Characteristic of low rank coal from Warukin Formation, South Kalimantan and their implication for coal liquefaction

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Abstract. The research was conducted on petrology and geochemistry of coal at Warukin Formation, Barito Basin, in South Kalimantan. Research is focused on composition and behavior of low rank coal toward its liquefaction. The sampling location is in the coal mining of PT. Adaro Indonesia which involves some mining location such as Wara, Tutupan and Paringin area. The sampling was conducted in seam Wara 110, Wara 120, Wara 200, Tutupan 210 and Paringin 712 with ply by ply method. Sample analysis consists of proximate and ultimate properties, composition of maseral, reflectance vitrinite, as well as composition of mineral, major element and organic geochemistry. Experiment of coal liquefaction was conducted on the autoclave with temperature and pressure of 120°C and 14.17 psi. The problems are focusing on influence of maceral, mineralogy and geochemistry low rank coal of Warukin formation in Barito Basin on coal liquefaction, behavior of coal liquefaction to the change in variable of time to result of coal liquefaction yield.

The physical and chemical characteristics of coal in Wara seam content are ash (< 7 %) adb, inherent moisture (< 31%) adb, volatile matter (< 5%) adb and fixed carbon (< 33%) adb. Then in Tutupan and Paringin are ash < 3% adb, inherent moisture < 21% adb, volatile matter < 48% adb and fixed carbon < 40 % adb. Composition element in Wara coal are carbon < 64 % adb, hydrogen < 7 % adb, oxygen < 34% adb and nitrogen < 1% adb, then in Tutupan and Paringin seam consist of carbon (< 65 % adb), hydrogen (< 6 % adb), oxygen (< 32% adb) and nitrogen < 2% adb. The content of maseral in Wara seam coal consist of vitrinite, liptinite, inertinite maseral group which are 81%, 51% and 27% respectively. Result of coal liquefaction on Wara seam with time reaction of 30 minutes is 48.60 % and for 60 minutes is 51.27%. The result of liquefaction is decreasing on reaction time of 90 minutes and 120 minutes, which are 46.72%, 35.51% respectively. The liquefaction conversion obtained from Tutupan and Paringin seam within reaction time 30 minutes and 60 minutes are 8.22% and 15.46% respectively. The conversion is decreasing on reaction time 90 minutes and 120 minutes which of 6.23% and 5.54% respectively. The coal with more lignite is easier to be liquefied than sub-bituminous because the coal has higher hydroxyl group.

1. Introduction
The liquefaction of coal has shown the correlation between the percentage of conversion and the maceral content in the coal. The more the percentage of vitrinite and liptinite in coal, the more the
percentage of conversion. Therefore, more content maceral in coal will increase the ratio of H/C [1]. [2]; [3] and [4]. The variables normally used for liquefaction processes include: reaction time, process temperature and type of catalyst reported by [5], [6], [7], [8], [9]. The presence of iron-based catalysts in the liquefaction of low rank coal has increased the conversion [6], [7], [8] and [9].

The liquefaction of Indonesia’s low rank coal has been reported by [5], [6], [7], [8], [10], [11] and [12]. However, the study of liquefaction on properties, mineralogy, and geochemical of maceral for Indonesia low rank coal has not been reported. Therefore, in this study the characteristics of low rank coal will be observed to the liquefaction process.

Coal samples in this study were taken from mining sites of Adaro Indonesia Company. The sites are located in Wara, Tutupan and Paringin, Barito Basin of South Kalimantan. Based on a report, the deposits of low rank coal much spread in the mining site. The experimental of liquefaction was conducted at low temperature in an autoclave. The method is different from previous liquefaction with high temperatures and pressures.

2. Geological Setting
Generally, Warukin Formation contains so many coal deposits interspersed by clay and sandstone. In the formation there are three separate blocks: Tutupan, Wara, and Paringin. The length of Tutupan block about 20 km, extending from East-Sea to West [13]. The thickness of coal layer on the Tutupan block up to 50 meters with a slope of 30° to 50°. In the Paringin block there is one main layer with a minor layer. In the block the coal has thickness of 38 m with slope ranging from 10° to 25°. In the Wara block there are three layers of coal with the slope of layer 10° to 35° with thickness of 12 to 14 m [13].

The Wara, Tutupan dan Paringin block were formed and limited by the movement of two parallel-trending (Thrust Fault). The fault in the western side of the hill is known as the rising fault of Dahai, limiting the Dahor Formation in the West and the Warukin Formation in the East. Another fault that limits the eastern side of the hill is the fault rises in Tanah Abang-Tepian Timur. Cesarean data are identified from seismic data and drilling of oil wells.

3. The Quality Of Low Rank Coal At Barito Basin
Generally, the properties of coal in Warukin Formation are humidity ranges between 12.60-22.20%, ash content ranges between 4.39-21.50%, the calorific value ranges from 4,279 cal/g-5,630 cal/g. The total sulfur content in the coal range of 0.18-0.32% implies that the coal was deposited in the terrestrial environment [14].

The results of this study show that coal mining of the Warukin Formation, Barito Basin as follows. The layer 100 consists of vitrinite (telokolinite, desmokolonite, korpogelinite) = 68%, liptinite (sporinite, resinite, suberinite) = 5.4% and inertinite (fusinite, semifusinit, sclerotinite) = 25%. The layer 200 consists of vitrinite (telokolinite, densinite, desmokolonite, corpogelinite) = 80.2%, liptinite (sporinite, kinetite, resinite, suberinite) = 10.6% and inertinite (inertodetrinit, sclerotinit) = 7.2%. Finally, the layer 300 consists of zitinite (telokolinite, densinite, desmokolonite, corpogelinite) = 84.8%, liptinite (resinite, suberinite) = 3.0% and inertinite (inertodetrinit, sclerotinit, semifusinit) = 10.0% [15].
Proximate analyzes include ash content, inherent moisture (IM) and volatile matter (VM) characterization. The ash content was observed on the residue of coal burning. The coal ash is minerals formed in conjunction with coal formation and it is a main part of coal. Physically, IM is present in the internal pore structure of coal and has a vapor pressure lower than normal vapor pressure. The IM is a basic characteristic of coal and when the content in coal is high, the coal is low rank [16]. The VM, essentially consists of flammable gases such as hydrogen, carbon monoxide and methane as well as condensable vapors such as tar and vapors such as carbon dioxide and water formed by the thermal degradation and the calcination of coal substances and dehydration of minerals. The coal VM content is closely related to coal rank and is an important parameter in coal classification. The result of proximate analysis showed that the ash content and congenital in Wara formation had a high value, ie 19.96-30.90% compared with the water congenital in the Tutupan 210 and Paringin 712 layers of 12.89 to 20.40% (Table 2).

| Layer code | Ash (%) | IM (%) | VM (%) | FC (%) | FR |
|------------|---------|--------|--------|--------|----|
| Wara 110   | 1.24-1.74 | 19.96-29.43 | 40.60-49.46 | 26.69-31.450.54-0.70 |
| Wara 120   | 3.57-6.11  | 21.27-30.90  | 35.28-49.67  | 19.29-28.940.39-0.82 |
| Wara 200   | 0.68-0.94  | 20.89-28.99  | 39.57-48.20  | 29.50-32.070.61-0.77 |
| Tutupan 210 | 1.31-2.87  | 16.40-20.40  | 44.80-47.70  | 32.50-35.100.71-0.78 |
| Paringin 712 | 1.03-1.72  | 12.89-18.77  | 45.22-46.93  | 34.29-39.460.75-0.85 |

IM = Inherent moisture
VM = Volatile matter
FC = Fuel ratio
FR = Fuel ratio

Table 1. The results of proximate analysis on Wara, Tutupan, and Paringin seam

Based on the genes, the high content of the congenital water content of the Wara layer reflects low caloric values, while the Tutupan 210 and Paringin 712 layers have a higher caloric value. The relationship between water content and calorific value in coal has also been proposed by [17] and [18].

To reveal the chemical elements contained in the coal it was conducted the ultimate analysis on the coal. The results show that hydrogen, oxygen, nitrogen and carbon exist in the coal. Hydrogen is contained in coal in the form of an aliphatic and aromatic groups. During the coal formation the amount of hydrogen gradually diminishes due to the evolution of methane gas. Thus, the hydrogen content is an important parameter and determines the rank of coal. Oxygen exists in coal as hydroxyl, carboxyl, methoxyl and carbonyl groups as well as fundamental structural units known as non-reactive oxygen. The oxygen content decreases as water vapor and carbon oxide during the coal formation,
hence oxygen is an also important parameter of coal rank [16]. Besides, the nitrogen is typically has a concentration of 0.5-2% and not related to coal rank, although some of the nitrogen may be lost during the coal formation.

4. Methods
Coal samples Wara 100, Wara 120, Wara 200, Tutupan 210 and Paringin 712 were collected. Rawa samples is proximate and ultimate that is inherent moisture, Ash, Volatile Matter (VM) anf Fixed Carbon (FC), then ultimate analysis that is determining element of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) were also carried out. Liquefaction process used size – 200 mesh, liquefaction conducted in an Autoclave and liquefaction temperature is 120 °C, pressure is 14 psi, catalyst used is alumina 0.03 g, hydrogen donor that is NaOH 0.1 g, and water solvent is 39 ml. Moreover, the liquefaction, the liquefaction temperature variables are 30, 60, 90 minutes, respectively. The mixture of coal, catalyst, hydrogen donor and solvent water is placed in tank with capacity of 50 ml. Then, this mixture is placed in the autoclave for liquefaction process.

5. Discussion
a. Coal ranking
Coal are vary based on their elements and degree of alteration that has occurred or the coal formation from origin plants. Most of the coal are humic resulting from the converting of plants under aerobic conditions of peat, then transformed to produce one of the coal varieties known as lignite, subbituminous, bituminous and anthracite. Several ways is used to classify the coal rank. The rank of the coal states the degree of conversion that has occurred. The larger the changes occurred the higher the rank of coal. The classification of coal has been explained by [19].

Based on the calculation of fuel ratio (FR) of coal in the formation area at Wara layer 110, Wara 120 and Wara 200 it is found that the FR of 0.53-0.68 means the coal classified as lignite coal. Besides, coal layer of Tutupan 210 and Paringin 712 which have value FR of 0.71-0.85 is classified as subbituminous coal. The value of FR is proposed by [20] which states that the value of FR of Indonesian coal is lower than 0.95 including lignite and subbituminous coal.

b. The relationship between ash, inherent moisture (IM) and volatile matter (VM).
The ash of a coal is an inorganic residue that occurs after coal is burned. The measurement of ash content is part of the standard proximate analysis. The VM content is determined based on the lost weight when the coal is heated under specific conditions, without air. This test is carried out under dry air at around 950 °C within 7 minutes and this test is part of the proximate analysis [21]. The analysis of coal layer on Wara 110, Wara 120, Wara 200, Tutupan 210 and Paringin 712 are shown in Table 1 [22]. The coal parameters are ash content, inherent moisture IM) and volatile matter (VM).

Figure 1. shows the relationship between ash content, IM, and VM in various layers of coal, ie Wara 110, Wara 120, Wara 200, Tutupan 210 and Paringin 712. It is seen that Wara 110, Wara 120 and Wara 200 are relatively higher in ash, IM, and VM than layer Tutupan 210 and Paringin 712. This results imply the fact that coal in Wara 110, Wara 120 and Wara 200 has transformed not longer than other layer as reported by [18], [21]. In addition, based on the value of IM, ie 19.96-28.99% and carbon tethered, ie 26.69-32.07%, it can be proved that the layer Wara 110, Wara 120 and Wara 200 (Table 5.1) is low rank coal hence lignite coal, while coal layer Tutupan 210 and Paringin 712 which have IM of 16.40-18.77% and carbon tethered is 32.50-39.46% (Table 5.1) could be classified as the middle rank coal hence subbituminous coal. The results has also been shown by [19].
Figure 1. The correlation of ash content, IM, VM

c. The relationship between the hydrogen content (H), oxygen (O) and carbon (C) in coal

The results of the ultimate analysis on layer Wara 110, Wara 120, Wara 200, Tutupan 210 and Paringin 712 coals are reported. The analysis include elements of coal such as hydrogen (H), oxygen (O) and carbon (C). Figure 2 shows the relationship between hydrogen, oxygen and carbon content in various layers of coal, ie Wara 110, Wara 120, Wara 200, Tutupan 210 and Paringin 712 layer. Based on observation results, Coal layers Wara 110, Wara 120 and Wara 200 are lignite, while layer Tutupan 210 and Paringin 712 are subbituminous coal [22].

Figure 2. The relation of hydrogen, carbon and oxygen
d. Characteristic of Coal Liquefaction Process

The coal liquefaction was carried out within 30, 60, 90 and 120 minute. Based on the experiments it can be seen that the optimal product of Wara 110, Wara 120 and Wara 200 layer occurred using reaction time of 60 minutes with results of 24.14-32.57%, 31.85-51.27%, and 19.54-34.50% respectively, meanwhile product of Tutupan 210 and Paringin 712 are optimal result of 11.61-18.35% dan 5.99-11.95% (Figure 3-6).

In addition, the product yield has been associated with the liquefaction time and the results show that the coal in Wara 110, Wara 120 and Wara 200 layers has increasing yield when reaction time of 30 minutes change to 60 minutes with of 4.42% , 4.91% and 11.99% respectively. The average percentage increase of coal in the Wara 120 layer is higher than the average percent increase in coal of Tutupan 210 and Paringin 712 layers which is 6.87% and 6.36% [22].

The coal in Wara 120 layer is classified as low rank which is lignite type. The coal is easily converted into liquid using liquefaction due to lignite type has as much as 15-25% of total oxygen content in hydroxyl groups. The hydroxyl group in coal has correlation with the degree of coal quality by which hydroxyl group will decrease when increasing of the carbon content [23].

The high rank coal has little or no hydroxyl group, while the substances are found in low rank coals [23]. The presence of hydroxyl groups increase the ratio of H/C. The coal liquefaction requires hydrogen donor therefore the higher the ratio the easier coal to be liquefied.

Figure 3. The correlation between H/C and liquefaction time 30 minutes
Figure 4. The correlation between H/C and liquefaction time 60 minutes

Figure 5. The correlation between H/C and liquefaction time 90 minutes
Figure 3-6 shows the relationship between the ratio of H / C to liquefaction products in Wara, Tutupan 210 and Paringin 712 layer. The percentage of liquefaction product has also been demonstrated by Whitehurst (1978) stating that coal with more hydrogen content produces a more product than coal with little hydrogen. In addition, low rank coal such as lignite produces more products than medium or higher rank coal such as subbituminus, bituminous or anthracite during liquefaction [24].

On the other hand, medium rank coal which is subbituminous coal, Tutupan 210 and Paringin 712 layers reach increasing only 6.87% and 6.36% respectively. The increasing of product percentage occurs when reaction time changed from 30 to 60 minutes. The results due to the longer the liquefaction process causes the coal contact with the solvent and the hydrogen donor getting longer so that the product results are also higher. In addition, the effect of time on the coal liquefaction has also been proposed by [6], [25], [26], who states that the longer the liquefaction time the higher the product.

The product will be optimum within 60 minute for all of layers, but liquefaction within 90 and 120 minutes the products are decreased. This decreasing is caused by a very rapid backlash. Similar studies have been conducted also by [27] suggesting that coal liquefaction products increased within 30 to 60 minutes and a decrease in 90 minutes. In addition, the research conducted by [27] reported that the decline of product in coal liquefaction is due to the polymerization or coagulation of coal during the liquefaction with increasing time.

6. Conclusion
The physical and chemical characteristics of coal in Wara seam content are ash (< 7 %) adb, inherent moisture (< 31%) adb, volatile matter (< 5%) adb and fixed carbon (< 33%) adb. Then in Tutupan and Paringin are ash < 3% adb, inherent moisture < 21% adb, volatile matter <48% adb and fixed carbon < 40 % adb. Composition element in Wara coal are carbon < 64 % adb, hydrogen < 7 % adb, oxygen < 34% adb and nitrogen < 1% adb, then in Tutupan and Paringin seam consist of carbon (< 65 % adb), hydrogen (< 6 % adb), oxygen (< 32% adb) and nitrogen < 2% adb. The content of maseral in Wara seam coal consist of vitrinite, liptinite, inertinite maseral group which are 81%, 51% and 27%
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Acknowledgments
This research is supported by Adaro Indonesia Inc. We express our deepest gratitude to the management of Adaro Indonesia Inc. for giving us permission as well as support during the field research.

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