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Mechanistic analysis of ultrasound-assisted biodiesel synthesis with Cu_2O catalyst and mixed oil feedstock using continuous (packed bed) and batch (slurry) reactors

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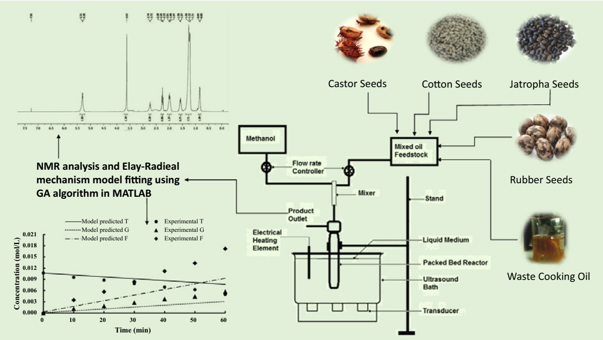
HIGHLIGHTS

- Statistical optimization of transesterification with Cu_2O catalyst in packed bed reactor.
- Kinetic analysis of transesterification using model based on Eley-Rideal mechanism.
- Methanol adsorption on the catalyst is the slowest and rate-limiting step.
- Sonication enhances reaction kinetics of process but not methanol adsorption on catalyst.
- Activation energy of the overall process largely contributed by mass transfer steps.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper has investigated the mechanistic issues of ultrasound-assisted transesterification process using solid Cu_2O catalyst and mixed feedstock of non-edible oils. The optimum conditions for transesterification have been determined using statistical experimental design in packed bed catalytic reactor. The kinetic constants of different steps of transesterification process have been determined using kinetic model based on Eley-Rideal mechanism coupled to time profiles of reactants and products of transesterification in batch slurry reactors. The batch experiments have been performed at optimum conditions predicted by statistical experimental design: alcohol/oil molar ratio = 10.6, temperature = 62.5 °C, catalyst concentration = 7.25 wt% oil. It is revealed that adsorption of methanol is the slowest and rate determining step of transesterification process. Sonication enhanced the kinetics of reaction steps of transesterification process, but its effect on methanol adsorption on Cu_2O catalyst was adverse. The activation energy of overall transesterification process was 90.14 kJ/mol; while, the sum total of activation energies of the three reaction steps of triglyceride conversion was 40.98 kJ/mol. These results essentially point to strong mass transfer influence on Cu_2O-catalyzed transesterification process, even in presence of

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sonication. The adsorptive mass transfer of methanol to catalyst sites is not enhanced by microturbulence generated by sonication. Two probable causes leading to this effect are: discrete and intermittent nature of acoustic (or shock) waves generated by the transient cavitation, and secondly, the high temperature of reaction that offsets the methanol adsorption on catalyst websites.

1. Introduction

Biodiesel has emerged as a potential alternate liquid transportation fuel in the past two decades. The large-scale production of biodiesel is hampered by unattractive economy (Aransiola et al., 2014). Two factors that influence feasibility and viability of the biodiesel process are cost of feedstock and sufficient availability of feedstock all through the year. Possible solution to the first issue is use of non-edible oil feedstock (such as *Neem, Karanja, Kususm, Jatropha, Rubber seeds, Cassava, Mahua,* etc.), which are far cheaper than the edible oils (Reshad et al., 2015). The solution to second issue is feedstock flexibility or possibility of use of mixed feedstock for the process, as sufficient oil of single species or type may not be available in required quantities. The base catalyst for the transesterification process is in either homogeneous (NaOH or KOH) (Drapcho et al., 2008) or heterogeneous (CaO, MgO or Mg–Al hydrotalcites) (Gao et al., 2010) form. The latter form of catalyst is more beneficial, as it does not cause contamination of glycerol (the side product of transesterification), thus making it merchantable byproduct. However, the transesterification reaction system with heterogeneous solid catalyst suffers from drawback of slow kinetics due to mass transfer limitations of three phase (liquid–liquid–solid) reaction system (Choudhury et al., 2014). The previous studies have employed alkali or alkaline earth metal oxides like CaO, $Ba(OH)_2$, basic zeolites as the catalyst for transesterification (Lukic et al., 2009; Alonso et al., 2009; Zabeti et al., 2010; Takase et al., 2014). Moreover, most of these studies have been conducted in batch mode with mechanical shaking of reaction mixture. Biodiesel synthesis in continuous process using packed bed solid base catalyst has also been reported by few authors, and a summary of this literature in this area is given in Table 1.

The present study has addressed the matter of biodiesel production using new solid catalyst of cuprous oxide and mixed feedstock of five non-edible oils, viz. cotton seed oil, castor oil, Jatropha curcus oil, rubber seed oil and waste cooking oil. The approach adopted in this study is two-fold, viz. (1) statistical optimization of the transesterification process in a continuous packed bed reactor with Cu_2O catalyst, coupled with sonication (or ultrasound irradiation), and (2) kinetic and mechanistic analysis of transesterification process using mathematical model based on Eley-Rideal mechanism. For this purpose, the experiments have been conducted in batch mode using slurry reactor coupled with sonication. The experimental data has been fitted to kinetic model to obtain the value of kinetic parameters. An additional objective of this study is to gain mechanistic insight into the process intensification (in terms of enhancement of reaction kinetics) induced by ultrasound. Hence, the experiments in batch mode have been conducted using mechanical agitation as well as sonication, and the kinetic parameters for sonication and mechanical agitation have been compared. This analysis has assisted in discriminating between the roles of mass transfer and reaction kinetics, and has provided insight into the physical mechanism of ultrasound-assisted transesterification process, as explained in the subsequent sections.

2. Material and methods

2.1. Chemicals, reagents and feedstock preparation

Following chemicals have been used in the experiments: Methanol (AR grade, purity 99%, Merck, India), sulfuric acid (98%, Merck, India), Cu_2O (AR grade, purity 92%, Himedia, India). Anhydrous methanol was prepared by distillation.

Crude *Jatropa curcus* oil and crude castor oil were procured from local farmers. Waste cooking oil was collected from a restaurant on institute campus. Crude cotton seed oil was a gift from M/s. Govind Krupa Oil Industry (Amravati, Maharashtra, India). Rubber seeds were purchased from local farmers, and oil was extracted from the seeds using Soxhlet extraction method with *n*-hexane as solvent. All oils were tested for density, acid value (AV), saponification value (SV), and average molecular weight of the oil was determined as (Deng et al., 2010):

$$\text{Average molecular weight} = 56.1 \times 3 \times 1000/(SV - AV) \quad (1)$$

The feedstock for transesterification was prepared by blending different oils as follows: *Jatropha* oil (15% v/v), castor oil (25% v/v), rubber seed oil (20% v/v), cotton seed oil (25% v/v), and waste cooking oil (15% v/v). The basic properties of all individual oils and blended feedstock are given in Table 2.

2.2. Catalyst preparation and characterization

The fine powder of Cu_2O catalyst, as received from supplier, was initially dried in hot air oven at 120 °C for 3 h to remove moisture. Dried or de-moisturized catalyst was cooled to ambient temperature, and was characterized using X-ray diffraction (XRD) (Bruker, Model: D8 Advance) for identification of different phases in the catalyst. The surface area of the catalyst was determined using surface area and pore size analyzer (Quanta chrome, Model: Autosorb-IQ MP) and Field-emission scanning electron microscopy (FE-SEM, Zeiss, Model: Sigma). Due to fine size, direct packing of catalyst in reactor bed was not possible, as voidage of such bed would be too small to have proper flow of methanol/oil mixture. As a solution to this issue, the catalyst was used in supported form as follows: glass beads (diameter 3–5 mm, Himedia, India) were used as the catalyst support. These beads were coated with a film of Cu_2O particles. For firm adherence of the Cu_2O powder onto the surface of the glass beads, glutaraldehyde was employed as a surface binding agent. Cu_2O-coated glass beads were dried in hot air oven at 120 °C for 3 h, and were used for making up the packed catalyst bed after cooling.

2.3. Experimental setup and protocol

Experiments in the present study were carried out in three parts: (1) reduction in the free fatty acid (FFA) content of the mixed oil feedstock by preliminary esterification, (2) transesterification of mixed oil feedstock in continuous packed bed reactor and optimization of process variables using statistical design of experiments (DoE), and (3) determination of kinetic and Arrhenius