Modeling and simulation of batch kinetics of non-edible karanja oil for biodiesel production: A mass transfer study

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HIGHLIGHTS

- Alcoholysis reaction of non edible oil to biodiesel at different temperatures.
- Modeling simulations of mass transfer, pseudo homogenous and equilibrium kinetics.
- Mixing speed and temperature influences the mass transfer resistance.
- Development of overall kinetic model.

GRAPHICAL ABSTRACT
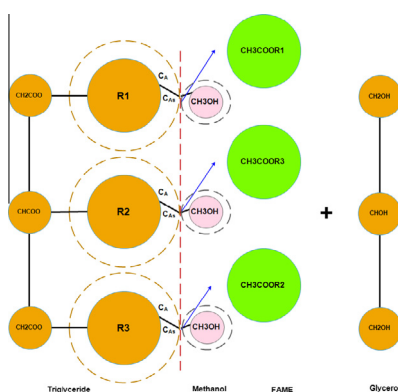
ABSTRACT

Alcoholysis reaction for non-edible karanja vegetable oil is investigated in the presence of potassium hydroxide catalyst. The mass transfer and chemical kinetics studies were conducted in a batch reactor together with the effect of temperature on overall reaction kinetics at optimized molar ratio of oil to methanol (1:6) and 1% catalyst weight at a mixing speed of 600 rpm. The overall karanja alcoholysis reaction is modeled based on three control mechanisms, an initial mass transfer regime followed by irreversible pseudo second order and finally a reversible second order equilibrium reaction. A higher mass transfer resistance was observed as compared to that of edible oils (sunflower and rapeseed) which was attributed to the presence of impurities, especially gums that alter the fundamental physical properties of the oil. At high temperatures equilibrium reaction rate is more dominant than the irreversible pseudo homogeneous reaction, thereby making the alcoholysis reaction initially irreversible reaction controlled. The study establishes that time and temperature are the main parameters influencing the mass transfer and reaction rate, with the volumetric mass transfer coefficients as 51×10^{-3}, 135×10^{-3} and $334 \times 10^{-3} \, min^{-1}$ at temperatures of 35 °C, 45 °C and 55 °C respectively. The results are subsequently used to predict the mass transfer effect at lower temperatures and higher scale of operation as a function of mixing speed.

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Nomenclature

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a	interfacial area (m^2/m^3)	k'_2	reaction rate constant for reverse second order reaction ($l/kmol/min$)
a_i	interfacial area, i = A, C, E (m^2/m^3)		
A	pre exponential factor	k_7	shunt reaction forward rate constant ($l/mol/min$)
$c_{1,2}$	integral constant	k_8	shunt reaction backward rate constant ($l/mol/min$)
C_i	concentration of component in reaction mixture, i = A, B, C, D, E, F (mol/l)	M	initial molar ratio of methanol to TG
		M_i	initial to final molar concentration ratio, i = A, C, E
C_{Ao}	initial concentration of A in the reaction mixture (kmol/l)	M_{ij}	ratio of molar concentration, i, j = A, B, C, D, E, F
		$N_{1,2}$	mixing speed (rpm) index 1; present work and 2; large scale operation
$D_{1,2}$	impeller diameter, index 1; present work and 2; large scale operation	$-r_i$	rate of disappearance, i = A, C, E
E_a	activation energy (kJ/kmol)	R	gas constant (kJ/kmol)
G	gibbs free energy (kJ/kmol)	t	time (min)
k	equilibrium rate constant for alcoholysis reaction	t_1	time duration in pseudo homogeneous regime (min)
k_c	mass transfer coefficient (m/min)	t_2	time duration in equilibrium controlled regime (min)
k_{ci}	mass transfer coefficient, i = A, C, E (m/min)	T	temperature (K)
k'_c	volumetric mass transfer coefficient (1/min)	x_A	conversion of TG
k_i	elementary forward reaction rate constants, i = 1, 3, 5 ($l/mol/min$)	*Subscripts*	
		A	triglyceride (TG)
k_j	elementary backward reaction rate constants, i = 2, 4, 6 ($l/mol/min$)	B	methanol
		C	di-glycerides (DG)
k_{ij}	equilibrium constant for reactions, k_i/k_j	D	FAME
k_1	irreversible reaction rate constant for pseudo homogenous reaction regime ($l/mol/min$)	E	mono-glycerides (MG)
		F	glycerol
k_2	reaction rate constant for forward second order reaction ($l/kmol/min$)		

1. Introduction

Increased exploitation of crude oil resources has resulted in the deterioration of ambiance and caused global warming. Therefore, it becomes significantly important to look for readily available resources that are technically and economically competent within the environmental acceptance. Biodiesel is one such promising alternative fuel [1].

Selection of a vegetable oil for biodiesel production depends on the feedstock availability and its cost. India and other developing countries with the insufficient edible oil production, the use of edible oil for biodiesel production is not feasible. The non-edible vegetable oils like *Simarouba* (*Simaroubaindica*), *Mahua* (*Madhucaindica*), *karanja* (*Pongamia pinnata*), *jatropha* (*Jatropha curcas*) and *Polanga* (Calophyllum inophyllum) are the possible sources for biodiesel production [2]. Among them, *karanja* with a total output capacity of 200 million tons per year is a potential feedstock for biodiesel [3]. Chemically, biodiesel is a mixture of mono-alkyl esters with long chain fatty acids and is produced by alcoholysis/transesterification reaction. In alcoholysis reaction, the displacement of an alcohol from an ester by another in presence of catalyst (homogenous or heterogeneous) and is presented by Eq. (1) as:

$$RCOOR^1(Ester) + R^2OH(Alcohol) \overset{catalyst}{\Longleftrightarrow} RCOOR^2(Ester) + R^1OH(Alcohol) \quad (1)$$
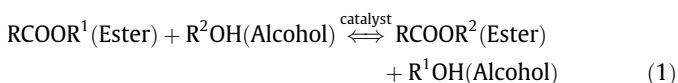
The reaction depends on various parameters: type of feedstock and alcohol, oil to alcohol molar ratio, reaction temperature, catalyst type and their concentration and agitation intensity. Several studies have been carried out on biodiesel production with variation in parameters to obtain the optimized conditions [4,5–7]. It is well known that biodiesel reaction is reversible in nature, and to shift the equilibrium reaction in forward direction the possible ways are either to use excess alcohol or to remove one of the

products continuously [5]. The key factor for process viability of alcoholysis process is the free fatty acid (FFA) and moisture contents present in the oil. For the completion of reaction FFA content in oil should be less than 3% [4,5]. The oils with high FFA content cannot be catalyzed directly by alcoholysis reaction because the alkali catalyst employed will be consumed in neutralizing FFA already present in the feed oil. A two-step mechanism is mandatory for processing biodiesel from unrefined oils that have significant FFA concentration. Initially, FFA is converted to Fatty acid methyl ester (FAME) by acid catalyzed pretreatment step and a second step of alcoholysis in the presence of an alkali catalyst. FFA will show a negative influence on base catalyzed biodiesel reaction by resulting in a side saponification reaction of the base catalyst and FFA.

For designing and developing a process for biodiesel production proper understanding of the reaction kinetics mechanism plays an important role. Generally for an alcoholysis reaction three consecutive reversible reactions is the most accepted mechanism [8–11]. Other possible mechanisms reported are; three consecutive reactions with side saponification reaction [12]; three consecutive reactions with pseudo second order kinetic model for forward reaction [13] and a single step shunt reaction mechanism [14]. Along with the chemical reaction kinetics, mass transfer also plays a significant role in biodiesel processing. In alcoholysis of oil, the immiscibility of methanol and TG leads to a mass transfer resistance [15]. The triglyceride mass transfer limitation is due to the small available active specific catalyst surface, which is mainly covered by adsorbed molecules of methanol. Noureddini and Zhu proposed a reaction mechanism consisting of an initial mass transfer controlled region followed by a kinetically controlled region [9]. Mass transfer limitation between the polar methanol/glycerol phase and non-polar oil phase characterize slow reaction rates at initial and final reaction stages of base catalyzed transesterification [16]. Mass transfer limitation affects the catalytic activity and results on slow reaction rate between methanol and oil phase