Low-Calorie Coal Liquefaction Products as an Alternative Fuel Oil

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Abstract: *Liquefaction of low-rank coal has been done to optimize the utilization of low-rank coal, which is less economical for obtaining alternative fuel oil. Coal samples were taken from the Bukit Pinang coal mine, Samarinda Ulu, East Kalimantan. Coal was liquefied using the NEDOL procedure at PUSPITEK, Serpong, South Tangerang, Indonesia. This Bukit Pinang coal liquefaction produces five fractions consisting of Naphta, Light Oil (LO), Middle Oil (MO), Heavy Oil (HO), and Coal Liquid Bottom (CLB) fractions. The liquefaction yield was dominated by the HO and CLB fractions (> 50% by weight). The naphtha, MO and LO fractions were fractionated using* SiO_2 GF_{254} *Thin Layer Chromatography (TLC) plate. It produced aliphatic and aromatic hydrocarbon fractions. Aliphatic hydrocarbon fractions were analyzed using a Gas Chromatography-Mass Spectrometer (GC-MS), while the aromatic hydrocarbon fractions were not analyzed. Mass spectrum studies showed that the components consisted of* n*-alkanes, isoalkanes (branched alkanes), cycloalkanes and alkyl cycloalkanes. The aliphatic hydrocarbon components resulting from the liquefaction of low-rank coal showed its equivalence with the components that make up fuel oil. Therefore, this coal liquefaction can be suggested as an optimization for low-rank coal, which is less economical.*

Keywords: *coal liquefaction; Naphtha; Light Oil (LO); Middle Oil (MO); aliphatic hydrocarbon*

■ INTRODUCTION

Oil or liquid fuels are still the primary energy sources in Indonesia, especially in the transportation sector. Continuing economic growth causes the consumption of these fuels to increase. On the other hand, data from the government shows that oil reserves are decreasing. In 2016, Indonesia had 7.25 MMSTB (Million Stock Tank Barrels) in oil reserves. However, in 2020, 4.17 MMSTB remained [1]. It means that someday Indonesia will need more oil imported from another country to fulfill its daily needs. This phenomenon would be problematic due to volatile global energy prices caused by global challenges [2-4]. This predicament necessitates the move from oil to alternative energy sources. Another abundant fossil energy source in Indonesia, coal, holds a respectable alternative energy position [5].

Although coal and oil have different forms, they contain hydrocarbon as the main element [6]. Low-rank coals dominate coal reserves; lignite, sub-bituminous and bituminous are primarily found in the Sumatera basins and Kalimantan. Low-rank coals have low calorific values (< 5100–6100 KJ) [7-8]. Low-rank coal is ineffective if used directly as solid fuel because the energy produced is relatively small and cheap. However, this coal is easy to liquefy. Liquefaction of coal not only changes its form into a liquid, more like oil fuels, and enhances the calorific value. Thereby, it can increase the economic value of coal. Coal liquefaction has been widely practiced as an implication of producing liquid fuel [9-13]. Liquefaction of coal can be done directly or indirectly. One standard coal liquefaction process is the direct coal liquefaction (DCL) method. Direct coal liquefaction (DCL) has attracted much attention because of its abundant coal reserves, and liquefied coal is cleaner for the environment than solid coal [9-12].

The Direct Coal Liquefaction (DCL) process works well at 400–470 °C under a pressure of 7–20 MPa H_2 in a hydrogen donor solvent and a suitable catalyst. The DCL method requires feed coal with total vitrinite and axinite content of more than 80% and a H/C ratio of more than 0.66 [13]. Meanwhile, coal with more inertinite or less volatile content does not work well for the DCL process [14-16]. Coal of different grades has various uses in industry. Bituminous coal with a volatile content is suitable for combustion [17]. Anthracite coal is required for carbon material [18]. In addition, coal with the same rank will have different qualities. It depends on the coal depositional environment (coalification) [19]. Therefore, it is crucial to know the correlation between fossil coal's organic components and coal liquefaction products' hydrocarbons [1].

The products of direct liquefaction of sub-bituminous can be grouped based on differences in their boiling points into naphtha fraction, light oil (LO) fraction, middle oil (MO) and heavy oil (HO). The components of liquid coal are organic compounds. It consists of *n*-alkanes (n-C_7-n-C_{13}), isoalkanes, cycloalkanes, phenols, alkylbenzenes and polycyclic aromatic hydrocarbons (PAHs) (naphthalene and indene) [12]. The organic components of liquid coal are derived from the macromolecular structure of coal and biomarkers, which are decomposed through the thermal breakdown reaction of coal [20]. Indirect liquefaction through gasification integrated with the Rectisol/Fischer-Tropsch process produces alternative diesel fuel [21].

Coal liquefaction is an attempt to increase the relatively low H/C ratio of coal, values between 0.3–0.8, to approach a higher oil H/C ratio, reaching 0.9–1.3 through the addition of hydrogen by a donor catalyst. The characteristics of coal suitable for liquefaction have a high concentration of moisture matter and a H/C ratio > 0.75 with a vitrinite reflectance index < 0.80% and a vitrinite + liptinite content > 60% [14,22]. Meanwhile, coal with more inertinite or less volatile content does not work well for the DCL process [14-16]. Coal's maceral and mineral composition are related to the magnitude of the conversion of coal organic matter into liquid fuel. The characteristics of coal content with more lignite are more straightforward to melt than sub-bituminous [15].

An in-depth understanding of the presence of maceral in coal is carried out through the relationship between the macromolecular structure of coal and biomarkers produced in coal liquefaction. The relationship is in the old coal depositional environment, the origin of the source of coal-forming organic compounds and coal maturity [16-19,23-26]. The biomarkers found in the liquefaction products are accessible biomarkers that do not undergo decomposition or are bound to the coal matrix and released during liquefaction.

One of the low-rank coals that have the potential to be liquefied is coal from the Bukit Pinang coal mine, Samarinda Ulu, East Kalimantan. The chemical components of coal have never been disclosed, making it impossible to evaluate its feasibility of diversifying to liquid fuels. This paper discusses in depth the aliphatic hydrocarbon fraction, a fraction of the biomarkers of Bukit Pinang coal. The aliphatic hydrocarbon fraction will consider the accuracy of coal-type segregation for coal liquefaction.

■ EXPERIMENTAL SECTION

Materials

The primary materials in this research consist of coal and limonite catalysts. A coal sample was obtained from Bukit Pinang, Samarinda Ulu. Limonite SH was derived from Agency for the Assessment and Application of Technology (BPPT), PUSPITEK, Serpong, South Tangerang. Heavy oil as a carrier medium of coal dan catalyst was prepared in the reactor. Organic solvents such as *n*-hexane and dichloromethane for analysis EMSURE were also used in this study. Silica gel GF_{254} was used for TLC purposes.

Instrumentation

Identification of biomarkers in coal samples using GC-MS equipment (Agilent 7890A). This apparatus was equipped with a 7683B automatic sampler, an on-column injection chamber, and a fused silica capillary column (60 m ×0.25 mm i.d.) coated with 95% methyl/5% phenyl silicone phase (HP-5 ms, film thickness 0.25 µm). Helium was used as a carrier gas. The GC was coupled with an Agilent 5975C mass selective detector (MSD).

Procedure

Coal liquefaction and fractionation

Coal samples from Bukit Pinang, as much as seventy-five grams (75 g), Samarinda Ulu were liquefied using the NEDOL procedure [27] with limonite SH as a catalyst. The Coal Liquefaction was performed at Laboratory BPPT, PUSPITEK, Serpong, South Tangerang. The liquid product (slurry) was then fractionated using vacuum distillation at 10 mmHg based on the difference in the boiling points of each fraction. The results of the fractionation are Naphtha fraction which evaporates at a temperature of 30–180 °C, LO at a temperature of 180–220 °C, MO at a temperature of 220–350 °C, HO at a temperature of 350–538 °C and coal liquid bottom (CLB) at > 538 °C. The naphtha product was directly analyzed using GC-MS. The LO and MO products were further fractionated to obtain aliphatic and aromatic hydrocarbon fractions. The chemical components and biomarkers of Naphtha, LO and MO fractions were identified using GC-MS. In this paper, only aliphatic hydrocarbon biomarkers from coal-owned biomarkers are discussed.

Gas chromatography-mass spectrometer analysis

The GC–MS settings were as follows. The aliphatic fraction was diluted in n-hexane and analyzed through coupled GC–MS for biomarker composition. The GC oven was programmed as follows: a temperature of 80 °C was maintained for 5 min, increased to 100 °C at the rate of 10 °C/min, increased further to 300 °C at the rate of 4 °C/min, and maintained for 35 min. The mass selective detector operated at an ion source temperature of 230 °C, ionization energy of 70 eV, and cycle time of 1 s in a mass range from 45 to 1100 Da.

■ RESULTS AND DISCUSSION

Coal Liquefaction Products

The coal (75 g) liquefaction produces coal slurry with a composition of Naphtha fraction (1.43%); the fraction of Light Oil (LO) (6.84%); Middle Oil (MO) fraction (2.3%); Heavy Oil (HO) fraction (25.41%) and Coal Liquid Bottom (CLB) fraction (33.72%). The data illustrates that Bukit Pinang sub-bituminous coal liquefaction products are dominated by Heavy Oil and Coal Liquid bottoms with a total percentage of > 50%.

The success of the coal liquefaction process is determined by the H/C ratio of the coal to be liquefied and the hydrogen donor solvent used. Based on the ultimate and proximate analysis of Bukit Pinang coal, Samarinda Ulu, it is known that the H/C ratio is 0.89, and the volatile content is 50.7%, as an indicator of coal suitable for liquefaction. However, the resulting CLB product is more dominant than LO and MO. The oil yield obtained in this study is lower when compared with the coal liquefaction of Xinjiang, China which has a H/C ratio > 0.68, 73.9% [6]. It may be due to the less-than-optimal active hydrogen donated by the solvent. It cannot inhibit the reaction between free radicals formed in the coal liquefaction [20,28]. As a result, CLB products are more dominant than LO and MO products [2].

Identification of Aliphatic Hydrocarbon Fractions

The results of identifying the chemical components of the aliphatic hydrocarbon fraction of Naphtha, LO, and MO products are shown as Total Ion Chromatogram (TIC) as shown in Fig. S1–S3 and Table 1. The structure of all compounds was elucidated through the fragmentation reaction, then compared to the previously published papers. They were *n*-alkanes, isoalkanes (branched alkanes) and cycloalkanes. Conversion of retention time (in Fig. S1–S3) into temperature is carried out based on the oven temperature program, as follows:

$$80\ ^{\circ}\mathrm{C}\ (5\ \mathrm{min})\ \xrightarrow{10^{\circ}\mathrm{C/min}}\ 100\ ^{\circ}\mathrm{C}\ \xrightarrow{4^{\circ}\mathrm{C/min}}\ 300\ ^{\circ}\mathrm{C}\ (35\ \mathrm{min})$$

The oven temperature is 80 °C starting at the retention time = 0 min. The temperature was maintained at 80 °C for 5 min, which means that until the 5th min, the oven temperature was still 80 °C. Furthermore, the temperature was increased by 10 °C/min to 100 °C. It means that at a temperature of 100 °C, the retention time was increased by 2 min (Rt = 7 min). Furthermore, the

Table 1. TIC aliphatic hydrocarbon fractions of Naphta, LO, and MO

No	Compound	Compound name	Molecular formula	M+	Composition (%)		
					LO	MO	Naphta
1	C_7	*n*-Methly-cyclohexane	C_7H_{14}	98	-	-	0.42
2	*i*-C_9	Iso-nonane	C_9H_{20}	128	-	-	1.47
3	C_8	*n*-Ethyl-cyclohexane	C_8H_{16}	112	-	-	0.76
4	*i*-C_{10}	Iso-decane	$C_{10}H_{22}$	142	-	-	12.49
5	C_9	*n*-Propyl-cyclohexane	C_9H1_8	126	-	-	3.22
6	*i*-C_{11}	Iso-undecane	$C_{11}H_{24}$	156	-	-	3.07
7	C_{11}	*n*-Pentyl-cyclohexane	$C_{11}H_{22}$	154	-	-	2.08
8	*n*-C_{10}	*n*-Decane	$C_{10}H_{22}$	142	-	-	25.52
9	*i*-C_{12}	Iso-dodecane	$C_{12}H_{26}$	170	-	-	1.72
10	C_{12}	*n*-Hexyl-cyclohexane	$C_{12}H_{24}$	168	-	-	0.41
11	C_{10}	Methyl-*n*-propyl-cyclohexane	$C_{10}H_{20}$	140	-	-	2.07
12	*n*-C_{11}	*n*-Undecane	$C_{11}H_{24}$	156	9.58	-	-
13	C_8	*n*-Ethyl-cyclohexane	C_8H_{16}	112	0.11	-	-
14	*n*-C_{12}	*n*-Dodecane	$C_{12}H_{26}$	170	26.7	2.55	10.62
15	C_9	*n*-Propyl-cyclohexane	C_9H_{18}	126	0.22	-	-
16	*n*-C_{13}	*n*-Tridecane	$C_{13}H_{28}$	184	24.81	7.70	6.06
17	C_{10}	*n*-Butyl-cyclohexane	$C_{10}H_{20}$	140	0.14	0.08	-
18	*n*-C_{14}	*n*-Tetradecane	$C_{14}H_{30}$	198	16.2	11.77	2.04
19	C_{11}	*n*-Pentyl-cyclohexane	$C_{11}H_{22}$	154	0.08	0.08	1.37
20	*n*-C_{15}	*n*-Pentadecane	$C_{15}H_{32}$	212	9.52	12.77	0.97
21	C_{12}	*n*-Hexyl-cyclohexane	$C_{12}H_{24}$	168	0.04	0.11	0.41
22	*n*-C_{16}	*n*-Hexadecane	$C_{16}H_{34}$	226	5.83	14.29	1.04
23	C_{13}	*n*-Heptyl-cyclohexane	$C_{13}H_{26}$	182	-	0.13	-
24	*n*-C_{17}	*n*-Heptadecane	$C_{17}H_{36}$	240	3.94	16.90	0.59
25	C_{14}	*n*-Octyl-cyclohexane	$C_{14}H_{28}$	196		0.07	-
26	*n*-C_{18}	*n*-Octadecane	$C_{18}H_{38}$	254	2.41	12.96	0.49
27	C_{15}	*n*-Nonyl-cyclohexane	$C_{15}H_{30}$	210		0.03	-
28	*n*-C_{19}	*n*-Nonadecane	$C_{19}H_{40}$	268	0.27	8.43	0.35
29	*n*-C_{20}	*n*-Eicosane	$C_{20}H_{42}$	282	0.15	5.09	0.29
30	*n*-C_{21}	*n*-Heneicosane	$C_{21}H_{44}$	296	-	3.03	-
31	*n*-C_{22}	*n*-Docosane	$C_{22}H_{46}$	310	-	1.75	-
32	*n*-C_{23}	*n*-Tricosane	$C_{23}H_{48}$	324	-	1.01	-
33	*n*-C_{24}	*n*-Tetracosane	$C_{24}H_{50}$	338	-	0.68	-
34	*n*-C_{25}	*n*-Pentacosane	$C_{25}H_{52}$	352	-	0.36	-
35	*n*-C_{26}	*n*-Hexacosane	$C_{26}H_{54}$	366	-	0.49	-

oven temperature was increased by 4 °C/min until the oven temperature was 300 °C. It means that for every 4 °C increase in oven temperature, the retention time increased by 1 min. The temperature of 300 °C was maintained for 35 min. It means the retention time moved without being accompanied by an increase in oven temperature.

The *n*-Alkane and Isoalkane

The distribution of *n*-alkane and isoalkane compounds in each aliphatic hydrocarbon fraction of Naphtha, LO and MO products from the coal liquefaction of Bukit Pinang, Samarinda Ulu is shown in Fig. S4, S5, and S6 or Table 2. Identification of *n*-alkane compounds was carried out based on the fragmentogram

Table 2. Aliphatic hydrocarbon *n*-alkane and isoalkane fraction of Naphta, LO, and MO

No	Compound	Compound name	Molecular formula	M+	Composition (%)		
					LO	MO	Naphta
1	*i*-C_9	Iso-nonane	C_9H_{20}	128	-	-	1.65
2	*i*-C_{10}	Iso-decane	$C_{10}H_{22}$	142	-	-	13.99
3	*i*-C_{11}	Iso-undecane	$C_{11}H_{24}$	156	-	-	3.44
4	*i*-C_{12}	Iso-dodecane	$C_{12}H_{26}$	170	-	-	1.93
5	*n*-C_{10}	*n*-Decane	$C_{10}H_{22}$	142	-	-	28.59
6	*n*-C_{11}	*n*-Undecane	$C_{11}H_{24}$	156	9.64	-	25.23
7	*n*-C_{12}	*n*-Dodecane	$C_{12}H_{26}$	170	26.86	2.56	11.90
8	*n*-C_{13}	*n*-Tridecane	$C_{13}H_{28}$	184	24.95	7.74	6.79
9	*n*-C_{14}	*n*-Tetradecane	$C_{14}H_{30}$	198	16.30	11.83	2.28
10	*n*-C_{15}	*n*-Pentadecane	$C_{15}H_{32}$	212	9.58	12.83	1.09
11	*n*-C_{16}	*n*-Hexadecane	$C_{16}H_{34}$	226	5.86	14.36	1.17
12	*n*-C_{17}	*n*-Heptadecane	$C_{17}H_{36}$	240	3.96	16.98	0.66
13	*n*-C_{18}	*n*-Octadecane	$C_{18}H_{38}$	254	2.43	13.02	0.55
14	*n*-C_{19}	*n*-Nonadecane	$C_{19}H_{40}$	268	0.27	8.47	0.40
15	*n*-C_{20}	*n*-Eicosane	$C_{20}H_{42}$	282	0.15	5.12	0.32
10	*n*-C_{21}	*n*-Heneicosane	$C_{21}H_{44}$	296	-	3.05	-
11	*n*-C_{22}	*n*-Docosane	$C_{22}H_{46}$	310	-	1.76	-
12	*n*-C_{23}	*n*-Tricosane	$C_{23}H_{48}$	324	-	1.02	-
13	*n*-C_{24}	*n*-Tetracosane	$C_{24}H_{50}$	338	-	0.68	-
14	*n*-C_{25}	*n*-Pentacosane	$C_{25}H_{52}$	352	-	0.36	-
15	*n*-C_{26}	*n*-Hexacosane	$C_{26}H_{54}$	366	-	0.20	-

Table 3. Composition of *n*-alkane and isoalkane of Naphtha, LO, and MO products

Liquefaction product	Temp. range (°C)	*n*-alkanes (C_nH_{2n+2})	Isoalkanes (C_nH_{2n+2})	Max. intensity (*n*-alkanes)	Min. intensity (*n*-alkanes)
Naphtha	30–180	*n*-C_{10}-*n*-C_{20}	*i*-C_9–*i*-C_{12}	*n*-C_{10}-*n*-C_{11}	*n*-C_{20}
LO	180–220	*n*-C_{11}-*n*-C_{20}	-	*n*-C_{12}	*n*-C_{20}
MO	220–350	*n*-C_{12}-*n*-C_{26}	-	*n*-C_{17}	*n*-C_{26}

m/z 57. It was obtained from the GC-MS instrument software to analyze the *m/z* 57 value from the chromatogram.

Identification of *n*-alkane compounds from Naphtha products showed that the distribution of *n*-alkane homologs (*n*-C_{10}-*n*-C_{20}), LO products contained *n*-alkane homologs (*n*-C_{11}-*n*-C_{20}) and MO products contained *n*-alkane homologs (*n*-C_{12}-*n*-C_{26}). Only the naphtha products contain isoalkanes (*i*-C_9-*i*-C_{12}), as indicated by peaks 1–4 (Fig. S4). The composition of the *n*-alkane and isoalkane products of Naphtha, LO and MO is listed in Table 3.

Based on the *n*-alkane composition identified in the Naphtha, LO and MO products, there appear to be suitability for the raw material requirements for gasoline, kerosene, and diesel fuel formulations [29]. The small intensity of the *n*-alkane medium chain, such as *n*-C_{20} in Naphtha and LO products, is shown in Table 3. It is caused by Naphtha products obtained in the low fractionation distillation temperature range (30–180 °C). Thereby, *n*-C_{20} has fractionated in quantity the minimum. The liquefaction product shows that n-C_{10}-*n*-C_{11} represents the maximum intensity of Naphtha products, *n*-C_{12} for LO products, and *n*-C_{17} for MO products. The maximum intensity of each product shows the characteristics of each product. Naphtha products consist of *n*-alkanes (paraffin), short-medium chains (n-C_{10}-n-C_{20}) and isoalkanes (iC_9-iC_{12}). The formation of *n*-alkanes in Naphtha, LO, and MO products can occur through the thermal cracking reaction of long-chain *n*-alkanes [10,30-31].

Aliphatic hydrocarbon compounds are branch chains in coal's macromolecular structure. The lower the coal maturity, the longer the aliphatic carbon chain, so the degradation reaction produces more long-chain alkanes. Medium chain *n*-alkane homologs such as n-C_{10}-n-C_{20} were obtained in Naphtha products. Thereby Bukit Pinang coal, Samarinda Ulu is immature coal. The distribution of *n*-alkane medium chain (n-C_{10}-n-C_{20}) in Naphtha and LO products, *n*-alkane medium-long chain (n-C_{12}-n-C_{26}) in MO products, is a characteristic of the cracking process of the macromolecules structure of immature coal [32].

The thermal cracking of Bukit Pinang coal produces *n*-alkane (n-C_{10}-n-C_{26}) hydrocarbons dominated by long-chain *n*-alkanes. Long-chain *n*-alkanes are precursors for forming short-chain *n*-alkanes in coal and petroleum liquefaction products. It is the case with *n*-alkane cracking (n-$C_{22}H_{46}$) contained in petroleum at 350 °C for 24 h producing short-chain *n*-alkanes (n-C_6-n-C_9) [30] and cracking *n*-pentadecane (n-$C_{15}H_{32}$) produces short-chain *n*-alkanes (n-C_7-n-C_8) [33]. The liquefaction of Bukit Pinang-Samarinda Ulu coal, which took place at a temperature of 450 °C for 24 h, resulted in short-medium *n*-alkanes for Naphtha and LO products and medium-long chain *n*-alkanes for MO products. Although liquefaction is carried out at a higher temperature (450 °C) than the cracking temperature of *n*-alkanes (n-$C_{22}H_{46}$) in the petroleum fraction (350 °C) for 24 h, it turns out that Bukit Pinang's liquid coal product does not produce short-chain *n*-alkanes the same one. Bukit Pinang coal has a low maturity, so it is estimated to have a long *n*-alkane side chain in its macromolecular matrix. Thus, cracking produces short-medium chain *n*-alkanes in Naphtha and LO products, while medium-long chain *n*-alkanes are produced in MO products.

The distribution of short-medium *n*-alkanes (n-C_{10}-n-C_{20}) in Naphtha and LO products resulting from the liquefaction of Bukit Pinang coal has similarities with the Arjuna Basin petroleum hydrocarbon component, West Java [34] and liquid oil produced through the pyrolysis of Talang Akar coal [35]. The chemical composition of the Bukit Pinang coal liquefaction product also has similarities with the raw material components of commercial fuel formulations [29]. Thus, the *n*-alkane component produced has similarities with the components of the gasoline, kerosene and diesel fuel formulations. The similarity of precursors for forming short-chain *n*-alkanes between coal and petroleum liquefaction products supports the potential for liquified coal liquefaction products to be formulated as a liquid fuel source.

Isoalkane Compounds

The isoalkanes in the sub-bituminous coal liquefaction products of Bukit Pinang, Samarinda Ulu, were only found in the Naphtha products and not in the LO and MO products. The presence of isoalkanes in Naphtha products is indicated by peaks 1, 2, 3 and 4, as shown in Fig. S4. These compounds were identified based on the *m/z* 57 fragmentogram. The fragmentation pattern was characterized by increased intensity of specific characteristic fragment peaks [31]. Based on the mass spectrum data, peak (1) with [M+] ion at *m/z* 128 was identified as 2,6-dimethyl heptane (i-C_9H_{20}), peak (2) with *m/z* 128 was identified as compound 4-methyl-octane (C_9H_{20}). Peak (3) with *m/z* 142 as 2,6-dimethyl-octane ($C_{10}H_{22}$), and peak (4) with *m/z* 156 identified as 2,6-dimethyl-nonane ($C_{11}H_{24}$). The distribution of short-chain isoalkanes (i-C_9-i-C_{11}) in liquefaction products was thought to originate from the thermal cracking process of heavier isoprenoids such as pristane and phytane. This compound was found as a biomarker in the coal extract of Bukit Pinang, Samarinda Ulu.

Short-chain isoalkane groups are also found in petroleum formed during the catagenesis stage [31]. One of the essential isoalkane compounds in fuels is iso-octane. The iso-octane compound is an indicator of the quality of the fuel type of gasoline as an octane number value. The presence of isoalkane compounds in Naphtha products causes this product to be more profitable as gasoline fuel. It is due to isoalkane components reducing the engine's tendency to knock it. The tendency for gasoline to provide this anti-knock property increases if there is branching in the alkane structure [36-38]. This isoalkane component is not produced in the LO and MO products analyzed. Therefore, Naphtha products are more suitable as gasoline and kerosene fuel components than LO and MO products. However, some conversion processes can also convert *n*-alkanes to isoalkanes or aromatic compounds in the application of petroleum as fuel. Thus, LO and MO products containing straight-chain alkane compounds can still be used as fuel through this conversion and then obtained isoalkanes (i-C_9-i-C_{11}) and *n*-alkanes (n-C_{10}-n-C_{20}) in Naphtha products, n-C_{11}-n-C_{20} in LO products, and n-C_{12}-n-C_{26} in MO products, supporting the potential of Bukit Pinang coal to be liquefied.

Cycloalkane Compound

The presence of cycloalkanes in the aliphatic hydrocarbon fraction was identified based on the *m/z* 83 fragmentogram, Fig. S7, S8, and S9 or Table 4. The base peak *m/z* 83 was formed due to the release of $C_6H_{11}^+$ fragments from *n*-alkyl cyclohexane compounds [10].

Based on mass spectrum data analysis (Table 4), the presence of cycloalkanes in Naphtha products was identified as *n*-methyl-cyclohexane (C_7) *n*-ethyl-cyclohexane (C_8), *n*-propyl-cyclohexane (C_9), *n*-pentyl-cyclohexane (C_{11}), *n*-hexyl-cyclohexane (C_{12}), methyl-*n*-propyl-cyclohexane (C_{10}), methyl-*n*-butyl-cyclohexane (C_{11}), methyl-*n*-pentyl-cyclohexane (C_{12}). The cycloalkanes identified in this Naphtha product were compatible with the gasoline fuel component [29]. The presence of LO cycloalkanes is shown in Fig. S8.

Alkyl cycloalkanes showed the presence of cycloalkanes in LO products. It is consist of *n*-ethyl-cyclohexane (C_8), *n*-propyl-cyclohexane (C_9), *n*-butyl-cyclohexane (C_{10}), *n*-pentyl-cyclohexane (C_{11}), *n*-hexyl-cyclohexane (C_{12}). Fig. S9 shows the fragmentogram of the existence of cycloalkanes in MO products.

The cycloalkane compounds in MO products were identified as *n*-butyl-cyclohexane (C_{10}), *n*-pentyl-cyclohexane (C_{11}), *n*-hexyl-cyclohexane (C_{12}), *n*-heptyl-cyclohexane (C_{13}), *n*-octyl-cyclohexane (C_{14}), and *n*-nonyl-cyclohexane (C_{15}). The distribution of cyclohexane compounds in Naphtha products showed C_7-C_{12} (C_7H_{14}-$C_{12}H_{24}$). LO products contain C_8-C_{12} (C_8H_{16}-$C_{12}H_{24}$), and MO products contain C_{10}-C_{15} ($C_{10}H_{20}$-$C_{15}H_{30}$). The distribution of cyclohexane compounds in Naphtha, LO, and MO products showed

Table 4. Cycloalkane compound of Naphta, LO, and MO

No	Compound	Compound Name	Molecular formula	M+	Composition (%)		
					LO	MO	Naphta
1	C_7	*n*-methyl-cyclohexane	C_7H_{14}	98	-	-	3.08
2	C_8	*n*-ethyl-cyclohexane	C_8H_{16}	112	18.81	-	5.62
3	C_9	*n*-propyl-cyclohexane	C_9H_{18}	126	36.75	-	23.89
4	C_{11}	*n*-pentyl-cyclohexane	$C_{11}H_{22}$	154	24.37	-	15.44
5	C_{12}	*n*-hexyl-cyclohexane	$C_{12}H_{24}$	168	13.62	-	23.45
6	C_{10}	methyl-*n*-propyl-cyclohexane	$C_{10}H_{20}$	140	-	-	15.34
7	C_{11}	methyl-*n*-butyl-cyclohexane	$C_{11}H_{22}$	154	-	-	10.14
8	C_{12}	methyl-*n*-pentyl-cyclohexane	$C_{12}H_{24}$	168	-	-	3.05
9	C_{10}	*n*-butyl-cyclohexane	$C_{10}H_{20}$	140	6.45	15.22	-
10	C_{11}	*n*-pentyl-cyclohexane	$C_{11}H_{22}$	154	18.81	16.06	-
11	C_{12}	*n*-hexyl-cyclohexane	$C_{12}H_{24}$	168	36.75	21.85	-
12	C_{13}	*n*-heptyl-cyclohexane	$C_{13}H_{26}$	182	-	25.62	-
13	C_{14}	*n*-octyl-cyclohexane	$C_{14}H_{28}$	196	-	14.76	-
14	C_{15}	*n*-nonyl-cyclohexane	$C_{15}H_{30}$	210	-	6.49	-

short-chain alkanes are also equivalent to *n*-alkanes and isoalkanes. The distribution of cyclohexane (C_7-C_{12}) in Naphtha products, C_8-C_{12} components in LO products and C_{10}-C_{15} components in this MO product supports the potential of immature coal to be liquefied. Based on the analysis of the coal liquefaction products of Bukit Pinang, East Kalimantan, Indonesia, the presence of aliphatic hydrocarbon compounds in Naphtha, LO, and MO products can be seen in the following Table 5.

According to Table 5, Naphtha and LO products have the same chemical composition as gasoline and kerosene fuels, while MO products have similar chemical components to kerosene and diesel fuels [29,39]. Therefore, the liquefaction of immature coal of Bukit Pinang, East Kalimantan, Indonesia, is produced liquid coal. It is considered to be formulated as a source of liquid fuels.

Naphthene or cycloalkane is thermo radical. It is derived from and cyclization of heavy *n*-alkane and fatty acids in sediments of organic matter (kerogens from petroleum or coal). In nature, this process occurs during the catagenesis stage with the help of minerals in the soil [30,40]. Cyclohexane with linear alkyl substituents is a significant component in crude oil [30]. The presence of cyclohexane compounds in liquid coal is thought to originate from radical reactions that occur during the coal liquefaction process. High temperature and pressure allow the heavy *n*-alkane (C_7-C_{33}) and fatty acid to cyclize to form cyclohexane and alkyl cyclohexane.

Alkyl cycloalkane compounds are the main components in crude oil [30]. It was produced in the liquefaction process of the Black Thunder sub-bituminous coal, Wiyodak and Anderson Basins [41] and in the light oil fraction from liquefaction bituminous coal Shenhua Shangwan [12]. Therefore, alkyl cycloalkane, *n*-alkanes and isoalkanes in liquid coal have similarities with the chemical composition of the petroleum and the light oil fraction from coal liquefaction. Thus, low-rank sub-bituminous and bituminous coal can be liquefied as alternative fuel oil.

Table 5. Chemical components of Bukit Pinang coal liquefaction products

Products	*n*-alkanes	isoalkanes	Cyclohexane
Naphtha	n-C_{10}-n-C_{20}	iC_9-iC_{12}	C_7-C_{12}
LO	n-C_{11}-n-C_{20}	---	C_8-C_{12}
MO	n-C_{12}-n-C_{26}	---	C_{10}-C_{15}

Correlation of Coal Biomarkers with Their Liquefaction Products

Biomarker plays a vital role in the coal liquefaction process to determine the macromolecular character of coal to be liquefied. The biomarker is a fossil compound formed during peatification and coalification. It can be extracted in organic solvents, while the chemical composition of liquid coal is produced from the thermal cracking of coal macromolecules into smaller molecules [20]. Some organic compounds in liquid coal can be extracted from radical reactions and rearrangement of biomarkers commonly found in immature coal, such as isoalkanes derived from pristane and phytane [31,42-43]. It is also thought that the isoalkane compounds found in the coal liquefaction process were obtained through the thermal degradation of compounds with a styrene skeleton in the form of 13b(H)-diacholest-24-ene and 24-diastigmastene usually found as biomarkers in immature coal extracts. In addition, isoalkane compounds contained in coal liquefaction products are also produced from compounds with a styrene skeleton typically found in immature coal extracts. This process is carried out at high temperatures [30].

Short-chain *n*-alkane compounds can also originate from long-chain *n*-alkanes (nC_{11}-n-C_{35}) [10,30-31,33]. However, some other organic compounds produced in the coal liquefaction process are formed purely from the breakdown of coal macromolecules. Furthermore, it is followed by radical rearrangements and the formation of *n*-alkanes, isoalkanes, cycloalkanes and alkyl cyclohexane compounds. Cyclohexane compounds with linear alkyl substituents produced in coal liquefaction products are a significant component in petroleum [9,11,20,30,41,44].

Excellent and clean liquid coal claims to use coal as a substitute for liquid fuel from petroleum. The reactivity of the reaction in the coal liquefaction process is related to the macromolecular structure of the coal

[20]. It contains polycyclic aromatic units and hydroaromatic rings. It is linked to methylene, ethylene and ether groups. Thereby, breaking these bonds will lead to the depolymerization of macromolecules [45].

The coal liquefaction process is the depolymerization of the coal macromolecular structure. It breaks the bonding of the basic coal constituent units to produce hydrocarbon compounds such as those in petroleum [44]. This reaction occurs in three stages: dissolution, bond breaking and retrogressive [20].

The dissolution (first stage) is the dissolving of solid coal into liquid. The bonds that connect the basic units of the coal constituents become unstable at temperatures above 350 °C so that they undergo thermal cracking producing reactive free radical fragments. The amount of hydrogen supplied by the donor solvent or catalyst is balanced by the number of free radical fragments resulting in the size of the free radical being small and stable so that it dissolves in the solvent. The breaking process will end if the reactive bonds and hydrogen available as stabilizers are used up [20].

The second stage is a stronger bond termination reaction, such as the aryl bond in the aromatic ring. The bond-breaking reaction can be carried out directly by the reactive hydrogen that attacks the bond. Indirectly, the bond-breaking and aromatic ring opening reactions are broken thermally.

The third stage is a retrogressive reaction, in which unstable free radical fragments join with other molecules to produce thermally stable bonds. The combination reaction repeatedly occurs, producing large molecules resistant to depolymerization. Therefore, the dissolution of depolymerized molecules aims to break the trap. It also minimizes the macromolecular interaction of coal components or coal-derived products. This third stage produces a degradation product in the form of aliphatic hydrocarbons [20].

Organic compounds (*n*-alkanes, isoalkanes, alkyl cyclohexane, bicyclic alkanes and tricyclic alkanes) produced in this coal liquefaction process are also common biomarkers found in coal [12,43]. Therefore, biomarker identification considers the feasibility of coal being liquefied.

CONCLUSION

Liquefaction process of Bukit Pinang, Samarinda Ulu coal, producing Naphtha product (1.43%); Light Oil (LO) (6.84%); Middle Oil (MO) (2.3%); Heavy Oil (HO) (25.41%) and Coal Liquid Bottom (CLB) (33.72%). Naphtha product contains short-medium *n*-alkanes (n-C_{10}-n-C_{20}), isoalkanes (i-C_9-i-C_{12}), and alkyl cycloalkanes (C_8-C_{13}). The LO product contains medium-long chain *n*-alkanes (n-C_{11}-n-C_{20}) and alkyl cyclohexane (C_8-C_{12}). The MO product contains *n*-alkanes (n-C_{12}-n-C_{26}) and alkyl cyclohexane (C_{10}-C_{15}). The chemical components of the Naphtha, LO, and MO products are similar to those of gasoline, kerosene and diesel oil. These results indicate that the coal liquefaction product can be applied as alternative liquid fuel oil.

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AUTHOR CONTRIBUTIONS

The contribution of each author in this manuscript is described as follows. Yulfi Zetra and Rafwan Year Pery Burhan conceptualized this research. Yulfi Zetra, Anis Febriati, and Dyah Nirmala co-wrote the manuscript draft and reviewed and edited it. In addition to validating the manuscript draft, Arizal Firmansyah also reviewed and edited it. Rafwan Year Perry Burhan carried out the design or methodology and supervision of the entire research. The task of validating the manuscript was also handled by Zjahra Vianita Nugraheni, who helped to correct it simultaneously. All authors agreed to the final version of this manuscript.

REFERENCES

[1] British Petroleum, 2021, *Statistical Review of World Energy 2021*, BP Energy Outlook 2021, 70th Ed., 8–20.

[2] Widyastuti, N.L., and Nugroho, H., 2020, Dampak Covid-19 terhadap industri minyak dan gas bumi: Rekomendasi kebijakan untuk Indonesia, *Jurnal Perencanaan Pembangunan*, 4 (2), 166–176.

[3] Kuncoro, H., 2011, The Volatility of world crude oil prices, *Econ. J. Emerging Market*, 1 (3), 1–15.

[4] Song, Y., Chen, B., Wang, X.Y., and Wang, P.P., 2022, Defending global oil price security: Based on the perspective of uncertainty risk, *Energy Strategy Rev.*, 41, 100858.

[5] Gallagher, K.S., Bhandary, R., Narassimhan, E., and Nguyen, Q.T., 2021, Banking on coal? Drivers of demand for Chinese overseas investments in coal in Bangladesh, India, Indonesia and Vietnam, *Energy Res. Soc. Sci.*, 71, 101827.

[6] Xu, Y.Y., Sun, Z.Q., Fan, X., Ma, F.Y., Kuznetsov, P.N., Chen, B., and Wang, J.F., 2021, Building methodology for evaluating the effects of direct coal liquefaction using coal structure-chemical index, *Fuel*, 305, 121568.

[7] Arinaldo, D., and Adiatama, J.C., 2019, *Dinamika Batu Bara Indonesia: Menuju Transisi Energi yang Adil*, Institute for Essential Services Reform (IESR), Jakarta, Indonesia.

[8] Soelistijo, U.W., Wibowo, A.P., and Abdullah, M., 2013, The contribution of low rank coal liquefaction in Indonesian economy in 2025, *Procedia Earth Planet. Sci.*, 6, 301–310.

[9] Zhang, G., Qiao, X., Miao, X., Hong, J., and Zheng, J., 2013, Effect of coal to liquid fuel on combustion and emission in a heavy-duty diesel engine, *Proc. Inst. Mech. Eng., Part D*, 227 (4), 481–489.

[10] Feng, Z., Bai, Z., Hou, R., Guo, Z., Kong, L., Bai, J., and Li, W., 2021, Co-pyrolysis of mild liquefaction solid product and low rank coals: Products distributions, products properties and interactions, *Fuel*, 306, 121719.

[11] Li, X., Li, L., Li, B., Feng, J., and Li, W., 2017, Product distribution and interactive mechanism during co-pyrolysis of a subbituminous coal and its direct liquefaction residue, *Fuel*, 199, 372–379.

[12] Bai, Z., Huang, P., Wang, L., Cao, H., Zhang, X., and Li, G., 2021, A study on upgrading light coal tar to aerospace fuel, *J. Fuel Chem. Technol.*, 49 (5), 694–702.

[13] Liu, H., Jiang, S.S., Guo, H.S., Han, S., Yang, C., and Jiang, J.Z., 2016, A new kind of pour point depressant: Diesel from direct coal liquefaction, *Fuel Process. Technol.*, 149, 285–289.

[14] Singh, A.K., and Kumar, A., 2017, Liquefaction behavior of Eocene lignites of Nagaur Basin, Rajasthan, India: A petrochemical approach, *Energy Sources, Part A*, 39 (15), 1686–1693.

[15] Nompo, S., Sardi, B., and Arif, M., 2020, Karakteristik batubara peringkat rendah formasi bobong dan implikasinya terhadap coal liquefaction, *Jurnal Geomine*, 8 (1), 17–24.

[16] Tewari, A., Dutta, S., and Sarkar, T., 2017, Biomarker signatures of Permian Gondwana coals from India and their palaeobotanical significance, *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, 468, 414–426.

[17] Liu, B., Vrabec, M., Markič, M., and Püttmann, W., 2019, Reconstruction of paleobotanical and paleoenvironmental changes in the Pliocene Velenje Basin, Slovenia, by molecular and stable isotope analysis of lignites, *Int. J. Coal Geol.*, 206, 31–45.

[18] Wang, S., Tang, Y., Schobert, H.H., Jiang, Y., Yang, Z., and Zhang, X., 2018, Petrologic and organic geochemical characteristics of Late Permian bark coal in Mingshan coalmine, Southern China, *Mar. Pet. Geol.*, 93, 205–217.

[19] Guo, Q., Littke, R., and Zieger, L., 2018, Petrographical and geochemical characterization of sub-bituminous coals from mines in the Cesar-Ranchería Basin, Colombia, *Int. J. Coal Geol.*, 191, 66–79.

[20] Wang, Z., Wang, Q., Hu, R., Pan, C., Wang, X., Ren, S., Lei, Z., Kang, S., Yan, J., and Shui, H., 2019, Effect of thermal extraction on hydro-liquefaction property of residual coal, *Fuel*, 251, 474–481.

[21] Ra, H.W., Mun, T.Y., Hong, S.J., Chun, D.H., Lee, H.T., Yoon, S.M., Moon, J.H., Park, S.J., Lee, S.H., Yang, J.H., Kim, J.K., Jung, H., and Seo, M.W., 2021, Indirect coal liquefaction by integrated entrained flow gasification and Rectisol/Fischer–Tropsch processes for producing automobile diesel substitutes, *Energy*, 219, 119597.

[22] Yang, T., Zheng, J., Liu, C., Tang, F., Li, C., Deng, W., Yang, N., and Wang, X., 2022, Utilization of coal liquefaction solid residue waste as an effective additive for enhanced catalytic performance, *Fuel*, 329, 125454.

[23] Lin, Y., Wang, S., Sha, Y., and Yang, K., 2020, Organic geochemical characteristics of bark coal in Changguang area: Evidence from aromatic hydrocarbons, *Int. J. Coal Sci. Technol.*, 7 (2), 288–298.

[24] Lv, J.H., Wei, X.Y., Zhang, Y.Y., and Zong, Z.M., 2020, Occurrence and distribution of biomarkers in Baiyinhua lignite, *Fuel*, 271, 117525.

[25] Rybicki, M., Marynowski, L., and Simoneit, B.R.T., 2020, Composition of organic compounds from low-temperature burning of lignite and their application as tracers in ambient air, *Chemosphere*, 249, 126087.

[26] Guo, Q., Littke, R., Sun, Y., and Zieger, L., 2020, Depositional history of low-mature coals from the Puyang Basin, Yunnan Province, China, *Int. J. Coal Geol.*, 221, 103428.

[27] Hirano, K., 2000, Outline of NEDOL coal liquefaction process development (Pilot plant program), *Fuel Process. Technol.*, 62 (2-3), 109–118.

[28] Shen, T., Wang, Y., Liu, Q., Liu, J., and Liu, Z., 2021, A comparative study on direct liquefaction of two coals and hydrogen efficiency to the main products, *Fuel Process. Technol.*, 217, 106822.

[29] Wang, S., Kim, H., Lee, D., Lee, Y.R., Won, Y., Hwang, B.W., Nam, H., Ryu, H.J., and Lee, K.H., 2021, Drop-in fuel production with plastic waste pyrolysis oil over catalytic separation, *Fuel*, 305, 121440.

[30] Kissin, Y.V., 1990, Catagenesis of light cycloalkanes in petroleum, *Org. Geochem.*, 15 (6), 575–594.

[31] Kissin, Y.V., 1993, Catagenesis of light acyclic isoprenoids in petroleum, *Org. Geochem.*, 20 (7), 1077–1090.

[32] Al Sandouk-Lincke, N.A., Schwarzbauer, J., Hartkopf-Fröder, C., Volk, H., Fuentes, D., Young, M., and Littke, R., 2014, The effect of different pyrolysis temperatures on organic microfossils, vitrain and amber–A comparative study between laser assisted- and Curie Point-pyrolysis-gas chromatography/mass spectrometry, *J. Anal. Appl. Pyrolysis*, 107, 211–223.

[33] Mango, F.D., 1997, The light hydrocarbons in petroleum: A critical review, *Org. Geochem.*, 26 (7-8), 417–440.

[34] Horsfield, B., Yordy, K.L., and Crelling, J.C., 1988, Determining the petroleum-generating potential of coal using organic geochemistry and organic petrology, *Org. Geochem.*, 13 (1-3), 121–129.

[35] Noble, R.A., Wu, C.H., and Atkinson, C.D., 1991, Petroleum generation and migration from Talang Akar coals and shales offshore N.W. Java, Indonesia, *Org. Geochem.*, 17 (3), 363–374.

[36] Kumar, T., Mohsin, R., Abd. Majid, Z., Abdul Ghafir, M.F., and Wash, A.M., 2020, Experimental study of the anti-knock efficiency of high-octane fuels in spark ignited aircraft engine using response surface methodology, *Appl. Energy*, 259, 114150.

[37] Dias, T., Oliveira, R., Saraiva, P., and Reis, M.S., 2020, Predictive analytics in the petrochemical industry: Research Octane Number (RON) forecasting and analysis in an industrial catalytic reforming unit, *Comput. Chem. Eng.*, 139, 106912.

[38] Zhou, Z., Kar, T., Yang, Y., Brear, M., Leone, T.G., Anderson, J.E., Shelby, M.H., Curtis, E., and Lacey, J., 2021, The significance of octane numbers to drive cycle fuel efficiency, *Fuel*, 302, 121095.

[39] Wang, S., Lee, D., Kim, H., Hwang, B.W., Nam, H., and Ryu, H.J., 2022, Separation of MSW pyrolysis fuel using 20 kg scale vacuum distillation system and its potential application as petro-chemical substitute, *J. Environ. Chem. Eng.*, 10 (5), 108416.

[40] Xie, H., Dong, G., Formolo, M., Lawson, M., Liu, J., Cong, F., Mangenot, X., Shuai, Y., Ponton, C., and Eiler, J., 2021, The evolution of intra- and inter-molecular isotope equilibria in natural gases with thermal maturation, *Geochim. Cosmochim. Acta*, 307, 22–41.

[41] Ji-Zhou, D., Vorkink, W.P., and Lee, M.L., 1993, Origin of long-chain alkylcyclohexanes and alkylbenzenes in a coal-bed wax, *Geochim. Cosmochim. Acta*, 57 (4), 837–849.

[42] Dawson, K.S., Schaperdoth, I., Freeman, K.H., and Macalady, J.L., 2013, Anaerobic biodegradation of the isoprenoid biomarkers pristane and phytane, *Org. Geochem.*, 65, 118–126.

[43] Nunes, N.M.M., Ade, M.V.B., Rodrigues, R., de

Assis, F.B., Nascimento, F., and Leite, R.T.N., 2017, Oil biodegradation in siliciclastic Reservoir: An example from Paleogene, Oliva Block, North of Santos Basin, Brazil, *Anu. Inst. Geocienc.*, 40 (3), 222–231.

[44] Kuznetsov, P.N., Kamenskiy, E.S., and Kuznetsova, L.I., 2020, Solvolysis of bituminous coal in coal- and petroleum-derived commercial solvents, *ACS Omega*, 5 (24), 14384–14393.

[45] Lin, X., Yin, J., Ding, X., Wang, Y., and Xu, Z., 2021, Study on the transformation characteristic of heteroatoms during liquefaction of Naomaohu coal, *J. Fuel Chem. Technol.*, 49 (5), 656–663.