Indonesian Journal of Agricultural Sciences (2001), 1, 5-10. Green Digital Press.
Copyright © 2001 Indonesian Agricultural Sciences Association

Chemical modification of crude palm oil by palladium catalyzed hydrogenation

Marwan

Chemical Engineering Department, Syiah Kuala University, Darussalam, Banda Aceh 23111, Indonesia

(*Received April 13, 2001; Final Revision May 22, 2001; Accepted June 4, 2001*)

Abstract

Hydrogenation of crude palm oil using in-house prepared 1% palladium on activated carbon catalyst was studied in a stirred type reactor in attempt to establish kinetics regime of the reaction. Preliminary runs showed hydrogenation raising to similar effect on oil color as bleaching and the use of bleached oil was preferable due to less catalyst deactivation by oil impurities. Initial rate analysis indicates that the reactions occurred in kinetics regime at stirring speeds above 1000 rpm and catalyst loadings less than 0.4 g/L. Arhenius plot analysis confirms kinetics regime finding. The reaction mechanism was proposed to follow Langmuir-Hinshelwood kinetics.

Keywords: palm oil; hydrogenation; palladium; hardening

Introduction

A growing concern on sustainable development concept has led to more attention on utilization of agriculture products. Palm oil as one of prominent agro-products in Indonesia has huge potential to be a source of various industrial raw materials. Palm oil is made up mostly of glyceridic materials with some non glyceridic ones in small or trace quantities. One of its common modifications to meet the downstream process requirements is by use of partially catalytic hydrogenation method, a process aiming to render it more solid, and to improve its stability against oxidation.

There has been strong recommendation to study the use of palladium (Pd) as an alternative catalyst for edible oil hydrogenation (Koetsier and Lok, 1998, Tackle *et al.* 1996). Pd is an extremely active hydrogenation catalyst, known to be up to a hundred times more active than nickel (Ni) for edible oil hydrogenation (Grau *et al.* 1988). The current research investigated the use more active catalyst of Pd, instead Ni in the traditional processes. Previous experiences suggest that it is important to perform the reactions under kinetics controlling reaction rates, to obtain better selectivity towards mono-unsaturated fatty acids, even in the form of *cis*-isomer (Winterbottom *et al.* 1997). Therefore, this work was attempted to establish this requirements when using Pd catalyst. Hydrogenation of crude palm oil (CPO) using in-house prepared 1% Pd on activated carbon (Pd/C) catalyst was carried out in a stirred type reactor. By partially hydrogenation of the oil, unsaturated acids will be reduced up to a point where physical texture of the oil is completely solid at room temperature. The hydrogenated oil can be used as a solid fraction in preparation of shortening and margarine.

Correspondence: Marwan, Chemical Engineering Department, Faculty of Engineering, Syiah Kuala University, Darussalam, Banda Aceh 2311, Indonesia.
Phone: +62-651-51977; Fax: +62-651-52222.
E-mail: marwan@yahoo.com

Materials and Methods

Fresh CPO used was kindly supplied by PTP I Tanjong Seumantouh (Aceh, Indonesia) with its properties shown in Table 1. CPO was kept under nitrogen in dark plastic bottles to avoid oxidation and reduction. Hydrogen gas was purchased from PT. Aneka Gas (Indonesia). The catalyst precursor

was sodium tetrachloropalladate (II) from Aldrich (UK). Catalyst support was prepared from a block of activated carbon, obtained from local market. The solvent for catalyst preparation was acetone (Aldrich, UK). The reaction was carried out in a 1-L reactor of Juvo GmbH (Germany) connected to an oil thermostat. The vessel pressure was controlled from a gas regulator fitted on hydrogen cylinder. The operation was on batch basis with respect to the oil, while hydrogen was supplied continuously according to its consumption rate by the reaction.

Table 1. Chemical and physical properties of the CPO

Characteristics	Value
C14-0 (Myristic acid)	0.82%
C16-0 (Palmitic acid)	46.69%
C18-0 (Stearic acid)	3.43%
C18-1 (Oleic acid)	38.29%
C18-2 (Linoleic acid)	10.44%
C18-3 (Linolenic acid)	0.16%
Iodine value	51.15
Carotenoids	562.34 ppm
Melting point	41.5^{o}C

The experimental setup is as shown in Figure 1. Firstly, the reactor vessel was filled with 400 mL CPO and catalyst at a given loading. Headspace of reactor was flushed with nitrogen and then hydrogen prior to the reaction. While the temperature was adjusted with lubricant oil flowing through the jacket, the reactor was pressurized with hydrogen. The reaction was started by switching the stirring motor on and fixed at a given speed. 10 mL liquid sample was collected at a certain time interval. To avoid significant change of reacting volume, up to 5 samplings were done except for the observation of melting point changes. The experiments were carried out at temperatures from 50 to 100°C, pressures from atmospheric to 6 barg, catalyst loadings from 0.1 to 0.5% and stirring speeds from 500 to 1500 rpm.

The Pd/C catalyst was prepared by incipient wetness method. Firstly, activated carbon block was crushed, milled and sieved to obtain a particle size range of 100/150 mesh. Meanwhile, a certain amount of Pd salt to give 1% catalyst loading was dissolved in acetone. The powdered activated carbon was poured into the salt solution and the mixture was stirred for one hour. Then, the solvent was evaporated by heating. Finally, dried powder was calcined in a furnace at a temperature of 250°C for 2 hours. Catalyst reduction was not carried out since it would reduce easily even at room temperature during initial stage of the reaction (Marwan, 1998). For use in most runs, CPO was bleached using bleaching earth under physical treatment. The bleaching earth loading was 5% weight. The mixture of CPO and bleaching earth were stirred mechanically in a 500 mL beaker glass for 6 hours. The temperature was 50°C. Bleached oil was then kept on dark bottles.

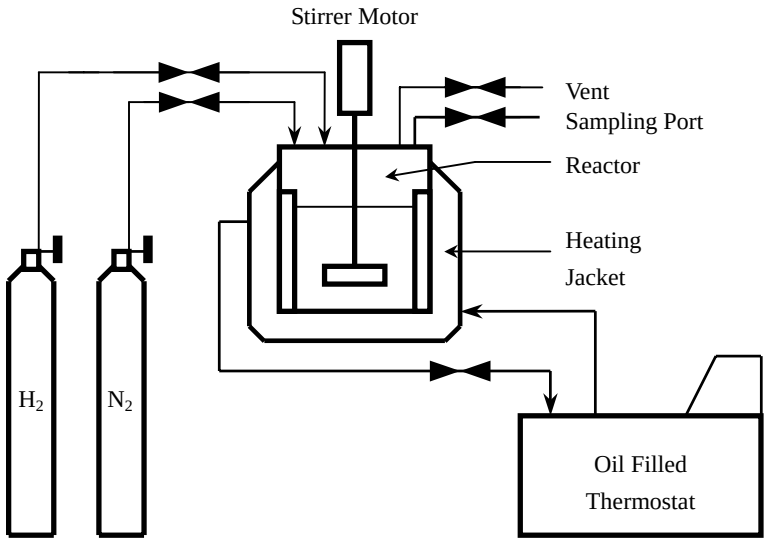

Figure 1. Scheme of experimental apparatus

Prior to analysis, the oil samples were separated from catalyst particles using filter papers. The filtered samples were analysed for iodine value (IV) and melting point, according to standard methods described in literature (Hui, 1996). Analysis was not replicated due to small amount of samples. Kinetics of the reaction were analysed based on the initial reaction rates found from the plots of iodine value against time.

Results and Discussion

Preliminary Observations

Noble metal catalysts are sensitive to some metal ions, *i.e.* they may occupy active sites permanently, thus reducing catalyst activity, even in some cases providing better selectivity towards desired products. Figure 2 shows a higher reduction rate with bleached oil, suggesting that the presence of impurities in the initial oil has poisoned the catalyst to some extent. Bleaching process did not only reduce the oil color, but also removed some trace metals from oil. Some trace metals such as ferrous and potassium are already recognized present in the fresh CPO. It is suggested to use bleached or refined palm oil for hydrogenation to avoid or minimize catalyst deactivation.

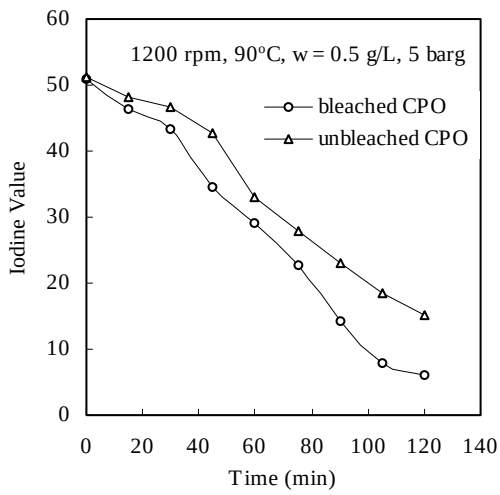

Figure 2. Iodine value vs. time in hydrogenation of bleached and unbleached palm oils

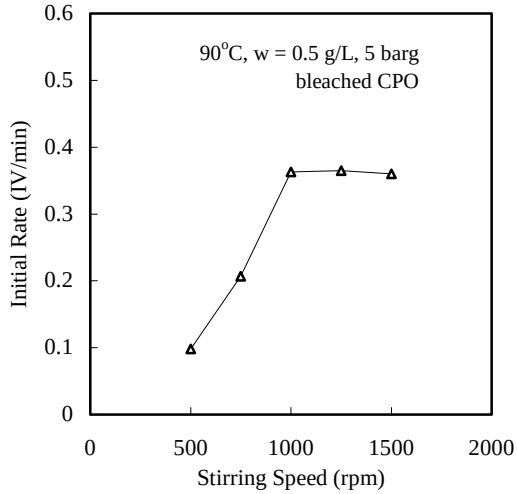

Figure 3. Reaction rate at various stirring speeds

During hydrogenation process, the unsaturated fats that have lower melting point will be reduced, starting from the most unsaturated bond. It was observed that melting point increased almost linearly from 41°C to 57°C at final iodine value (IV) of 6.5 as the reaction was progressing. Higher content of unsaturated fats in form of linoleic has resulted in lower melting point of initial oil. While the reaction proceeded, linoleic was converted to more saturated fats mainly to oleic acid and then to stearate which both have higher melting points. As the results, melting point of hydrogenated oil increased. For effective reaction, the reaction should be carried out at above possible highest melting point, otherwise the oil would solidify resulting in mixing problem and poor hydrogen transfer into the oil. Therefore, other runs were carried out at temperatures of 60°C or above.

A change in the oil color during hydrogenation was observed, where deep orange-red color in initial unbleached CPO significantly reduced to clear yellow in final product. It is well known that the presence of carotenoids in form of α- and β-carotenes, precursor of vitamin A, in CPO has caused deep orange-red color. Possibly, carotenoids which also contain unsaturated bonds were hydrogenated during the reaction to give similar effect as bleaching. However, such situation is unexpected since carotenoids give better nutritional effect in form of vitamin A and also increase oil stability against oxidation. To minimize the lost of

these important ingredients, it is suggested to conduct the reaction at higher pressures and keep the temperature low (Hui, 1996). At ambient, the hydrogenated oils were in the form of yellowish soft solid.

Identification of Kinetics Regime

The prime objective of the present work was to investigate the kinetics of the reaction using an in-house prepared Pd/C catalyst. This being a multiphase system, it was important to ensure that mass transfer and hydrodynamic factors were either eliminated or accounted for in determining the kinetics. For this purpose, a fine size of catalyst particles was prepared so as to eliminate intraparticle and liquid-particle mass transfer resistances. Also, the data were obtained under stirring speeds well beyond the critical speed of agitation required for complete suspension of particles. The reaction rate analysis for kinetics study was based on the change of iodine value with time at initial stage of the reaction in order to eliminate the influence of products and catalyst deactivation. Iodine value represents the content of unsaturated triglycerides, measured as milligram iodine reacting with a gram of oil. Although this method is not accurate as a measure of rate, iodine value is acceptable to be used as a practical way.

Figure 3 shows that an increase in stirring speed accelerated the reaction rate up to the speed of 1000 rpm, beyond which the rates were independence of stirring speed. Therefore, at above 1000 rpm the rates were not controlled by hydrogen mass transfer, but by surface reaction kinetics. Therefore, the stirring speed of 1200 rpm was used to ensure the observations under kinetics controlling rates.

Figure 4 exhibits the fact that the reactions at catalyst loadings more than 0.4 g/L led to mass transfer controlling reaction rates. To perform the reaction under kinetics regime, the catalyst concentration must be kept less than 0.4 g/L. To ensure the kinetics regime the following runs were carried out at a loading of 0.2 g/L. Minimum loading was observed at 0.05 g/L, suggesting that the catalyst was poisoned by the impurities present in oil, even it was already bleached. The amount of 0.05 g/L of the catalyst charged into the reactor has been acting as poison sink. It appears in Figure 5 that pressure had strong influence on the reaction rate. As hydrogen partial pressure increased, the rates became more intense linearly suggesting first order reaction with respect to gas.

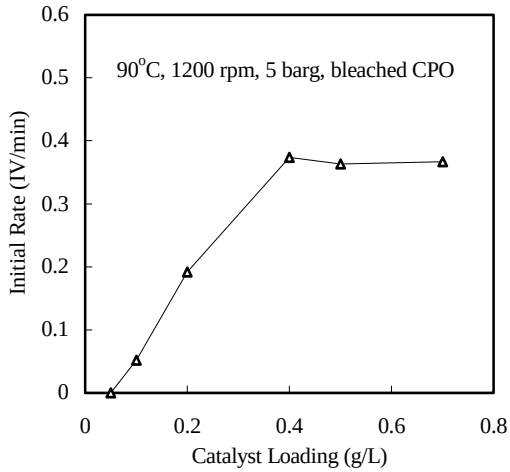

Figure 4. Reaction rate at various catalyst loadings

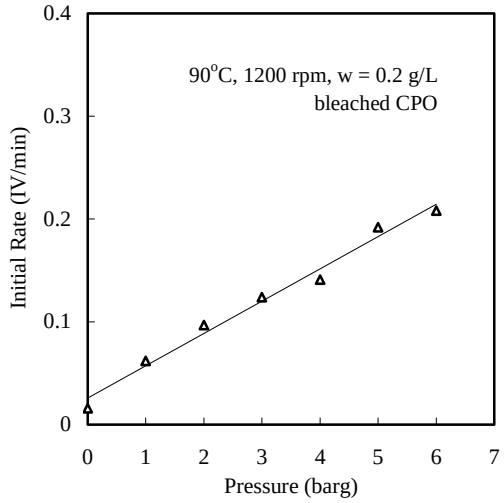

Figure 5. Reaction rate at various H_2 pressures

The temperature dependence of reaction rate was analysed based on Arhenius relationship. The apparent activation energies found were 11.5 and 9.4 kcal/gmol for catalyst loadings of 0.2 and 0.5 g/L, respectively. The former indicates that the reaction took place under kinetics control, while the latter exhibits the presence of mass transfer resistance, especially at oil-catalyst film. This confirms the finding in the effect of catalyst loading on reaction rates.

Kinetics Analysis

Since the rate was based on initial rate in term of IV, the discussion relates to linoleic conversion as a major reactant in initial stage. Figure 2 also suggests the presence of two reaction steps, *i.e.* firstly dominated by conversion of linoleic to oleic, and secondly predominantly reduction of oleic to stearate. Such mechanism can be proposed since over a very active Pd catalyst adsorptive characteristics of these acids are quite distinct with the adsorption strength order: linoleic>>oleic>>stearate (Winterbottom *et al.* 1997). It means that when linoleic is still presence in oil, oleic has no access to catalyst surface until all linoleic almost completely consumed. This also results in negligible direct conversion of linoleic to stearate. In addition, linoleic is less reactive than oleic. Both considerations contribute to the assumption of pseudo zero-order for linoleic.

Although then the order with respect to hydrogen was one, the power law seems not adequate to represent reaction kinetics model. Our previous work suggests that hydrogen can occupy any active site available on Pd surface (Marwan, 1998). Thus hydrogen must compete with linoleic for active site, with linoleic being more strongly adsorbed. Increased H_2 pressures giving more dissolved hydrogen in oil have enhanced its competitiveness. This argument leads to the Langmuir-Hinshelwood kinetics as a more reasonable model since this model also includes adsorption factors. Denoting S_1 and S_2 as surface sites for linoleic (L) or oleic (O) and adsorbed hydrogen, respectively, the following sequence of kinetic steps is suggested for conversion of linoleic to oleic acid:

$$L + \underline{S_1} \overset{K_1}{\Leftrightarrow} \underline{LS_1} \qquad \text{(i)}$$

$$H_2 + \underline{2S_2} \overset{K_2}{\Leftrightarrow} \underline{2HS_2} \qquad \text{(ii)}$$

$$\underline{LS_1} + \underline{2HS_2} \overset{k_3}{\rightarrow} \underline{O-S_1} + \underline{2S_2} \qquad \text{(iii)}$$

$$\underline{O-S_1} \overset{K_4}{\Leftrightarrow} O + \underline{S_1} \qquad \text{(iv)}$$

Underlined items represent surface active centres. Step (iii) is rate-determining. The rate expression applicable for above steps with $K_1 >> K_4$ (*i.e.* linoleic acid is more strongly adsorbed than oleic) is proposed as follows:

$$r = \frac{k_3 K_2 C_{H_2}}{\left(1 + K_2^{1/2} C_{H_2}^{1/2}\right)^2}$$

where K_2 is adsorption constant of hydrogen and k_3 is rate constant.

Conclusions

Partial hydrogenation of CPO over powdered 1% Pd/C catalyst was carried out with kinetics controlling rates obtainable at stirring speeds above 1000 rpm and catalyst loadings less than 0.4 g/L. Temperature dependence of the hydrogenation rate was analysed to give activation energies of 9.4-11.5 kcal/gmol, confirming kinetics controlling rates. The reaction mechanism was proposed to follow Langmuir-Hinshelwood kinetics.

Acknowledgements

The author wish to thank Indonesia Toray Science Foundation (ITSF) for a research grant (1999) and Japan International Cooperation Agency (JICA) for financial support allowing presentation part of this paper in the 5th Symposium on Agricultural Science and Biochemical Engineering, March 11th, 2001 in Tokyo (Japan).

References

Grau, R.J., Cassano, A.E. and Baltanas, M.A. (1988). Catalyst and network modeling in vegetable oil hydrogenation processes. *Catal. Rev. Sci. Eng.* **30**, 1.

Hui, Y.H. (1996). Bailey's industrial oil and fat products. 5th ed., Wiley, New York.

Koetsier, W.T. and Lok, C.M. (1998). Trends in edible oil hydrogenation catalysts development. *SCI Lect. Pap. Ser.* **96**, 1-4.

Marwan (1998). A study of the selective hydrogenation of 2-butyne-1,4-diol in various forms of three-phase reactor. PhD Thesis, University of Birmingham, U.K.

Tackle, T., Wieland, S. and Panster, P. (1996). Hardening of fats and oils in supercritical CO_2, in *High Pressure Chemical Engineering*, P.R. von Rohr and C. Trepp (eds), Elsevier, Amsterdam.

Winterbottom, J.M., Marwan, Viladeval, J., Sharma, S. and Raymahasay, S. (1997). Selective catalytic

hydrogenation of 2-butyne-1,4-diol to cis-2-butene-1,4-diol in mass transfer efficient slurry reactors, *Studies in Surface Sci. Catal.* **108**, 59-69.