The potential of liquid fuel production from lignite using bio-solubilization method in Indonesia

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Abstract. Indonesian coal reserves amounted to 20.98 billion tons, which was dominated by lignite of 59%. Its abundance, various usage, and relatively cheaper price is some of the many profitable traits for it to be used as an energy source for many industries especially in Indonesia. However, most of the type of low-quality lignite (96.4%) may result in a serious case of air pollution. For this reason, direct combustion is not an ideal process to extract energy from coal for environmental protection. This study aims to research the potential of lignite conversion into liquid fuel which considerably has less emission. A process called bio-solubilization utilizes the role of microorganisms to convert solid coal into liquid fuel/chemical compounds while still producing environmentally friendly by products. Furthermore, lignite contains simple aromatic compounds which is a favourable condition to optimize the process. Through several study review, it seems that there are still many microorganisms’ behaviours which need to be investigated further to ensure a steady process of solubilization, regardless the great potential of bio-solubilization. However, there is a hope of liquid coal production yield optimization, one of which is by pretreatment process which helps in increasing the susceptibility of brown coal to microbial solubilization.

1. Introduction
Coal is one of the most widely used energy sources in the world, along with the increasingly limited oil and natural gas reserves. The US Department of Energy's International Energy Outlook 2009 report shows that coal, oil and natural gas reserves as of the end of 2007 were amounted to 462.6, 164.5 and 163.3 trillion tons. Assuming the level of consumption as of 2007, coal reserves will meet energy requirements for the next 146 years, oil for the next 50 years and natural gas for the next 63 years [1]. Indonesian coal reserves amounted to 20.98 billion tons, which was dominated by lignite (low heat content) of 59%, subbituminous (medium heat content) of 27%, and bituminous reached 14%, while anthracite was less than 0.5% [2]. Coal is widely used for generating electricity and heat.

Generally, the type of coal used widely is of low quality lignite (96.4%) which may result in a serious case of air pollution. Emissions from lignite combustion come mainly in the form of sulphur oxide ($SO_x$), nitrogen oxides ($NO_x$), carbon dioxide ($CO_2$) and heavy metals [3]. For this reason, direct combustion is not an ideal process to extract energy from coal in terms of environmental protection. Therefore, a new technology is needed to overcome this issue, one of which is bio-solubilization.

Bio-solubilization is a process which utilizes microorganisms to dissolve or liquefy coal in order to obtain energy source while producing clean products. This bio-solubilization product, which comes in
the form of a black liquid, saves 97.5% of the calorific value of raw lignite [4]. Compared to thermal liquefaction, bio-solubilization has several advantages, namely the process can be carried out under conditions of atmospheric temperature and pressure, and microbes can use hydrogen from water and do not require external energy of hydrogen to form solubilized lignite. The combustion process does not produce SOx and NOx which makes it environmentally more friendly [5]. For the above reasons, coal bio-solubilization becomes a topic which requires more elaborate studies.

2. Coal bio-solubilization

Bio-solubilization is a promising technology by utilizing microbes to isolate or liquefy coal solids to obtain an energy source with clean products. The bio-solubilization product in the form of a black liquid stores 97.5% of the heating value of raw lignite. Compared with coal thermal liquefaction, bio-solubilization has several advantages, namely the process carried out under conditions of temperature and atmospheric pressure, microbes can use hydrogen from water and do not require external hydrogen energy [5].

![Figure 1. Bioconversion of lignite through solubilization and depolymerization.](image)

Figure 1 shows the process of bioconversion of lignite through the activity of microorganisms, namely the process of solubilization and depolymerization. Coal solubilization does not result in a substantial decrease in the molecular mass of coal humic substances; on the contrary, it may even be accompanied with polymerizing reactions and an increase in the predominant molecular mass [6]. It is known that bacteria and fungi are known to solubilise low-rank coal converting it to water-soluble products with little apparent change in chemical structure and composition [7]. There are several types of bacteria and fungi that can convert solid coal into liquid production by minimizing the initial total energy content [8]. The study literature from about 3100 cultivation experiments made by [6] found that any secreted enzyme from many bacteria are able to convert coal substances to a more hydrophilic status, i.e., they become more water-soluble, and were then taken up by the bacterium. As for fungi, the study of [6] found that there are some fungal organisms, both deuteromycetes and basidiomycetes, which are capable of modifying the physio-chemical structure of hard coal and even liberating low-molecular mass compounds.

3. Research methods

The method used in this study was carried out through several stages (refer to Figure 2) and will be describe as follows.
3.1. Literature study
In this research, literatures related to lignite and the bio-solubilization process will be the source of data in determining which measures can be taken in order to obtain the optimal solubilization process. The literatures that will be used mostly come in the form of research journals and other scientific sources related to the study.

3.2. Identification and analysis of lignite characteristics
The identification stage of lignite characteristics such as chemical compounds and its elemental composition would be a useful resource regarding what opportunities can be taken in order to optimally utilize lignite by using bio-solubilization method.

3.3. Identification of pre-treated lignite
The low amount of solubilization products and long conversion time are some issues that may hinder the development of coal bio-solubilization. One way to accelerate the bio-solubilization process is by doing a pretreatment. This stage will look into available pretreatment options and identify which one could help to tackle this issue.

3.4. Identify the pattern of the process of lignite solubilization based on its carbon content
The solubilization process will include several carbon chain cleavages, typically carbon chain. The microorganisms used in bio-solubilization generally are microbes and molds which might have different pattern of coal liquefaction. Thus, this stage will identify the patterns of both the microbes and the molds and compare the result of each process.

3.5. Review opportunities for liquid fuel production through bio-solubilization
This stage is especially intended for results and discussion section (section 4). All the previous stages finding will be describe and discuss thoroughly here.

4. Results and discussion
This section will be separate into two sections of the results section which based on the identification stages finding, and the discussion section which based on the results.
4.1. Results

The identification and analysis of lignite characteristics has resulted in several findings as follows. The nature of the lignite elements composition, based on the study of Romanowska [9], is shown by the following table 1.

Table 1. Elemental composition of brown coal.

| Element | C (%) | H | N | S | O | Atomic Ratio |
|---------|-------|---|---|---|---|--------------|
|         | 46.24 | 5.39 | <0.30 | 0.85 | 30.00 | 1.40         |

There are two main methods of coal pretreatment which are commonly used, namely chemical pretreatment and physical pretreatment. One way of chemical pretreatment is done by adding nitric and peroxide acids into the coal. This treatment causes changes in the coal’s functional groups and increases enzyme adsorption sites [5]. As mentioned in other studies by Hofrichter M and Fakoussa, the effect of giving acidic compounds to coal on the contact ability of enzymes from microorganisms that can facilitate the process of solubilization [6]. In general, coal solubilization and probably also depolymerization of coal facilitated when oxidatively pretreated or naturally highly oxidized coals (e.g., weathered lignite, leonardite) are exposed to microbes. Artificial oxidative pretreatment can be performed in the laboratory using nitric acid (HNO₃), hydrogen peroxide (H₂O₂), ozone (O₃), or radiation. In addition to chemical pretreatment, a physical pretreatment was carried out by utilizing gamma irradiation. Coal irradiation will cause complex bonds to break increasing enzyme adsorption sites. The result of the elemental composition analysis of the pretreated brown coal can be seen in the following table 2.

Table 2. Elemental composition of pretreated brown coal.

| Element | C (%) | H | N | S | O | Atomic Ratio |
|---------|-------|---|---|---|---|--------------|
|         | 44.00 | 4.00 | 3.40 | 0.72 | 32.40 | 1.09         |

Source:[9]

Based on the study of coal pre-treatment [9], the nitric acid pretreatment of brown coal could reduce the contents of carbon, hydrogen and sulphur and increased the contents of oxygen (from 30.0 to 32.4%) and nitrogen (from 0.3 to 3.40%). It is because lignite oxidation is based on chemical reactions between nitric acid and functional groups of brown coal, e.g. carboxylation of aromatic rings, oxidation of side alkyl chains (linked to aromatic rings) to esters, aldehydes and ketones and their nitrations. These changes in the structure of lignite favour its bio-solubilization and increase effectiveness of the latter. The residues that remained after bio-solubilization of the oxidized brown coal were characterized by the lower content of the analysed elements. Products of bio-solubilization were characterized by increased levels of oxygen and nitrogen, reduced concentrations of carbon and sulphur as well as increased (compared to the nitric acid-pretreated carbon) atomic ratios H/C, O/C and N/O. These results suggest...
that the H/C ratio increased from 1.09 for the nitric acid-pretreated carbon to 1.63 for the product generated by G. alkanivorans S7 and to 1.53 for its counterpart produced by B. mycoides NS1020.

The study about characterization of bio-solubilization product by indigenous mold from mining land in South Sumatera [10] found that the mold secreted extracellular enzymes to break coal substrate molecules into simpler compounds. The more enzymes that bind to the substrate, the reaction speed increases and more enzyme-substrate complexes are formed. This causes more and more products to be formed. In the reaction the enzyme (Enzyme) will hold a bond with the substrate (S) and form an enzyme-substrate complex (EnzS) where (EnzS) will be broken down into the product (P) and free enzyme (Enz) as described by the following formula.

\[ \text{Enz} + \text{S} \xrightleftharpoons{} \text{EnzS} \xrightarrow{} \text{Enz} + \text{P} \]

The bio-solubilization reaction process that occurs both by molds and bacteria that break the conjugate bonds in aromatic coal compounds into simpler compounds can be seen in the following figure 4.

Based on a comprehensive work of the previous stages, there are some studies which demonstrate the ability of both molds and bacteria to dissolve coal and produce liquid fuel products. Specifically for study [10], it is found that the molds are able to decrease the percentage of long carbon chain and on the contrary the percentage of short carbon chain is increasing. The components where the percentage of short-chain carbon increases, i.e. C_9H_{18}, C_{10}H_{20}, C_{12}H_{26}, and C_{14}H_{30}. Gasoline has a carbon atom of 9 to 12, while diesel has a carbon chain length of 10 to 13. Based on the experimental results of Jannah it also found that molds were able to dissolve complex coals into compounds with 9 to 13 carbon chains with a high enough percentage. The highest percentage of hydrocarbon compounds equivalent to gasoline and diesel can reach up to 74.97% and 72.58% [10].

As for study Romanowska and Strzelecki, there are two bacteria of G. alkanivorans S7 and B. mycoides NS1020 which capable of degrading crude oil hydrocarbons, and were found to solubilize brown coal. Nitric acid-pretreatment of lignite increased bio-solubilization efficiency by around 89%. Preliminary analysis of extracellular substances, responsible for this phenomenon, showed that B. mycoides NS1020 synthesized alkaline, thermostable compounds while G. alkanivorans S7 produced not only alkaline compounds but presumably also enzyme [9].

4.2. Discussion

In fact, the idea of coal utilization as substrate for microbes is not new. For example, as what already reviewed by [6] that as early as 1908 Potter reported that bacteria acted as biocatalytic agents in the oxidation of amorphous brown coal. However, it is relatively only few microbiologists, and perhaps even fewer geochemists and fuel scientists, have seriously considered that microorganisms might be able to modify the physio-chemical structure of coal. There are two main reasons for this.
Microbiologists usually prefer simple sugars, organic acids and the like as substrates for microbial activity, and they try to avoid the use of too complex substrates such as coal.

Nevertheless, there are several reasons to investigate microbial activities towards coal, aside from coal importance as fossil fuel which is comparable to crude oil. The worldwide coal deposits are considerably larger than those of oil, and for that matter, according to Indonesian Ministry of Energy and Mineral Resources, Indonesia has coal resources at around 120.5 billion tons and proven oil resources at around 3.69 billion barrels. This translates into about 146 remaining years of coal and 23 years of oil reserve [12], and Indonesia's level of low-rank coal quality in 2016 was 50% of the total reserves for all types of coal quality) [2]. Thus, this amount of coal is worth used as the main resource of raw materials (feedstock) especially for energy industry in Indonesia. In addition, when talking about coal liquefaction technology, bio-solubilization process can be classified as the most energy efficient technology with products worth classified as a clean energy source as explained by Shi et al. [5].

As can be seen in Figure 4, bacteria and molds break the conjugate bonds in aromatic coal compounds into simpler compounds. Lignite constituent is composed of aromatic compounds, and it has the simpler organic compound and lesser aromatic compounds compare to other coal types (see Figure 3) which become the advantage for bio-solubilization. Yet, Hofrichter and Fakoussa stated that lignite actually has an even more complex structure than hard coal because it consists of several distinct classes of constituents [6]. These include the mainly hydrophobic bitumen, the alkali-soluble humic and fulvic acids, and the insoluble residue designated as matrix or humin. Some studies have done investigations regarding the humic substances in lignite, compared for example with research into humic acids from water or soil. Even though some Australian, American and East European lignites have been characterized, these results cannot be transferred to lignites of other origins, because the coal diagenesis differs strongly with each coal deposit depending on plant input, coal generating conditions, etc.

It also seems that microorganism has its own reaction on lignite, as studied in Hofrichter and Fakoussa that with respect to the origin of coal from fossil lignocelluloses, the activities of ligninolytic fungi and their extracellular enzymes are considered in particular [6]. This also mentioned by Jannah which study the characteristic of bio-solubilization products of Lahat mining lignite after incubated by its indigenous molds. It is found that each mold would have different ability in coal solubilization although given the same coal substrate and condition. It is because they will produce different types of enzyme, and this is very important to be able to identify which enzyme of which mold that suitable the most to its substrate [10].

As it has been understood that usually the microorganisms grow slowly on coal particles. However, the impact of pretreatment process should not be underestimated as it shows the ability in encouraging growth of the microorganisms. This effect of pretreatment has been recognized by Hofrichter and Fakoussa where the growth of microorganisms is noticeably stimulated when naturally weathered or chemically pre-oxidized coals are used [6]. It is likely that the oxidation enhances the bioavailability of available compounds. Other similar finding by Romanowska and Strzelecki also showing satisfactory results where chemical pretreatment of nitric acid gives much faster brown coal conversion (bio-solubilization) than crude coal which was around two-fold higher [9]. This has confirmed that nitric acid pretreatment increased the susceptibility of brown coal to microbial solubilization. It was also observed that brown coal pretreatment with oxidizing agents causes loosening of its structure and gives rise to more efficient solubilization.

As for the characteristics of the bio-solubilization product, it was proven to shows similarities with fuel types of gasoline and diesel. The study result of Jannah has found that molds are able to solubilize lignite into compounds with carbon chains of 9 to 13. Moreover, the percentage area of hydrocarbon compounds equivalent to gasoline and diesel fuel that can be produced is 74.97% and 72.58%, respectively. This results has shown a great potential of lignite bio-solubilization although the development of application technology itself is still in laboratory-scale research studies, but it does not rule out the possibility of implementing it at both the pilot scale and the field scale [10].
5. Conclusions
Based on the results achieved from this study, it can be concluded that lignite has a considerable abundance in Indonesia, amounting to half of the total coal content for the overall quantity. Lignite chemical structure which contains simpler aromatic compounds is one reason why development of optimal bio-solubilization process is still worth to be studied. It seems that there are still many microorganisms’ behaviours which need to be investigated further to ensure a steady process of solubilization, regardless the great potential of bio-solubilization. However, there is a hope of liquid coal production yield optimization, one of which is by pretreatment process which helps in increasing the susceptibility of brown coal to microbial solubilization and stimulates faster process.

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