

Acid-catalyzed production of biodiesel from waste frying oil

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Abstract

The reaction kinetics of acid-catalyzed transesterification of waste frying oil in excess methanol to form fatty acid methyl esters (FAME), for possible use as biodiesel, was studied. Rate of mixing, feed composition (molar ratio oil:methanol:acid) and temperature were independent variables. There was no significant difference in the yield of FAME when the rate of mixing was in the turbulent range 100 to 600 rpm. The oil:methanol:acid molar ratios and the temperature were the most significant factors affecting the yield of FAME. At 70 °C with oil:methanol:acid molar ratios of 1:245:3.8, and at 80 °C with oil:methanol:acid molar ratios in the range 1:74:1.9–1:245:3.8, the transesterification was essentially a pseudo-first-order reaction as a result of the large excess of methanol which drove the reaction to completion ($99 \pm 1\%$ at 4 h). In the presence of the large excess of methanol, free fatty acids present in the waste oil were very rapidly converted to methyl esters in the first few minutes under the above conditions. Little or no monoglycerides were detected during the course of the reaction, and diglycerides present in the initial waste oil were rapidly converted to FAME.

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1. Introduction

Biodiesel oil, having the chemical structure of fatty acid alkyl esters (usually methyl esters, FAME¹), is a clean burning fuel produced from renewable domestic sources such as vegetable oils and animal grease. It is biodegradable, non-inflammable, non-toxic and has a favorable combustion–emission profile, producing much less carbon monoxide, sulfur dioxide and unburned hydrocarbons than petroleum-based diesel [1]. These properties make biodiesel a good alternative fuel to petroleum-based diesel oil.

The cost of biodiesel, however, is higher than that of petroleum-based diesel: US \$1.4–2.4/US gal. biodiesel, compared to US \$1.0–1.5/US gal. petroleum diesel [2]. The

higher cost of biodiesel is due to its being produced mostly from expensive high-quality virgin oil. Use of low-cost feedstock such as waste frying oils and non-edible oils in an acid-catalyzed process should help make biodiesel competitive in price with petroleum diesel [3].

Although the acid-catalyzed reaction requires a longer reaction time and a higher temperature than the alkali-catalyzed reaction, acid catalysis is more efficient when the amount of free fatty acids in the oil exceeds 1% [4–7]. An economic analysis study has shown that the acid-catalyzed procedure, being a one-step process, is more economical than the alkali-catalyzed process, which requires an extra step to convert free fatty acids to methyl esters, thus avoiding soap formation [3,7].

In a study of the acid-catalyzed transesterification of soybean oil, Canakci and Van Gerpen [6] found that the yield of FAME increased with increasing methanol:oil molar ratio, with increasing temperature and with the amount of catalyst. Also, the transesterification reaction was inhibited by the presence of water in the oil phase. High molar ratios of methanol:oil were found necessary to drive the transesterification reaction to completion [6,7].

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¹Abbreviations: DG, diacylglycerol (diglyceride); ESS, extra sum of squares of residuals test; FAME, fatty acid methyl esters; FFA, free fatty acids; GPC, gel permeation chromatography; MeOH, methanol; MG, monoacylglycerol (monoglyceride); TG, triacylglycerol (triglyceride); TGE, triglyceride molar equivalents.

Although the kinetics of the alkali-catalyzed transesterification of oils have been studied [8], detailed kinetic studies of the acid-catalyzed transesterification of waste frying oil have not been carried out previously. Results of such studies are needed to quantify the effects of some important factors affecting the yield and purity of biodiesel, and to obtain suitable kinetic models for better understanding of the transesterification mechanism. The present study is concerned with the effects of feed composition, temperature, and rate of mixing on the kinetics of the acid-catalyzed transesterification reaction, and the determination of the optimal conditions for the reaction.

2. Materials and methods

2.1. Experimental design

The effects of mixing rate, feed composition and temperature on the rate and extent of conversion of oil

to FAME in the acid-catalyzed transesterification reaction were investigated. The response variables chosen were: %yield of FAME at 240 min (X_{240}), overall first-order reaction rate ($k \text{ min}^{-1}$), and time to reach 50% of the maximum yield ($t_{1/2} \text{ min}$).

In order to drive the equilibrium of the transesterification reaction to 100% conversion, the molar ratio of methanol:oil was maintained in the range 50:1 to 250:1. To prevent scorching of the oil by the acid, the acid concentration in the methanol was kept in the range of 0.5–1 M (1.5–3.5 mol% of H_2SO_4 in the total oil–methanol–acid mixture). The constraints on the feed composition are shown in Fig. 1. The actual feed compositions used in nine runs are given in Table 1. All runs were carried out at 70 and 80 °C and one of these runs (run #9, the center point of constraint) was replicated at both temperatures. Run #9 was also carried out at three different stirring speeds: 100, 400, and 600 rpm, to investigate the effect of mixing rate.

2.2. Experimental procedures

2.2.1. Apparatus

The apparatus used for the transesterification reaction was a 5-L stainless-steel jacketed reactor, equipped with an internal cooling coil, a variable speed two-blade propeller turbine agitator, sampling port and a reflux condenser using cold tap water to condense methanol vapor (to prevent buildup of excessive pressure). The temperature of the reactor was controlled and maintained at 70 or 80 °C by means of LabView™ software.

2.2.2. Procedure

Methanol (reagent grade, ACP Chemicals Inc.), concentrated sulfuric acid (ACS grade, BDH Chemicals Inc.) and waste frying oil (from a local restaurant, Sam's University Tavern, Ottawa) were used in the experiments. The waste oil (canola oil, derived from rapeseed oil (*Brassica napus* ssp. *oleifera*), free of erucic acid) contained 6% by weight of free fatty acid (FFA), 12% of diglyceride (DG), 82% triglyceride (TG) and

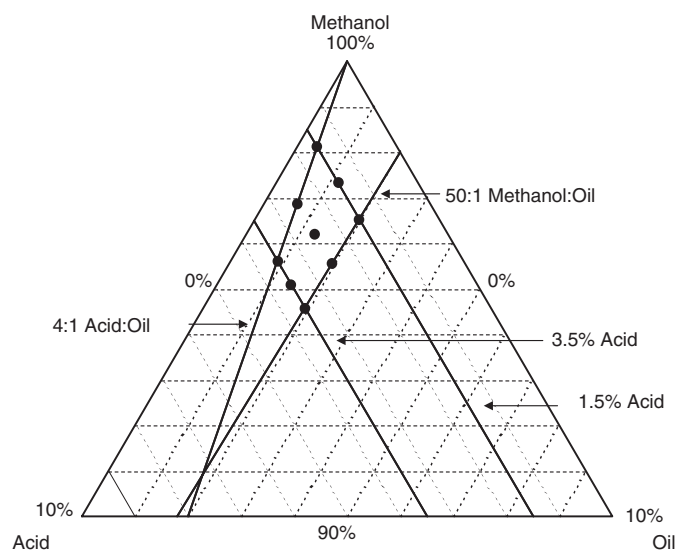


Fig. 1. Constrained mixture design region of feed compositions. ●, indicates run compositions.

Table 1
Yield (mol%) of FAME at 4 h (X_{240}) and first-order rate constant (k) at various feed compositions and temperatures

Feed composition					70 °C		80 °C		
Run	Oil (mol%)	MeOH (mol%)	Acid (mol%)	Oil:MeOH:Acid (molar ratio)	Total volume (L)	X_{240} (mol%)	k (min^{-1})	X_{240} (mol%)	k (min^{-1})
1	0.4	98.1	1.5	1:245:3.8	2.24	99.0	0.0116	99.4	0.0260
2	0.9	95.6	3.5	1:106:3.9	2.56	72.3	0.0057	97.4	0.0124
3	1.9	94.6	3.5	1:50:1.8	2.31	53.9	0.0118	81.1	0.0088
4	2.0	96.5	1.5	1:48:0.8	2.29	46.0	0.0085	71.0	0.0095
5	0.6	96.9	2.5	1:162:4.2	2.37	87.0	0.0087	98.9	0.0169
6	1.4	95.1	3.5	1:68:2.5	2.53	59.6	0.0098	87.7	0.0069
7	1.2	97.3	1.5	1:81:1.3	2.28	50.6	0.0185	71.9	0.0096
8	1.9	95.6	2.5	1:50:1.3	2.64	59.2	0.0140	97.2	0.0101
9	1.3	96.2	2.5	1:74:1.9	2.73	64.7	0.0085	95.8	0.0101
10	1.3	96.2	2.5	1:74:1.9	2.73	66.5	0.0096	98.8	0.0110

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