



## Synthesis of Biokerosene through Electrochemical Hydrogenation of Terpene Hydrocarbons from Turpentine Oil

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**Abstract.** Indonesia possesses great potential for developing renewable resources as alternative fuels. For example, turpentine oil obtained from *Pinus merkusii*, which contains mostly monoterpene hydrocarbons (C<sub>10</sub>H<sub>16</sub>). The oil is highly suitable to be processed for biokerosene or even jet biofuel. It consists of hydrocarbons within the range of C<sub>10</sub> to C<sub>15</sub>. However, it contains insufficient H and thus needs to be upgraded. In the present work, electrochemical hydrogenation was used for upgrading. In the electrochemical cell, stainless steel, silver, and carbon were used alternately for the anode, while copper and silver Raschig rings were used for the cathode. An electrolyte solution of cuprous ammonium formate was utilized not only as a source of H but also to draw the unsaturated hydrocarbons into the aqueous phase. The electrolyte : oil ratio (up to 2:1), electrolyte concentration (between 0.4 and 2 M) and reaction time were varied throughout the experiments. The bromine number (unsaturation level) of the turpentine oil, which was initially 1,86 (mole Br<sub>2</sub>/mole), was lowered significantly to 0.69-0.90. Promising increase of smoke point values were observed from 11 mm to 16-24 mm, indicating a higher H content of the processed oil, thus making it suitable as a substitute for petroleum kerosene.

**Keywords:** *biokerosene; cuprous ammonium formate; electrochemical hydrogenation; smoke point; turpentine oil.*

### 1 Introduction

Many serious negative environmental impacts, especially the alarming concern of global warming, result from the use of non-renewable fossil fuels as the world's primary energy source. The awareness of the need for renewable as well as more environmentally friendly fuel resources has triggered an intensive search for biomass-based alternative fuels worldwide. In Indonesia, one of developments in searching for alternative fuels is the utilization of plant origin or derived oils, one of which is turpentine oil from pine tree plantations.

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Received September 2<sup>nd</sup>, 2015, 1<sup>st</sup> Revision November 13<sup>th</sup>, 2015, 2<sup>nd</sup> Revision August 29<sup>th</sup>, 2016, Accepted for publication November 20<sup>th</sup>, 2016.

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Terpene hydrocarbons are naturally found in plant exudates. They are carbon compounds that consist of 2 or more units similar to isoprene or 2-methyl-1,3-butadiene,  $C_5H_8$  [1] and thus have a general molecular formula of  $(C_5H_8)_n$ .  $C_{10}H_{16}$  (monoterpenes) and  $C_{15}H_{24}$  (sesquiterpenes) are terpene hydrocarbons and have similar number of C atoms as hydrocarbons found in kerosene or jet fuel. Turpentine oil, which mainly consists of monoterpenes, is relatively volatile. Pine gum separation by vacuum distillation produces turpentine oil in the form of distillate (about 13-25%) and rosin as the bottom product (about 70-75%). In turpentine oil,  $\alpha$ -pinene is the major component. The composition of Indonesian turpentine oil from *Pinus mercurii* is shown in Table 1 [2].

**Table 1** Terpene Hydrocarbon contents in Indonesian turpentine oil.

Component	% mass
$\alpha$ -pinene	65-85
$\beta$ -pinene	1-3
Camphene	$\approx 1$
3-Carene	10-18
Limonene	10-18

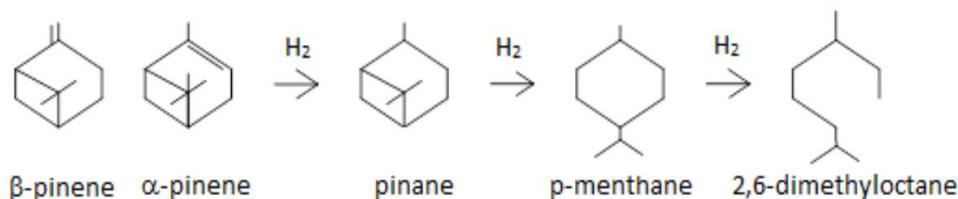
Kerosene and jet fuel are hydrocarbon fractions from petroleum refining with a boiling range between 175 and 250 °C. The major components of kerosene and jet fuel are alkane and cycloalkanes hydrocarbons between  $C_{10}$  and  $C_{15}$  [3]. One of the most important properties of kerosene and jet fuel is the smoke point. The smoke point is the height of the tallest flame without causing any noticeable smoke when the oil is burned in a standard oil lamp. Kerosene must have a minimum smoke point of 18 mm, while the smoke point of jet fuel must be at least 24 mm. Since jet fuel is burnt in aircrafts at an altitude of thousand of meters above sea level, it must also have a freezing point no higher than -40 °C, while kerosene is only required to be remain liquid at room temperature.

Monoterpene hydrocarbons have too low smoke points because their hydrogen contents are inadequate. Therefore, hydrogen addition is required to upgrade the turpentine oil so that its quality resembles that of kerosene or even jet fuel. The hydrogen addition process is called hydrogenation (shown in simple form in Figure 1). The hydrogenation of monoterpenes will increase the hydrogen content so that the smoke point of the turpentine oil is upgraded to resemble kerosene or jet fuel.



**Figure 1** Simple hydrogenation reaction.

An example of the hydrogenation process of some components found in turpentine oil is shown in Figure 2.



**Figure 2** Hydrogenation of  $\alpha$ -pinene and  $\beta$ -pinene compounds.

Hydrogenation can be carried out via several methods, namely: conventional catalytic hydrogenation using high-pressure hydrogen gas; catalytic transfer hydrogenation with the help of hydrogen donor solution and solid catalyst [4]; and electrochemical hydrogenation. In this study, catalytic electrochemical (electrocatalytic) hydrogenation [5] was chosen for a number of reasons. This process does not utilize high-pressure hydrogen gas so that it eliminates high risk as well as high capital cost, which makes it more suitable for small-scale industrial applications.

In general, electrocatalytic hydrogenation uses the cathode as the electrode as well as a catalyst for the chemisorption of reactants. At the cathode, adsorbed H is generated by the electrochemical reduction of water, which then reacts with the adsorbed unsaturated molecules [6] as shown in Eqs. (1) and (2):



Besides the reaction shown above, a side reaction that will ineffectively lead to a higher electricity consumption may also happen at the cathode. Eq. (3) shows a hydrogen formation reaction from two adsorbed H atoms:

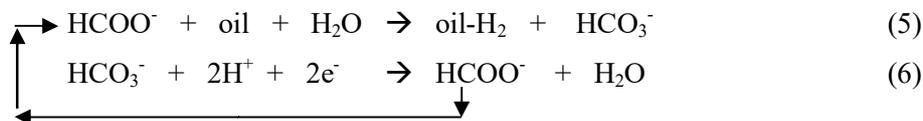


This reaction needs to be avoided by using an optimum voltage, which can be experimentally determined. At the other electrode (anode), an oxidation reaction occurs as shown in Eq. (4),



In their study on electrocatalytic hydrogenation of soybean and canola oils using Pt mesh as hydrogenation catalyst as well as the cathode, Mondal and Lalvani [7-9] utilized formate ion (supplied as formic acid) as a mediator for

transferring hydrogen atoms. The mechanism of the formate-assisted electrocatalytic hydrogenation cycle is provided in Eqs. (5) and (6):



In our previous investigation [10], the hydrogenation of turpentine oil with formate ion–formic acid as H transfer mediator was conducted, with a significant decrease in Bromine number.

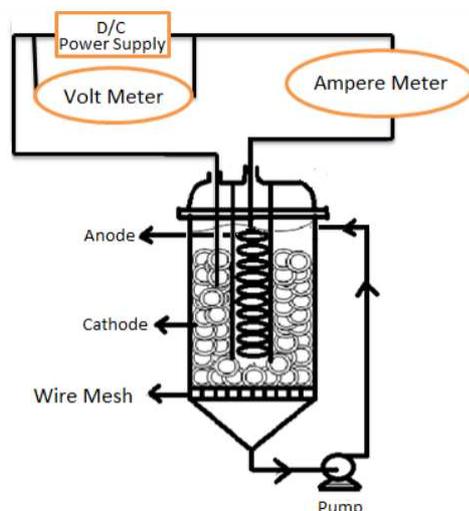
In this study, an electrolyte solution of cuprous ammonium formate was utilized to accelerate and increase the extent of hydrogenation, since the  $\text{Cu}^+$  ions are capable of drawing the unsaturated ( $\pi$ ) bonds of the terpenes into the aquatic phase and thus reduce the mass transfer resistance of the hydrogenation process.

## 2 Experiment

Hydrogenation was carried out in an electrochemical cell filled with a circulated mixture of electrolyte and turpentine oil. Turpentine oil was used as the source of the terpene hydrocarbons because of the abundant amount of turpentine oil in Indonesia. In December 2012, PT Perhutani (Indonesia State Owned Forestry Enterprise) produced 15,340 tons of turpentine oil [11]. The turpentine oil used as the hydrocarbon source in this experiment was obtained from PT Perhutani.

The electrolyte was cuprous ammonium formate solution in a water-methanol mixture with varied concentrations of 0.4 M, 0.75 M and 2 M. Several materials were tried as anode and cathode. Stainless steel, silver, and carbon were used alternately as the anode, and a bed of copper and silver Raschig rings as the cathode. Electricity was discharged into the cell through a DC power supply at an optimal constant voltage. Figure 3 presents the equipment set-up used for the electrocatalytic hydrogenation.

Electrocatalytic hydrogenation was carried out at the following volume ratios of electrolyte solution to turpentine oil, 2:5, 1:1, and 2:1. Moreover, the hydrogenation was also investigated with variation of the concentration of electrolyte solution (0.4 M, 0.75 M, and 2 M). The unsaturation level of the oil was measured by bromide-bromate titration, while the smoke test was conducted using a commercially available kerosene oil-lamp.



**Figure 3** Electrocatalytic hydrogenation cell.

### 3 Results and Discussion

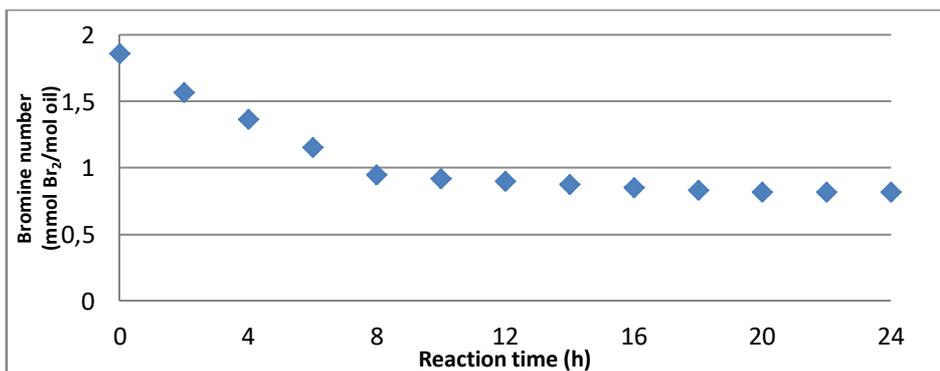
In several preliminary tests, the optimum voltage for the electrocatalytic hydrogenation of turpentine oil was determined from the current vs. voltage profile at a certain operating condition. The current flowed through the cell was initially proportional to the given potential difference, showing that the total transfer rate of electrons was slower than the ionic mass transfer between the electrodes and the solution. However, after a certain voltage, the current did not change significantly as the process had been mass transfer limited. Just above this critical voltage, the formation of  $H_2$  gas (bubbles) at the cathode surface became obvious. Table 2 summarizes the optimum voltage under various experimental conditions.

The bromine number of the unprocessed turpentine oil was determined titrimetrically using bromide-bromate titration and the analysis showed that the initial bromine number of the oil was  $1.865 \pm 0.009$  mole  $Br_2$  / mole. The theoretical values of turpentine oil from Indonesian *Pinus mercusii* (based on Table 1) should be between 1-2 mole  $Br_2$ /mole since 1 mole of  $Br_2$  represents 1 mole of unsaturated bond. The higher bromine number is consistent with the findings for several terpenes analyzed by the same method [12]. In order to evaluate the necessary extent of hydrogenation of the turpentine oil, the same analysis was done on cyclohexane and kerosene samples; the results showed that their bromine numbers were similarly low, i.e. 0.034 and 0.049, respectively.

**Table 2** Optimum operating voltage.

Cathode	The volume ratio of electrolyte : turpentine	Concentration of electrolyte solution	Anode	Optimum voltage (Volt)
Copper	1:1	2 M	Stainless Steel	12
Copper	2:1	2 M	Stainless Steel	12
Copper	2:5	2 M	Stainless Steel	10
Silver	1:1	0.4 M	Stainless Steel	10
Silver	1:1	0.75 M	Stainless Steel	12
Silver	1:1	0.75 M	Silver	18
Silver	1:1	0.75 M	Carbon	10

In general, after being electrocatalytically hydrogenated, the turpentine oil showed a significant decrease in bromine number (see Figure 4). Similar bromine number trends were found for all electrolyte : oil ratios when the reaction times of the hydrogenation process were varied as follows: 2, 4, 6, 8, 10, and 12 hours. Initially, there was a relatively rapid decrease of the bromine number. After 8 hours, however, the decrease of the bromine number became unnoticeable.



**Figure 4** Bromine number of hydrogenated oil at various reaction times (copper cathode, electrolyte : oil = 2:1).

The slow progress of hydrogenation was probably due to the steric hindrance effect of cyclic unsaturated bonds (in  $\alpha$ -pinene, carene, and limonene). Therefore, the cyclic double bonds were practically unreactive towards electrocatalytic hydrogenation compared with the hydrogenation of aliphatic double bonds (in  $\beta$ -pinene and limonene) that occurred during the first 8 hours of the process. Furthermore, extra runs were carried out for the hydrogenation using ratio of 2:1 (the highest electrolyte proportion in the mixture) with reaction time variation until 24 hours. The results revealed that the bromine number of the processed oil leveled off at around 45% of the initial value after

16 hours reaction time. As expected, the use of cuprous ammonium formate solution showed a significant improvement in comparison with a similar study using formate-formic acid solution [10], since the decrease of the bromine number was doubled from the 24% decrease previously obtained.

Electrocatalytic hydrogenation was carried out at the following volume ratios of electrolyte solution to turpentine oil, 2:5, 1:1, and 2:1. Then, the hydrogenation was further investigated with variation of the concentration of electrolyte solution (0.4 M and 0.75 M). The complete test results at various electrolyte : oil ratios, electrolyte solution concentrations, reaction times, and different electrodes are presented in Table 3.

**Table 3** Bromine number and smoke point of turpentine and processed oil at various reaction conditions.

Cathode	Volume ratio of electrolyte : turpentine	Electrolyte concentration	Anode	Reaction time (h)	Bromine number (mole Br <sub>2</sub> / mole of turpentine)	Smoke point (mm)
Pure Turpentine					1.865	±11
Copper	2:5	2 M	Stainless Steel	12	1.128	±14
Copper	1:1	2 M	Stainless Steel	12	0.907	±16
Copper	2:1	2 M	Stainless Steel	12	0.904	±16
Copper	2:1	2 M	Stainless Steel	24	0.820	±20
Silver	1:1	0.4 M	Stainless Steel	12	0.752	±22
Silver	1:1	0.75 M	Stainless Steel	12	0.679	±24
Silver	1:1	0.75 M	Stainless Steel	4	1.014	±17
Silver	1:1	0.75 M	Silver	4	1.121	±16
Silver	1:1	0.75 M	Carbon	4	1.134	±16
Kerosene					0.049	±21.5

The experimental results using the copper cathode showed that the proportion of electrolyte solution used significantly affected the final bromine number of the product and hence the degree of hydrogenation of the monoterpenes. Increasing

the concentration of electrolyte solution resulted in higher mass (ion) transfer capability between the electrolyte solution and the turpentine oil, so the hydrogenation rate was increased. However, beyond a ratio of 1:1 there was no visible effect. Thus the ratio of 1:1 was sufficient to effectively assist the hydrogenation process. In these experiments, the smallest bromine number was found at a ratio of 2:1 with the bromine number decrease of the turpentine oil at 56% (from 1.865 to 0.820). However, by taking the amount of electrolyte and the needed reaction time into account, a ratio of 1:1 and 12 hours of reaction time can be considered the best option for lowering the bromine number of the oil to 0.907.

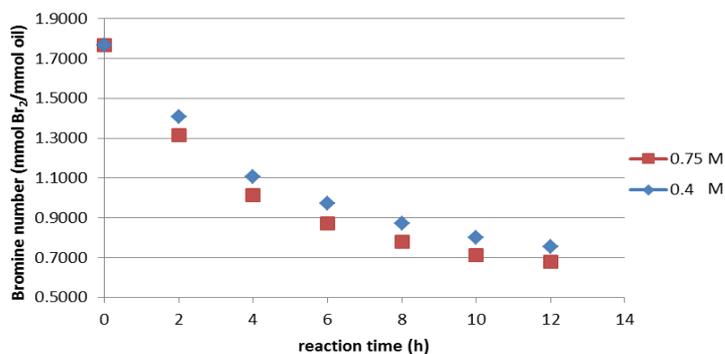
Hydrogenation with the silver cathode under various concentrations of electrolyte solution was used to determine whether the electrolyte concentration affected the hydrogenation process. The results showed that a higher concentration of electrolyte solution speeded up the hydrogenation process, since it contains more formate and  $\text{Cu}^+$  ions needed for the process. The processed oil from the silver cathode experiment (with lower electrolyte concentration) was much better than the one from the copper cathode, because copper is probably not effective in saturating the inner unsaturated bonds within the cyclic chain.

As we found in the hydrogenation process with the copper cathode, the rate of hydrogenation leveled off after 8 hours reaction time. The gradually slower rate of hydrogenation was probably due to the low concentration of  $\text{H}^+$  in the electrolyte solution, because most of the  $\text{H}^+$  in the electrolyte solution had been used after 8 hours. The results of the hydrogenation process with the silver cathode are presented in Figure 5.

In addition, several different anodes were also evaluated in this experiment to see the effect of the anode electrode. A more stable anode was explored because the stainless steel oxidized during the hydrogenation process, which resulted in the contamination of the processed oil with iron (Fe). This could be identified during the smoke point test, where the flame showed a yellow-red color coming from the iron. Meanwhile, the experiments using a silver or C anode produced a comparable (only slightly inferior) quality without contaminating the processed oil.

Finally, smoke point tests were conducted on the processed turpentine oil samples (hydrogenated for 12 hours). The smoke point test results are also shown in Table 3. From the smoke point tests it can be concluded that a lower bromine number of the hydrogenated turpentine oil translates into a higher smoke point due to the higher hydrogen content in the processed oil. The experiment with a silver cathode with electrolyte to oil ratio of 1:1 and 0.75 M

electrolyte concentration produced oil with a higher smoke point than that of kerosene. However, further investigation is necessary to decrease the bromine number of the processed oil even lower, so that the resulting oil may have a smoke point that resembles that of jet fuel.



**Figure 5** Bromine number of hydrogenated oil at various reaction times (silver cathode).

#### 4 Conclusion

Electrocatalytic hydrogenation can be used to increase the H content and thus lower the unsaturated bonds in turpentine oil as indicated by the increase in the smoke point values of the processed oil. Cuprous ammonium formate electrolyte solution is an excellent medium for assisting or improving the hydrogenation process compared with formate-formic acid solution since it may absorb the unsaturated hydrocarbons into the aqueous electrolyte phase containing the H transfer agent. With a copper cathode, the hydrogenation process using an electrolyte to oil ratio of 1:1 and a 12-hour reaction time can be considered the best option for lowering the bromine number of the oil from 1.865 to 0.907, with a smoke-point increase from 11 mm to 16 mm. Meanwhile, with a silver cathode, the bromine number can be lowered even further, to 0.679 mm, thus increasing the smoke point to 24 mm, which is higher than that of kerosene.

#### Acknowledgements

The authors are thankful for the financial support of LPPM UNPAR, through which the necessary reagents and apparatus were acquired.

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