

## BIO-OIL FROM RUBBER WOOD: EFFECTS OF UPGRADING CONDITIONS

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**Abstract.** Despite its prominent potential, the use of rubber wood (*Hevea brasiliensis*) for bio-oil production has not been fully investigated. This study reported experimental results of the bio-oil production and upgrading from rubber wood using fast pyrolysis technology. The effects of catalyst nature (vermiculite and dolomite), upgrading temperature and bio-oil/catalyst ratio on the product quality were deeply investigated. The results showed that dolomite was suitable to be used as a catalyst for bio-oil upgrading. At 600 °C and a bio-oil/catalyst ratio of 1:1, the bio-oil yield was maximized, while at 400 °C and a ratio of 1:3, the bio-oil heating value was maximized. Depending on usage purposes, a yield-oriented, heating value-oriented or in-between bio-oil upgrading solution could be considered.

**Keywords:** Bio-oil production, catalyst upgrading, fast pyrolysis, rubber wood.

**Classification numbers:** 2.8.3, 3.4.1, 3.7.1.

### 1. INTRODUCTION

The use of renewable energy sources, especially biomass, is considered an effective way to deal with the depletion of energy sources. Among all biomass types, woody by-products provide high energy benefits. Rubber trees (*Hevea brasiliensis*) are native to the Amazon forest but now are widely planted in wet tropic regions. Typically, the rubber tree is grown for milky latex, and trunks are used for timber in many countries in the world. The world's rubber tree production is 14 million tons per year in 2017 [1]. This shows that the production of rubber wood is large, thus, the use of rubber wood as a biomass source to generate energy is entirely possible. However, the current use of this type of biomass has not been properly evaluated.

Fast pyrolysis is the process of thermal decomposition in the absence of oxygen. It requires very high heating and heat transfer rates at the reaction interface, and temperatures typically

around 500 °C [2]. Along with that is the short residence time of the vapor (less than 2 seconds) and rapid cooling. The main product of this process is bio-oil, which accounts for 75 wt% on a dry basis, and by-products such as char and gas [3]. There are various types of fast-pyrolysis reactors used and experimented, such as fluidized-bed, circulating fluidized-bed, rotating cone, fixed bed, vacuum, free fall, and entrained flow reactors [4].

The use of rubber wood for bio-oil production was highly recommended in the literature. Rueangsan *et al.* investigated the fast pyrolysis of rubber wood in a free-fall reactor and results showed that a high yield of bio-oil could be obtained [5]. Nevertheless, the bio-oil produced from fast pyrolysis generally has some limitations, such as high water and oxygen content accompanied with low pH and heating value. This means that the bio-oil is usually acidic and corrosive [3]. Thus, to be able to use bio-oil as a fuel, the upgrade of bio-oil is essential. Well-known methods to improve the quality of bio-oil include hot-vapor filtration and catalytic upgrading [5]. By using hot vapor filtration, fine char will be removed in the final bio-oil. However, Pattiya and Sukkasi showed that the use of hot vapor filter may reduce bio-oil production as well as its heating value [6]. In contrarily, with catalytic upgrading, the oxygen in the bio-oil will be removed by defending H<sub>2</sub>O, CO<sub>2</sub> or/and CO hence improving the bio-oil's heating value. However, as catalysts are often environmental unfriendly and expensive, the main challenge of this technique is to find a natural and locally available material that can be used as a catalyst [7, 8]. In this circumstance, dolomite and vermiculite are suitable candidate for catalyst upgrading of bio-oil, as reported by some studies [9, 10, 11]. Dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) could contribute to the deoxygenation of bio-oil, hence increasing the O/C ratio in the upgraded bio-oil.<sup>[8]</sup> Meanwhile, vermiculite - a compound with main components of SiO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> - is effective in the dehydration of methanol and ethanol, and therefore could also be a potential catalyst for bio-oil upgrading [9]. Up to the present, catalytic upgrading of rubber wood bio-oil using vermiculite and dolomite has not been reported.

The aim of this study was thus to investigate the effect of different catalytic upgrading conditions using vermiculite and dolomite on the quality of rubber wood bio-oil.

## **2. MATERIALS AND METHODS**

### **2.1. Feedstock preparation**

Rubber wood (*Hevea brasiliensis*) collected from wood processing factories was used for this study. The material was sun-dried, crushed and sieved to a size of less than 600µm. The moisture content of these feedstocks was firstly determined following the ASTM E1756-08 standard. The biomass sample was then dried in an oven (Mettler Model 800 Class B) at 105 °C for 24 hours to remove their moisture content to less than 10 %. By doing this, the water content of the product bio-oil can be reduced because the amount of water contained in the original biomass will end up in the bio-oil. The high water content in bio-oil will reduce the lower heating value of the liquid, increase ignition delay and reduce the combustion rate by reducing flame temperature [3]. The samples were then stored in air-tight boxes at room temperature for further analysis.

### **2.2. Feedstock characterization**

Proximate analysis, ultimate analysis, and calorific values were conducted to characterize the biomass feedstock. The volatile matter was determined following the ASTM D 3175-07

standards. The ash content was determined following the ASTM D 3174-04 standard. The fixed carbon content was calculated by difference. The higher heating value of biomass feedstocks was evaluated using the Parr 6200 Calorimeter, following the procedure described in the National Renewable Energy Laboratory (NREL) protocol. The Carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O) contents in samples were determined using the PerkinElmer 2400 Series II Elemental Analyzer.

### 2.3. Catalyst activation

Before being used as a catalyst, natural dolomite was activated by calcination at a temperature of 900 °C for 6 hours. The activated dolomite was then stored in a desiccator to prevent carbonization and dehumidification from the air. Meanwhile, vermiculite was activated by both physical and chemical methods, in order to find the optimal method for the bio-oil upgrading. For physical activation, vermiculite was sieved and calcined at a temperature of 900 °C for 4 hours. For chemical activation, the procedure described by Alves was used [10]. Vermiculite was mixed with H<sub>2</sub>SO<sub>4</sub> at 3M in the ratio of 1 g/10 ml. The mixture after stirred and heated at 95 °C in 4 hours was added with water. The solid was then collected under vacuum filter, and was washed exhaustively with water until the pH became neutral. Finally, all the collected solid was dried in the oven at 105 °C within 24 hours to remove its moisture content.

### 2.4. Bio-oil production

The production of bio-oil via fast pyrolysis was carried out in a fixed bed reactor. The system includes a biomass hopper, a two-staged feeder, a vibrating reactor (7.32 cm in diameter and 185 cm in length), a cyclone separator, and a bio-oil product collection unit (Figure 1). Prior to condensation, pyrolysis vapor was separated from coal in a cyclone separator. The heating area was surrounded by a ceramic fiber blanket, the whole gas product was conducted through the water-cooled condenser and the electrostatic precipitator (ESP) before being collected in the liquid form.

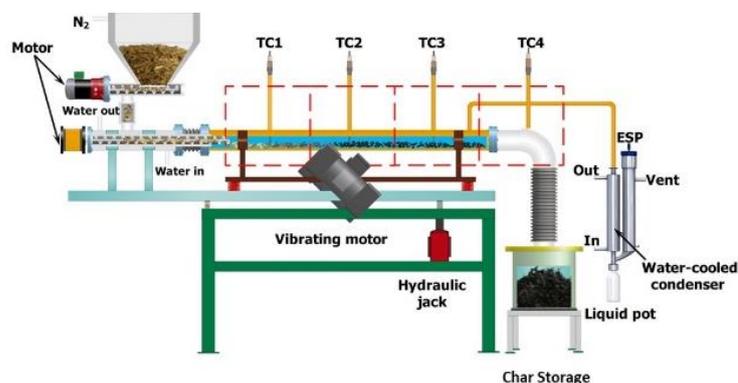


Figure 1. Fast pyrolysis system.

Experiments were conducted at a temperature of 450 °C, an N<sub>2</sub> flow rate of 2 Nlmin<sup>-1</sup> and a biomass feeding rate of 400 gh<sup>-1</sup>, respectively. Besides, the temperature of the cyclone and the transfer line was always kept at 420 °C, the cooling water temperature was 25 °C, and the running time was 1 h. We demonstrated in our previous study the stability and the efficiency of the system for bio-oil production under these operating conditions [7].

## 2.5. Bio-oil upgrading

A fixed-bed system was used for the bio-oil upgrade process. It consists of a bio-oil container (1), a fixed-bed reactor (7.3 cm in diameter and 42 cm in height) (3) and a bio-oil product collection unit (8) (Figure 2). In the container, the bio-oil is evaporated by heat and then passed through the fixed-bed reactor, where the bio-oil vapor is exposed to the catalyst and filtered by the glass wool (2) placed inside the reactor. The upgraded bio-oil in the form of vapor is then condensed and collected as a liquid with the help of a condenser (6) and an ESP (7). The temperature was precisely controlled with the help of thermal couples (5, 9).

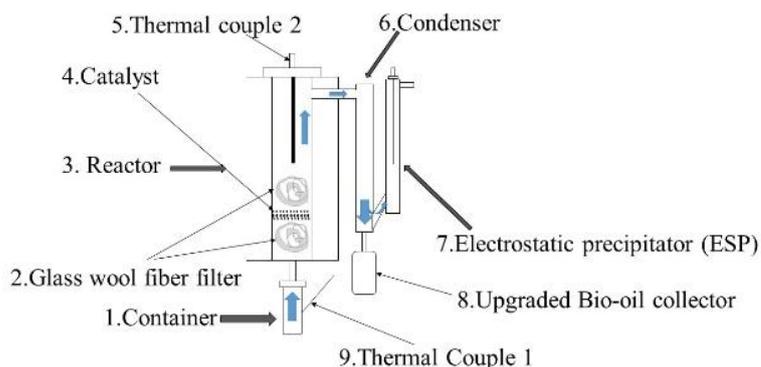


Figure 2. Upgrading bio-oil system.

Three independent variables were considered in the bio-oil upgrade process: (1) the type of catalyst (dolomite and vermiculite), (2) the reactor temperature and (3) the mass ratio between the bio-oil and the catalyst. The upgrading temperatures varied from 400 °C to 700 °C. The mass ratio between bio-oil and catalyst varied from 1:1 to 1:4. The temperature of 600 °C and ratio 1:3 of bio-oil/catalyst was chosen as reference operating conditions for studying the effect of each parameter on the quality of the bio-oil product. For each experiment, 50 g of bio-oil was introduced to the reactor, the running time was kept in 30 minutes and the temperature of the condenser using ethanol was fixed at -10 °C. The product yields were calculated using the mass balances of the initial and final products.

The liquid is formed by rapid cooling, and is the product of bio-oil upgrade by catalyst:

$$\text{Liquid yield (wt\%)} = \frac{m_{\text{liquid}}}{m_{\text{bio-oil}}} \times 100 \% \quad (1)$$

Char is the remaining part of bio-oil after the upgrade process:

$$\text{Char yield (wt\%)} = \frac{m_{\text{char}}}{m_{\text{bio-oil}}} \times 100 \% \quad (2)$$

when the bio-oil is heated up, many types of reactions that occur during this process such as thermal decomposition reactions, which led to the formation of solid carbonaceous materials (coke) as a result of radical recombination and/or polymerization reactions [11].

$$\text{Coke yield (wt\%)} = \frac{m_{\text{coke}}}{m_{\text{bio-oil}}} \times 100 \% \quad (3)$$

The gas yields were calculated by difference

$$\text{Gas yield (wt\%)} = 100 \% - \text{Char yield} - \text{Liquid yield} - (\text{Coke yield}) \quad (4)$$

### 3. RESULTS AND DISCUSSION

#### 3.1. Feedstock characterization

The characteristics of rubber wood were given in Table 1. The properties of rubber wood are shown in Table 1. From proximate analysis it was observed that the water content, volatile matter and fixed carbon were 1.59 wt%, 81.02 wt% and 15.02 wt% respectively. These values are similar to those already described for Rubber wood samples in the other studies [11, 12]. In addition, the C, H, N, O contents and the HHV value were similar to the ones described in the literature [12, 13]. Rubber wood contains a small amount of ash (2.37 wt%) making it more favorable for thermochemical conversion. The low ash content minimizes problems in the combustion process such as slagging, bed agglomeration, fouling, and corrosion in the combustion devices [14]. As a result, we can see that rubber wood has a high volatile content and a relatively low nitrogen content, which is quite suitable for their applications in gasification and pyrolysis. Furthermore, HHV is considered to be an important property of solid biofuels and HHV of rubber wood is  $17.8 \text{ kg}^{-1}$ , it is considered to be one of the highest heating biomass to be found [15].

Table 1. Characteristics of rubber wood.

Proximate	(wt.%)	Ultimate analysis (wt.%, daf.)	
Moisture (as received)	1.59	C	39.90
Volatile matter (db.)	81.02	H	3.70
Fixed carbon <sup>a</sup> (db.)	15.02	N	0.65
Ash (db.)	2.37	O <sup>a</sup>	
<b>Heating value (MJ.kg<sup>-1</sup>, db.)</b>		17.80	

db: dry basis, daf: dry ash free basis.

#### 3.2. Product yield of non-catalytic upgraded bio-oil

The product obtained from rubber wood using the vibrating reactor included the gaseous fraction (34.0 %), the liquid fraction (46.0 %), and the solid fraction (20.0 %). Comparing to the work of Fukada using the same type of rubber wood in a vacuum pyrolysis system at the same operating conditions [13], our system provided a better bio-oil yield. The liquid fraction was then submitted to the upgrading process (without catalyst) to remove moisture content and impurities. The final product could then be separated into three parts: the coke and gas (30.9 %) that was removed from the bio-oil, the “dark” bio-oil (5.1 %) that is known to have a high heating value and is comparable with fossil fuels, and the “light” bio-oil (64.0 %) having a poorer heating value (Figure 3a) [7]. The upgraded bio-oil (without catalyst) was served as a basis for comparison with the catalytic upgraded ones.

#### 3.3. Bio-oil upgrading

##### 3.3.1. Vermiculite

When using chemically activated vermiculite to upgrade bio-oil, the catalyst was too light and small so it was easy to get caught in the vapor and went into the final product, forming a

layer of impurity on the upper part in the final product (Figure 3b). Therefore, chemically activated vermiculite was not suitable for upgrading bio-oil produced from rubber wood.

For the case of physically activated vermiculite, the yield of the upgraded bio-oil was much lower compared to that of non-catalytic bio-oil (59 % compared to 69.1 %) (Figure 3c). The lower bio-oil yields in this study could be mainly due to catalytic activity of the catalysts that promoted the deoxygenation reactions (decarboxylation, decarbonylation etc.), which causes the increase of gas yield [16]. Moreover, the presence of the catalyst which is the cause of coke formation, with the present of coke not only makes the catalyst not effective in the upgrade of bio-oil but also reduce the quality of bio-oil after the upgrade, the higher heating value of the bio-oil was also lower (26.01 MJ.kg<sup>-1</sup> compared to 28.88 MJ.kg<sup>-1</sup>) (Table 2). Therefore, both physically and chemically activated vermiculite materials were not suitable to be used as a catalyst for the rubber wood bio-oil upgrading.



Figure 3. (a) Upgraded bio-oil without catalyst (b) Bio-oil upgraded with chemically activated vermiculite and (c) Bio-oil upgraded with physically activated vermiculite.

### 3.3.2. Dolomite

The bio-oil upgraded with dolomite at the reference condition gave a more satisfactory result, with no impurities found in the final product. Therefore, it was subjected to further experiments to investigate the effect of bio-oil/catalyst ratio and upgrading temperature.

#### 3.3.2.1. Effect of bio-oil/catalyst ratio

The effect of bio-oil/catalyst ratio on the bio-oil yield and heating value was presented in Figure 4 and Table 2. Results showed that the ratio 1:1 gave the best bio-oil production yield.

Nevertheless, the ratio 1:2 gave the best heating value of the bio-oil product at the temperature of 600 °C (Table 2).

Besides, the coke yield in upgrading process increased from 16 wt.% to 40 wt.% as the bio-oil/catalyst ratio decreased from 1:1 to 1:4. Wang et al. also found that the coke yield of their upgrading bio-oil process increased from 0.19 wt.% to 2.70 wt.% when applying the catalytic method to upgrade bio-oil [17]. The addition of catalyst promoted catalyst thermal cracking, which decreased the bio-oil yield. The possible reason for it was that the formation of coke reduced the catalyst activity and led to a decrease of cracking reaction.

Results highlighted difficulties in the production of high-quality bio-oil while maintaining a high product yield. Nevertheless, depending on the usage purposes, different upgrading

conditions could be selected to maximize either the bio-oil's yield or its heating value, or a "compromised" solution could also be proposed.

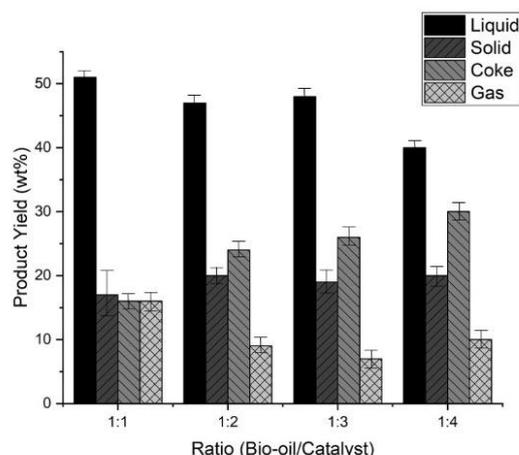


Figure 4. Effect of bio-oil catalyst ratio on product yields (temperature: 600 °C).

Table 2. Effect of bio-oil catalyst ratio on product heating value (temperature: 600 °C).

Bio-oil/catalyst ratio	Heating value (MJ.kg <sup>-1</sup> )
1:1	29.85
1:2	31.94
1:3	24.54
1:4	30.76
Non-catalyst	28.88
Vermiculite (physical activation)	26.01

### 3.3.2.2. Effect of upgrading temperature

The effect of upgrading temperature on the product yield was presented in Figure 5. Results showed that the temperature of 600 °C gave the best product yield. This result is quite similar to the result of Valle *et al.* when using dolomite as a catalyst [8].

When the bio-oil is heated up, many types of reactions that occur during this process such as thermal decomposition reactions, which led to the formation of solid carbonaceous materials (coke) as a result of radical recombination and/or polymerization reactions [11].

The catalytic temperature significantly influenced the bio-oil yield. The yield of bio-oil shows an increasing trend as the catalyst temperature rises from 400 °C to 600 °C. In addition, along with the increase in temperature, gas yield also increases when the upgrade temperature is raised from 500 °C to 600 °C. However, the yield of coke presented an opposite trend, and decreased as catalytic temperature increased. Because of this is an endothermic reaction, the high temperature promoted secondary cracking of large molecules.

The bio-oil seems to be more sensitive to the upgrading temperature compared to the bio-oil/catalyst ratio. The bio-oil obtained the highest heating value at the temperature of 400 °C (Table 3). The more the upgrading temperature was increased, the more the bio-oil's heating value was decreased. Moreover, when increasing the temperature of the reactor to 700 °C, there

was almost no presence of the “dark” fraction. This shows that when the temperature is too high, the organic compound in bio-oil is gasified, resulting in a lower heating value.

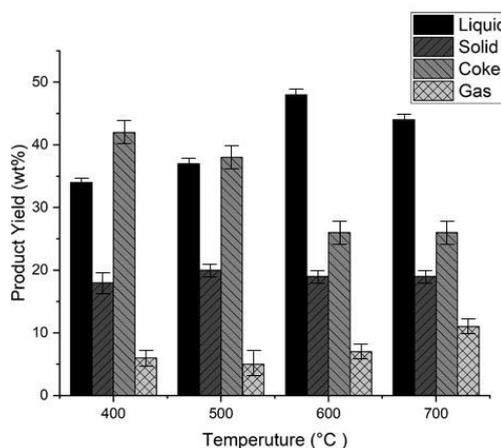


Figure 5. Effect of reactor temperature on product yields (ratio 1:3).

Table 3. Effect of upgrading temperature on product heating value (ratio 1:3).

Temperature (°C)	Heating value (MJ.kg <sup>-1</sup> )
400	33.49
500	31.75
600	24.54
700	20.01

#### 4. CONCLUSION

Bio-oil from fast pyrolysis of rubber wood was successfully produced and upgraded using natural and inexpensive dolomite as a catalyst. The bio-oil yield was maximized at a temperature of 600 °C and a bio-oil/catalyst ratio of 1:1. Meanwhile, at 400 °C and a ratio of 1:3, the bio-oil heating value was maximized. Depending on the usage purposes, operators could select suitable operating conditions for the bio-oil upgrading. For usual heating purposes, the conditions that maximize the product yield can be prioritized, while for advanced purposes such as fuel or power production, the conditions that maximize the product heating value are highly recommended.

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