INDONESIAN MINING JOURNAL Vol. 13, No. 1, February 2010 : 8 - 15

EVALUATION OF IRON ORE FROM SOUTH KALIMANTAN AND TAILING OF PT. FREEPORT AS CATALYST PRECURSORS FOR DIRECT COAL LIQUEFACTION

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ABSTRACT

Research on catalyst derived from minerals for coal liquefaction reaction remains attractive since Indonesia has various kinds of minerals which are suitable to be used as catalyst precursors. In this research, iron ore from South Kalimantan and tailing of PT. Freeport were examined their activities to find the most suitable catalyst precursor for coal liquefaction reaction. Experiments were performed using a 0.5 litre batch type autoclave equipped with a horizontal shaking unit (54 times per minute) at reaction temperature, initial hydrogen pressure and reaction time of 400ºC, 10 MPa and 1 hr, respectively. The result showed that tailing produced lower oil yield and coal conversion than those of iron ore. Tailing is suspected to experience slower hydrogen transfer rate during coal liquefaction since it produced larger pyrrhotite crystal size than that of iron ore.

Keywords: coal liquefaction, catalyst precursor, iron ore, tailing of PT. Freeport

INTRODUCTION

The high dependence of most modern industrial and transport systems on oil has led to use up of oil reserve. World oil production was about 4 billion barrels in 1950 and sharply increased to 28 billion barrels in 2000 however there was no large oil reserve has ever been found (Metz, 2007) since 1970. Thus, since the year, the growth of oil demand has outpaced the growth of oil reserve. Moreover, Energy Information Agency has predicted that world oil production will peak in the year 2037 followed by a drastic decrease of oil production after 2037 (Wood, 2003) due to limited oil reserve.

The issue of peak oil has led some countries to increase their energy security by reducing the dependency on oil through development of renewable energy (go-renewable), nuclear (go nuclear) and coal (back to coal). Due to abundant coal reserve in the country, Government of Indonesia (GOI) has set up a national energy policy (Presidential Regulation No. 5 of 2006) among which to increase the share of coal in the energy mix from 14% in the year 2005 to 33% in the year 2025. The policy also states that 2% of energy should come from synthetic oil from coal.

To implement the coal liquefaction program, GOI in cooperation with the Government of Japan has conducted joint research for the development of coal lquefaction technology and feasibility study for the construction of coal liquefaction plant. Under the cooperation, a new coal liquefaction process namely improved BCL (Brownn Coal Liquefaction) process was successfully developed. The new process is expected to be more energy efficient with lower invesment cost than the proven BCL technology developed in Australia (Huda, 2007).

Several coal liquefaction processes including BCL use iron minerals as their catalyst precursor (Hirano. 1999). Iron minerals are generally used together with molecular sulfur which are transformed into pyrrhotite under coal liquefaction con-

Received : 13 November 2009, first revision : 21 December 2009, second revision : 25 January 2010, accepted : February 2010

ditions. Pyrrhotite ($Fe_{1-x}S$) is believed to be the active phase that catalize coal liquefaction reaction (Kaneko, 1998). Thus, iron minerals (iron oxyde/hydoxide) themselves do not catalyze coal liquefaction, but play as precursors for the catalysts.

Investigation of several Indonesia iron mineral as catalyst for coal liquefaction also has been conducted (Hirano, 2001). Soroako limonite was reported more active for direct coal liquefaction catalyst than Australia Yandi Yellow limonite (Kaneko, 2002). Nevertheless, research and development of coal liquefaction catalyst derived from minerals is remain attractive since Indonesia has various kinds of minerals which may suitable to be used as catalyst precursors. In this research, iron ore from South Kalimantan and tailing of PT Freeport will be examined their activities for coal liquefaction process. The objective of this research is to compare the activity of both catalyst precursors for coal liquefaction reaction. The use of tailing or iron ore with deposit located close to coal liquefaction plant is expected to reduce the cost of catalyst for the plant.

EXPERIMENTAL

Materials

The coal used for experiment is Mulia coal which was obtained from Arutmin Coal Mining in South Kalimantan. The analyses of Mulia coal is shown in Table 1. The coal was pulverized to less than 200 mesh and dried at 150ºC for 2 hrs before use. The liquefaction solvent was obtained from Takasago Coal Liquefaction Centre (TCLC), Japan. It is a recycle solvent which has been used for coal liquefaction study in TCLC. The analysis of the solvent are shown in Table 2.

Two catalyst precursors, iron ore from South Kalimantan and tailing of PT. Freeport Indonesia, were used for the experiments. The tailing was taken from rivers surrounding PT. Freeport mining however it has been up graded to increase the concentration of its valuable mineral. The precursors were ground in a ball mill for 1 hr and screened into four fractions of -140+200, -200+250, -250+325 and -325+400 mesh prior to the sulfidation and liquefaction test and analysis.

Analysis of Catalyst Precursors

To determine the formation of pyrrhotite, catalyst precursors before and after sulfidation reaction were subjected to XRD analyses (SHIMADZU, Maxima 7000, kV 40, mA 30). Optical microscope (Microscope, Nikon eclipse E 600 Pol) and Atomic Absorption Spectrofotometer (AAS Variant, AAS Spectr AA 240 FS)) were used to analyse minerals and chemicals composition of the catalyst precursors. SEM-EDX (JEOL 6360 – JED 2300) was also used to identify the morphology of the catalyst.

Coal Liquefaction

The equipment used for liquefation tests was a 0.5 l batch autoclave equiped with a horizontal shaking unit (54 times per minute) at reaction temperature, initial hydrogen pressure and reaction

Table 1. Analysis of Mulia Coal

Proximate	Total Moisture	Moisture	Ash	Volatile Matter	Fixed Carbon
analyses	30.44% (ar)	26.05% (adb)	2.17% (adb)	36.44% (adb)	35.34% (adb)
Ultimate	C	H	O	N	S
Analyses (adb)	52.67%	6.78%	37.30%	0.91%	0.17%

Note: ar = as received basis; adb = air dried basis

Table 2. Analysis of TCLC solvent

Boiling range	(<180) °C		(180-300) °C		(300-420) °C		(>420) °C
(weight, %)	4.05		72.75		22.06		1.13
Element (weight, %)	C	H	N	S	O	H/C	O/C
	87.39	8.77	0.68	0.09	3.07	1.196	1.015

time of 400ºC, 10 MPa and 1 hr, respectively. The autoclave was heated from room temperature to 400ºC at heating rate of 5ºC/min. The influence of catalyst precursors types and sizes (-140+200, -200+250, -250+325 and -325+400 mesh) on coal liquefaction yields and products distribution were examined. The experiments were performed using 10 g coal (dry ash free/daf), 15 g of solvent, 0,3 g of Fe (weight ratio of Fe in catalyst/coal (daf)= 3/100) and 0,3424 g of sulfur (S/Fe=2 atomic ratio). Dry ash free (daf) is a basis of coal analysis which excludes all moisture and ash in coal. Ten stainless steel balls having diameter of 15 mm are also inserted into the autoclave to obtain a better mixing during shaking. After the reaction, liquid products and solid residue were extracted using hexane and toluene as solvent. Weight different between solid reactant (coal and catalyst precursors) and residue of hexane extraction is classified as oil, water and gas yield. Yield of asphaltene is calculated from weight different between residue of hexane and residue of toluene extraction. Asphaltene is hydrocarbon material which is insoluble in hexane but soluble in toluene. The total coal conversion was calculated by summation of oil, water and gas yield and asphaltene yield.

Sulfidation Test

Iron compound is transformed to Pyrhhotite during coal liquefaction. Pyrhhotite has been believed to be the active phase that catalyze coal liquefaction. To investigate the formation of pyrrhotite, catalyst precursors with size of -325 mesh were sulfidized at temperatures 350, 375, 400 and 425ºC in the absence of coal. The tests were conducted using the same autoclave and reaction conditions (hydrogen pressure, amount of Fe, S/Fe ratio, heating rate) as coal liquefaction experiment described above. After the reaction, autoclave was cooled rapidly to room temperature by removing its heating mantle and then air blowing was performed using electric compressor. The solid product (catalyst samples) were washed with tetrahydrofuran (THF) and subjected to XRD analysis. The mean crystallite size of pyrhotite formed during sulfidation was calculated with the Scherrer equation from a full width at half-maximum (fwhm) of the XRD peak. The smallest size fraction of catalyst precursor (-325+400 mesh) was used for sulfidation experiments since the experiments are usually conducted using very small size (less than 2mm) of catalyst (Kaneko, 1998).

RESULTS

Iron compound which is believed to catalyze coal liquefaction reaction is pyrrhotite. Natural iron minerals such as goethite, magnetite and pyrite are precursors to form pyrrhotite. Transformation of the iron minerals to pyrrhotite is influenced by type and purity of the iron minerals.

Table 3 presents types and percentage of mineral in iron ore and tailing determined using optical microscope. Actually iron ore contained goethite, magnetite and non-iron mineral of silica while tailing contained iron minerals of magnetite, pyrite and non-iron mineral of silica, plagioklas, carbonate, and clay. The main mineral in the iron ore was goethite while that in the tailing was magnetite. The total amount of iron minerals (goethite+magnetite) in the ore was larger (>95%) than that of iron minerals in the tailing (magnetite+pyrite) which is less than 84%. Minerals are evenly distributed in each size fractions, except that in the tailing with size fraction of -325+400 mesh which contained considerably low concentration of magnetite. It is also suspected that some minerals in the tailing may not all originated from waste of PT. Freeport mineral processing plants since tailing sample was taken from a river.

Table 3. Optical microscopy results of iron ore and tailing

Screen Size (mesh)	Average Particle Size (mm)	Iron Ore (%)			Tailing (%)		
		Ghoetite	Magnetite	Total	Magnetite	Pyrite	Total
-140+200	90	90.1	5.3	95.3	65.7	17.8	83.5
-200+250	69	89.6	6.3	95.9	61.1	12.4	73.5
-250+325	54	91.0	5.1	96.1	58.9	11.3	70.2
-325+400	41	87.0	8.2	95.2	18.8	13.3	32.1

Table 4 shows the amount of elemental iron (Fe) in the tailing based on the result of chemical analysis. There is only a small different in Fe concentration on both ore and tailing. The concentration range of Fe in the ore was from 54.7% to 56.7% while that in the tailing was from 53.1% to 60.6%. It is found here that the concentration of Fe in tailing at size fraction of -325+400 mesh remain high although the concentration of magnetite in the fraction is the lowest (Table 3). It is most likely, at very fine particle size, magnetite was easily covered by clay or other non metallic mineral in tailing which hinders its identification by optical microscope.

Table 4. Chemical analyses results of ore and tailing.

Average Size (mm)	Fe (% wt.)	
	Iron Ore	Tailing
90	56.69	60.6
69	56.41	56.4
54	57.30	55.9
41	54.73	53.1

Figure 1 illustrates XRD pattern of iron ore and tailing at particle size of 41 mm before sulfidization and after sulfidization at 400°C (S400°C). Goethite (G) is the only mineral in the ore identified by XRD although magnetite and silica (quartz) appeared during observation using optical microscope (Table 3). Sulfidation process at 400°C converted goethite in the ore to pyrrhotite (P) almost completely. Tailing contained magnetite, pyrite and quartz. Sulfidation process at 400°C could not transform magnetite to pyrrhotite completely. Magnetite and pyrhotite peaks remain co-existed after sulfidation.

Figure 2 presents the size of pyrrhotite crystal calculated using Scherer equation. The size of pyrrhotite from both ore and tailing at sulfidation temperature of 425°C was almost the same (25.5 nanometer). At lower sulfidation temperatures, sizes of pyrrhotite crystal derived from ore was smaller than that from tailing, however the sizes of pyrrhotite crystal derived from ore is rapidly increase with increasing sulfidation temperature. The presence of clays in the tailings is one of the reason why pyrrhotite crystal growth derived from tail-

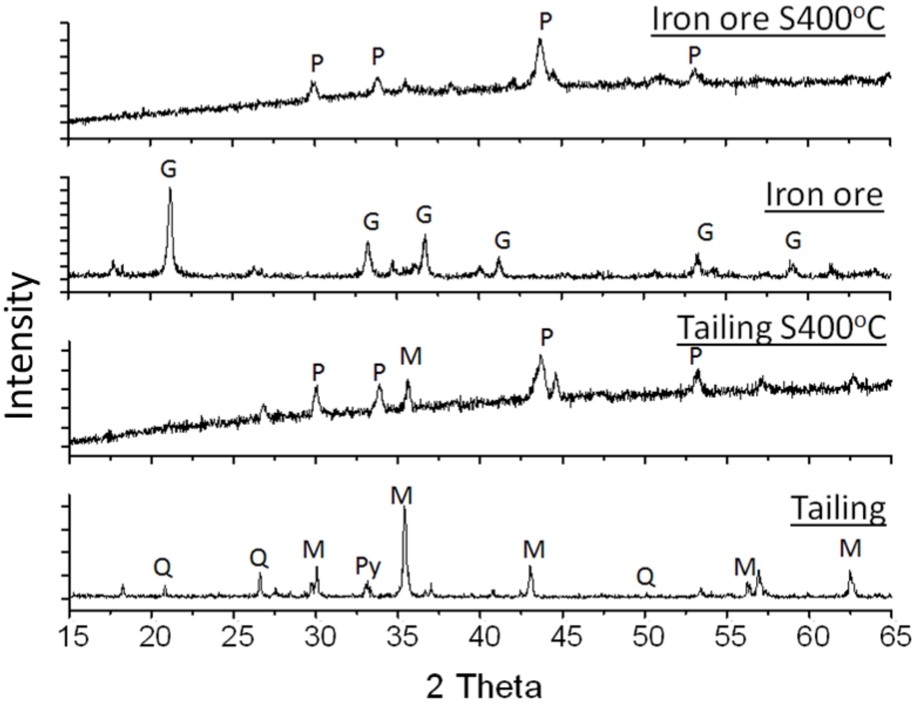

Figure 1. XRD pattern of iron ore and tailing before sulfidization and those after sulfidization at 400˚C (S400˚C)

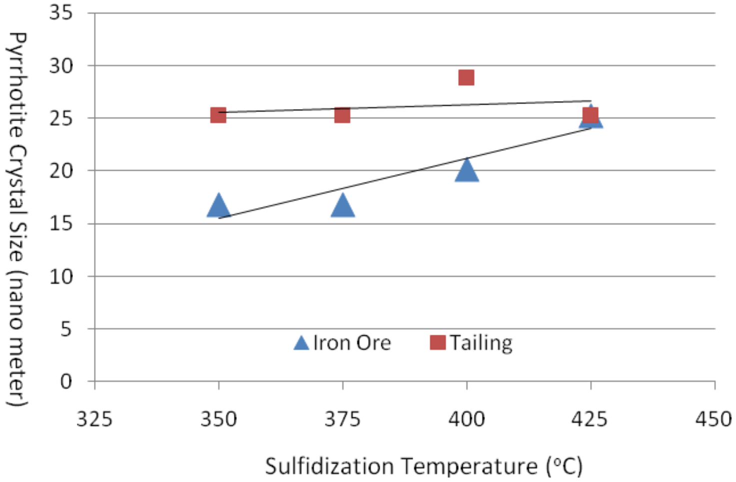

Figure 2. Crystal sizes of pyrrhotite derived from iron ore and tailings at several sulfidation temperatures

ings is slower than that from ore. Clay is an alumunium containing material which may form Fe-O-Al bond with iron minerals to inhibit the growth of pyrhotite crystal (Kaneko, 1998). Crystal growth will achieve maximum rate at certain temperature depend on molecular transport rate and nucleation rate (Okui, 1990). The crystal growth at temperature higher than 425°C was not studied here since the coal liquefaction reaction is conducted at temperature of 400°C.

The influence of catalyst precursors on coal conversion and product distribution of coal liquefaction reaction is presented in Figure 3. Coal conversion using ore as catalyst precursor was higher than that of using tailing. In case of ore, the conversion continued to increase with decreasing particle sizes. While for tailing, coal conversion increased from 66% to 74% with decreasing tailing size from 90 mm to 54 mm however futher reduction of particle size from 54 mm to 41 mm de-

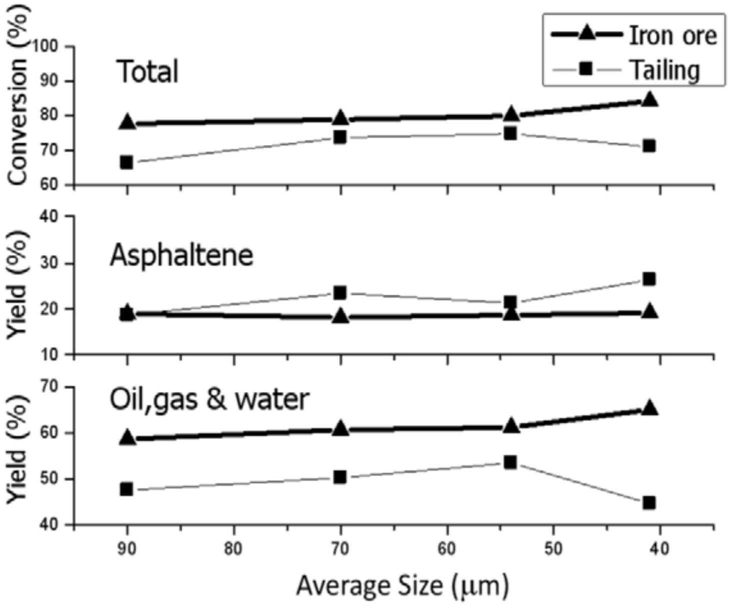

Figure 3. Influence of catalyst size on distribution liquefaction product

creased coal conversion. Catalyst precursor also influence product distribution. Catalyst precursors derived from ore produced more oil while that of derived from tailing produced more asphatene. It is assumed here that coal liquefaction reaction at the same temperature produces the same quantity of gas and water.

DISCUSSION

The objective of coal liquefaction is to produce smaller molecule of hydrocarbon (oil) from larger molecule of coal through reaction at high temperature and high pressure of hydrogen. The mechanism of coal liquefaction reaction is very complex. It can be described simply as reactions that progress through four stages as follows (Suzuki, 1994;Huang, 1998):

1) Extraction a part of coal which is soluble in organic solvent
2) Thermal decomposition of coal to produce free radicals
3) Stabilization of Free radicals through reactions with hydrogen to produce preasphaltene, asphaltene and oil
4) Hydrocracking preasphaltene and asphaltene to yield light oil

The first stage, solvent extraction, is very rapid reaction and require relatively low activation energy (Huang, 1998). Types of coals, types of solvents and reaction temperature determine products characteristics of this stage. The next stage, thermal decomposition, involve breaking of several kinds of chemical bond in coal therefore reaction rate in this stage is slower than that in the first stage. The results of thermal decomposition stage is influenced very much by reaction temperature. Stabilization of free radicals, the third stage, is required to prevent retrogressive reaction that transforms free radical to solid coke. Hydrogen to stabilize the radicals may be obtained from a hydrogenated solvent and from hydrogen molecule that has been activated by catalyst. Preasphaltene and asphaltene produced during solvent extraction and radical stabilization stages which may experience hydrocracking reaction (the forth stage) depend on their reaction conditions and catalysts.

It was found that tailing produced lower oil yield and coal conversion than those of ore. Since both catalyst precursors were tested using the same coal and experimental conditions, the amount of oil and coal conversion during solvent exraction and thermal decomposition stages should be the same. Thus, different results of coal liquefaction reaction using both catalyst precursors found here were caused by different behavior of both catalysts during free radicals stabilization and liquid products hydrocracking stages. The roles of catalyst in both stages are to accelerate solvent hydrogenation reactions, to activate hydrogen molecules in order to allow the molecules react directly with free radicals and to accelerate hydrogen transfer from solvent to free radicals (Ikenaga, 1997). In the both stages, tailing is suspected to experience slower hydrogen transfer rate than that of iron ore since tailing produced larger pyrrhotite crystal size (Figure 2) and it is not all iron minerals in the tailing transformed to pyrrhotite during coal liquefaction. Slower hydrogen transfer from gas phase to solvent may resulted in hydrogen deficient solvent which reduce the rate of asphatene hydrogenation to yield oil. Hydrogen deficient solvent also affect coal conversion since hydrogen assist coal hydrocracking reactions, therefore total oil yield and coal conversion using tailing as a catalyst precursor was lower.

Coal conversion also decreased when particle size of the tailing was reduced from 54mm to 41mm. It was also observed that at particle size of 41mm, magnetite minerals in the tailing were covered by non-iron minerals so that hardly to be identified by optical microscope (Table 3). It seems that non-iron mineral in the catalyst precursors inhibited adsorption of hydrogen molecule inside catalyst hence lowering of their coal conversion.

Figure 4 presents photographs of typical catalyst precursor before sulfidation experiment determined using optical mycroscope and after sulfidation experiment determined using SEM. The average particle size of catalyst precursors before sulfidation (Figure 4a) was about 41 mm and it was reduced to size less than 30 mm after the sulfidation experiments (Figure 4b). Stainless stell balls in the shaking type autoclave obviously ground the catalyst further to smaller size. Therefore the initial size of catalyst precursors (41mm to 90mm) has little influence to coal conversion (Figure 3). The influence of catalyst particle size can be examined clearly if the particle sizes of catalysts before and after reaction remain the same.

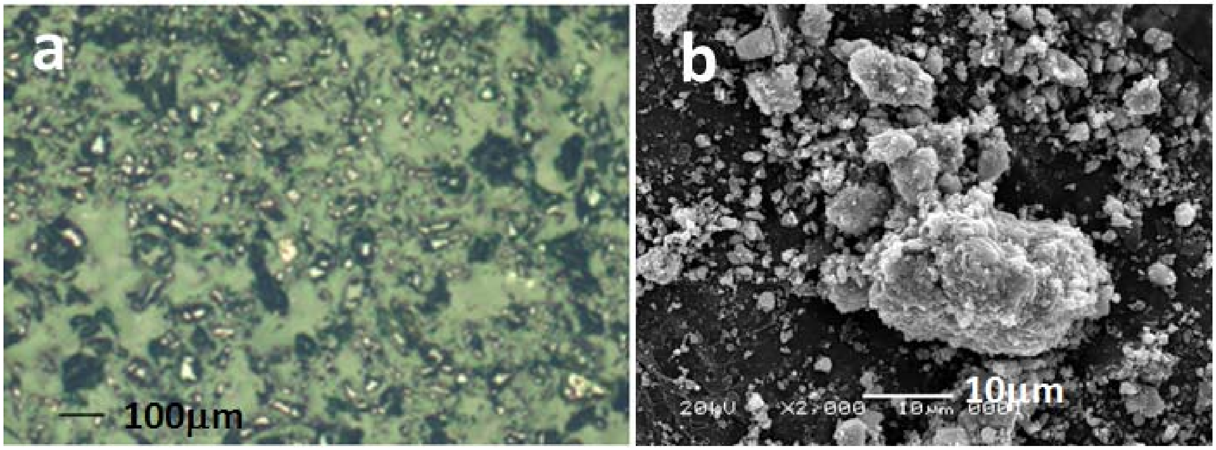

Figure 4. Size of catalyst precursor before (a) and after (b) sulfidation test

CONCLUSION

Iron ore from South Kalimantan and tailing of PT. Freeport Mineral Processing Plant had been investigated their catalytic activities for coal liquefaction reaction. The investigation concludes as follows:

a. Examination using optical microscope revealed that South Kalimantan iron ore contained more than 85% of ghoetite or more than 95% of iron minerals (goethite plus magnetite) while tailings from PT Freeport contained less than 84% of iron minerals (magnetite plus pyrite).

b. Sulfidation process at 400°C transformed iron minerals in ore into pyrrhotite completely however such complete transformation was not observed for iron mineral derived from tailing. XRD peak of magnetite derived from tailing was remain observed after the sulfidation process. Goethite is more easily transformed to pyrrhotite than that of magnetite.

c. At sulfidation temperatures less than 425°C, pyrrhotite crystal sizes formed from iron ore was smaller than that from the tailings however the sizes of pyrrhotite crystal derived from iron ore was rapidly increase with increasing sulfidation temperature. It is suggested that non-iron minerals in tailing prevent crystal growth of pyrrhotite.

d. In the liquefaction reaction, tailing produced lower oil yield and coal conversion than those of ore. Tailing is suspected to experience slower hydrogen transfer rate during coal liquefaction since tailing produce larger pyrrhotite crystal size than that of ore.

REFERENCES

Hirano, K. and Kanda, Y., 2001. Study on industrial catalyst for bituminous coal liquefaction. *Fuel Processing Technology,* vol.72.

Hirano, K., Kouzua, M., Okada, T., Kobayashi, M., Ikenaga, N. and Suzuki, T., 1999. Catalytic activity of iron compounds for coal liquefaction. *Fuel,* 78. p1867–1873.

Huang, H., Wang, K., Wang, S., Klein, M.T. and Calkins, W.H., 1998. Studies of coal liquefaction at very short reaction times. *Energy & Fuels*, vol.12. p95-101.

Huda, M., 2007. Teknologi BCL untuk Pencairan Batubara Indonesia. *Majalah Mineral & Energi*, vol.5 no.2.

Ikenaga, N., Kan-nan, S., Sakoda, T. and Suzuki, T., 1997. Coal hydroliquefaction using highly dispersed catalyst precursors. *Catalysis Today,* vol.39. p 99-109.

Kaneko, T., Sugita, S., Tamura, M., Shimasaki, K., Makino, E. and Silalahi, L.H., 2002. Highly active Limonite catalyst for direct coal liquefaction. *Fuel,* Vol.81. p1541-1549.

Kaneko, T., Tazawa, K., Koyama, T., Satou, K., Shimasaki, K. and Kageyama, Y., 1998. Transformation of iron catalyst to the active phase in coal liquefaction. *Energy & Fuels*, vol.12. p 897-904.

Metz, B., Davidson, O., Bosch, P., Dave, R. and Meyer, L., 2007. *Climate change mitigation technology*. Cambridge University Press.

Okui, N., 1990. Maximum crystal growth rate and its corresponding state. *Polymer Bulletin*, Vol. 23, Number 1 / January.

Suzuki, T., 1994. Development of Highly Dispersed Coal Liquefaction Catalysts. *Energy & Fuels*,vol.8. p341-347.

Wood, J.H., Long, G.R. and Morehouse, D.F., 2003. Long-term world oil supply scenarios. Energy Information Agency. *http://www.eia.doe.gov/pub/oil_gas/petroleum/feature_articles/2004/worldoilsupply/oilsupply04.html*