



Kinetic study of soybean oil methanolysis using cement kiln dust as a heterogeneous catalyst for biodiesel production



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ABSTRACT

Biodiesel may be produced through transesterification reaction between triglycerides and light alcohols in presence of different catalysts. This paper presents a study of kinetics of soybean methanolysis using cement kiln dust (CKD) as a heterogeneous catalyst. All reactions took place at a constant methanol to oil molar ratio of 12:1 and catalyst loading of 3.5%. The study consists of three phases; the first one is to consider the reaction following irreversible homogeneous kinetic models (1st and 2nd orders) due to using high excess of methanol. The second is to add the backward reaction term to the power law models. Finally, models for heterogeneous catalysts such as Eley–Rideal and Langmuir–Hinshelwood models are suggested to describe reaction kinetics. Least squares method, Runge–Kutta methods for ordinary differential equations and Levenberg–Marquardt algorithm for minimizing objective function were used to obtain the parameters of each suggested model in each phase. Calculation of determination coefficient (R^2) and minimization of squared error summation method were used to determine which model is the best one to fit the experimental data. Eley–Rideal kinetic model was the best model amongst the suggested models. Fisher and Chi-square criteria were used to check the reliability of generated rate equation. The rate differential equation was solved to obtain the main engineering factors controlling the reaction.

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1. Introduction

Biodiesel is a mixture of monoalkyl esters produced through transesterification reaction between triglycerides and light alcohols such as methanol and ethanol. Triglycerides sources can be virgin or used edible oils [1] or non edible oils [2,3].

Typical edible oils which are widely used for biodiesel production are soybean and sunflower oils; also, these oils can be utilized as feedstocks after being used in cooking or frying [4]. Recently, there is a general interest amongst research studies to produce biodiesel from non edible sources [5,6]. Some of the famous non-edible oils used are karanja oil [7], pongamia oil [8,9] jatropa oil [9] and oils extracted from microalgae [10]. These studies aim to optimize different reaction parameters as well [11,7]. They are concerned about the optimization of these conditions in the sake of the development of biodiesel mass production. Factorial design and response surface methodology concepts are widely used

techniques for studying different factors affecting transesterification as well as their optimization [12,8].

Kinetics of transesterification reactions are well studied by many researchers [13–15]. These studies are concerned in generating expressions for reaction rate to help designing a proper reactor to produce biodiesel from triglycerides. Reaction rates take different forms according to the catalyst used [16]. In the case of homogeneous catalyzed transesterification the reaction rate can take the form of power law rates (i.e. first or second order) [17]. On the other hand, in the case of using heterogeneous catalysts, reaction rate takes other forms [18]. These formulas are elaborated taking into consideration the different mechanisms of reaction and the controlling step of this reaction [19]. In the case of using solid catalyst, controlling step can be the reaction step adsorption of reactants, desorption of products or a mass transfer step [20]. Mass transfer steps include the external and internal diffusion relative to the catalyst pellet [21].

There are two famous mechanisms which are: Eley–Rideal mechanism and Langmuir–Hinshelwood mechanism. The former mechanism involves the reaction of an adsorbed molecule on a certain site with another molecule in fluid phase to produce two products one of them is adsorbed while the other one is free in

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Nomenclature

Abbreviations

%x	Percentage conversion
TG	Triglyceride (soybean oil)
MA	Methanol
DG	Diglyceride
MG	Monoglyceride
FAME	Fatty acid methyl ester (biodiesel)
CA	Concentration of component a (mol L^{-1})
DAB	Diffusivity of a in B
Deff	Effective diffusivity
GL	Glycerol
r	Rate ($\text{mol L}^{-1} \text{h}^{-1}$)
t	Time (h)
(k_1)	Rate constant of forward reaction of $\text{TG} \rightarrow \text{DG}$
(k_2)	Rate constant of backward reaction of $\text{TG} \rightarrow \text{DG}$
(k_3)	Rate constant of forward reaction of $\text{DG} \rightarrow \text{MG}$
(k_4)	Rate constant of backward reaction of $\text{DG} \rightarrow \text{MG}$
(k_5)	Rate constant of forward reaction of $\text{MG} \rightarrow \text{G}$
(k_6)	Rate constant of backward reaction of $\text{MG} \rightarrow \text{G}$
(k_t)	Rate constant of forward reaction of $\text{TG} \rightarrow \text{G}$ (overall reaction)
(k_{t-})	Rate constant of backward reaction of $\text{TG} \rightarrow \text{G}$ (overall reaction)
K	Rate constant includes the constant methanol concentration
(k_{ad})	Rate constant of forward reaction of adsorption of methanol
(k_{ad-})	Rate constant of backward reaction of adsorption of methanol (ER)
(k_s)	Rate constant of forward reaction of surface reaction (ER)
(k_{s-})	Rate constant of backward reaction of surface reaction (ER)
(k_d)	Rate constant of forward reaction of desorption of glycerol (ER)
(k_{d-})	Rate constant of backward reaction of desorption of glycerol (ER)
S	Active site
Sp	Particle surface area
(Kad')	Equilibrium constant of reaction of adsorption of methanol (ER)
(Kd')	Equilibrium constant of reaction of desorption of glycerol (ER)
Ct	Concentration of total active sites
Cv	Concentration of empty active sites
K', K'' and K_i	Constants
km	Mass transfer coefficient
E	Activation energy
A_0	Pre-exponential factor
R	Universal gas constant
V_p	Particle volume
η	Effectiveness factor
ε	Porosity
τ	Tortuosity
ρ	Density
μ	Viscosity
φ	Thiele modulus
d_p	Particle diameter
ω	Angular velocity
UL	Linear velocity

D_r	Reactor diameter
Sh	Sherwood number
Re	Reynolds number
Sch	Schmidt number

the fluid phase [22]. On the other hand, Langmuir–Hinshelwood mechanism involves single site mechanism or dual-site mechanism surface reaction [23].

Noureddini and Zhu [24], Bambase et al. [25], Karmee et al. [26] and Vicente et al. [27] suggested a second-order reaction mechanism during the transesterification of soybean oil using homogeneous catalyst. Darnoko and Cheryan [28] reported that the reaction mechanism would be of second-order in the early stages of reaction shifting to first order mechanism in latter stages.

All previously cited works assumed that the reaction is kinetically controlled and that the side reactions – saponification and neutralization of free fatty acids – are negligible [29]. However, Bambase et al. [25], Darnoko and Cheryan [28] and Noureddini and Zhu [24] selected the step of triglyceride conversion to diglyceride as controlling step while Karmee et al. [26] suggested the conversion of diglyceride to monoglyceride as determining step and Vicente et al. [27] selected conversion of monoglycerides to glycerol reaction as being the controlling step.

Dossin et al. [30] and Hattori et al. [31] reported methanol adsorption step as the main controlling step using heterogeneous catalyst, while Xiao et al. [32], Dossin et al. [30] and Hattori et al. [31] suggested surface reactions step. Eley–Rideal (ER) and Langmuir–Hinshelwood–Hougen–Watson (LHHW) mechanisms are the proposed mechanisms for heterogeneously catalyzed transesterification. On using a solid catalyst that contains Lewis acid/base sites the reaction can be described by LHHW model [32]. Dossin et al. [30] and Hattori et al. [31] claimed that ER kinetic model was suitable for heterogeneous base catalysts. Both LHHW and ER models are not suitable for describing reactions catalyzed by a heterogeneous catalyst leaches into the reaction mixture as this catalyst cannot be considered totally heterogeneous, so these reactions can follow the models proposed for homogeneous reactions (i.e. first and second order kinetic models) [29,33].

MacLeod [34] fitted power law, ER and LHHW models with the experimental data obtained by using alkali metals doped on metal oxides (e.g. Li–CaO) as solid catalysts. Due to catalyst leaching, homogeneous contribution was found to be significant so the second order model was used to describe the reaction kinetics as an initial solution. On comparing the fitted data with experimental data there results are not compatible so this model was not representative. It was found that ER was the best model to represent the reaction kinetics as it had lower sum of squares error than LHHW model. However, even the ER model cannot be considered to be totally appropriate due to leaching which make the reaction partially homogeneous.

Recently the kinetics of methanolysis reaction over complex heterogeneous catalysts, prepared through simple synthesis process or derived from sustainable sources, was investigated [35]. When $\text{K}_2\text{O}/\text{NaX}$ was used for catalyzing the methanolysis of safflower oil, it was found that the best kinetic model to fit the experimental data is a model based on Eley–Rideal mechanism while the rate determining step was assumed to be the methanol adsorption step [36]. In 2013, Kumar and Ali [37] investigated the transesterification of Low-quality triglycerides over a Zn/CaO and they observed that the reaction follows a pseudo first order kinetic model. Feyzi and Khajavia [38] studied the kinetics of biodiesel synthesis from sunflower oil using Ba–Sr/ZSM-5 nano-catalyst where they found out that the reaction can be described by pseudo

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