



# Reaction kinetics with catalyst deactivation in simultaneous esterification and transesterification of acid oils to biodiesel (FAME) over a mesoporous sulphonated carbon catalyst



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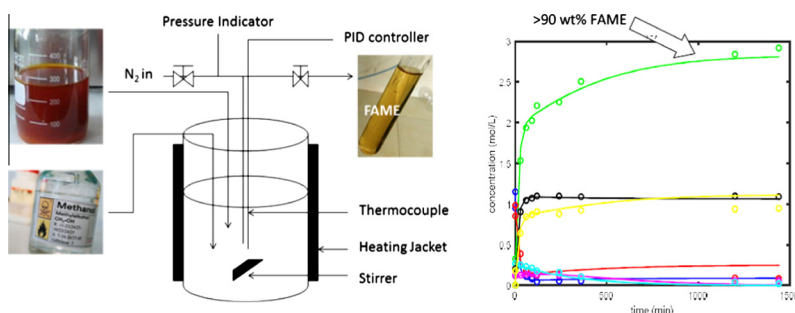
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## HIGHLIGHTS

- Kinetics of simultaneous esterification and transesterification of natural acid oils.
- The composition of feedstock influences the methanol solubility.
- One-step biodiesel production over a mesoporous sulphonated catalyst.
- Catalyst deactivation modeling.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this work, a careful analysis of the reaction kinetics upon simultaneous esterification and transesterification of acidic oils over a mesoporous sulphonated carbon catalyst is discussed. A batch reactor system was used and the synthesized carbon catalyst were characterized by  $N_2$ -physisorption, transmission electron microscopy, elemental analysis and  $NH_3$ -TPD. A second order pseudo-homogeneous kinetic model was proposed which explained the experimental results obtained for three different feedstock oils with  $\geq 98\%$  accuracy. The rate constants ( $k$ ), activation energies ( $E_a$ ) and equilibrium constants ( $K_{eq}$ ) of the individual reactions were determined by regression analysis which confirmed that the reaction steps were kinetically controlled and not limited by inter-particle diffusion or external mass transfer limitations ( $E_a > 25 \text{ kJ mol}^{-1}$ ). Furthermore, the composition feedstock was found to have a distinct effect on the solubility of methanol and oil phase which influenced  $k$ ,  $K_{eq}$  and  $E_a$  values, eventually determining the final biodiesel (FAME) yield. To account for the loss of activity upon catalyst reuse, a deactivation model was also proposed which explained our results with  $\sim 94\%$  accuracy. In fact, the loss of activity was accounted for by incorporating a concentration-independent 'deactivation constant'  $k_d$  in the reaction rate equations. Moreover, under optimized reaction conditions (120 °C and 20:1 methanol-to-FFA molar ratio), FAME yields up to 79–91 wt% could be obtained in one step process from oils containing 21–41 wt% FFA.

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## 1. Introduction

Free fatty acid (FFA) containing acid oils (i.e. waste oils or crude vegetable oils) are attractive low cost feedstocks for production of biodiesel as compared to expensive refined vegetable oils. However, the production of biodiesel from such oils is especially challenging because of the presence of moisture and the natural variation of FFAs levels in such oils depending on the source. Traditional conversion of such feedstock to biodiesel is accomplished via a two-step acid-base catalyzed esterification–transesterification process at industrial scale [1–4]. Albeit a one-step transesterification process taking advantage of a homogeneous acid (like  $\text{H}_2\text{SO}_4$ ) might prove to be more economical than a two-step acid–base catalyzed process, the latter one is also compatible with feedstocks containing FFA amounts of 5 wt% or more. Further, the process is extremely slow and requires large excess of methanol and, consequently, a reaction time of ~48 h or longer to achieve desired conversions levels (greater than 95%) [5]. Besides, the process suffers from all the drawbacks of a homogeneous process (generation of large volumes of neutralization waste, high downstream processing costs, etc.) and, in addition, requires larger reactor capacity and gives rise to a greater risk of sulfur contamination in biodiesel. All these facts render the process far less attractive [1,5]. As an alternative, a supercritical process eliminates the need of a catalyst and also produces high quality FAME with high yields and in short reaction times but, at the same time, requires high energy input per ton biodiesel and high equipment investment. Consequently, all these consideration offset the possible advantages [6]. Heterogeneous catalysis, on the other hand, and solid acid catalysts in particular (due to their tolerance to FFA), allow for a number of process advantages in terms of developing an economical process for biodiesel production from acid oils [3,4,7]. Like homogeneous solid acids, heterogeneous acid catalysts can also catalyze both the esterification and transesterification reactions, simultaneously. Consequently, this allows for utilization of lower cost FFA containing feedstocks [3,7]. Moreover, a recent process simulation study indicated that a heterogeneous acid catalyzed process based on acid oils might be the most economical approach compared to the supercritical and traditional homogeneous processes [8].

In recent years, many groups have investigated different solid acid catalysts such as sulfated zirconia [7,9], zeolites [10], heteropolyacids [11], ion exchange resins [12] and also sulfonated carbons [3,13–15]. Although the range of temperatures, pressures and composition of feedstock studied varied significantly, the overall results were positive and with most catalysts >90% conversion was achieved [16]. Among the different solid acids reported so far, sulfonated carbon materials or  $-\text{SO}_3\text{H}$  functionalized carbons were among the most active and economically attractive catalysts for biodiesel production, as reviewed by Konwar et al. [17]. They resemble  $\text{H}_2\text{SO}_4$  in terms of acidity, activity and also offer high operational stability (>240 °C) and reusability; moreover they could be prepared from any carbonaceous source. Still, their textural properties can be easily tuned by changing carbonization/activation conditions thus leading to lower preparation costs [3,13,17]. As such, these  $-\text{SO}_3\text{H}$  containing solid acids or sulfonated carbons could have an important role in the realization of an economical biodiesel production process from acid oil feedstocks [17]. The main advantage of these carbon catalysts remains in the fact that they could be integrated into the biorefining concept if derived from the in situ wastes generated within such processes/industries (e.g. e-oiled cakes, seed hulls, residual lignin, etc.) [3,14]. In fact, the number of articles reporting the catalytic applications of sulfonated carbons for biodiesel production has increased in recent years [16,17]. However, papers including a study of the reaction

kinetics of sulfonated carbon catalyzed processes are quite scarce [4,18]. Kinetic models are vital for understanding the reaction pathways and can be used to predict even the smallest changes in the amount of specific products during a reaction process. Thus, an experimental study and subsequent mathematical modeling of the reaction kinetics is considered one of the most crucial steps in the chemical process development for industrial applications. In fact, the mechanism and reaction kinetics of acid catalyzed fatty acid esterification and neat vegetable oil transesterification are individually rather well-studied (Scheme 1) [19–27]. In spite of that, only the kinetics of fatty acid esterification in vegetable oil and neat vegetable oil transesterification have been extended to biodiesel production in heterogeneous systems [28,29]. Further, the investigation of quantitative kinetics and modeling of simultaneous esterification and transesterification of acidic oils have rarely been performed. In addition, the published studies were seldom based on a semi-empirical approach, either using pure fatty acids [4] or simulated acid oils (mixture of free fatty acid and triglycerides) [18] as feedstock. However, in reality the acid oils (waste cooking oil or crude vegetable oils) are more complex mixtures containing significant proportions of monoglycerides (MG) and diglycerides (DG) in addition to the FFA and triglycerides (TG). FFA and MG are reported to have significant impact on the mutual solubility of an alcohol and an oil which can influence the reaction rates [3,30].

The objective of this work was to demonstrate the applicability of a biodiesel waste-derived mesoporous sulfonated carbon catalyst in one-step biodiesel production by experimental investigation of the reaction kinetics of simultaneous esterification and transesterification of acid oil feedstock. The influence of the reaction temperature, feedstock composition and the initial molar ratio of the reactants on reaction kinetics were studied and the results were described by a simple pseudo-homogeneous kinetic model. Also, the reaction kinetics were studied for spent catalyst and a catalyst deactivation model was proposed to explain the loss of catalyst activity upon reuse.

## 2. Experimental section

### 2.1. Materials

Ortho-phosphoric acid (88%, Sigma), sulfanilic acid (99%, Merck), stearic acid (Merck, 97%),  $\text{H}_3\text{PO}_2$  (aq. 30–32%, SRL), HCl (35%, Merck),  $\text{Na}_2\text{SO}_4$  (99.5%, Merck),  $\text{NaNO}_2$  (98%), acetone (99.5%, Sigma), ethanol (99.9%, Merck), heptane (HPLC, Sigma), pyridine (HPLC, Merck), FAME mix (Supelco), methyl heptadecanoate (99%, Supelco), N-methyl-N-trimethylsilyltrifluoroacetamide (98%, Sigma) and ASTM® D6584 Individual Standard Solution (Supelco) and Internal Standards Kit (Supelco) were purchased from commercial sources and used as received.

The acid oil feedstock, mechanically extracted and naturally aged (~4 months) *Mesua Ferrea* Linn oil (I) was supplied by the Biofuel Laboratory of Department of Energy, Tezpur University while the alternative oils II and III were prepared by calculated addition of stearic acid (C18:0) to oil I. The composition of the raw materials are given in Table S1 (Supporting Information). The fatty acid composition was determined by gas chromatography on a Thermo Scientific TRACE 1300 chromatograph equipped with a FID detector and a TRACE TR-FAME GC column. The methyl esters were prepared according to AOCS Official Method 1998; Ce 1e62 and Ce 2e66 and the individual components were identified by comparison of retention times with the standard FAME mix and the wt% of the individual fatty acids were calculated based on the methyl heptadecanoate internal standard.

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