



Alkali transesterification of linseed oil for biodiesel production

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HIGHLIGHTS

- ▶ Alkali catalyzed transesterification of linseed oil.
- ▶ Effect of the process parameters on equilibrium conversion.
- ▶ Development of a reversible kinetic model for transesterification.
- ▶ Optimization of the kinetic parameters.
- ▶ Simulating the effect of process parameters using optimal kinetics.

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ABSTRACT

The use of renewable vegetable oils derived from plant seeds has gained attention worldwide due to soaring petroleum-crude prices. Physical and/or chemical transformations are used to improve the vegetable oil properties to make it compatible for use in existing engines. Transesterification process reduces the poly-unsaturation of these vegetable oils which results in diesel like fuel (biodiesel). Alkali-catalyzed transesterification is most commonly used process for oils with low free fatty acids and low moisture content. In this study, the kinetics and simulation of alkali-catalyzed transesterification of linseed oil in a batch reactor is reported. The effects of temperature, catalyst concentration, and molar ratio of methanol to triglyceride were investigated experimentally. The equilibrium conversions of triglycerides were observed to be in the range of 88–96%. The equilibrium conversions were achieved within 40 min in all experiments. Increasing the temperature and molar ratio increased the equilibrium conversions; while catalyst concentration had no significant effect. A reversible kinetic model was applied to the observed conversion data. Model parameters for forward and backward reactions were estimated and optimized. Various simulations were also carried out at different conditions to show that beyond a critical molar ratio no significant effect on transesterification kinetics was observed. Characterization of biodiesel produced from linseed oil showed similar properties to mineral diesel.

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1. Introduction

The production and use of petroleum has dominated the chemical process industries. Currently, the limited petroleum reserves are being rapaciously consumed which also leads to various environmental issues [1]. Thus, alternative fuels which are renewable and are also environment friendly are being investigated. Considering the world's insatiable appetite for petroleum, one of the best large-scale renewable sources possible are vegetable oils derived from natural plant seeds. The direct use of vegetable oils in diesel engines poses many problems in the long run. Efforts have been made to develop vegetable oil derivatives that approximate the properties and performance of mineral diesel [2,3].

Transesterification of vegetable oils using alcohol in a catalytic environment is a chemical process to produce diesel-like liquid, biodiesel. Chemically, biodiesel is mono-alkyl esters (fatty esters) of long chain fatty acids [3,4]. Transesterification process consists a sequence of three consecutive reversible reactions; conversions of triglyceride (TG) to diglycerides (DGs), DG to monoglyceride (MG) and MG to glycerol (GLY). Overall three moles of alcohol are required and one mole of monoalkyl ester is obtained in each step. Glycerol is the byproduct. Higher molar ratio than required by stoichiometry is required to shift the equilibrium in forward direction. Transesterification reaction is sensitive to reaction parameters such as the alcohol used, the molar ratio of alcohol to oil (MR), temperature of the reaction (T), catalyst and catalyst amount ($C\%$ w/w of oil), and the stirring rate (SR) [5–9]. The optimal values of these reaction parameters are dependent upon the feedstock characteristics.

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Nomenclature

a	initial moles of triglyceride (TG)	MW_{LSO}	mol wt. of linseed oil (872.54 gm/gm mole)
a	order of the reaction wrt to TG	MW_{LME}	molecular weight of LME (292.18 gm/gm mole)
a'	moles of alkyl ester (biodiesel) formed	$MW_{Methanol}$	mol wt of methanol (32.04 gm/gm mole)
b	order of the reaction wrt to methanol (MeOH)	MW_{oleic}	molecular weight of oleic acid (282 gm/gm mole)
c	order of the reaction wrt to linseed methyl ester (LME)	R	universal gas constant (1.98E–03 kcal/g mol K)
C_A	concentration of TG at time t (moles/l)	SG_{LME}	specific gravity of LME (0.852)
C_{A0}	initial concentration of TG (moles/l)	T	temperature ($^{\circ}\text{C}$ or K)
C_B	concentration of MeOH (moles/l)	t	reaction time (min)
C_C	concentration of LME (moles/l)	V_0	initial volume of oil used (1 l)
C_D	concentration of glycerol (moles/l)	V_B	volume of H_2SO_4 required for titration of blank sample (ml)
d	order of the reaction wrt to glycerol (GLY)	$v_u (v)$	volume of upper layer (ml)
E_a	activation energy (kcal/gm mol)	W	weight of oil sample (gm)
EW_{KOH}	equivalent weight of KOH (56.11 gm/gm mol)	w	weight of LME produced (gm)
K	equilibrium rate constant (min^{-1})	W_{LSO}	weight of linseed oil (903 gm)
k	rate constant (min^{-1})	x	amount of the catalyst (gm)
k_0	frequency factor (min^{-1})	X_A	conversion of TG into LME
K_1	forward rate constant (min^{-1})	X_f	KOH needed to neutralize (ml)
K_2	backward rate constant (min^{-1})	X_i	volume of H_2SO_4 required for titration of sample (ml)
N	normality		
Na	normality of acid		
m	molar ratio of alcohol to oil		

Free fatty acid (FFA) and moisture content are key parameters for determining the viability of vegetable oils to be used in transesterification process [10]. Alkali [4,5,7,8,11–14], acid [15–17] or enzyme [18–22] catalyzed transesterification studies have been reported. Recently, studies are also reported with heterogeneous catalysts [23–27], supercritical alcohols [28] and Biox cosolvent process [29,30]. Enzymatic catalysts are able to effectively catalyze the transesterification in either aqueous or non-aqueous systems at room temperature, but the cost and the time to reach equilibrium conversion are much more than that for alkali or acid catalyzed. If the oil has high FFA content acid catalyzed transesterification is suitable [16]. Higher the acidity of the oil, smaller is the conversion efficiency, and a two-step esterification–transesterification process is required [15,17]. For low FFA (less than 3%) and moisture contents, alkali catalyzed transesterification is recommended [7,10].

The process developed by Freedman et al. [14] for alkali-catalyzed transesterification is widely referred for experimental details and protocols for batch-scale transesterification process. The molar ratio (MR) is associated with the type of catalyst used. An acid catalyzed reaction requires higher molar ratio (30:1) than alkali catalyzed reaction (6:1) to achieve the same ester yield for a given reaction time [14]. Two-step alkali transesterification of different characteristic feedstocks (oils and fat) and MR 6:1–30:1 to achieve 99.5% conversion was reported by Tanaka et al. [31]. Transesterification of peanut, cotton-seed, sunflower and soybean oils, at 60°C with 6:1 MR (methanol-oil) and 0.5% sodium methoxide, achieved the same conversion values for the four oils (93–98%) after 60 min [5]. For achieving maximum conversions, a molar ratio of 6:1 is also recommended by others in the literature [10,32]. Higher molar ratio makes subsequent separation and washing difficult. The rate of the transesterification process is strongly influenced by reaction temperature. However, the reaction proceeds to near completion even at room temperature in sufficient time [2,10]. Darnoko and Cheryan [11] investigated alkali catalyzed palm oil transesterification in a batch reactor. They reported that the rate of reaction increased with temperature up to 60°C and further increase in temperatures did not reduce the time to reach the maximum conversion.

Freedman et al. [14] studied the kinetics of soybean oil transesterification with two alcohols, methanol and butanol, and two types of catalysts, acid and alkali. It was reported that with both catalysts, the

forward reaction followed pseudo first-order kinetics for Butanol ($MR = 30:1$). However, with alkali catalyst the forward reaction followed consecutive second-order kinetics for Butanol ($MR = 6:1$). The reaction of methanol and SBO ($MR = 6:1$) with 0.5% sodium methoxide at 20 – 60°C was a combination of both pseudo second-order consecutive and fourth-order shunt reactions. The rate constants increased with an increase in the amount of catalyst used and activation energies ranged from 8–20 kcal/gm mol. Kinetic models with alkaline catalysis fitted better a pseudo second-order reaction, while for the acid catalysis pseudo first-order reaction provided a best fit [33]. The three step-wise reversible transesterification kinetics of soybean oil under variable mixing conditions was reported by Nouredini and Zhu [34]. A reaction mechanism consisting of an initial mass-transfer controlled region followed by a kinetically controlled region was proposed. The variations in mixing intensity appeared to affect the reactions parallel to variations in temperature. Similar mechanism for sunflower oil methanolysis was studied by Vicente et al. [35]. The kinetically controlled region followed a second order mechanism for the forward and reverse reactions and the system was described as a pseudo homogeneous catalyzed reaction. Darnoko and Cheryan [11] simulated pseudo second order irreversible kinetics for palm oil, for reaction time less than 30 min. Activation energies 14.7, 14.2, and 6.4 kcal/gm mol for TG, DG, and MG hydrolysis reactions were reported, respectively.

vBiodiesel is being produced from edible oils in developed countries [1,3]. Use of edible vegetable oils for biodiesel production is not feasible in developing countries. Biodiesel production in India has been catered mainly from non-edible oils like linseed oil, rice-bran oil, castor oil, jatropha oil, karanja oil, etc. [1]. In this study, linseed oil was transesterified in alkali catalyzed environment. The effect of the process conditions on equilibrium conversion was studied. An overall reversible kinetic model was developed and the kinetic parameters were estimated and optimized.

2. Methodology

2.1. Material used

Vegetable oils (linseed oil, rice-bran oil and castor oil) were purchased from the local market (Kanpur, India); NaOH and methanol

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