

Methanol-Based Transesterification Optimization of Waste Used Cooking Oil over Potassium Hydroxide Catalyst

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Abstract: Problem statement: Waste used Cooking Oil (WCO) harmfully affected to environment and human's health can be a feedstock for producing biodiesel. **Approach:** The conversion of Fatty Acid and Free Fatty Acid (FFA) of WCO with 15.0% w/w FFA content to biodiesel was studied through transesterification reactions. This work investigated the effects of alcohol and catalyst quantity, reaction time and temperature on the FFA conversion and biodiesel production and also determines the optimum condition. **Results:** The optimum use of 5% w/w potassium hydroxide (KOH) catalyst at 70°C for 2 h yielded 88.20% FFA conversion and 50% biodiesel recovery of WCO. For the reaction rate analysis, based on Arrhenius equation, the activation energy of 47.07 kJ.mol⁻¹ and the pre-exponential factor of 7.58×10¹⁰ min⁻¹ were obtained using pseudo first-order model. In addition, the produced biodiesel was blended with diesel in the volumetric proportions of 5:95 (ExB5), 20:80 (ExB20) and 50:50 (ExB50) and characterized by FT-IR, in order to compare to biodiesel blend sold in local gas station (B5). It was observed that the ExB5 has exhibited the same functional group as of the B5. **Conclusion:** The produced biodiesel may be used in diesel engines if other properties are tested for compatibility. This provides one more choice for alternative energy and commercialization.

Key words: Wasted used cooking oils, free fatty acid, transesterification, esterification, biodiesel

INTRODUCTION

Waste used Cooking Oil (WCO) is a residue from a variety of sources, e.g., restaurants, food industrial or domestics, which not only harms human's health but also causes environmental problems. However, WCO can be used as a raw material for biodiesel production. By this manner, the production of biodiesel from WCO to partially substitute petroleum diesel is an alternative way for environment protection and energy security.

General vegetable oils or animal fats comprise the main constituent of Triglycerides (TGs) with lower density compared to water and may be solid or liquid at normal room temperature. TGs are esters of saturated and unsaturated monocarboxylic acids with the trihydric alcohol glyceride. These esters are collectively called triglycerides, which can react with alcohol in a presence of catalyst, widely known as transesterification process (Balat and Balat, 2010). Figure 1 shows that a triglyceride reacts with short chain alcohols such as methanol and ethanol in the presence of a catalyst to produce Fatty Acid Methyl Esters (FAMES) or Fatty

Acid Ethyl Esters (FAEEs) and glycerol (Encinar *et al.*, 2007) where R₁, R₂, R₃ represent long chain of fatty acid.

Generally, there are five main types of chains in vegetable oils and animal oils, i.e., palmitic, stearic, oleic, linoleic and linolenic (Chhetri *et al.*, 2008). When the triglyceride is decomposed, stepwise to diglyceride, monoglyceride and ultimately to glycerol, one mole of fatty acid ester is liberated in each step. Methanol is preferably used for the transesterification due to its low cost and advantages in physical and chemical properties, i.e., polarity and small molecule (Sanli and Canakci, 2008). In addition, it can easily react with triglycerides and catalyst can be dissolved faster than other alcohols.

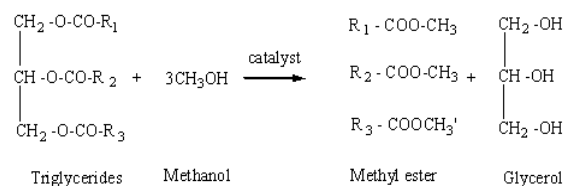


Fig. 1: The transesterification of triglyceride with methanol

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F = Concentration coefficient of the KOH standard solution
 g = Sample weight (g)

Gas chromatography: The quantitative analysis of the WCO biodiesel was carried out using a temperature programmed Varian CP-3800 gas chromatograph. One microliter of the clean treatment upper oil layer was dissolved in 10 mL n-heptane and 1 μ L internal standard solution (heptadecanoic acid methyl ester, conforming to EN 14103 standard) for GC analysis. On each run, the 1 μ L sample was injected into the GC at the temperature of 140°C and held for 5 min. The GC's oven was heated at 10°C.min⁻¹ rate to 250°C. Helium was used as a carrier gas, operated at 10 bar pressure and 20 mL.min⁻¹ flow rate. The injector and the Flame Ionization Detector (FID) were set up to the operating temperature of 250°C. Calibration standards were prepared from a known concentration of methyl esters solution. The standards were used to plot a calibration curve in determining the methyl esters (Madras *et al.*, 2004).

Fourier Transform Infrared spectroscopy (FTIR) determination: The WCO biodiesel content in a blended fuel was determined by infrared spectroscopy. Initially, the measurement of absorbance was performed using 16 scans in the range of 4000 cm⁻¹ down to 400 cm⁻¹ with 4 cm⁻¹ resolution. The WCO biodiesel-diesel mixtures were tested in the volumetric proportions of 50:50 (ExB50), 20:80 (ExB20) and 5:95 (ExB5). All absorbance measurements were performed with a Fourier Transform Infrared Spectrometer (FTIR) JASCO model 4100.

RESULTS

Effects of methanol content: Methanol is an important reactant used in the process of esterification of FFA and transesterification of fatty acids; it merges with triglycerides and FFA to form methyl esters. The effect of methanol-to-WCO weight ratio on the conversion of FFA and biodiesel obtained is shown in Fig. 4, at 5.0 wt% KOH, 70°C reaction temperature and 2 h reaction time.

Effects of catalyst amount: The amount of catalyst can affect the transesterification (Santos *et al.*, 2009), resulting in different FFA conversion and biodiesel yield as shown in Fig. 5.

Effects of reaction time: The effects of reaction time were investigated using the optimal parameters obtained from the investigation of methanol and catalyst amount effects. The time was varied from one to five hours as the results are shown in Fig. 6.

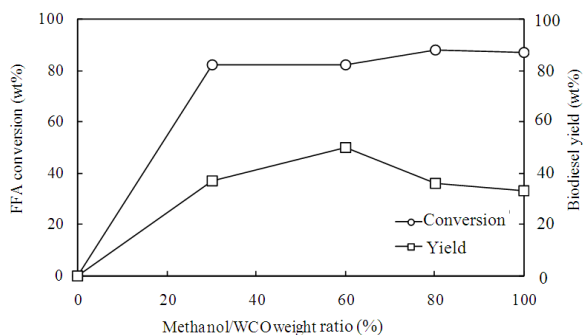


Fig. 4: Effect of methanol/WCO weight ratio on the FFA conversion and biodiesel yield, 5.0 wt% KOH, 70°C temperature, 2 h reaction time

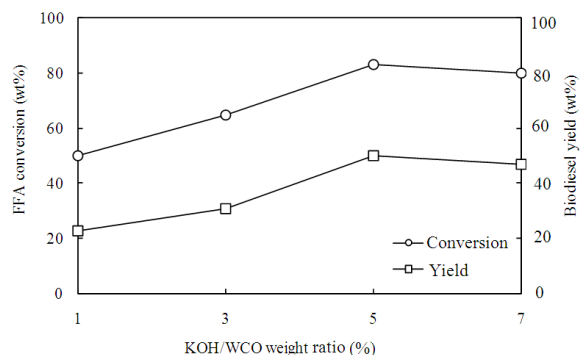


Fig. 5: Effect of KOH/WCO weight ratio on the FFA conversion and biodiesel yield, 60 wt% methanol, 70°C temperature, 2 h reaction time

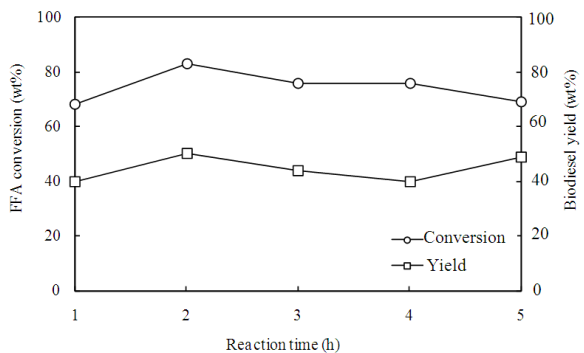


Fig. 6: Effect of reaction time on the FFA conversion and biodiesel yield, 60 wt% methanol, 5.0 wt% KOH, 70°C temperature

Effects of reaction temperature: In studying the effect of reaction temperature (Fig. 7), the experiments were conducted using the obtained optimum amounts of

catalyst and methanol/WCO weight ratio, while reaction time was maintained at 2 h. The reaction temperature affected on the biodiesel yield were varied from 50-100°C in the condensed flask to avoid methanol phase changed (methanol boiling point at 64°C). Figure 8 shows the optimum point for biodiesel yield and FFA conversion at 70°C reaction temperature.

WCO biodiesel and commercial biodiesel comparison: Figure 9a shows the Infrared (IR) spectra of WCO before and after treatment (B100). The IR-spectra of WCO biodiesel-diesel blends and commercial Biodiesel (B5) in Fig. 9b-d shows an absorption peak measurement (Aliske *et al.*, 2007).

DISCUSSION

It has seen in Fig. 4 that the use of low methanol amount of 0.5 wt% led to the FFA conversion become incompleated and resulted in a low yield of biodiesel. The yield increased and reached optimum reactions at a methanol amount of 60 wt%. At higher methanol amount, the FFA conversion increased but the yield decreased. This is due to the transesterification was reversible (Shu *et al.*, 2010) as the additional methanol accelerates considerably an adjustment of the new equilibrium. A high amount of methanol interferes the separation of glycerol due to an increase in solubility (Maceiras *et al.*, 2009) while the glycerol remaining in the solution drives the reaction equilibrium back, resulting in the lower yield of biodiesel (Kotwal *et al.*, 2009).

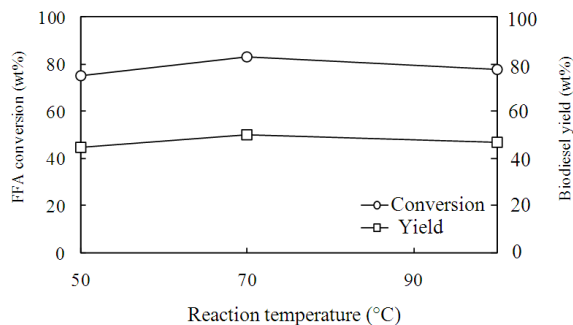


Fig. 7: Effect of reaction temperature on the FFA conversion and biodiesel yield, 60 wt% methanol, 5.0 wt% KOH, 2 h reaction time

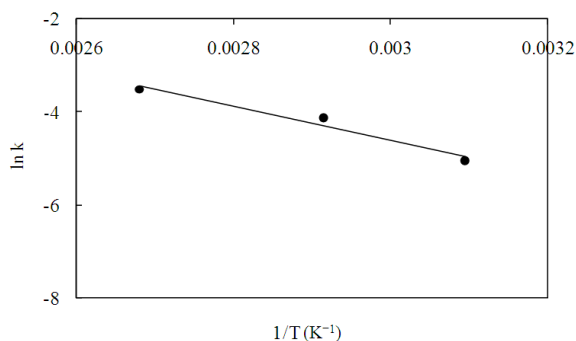


Fig. 8: Arrhenius plot for transesterification rate constant of WCO methyl ester with 60 wt% methanol, 5.0 wt% KOH, 2 h reaction time

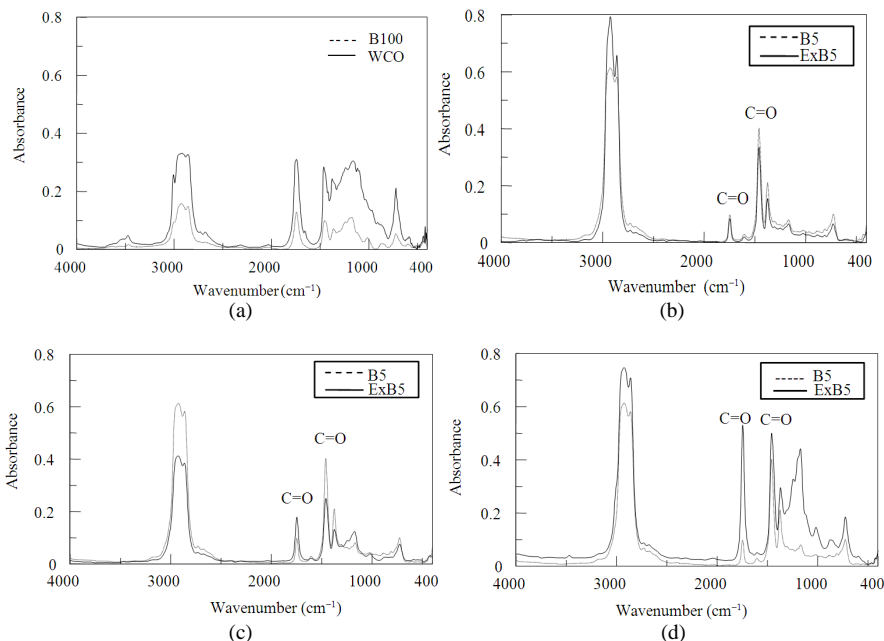


Fig. 9: Spectra comparison of WCO biodiesel-diesel blends and commercial B5 biodiesel blends: (a) B100 and WCO (b) B5 and ExB5, (c) B5 and ExB20 and (d) B5 and ExB50

In Fig. 5, at the KOH/WCO weight ratios of 1 and 3, the WCO incompletely converted to biodiesel. In this experiment, the maximum conversion of FFA and biodiesel yield occurred at KOH/WCO weight ratio of 5. When the amount of KOH/WCO weight ratio exceeded 5 wt%, the conversion of FFA decreased. Although higher amounts of KOH were added, the biodiesel yield decreased as the reverse reaction (Ataya *et al.*, 2007). In addition, more soap was observed, as the excess KOH favored the saponification reaction. This was observed at the catalyst concentration of 7.0 wt%.

It was observed from Fig. 6 that at 1 h reaction time, the FFA conversion and biodiesel yield seemed not to reach their completion. This may be due to the esterification reactions are faster than transesterification reactions (Leung *et al.*, 2010). However, biodiesel yield increased as the time was lengthened to 2 h. With the longer reaction period of up to 3 h, the decreased yield and more soap formation were observed during washing. This occurred as a result of the hydrolysis of esters which tends to cause more fatty acids to form soap (Pena *et al.*, 2009). The optimum yield was observed at the reaction time of 2 h.

In Fig. 7, at 100°C, the yield slightly inclined, owing to high temperatures favoring the side reaction of transesterification, i.e., hydrolysis and saponification (Pena *et al.*, 2009). The saponification was also observed during washing with warm deionized water. It has to be noted that lower temperatures may require longer reaction time for the completion of the reaction, as found by the slow forming of the phase change. However, at higher temperature, it may require a shorter time to complete due to the fast forming of phase change.

In order to quantify the temperature effect on the reaction and evaluate the apparent activated energy of the reaction, the experimental results were further analyzed in terms of the kinetics of WCO methyl esters. As the operating parameters for the reaction were fixed at 60 wt% methanol, 5.0 wt% KOH and 2 h reaction time, the reaction data were fitted to a first-order model in the form of Arrhenius rate equation (Jain and Sharma, 2010) as:

$$k = A \times e^{-\frac{E_a}{RT}} \quad (3)$$

Where:

A = Pre-exponential factor

E_a = Apparent activation energy

R = Gas constant

T = Reaction temperature in Kelvin

The plot of $\ln k$ versus $1/T$ in Fig. 8 with the slope of activation energy confirms the pseudo first-order reaction kinetics.

The apparent activation energy in the reaction temperature range from 323-373 K was 47.07 kJ.mol⁻¹ and the corresponding pre-exponential factor was 7.58×10¹⁰ min⁻¹. The obtained activation energy was comparable to that in the published work which used two step H₂SO₄ and NaOH catalysts (E_a = 49.3 kJ.mol⁻¹) (Jain and Sharma, 2010) and calcium and lanthanum oxides catalyst (E_a = 87.8 kJ.mol⁻¹) (Yan *et al.*, 2009) transesterification of vegetable oils. The E_a from this work represents an energy required for the transesterification of WCO that is favorable for biodiesel production from high FFA oils.

It was observed from Fig. 9b-d that WCO biodiesel for all proportions and B5 showed many overlap peaks. The prominent peaks from 1850-1450 cm⁻¹ wave number correspond to carbonyl group of ester (C=O) absorption (Nabi *et al.*, 2006) The ester absorbance shown in high intensity for all the WCO biodiesel blends and the ExB5 seem quite perfect in overlapping to the commercial B5 over the range of 4000-400 cm⁻¹ wave number.

CONCLUSION

The transesterification of WCO over KOH catalyst to biodiesel was studied and presented. The operating parameters such as methanol content, catalyst amount, reaction time and reaction temperature were found to affect the reaction. The optimum FFA conversion and biodiesel yield were obtained at 60 wt% methanol/WCO weight ratio, 5 wt% KOH, 2 h reaction time and 70°C reaction temperature. At this condition, the reaction gave comparatively low activation energy. The infrared absorbance measurement to determine the produced WCO biodiesel performance and its blends in the volumetric WCO biodiesel: diesel proportions of 5:95 (ExB5), 20:80 (ExB20) and 50:50 (ExB50) were determined by FTIR. The spectra obtained indicated peaks of WCO biodiesels and B5 overlapped the carbonyl (C=O) absorption peak. The results of IR spectra make this proportion WCO biodiesel compatible to the B5 biodiesel blends sold in Thailand. This can be considered as an alternative environmentally-friendly fuel for diesel engines.

ACKNOWLEDGEMENT

The researchers thank Kasetsart University Siracha Campus for the financial support to this project (Contract No. 532101) and the Faculty of Resources

and Environment for the provision of laboratory equipments. Senior project students Ms. Doungchai Moolsorn and Ms. Nuttaramunya Chantraparakul are acknowledged for their experimental assistance.

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