

Bimetallic Ag-Ni on SiO₂ Catalyst for Kapok Seed Oil Hydrogenation

Fitri Hadiah^{#,*}, Tirta Prakoso^{*}, Subagio^{*}, Tatang Hernas Soerawidjaja^{*}

[#] *Chemical Engineering Department, University of Sriwijaya, Palembang, Indonesia*

¹giftri@yahoo.com

^{*} *Chemical Engineering Department, Institute of Technology Bandung, Bandung, Indonesia*

²subagjo@che.itb.ac.id

³tirta.prakoso@gmail.com

⁴hstatang@yahoo.com

Abstract— Bimetallic Ag-Ni on SiO₂ prepared by precipitation was used as catalyst for kapok seed oil hydrogenation. The catalytic-transfer hydrogenation (CTH) was performed in a batch reactor at 76°C, catalysts loadings of 1-4%w, using potassium formate as hydrogen donor. The best condition for kapok seed hydrogenation is at 76 °C temperature, 16 hours reaction time, with 1% catalyst, 10 M potassium formate, and 2:1 ratio of potassium formate to the double bond. CTH using higher concentration of potassium formate could eliminate almost all of the cyclopropenoid acid. The bimetallic Ag-Ni catalyst is proposed as a promising candidate for selective edible oil hydrogenation.

Keywords— Ag-Ni bimetallic, cyclopropenoid acid, catalytic-transfer hydrogenation, kapok seed oil, potassium formate.

I. INTRODUCTION

Kapok (*Ceiba pentandra*) is 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. Kapok seed oil (KSO) contains palmitic acid (20-24%), oleic acid (21-22%), linoleic acid (33-58%), and cyclopropenoid acid (10-14%; sterculic acid (3-4%) and malvalic acid (7-8%)) [2,3,4]. The Iodine value of KSO is 86-110 g I₂/100-g oil.

Linoleic and cyclopropenoid 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 conventional processes involves elevated temperature (about 150–225°C) and high pressure (10–60 psig) [5], 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 [6]. 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 [7, 8]. 10%-Pd/C was also used with other hydrogen donors such as formic acid and triethylamine formate [7]. 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 [9]. 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 [10]. 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 [11, 12]. This indicates that Ag based catalyst is a potential alternative for CTH catalyst.

Precipitated bimetallic catalysts give rise to total conversion from 373 K of benzene hydrogenation, a temperature at which conversion hardly reaches 30% for the impregnated catalysts [13, 14]. The synergism between Ag and Ni in transfer hydrogenation eliminates the need for external hydrogen [15]. Previous researchs reinforces the hypothesis that the bimetallic Ag-Ni can be developed as a catalyst-transfer catalytic hydrogenation of vegetable oils. Appropriate operating conditions would determine the success of hydrogenation.

Potassium formate has been chosen as the hydrogen donor in the present research on the CTH of KSO and CNO, because of its high solubility in water (330g/100g H₂O). High concentration of potassium formate (10 M) can increase the rate of vegetable oils hydrogenation [16]. Potassium formate (KCOOH) reacts with hydrogen acceptors (A) in the present of catalyst according to equation (1).



II. METHODS

A. Material

Kapok seed oil (KSO) with an acid value of about 18 mg KOH/g (obtained from a producer in Semarang, Indonesia). Ethanol and potassium carbonate technical grade (Bratachem), and formic acid (Merck) were used.

B. Catalyst Preparation

5.5 g KCOOH were dissolved in 25 ml distilled water. Silica gel, average pore diameter 150 Å (24 grams) was wetted with this solution. Candidate catalyst was dried at room temperature for 12 hours. Meanwhile, 8.2 g Ni(NO₃)₂.6H₂O and 1.6 g AgNO₃ were dissolved in 25 ml distilled water. Candidate catalyst and nitrate solution were stored at freezer for 12 hours. The candidate catalyst was then wetted with nitrate solution, and dried at room temperature. Candidate catalyst then filtered on cold Buchner funnel and washed 5 times with cold distilled water. The catalyst was dried first at room temperature and then in vacuum oven at 75°C until it turned black.

C. Hydrogenation Experiment

The following catalysts were used in the CTH of kapok seed oil (*Ceiba pentandra*) with potassium formate (KOOCH) solutions as hydrogen donor. The CTH was performed in a batch reactor, at 76°C, atmospheric pressure, and 16 hours reaction time. Isopropanol was used as solvent with ratio 5:1 to fatty oil. Fig. 1 shows a schematic diagram of the CTH apparatus. At the end of the 16 hrs reaction time, hydrogenated fatty oil was separated from the ethanol and KCOOH/KHCO₃. It was then washed with distilled water to remove traces of KCOOH/KHCO₃, until the pH of wash water

was neutral. The iodine value of the fatty oils was measured using Wijs method. Cyclopropanoid acid was determined with Besson test.

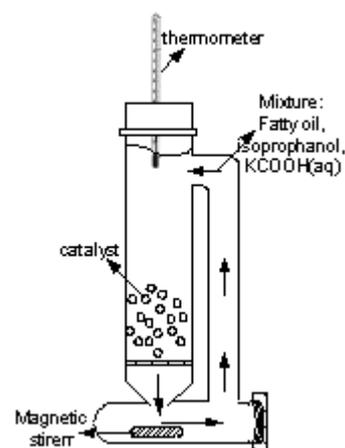


Fig. 1 Schematic diagram of CTH of fatty oil system

III. RESULT AND DISCUSSION

The BET surface area of Ag-Ni/SiO₂ catalyst is 283.47 m²/g and the average pore size is 137.36 Å. Thus very large average pore size increasing the adsorption rate of the unsaturated fatty acids, which has molecule size around 25 Å. Table 1 lists the results of kapok seed oil hydrogenation with Ag-Ni/SiO₂ catalysts. The lowest KSO iodine value (IV) was 39.88 g I₂/100-g oil. These values were lower than IV of future biodiesel feedstock standard in Indonesia (80 g I₂/100-g oil). The effects of hydrogen donor concentration and catalyst loading to reduction in iodine value is shown in Fig.2. Iodine number reduction in Ni-Ag bimetalic catalyst shows that silver existence would increase nickel hydrogenation activity in condition (temperature and pressure) where nickel actually less active.

Besson test [17] for hydrogenated kapok seed oil results were always positive in all sample using 10 M KCOOH, but the results were always negative in all sample that using 6 M and 4 M KCOOH, indicating that usage of Ag-Ni bimetal and hydrogen donor of 10 M will hydrogenate all cyclopropanoid acids.

TABLE I
IODINE VALUE OF KSO HYDROGENATED

KCOOH	Catalyst (%w)		
	1%	2%	4%
Iodine Value (g I ₂ /100 g oil)			
4 M	81.65	91.20	82.79
6 M	100.89	101.25	93.52
10 M	39.88	61.18	87.82

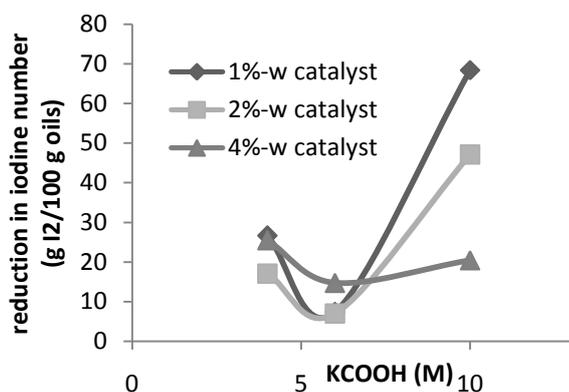


Fig. 2 The effects of hydrogen donor concentration and catalyst loading to reduction of iodine value

The greater catalyst loading used yielding reduction in iodine number except for KCOOH 6M and 4% catalyst ratio. This exception allegedly caused by physical factor i.e. oil viscosity and catalyst ratio (the catalyst were in powder form so the greater catalyst ratio would make the mixture more viscous). Further, the more viscous the mixture, the substances in the reactor would be more difficult to be homogenous.

Higher KCOOH concentration and catalyst loading would also make hydrogen concentration increased. Not all of the hydrogen formed in the reactor adsorbed on the catalyst surface making hydrogen bubbles that would hinder mixing of substances in reactor. This phenomenon was observed directly in reactor, showing circulation suspension when there were much hydrogen produced that would be resumed when the hydrogen bubble decreased. This unstreamlined circulation lead to less contact between hydrogen donor, the double bond, and the catalyst, making the hydrogenation process hampered.

IV. CONCLUSIONS

The best condition for kapok seed hydrogenation is at 76 °C temperature, 16 hours reaction time, with 1% catalyst, 10 M potassium formate, and 2:1 ratio of potassium formate to the double bond. Silver promotes the activity of nickel at temperature and pressure at which nickel is usually inactive. CTH using higher concentration of potassium formate could eliminate almost all of the cyclopropenoid acid.

ACKNOWLEDGMENT

The authors gratefully acknowledge the support of “Hibah Disertasi” from DIKTI Indonesia.

REFERENCE

- [1] N. Norazahar, S. Yusup, M.M. Ahmad, S. Abu Bakar and J. Ahmad, “Parametric Optimization of Kapok (Ceiba Pentandra) Oil Methyl Ester Production using Taguchi Approach”, *International Journal of Energy And Environment*, 6:6, pp. 541-548, 2012.
- [2] G.G. Shone, “Adverse effect of cyclopropenoid fatty acid”, *Symposium Proceeding Nutritional and Toxicity Problems Associated with Fats*, pp. 37-38, 1996.
- [3] S.K. Berry, “Cyclopropenoid fatty acid in some malayan edible seeds and nuts”, *Journal of Food Science and Technology*, 17(5), pp. 224-227, 1980.
- [4] Ceiba petandra., Prota 16: Fibres/Plantes à fibres Record display,

http://database.prota.org/PROTAhtml/Ceiba%20pentandra_En.html, download at June 8 2013.

- [5] TH. Soerawidjaja, “Prospek dan Tantangan Pengembangan Industri Biodiesel di Indonesia” National Seminar Proceeding “Energi Hayati Sebagai Solusi Krisis Energi: Peluang dan Tantangannya di Indonesia” UNS Surakarta, April 8, 2006.
- [6] K. Mondal and S. B. Lalvani, “Electrochemical Hydrogenation of Canola Oil Using a Hydrogen Transfer Agent”, *Journal of American Oils Society*, 80:11, pp.1135-1141, 2003.
- [7] A. Thomas., “Fats and Fatty Oils”, *Ullmann Encyclopedia of Industrial Chemistry*, 6:A10, pp. 173-245.
- [8] A. Smidovnik, A.Stimac, and J. Kobe., “Catalytic transfer hydrogenation of soybean”, *JAOCS*, 69 (5), pp.405-409, 1992.
- [9] A. Smidovnik, M.Naglic, and T. Koloini., “Kinetics of catalytic transfer hydrogenation of soybean oil”, *JAOCS*, 71 (5), pp.507-511, 1994.
- [10] R. Scheider, LRS. Lara, and M. Martinelli., “An alternative process for hydrogenation of sunflower oil”, *Orbital The Electronis Journal of Chemistry*, 2(2), 2010.
- [11] W. Chemie., “Process for the production of saturated aldehydes”, *United Kingdom Patent no. GB 1 065 628*, 1967.
- [12] RN. Keller., “Coordination compounds of olefins with metallic salts”, *Chemical Reviews*, 28(2), pp. 229 – 267, 1941.
- [13] R. Wojcieszak, S. Monteverdi, J. Ghanbaja, M.M. Bettahar., “Study of Ni–Ag/SiO₂ Catalysts Prepared by Reduction in Aqueous Hydrazine”, *Journal of Colloid and Interface Science*, 317, pp. 166–174, 2008.
- [14] M.M. Bettahar, R. Wojcieszak, S. Monteverdi., “NiAg catalysts prepared by reduction of Ni²⁺ ions in aqueous hydrazine II. Support effect”, *Journal of Colloid and Interface Science*, 332, 416–424, 2009.
- [15] A. M. Hengne, A.V. Malawadkar, N. S. Biradar and C. V. Rode., “Surface synergism of an Ag–Ni/ZrO₂ nanocomposite for the catalytic transfer hydrogenation of bio-derived platform molecules”, *RSC Advances*, 4, 9730–9736, 2014.
- [16] O. Arkad, H. Wiener, N.Garti, Y. Sasson., “Catalytic transfer hydrogenation of soybean oil methyl ester using inorganic formic acid salts as donors”, *J. Am. Oil Chem. Soc.*, 64 (11), 1529-1532, 1987
- [17] V.C. Mehlenbacher., “Color test for kapok oil”, *Oil and Soap* 13(6) 136– 138, 1936.