Catalytic Transfer-Hydrogenation of Fatty Oil

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ABSTRACT

Polyunsaturated fatty acids are the main cause of the poor thermal and oxidative stabilities of fatty oils as well as biodiesels. The conversion of polyunsaturated to monounsaturated fatty acid moieties are normally carried out via hydrogenation. The most conventional hydrogenation process uses gaseous hydrogen at relatively high temperature and pressure in the presence of metal catalysts. Catalytic-transfer hydrogenation is an alternative method for oil hydrogenation which does not require the presence of hydrogen and can be carried out at atmospheric pressure.

This paper describes the catalytic transfer-hydrogenation of kapok seed oil (*Ceiba pentandra*) and candlenut oil (*Aleurites moluccana*) by potassium formate (KOOCH) solutions using the following catalysts: Ag–Cu_2O, Ag–Cu_2O/Pumice, Ag–Cu_2O–Pd/Pumice, and Pd/C 5%. None of the catalysts were found effective and kapok seed oil hydrogenated using 5%-Pd/C catalyst turned into gel, most probably due to the polymerization reactions of sterculic and malvalic acid

Keywords: catalytic-transfer hydrogenation, unsaturated fatty acid, potassium formate

1. INTRODUCTION

Kapok (Ceiba pentandra) and candlenut oil (*Aleurites moluccana*) are potential alternative raw materials for biodiesel production in Indonesia. The kapok tree can produce between 500 to 4000 fruits at one time, with each fruit containing 200 seeds [1]. The seeds are brownish black in color, enclosed within lint fiber and contains 25-28% of oil, similar to the characteristic of cotton seed oil. Candlenut tree can produce 30–80 kg of nuts, and kernel yield oil at 60 to 66% of their weight.

Kapok seed oil (KSO) contains palmitic acid (20-24%), oleic acid (21-225), linoleic acid (33-58%), and cyclopropenoid acid (10-14%; sterculic acid (3-4%) and malvalic acid (7-8%)) [2,3,4], while candlenut oil (CNO) contains palmitic acid (4-9%), stearic acid (4-7%), oleic acid (10-35%), linoleic acid (33-485) and linolenic acid (23-35%) [5]. The Iodine value of KSO is 86-110 g I_2/100-g oil and CNO is 136-167 g I_2/100-g oil. Linoleic and linolenic acids contain more than one double bond (poly-unsaturated fatty acid) making them susceptible either to oxidative degradation leading to the appearance of undesirable compounds or to thermal oligo-/polymerization causing gum formation. Although cyclopropenoid acid has lower iodine number but this type of fatty acid has also a poor oxidative stability. For the sake of utilization of fatty oils in liquid fuel production, the polyunsaturated bonds and the cyclopropenoid acids in the fatty acid chains should be converted into monounsaturated ones. The conventional method of doing this is by direct catalytic hydrogenation using hydrogen gas at relatively high temperature and pressure with the aid of nickel as catalyst. The presence of free gaseous hydrogen at high temperature and pressure in this process carry the risk of explosion.

Hydrogenation of edible oils in commercial gaseous processes involves elevated temperature (about 150–225°C) and high pressure (10–60 psig) [6], which leads to excessive equipment costs and operational problems. High-temperature hydrogenation also favors the production of trans-fatty acid (FA). Recent studies have implicated trans-FA in increasing cholesterol levels in the blood and enhancing blood lipoprotein. There is also evidence that trans-FA may be associated with the development and acceleration of coronary heart disease. Trans-FA also increases the viscosity and melting point of the oils [7]. The key to lowering the trans-FA in edible oils is by accomplishing hydrogenation at low temperatures. The gaseous hydrogenation process is not effective at low temperatures. Catalytic-transfer hydrogenation is an alternative method that looks promising to enable the process to be carried out at low pressure and temperature without the presence of gaseous hydrogen.

Catalytic-transfer hydrogenation (CTH) using palladium-based catalyst was proven to work at moderate temperature. CTH with 10%-Pd/C as catalyst and sodium formate as hydrogen donor reduced the iodine value of soybean oil [8, 9]. 10%-Pd/C was also used with other hydrogen donors such as formic acid and triethylamine formate [8]. Palladium catalyst with lower concentration has been used as catalyst for the CTH of sunflower oil with limonene as hydrogen donor. At Pd-to-oil ratio of 0.5-1%, linolenic acid and linoleic acid in sunflower oil were converted mainly into oleic acid, thus fulfilling the goal of partial hydrogenation [10]. Although palladium is an effective catalyst, but the high price of palladium becomes an obstacle for CTH. Therefore further CTH research is needed to find a cheaper but effective catalyst that could work at moderate temperature and pressure.

Silver (Ag) and Copper (Cu) added to Palladium (Pd) catalysts on pumice support (Pd concentration 0.05 to 0.5%) will promote the activity of Pd in the selective hydrogenation of -CH = CH- bonds in liquid unsaturated aldehyde at temperatures around 100°C [11]. The present of Cu^+ or Ag^+ ion in formic salt solution as hydrogen donor of fatty oil CTH will be useful because it is already known that Ag(I) ion and Cu(I) ion react with unsaturated chain (olefin) to form complexes. This complexes formation causes unsaturated fatty acid chain to be absorbed in formic salt solution [12, 13]. This indicates that Ag-Cu_2O-based catalyst is a potential alternative for CTH catalyst.

Potassium formate has been chosen as the hydrogen donor in the preesent research on the CTH of KSO and CNO, because of its high solubility in water (330g/100g H_2O). High concentration of potassium formate (10 M) can increase the rate of vegetable oils hydrogenation [14]. Potassium formate (KCOOH) reacts with hydrogen acceptors (A) in the present of catalyst according to equation (1).

$$KCOOH + H_2O + A \rightarrow KHCO_3 + H_2A \qquad (1)$$

2. METHODS

Materials

Kapok seed oil (KSO) with an acid value of about 18 mg KOH/g (obtained from a producer in Semarang, Indonesia), candle nut oil (CNO) with an acid value about 10 mg KOH/g (pressed in our own laboratory), ethanol and potassium carbonate technical grade (Bratachem), and formic acid (Merck) were used. The catalyst, 5%-Pd/C was from Sigma Aldrich.

Catalyst preparation

Treated Pumice: To increase its surface area, natural pumice (about 1 mm size) was soaked in 3N HCl for 5 hours (two times), filtered and washed with distilled water and finally dried at 110°C for 5 hours.

Ag–Cu_2O: Modification of Cu_2O base catalyst method [14]; 125g $Cu(NO_3)_2.3H_2O$, 88 g $AgNO_3$ and 250 g dextrose were dissolved in 1250 ml of distilled water. 250 ml of 40 %-NaOH solution was then added to coprecipitate Ag–Cu_2O, which was then aged by heating at 85°C for 30 minutes. The aged coprecipitate was filtered and washed with distillate water. The catalyst was then dried first at room temperature and then in a vacuum desiccator for 12-16 hours.

Ag–Cu_2O/Pumice: 2.5g $Cu(NO_3)_2.3H_2O$ and 1.76 g $AgNO_3$ were dissolved in 25 ml distilled water. Treated pumice (24 grams) was wetted with this solution (dry impregnation). Candidate catalyst was dried at room temperature for 12 hours and then stored at freezer for 12hours. The candidate catalyst was then soaked in 120 ml potassium formate 0.3 M, stirred for about 5-10 minutes, filtered on cold Buchner funnel and washed 3 times with distilled water. The catalyst was dried first at room temperature and then in vacuum oven at 75°C for 5 hours.

Ag–Cu_2O-Pd/Pumice: Based on Pd-Cu_2O production method [11], 2.5 ml glacial acetic acid was diluted with 10 ml distilled water and 0.505 g $Pd(CH_3COO)_2$, 1.055 g $Cu(CH_3COO)_2$

and 0.375 $AgCH_3COO$ were then dissolved in the solution. Treated pumice (24 grams) was wetted with these solution and then dried at room temperature for about 12 hours,and finally reduced with hydrogen-free oxygen at 100-120°C. Palladium concentration in this catalyst is around 0.5%.

KCOOH preparation

K_2CO_3 (248.5 grams) was dissolved in 1 liter distilled water and stirred gently. Formic acid (136.5 ml) was added slowly. After the CO_2 evolution was complete, the solution was evaporated to dryness and the solid obtained was then dried in oven at 150°C for 48 hours.

Hydrogenation experiment

The following catalysts were used in the CTH of kapok seed oil (*Ceiba pentandra*) and candlenut oil (*Aleurites moluccana*) with potassium formate (KOOCH) solutions as hydrogen donor : Ag–Cu_2O, Ag–Cu_2O/Pumice, Ag–Cu_2O–Pd/Pumice, Pd/C 5% and Pd/C 0.5%. The CTH was performed in a batch reactor, at 40°C, KCOOH 10 M (2 mol KCOOH/ mol double bond), atmospheric pressure, and 16 hours reaction time [14]. Ethanol was used as solvent with ratio 5:1 to fatty oil. Figure 1 shows a schematic diagram of the CTH apparatus.

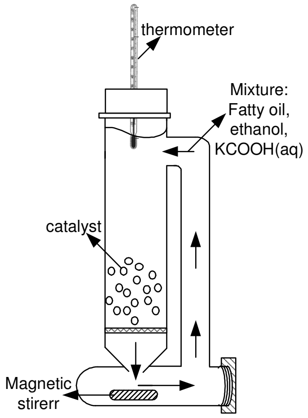

Fig. 1 Schematic Diagram of CTH of Fatty Oil System

At the end of the 16 hrs reaction time, hydrogenated fatty oil was separated from the ethanol and $KCOOH/KHCO_3$. It was then washed with distilled water to remove traces of $KCOOH/KHCO_3$, until the pH of wash water was neutral. The iodine value of the fatty oils was measured using Wijs method.

3. RESULTS

The present work tested the activity of Ag-Cu_2O-based catalysts as potential catalysts for catalytic-transfer hydrogenation. Pd/C 5% from Sigma Aldrich was also tested for comparison.

Characteristics of the tested catalysts, analyzed with BET method, are shown in Table 1.

Table 1 Catalysts Characteristics

Catalyst	Surface Area (m^2/g)	Average Pore Diameter (Å)	Total Pore Volume (cc/g)
Ag-Cu_2O	5,816	1,7487 x 10^2	2.543 x 10^{-2}
Ag-Cu_2O-Pd/pumice	3,122	5,7021x10^1	4,451 x 10^{-3}
Ag-Cu_2O /pumice	4,180	5,542 x 10^1	5,793 x 10^{-3}

Table 2 lists the results of CNO and KSO hydrogenation with Ag-Cu_2O based catalysts. The iodine values of hydrogenated KSO and CNO show that the three Ag-Cu_2O base catalysts were ineffective at reaction temperature 40°C. The lowest KSO iodine was only 95.51 g I_2/100-g oil, and CNO iodine value was only 156.15 g I_2/100-g oil. These values were still higher than IV of future biodiesel feedstock standard in Indonesia (80 g I_2/100-g oil).

CTH of KSO and CNO utilizing Ag-Cu_2O as catalyst yielded blue $KHCO_3/KCOOH$ solution, because Cu^+ ions in the catalyst was oxidized to Cu_2^+ ions that is soluble in the $KHCO_3/KCOOH$ solution (Figure 2). The formations of $Cu_2{}^+$ ion is due to the nature of Cu^+ ion which is less stable and tend to disproportionate in solution according to equation 2.

$$Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu^0(s) \qquad (2)$$

The present of Cu^{2+} and Cu^0 in $KHCO_3/KCOOH$ solution becomes an impediment on the KCOOH regeneration process, because these ions are difficult to separate.

Table 2 Iodine Value of CNO and KSO after CTH with Ag-Cu_2O based catalysts

Catalysts	CNO		KSO	
	Iodine Value (IV_f) g I_2/100-g oil	Δ IV	Iodine Value (IV_f) g I_2/100-g oil	Δ IV
Untreated fatty oil (IV_i)	**166.59**		**108.29**	
Ag-Cu_2O 2%b oil	162.18	4.41	95.51	12.78
Ag-Cu_2O/ pumice 2% b oil	156.15	10.44	97.35	10.94
Ag-Cu_2O-Pd/pumice 2%b oil	164.08	2.51	97.35	10.94

Conditions: 40°C and atmospheric pressure, KCOOH 10 M (2 mol KCOOH/ mol double bond), catalyst 2% b oil, reaction time 16 h.
Δ IV = IV_i-IV_f

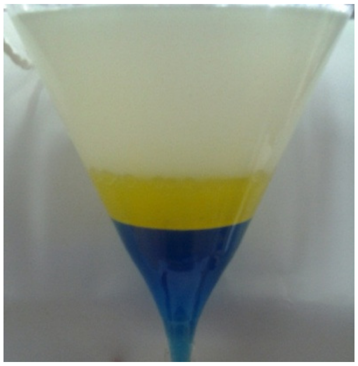

Fig.2 CTH Mixture Product, Upper Layer: Ethanol, Middle Layer: Fatty Oil, and Bottom Layer: Blue $KHCO_3$/KCOOH solution

Commercial 5%-Pd/C catalyst which has greatest palladium concentration was also ineffective in hydrogenation of CNO at reaction temperature (40°C). KSO hydrogenated using 5 %-Pd/C as catalyst result in lower IV (63.08 g I_2/100-g oil), but the product became sticky, viscous and turned into gel in the following day. These phenomenon occurred because the sterculic and malvalic acid were bind to each other to form polymer [16]. Rinehart dan Mills [17-18] proposed some type of polymerization products or reactions of malvalic and sterculic acid shown in Figure 3. Figure 4 shows the picture of KSO polymer.

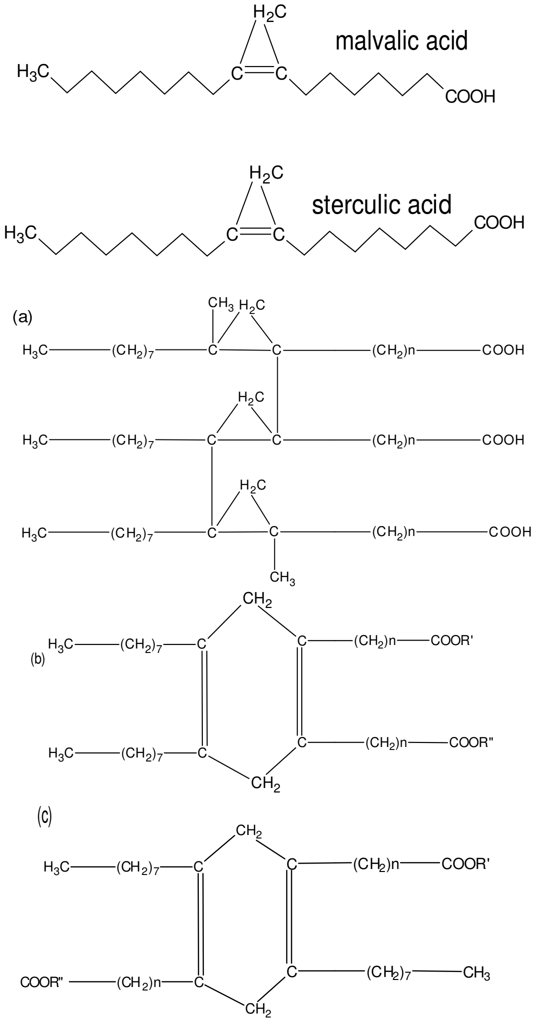

Fig. 3 Sterculic and Malvalic Acid. (a,b,c) The Possibility of Polymerization Product of Malvalic and Sterculic Acid [17-18]

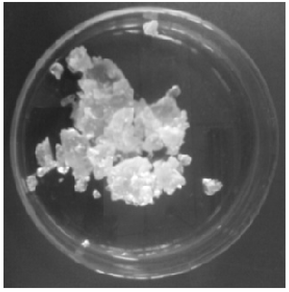

Fig. 3 KSO after CTH using Pd/C 5% as catalyst (KSO polymer)

Table 3 Iodine Value of CNO and KSO after CTH with Pd/C 5% catalysts

Catalysts	CNO	KSO

	Iodine Value (IV_f) g I_2/100-g oil	**Δ IV**	**Iodine Value (IV_f) g I_2/100-g oil**	**Δ IV**
Untreated fatty oil (IV_i)	**178.74**		**108.29**	
Pd/C 5%	161.87	16.87	63.08	45.21

Conditions: 40°C and atmospheric pressure, KCOOH 10 M (2 mol KCOOH/ mol double bond), catalyst 0.05% b oil, reaction time 16 h.
$\Delta IV = IV_i - IV_f$

4. CONCLUSION

The catalysts Ag-Cu_2O, Ag-Cu_2O/pumice, Ag-Cu_2O-Pd/pumice and 5%-Pd/C were all ineffective for the catalytic-transfer hydrogenation (CTH) of KSO and CNO oils using potassium formate 10 M as hydrogen donor and 40°C reaction temperature. KSO hydrogenated using 5%-Pd/C as catalyst turned into gel due to the polymerization reactions of sterculic and malvalic acid.

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