely reported. It can provide an additional volumetric compactness and let the drying process be easily adapted to a part of the existing high pressure operation units. To materialize this concept, flash drying or pneumatic drying can be one of the best options due to its high heat transfer rate and short contact time of just a few seconds, whereas ten to sixty minutes is for the contact time in the rotary dryer and fluidized bed dryer [2,5,10]. It also has an advantage of low maintenance cost owing to a small number of moving parts [2].

Regarding the flash dryer hydrodynamic design, many industrial and academic approaches have focused on up-flow or riser type, which has a hydrodynamic effect of both gas and solid flows against gravitation [4,10-12]. Down-flow or downer type flash drying has rarely been investigated, although it provides a concurrent flow of gas and solid to gravity [13]. It can diminish solid back-mixing that causes both long exposure of the coal to a high temperature and subsequent tar devolatilization. Thus, it can also eliminate the risk of plugging in the process line of down-stream operation units caused by the tar condensation [14].

This study firstly demonstrates that down-flow flash drying of the low rank coal with pressurized synthesis gas is a feasible approach for both supplying moisture from the coal to the down-stream and upgrading the low rank coal. To validate the idea, we investigated the efficiency of drying, the change in hydrocarbon compositions in the outlet gas and chemical and physical property changes of the coal using thermal and spectroscopic methods

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with BET and elemental analyses.

MATERIALS AND METHODS

1. Coal Samples and Analysis

Indonesian low rank coal was chosen for this study. The raw coal was pulverized and sieved to a size smaller than 1,000 μm . The results of proximate and ultimate analysis of the coal sample are shown in Table 1. The proximate analysis was conducted with

Table 1. Analyses of the coal sample

| Samples | Indonesian coal |
|--------------------------------|-----------------|
| Proximate analysis (ar, mass%) | |
| Moisture | 20.86 |
| Volatile matter | 34.00 |
| Fixed carbon | 37.71 |
| Ash | 7.43 |
| Ultimate analysis (daf, mass%) | |
| C | 71.44 |
| H | 5.36 |
| O* | 21.43 |
| N | 1.48 |
| S | 0.29 |
| Caloric value (kcal/kg) | |
| As received | 4,584 |
| Dry basis | 5,792 |

Notes: ar - as received; daf: dry ash free, Calculated by difference

TGA-DSC1 thermogravimeter (LECO) and the ultimate analysis was done with TruSpec Elemental Analyzer (LECO). Those analyses showed high oxygen content even with a dry ash-free basis, which results in a low heating value of the sample.

2. Drying Characterization

The drying experiments were conducted in a down flow dryer as shown in Fig. 1. The coal and gas were fed to an insulated vertical stainless steel tube (an internal diameter (ID) of 38 mm and 5 meters long) from a feed hopper and controlled to a flow rate of 4 kg/hr by a motor speed of the calibrated screw feeder. Nitrogen was provided from a storage cylinder for carrying the coal with a flow rate of 0.1 kg/hr by a mass flow controller, and syngas was fed at a rate of 14 kg/hr in the same way but separately provided and heated by an electric heater prior to the dryer. The velocity of syngas in a pressurized down-flow dryer was calculated to be 1.2 m/sec at the entrance. The operating variables are summarized in Table 2. The synthesis gas consists of CO, H₂, CO₂, CH₄ and N₂ with their fractions of 25%, 26%, 20%, 2% and 27%, respectively, to simulate the output of the pilot scale gasifier. The temperature of synthesis gas was measured by the thermometer gauge prior to the injection point of the coal and used as an initial syngas temperature. Five thermocouples were located in the dryer with the thermowell to check the gas temperature inside the dryer. The dried coal was separated from gas and moisture by a cyclone and a sintered metal porous filter at the downstream and was finally sent to a hopper for storage and sampling. Coal fines were collected from the filter chamber bottom after the experiment.

The moisture content of the coal is measured by Satorius balance of MA-150. The moisture content can be expressed through

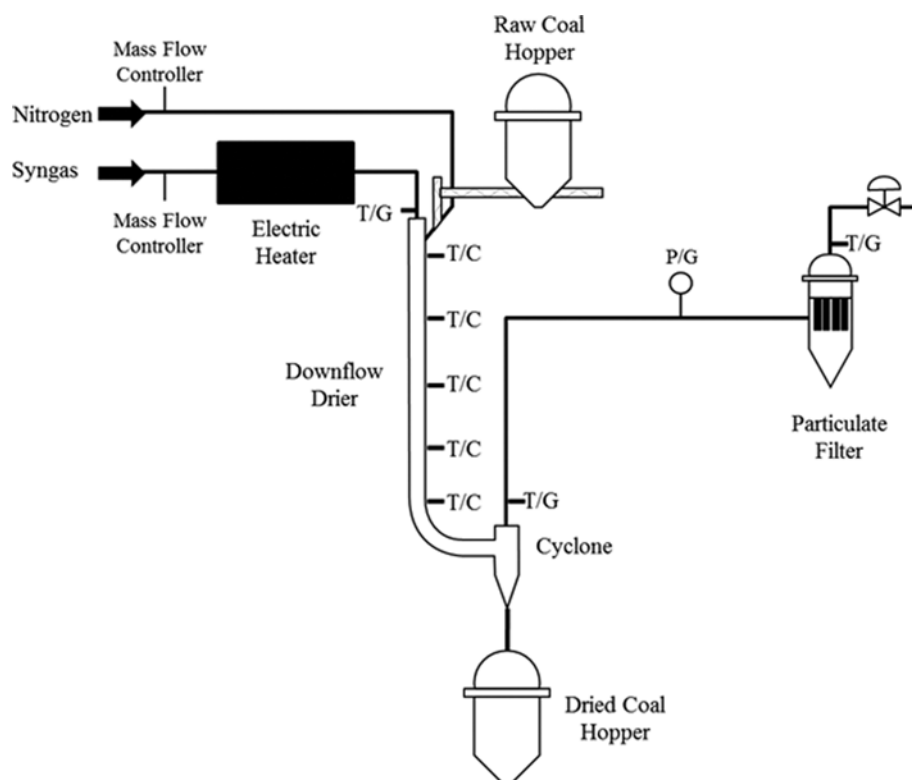


Fig. 1. Schematic of the vertical down-flow drying process.

Table 2. Experimental variables and ranges

| Variable | Range |
|--|---------|
| Coal feed rate (kg/h) | 4-5 |
| Coal particle size (μm) | 40-1000 |
| Operating pressure (bar) | 9 |
| Initial gas temperature ($^{\circ}\text{C}$) | 350-500 |
| Out gas temperature ($^{\circ}\text{C}$) | 212-278 |
| Transport nitrogen flow rate (kg/h) | 0.1-2 |
| Syngas flow rate (kg/h) | 14-18 |
| Initial gas velocity in dryer (m/sec) | 1.0-1.3 |

following equation:

$$X_t = \frac{m_t - m_0}{m_0} \quad (1)$$

where X_t is the instantaneous moisture content of the sample, m_t is the weight of the sample at time t and m_0 is the moisture free sample weight. Dimensionless moisture ratio (DMR) can be obtained by the following equation:

$$\text{DMR} = \frac{X_t - X_e}{X_0 - X_e} \quad (2)$$

where X_0 is the initial moisture content of the sample and X_e is the equilibrium moisture content. The equilibrium moisture content is the maximum inherent moisture content under a certain temperature and humidity. Since the value of equilibrium moisture content X_e is much smaller than X_t and X_0 in the high temperature drying process, the dimensionless moisture ratio can be simplified as X_t/X_0 [15,16].

$$\text{DMR} = \frac{X_t}{X_0} \quad (3)$$

3. Physical and Chemical Structure Change Measurements

Both BET surface area and pore volume of the coal samples were determined by nitrogen adsorption using Micromeritics ASAP 2020. The BET measurements were carried out with oven-dried 0.2 g sub-sample, which was further degassed under a vacuum condition at 50°C for 24 h to ensure complete drying and removal of adsorbed gases. Nitrogen surface area and pore volumes were calculated using the BET Method [17].

Since the initial temperature of the drying medium gas is much higher than the pyrolysis temperature of the lignite, it can cause tar devolatilization and change in the coal structure. To determine the degree of the change, the difference of the hydrocarbon compositions in drying medium gas was measured by Agilent 7890-RGA model gas chromatography.

FTIR spectroscopy was used for determining the chemical structure change during the drying step of coal. In this work, infrared (IR) spectra of wet coal and dried coal samples were obtained with a Thermo Fisher Nicolet IS5 mid-FTIR (Fourier transform infrared) spectrometer with $4,000\text{--}800\text{ cm}^{-1}$ region. The bands in the IR spectra were assigned according to the previous study [18]. The oxygen and hydrogen contents of dried coal sample were measured by the ultimate analysis and compared with those of the original coal sample.

Moisture re-adsorption tests were conducted at constant relative humidity and temperature according to a test method based on ASTM D1412. Equilibrium moistures were measured at relative humidity of 20%, 60%, and 98% for each case at 30°C in a humidity-controlled chamber for longer than three days [27].

RESULTS AND DISCUSSION

1. Drying Characteristics

To examine the effect of the initial temperature of drying gas medium on the drying performance, experiments were conducted at different initial synthesis gas temperatures (350, 400, 450 and 500°C). The effect of coal particle sizes was also investigated with the size ranges of 40-200, 200-500 and 500-1,000 μm , respectively. As shown in Fig. 2(a), the moisture ratio gradually decreased with the temperature rise. The higher was the synthesis gas temperature, the lower became moisture contents. When the drying temperature increases, the heat transfer into the coal particle and the evaporation rate of moisture inside the particle are enhanced, resulting in high drying performance. It also showed that the dimensionless moisture ratio (DMR) was reduced with the decreasing particle size. Since the low rank coal with smaller particles has a larger external surface area and facilitates the heat transfer from the drying medium to the center of particles and moisture evaporation from the inside of the coal particle to the surface [17], it would increase degree of drying. However, the effect of particle size was

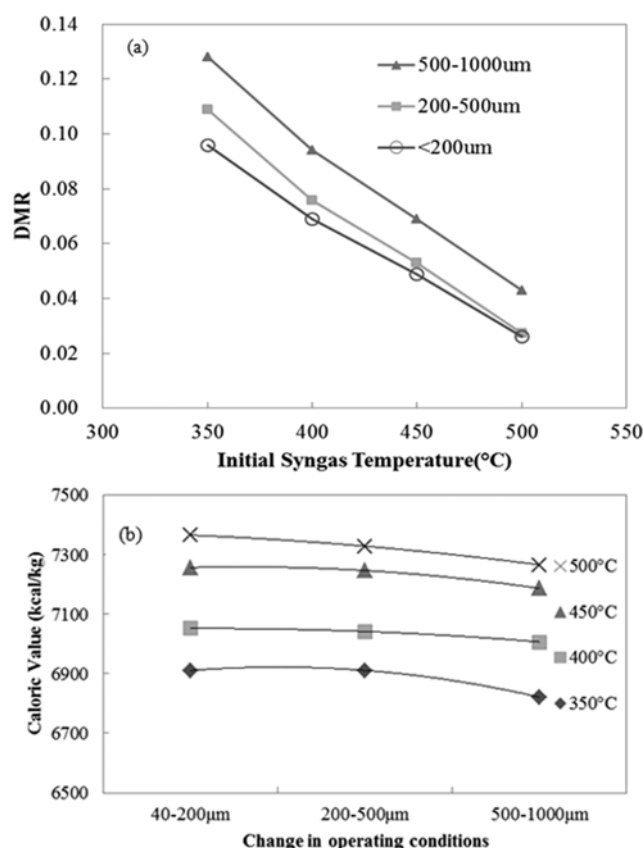


Fig. 2. Dimensionless moisture ratio (DMR) changes (a) and caloric values (b) with varying initial gas temperature.

not much pronounced compared to the temperature effect on the DMR change.

Fig. 2(b) illustrates that the caloric value of the coal was improved as the initial temperature rose. As the moisture of the coal was reduced down to 1.5% from 20%, the coal became more carbon-intensive with less oxygen content and provided a higher heating value (7,000 kcal/kg) on the weight basis.

2. Chemical Structure Change

Although the degree of tar evaporation is low, the chemical structure of surface and internal pore of the coal can be altered by the elevated pressure and temperature. The change in the chemical structure of coal surface was reported to be predominantly in the formation and destruction of the oxygen containing polar functional groups (including carboxyl, hydroxyl and carbonyl) [18]. During the experiment, the temperature of the coal particle gradually rose and the temperature of drying gas medium decreased with both coal and gas flow concurrently downward. The gas was cooled to 189 °C–278 °C at the outlet of cyclone and thus the temperature of the coal particle could be presumed to be lower than this temperature.

FTIR analysis results of both raw coal and dried coal samples are shown in Fig. 3. After the drying process, the hydroxyl functional group wavelength region ($3,700\text{--}3,100\text{ cm}^{-1}$) was significantly reduced, while aliphatic C-H stretching ($3,000\text{--}2,800\text{ cm}^{-1}$), carbonyl ($1,850\text{--}1,500\text{ cm}^{-1}$) and carboxyl functional group ($1,700\text{--}$

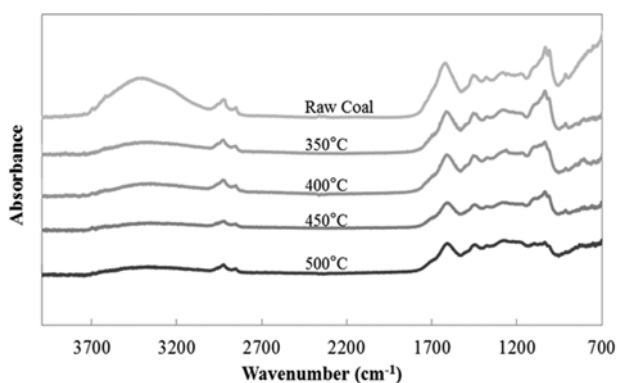


Fig. 3. FTIR spectra of as-received coal and dried coals at different temperatures.

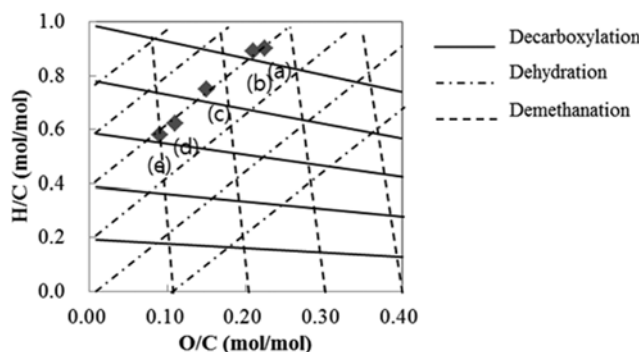


Fig. 4. Characterization of dried coal in revealed coal band (O/C and H/C ratios are determined on the dry ash free basis).

$1,600\text{ cm}^{-1}$) were not much changed. As carboxylic acid and carbonyl group disappeared significantly at a temperature higher than 200 °C for 10 minutes as reported in the literature [18,22], the temperature of the coal particle in the experiment could be below the range owing to a short residence time of less than 10 seconds. Reduction in the polar group leads to a reduction in the oxygen content and moisture-holding capacity of the coal [22,26]. Another indicator, the O/C and H/C ratios of the present samples from the ultimate analysis were shown in the Krevelen coal band [24] as portrayed in Fig. 4. The O/C and H/C atomic ratios were reduced by elevating the initial temperature of the drying synthesis gas medium. They were following the dehydration line, indicating most of the chemical change is due to the removal of hydroxyl functional group [25] rather than decarboxylation and demethanation. Thus, the carbon loss is not significant during the drying. It can also be said that the lower O/C atomic ratio at the higher drying temperature increased the caloric value of the dried coal.

The parameters of H/C and O/C ratios of the coal upgraded at 450 °C reached the values of 0.62 and 0.11, respectively. They were similar to those of 0.60 and 0.12, observed by the steam treatment process for the low rank coal at the similar temperature but with a much higher pressure of 7 MPa (K-Fuel) [27].

3. Hydrocarbon Devolatilization

Due to the exposure of the coal to the high temperature drying gas medium, it is necessary to determine the degree of hydrocarbon or tar evaporation in the drying medium after drying and a potential risk of tar condensation of hydrocarbon components in the downstream lines. The loss of useful volatile hydrocarbons from the low rank coal also increases the risk of fire from the ignition of volatile organic compounds.

The degree of hydrocarbon devolatilization in the coal was evaluated from the change in hydrocarbon compositions in the drying medium with different initial temperatures at the downstream as shown in Fig. 5. From the graph, it can be seen that the amount of hydrocarbon contents did not change significantly and the main change of chemical structure in the coal occurred from dehydration rather than demethanation and decarboxylation. One of the reasons is that the pressurized atmosphere suppresses the evaporation of the hydrocarbon volatile matter even with high tempera-

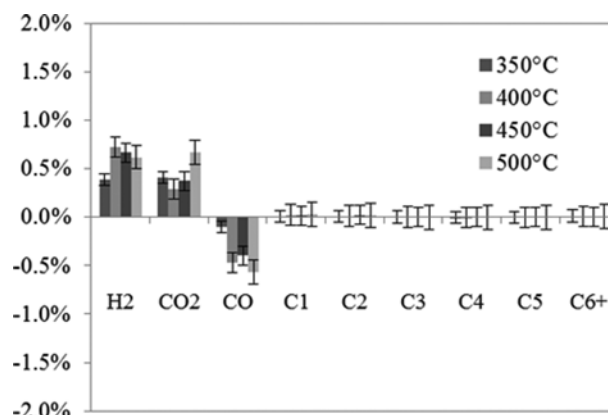


Fig. 5. Hydrocarbon composition changes in the drying synthesis gas medium with varying initial synthesis gas temperatures.

tures. This hypothesis is supported by the previous investigation, which described total yields of the volatile matter and tar decreased with the increasing pressure [20,23]. Another aspect is that the temperature of the coal particle may not be so high as the initial temperature of the drying medium with a short residence time of no longer than 10 seconds, while the tar yield begins to increase at 350–500 °C in a fixed bed or moving bed pyrolysis with a longer residence time of several minutes [15,23]. The gas formation by tar cracking occurs above 500 °C [15], and it is inferred that the increment in light hydrocarbons of outlet gas under the lower temperature is negligible. The temperature of the coal particles in the present work can be lower than that of the drying syngas medium due to absorbed heat latently by the moisture evaporation.

4. Structural Changes

The high drying temperature can also cause the physical property change of the low rank coal. The BET specific surface areas (m^2/g) of the raw and dried coal samples are shown in Fig. 6. The higher the drying gas medium temperatures, the lower the surface area is. The decrease in the surface area and pore volume may be explained by consideration of the shrinkage and plugging of macropores and mesopores [28]. The porous structure of the low rank coal is mainly comprised of mesopores with a small portion of macropores as shown in Fig. 7 [29]. Therefore, the surface area and pore volume of the low rank coal are reduced by the changes of pore structures in the mesopores due to the increase in the drying temperature.

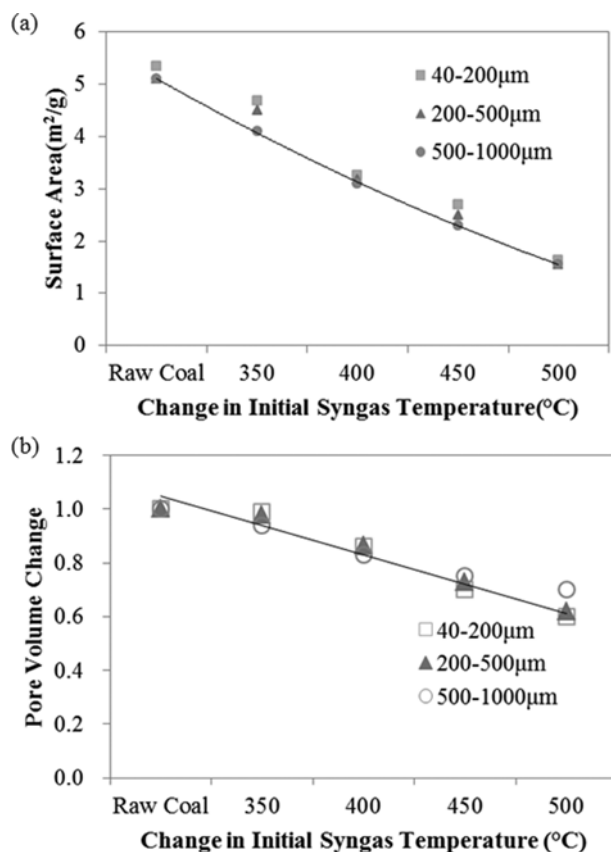


Fig. 6. (a) Surface area and (b) pore volume changes upon drying.

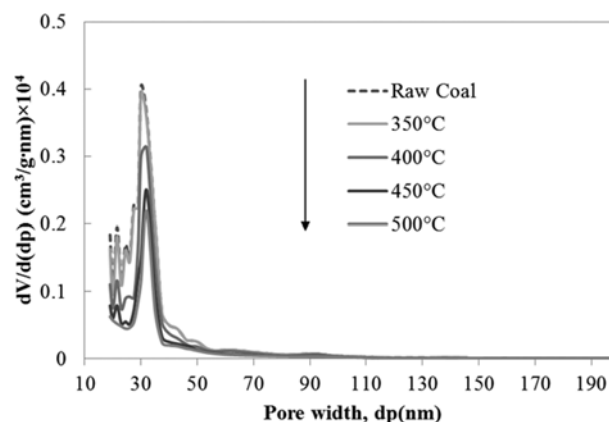


Fig. 7. Pore size distributions - pore volume vs. pore diameter.

5. Moisture Re-adsorption Characteristics of Dried Coal

The chemical and physical changes of the coal structure affect its moisture re-adsorption characteristic. Fig. 8(a) shows that the equilibrium moisture (a relative humidity 98% at 30 °C) reduced as the drying temperature increased. As seen from Fig. 8(b) of moisture re-adsorption curves, the dried coal at an initial temperature 400 °C tends to saturate with the atmosphere at the moisture content of approximately 11%, while the raw coal tends to equilibrate with the atmosphere at that of approximately 18% which is higher than that of the dried coal sample. This difference also implies that

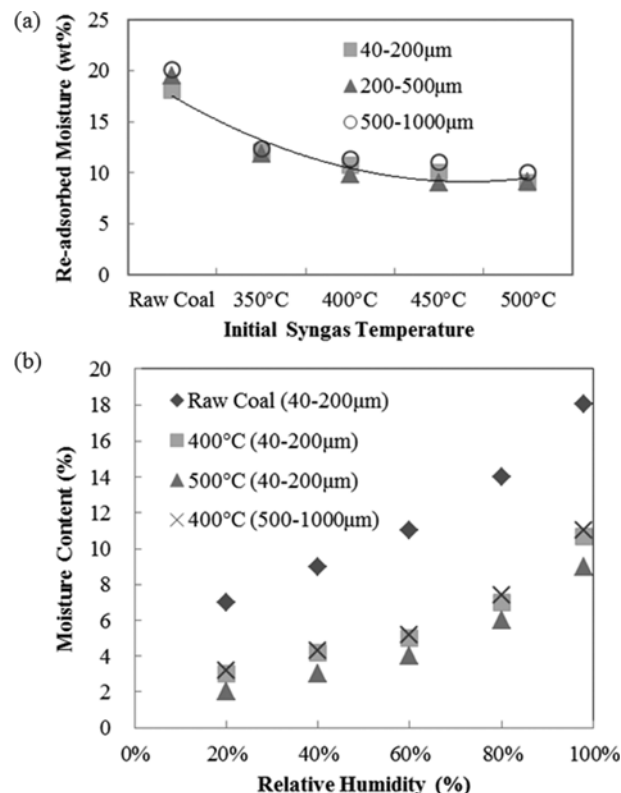


Fig. 8. (a) Re-adsorption moisture content (%) at relative humidity 98% and 30 °C and (b) moisture desorption and re-adsorption isotherms.

irreversible structure changes of the coal have taken place during the drying process [30].

It is concurrent with a previous study [22] describing that the water molecules interact with the surface of coal by hydrogen bonds with oxygen-containing functional groups. The hydrogen bonds include the intra-molecule hydrogen bonds in the coal and coal-water hydrogen bonds formed by carboxyl and hydroxyl groups in the coal [31]. The proportional relationship between equilibrium moisture content (moisture-holding capacity of coal) and polar groups is due to the fact that the polar groups (carboxyl, hydroxyl, and carbonyl) have greater affinity to chemically bind with the moisture, making the surface more hydrophilic and the coal retains more water molecules.

CONCLUSIONS

A flash drying process of the low rank coal with synthesis gas in a pressurized down-flow dryer has been investigated. The drying experiments were carried out under the initial temperature of the drying agent of 350 to 500 °C and 9 bars. The moisture removal reached 97% and the remaining water molecules were inherently bound inside the pores of the coal. The caloric value of the coal was increased as hydroxyl functional groups on the surface of the coal were reduced. While the coal surface is less hydrophilic, the outlet moisture laden synthesis gas has a low level of tar enough to be a feedstock in the downstream process without further treatment because the drying process was performed at an elevated pressure (9 bars) in short time intervals (<10 seconds). Accompanying the reduction of specific surface area and hydrophilicity of the coal, the proposed method irreversibly decreased moisture re-adsorption, which can inhibit a spontaneous combustion of the low rank coal.

REFERENCES

1. K. Burnard and S. Bhattacharya, Power Generation from Coal: Ongoing Developments and Outlook, International Energy Agency (IEA), Paris, France, http://www.iea.org/papers/2011/power_generation_from_coal.pdf (2011).
2. H. Osman, S. V. Jangam and S. Mujumdar, *Drying Technology*, **29**, 1763 (2011).
3. X. Li, R. K. Rathnam, J. Yu, Q. Wang, T. Wall and C. Meesri, *Energy Fuels*, **24**, 160 (2010).
4. W. G. Willson, D. Walsh and B. W. Irwin, *Int. J. Coal Preparation and Utilization*, **18**, 1 (1997).
5. N. Nikolopoulos, I. Violidakis, E. Karampinis, M. Agraniotis, C. Bergins, P. Grammelis and E. Kakaras, *Fuel*, **155**, 86 (2015).
6. H. Katalambula and R. Gupta, *Energy Fuels*, **23**, 3392 (2009).
7. X. Li, H. Song, Q. Wang, C. Meesri, T. Wall and J. Yu, *J. Environ. Sci. Suppl.*, 127 (2009).
8. L. Pan, P. Liu, L. Ma and Z. Li, *Energy Policy*, **48**, 93 (2012).
9. P. J. Wilver and C. A. Brumbaugh, *Proceedings of the 13th Biennial Lignite Symposium*, Bismarck, ND, May 21-23 (1985).
10. S. D. Kim, S. H. Lee, Y. J. Rhim, H. K. Choi, J. H. Lim, D. H. Chun and J. H. Yoo, *Korean Chem. Eng. Res.*, **50**, 106 (2012).
11. K. Zhang and C. You, *Korean J. Chem. Eng.*, **29**, 540 (2012).
12. T. J. Jamaledine and M. B. Ray, *Ind. Eng. Chem. Res.*, **49**, 5900 (2010).
13. Y. J. Kim, J. H. Bang and S. D. Kim, *Canadian J. Chem. Eng.*, **77**, 207 (1999).
14. S. Anisa and Z. A. Zainal, *Renewable and Sustainable Energy Reviews*, **15**, 2355 (2011).
15. G. H. Ko, D. M. Sanchez, W. A. Peters and J. B. Howard, *Twenty-Second Symposium (International) on Combustion/The Combustion Institute*, 115 (1988).
16. L. Jin, Y. Li, L. Lin, L. Zou and H. Hu, *Fuel*, **152**, 80 (2015).
17. G. N. Okolo, R. C. Everson, H. W. J. P. Neomagus, M. J. Roberts and R. Sakurovs, *Fuel*, **141**, 293 (2015).
18. A. Tahmasebi, J. Yu, Y. Han, F. Yin, S. Bhattacharya and D. Stokie, *Energy Fuels*, **26**(6), 3651 (2012).
19. K. S. Vorres, *Energy Fuels*, **8**, 320 (1994).
20. G. H. Ko, W. A. Peters and J. B. Howard, *Fuel*, **66**, 1118 (1987).
21. E. M. Suuberg, PhD Thesis, MIT (1977).
22. J. Yu, A. Tahmasebi, Y. Han, F. Yin and X. Li, *Fuel Processing Technol.*, **106**, 9 (2013).
23. C. Zeng, G. Favas, H. Wu, A. L. Chaffee, J. Hayashi and C. Li, *Energy Fuels*, **20**, 281 (2006).
24. D. W. van Krevelen, *Coal, Typology, Physics, Chemistry, Constitution*, 3rd Ed., Elsevier, Amsterdam, 673 (1993).
25. Y. Mahidin, Y. Ogaki, H. Nakata and H. Usui, *J. Chem. Eng. Japan*, **36**(7), 769 (2003).
26. Y. Sato, S. Kushiya, K. Tatsumoto and H. Yamaguchi, *Fuel Processing Technol.*, **85**, 1551 (2004).
27. G. R. Couch, Report of IEA Coal Research, IEACR/23, London (1990).
28. Y. S. Nugroho, A. C. McIntosh and B. M. Gibbs, *Fuel*, **79**, 1951 (2000).
29. C. E. Salmas, A. H. Tsetsekou, K. S. Hatzilyberis and G. P. Androutsopoulos, *Drying Technol.*, **19**, 35 (2001).
30. X. Li, H. Song, Q. Wang, C. Meesri, T. Wall and J. Yu, *J. Environ. Sci.*, 127 (Supplement) (2009).
31. K. Miura, K. Mae, W. Li, T. Kusakawa, F. Morozumi and A. Kumano, *Energy Fuels*, **15**, 599 (2001).