INDONESIAN MINING JOURNAL Vol. 14, No. 2, June 2011 : 74 - 81

THE EFFECT OF HYDROGEN PRESSURE ON THE PREPARATION OF ARTIFICIAL CAKING COAL FOR COKE BINDER

NINING S. NINGRUM, MIFTAHUL HUDA and HERMANU PRIJONO
R & D Center of Mineral and Coal Technology
Jl. Jenderal Sudirman No. 623 Bandung 40211,
Tel. (022) 6030483, 6038027, Fax. (022) 6003373
e-mail: ninings@tekmira.esdm.go.id

ABSTRACT

Binder of carbon compounds can be made through hydrogenation process and/or coal extraction. Hydrogenation of coal converts the steam coal into caking one which functions as a binder or additive in the making of coke while the extraction of coal produces good quality pitch. Some coals from Tanito Harum, Baramarta and Bukit Asam were used as raw materials for binder making. Observations included effect of hydrogen pressure on the total carbon and ash contents and free swelling index as well. Coal hydrogenation was performed in a 5-litre batch type autoclave at reaction temperature of 400ºC. The initial hydrogen pressure varies from 5 to 30 bars and to 1 hour reaction time. The next stage was the distillation of hydrogen product. It can be concluded that all non-caking coals used in the experiments can be converted into caking coal to be used as a binder in the coke making. The ash content within coal considerably affects the resulting binder product; binder that has low ash content is preferred.

Keywords: artificial caking coal, hydrogenation, coke binder

INTRODUCTION

According to Benk et al. (2008), the need for coke in the world will increase with the increasing demand for iron and steel. Demand of steel in Indonesia has outpaced domestic production. In 2006, Indonesia consumed about 6.2 million tons of steel and produced only 3.8 million tons. In 2011, it is predicted that the demand and domestic production of steel will be around 8 to 9 million tons and 4 to 5 million tons respectively. In order to reduce the amount of imported steel, Indonesia should increase domestic production of steel as well as improve efficiency of iron and steel making processes.

Krakatau Steel, the largest integrated iron and steel company in Indonesia, is planning to expand its production capacity and its efficiency by installing several blast furnaces. Currently the company uses expensive natural gas and imported iron-ore pellet for producing the iron. The use of blast furnace will reduce the amount of imported iron ore pellet. However, blast furnace uses strong cokes that must be produced by carbonization of imported coking coals. Indonesian coal are mainly non coking coals although few of caking coals may be found in some parts of Indonesia. Caking coal fuses and forms a plastic mass that swells and resolidifies into a porous solid during heating under inert atmosphere. A coking coal is caking coal, which yields a solid product (coke) with properties suitable for use in blast furnace. Non-caking coals usually low rank coals (sub-bituminous and lignite), that does not fuse together or solidify as coke when heated.

Figure 1 illustrated the mechanism of Artificial Caking Coals (ACC) that is synthesized from non-coking coal. Coal consists of clusters of aromatic carbon rings with appreciable amount of hydro aromatic carbon. The individual cluster is joined by various types of bonds, including short aliphatic bridges, ether linkages, sulfide or disulfide linkages and biphenyl linkages as well. ACC may be synthesized from non-caking coal at temperature about 400ºC, in the presence of transferable hydrogen. At such a temperature, coal releases CO_2

Received : 01 February 2011, first revision : 20 April 2011, second revision : 24 May 2011, accepted : June 2011

and H_2O and forms free radicals. Hydrogen stabilizes free radicals to prevent retrogressive reaction and to maintain plasticity of coals. Other reactions such as cracking, polymerization, condensation and polyaromatization may take place. After cooling a residue of high aromaticity, high hydrogen and low oxygen content will be produced. Such a residue is expected to have plastic properties and ability to be used as binder or coking additives (Steel Handbook, 1982). The objective of this research is to synthesize the ACC from Indonesia non-caking coal. The plastics property of the ACC will be examined using crucible swelling number or free swelling index methods.

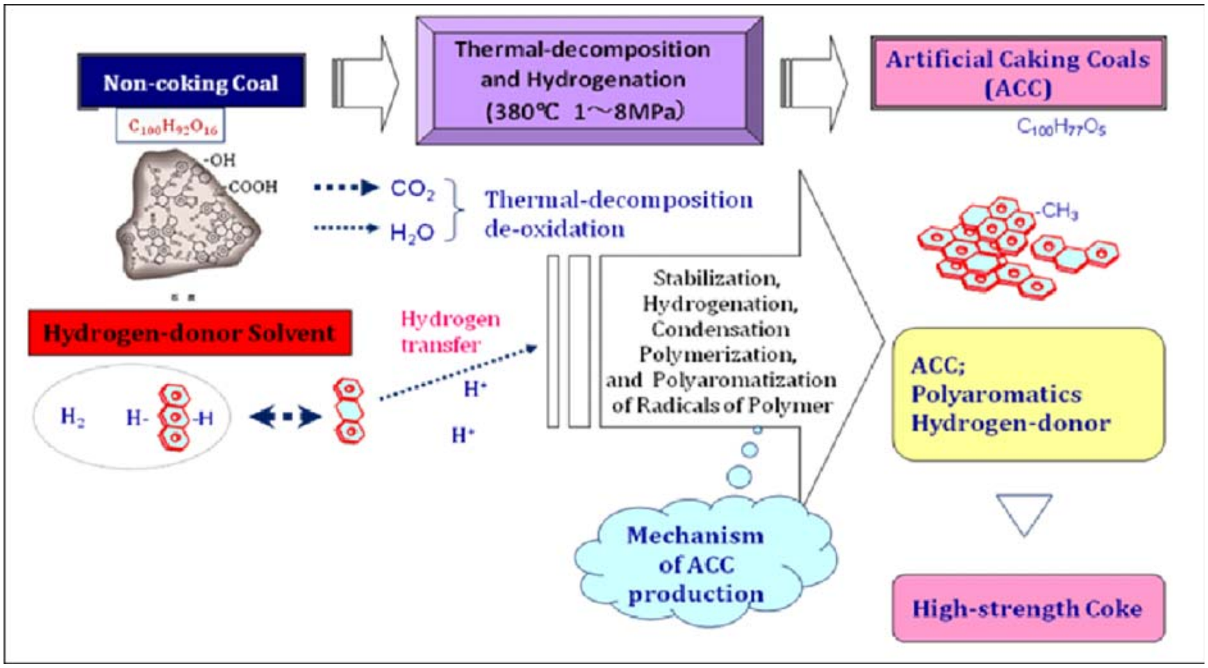

Figure 1. Scheme of artificial caking coal production

METHODOLOGY

Materials and Equipments

Coals from 3 coal mining areas in Indonesia, namely Tanito Harum (TH) East Kalimantan, Baramarta (BM) South Kalimantan and Bukit Asam (AL) South Sumatera were used in this study. The coals were pulverized into -170+200 mesh and dried at 150ºC for 2 hours prior to using them for the expeiments. Laterite iron ore from South Kalimantan was used as a catalyst. The particle size of catalysts was less than 325 mesh (Ningrum, 2010). The solvent was derived from coal tar with boiling point of 250-350ºC. Other materials are sulfur and hydrogen. The main equipment used is a 5-liter capacity autoclave, equipped with an agitator stirrer, temperature and pressure controller and distillation unit.

Procedure

The autoclave was heated from room temperature to 400ºC at heating rate of 5ºC/min. The influence of initial pressure and coal type on characteristics of the product were examined. Each experiments used 400 g coal (dry ash free/daf), 600 g of solvent, 12 g of Fe (weight ratio of Fe in catalyst/coal (daf) = 3/100) and 13.71 g of sulfur (S/Fe=2 atomic ratio). The initial pressure of hydrogen varied from 10 to 30 bars along with reaction time from 30 to 60 minutes. After the reaction time, the autoclave was cooled and depresurrized to atmospheric pressure. The liquid products were separated from solid residue by distillation and fractioned based on their boiling point into fractions of 150-250ºC and 250-350ºC. The fraction of 250-350ºC was re-used for solvent of the next experiments. The procedure of experiment is illustrated in Figure 2.

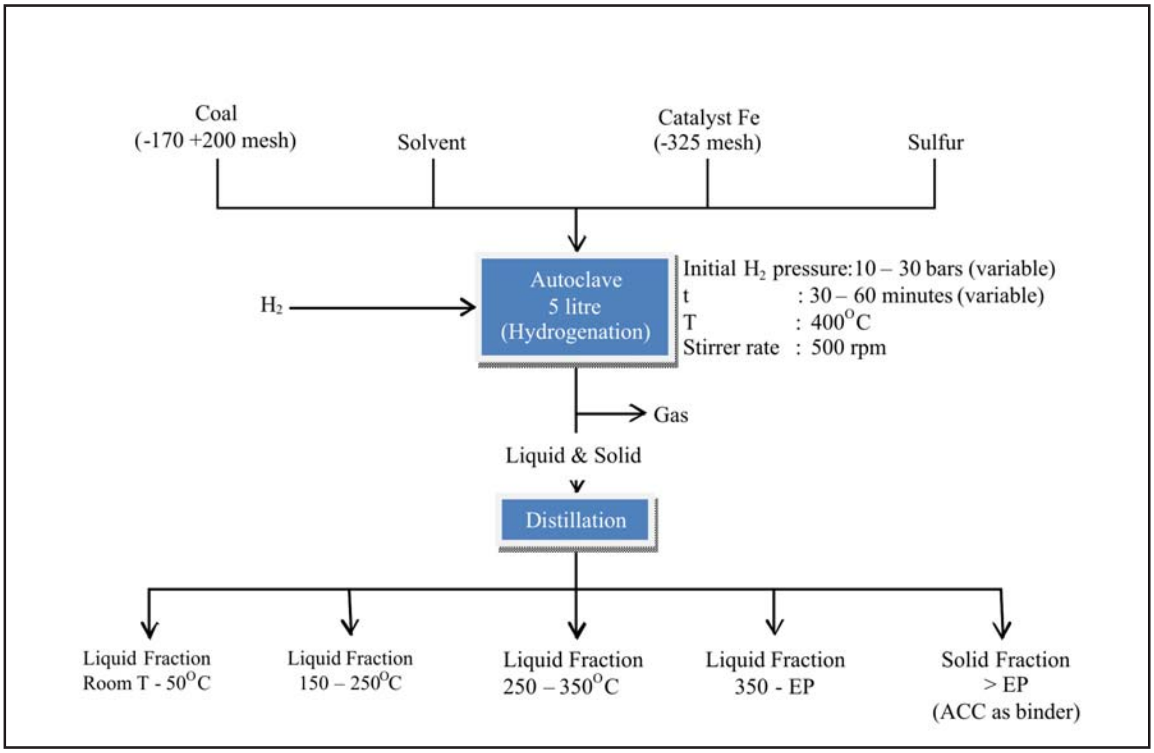

Figure 2. Flow diagram of ACC making

RESULTS AND DISCUSSION

Characterization of Coal

Prior to conducting the research of carbon materials for binder making, coal which was used as raw material was analyzed to find out its characteristics. The analyses included proximate and ultimate analyses as well as calorific value and free swelling index (FSI) of coal. Those need to be evaluated as it will influence the process of binder making. The results are shown in Table 1.

Table 1. Proximate, ultimate, calorific value and FSI of coal

Analysis Parameters	COAL			Method
	TH	BM	AL	
Proximate				
Moisture (% adb)	11.5	4.84	10.89	ASTM D.3302
Ash (% adb)	2.61	6.55	5.62	ASTM D.3174
Volatile matter (% adb)	40.66	42.92	39.52	ISO 562
Fixed carbon (% adb)	45.23	45.69	43.97	ASTM D.3172
Ultimate				
Carbon (% daf)	79.52	83.95	78.39	ASTM D.5373
Hydrogen (% daf)	5.31	5.98	4.76	ASTM D.5373
Nitrogen (% daf)	1.68	1.49	1.32	ASTM D.5373
Sulfur (% daf)	0.22	0.34	0.24	ASTM D.4239
Oxigen (% daf)	13.27	8.24	15.29	ASTM D.3176
Atomic ratio of O/C	0.1252	0.0736	0.1464	
Atomic ratio of H/C	0.8017	0.8548	0.7281	
Calorific value (cal/g adb)	6437	7111	6426	ASTM D.5865
Free swelling index (FSI)	0	1	0	ASTM D.720

Table 1 shows that the three coals retain high calorific value, performed by their calorific value around 6100-7100 cal/g. The calorific value of BM coal is slightly higher than that of TH and AL coals. It is strongly affected by its low inherent moisture content. Based on the ultimate analyses, the carbon content of BM coal is the highest compared to TH and AL coals. The higher the coal rank, the higher the carbon content results in the hydrogen and oxygen content are lower. Oxygen occurs naturally in coals as hydroxyl, carbonyl, methoxyl and carbonyl groups. Similar to hydrogen, the oxygen content of coal is depleted during the natural ageing process, by the evolution of water vapor and oxides of carbon, and it thus a strong function of coal rank (Grainger and Gibson, 1981). In addition to proximate and ultimate, calorific value and FSI analyses; the petrography analyses was also conducted. The results are shown in Table 2.

Table 2. Maceral analysis result

Analysis Parameters	Coal		
	TH	BM	AL
Vitrinite	**65.8**	**74.6**	**69**
Telovitrinite (% vol)	38.2	28.4	21.2
Detrovitrinite (% vol)	27.2	46	43.4
Gelovitrinite (% vol)	0.4	0.2	4.4
Exinite	**18.2**	**13.2**	**8.4**
Sporinite (% vol)	0.4	1.6	0.4
Cutinite (% vol)	6.4	-	1
Resinite (% vol)	9.2	11	5.6
Alginite (% vol)	0.6	0.2	0.2
Suberinite (% vol)	1.6	0.4	1.2
Inertinite	**15.6**	**8.8**	**11.8**
Fusinite	-	-	1
Semifusinite (% vol)	4.2	1	3.6
Sclerotinite (% vol)	8.4	5.6	5.2
Inertodetrinite (% vol)	3	2.2	2
Mineral Matter	**0.4**	**3.4**	**10.8**
Oxide	-	-	1
Clay	0.4	3	2.4
Pyrite	-	0.4	7.4
Mean of Rv	**0.5**	**0.48**	**0.49**

The dominant maceral of those three coals was vitrinite ranging between 66 and 75% vol. Vitrinite consists of three maceral groups. Those are telovitrinite, detrovitrinite and gelovitrinite (Bustin et.al. 1983). There is slightly difference in telovitrinite content between those three coals. The telovitrinite of TH coal (38.2% vol) is higher than that of BM coal (24.8% vol) and AL (21.2% vol). Telovitrinite is one of the main sub-macerals in high rank coal. It is derived from wood tissue that has a high reflectance. Fluorescence does not appear in the light. It also has high cellulose content (Falcon and Snyman, 1986). The content of this telovitrinite is predicted to affect the compressive strength of coke. The content of the cutinite especially exinite on TH coal also appears higher than those in maceral content of BM and AL coal. Cutinite is one of sub-macerals of the exinite group; a sub maceral that is most resistant to pressure. By combining cutinite and telovitrinite, it will likely make the maceral structure of coking coal more compact.

Effect of Initial Hydrogen Pressure on Carbon Content

The experiment results of binder-making from Indonesian coal are showed in Figure 4, 5, 6 dan 7. Observations were carried out on the effect of hydrogen pressure on the content of carbon, FSI, the atomic ratio of O/C, the atomic ratio of H/C and the ash content of hydrogenated coal.

Reaction pressure is usually the initial hydrogen pressure. The initial hydrogen pressure is a partial pressure of hydrogen used. The pressure affects autoclaves operating pressure or other type of reactor used. In this study, it was observed that the influence of initial hydrogen pressure to carbon content of hydrogenation products is showed in Figure 4.

A high initial hydrogen pressure is expected to accelerate the heating rate at the specified operating temperature and will increase the carbon content and hydrogen consumption. Figure 4 indicates that commonly carbon content of hydrogenated coal increases with increasing initial hydrogen pressure but not evently. Start from 10 bar, the carbon content of TH, BM and AL hydrogenated coal increases. The highest carbon content of TH hydrogenated coal on hydrogen pressure of 25 bars is 91.00%. At 25 bar pressure, the carbon content of AL coal amounted to 89.21%. The highest carbon content of BM coal obtained on hydrogenation with the pressure of 15 bars is 87.92%.

The initial carbon content of coal does not guarantee the increase carbon content of the hydrogenation product. This is evident from the results of the experiment in Figure 4. BM Coal has 83.95% carbon content, while the carbon content of TH and AL coal are 79.52 and 78.39% respectively. The hydrogenation product shows that the highest carbon content of TH coal is 91.00%. It is believed that there are other compounds in coal that affect the quality of hydrogenation products such as coal moisture content.

Effect of Initial Hydrogen Pressure on FSI

Caking coal states the ability to clot and swell during carbonization process. The test is associated with a rapid heating rate. The test to measure the caking properties is the FSI as a useful guide to assess the minimum limit of coking coal.

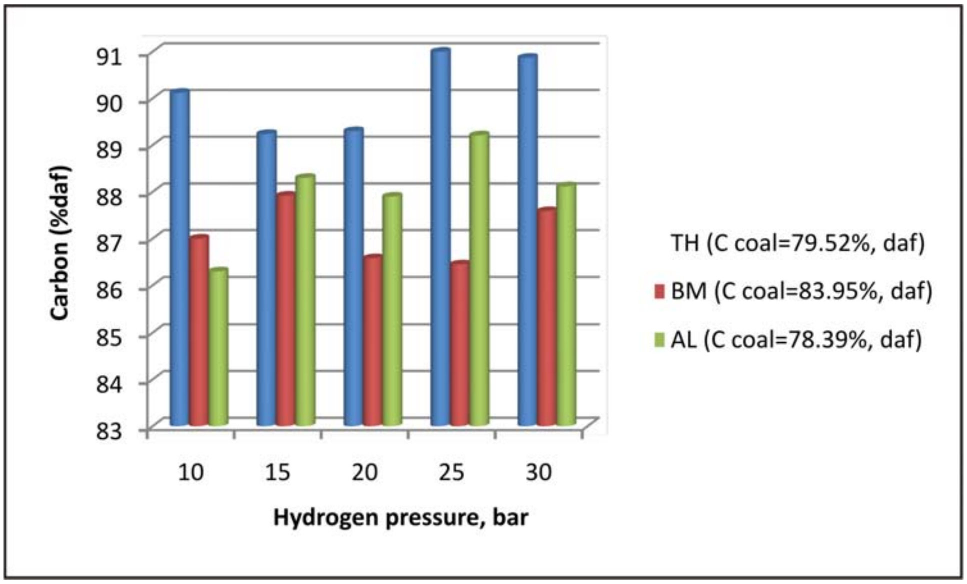

Figure 4. The effect of hydrogen pressure on the total carbon

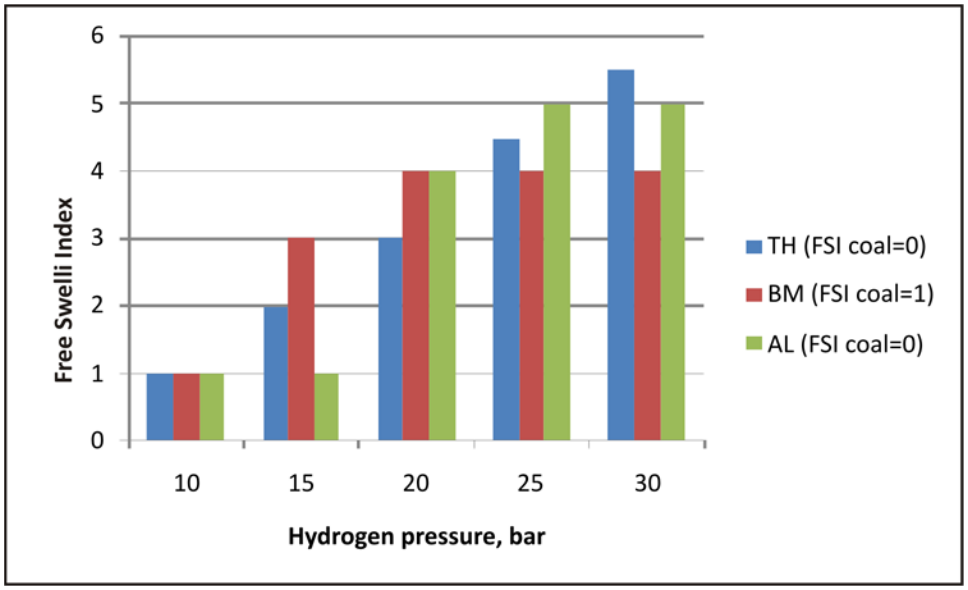

Figure 5. The effect of hydrogen pressure on the free swelling index

According to ASTM Standards D720-91 (2009), the FSI limits for coke making is the coal with the FSI ranges from 5 to 9. Based on the observations of the effect of hydrogen initial pressure to the FSI (Figure 5), it indicates that the increase of initial pressure of hydrogen results in increasing the FSI up to > 5. Increasing the hydrogen pressure up to 20 bars results in the increase of the FSI of BM hydrogenated coal from 0 to 4 and the FSI of AL hydrogenated from 0 to 5. FSI that is bigger than >5 for TH hydrogenated coal can be obtained at a hydrogen pressure of 30 bar.

From the observation it is showed that the TH coal has apparently better caking character than that of BM and AL coal. FSI of TH coal continues to increase with the increase of hydrogen pressure; while in BM coal, the increase of swelling stops at 20 bar hydrogen pressure and AL coal the swelling discontinue at 25 bar of hydrogen pressure. This condition is probably affected by its maceral composition. According to Bustin et al. (1981), the FSI is higher for bright or high vitrinite samples than that of dull or high inertinite materials. Vitrinite, exinite and some inertinite macerals melt when heated. The remainding of inertinite as well as most of the mineral matter is essentially unaltered. The TH coal has a high vitrinite and inertinite but low mineral matter as shown in Table 2.

Relation of Atomic Ratio of H/C and O/C to Hydrogenation Product

Coal, as a whole, is strongly aromatic. Two important aromaticity values need to be considered. The percentage of hydrogen atoms is directly bound to aromatic carbons and the percentage of aromatic carbon atoms. Chemically structure, coal is a hydrocarbon that consists of atom variation (Nowacki. 1979). Carbon atoms in coal are commonly 65-75% of aromatic carbon, 15-25% of hydroaromatic carbon and 5-10% of alifatic carbon. It is indicated that commonly carbon aromaticity is one of the more important structural parameters of coal.

Atomic ratio of hydrogen to carbon in coal ranges from 0.3 to 0.8. It is expected that the higher the rank of a coal, the higher the carbon content; however oxygen, hydrogen content and aromaticity decrease. Consequently, atomic ratio of H/ C also decreases with the increase of the coal rank.

Figure 6 presents the effect of initial hydrogen pressure on atomic ratio of O/C and atomic ratio of H/ C. The atomic ratio of O/C of hydrogenated coal significantly decreases with the increase of initial hydrogen presure. The atomic ratios of hydrogen to carbon in hydrogenated coal vary from 0.73 to

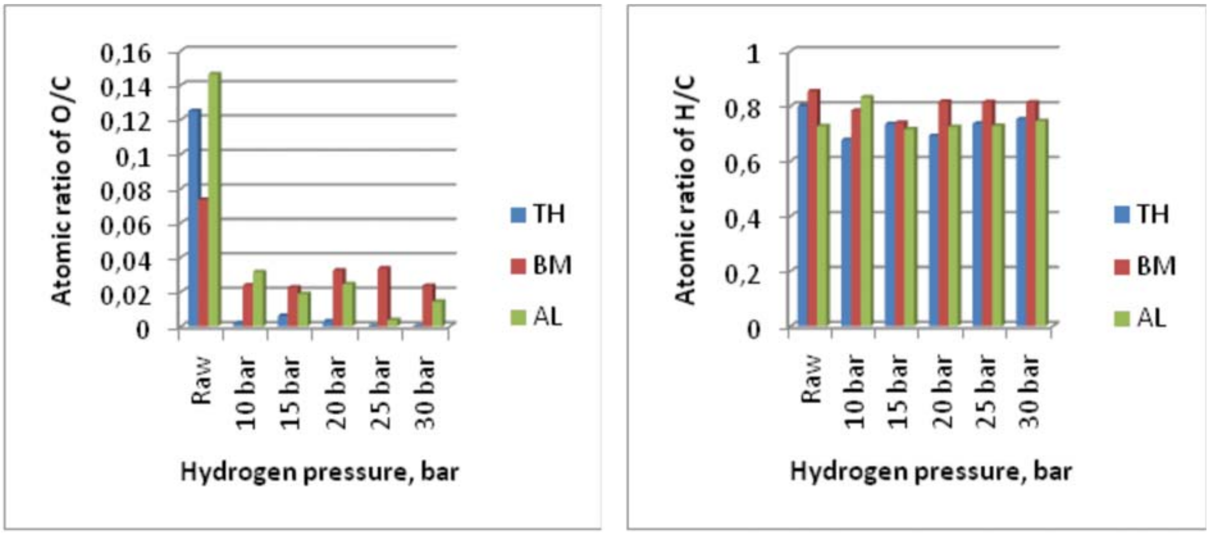

Figure 6. Effect of initial hydrogen pressure on atomic ratio of O/C and on atomic ratio of H/C

0.85. Figure 6 shows that the atomic ratios of hydrogen to carbon of hydrogen coal are between 0.67 and 0.82. It slightly decreases if compared to the atomic ratio of hydrogen to carbon of coal. This indicates that the rank of TH, BM and AL coals increase.

Observation of Ash Content in Hydrogenated Coal

Ash in coal is included as the unwanted material because in coal utilization, primarily as a fuel in a power plant, produces the fly and bottom ashes that cause pollution to the surroundings. Currently, coal ash is utilized for cement manufacturing and paving blocks. In the cement industry, ash is absorbed into the clinker product. In the coke manufacturing, the ash content should preferably be low in terms of reducing the slagging load and associated inefficiencies in the blast furnace.

Figure 7 reflects the increase of ash content in TH, BM and AL coals which have been hydrogenated with varied initial hydrogen pressure. A striking increase can be seen in the BM hydrogenated coal at 10 bars initial pressure. The increase is more than 3 times from the initial (6.55%), namely up to 19.73%. The increase of ash content is supposed to occur at the catalyst process and sulfur addition. The catalyst added is limonite from Soroako and will become an ash after the process because the limonite is an inorganic mineral. Some sulfur occurs as H_2S and will partly become pyrite and mix with coal ash and catalyst.

From Figure 7, it can be seen that the pressure of 15 bars represents good conditions for TH coal. In those circumstances, increasing the ash content could be reduced, approximately to 5.8% (initially 2.61% up to 8.40%). For BM coal the best hydrogen pressure is 25 bars, while the AL coal is 20 bars. To get the low ash content binder it is suggested using coal of low ash content less than 5%. According to the research conducted by Sharma et al. (2002), the characteristics of coal used, including ash content, will affect the strength of coke.

CONCLUSIONS AND SUGGESTIONS

Conclusions

Based on their proximate and ultimate analyses, calorific value and FSI; it reveals that the TH, BM and AL coals are sub-bituminous ones performing calorific value between 6000 and 7200 cal/g (adb). According to the microscope analyses, it is indicated that the maximum vitrinite reflectance (Rv max) of those coals are between 0.48 and 0.50. Most of the macerals in such coals are reactive ones that will affect coke structure.

Initial pressure of hydrogen increases the carbon content and hydrogen consumption. The carbon

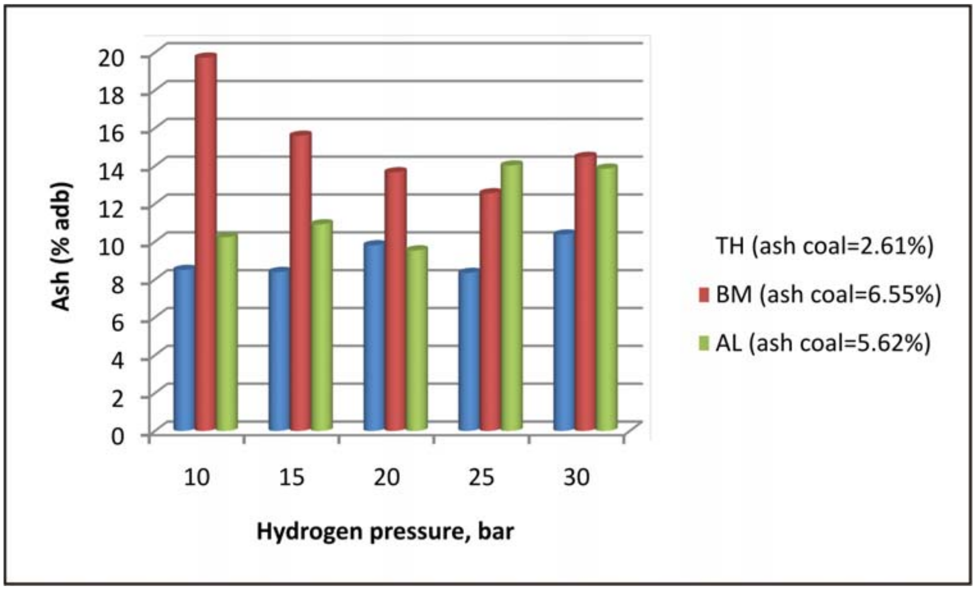

Figure 7. The effect of hydrogen pressure on the ash content

content of hydrogenated coal increases fluctuatively with the increase of initial hydrogen pressure. The highest carbon content of TH and AL hydrogenated coals on hydrogen pressure of 25 bars are 91.00% and 89.21% respectively. The highest carbon content of BM coal obtained by hydrogenation with the pressure of 15 bars is 87.92%.

Caking characteristics can be seen from the FSI test. The values increase in line with the increase of hydrogen initial pressure. The TH hydrogenated coal has good caking properties at hydrogen pressure of 30 bar and FSI > 5

The study show that Indonesian non caking coals can be converted into the caking ones. The artificial caking coal may be used as blending materials for coke making.

The ash content of the coal considerably affects the binder product. Binders with low ash content are preferable.

Suggestions

The research needs to be continued to get the best binder for coke making by observing several parameters such as coal type, coal particle size and temperature as well.

The materials used for this study should retains low ash content. Meanwhile, the process is not necessary use a catalyst since the material significantly affects the ash content of binder product.

ACKNOWLEDGEMENTS

The authors wish to thank the Research and Development Center for Mineral and Coal Technology that has provided fund and facilities to conduct this research. Thanks also extended to PT. Tanito Harum, PD. Baramarta and PT. Bukit Asam for providing the coal as raw material in this experiment.

REFERENCES

ASTM Standard D720-91, (2009). *American Society for testing Materials*, New York, pp. 326-330.

Benk, A., Talu, M. and Coban, M., 2008. Phenolic resin binder for the production of metallurgical quality briquettes from coke breeze: Part I, *Fuel Processing Technology, Vol 89, Issue 1*, pp. 28-37.

Bustin, R.M., Cameron, A.R., Grieve, D.A and Kalkreuth, W.D., 1983. *Coal petrology, its principles methods and application,* Geological Association of Canada, Short Course Notes 3, 230 p.

Falcon, R.M.S. and Snyman, C.P., 1986. An Introduction to coal petrography: Atlas ofl petrographic constituents in bituminous coal of Southern Africa, The Geological Society of South Africa, *Review paper Number 2,* 27 p, 39 plates.

Grainger, L and Gibson, J., 1981. *Coal Utilisation, Technology, Economic and Policy*, London, 503 p.

Ningrum, N.S., 2010, Pengaruh ukuran partikel katalis bijih besi dan rasio atom S/Fe terhadap produk pencairan batubara. *Prosiding Seminar Nasional XIII "Kimia dalam Pembangunan"*, Yogyakarta, hal 9-18.

Nowascki, P., 1979, *Coal Liquefaction Processes*, Noyes data corporation, USA, 339 p

Sharma, A.K., Das, B.P. and Tripathi, P.S.M., 2002. Influence of properties of bituminous binders on the strength of formed coke, *Fuel Processing Technology, Vol 75, Issue 3*, pp. 201-241.

Steel Handbook, 1982. *Iron Making & Steel Making Vol. II,* Japanese Patent No. 666580 (PCT/JP2006/304011), 212 p.