Lipase catalyzed transesterification of tung and palm oil for biodiesel

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Abstract: The tung oil and palm oil were subjected to enzymatic transesterification. Immobilized lipase (Novozyme 435) was used at 10 % w/v vs. oil. The reactions were conducted at 40°C to 60°C with methanol and ethanol at a molar ratio of 1:3 for 24 hours. Temperature was found critical for the conversion efficiencies. Under 55°C after 24 hour, the optimal conversions of tung oil and palm oil fatty acid methyl esters (FAMEs) were 48 % and 63 %. The optimal conversions for tung oil and palm oil fatty acid ethyl esters (FAEEs) at 50°C were 20 % and 55 % respectively at 50°C. It was found the effciencies of FAEEs conversion were lower than the ones of FAMEs conversion. It was found that the tung oil consisted of 80 % unsaturated fatty acids, and palm oil consisted by just over 50% saturated fatty acids, by contrast. The results showed that the fatty acid composition of oil could directly impact on the efficiencies of enzymatic transesterification. A numerical model was derived to describe the reaction in this two-phase system. It was found that fitted mass transfer coefficients and rate constants of the pseudo-steady-state second order reaction were consistent to experimental results.

Keywords: *Biodiesel, Lipase, Palm oil, Transesterification, Tung oil.*

1. Introduction

Tung Tree (*Vernicia fordii*) is widely distributed in Taiwan, as well as in southern China, Burma, and northern Vietnam. Its seed oil, as known as tung oil, had been conventionally used in lamps for lighting, as well as an ingredient for wood paint and varnish. Currently, non-edible oils have been more favourable to serve as biodiesel feedstocks to avoid competitions with food sources under increasing population pressures. The utilization of seed oil from tree sources can have synergistic benefits with afforestation, like carbon sequestration and climate mitigation. Lipase transesterification of triglycerides is an eco-friendly alternative to chemical process due to a lower process temperature and an improved selectivity [1, 2]. In addition, many operational advantages of using immobilized lipase were reported [3, 4]. Few catalytic transesterification of tung oil were reported [5], and even fewer lipase transesterification of tung oil for biodiesel production was reported [6].

In order to characterize the enzymatic transesterification for tung oil, various temperatures were employed with methanol and ethanol. The results were compared to the ones of the palm oil. In contrast to mono-phase three-step reactions [7-9], fewer models were considering two-phase mass transfers for immobilized lipases [10, 11]. A numerical model, considering dual phase mass transfer coefficients and rate constants of the pseudo-steady-state second order reaction, was derived to describe the reaction in this two-phase system. No other published studies compared the differences for transesterification by immobilized lipases between two plant oils with different degree of unsaturation in a two-phase system.

2. Methodology

2.1. Experimental

2.1.1. Materials and analytical methods

The locally obtained tung and palm oils were de-waxed by dichloromethane [12]. Their fatty acid contents were verified using a G C/MS following protocols described by Chinese National Standard (CNS) 15051 (2007) and ISO 5508 (1990). The composition is listed in Table 1. Lipase immobilized onto catalytic exchange resins (Novozyme 435, B aesvegard, Denmark) was used without further treatments.

Table 1. Fatty acids composition of tung oil and palm oil.

Plants	C16:0	C18:0	C18:1	C18:2	C18:3$^{\Delta 9,11,13}$
Tung oil	2.67	2.4	7.88	6.6	80.46
Palm oil	52.71	3.8	36.73	6.7	--

2.1.2. Reaction Conditions

Tung and palm oils were subjected to enzymatic transesterification, with parameters from the studies cited in a recent review [13]. Immobilized lipase was used at 10 % w/v vs. oil [14]. The reactions were conducted at the oil to alcohol molar ratio for 1:3. The reaction temperature was set at 40^{o}C, 45^{o}C, 50^{o}C, 55^{o}C, 60^{o}C with methanol for 24 hours. A stirring rate of 700 rpm was applied. Conversions by enzymatic transesterification were also quantified using a GC/MS based on the above protocols.

2.2. Numerical model

2.2.1. Mass transfer

Lipase was a water-soluble enzyme, and the catalyst particles are surrounded by a hydrophilic film consisting of methanol/ethanol and glycerol. The immiscible mixture of methanol/ethanol and tung/palm oil formed a film consisting mass transfer resistance:

$$-\frac{dC_A}{dt} = k_1(C_A - C_{As}) \quad (1)$$

where k_1 was the mass transfer coefficients of tung/palm oils; C_A and C_{AS} were the tung/palm oil concentrations in the oil phase and on the interfacial area, respectively, and t was time. In a mass-transfer limiting case, C_{AS} could be ignored:

$$-\frac{dC_A}{dt} = k_1 C_A \quad (2)$$

$$-\frac{dC_{A0}(1-X_A)}{dt} = k_1 C_{A0}(1-X_A) \quad (3)$$

$$\frac{dX_A}{dt} = k_1(1-X_A) \quad (4)$$

X_A was the conversion of tung/palm oils.

2.2.2. Pseudo steady-state second order reaction

After mass transfer resistance was overcome, a pseudo steady-state second order reaction was assumed:

$$-\frac{dC_A}{dt} = k_2 C_A{}^2 \tag{5}$$

$$-\frac{dC_{A0}(1-X_A)}{dt} = k_2 C_{A0}^2 (1-X_A)^2 \tag{6}$$

$$\frac{dX_A}{dt} = k_2 C_{A0} (1-X_A)^2 \tag{7}$$

k_2 was the rate constant of the pseudo-steady-state second order reaction; C_A and C_{A0} were the tung/palm oil concentrations at $t = t$ and $t=0$.

2.2.3. Numerical procedures

The parameters k_1 and k_2 were obtained from non-linear regression of the experimental oil conversion versus time data using Eq. (1-7) using SigmaPlot for Windows Version 10.0.

3. Results and Discussions

3.1. Effect of Alcohols

Figure 1 shows the effect of alcohols on the conversions of tung and palm oils at 50°C. The model fitted well with the experimental data. Conversions of tung oils at 24 hours were very sensitive to alcohol used in the transesterification: 40 % with methanol and 18 % with ethanol. Although conversions of palm oils at 24 hours were not very sensitive to alcohol used, the system using methanol demonstrated greater initial conversions for the first 12 hours than the one using ethanol.

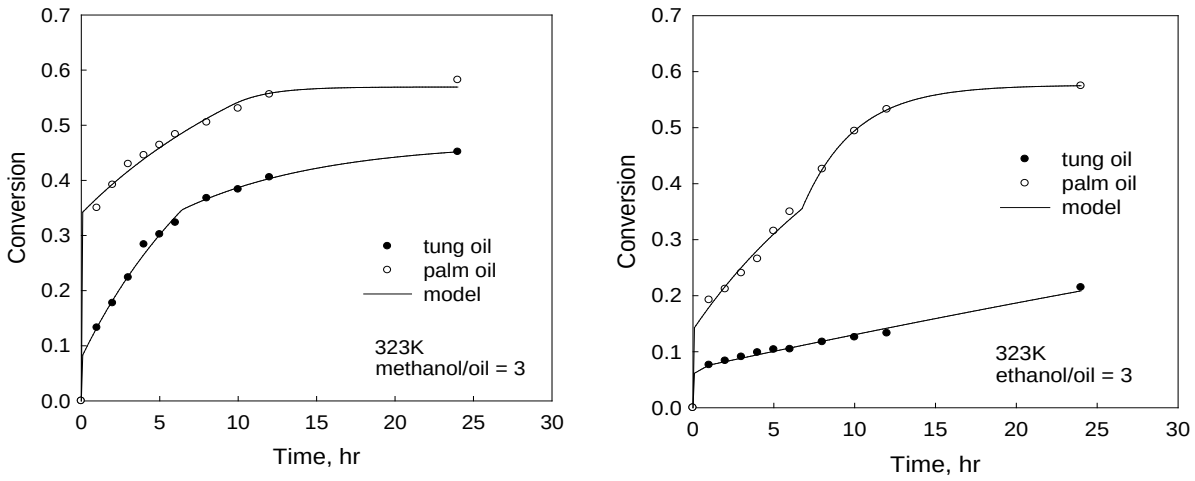

Fig. 1. Effect of alcohols on the conversions of tung/palm oils at 50°C. Left panel: methanols; right panel: ethanol.

3.2. Effect of Temperature

3.2.1. Reaction with methanol

Figure 2 shows the effect of temperature on the conversions of tung/palm oils using methanol from 45 to 55°C. The model fitted well with the experimental data. Conversions of both oils at 24 hours were slightly increased with this temperature increment. Again, greater initial conversions for the first 12 hours were shown for both oils.

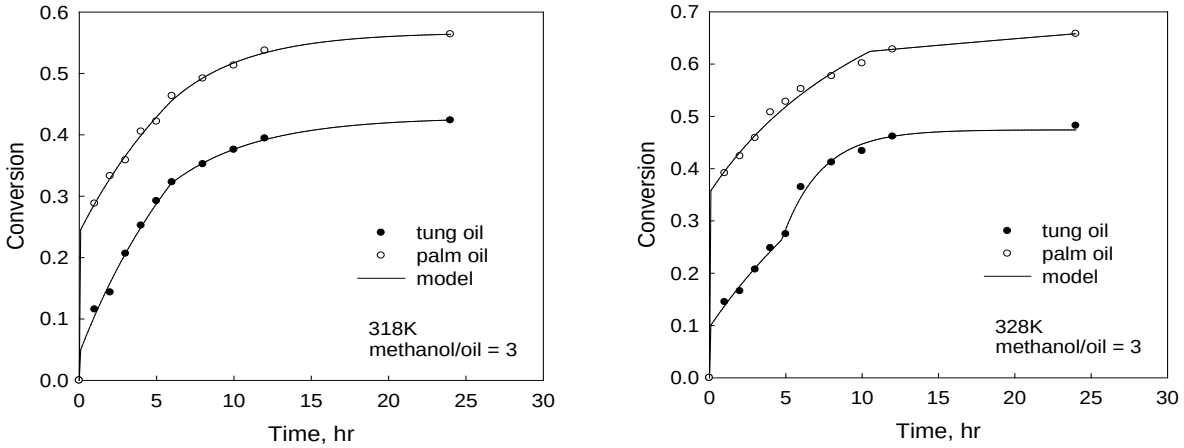

Fig. 2. Effect of temperature on the conversions of tung/palm oils using methanol. Left panel: 45°C; right panel: 55°C.

3.2.2. Reaction with ethanol

Figure 3 shows the effect of temperature on the conversions of tung/palm oils using ethanol from 40 to 50°C. The model fitted well with the experimental data. Conversions of both oils at 24 hours were increased with this temperature increment. Grater initial conversions for the first 12 hours were shown for both oils.

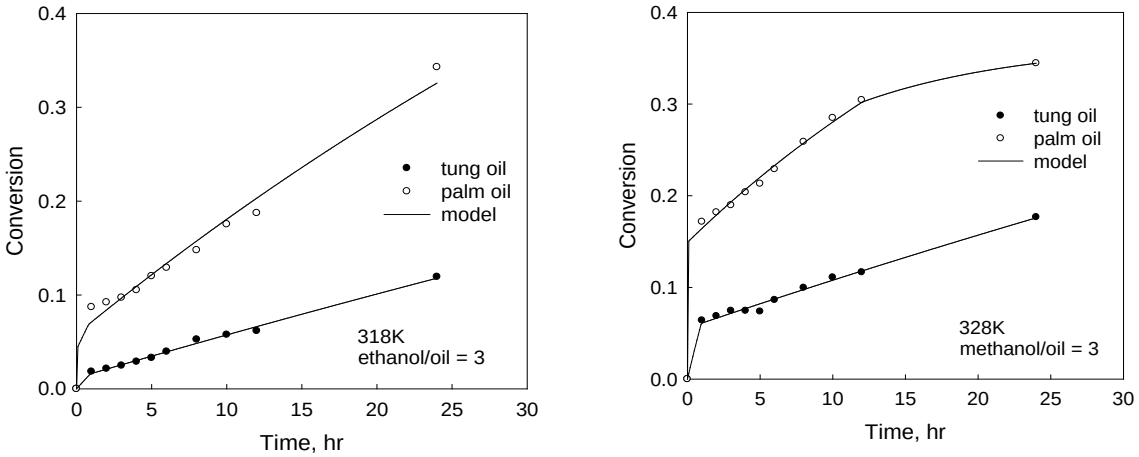

Fig. 3. Effect of temperature on the conversions of tung/palm oils using ethanol. Left panel: 45°C; right panel: 55°C.

3.3. Comparison of the kinetic parameters

Shown by Figure 1 to 3, the model fitted well with the experimental data for all cases. Trends of the obtained kinetic parameters were consistent to the conversions of experimental data. Then the physical meanings of the obtained kinetic parameters could be further discussed. Effect of reaction temperatures on the obtained kinetic parameters are listed in Table 2.

Table 2. Effect of reaction temperatures on the obtained kinetic parameters

T (°C)	Tung oil				Palm oil			
	Methanol		Ethanol		Methanol		Ethanol	
	k_1 (h^{-1})	k_2 ($M^{-1}h^{-1}$)	k_1 (h^{-1})	k_2 ($M^{-1}h^{-1}$)	k_1 (h^{-1})	k_2 ($M^{-1}h^{-1}$)	k_1 (h^{-1})	k_2 ($M^{-1}h^{-1}$)
40	214	0.050	0.0052	0.0076	--	--	--	--
45	378	0.072	8.6E-06	0.018	939	0.087	315	0.037
50	508	0.070	0.0391	0.019	1153	0.067	692	0.058
55	570	0.073	5.6E-06	0.068	1182	0.100	719	0.071
60	770	0.088	7.8E-06	0.041	915	0.093	250	0.061

The mass transfer coefficients (k_1) of tung oil with methanol were from 214 to 770 h^{-1}, generally less than 915 to 1182 h^{-1} of palm oil system. The highest mass transfer coefficients (k_1) of tung oil and palm oils were exhibited at 60 and 55°C, respectively. The mass transfer coefficients (k_1) of ethanol system were generally less than the ones of methanol system for both oils. The magnitude of order was similar for mass transfer coefficients (k_1) of palm oils but the differences between using methanol and ethanol were much greater for tung oils. The above finding for the difference caused by different alcohols was consistent to previous work using waste animal fats [15].

The reaction rate constants (k_2) of tung oil system using methanol were much greater than the ones using ethanol. However, the values in Table 2 for tung oils were of same magnitude of order. In the other hand, the reaction rate constants (k_2) of palm oil showed the same trend as tung oils. And the differences for palm oils were even smaller between methanol and ethanol. The above results implied that the safer ethanol could be employed for enzymatic transesterification.

The above finding suggested that the mass transfer of triglycerides into the surface of the immobilized lipase could play a deciding role for reduced conversions shown by Tung oils. The majority of highly unsaturated chain of Tung oils fatty acids may contribute higher affinities among tung oil triglycerides.

4. Conclusions and Recommendations

The present study showed that the fatty acid composition of oil could directly impact on the efficiencies of enzymatic transesterification. A numerical model with mass transfer coefficients and rate constants of the pseudo-steady-state second order reaction were successfully employed to describe the conversion. It was found that the mass transfer played a more important role than the one by reaction during enzymatic transesterification. The above finding suggested that the increased mixing could improve the processes for biodiesel conversion from tung oils.

References

[1] E. Hernandez-Martin, C. Otero, Different enzyme requirements for the synthesis of biodiesel: Novozym 435 and Lipozyme TL IM. Bioresource Technology 99, 2008, pp. 277-286.

[2] S. V. Ranganathan, S. L. Narasimhan, K. Muthukumar, An overview of enzymatic production of biodiesel, Bioresource Technology 99, 2008, pp. 3975-3981.

[3] V. M. Balcao, A. L. Paiva, F. X. Malcata, Bioreactors with immobilized lipases: state of the art, Enzyme and Microbial Technology 18, 1996, pp. 392-416.

[4] J. W. Chen, W. T. Wu, Regeneration of immobilized *Candida antarctica* lipase for transesterification, Journal of Bioscience and Bioengineering 95, 2003, pp. 466-469.

[5] J, Park, D. Kim, Z. Wang, P. Lu, S. Park, J. Lee, Production and characterization of biodiesel from tung oil, Biotechnology for Fuels and Chemicals 148, 2008, pp. 109-117.

[6] G. Z. Xu, B. L. Zhang, H. L. Liu, A study on immobilized lipase catalyzed transesterification reaction of tung oil, Agricultural Science in China 39, 2006, pp. 2089-2094.

[7] H. Noureddini, D. Zhu, Kinetics of transesterification of soybean oil, Journal of the American Oil Chemists' Society 74, 1997, pp. 1457-1463.

[8] D. Darnoko, M. Cheryan, Kinetics of palm oil transesterification in a batch reactor, Journal of the American Oil Chemists' Society 77, 2000, pp. 1263-1267.

[9] B. Freedman, R. O. Butterfield, E. H. Pryde, Transesterification kinetics of soybean oil, Journal of the American Oil Chemists' Society, 1986, 63, pp. 1375-1380.

[10] V. Calabro, E. Ricca, M. G. De Paola, S. Curcio, G. Iorio, Kinetics of enzymatic transesterification of glycerides for biodiesel production, Bioprocess and Biosystems Engineering, 2010, 33, pp. 701-710.

[11] S. Hari Krishna, N. G. Karanth, Lipases and lipase-catalyzed esterification reactions in nonaqueous media, Catalysis Reviews, 2002, 44, pp. 499-591.

[12] A. Randunz, G. H. Schmid, Wax esters and triglycerides as storage substances in seed of *Buxus sempervirens*, 2000, European Journal of Lipid Science and Technology, 102, pp. 734-738.

[13] S. V. Ranganathan, S. L. Narasimhan, K. Muthukumar, An overview of enzymatic production of biodiesel, Bioresource Technology, 2008, 99, pp. 3975-3981.

[14] S. Shah, M. N. Gupta, Lipase catalyzed preparation of biodiesel from Jatropha oil in a solvent free system, Process Biochemistry, 2007, 42, pp. 409-414.

[15] Y. Liu, H. Tan, X. Zhang, Y. Yan, B.H. Hameed, Effect of monohydric alcohols on enzymatic transesterification for biodiesel production, Chemical Engineering Journal, 2010, 157, pp. 223–229.