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Concentration-independent rate constant for biodiesel synthesis from homogeneous-catalytic esterification of free fatty acid

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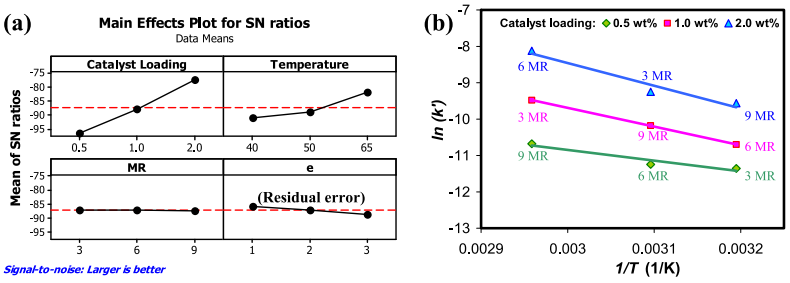
HIGHLIGHTS

- Rate constant dependency on reaction parameters is studied using Taguchi approach.
- Second-order rate constant (SRC) is modified for esterification of free fatty acids.
- Modified-SRC is reported as concentration-independent rate constant (CIRC).
- CIRC is shown to be equivalent to Brønsted–Bjerrum relation.
- CIRC-based kinetics predictions are found to be better than those based on SRC.

GRAPHICAL ABSTRACT

(a) Taguchi analysis for parametric effects on concentration-independent rate constant (CIRC or k').
(b) Arrhenius plots for CIRC (using standard L9 orthogonal array design).



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ABSTRACT

Dependence of the second-order rate constant (SRC) on the reactants' concentration, for esterification of fatty acids, is found empirically in the published reports. Taguchi method is used to study dependency of the rate constant on temperature, reactants' concentration, and catalyst loading for the synthesis of biodiesel from sulfuric acid-catalyzed esterification of free fatty acid (FFA) with methanol. On the basis of general literature on dependency of rate constant on reactants' concentration and the esterification-rate determining step, concentration term embedded in the units of SRC has been identified as catalyst concentration. Accordingly SRC has been modified to include the catalyst concentration in the rate law, which is consistent with the general mass-action rate law reported by Blum and Luus (1964) and Pekař (2011). Analysis of the modified rate constant showed it to be independent of the reactants' concentration. It is thus named as 'concentration independent rate constant (CIRC)'. The predictions of kinetics of the esterification of FFA are better using CIRC than other commonly used rate forms. The modified rate constant is shown to be equivalent to Brønsted–Bjerrum relation. Moreover, the modified rate constant is more general than the reported ones for esterification of fatty acids and it predicts kinetics well over a wide range of reaction parameters.

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1. Introduction

The cost of feedstock accounts for 60–80% of the total cost of biodiesel fuel (Haas et al., 2005; Zhang et al., 2003). Biodiesel production can be profitable if it is made from low-cost feed-stocks, but such feed-stocks generally contain large amounts of free fatty acids (FFA) (Canakci and Gerpen, 2001; Diaz-Felix et al., 2009; Ghadge and Raheman, 2005). A systematic study of the reaction kinetics of biodiesel synthesis from esterification of FFA is considered here. Reaction rate for kinetic study can be modeled as $k(T)[A]^x[B]^y$ for reactions represented by $xA+yB \rightarrow products$. This rate model is established over a century and a half ago and it

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follows the kinetic aspect of the law of mass action for an elementary reaction (Koudriavtsev et al., 2000). The exponents x and y are the stoichiometric coefficients for the reaction, and $k(T)$ is the rate constant, which is generally a function of temperature and independent of reactants' concentrations.

The empirical equation of Arrhenius for rate constant is well accepted in the study of kinetics parameters from experimental data. Collision and transition state theories are also used for theoretical calculation of rate constant (Holland and Anthony, 1989). These theories give an insight into the molecular dynamics of the reactions; especially transition state theory provides more details about the mechanistic approach at molecular level for the rate constant estimation. However, these theories suffer from many difficulties in estimation of practical values for rate constants (Holland and Anthony, 1989; Truhlar et al., 1996). Besides temperature, the apparent rate constant can also depend on other factors such as catalyst type, catalyst loading, solvent, and reactants molar ratio (Fogler, 2006; Jong et al., 2009; Leyes and Othmer, 1945; Yadav and Mehta, 1994). The above theories and the Arrhenius equation express the temperature dependency of rate constant clearly, but not the influence of the other factors.

The linear increase of rate constant with the catalyst concentration and molar ratio (MR) of alcohol to fatty acid are reported by Leyes and Othmer (1945), Ling and Geankoplis (1958), and Othmer and Rao (1950). Ling and Geankoplis (1958) reported a combined equation for the rate constant of homogeneous-catalyzed esterification of oleic acid with butanol as $k=93(0.401C_{Catalyst}+0.000368)(0.0133MR+0.042)(e^{16.76-7100/T})$ by relating the effects of catalyst concentration ($C_{Catalyst}$), molar ratio (MR), and temperature. This equation only holds at 100 °C and within the range of catalyst concentration and MR studied. Equivalent forms of the combined equation are also reported by Leyes and Othmer (1945) and Othmer and Rao (1950) for the esterification of fatty acids. However, Othmer and Rao (1950) mentioned that the combined equation obtained for the sulfuric acid-catalyzed esterification of oleic acid with butanol does not work for MR > 10, catalyst loading beyond the range of 0.5–1.2 wt%, and temperature other than 100 °C. Hence, such reported combined relations are specific to the reaction conditions under study.

The kinetics of complex reactions is studied by postulating several elementary reaction steps where each of the elementary reaction rate constants is strictly concentration independent. An overall (or apparent/effective/complex) rate constant can be obtained from the overall kinetics derived from the kinetics of elementary steps. Recently, based on reactivity and activity coefficients arguments, Jesudason (2008) concluded that the current form of elementary reaction rate constant is still incomplete. He strongly argued that, due to historical conventions, rate constant of elementary reactions is treated as strictly independent of reacting species concentration. He showed from molecular dynamics simulation (without using any transition states) that even the rate constant of elementary reaction depends on reacting species concentration in contrast to the current form of elementary rate constant.

Taguchi method is used in this study for a systematic study of reaction kinetics for biodiesel synthesis by homogeneous-acid catalytic esterification of free fatty acid with methanol to understand the effects of reaction parameters on rate constant. Taguchi method is a statistical analysis of a system and utilizes various standard orthogonal arrays for the design of experiments (Bagachi, 1993; Phadke, 2008). This method has been mainly used for optimization of process variables using signal-to-noise ratio as the decision making tool. The method not only minimizes the number of experiments, but also exploits the variation of all variables simultaneously in order to understand the impact of each of them on the process and identify interaction among the variables. The method is technically advanced and more systematic in approach than the conventional method of "one factor at a time" (Czitrom, 1999).

Several researchers (Chongkhong et al., 2007; Gan et al., 2012; Khan et al., 2010) have used the Taguchi method for optimization of reaction parameters (e.g., temperature, reactants proportion, reaction time, catalyst type, catalyst concentration, etc.) to reduce the FFA content in biodiesel production. Similarly, Taguchi methodology is applied for optimization of the reaction variables for obtaining the maximum yield of biodiesel from trans-esterification (Antolin et al., 2002; Wu and Leung, 2011; Yusup and Khan, 2010; Mahamuni and Adewuyi, 2010). In these kinds of studies, the yield of biodiesel or fatty acid conversion is treated as a response factor. The application of Taguchi method to study the effects of reaction variables on rate constant for biodiesel production from the low-cost feed-stocks has not been studied.

In the esterification reactions of fatty acids, the catalyst loading term is explicitly expressed in rate equation for heterogeneous catalysis (Gangadwala et al., 2003; Izci et al., 2009; Tesser et al., 2005). In the homogeneous catalysis, however, there is yet no consensus on the inclusion of catalyst loading in rate equation; in some reports catalyst loading appears in the rate equation (Bart et al., 1994; Boucher et al., 2008; Jong et al., 2009; Liu et al., 2006) and in some others it does not (Aafaqi et al., 2004; Berrios et al., 2007). This reported contradiction is also examined in this work.

Sulfuric acid-catalyzed esterification of oleic acid (mixed as free fatty acid in refined sunflower oil) with methanol is carried out as a model reaction for this study. Taguchi approach guided modification of the conventional rate constant to a concentration-independent rate constant (CIRC). Using CIRC and Taguchi orthogonal array design, a method is shown to predict kinetics of biodiesel synthesis at different levels of reaction parameters.

2. Experimental section

2.1. Materials

Methanol (GR grade, moisture < 0.02%), water (HPLC grade), sulfuric acid (98% GR), pure oleic acid, oxalic acid dihydrate (GR grade), *n*-hexane (HPLC grade), and phenolphthalein indicator are supplied by Merck India Ltd. Refined sunflower oil (max. 0.1 wt% FFA) is purchased from Liberty Oil Mills Ltd., Mumbai, India. Potassium hydroxide (extra pure AR) is obtained from Sisco Research Laboratories Pvt. Ltd., Mumbai, India.

2.2. Taguchi design of experiments, experimental procedure, sample analysis, and data interpretation

The details of the design, procedure, and the analysis are given elsewhere (Hassan and Vinjamur, 2013). In this study, the standard L9 (3^4) orthogonal array of experiments (see Table 1) is conducted for sulfuric acid-catalyzed esterification of 50 wt% oleic acid (mixed as FFA in sunflower oil) with methanol. Each experiment in the L9 array is carried out three times and the average value of conversion is taken for analysis. Uncertainty in the measured conversion of the FFA is within ± 2%.

3. Results and discussion

3.1. Rate model and initial reaction kinetics

Esterification reaction of oleic acid with methanol is: *Oleic Acid + Methanol ↔ Methyl Oleate + Water.* For esterification reactions, several kinetics have been reported: reversible second-order (Aafaqi et al., 2004; Bart et al., 1994), second-order for forward reaction with no backward reaction (Liu et al., 2006; Smith, 1939), and pseudo first order when large quantities of

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