Kinetics of ionic liquid-heteropolyanion salts catalyzed transesterification of oleic acid methyl ester: A study by sequential method

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ABSTRACT

The kinetics of ionic liquid-heteropolyanion (IL-HPA) salts catalyzed transesterification of oleic acid methyl ester (OAME) was studied via a sequential method. The method can be separated into two parts. The first part was to analyze the kinetics of transesterification of OAME catalyzed by a novel catalyst and to provide a way to simulate the reaction rate profile. The second part was to verify the appropriateness of kinetic parameters calculated in the first part. Kinetic parameters were properly determined and reaction rate profiles were adequately simulated by regarding transesterification as a second order reaction. A good agreement between the experimental data and theoretically predicted values is obtained. This method may be applicable to most of three-step consecutive reaction whose $t_{\mathrm{max,first\ intermediate}}$ and $t_{\mathrm{max,second\ intermediate}}$ at the maximum concentration are acquirable, representatively and reliably.

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1. Introduction

Synthetic esters, as a kind of bio-lubricant, derived from methyl esters and branched polyols exhibit better lubricity, more favorable viscosity and pour point and lower volatility than petroleum-based lubricants [1–3]. In addition to these advantages, the absence of hydrogen atom bonded on the α-carbon of the synthetic esters further affords excellent stability in thermal and oxidative processes, leading to the remarkable improvements in engine lifetime. To promote synthetic efficiency, processes for bio-lubricant production are usually carried out in the presence of homogeneous acid/alkali catalyst and organic solvent, which is inevitably troublesome for catalyst recovery and waste disposal [4–6]. Although solid catalyst may partially overcome these problems, several disadvantages, such as poor activity, rapid deactivation and pronounced mass transfer resistance, are also encountered, which limit its practical application in bio-lubricant production. During the past decades, a series of advanced catalytic techniques including phase-transfer catalysis [7–9], thermo-regulated phase-transfer catalysis [10] and liquid–liquid biphasic catalysis [11]—have been developed in bio-lubricant processes with improved handling convenience and environmental friendliness. Recently, a novel ionic liquid-heteropolyanion (IL-HPA) hybrid, which acts as a "reaction-induced self-separation catalyst", has been prepared and employed as acid catalyst in esterification [12]. Due to its high melting point and polarity, IL-HPA hybrid behaves as a homogeneous catalyst during reaction at high temperature and precipitates as gelatinous solid at low temperature, led to convenient recovery and recycle of used catalyst. A series of IL-HPA compounds with both high catalytic efficiency and convenient catalyst recovery for transesterification of oleic acid methyl ester (OAME) have been reported [13]. The overall reaction was shown in Scheme 1. In the presence of IL-HPA, 99.2% conversion and 92.5% yield of product were obtained within 3 h at 120 °C. This new catalyst can be easily recovered and reused for eight catalytic runs without losing catalytic performances.

Chemical kinetics, which is the study of rates of chemical processes, plays an important role in the field of scientific research. Kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction. In particular, kinetics analysis for the reactions such as transesterification involving a complex set of sequential bimolecular reactions that are often impossible to characterize at any significant level of detail become more and more attractive due to its practical interest. The kinetic analysis may capture the essence of the exceedingly

complex reaction set in a tractable mathematical way. Consequently, better understanding of the kinetics and estimating kinetic factors are necessary for operating this catalytic process. Generally, the derived kinetic parameters are dependent on not only the respective reaction conditions, but also the mathematical model employed [14]. A number of methods for kinetic analysis using different mathematical and methodological models have been developed, and they focused on the development of mathematical simulator to solve multiple rate equations [15,16]. Nevertheless, Levenspiel et al. suggested that, in sequential reactions, the parameters obtained from the equations described in terms of concentration of product *vs* concentration of reactant would be more accurate than that from mathematical simulator [17]. Two methods, differential and integral methods, have been attempted to

determine the kinetic parameters for catalytic reactions [18–20]. Approximation is always required in an integral method and several helpful techniques have been applied to minimize the error. On the other hand, the differential method needs less or even no approximation, but is quite sensitive to experimental noise due to the calculation of derivatives. In recent years, a novel methodology that uses experimental data at maximum reaction rate to reduce the error of approximation attracts great interests [21].

In this study, kinetic analysis of OAME transesterification catalyzed by IL-HPA hybrids was attempted by a sequential method, which was first reported by Huang et al. [21]. Transesterification of OAME consists of three consecutive reaction steps (Eqs. (1)–(3)). A kinetic model was proposed to determine the kinetic parameters rapidly and accurately. The experimental data at maximum concentration were employed to simulate the chemical kinetics and the accuracy of the developed sequential method was verified by comparison of experimental data with theoretically predicted values. More insights into catalytic nature of OAME transesterification catalyzed by these IL-HPAs were discussed.

2. Method

2.1. Chemicals

Pyridine (99%), 1,4-butane sultone (99%), phosphotungstic acid (AR) and trimethylolpropane (AR), oleic acid methyl ester (AR), ethyl acetate (AR), N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) (99%) were purchased from Sigma-Aldrich or Fluka and used without further purification.

2.2. Preparation of catalysts

IL-POMs were synthesized based on the previous report [20]. Pyridine (0.11 mol) and 1,4-butane sultone (0.10 mol) were
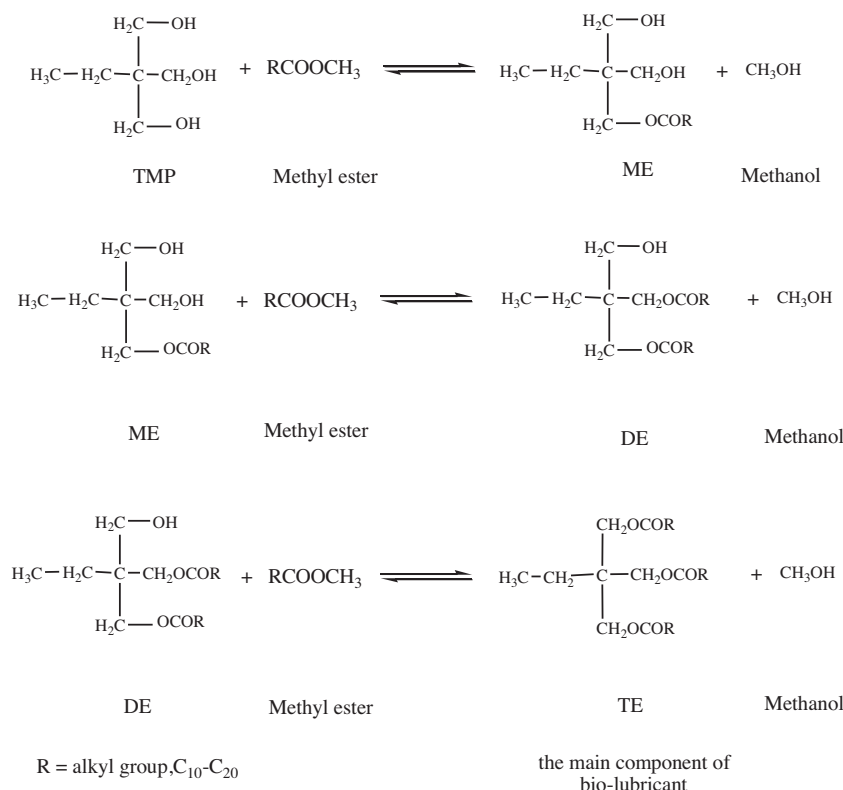
Scheme 1. The overall transesterification of oleic acid methyl ester for bio-lubricant production.