Parametric effects on kinetics of esterification for biodiesel production: A Taguchi approach

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HIGHLIGHTS

- Study of parametric effects on *FFA*-esterification kinetics for biodiesel production.
- Taguchi method with standard orthogonal array design is used in this study.
- Relative dominancy of parameters on X_{FFA} is time-dependent.
- Temperature dominates in the beginning but MR is more dominant in the later period.
- Catalyst amount: minimal effect, constant-effect to rate of X_{FFA} after 75 min.

GRAPHICAL ABSTRACT

Relative-contribution of reaction parameters to conversion of free fatty acids is a function of reaction time.
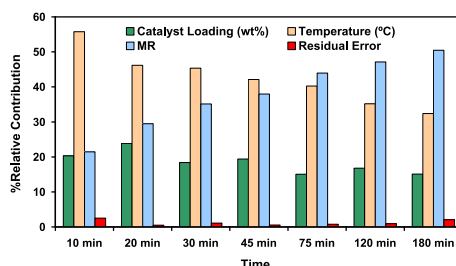
ABSTRACT

Parametric-effects on kinetics for biodiesel production from H_2SO_4–catalyzed esterification of free fatty acids (*FFA*) with methanol are evaluated at different intervals of reaction using Taguchi method. The parameters studied with orthogonal array design are catalyst loading, temperature, and methanol-to-*FFA* mole ratio (MR). Within the range of the parameters studied, each parameter has positive effect on conversion of *FFA* (X_{FFA}) throughout the reaction wherein trans-esterification of oil is found negligible. But relative-contribution of temperature to X_{FFA} declined ~23.5% (from 55.77% at 10 min to 32.39% at 180 min) and that of MR increased ~29% (from 21.46% at 10 min to 50.45% at 180 min). Catalyst loading has minimal effect on X_{FFA} throughout the reaction (contribution varied within 15–24%) and has constant effect on *FFA*-esterification rate beyond 75 min. The relative effect of reaction time (as an independent parameter) along with other parameters is also evaluated at different reaction-phases and the orders of parametric-effects are compared with the results of the detailed analyses (using Taguchi approach) of esterification-kinetics data of published works for biodiesel synthesis. The relative parametric-effects on kinetics are found to be a function of reaction duration; parametric-order changes as reaction progresses toward equilibrium. However, temperature and MR are the more dominant parameters than catalyst loading and reaction time. Taguchi additivity model is validated with experiments and the predictions deviated within ± 5%.

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1. Introduction

Biodiesel is a biodegradable, non-toxic, and environmentally benign fuel with low emission profiles (Xie et al., 2006). It is a mixture of alkyl esters of fatty acids synthesized mainly by two routes: (i) esterification of long chain fatty acids and (ii) trans-esterification of triglycerides (Ma and Hanna, 1999). Feed-stocks for biodiesel production should not contain $> 1\%$ free fatty acids (*FFA*) to prevent catalyst deactivation due to saponification of the *FFA* by base catalysts during trans-esterification (Freedman et al., 1984). High *FFA*, thus, increases the costs of downstream purification of the biodiesel. Therefore, a key challenge is

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cost-effective pretreatment of high *FFA* feed-stocks to reduce the *FFA* below the desired levels prior to the trans-esterification process. Understanding the effects and the significance of various process parameters such as temperature, catalyst loading, time, and molar ratio of reactants on the kinetics of esterification of *FFA* is important for this cost-effectiveness.

Typically, one-factor-at-a-time (OFAT) experiments are performed to study the parametric-effects on kinetics. Statistically designed experiments, however, have advantages over OFAT experiments (Czitrom, 1999): the latter require more number of experiments than the former for the same amount of information; the latter cannot detect interactions between the parameters and may miss optimal settings of the parameters. Taguchi method (Phadke, 2008; Bagachi, 1993), one of the standard statistical techniques, has been used by several researchers to analyze the parametric-effects on the trans-esterification (Yusup and Khan, 2010; Hassan et al., 2013; Antolin et al., 2002; Wu and Leung, 2011; Mahamuni and Adewuyi, 2010) and esterification processes (Chongkhong et al., 2007; Wang et al., 2007; Khan et al. 2010; Zhang et al., 2012). Optimization of the trans-esterification process using Taguchi method is reported on the basis of biodiesel yield. Recently, Hassan et al. (2013) have evaluated the relative significance and the contribution of individual parameters on the contents of biodiesel, triglycerides (TG), diglycerides, and monoglycerides (i.e., on the overall trans-esterification reaction kinetics) to maximize the biodiesel yield and its purity.

In the esterification process, Taguchi method is used for optimization of the reaction parameters to reduce the *FFA* content during biodiesel production. An L9 (3^4) experimental design, a three-level-four-factor orthogonal array of Taguchi method, is used by Wang et al. (2007) to investigate the effects of reaction parameters at 95 °C on the conversion of *FFA* (X_{FFA}) in ferric sulfate-catalyzed esterification of waste cooking oil (acid value: 75.92 ± 0.036 mgKOH/g). They obtained the optimal conditions as 4 h reaction time, 2 wt% catalyst, and 10:1 methanol-to-TG mole ratio for 97.20% X_{FFA}. Khan et al. (2010) used a similar L9-design for sulfuric acid-catalyzed esterification of high *FFA* containing equi-volume blend of crude rubber seed oil and crude palm oil. They reported the optimum conditions as 65 °C, 15:1 methanol-to-oil mole ratio, and 0.5 wt% H_2SO_4 to reduce the *FFA* content by 95% after 3 h of reaction. Gan et al. (2012) studied the effects of the parameters on X_{FFA} in waste cooking oil (WCO) using different ion-exchange resins, and reported the optimal parameters as 4 wt% catalyst Amberlyst-15, 65 °C, and 15:1 methanol-to-oil mole ratio using Taguchi orthogonal array design.

It can be inferred from Wang et al. (2007) that the effect of reaction time on X_{FFA} is larger than methanol-to-TG mole ratio. Khan et al. (2010) showed that the effect of temperature is larger than methanol-to-oil mole ratio. The effect of catalyst amount, however, is found to be minimal (Wang et al., 2007; Khan et al., 2010). From the L9-design of Zhang et al. (2012) study for esterification of oleic acid using Brønsted acidic ionic liquid supported onto Fe-incorporated SBA-15, the order of parameters is temperature > methanol-to-oleic acid mole ratio > catalyst amount > reaction time, on the basis of their relative significance. The effect of reaction time is found to be insignificant at 95% confidence level by Zhang et al. (2012), which contradicts the inference from Wang et al. (2007).

None of the studies (Chongkhong et al., 2007; Khan et al., 2010; Wang et al., 2007; Zhang et al., 2012) discussed above has carried out detailed Taguchi analyses such as signal-to-noise ratio (SN ratio) analysis, main effects plots, analysis of variance (ANOVA) for SN ratios, and range-analysis to evaluate the relative effects and contribution of parameters on esterification kinetics of *FFA*. Only range-analysis has been done by Wang et al. (2007) and Khan et al. (2010) to study the effects of parameters; and analysis of

perturbation of factors is used by Zhang et al. (2012). Chongkhong et al. (2007) have not used any statistical analysis for batch processing of H_2SO_4-catalyzed esterification of palm fatty acid distillate (PFAD – containing 93 wt% *FFA*); they selected only the starting reaction conditions for CSTR-based continuous production of biodiesel from their L9 experiments on the basis of maximum *FAME* content. However, Gan et al. (2012) have carried out the SN ratio analysis, the ANOVA, and the range-analysis in their study. They found that the catalyst type and methanol-to-oil molar ratio significantly influenced the *FFA* conversion; the catalyst amount and temperature did not have significant effect on the *FFA* conversion. This insignificant effect of temperature contradicts Khan et al. (2010) and Zhang et al. (2012) findings.

A detailed statistical Taguchi study is yet to be done to understand the relative significance and contributions of parameters for the esterification kinetics of *FFA*. Therefore, a rigorous statistical Taguchi approach is applied in this study for kinetics of sulfuric acid-catalyzed esterification of oleic acid (mixed as *FFA* in sunflower oil) with methanol for the entire reaction period. Also, the kinetics data of published works are analyzed in detail by the Taguchi method and compared with the results of this work to resolve the ambiguities of the relative effects of the parameters on esterification kinetics of *FFA*.

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 supplied by Sisco Research Laboratories Pvt. Ltd., Mumbai, India.

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

The details are given else where (Hassan and Vinjamur, 2013). For convenience of readers, however, the details are also provided in the supporting information. In this study, the standard L9 (3^4) orthogonal array of experiments (see Table 1) are 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. Uncertainty in measured conversion of *FFA* is within ± 2%.

3. Results and discussion

3.1. Reaction kinetics

In our previous study (Hassan and Vinjamur, 2013), a second-order reversible kinetic model best fitted the kinetics of H_2SO_4-catalyzed esterification of *FFA* with methanol. Fig. 1 shows reaction kinetics in terms of conversion of *FFA* (X_{FFA}) for all the L9 experiments. Rapid increase in X_{FFA} is observed in L9/3, L9/5, L9/6, L9/7, and L9/9 experiments in the initial periods of the reaction such that more than 50% X_{FFA} is achieved within 30 min. This observation is consistent with the rapid reduction in *FFA* content in the first 30 min at 60 °C and 1 wt% H_2SO_4 reported by Sendzikiene et al. (2004).