

A KINETIC STUDY ON FREE FATTY ACID ESTERIFICATION OF NEEM SEED OIL

J.M.K.T. Jayawardena and C.S. Kalpage

Department of Chemical and Process Engineering, University of Peradeniya

Introduction

Biodiesel is a renewable, alternative liquid biofuel processed (transesterified) from vegetable oils and animal fats. Oils and fats containing over 2% free fatty acids (FFA) are subjected to esterification before transesterification in order to reduce interference of FFA.

Neem seed oil is a potential feed stock for biodiesel production in Sri Lanka (Jayawardena and Kalpage, 2008). High FFA content (>14%) of this oil requires pretreatment before transesterification.

Kinetic studies of biodiesel processing reactions were reported for various precursors (Freedman *et al.*, 1986; Nouredini and Zhu, 1997; Berrios *et al.*, 2007). Results of these studies provide parameters that can be used to predict the extent of the reaction at any time under the given operating condition.

The main objective of this study was to apply the model proposed by Berrios *et al.*, (2007) for sunflower oil into neem seed oil esterification. Further, the dependency of specific rate constants k_1 and k_2 , on reactants (methanol to FFA molar ratio) was also investigated.

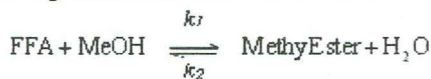
Materials and Methods

Materials: Neem seed oil was supplied by the NERD Center of Sri Lanka. All other chemicals were of

commercial grade, purchased from the local market.

Method: The reaction kinetic data reported by authors of this study were used for the modeling (Jayawardena and Kalpage, 2008).

The chemical reaction taking place during esterification is as follows.



H_2SO_4 was used as a catalyst. The kinetic model shown in equation [1] was used in the modeling of esterification reaction (Berrios *et al.*, 2007).

$$-\frac{d[\text{FFA}]}{dt} = k_1[\text{FFA}] - k_2[\text{ME}][\text{H}_2\text{O}]$$

[1]

where $[\text{FFA}]$, $[\text{ME}]$ and $[\text{H}_2\text{O}]$ are concentrations of free fatty acid, methyl ester and water in the reaction vessel, respectively. k_1 and k_2 are specific rate constants.

The equation [1] was solved assuming $[\text{ME}]$ and $[\text{H}_2\text{O}]$ are zero at $t = 0$ (Berrios *et al.*, 2007).

$$E = \frac{F_0 (e^{2k_2\alpha t} - 1)}{(\beta - 0.5) + (\beta + 0.5)e^{2k_2\alpha t}}$$

[2]

where

E = moles of FFA removed, mmol

$$F_0 = \text{FFA at } t=0,$$

$$\beta = \frac{\alpha}{K}, \quad K = \frac{k_1}{k_2} \quad \text{and} \quad \alpha = \sqrt{\left(\frac{K^2}{4}\right) + KF_0}$$

The experimental data were fitted to the model by optimizing k_1 and k_2 using Newton's Least Square Method (Kalpage, 2005). A sensitivity analysis was also performed and verified that the model can produce experimental data with high accuracy.

Results and Discussion

MeOH concentration was not considered as a time dependant parameter in the proposed mathematical model because of high initial excess MeOH load (molar ratio of methanol to FFA varied from 7:1 to 18:1 in this investigation). Moreover the model was derived by considering four major assumptions (Berrios *et al.*, 2007).

Plotted in Figure 1 are curves generated from the model and the experiment data.

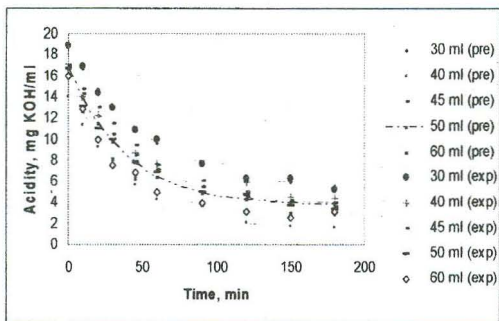


Figure 1 . Comparison of experimental data (exp) and predicted curves (pre) at different MeOH loads (test condition: 200ml oil and 0.5ml H₂SO₄ at 60 °C)

Rate constants for various MeOH to FFA ratios were plotted in Figure 2. It was observed that k_1 (s⁻¹) remained

greater than k_2 (ml.mmol⁻¹.s⁻¹) throughout the tested region. k_1 increases and k_2 decreases with increasing methanol load. This indicates that the forward reaction (i.e. esterification) is favoured by methanol load.

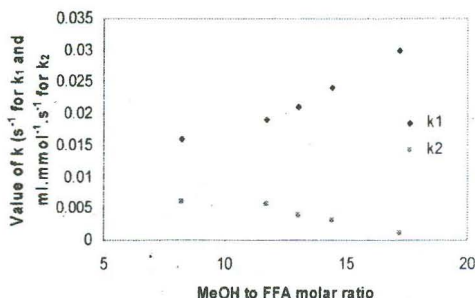


Figure 2. Rate constants for variable MeOH/FFA molar ratios (H₂SO₄ 0.5 ml, 60°C)

Rate constants (k_1 and k_2) at different temperatures were determined using experimental data. Shown in Figure 3 is experimental data and predicted curves of acid values.

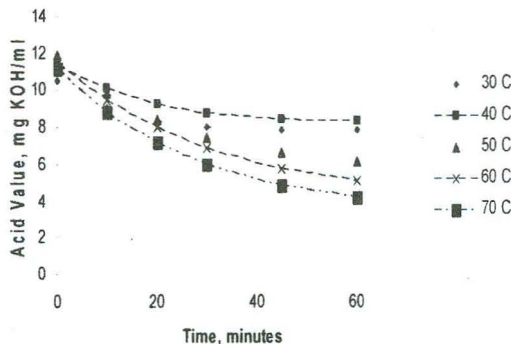


Figure 3. Experimental and predicted acid values at different operating temperatures

Effect of reaction temperature on reaction rate constants is shown in Figure 4.

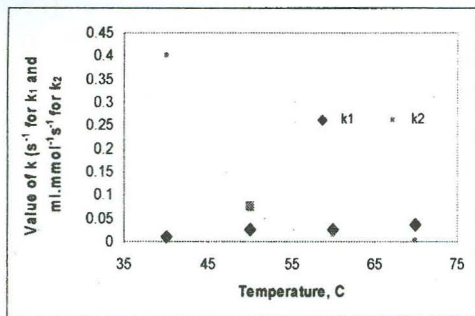


Figure 4. Effect of rate constants with variable reaction temperatures (Oil 100 ml, MeOH 20ml, H₂SO₄ 0.25 ml)

A retrograde behavior of rate constants was observed; k_1 was lesser than k_2 for temperatures below 54°C, and the phenomenon was reversed above the said temperature. This is the first time such observation is reported in literature. The retrograde behaviour is attributed to the reduced methanol concentration in the reaction vessel due to high evaporation rate as the boiling temperature of methanol is reached. However, further studies are required to confirm this explanation.

Conclusion

Main conclusions drawn from this study are given below:

1. Neem oil esterification can be modeled using the kinetic model proposed by Berrios *et al.*, (2007)
2. Rate constants k_1 and k_2 depend on methanol quantity in the reactor. High methanol dosage will promote the forward reaction rate.

3. A retrograde behavior k_1 and k_2 on temperature is reported for the first time in literature, but further studies are required to confirm the result.

Acknowledgements

Authors are willing to acknowledge the Dept. of Chemical and Process Engineering of the University of Peradeniya and Practical Action for the financial assistances and other support provided for the study.

References

- Berrios, M., Siles, J., Martin, M.A., and Martin, A. (2007). A kinetic study of the esterification of free fatty acids (FFA) in sun flower oil, *Fuel*, 86: 2383–2388.
- Freedman, B., Butterfield, R.O. and Pryde, E.H. (1986). Transesterification kinetics of soybean oil. *J. Am. Oil Chem. Soc.* 63:1375-1380
- Jayawardena J.M.K.T., and Kalpage C.S. (2008). Influence of operating parameters on the pre-treatment of *Azadirachta indica* (neem) seed oil as a feed stock for bio-diesel production, Proceedings of Peradeniya University Research Sessions, Vol. 13.
- Kalpage, C.S. (2005). Wastewater treatment by activated carbon: regeneration study by supercritical carbon dioxide, *PhD Thesis*, University of Birmingham, UK
- Noureddini, H., and Zhu, D (1997) Kinetics of transesterification of soybean oil, *Ibid.* 74:1457-1463.