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Overview of Obtaining Alternative Fuels in The Co-liquefaction Processes with Biomass and Coal in Malaysia


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1. Introduction

The extensive utilization of nonrenewable fossil fuels sources such as petroleum, coal and others has imposed a serious problem of energy depletion beyond the 21st century. Currently, our environment has been severely polluted and the instant effect such as climate change, acid rain, greenhouse effect, etc were the results of these problems. Therefore, it is crucial to balance between exploitation of energy resources and environment protection so that development can be sustainable for the human beings. Thus, a new alternative method should be proposed to overcome this problem, especially in the area of renewable energy. In many developing countries, there is an abundance of biomass and agricultural wastes like sawdust, rice and coconut husks, bagasse and animal dung. Unfortunately, these renewable sources were discharged daily due to its properties (wastes) and too expensive to dispose off. For instance, in Malaysia, a huge amount of biomass wastes from oil palm and rubber industries are being produced daily, estimated at not less than 4.5 million metric tonnes effluent per year.

The simplest way for the farmers to discharge the agricultural waste is by burning them. This practice will contribute to air pollution and increase the greenhouse gases effect. To overcome the waste properties of biomass, they are treated in two senses. First, biomass plant matter is used to generate electricity with steam turbines and gasifiers or produce heat, usually by direct
combustion. Second, biomass which includes plant or animal matter can be converted into fibers or other industrial chemicals, including biofuels. Vegetative biomass is generally composed of lignin, cellulose and hemicelluloses and varies in composition depending on plant species. Because of the nature of their chemical structures, biomass materials can easily be converted into biofuels and other useful chemicals in comparison to coals and other fossil energy sources. For instance, in Malaysia, rubber trees plantation cover more than 1.7 million hectares all over the country. These plantations produced agricultural waste that includes rubber seed, rubber seed pod, and rubberwood. Each hectare can produce an approximately amount of 150 – 160 kg of seeds. The search for a low-cost raw material with adequate fuel characteristics for biofuels production is an important step toward establishing a successful biofuels industry. Typically, rubber seed oil, which is nonedible, is considered as a prospective feedstock for alternative fuels production.

In recent years, the liquefaction potential of coals has been investigated to increase the yield of coal conversion processes and the quality of liquid fuels obtained from coal. However, the liquefaction process of coal and biomass materials known as co-liquefaction has not been developed in Malaysia. Typically, rubber seed oil, which is nonedible, obtained from rubber seed is considered as a prospective feedstock for alternative fuels production since it has been found to be rich in oil. Thus, these abundant biomass sources are potential candidates for the production of alternative fuels via co-liquefaction process, and the development of this technology becomes significant in both efficient utilization of resources and improvement of ecological environment. Owing to the fact that energy composition properties are rich in coal, poor in oil and little in gas [1], coal liquefaction to produce alternative petroleum in Malaysia is of great significance to energy security. Malaysian low-rank coals are chosen as the starting material in this study due to the fact that these coals are abundant, low grade and have lower energy content because of their low carbon composition. They are lighter (earthier) and have higher moisture levels. Hence, an attempt should be made for co-liquefaction of Malaysian coals and rubber tree wastes (rubber seed, rubber seed pod or rubberwood), especially for the production of alternative fuels or other chemical feedstocks.

2. World energy supply

Since 2004, there was no increase in world’s oil supply because of the unavailability of finding new sources and the declining output from older oil fields. The increasing production difficulties mean that the supply of oil will soon begin to decline and that, month by month, the decline will be at an accelerating pace [2]. World energy supply is largely dependent on conventional petroleum products and most of the expected increases in oil demand come from the motorized transport sector, with the largest growth from developing countries. Consequently, the transport sector will become responsible for about one-third of the world’s future greenhouse gas (GHG) emission growth and oil prices may reach dramatically high levels [3].
Coincidentally, a growing concern for fossil fuels exhaustion has shown up in the scientific community in the last decade or so. Because of oil, natural gas and coal are finite natural resources; thus the production of these fossil fuels will reach a peak and eventually start to drop. Then, the process of declining will be accelerated because extraction costs will increase after the fossil fuel resources have been consumed. Thus, the implementation of alternative sources becomes more and more important [4].

The depletion of fossil fuels and tighter environmental regulations has forced the world to adopt alternative renewable fuel sources such as hydro, wind and biomass [5], or others. The government expects that an investment through RM9.7 billion is required for the development of the electric utility sector until 2010 [6]. Analysts predicted that the government’s aim for 2,080 MW or 11% of all electricity generated nationwide in 2020 to be sourced from environment-friendly renewable energy and this will be a challenging and long-term task [7]. Hence, due to current demands in electricity and with recent developments in the energy sector, alternative renewable fuels must be recognized as an important energy source for the foreseeable future.

2.1. Biomass

Biomass is a local resource that can contribute to the diversification of energy supply and potentially create employment for cultivation, harvesting, transport and fuel preparation. The importance of biomass can clearly be seen from the action plan as reported by the European Commission. The commission has targeted to increase the usage of biomass from 289,000 TJ in 2003 to about 628,000 TJ in 2010, as reported in their 2005 “Biomass Action Plan”. The factors that led to almost double the biomass use was due to some important advantages that have been identified. These include (i) less dependence on short-term weather changes, (ii) low costs, (iii) an alternative source of income for farmers and finally (iv) able to promote regional economic structures [8].

Well-managed biomass yields carbon emission-saving fuels when substituted for fossil fuels. Amongst renewable energy sources, biomass appears to be the most important in terms of technical and economic feasibility. Since the content of both nitrogen and sulfur are low in biomass materials, the formation of NOx and SOx gases during combustion or firing the biomass materials is also low. The carbon dioxide released during combustion is equal to the amount of carbon dioxide intake when the plants grow up and this means produce almost no net carbon dioxide emission after combustion [1, 3, 4]. It is therefore today that biomass is considered a major future energy source for development and industry, arousing growing interest worldwide, not only for use in transport. Thus, the utilization and development of biomass energy could solve not only the energy issues, but could surely reduce the main environment problems such as pollution and greenhouse effects. Food crops containing starch/sugar/oil can be processed to produce biofuels where the conversion technologies and markets are readily available. Moreover, with the increasing petroleum prices, the commercial opportunity must be quickly taken into consideration.
Huge amount of biomass wastes in Malaysia, especially from rubber plantation are being produced daily. The use of biomass in direct liquefaction with the aim to ease the petroleum importation has been paid a major concern, especially among researchers. However, several drawbacks that affected the direct liquefaction of biomass are actually attributed to the nature of the biomass itself. These include source of biomass being seasonal and biomass normally having a relatively higher distributing area in comparison to its total amount. Eventually, these factors will directly affect the feedstock supply of biomass and of course limit its large-scale utilization.

Energy from biomass is a large untapped energy source and its direct liquefaction is possible [9-15]. Energy that can be derived from biomass actually exists in all three phases, i.e. (i) gas fuels (synthesis gas from gasification), (ii) liquid fuels (biodiesel, bio-oil and bio-ethanol) and (iii) solid fuels (for use in boiler combustion). However, in terms of energy output, commercially proven technology and versatility in a wide range of processes (biochemical or thermo-chemical), energy from biomass is proven to be the most feasible short-term solution to substitute fossil fuels in comparison to other underdeveloped technologies, namely, photo-voltaics and fuel cells [16].

2.2. Rubber seed oil

Peninsular Malaysia, compromising 12 of the 14 states in the Malaysian federation is among the world’s most important rubber growing area. Rubber tree is also grown in Sabah and Sarawak. Altogether, Malaysia produces almost 20% of the world’s natural rubber. More than half of Malaysia’s rubber comes from thousands of privately owned small landholdings, which are usually about 2 hectares. The rest is grown on big estates owned by various companies; each can cover over a 1000 hectares. Overall, Malaysia has about 1.7 million hectares of rubber plantation [10]. Rubber tree, or its scientific name is Hevea brasiliensis, belongs to the family Euphorbiaceae and was found to be the most economically important member of the genus Hevea. This is mainly due to the milky latex collected on the daily basis by using special knife tapping from its bark around the tree. In Malaysia, the leaves of the rubber tree fall by end of year, usually from December up to February and refoliate quickly after that, followed by flowering and also producing a large volume of seeds. These seeds, however, were left underutilized [11]. Because of environmental issues, researchers in Malaysia have pursued it quite extensively to evaluate the potential usage and applications of rubber tree wastes (mostly rubber seed, rubber seed pod and rubber wood) through various chemicals and biological determinations. Figure 1 shows the typical scenario of rubber tree plantation in Malaysia and Figure 2 shows the components of rubber tree wastes. Rubber seeds have been found to be rich in oil. Its content in the dried kernel varies from 35 to 45%. It is semi-drying and consists of 17 – 22% saturated fatty acids and 17 – 82% unsaturated fatty acids, and is comparable to drying oils commonly used in surface coating [17]. Rubber seed oil has been found to have potential applications in many areas, which include production of biodiesel as fuel for compression engines [18, 19], foaming agent in latex foam, in the synthesis of alkyd resin used in paints and coatings [17] and several other uses [20]. Thus, the potential of rubber seed to be further utilized in other areas such as co-liquefaction with coal to produce alternative fuels
and other useful products provides great opportunity. Table 1 shows the properties of rubber seed oil.

Figure 1. Typical rubber tree plantation scenario in Malaysia.

Figure 2. Components of rubber tree wastes: (a) young seeds, (b) ripe seeds, (c) fruit in an opened pod/pericarp and (d) kernel and shell of rubber fruits.
Fatty acid composition (%) Rubber seed oil

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Composition (%)</th>
<th>Specific Gravity</th>
<th>Viscosity at 40 °C (mm²/s)</th>
<th>Flash Point (°C)</th>
<th>Calorific Value (MJ/kg)</th>
<th>Acid Value (mg KOH/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic acid</td>
<td>10.2</td>
<td>0.9</td>
<td>66.2</td>
<td>198.0</td>
<td>37.5</td>
<td>34.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>8.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oleic acid</td>
<td>24.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>39.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linolenic acid</td>
<td>16.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Properties of rubber seed oil [18].

3. Energy demand scenario in Malaysia

The Malaysian government policy on energy utilization and consumption has approved to increase the coal base generation of electricity from 11% to about 33% by the year 1995 and 2020, respectively [21]. Moreover, the coal reserves in Malaysia, which are mainly located in the states of Sarawak (70% reserves), Sabah (28%) and other states (2% from Selangor, Perak and Perlis), have total reserves of about 1,050 million tonnes of various qualities, ranging from lignite to anthracite [21, 22, 23]. However, the only coal deposit being mined in Malaysia is from Kapit area, Sarawak.

Since early 1999, Tenaga Nasional Bhd. (TNB), the major electricity provider and Sarawak Electric Supply Co. (SESCO) have purchased 120,000 and 400,000 tonnes per annum (tpa), respectively, from Kapit coal mine [24]. SESCO operates the 100 MW Kapit minemouth coal-fired power station, where two 50 MW units supply electricity to the Sarawak grid. TNB has projected to double to 20 million tpa its coal import once two planned coal-fired plants (total of 1400 MW) are fully commissioned. Moreover, the construction work has started on the 2100 MW Pulau Bunting power station, which will burn 6 million tpa of coal. In order to secure low coal prices and improve the security of coal supply, TNB’s long-term plan is to buy 30 to 50% of its annual coal requirement from its Indonesian coal mining subsidiary, TNB Coal International Ltd., which owns the right to mine in five areas in South Kalimantan. Malaysia imported about 2.9 million tonnes of coals in 1999, i.e. 85% were steam coal and 15% anthracite and bituminous coal. This amount of coal was needed to fulfill the requirement for its cement and utility industries. Indonesia, Australia, China and South Africa were the major overseas suppliers [23].

3.1. Malaysian coals

Based on the statistics reported in The Eighth Malaysia Plan by the Department of Minerals and Geosciences, Sarawak; Mukah Balingian (MB) was identified as the second largest coal.
area in Malaysia with reserves of ca. 710 km² [6]. However, most of the known coal areas in the states of Sabah and Sarawak, including Mukah Balingian, are not commercially mined due to poor availability of infrastructure and located far inland [6], and most of the coal types are of low rank, i.e. sub-bituminous. Thus, the usage of abundant coal reserves was not optimized. Low rank coals (brown coal, lignite and lower sub-bituminous coals) are the most abundant fossil resources, but they have not been utilized in a large amount because of their low calorific values. This is mainly due to the presence of a large amount of oxygen functional groups in such coals, namely, carboxylic, -COOH; hydroxyl, -OH; carbonyl, -CO; etc. The traits of these coals are low price, relatively large porosity and high reactivity, which benefit their utilization for direct coal liquefaction (DCL) [25]. Owing to the fact that low rank coal contains less carbon, liquefaction process is one of the best options thus far to utilize them.

3.2. Characteristics of Mukah Balingian coal

From Table 2, it can be seen that MB coal has relatively high oxygen and volatile matter contents. The petrographic analysis of this coal shows a vitrinite reflectance value of 0.40% and thus can be categorized as a low rank coal, i.e. sub-bituminous C rank [26]. Further, previous work by Ismail et al. [27] using high pressure Temperature Programmed Reduction (TPR) on the pyrite-free MB coal also confirms that this coal is of a low rank by observing the organic sulfur distribution in the coal. Moreover, Rodriguez et al. [28] suggested that low rank coals are normally composed of small aromatic clusters and contain many cross-links and functional groups, and thus, are very reactive and undergo fast and extensive bond breaking during liquefaction.

<table>
<thead>
<tr>
<th>Ultimate analysis (wt% daf)</th>
<th>Proximate analysis (wt% as received)</th>
<th>(wt% db)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>63.9</td>
<td>Volatile matter 33.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.1</td>
<td>Fixed carbon 35.6</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.9</td>
<td>Ash content 4.8</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.5</td>
<td>Moisture 26.6</td>
</tr>
<tr>
<td>Oxygen¹</td>
<td>28.6</td>
<td>Fuel ratio² 1.1</td>
</tr>
<tr>
<td>H/C ratio</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>O/C ratio</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

Petrographic analysis (vol. %)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitrinite</td>
<td>60</td>
</tr>
<tr>
<td>Liptinite</td>
<td>31</td>
</tr>
<tr>
<td>Inertinite</td>
<td>8</td>
</tr>
<tr>
<td>Mineral matter</td>
<td>1</td>
</tr>
</tbody>
</table>

Vitrinite reflectance = 0.40%

O/C ratio = 0.3

[^1]: Calculated by difference.

Table 2. Characteristics of raw Mukah Balingian coal [29].
Moreover, the petrographic analysis shows that the composition of the coal is dominated by vitrinite that constitutes about 60% by volume of the whole rock, with 31% liptinite (formerly known as exinite), 8% inertinite and 1% mineral matter. Pyrite, however, is present in trace amount. The high content of reactive macerals, i.e., vitrinite and liptinite, that contributes up to 91% of the organic matter content, serves as an important characteristics for carbonization and liquefaction processes of coal [30]. Interestingly, this high value of reactive macerals is in accord with the value suggested by Van Krevelen [31], under the reactivity parameter group to characterize coal for direct liquefaction. It is also known that the vitrinite and liptinite can be extracted readily, which makes the extraction yield correlate broadly with its content [31].

3.3. Thermal behavior of Mukah Balingian coal

Another important characteristic of MB coal is the thermal behavior of decomposition under pyrolysis conditions via thermogravimetric analyser (TGA). The pyrolysis of raw MB coal via TGA at a heating rate of 20 °C min⁻¹ is shown in Figure 3. The TG curve (Figure 3(a)) of the raw coal shows the weight loss profile with the weight decreasing as temperature is increased from ambient to 1000 °C. The weight loss profile resembles that of a first-order reaction.

Figure 3. (a) TG and (b) DTG profiles for the thermal decomposition of pyrolysed raw MB coal [29].

Figure 3 (b) shows the differential weight loss (DTG) for the raw MB coal that consists of three main stages. This conforms to previous findings as reported by Probstein and Hicks [32].
Kastanaki et al. [33], Serio et al. [34] and Radovic et al. [35]. The first-stage pyrolysis, which occurs at temperatures ranging from ambient to 150 °C, involves the dehydration of water and releasing of gas composed of oxides of carbon from the coal. The second-stage pyrolysis, which occurs at temperatures of 200 – 550 °C, however, is due to the release of volatile matter such as hydrocarbon gases, light oils and tars, and is of interest in this study. Finally, the third-stage pyrolysis shows the appearance of some minor curves at temperatures ranging from 550 to 650 °C and from 700 to 800 °C, that were attributed to the release of heavier hydrocarbons and non-condensable gases, mainly hydrogen, and from thermal decomposition of carbonates that are abundant in low rank coals.

Also, from the DTG profile of the raw MB coal, it can be estimated that the softening temperature of this coal is around 350 °C. Merrick [36] suggested that with extraction using liquid solvents, the preferred extraction temperatures lie in the range where the coal starts to decompose thermally, and typically, the extraction is carried out at about 350 – 450 °C. Moreover, Van Krevelen [30] suggested that temperatures around 350 °C were found to be an indicative value for softening temperature in order to characterize coal for direct liquefaction. Thus, it can be suggested that MB coal would be a good feedstock and suitable for liquefaction and/or gasification processes and, hence, optimize the utilization of low rank Malaysian coal.

3.4. Potential of Mukah Balingian coal for liquefaction

In predicting potential conversion of coal, Guyot [37] investigated the relationship between coal properties and liquefaction potential. Guyot introduced a useful correlation called “petrofactor”, which derived from the correlations containing terms of factors based on the maceral composition and the maximum reflectance of vitrinite (as shown by Equation 1). A wide rank of coals ranging from brown coal, high-, medium- and low-volatile bituminous coals have been used to obtain potential conversion for all coals, where –2.5 was obtained from the slope of the correlation. The maximum reflectance of vitrinite functions as a rank parameter, whilst the reactive maceral content as the petrological parameter. Usually, the reactive maceral content is considered to be equal to the sum of vitrinite and liptinite. Figure 4 shows the correlation of potential coal conversion with petrofactor as suggested by Guyot [37], and the estimated coal conversion was approximated based on formula in Equation 2.

$$\text{Petrofactor} = 1000 \times \frac{\text{Maximum reflectance of vitrinite (\%)}}{\text{Total reactive maceral content (\%)}} \quad (1)$$

$$\text{Coal conversion} = 100 – 2.5 \times \text{Petrofactor} \quad (2)$$

The potential conversion of raw MB coal during liquefaction could be estimated using the “Petrofactor” proposed by Guyot [37] (refer Equations 1 and 2). The petrofactor value for the raw MB coal is calculated from Equation 1 and the potential conversion is then estimated using Equation 2. Table 3 shows the results of petrofactor value and estimated coal conversion of
raw MB coal. Thus, based on Equation 2, it is estimated that about 89% of raw MB coal would be converted during liquefaction process.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum reflectance of vitrinite</td>
<td>0.40%</td>
</tr>
<tr>
<td>Total reactive maceral content</td>
<td>(Vitrinite + Liptinite) = 91%</td>
</tr>
<tr>
<td>Petrofactor</td>
<td>$1000 \times \frac{0.40%}{91%} = 4.40$</td>
</tr>
<tr>
<td>Estimated coal conversion</td>
<td>$100 - 2.5 \times 4.40 = 89%$</td>
</tr>
</tbody>
</table>

Table 3. Petrofactor value and estimated conversion of raw MB coal [29].

4. Coal liquefaction

In order to reduce operation cost and capital, and also to increase coal liquefaction efficiency, the liquefaction processes were usually carried out at less severe conditions. However, in most of coal liquefaction, the temperature used was higher than 400 °C and at relatively higher pressures. Thus, many attempts have been made by researchers to establish and develop methods of liquefying coals at lower temperature and pressure. Mukah Balingian, a low rank Malaysian coal, was extensively used in liquefaction study [29]. In the investigation, three different types of pretreatments, i.e. solvent swelling, in-situ solvent soaking and heating and
microwave irradiation have successfully been applied to the untreated Mukah Balingian coal prior to liquefaction. The main objective of the pretreatments was to further enhance coal conversion (solid to liquid) and oil yield at less severe liquefaction conditions. The study found that all the applied pretreated coals showed an increase in both conversion and oil yield. A good coal-to-solvent contact and weakened coal structure were found to be equally important factors in determining high coal conversion and oil yield obtained during liquefaction [29].

Because of the increased demands and limited reserves of petroleum, the concern of energy security has made the direct coal liquefaction (DCL) become important in producing alternative transportation fuels. DCL is a technology to convert coal directly into transportation fuels and chemicals, which is conducted at high temperatures and pressures in the presence of solvents [1]. However, because DCL is usually conducted under severe reaction conditions with higher hydrogen consumption, it makes the cost of oil from DCL difficult to compete with that from crude oil, and thus the development of DCL is limited for large-scale applications [25].

On the contrary, biomass such as rubber seed is a cheap and renewable organic energy source; the liquefaction of biomass to convert into alternative transportation fuels has been paid more and more attention. Thus, a new alternative method should be proposed or investigated in order to overcome this crucial global issue.

5. Co-liquefaction of coal and biomass

One of the solution to the above-mentioned situations encountered with coal and biomass is by the co-liquefaction of both of them. This can also maintain the stability supply of the materials. Moreover, one of the advantages of using biomass is that it accelerates the thermal decomposition of coal macromolecular structure by reducing the severe reaction conditions, especially the temperature during liquefaction. By producing smaller molecular fragments, it enables the combination with the large fractions produced from coal decomposition and simultaneously terminate the cross-linking reaction between them (this is to avoid the production of larger molecular weight products). Thus, the yield of low-molecular-weight products will be increased, oil quality improved and eventually, will reduce the yield of the residue during co-liquefaction process [25].

Most of the research works done for alternative energy sources have shown that, in general, co-processing or known as co-liquefaction of coal with biomass-type wastes has a positive effect on the liquefaction yields and product quality [14, 15]. Co-liquefaction of coal with biomass has gained increasing research interest due to the growing concerns over greenhouse gas emissions [28]. Because biomass materials also contain abundant hydrogen, co-liquefaction of coal and biomass waste is one of the best and feasible option to reduce the consumption of hydrogen as well as to avoid severe reaction conditions during co-liquefaction. Till today, however, very limited research work has been carried out in this field.

The mechanism of co-liquefaction of coal and biomass is believed to be a radical process. Thus, the unstable free radical fragments which are formed during pyrolysis of coal and biomass
will be stabilized by active hydrogen contributed from biomass to form hydrogenation/lower-
molecular-weight products. Researchers anticipated that there is a synergistic effect (synergy
is two or more things functioning together to produce a result not independently obtainable)
in the co-thermolysis process, and the yield of solid products from co-thermolysis is different
from the arithmetic calculated value [1].

Hua et al. [38] carried out co-liquefaction of coal and rice straw and believed that there exists
a synergistic effect during co-pyrolysis of Shenfu coal and rice straw. Shui et al. [39] investigated
the co-liquefaction behavior of a sub-bituminous coal and sawdust. They found that the
thermolysis of Shenhua coal was accelerated by sawdust and more volatile matter was released
from the coal molecular structure during the co-thermolysis process. In another study, Guo et
al. [25] also investigated the synergistic effect existence in the co-liquefaction of coal and
biomass. They found that a positive synergistic effect during the process actually existed. Thus,
they concluded that the synergistic effect depends on several factors, i.e. (i) coal rank, (ii)
liquefaction conditions and (iii) different liquefaction products.

The liquefaction process of coal and biomass materials, which is known as “Co-liquefaction”,
has not been developed in Malaysia. The yields and quality (especially H/C ratio) of the liquid
products obtained from coal under less severe liquefaction conditions (at lower temperature
and pressure) can be improved with co-liquefaction of coal and biomass. Therefore, the cost
of oil produced from direct coal liquefaction can be reduced significantly. The process can
make full use of hydrogen in biomass, thus decreasing the consumption of hydrogen and
moderating the conditions of DCL [1].

Some important parameters for co-liquefaction are the materials used, the design of the reactor,
pressure, extraction solvent, temperature, holding time and catalyst used. Hua et al. [38]
reported that the rice straw contains 68.3 w/% of volatile matter and resulted in 60.3% of oil at
420 °C. However, rice straw contains high amount of silica. Shui et al. [39] reported that fir
sawdust contains 78.2 w/% of volatile matter and results in 55.2% of oil at 420 °C. However,
fir occurs in mountains over most of the range. Guo et al. [25] reported that poplar sawdust
contains 80.27 w/% of volatile matter and results in 59.19% of oil at 360 °C. However, high
tannic acid content is present in poplar. Basic properties of crude rubber seed oil and crude
palm oil blend as a potential feedstock for biodiesel production with enhanced cold flow
characteristics were studied by Yusup et al. [40] and the inspections determined that the rubber
seed oil can be used in the current diesel machines with no alteration required, confirming the
adaptability of the produced biodiesel to the current standards. This shows that the charac-
teristic of rubber seed as a biofuel material is more suitable than rice straw, fir sawdust, poplar
sawdust and other biomass that contains less oil.

Hua et al. also [38] suggest that the FeS catalyst used has a good catalytic hydrogenation activity
on rice straw, but the drawback of this catalyst is that it is low in basicity to reduce carboxylic
acid present in the vegetable oil. An alternative for the FeS usage as a catalyst is by using
dolomite. Dolomite is a natural rock found abundantly in certain areas of Malaysia and
Thailand. Due to its very low cost to produce and being easy to obtain, the main domestic
usage of dolomite is currently in the landfill site and in cement manufacturing. CaCO₃ and
MgCO₃ are the major components of dolomite with a small amount of silica and ferrite. In a
simple calcination process at high temperatures, the CO$_3$ group in pure CaCO$_3$ will decompose to produce CaO (which is highly basic) and MgO [41].

Guo et al. [25] state that the temperature is the most important factor during liquefaction. Shui et al. [39] reported that the main pyrolysis temperature range of Shenhua coal (a sub-bituminous coal) (362 – 750 °C) is much higher than that of sawdust (260 – 420 °C), and the releasing rate of volatile matter of Shenhua coal is much lower than that of sawdust. Hua et al. [38] reported that the pyrolysis temperature of Shenhua Coal is in the range of 360 – 750 °C; however, the pyrolysis temperature of biomass is in the range of 250 – 400 °C.

Hence, an attempt should be made for co-liquefaction of low-rank Malaysian coal and biomass wastes such as rubber tree wastes (rubber seed, rubber seed pod or rubberwood) for the production of alternative fuels and other important purposes such as chemical feedstocks. Working on the area of energy has now become the priority in most of laboratories worldwide. In Malaysia particularly, under the New Economic Model (NEM), innovation and research is regarded as crucial factor to propel the industry. The research in this area certainly contributes to the increases in energy sector that part of National Key Economic Area (NKEA). Furthermore, a competitive domestic economy can be created as part of Strategic Reform Initiative (SRI) [42].

6. Biofuels and alternative fuels

Today, the term biofuels mostly refers to ethanol and esterified vegetable oil. Scientifically, a biofuel is a type of fuel whose energy is derived from biological carbon fixation. Biofuels include fuels derived from biomass conversion, as well as solid biomass, liquid fuels and various biogases. It is known that especially agricultural-based alternative fuels have a considerable effect on decreasing net CO$_2$ emissions [43].

New products such as methanol, dimethyl ether, Fischer-Tropsch (FT) diesel and ethanol from lignocellulosic feedstock are benefitting from R&D programs. The most controversial such energy carrier is first-generation biofuels, i.e. biodiesel and bioethanol from sugar, starch and oil bearing crops or animal fats that in most cases can also be used as food and feed [44]. During the past years, researches on converting lignocellulosic biomass into bioethanol are actively undertaken, aiming to produce the second-generation biofuels, which has no competition with food and is thus sustainable [45]. A review from Akhtar et al. [46] on the process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass includes various parameters, including temperature, particle size, biomass feedstock, heating rate, density, pressure, residence time and reducing gas/hydrogen donors. In short, they found out that the major parameters that influence yield and composition of bio-oil are temperature, properties of solvent, solvent density and type of biomass.

A number of biofuels for transport are potentially available and are currently being used or investigated at different stages of development worldwide. A study in Australia [47] found out that the crop stubble – the fibrous stalk, leaf and chaff material left after grain (or other
products) has been harvested – is an agricultural source of lignocelluloses biomass for second-generation biofuels.

One of other such plants that were used for biofuels production is the once unpopular Jatropha Curcas (JC). JC is a perennial subtropical shrub that produces oil-rich seeds. A study by Jingura [48] on the technical options for optimization of production of JC as a biofuel feedstock in arid and semiarid areas of Zimbabwe proves that JC has been promoted extensively as an energy crop for biodiesel in the tropics.

![Diagram of co-liquefaction products](image)

**Figure 5.** Example of a complete fractionation process of co-liquefaction products.

Apart from the high oil content in the seed, JC was only planted for the fruit. It is not JC seeds that we found more massive when placed on a scale of comparison with the rubber seed. Unlike JC, rubber trees can produce both latex and high oil content seed. According to Kalam et al. [49], the flash point of JC oil is $229 ± 4$ °C which is higher than that of rubber seed oil with the
flash point of 198 °C. These properties can be an advantage to the rubber seeds as an alternative biomass in producing bio-oil or biofuel.

There are so many advantages associated with the use of rubber seed to produce biofuels including the large reserve for the production of nonedible products, do not necessarily require cultivation of new plantations, more profitable to farmers, and reinvigorate the economy of local communities. These advantages show great potential of rubber seeds as the biomass for biofuel productions. Several works have been done dealing with the production of biofuel from the rubber seed. A study by Melvin et al. [50] entitled, “A multi-variant approach to optimize process parameters for biodiesel extraction from rubber seed oil” shows that the discarded rubber seed from the hefty rubber plantation of Southern India is considered as the potential source for extracting oil for biodiesel production.

Therefore, alternative fuels, which are also known as nonconventional or advanced fuels, are any substances or materials that have the ability to be utilized as fuels. Commonly available alternative fuels include biodiesel (oil obtained from plant or fruit which was transsesterificed), bio-alcohols (methanol, ethanol and butanol), fuel cells, batteries, nonfossil methane, hydrogen, nonfossil natural gas, vegetable oil, propane and also other biomass sources. Figure 5 shows the example of a complete fractionation process of co-liquefaction products after liquefaction.

7. Problem statements

Huge amount of biomass wastes in Malaysia, especially from rubber plantations, are being produced daily. The rubber tree produces large volumes of seed, which is underutilized. Rubber seed would be a highly potential candidate for co-liquefaction process as it is absent in silica, easily collected and does not contain tannic acid. In addition, the oil content in the rubber seed is roughly around 40 – 60 %, which is suitable to replace other non-seed biomass. No study has been done on the rubber seed as the material in co-liquefaction process. The existence of synergystic effect between the coal and rice husk, fir sawdust and poplar sawdust was already known. However, the synergistic effect between the rubber seed and Mukah Balingian, a low rank Malaysian coal in the co-liquefaction process, has not yet been evaluated by any research works. And so far, there is no research on co-liquefaction of biomass and coal in Malaysia. It is also a must to investigate the synergistic effect between the coal and rubber seed.

Vegetable oil has the potential to supplement petroleum-based fuels; however, its high FFA, thereby its high viscosity, deters its usage in internal combustion engine directly. Dolomite has received, however, less attention in the basic catalyzed chemical syntheses, in spite of its high basicity, low cost, less toxicity and environmental friendliness. Thus, dolomite as reduction catalyst is a good option to reduce the amount of acid present in the rubber seed oil during the co-liquefaction process. The main pyrolysis temperature range of coal is much higher than that of biomass and the releasing rate of volatile matter of coal is much lower than that of biomass, causing different liquefaction temperature range. The temperature range will
be investigated to determine the temperature that can promote the highest conversion of both coal and biomass. From the co-liquefaction process with varied parameters, it is predicted that the percent of product yield will be more than the individual liquefaction of coal and rubber seed alone.

8. Significant contribution to knowledge

It is anticipated that a significant contribution could be made from this co-liquefaction process between rubber seed and coal, i.e.:

i. Contribution in terms of development and improvement of the co-liquefaction technique by using high pressure – high temperature reactor system.

ii. Valuable information of the extracts, i.e. alternative fuels obtained from the co-liquefaction processes would be useful to other areas and researchers.

iii. Provide useful information of Malaysian coal, especially in fuel chemistry area for Coal Bank data.

iv. As an alternative choice to conventional methods of energy consumption in Malaysia.

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