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Kinetics and thermodynamic analysis of levulinic acid esterification using lignin-furfural carbon cryogel catalyst

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ABSTRACT

The synthesis of ethyl levulinate, a fuel additive, by catalytic esterification of levulinic acid with ethanol over carbon cryogel has been investigated. The carbon cryogel catalyst, coupled with a large surface area and strong acidity, has been identified as an effective carbon-based catalyst for obtaining high ethyl levulinate yield of 86.5 mol%. The pseudo-homogeneous kinetic model is adopted to evaluate the different reaction orders. The first-order pseudo-homogeneous model is considered most suitable ($R^2 > 0.98$) while the selection of kinetic model is also clarified and supported by the linearity of the parity plot. The activation energy of the esterification reaction is estimated to be 20.2 kJ/mol. Based on the thermodynamic activation parameters, the reaction is classified as endergonic and more ordered. The results from this study could provide valuable information for reactor modeling and simulation purposes in the future.

1. Introduction

The derivatives of bio-fuel from renewable sources are appropriate for applications as transportation fuels and bio-based chemicals. Biodiesel, derived from many sources including waste oil, has been credited as a promising bio-fuel [1–3]. In addition, many processes have been conducted on lignocellulosic biomass to produce bio-fuels and bio-chemicals via thermochemical conversion [4]. The catalytic hydrolysis of biomass has been conducted to derive chemicals such as reducing sugar and 5-hydroxymethyl furfural (HMF) for further conversion to levulinic acid [5]. Levulinic acid is recognized as a building block and chemical platform [6]. Previous studies have reported the direct conversion of lignocellulosic biomass to levulinic acid using homogeneous and heterogeneous catalysts [5,7–10].

As a platform chemical, levulinic acid can be used to synthesize levulinate esters via esterification reaction with alcohol. Esters such as methyl, ethyl and n-butyl levulinate are produced using methanol, ethanol, and n-butanol, respectively as co-reactants [11–14].

The production of alkyl levulinate from levulinic acid as biomass-derived chemical has attracted great attention in the green energy sector. The reaction products could be separated and purified from the feedstock using separation methods such as reactive distillation [15] and membrane technology [16,17]. Levulinate esters have extensive application mainly as additives in gasoline and biodiesel, in γ-valerolactone (GVL) production, and also in flavoring and fragrance industries [18–20].

The application of carbon-based catalyst has attracted significant attention owing to its large surface area, high activity and thermal stability. The catalyst is prepared by modification of activated carbon [3,21,22] and sulfonation of carbonaceous material [23,24] mainly from biomass. The main motivation for synthesizing a new carbon cryogel is to tailor the properties of carbon-based catalyst more suited for esterification. Based on our previous studies, carbon cryogel synthesized from lignin and furfural gel demonstrated good reactivity in esterification [25,26]. Lignin and furfural, as major byproduct and derived chemicals from biomass processing, have advantages as green substitutes in gel synthesis. Previously, more toxic chemicals such as phenol or resorcinol and formaldehyde have been used for gel synthesis to produce carbon gel [27–30]. Therefore, it is envisaged lignin–furfural based carbon cryogel could substitute homogeneous acid catalysts, such as the strong H_2SO_4 acid, for esterification reaction.

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Modeling studies on kinetic and thermodynamic provide important parameters related to activity, reaction rate, and activation energy in heterogeneous reaction. The models should fit the experimental data at different reaction time and temperature and are very useful for scaling-up purposes [31]. Moreover, the kinetic parameters are needed in chemical process analysis and optimization of the reaction parameters for catalysis application in the industry [32,33].

The kinetic model is commonly developed based on simple power law for determining the reaction rate constant. Hoo and Abdullah [34] stated for rapid investigation on the reaction rate constant and activation energy of developed heterogeneous catalysts, the simple power law model has frequently been used. The pseudo-homogeneous approach is usually applied in determining the kinetic model [20,35–37]. The first-order kinetic model is frequently adopted to fit the data based on the assumptions made [38–40]. Previous studies on the levulinic acid esterification reported first-order and second-order kinetic models [20,31,35].

Thermodynamic study involves parameters such as enthalpy, entropy, and Gibbs free energy. Based on the activated complex theory, Ong et al. [41] have calculated the Gibbs free energy with the Eyring-Polanyi equation (generally known as Eyring equation). Similar equations has been used in previous studies for calculation of thermodynamic activation parameters [42–44].

In this paper, the kinetic and thermodynamic parameters of levulinic acid esterification with ethanol by using lignin-furfural carbon cryogel have been determined. The effects of internal and external diffusions were studied before conducting the kinetic analysis on the reaction at various temperatures and reaction time. The experimental data were interpreted using the pseudo-homogeneous kinetic model with different reaction orders. The kinetic parameters of the selected model were reported including the reaction rate constants, activation energy and the pre-exponential factor. In addition, the thermodynamic activation parameters namely the enthalpy of activation, entropy of activation and Gibbs energy of activation were determined for the levulinic acid conversion. Important basic information will be obtained through this study for process development of catalytic levulinic acid conversion to ethyl levulinate using carbon cryogel.

2. Materials and methods

2.1. Materials

Ethanol (C_2H_6O, 95%, QRec), sulfuric acid (H_2SO_4, 95–97%, QRec), lignin (alkali, Sigma-Aldrich Co.), and furfural ($C_5H_4O_2$, Merck) were used in gels synthesis. Levulinic acid ($C_5H_8O_5$, 98%, Merck), ethanol (C_2H_6O, 99%, Merck) and ethyl levulinate standard ($C_7H_{12}O_3$, 99%, Merck) were purchased with analytical grade and used as received for the esterification reaction.

2.2. Preparation and characterization of carbon cryogel

Lignin, furfural and distilled water were mixed with a ratio of 1:1:1 for gel synthesis following the methods described by Zainol et al. [25] and [26]. The mixture was homogenized and reaction was conducted at 90 °C for 30 min to synthesize the gel. Next, the gel was immersed in *t*-butanol for solvent exchange, pre-frozen for 24 h and freeze-dried for 8 h to form cryogel. Finally, the cryogel was calcined in the furnace at ambient atmosphere and 500 °C for 1 h to produce carbon cryogel.

The surface area of the carbon cryogel was evaluated by using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods based on nitrogen adsorption and desorption at −196 °C via Surfer instrument by Thermo Scientific. The total acidity of the carbon cryogel was measured by NH_3-TPD (Micromeritics AutoChem II 2920 V4.03) with thermal conductivity detector (TCD) and gas passing of 10% NH_3/He up to 900 °C. The TGA was analyzed by Perkin Elmer TGA 7 instrument at ramp temperature of 10 °C/min from 30 to 900 °C under nitrogen flow to evaluate the thermal stability.

2.3. Synthesis of ethyl levulinate

The esterification reaction of levulinic acid was conducted in a 100 mL high-pressure reactor. A series of carbon cryogel with particle size in the range of 100–300 μm were utilized in the experiment to determine if internal diffusion resistance was a controlling factor. Varying agitation speed from 100 to 300 rpm was studied to evaluate the effect of external diffusion on levulinic acid conversion. For a typical experiment, the agitation speed was fixed at 200 rpm and the reaction was conducted at 25 wt% of catalyst loading and 15 M ratio of ethanol to levulinic acid. For determining the kinetic and thermodynamic parameters, the reaction time and temperature range were from 0 to 180 min and 78–150 °C, respectively. The experimental runs were randomly selected and repeated to test the reproducibility of the data. The product samples were separated using vacuum filtration with 0.45 μm nylon membrane filter for further analysis.

2.4. Product analysis

A gas chromatograph system (GC-FID 7820A, Agilent Technology) was used to determine the number of moles of ethyl levulinate (EL) under the following conditions: HP-5 column (length, 30.0 m; diameter, 320.0 μm); injector temperature, 270 °C; column temperature, set from 80 to 170 °C (13 °C/min) and the 170–300 °C (40 °C/min); carrier gas, nitrogen (1.0 mL/min). The levulinic acid concentration was determined for the calculation of conversion with high performance liquid chromatography (HPLC) from Agilent Technology (1260 Infinity) with the following conditions: Hi-Plex H column (length, 300 mm; diameter, 7.7 mm); UV detector (210 nm); column temperature of 60 °C; auto-injector (20 μL injection volume) and mobile phase of 5 mM H_2SO_4 (0.6 mL/min).

The standard concentration of ethyl levulinate and levulinic acid were obtained from the standard calibration curves of the respective compounds. The conversion and product yield were calculated using eqs. (1) and (2):
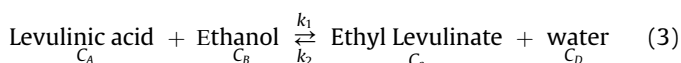
$$\text{EL yield (mol\%)} = \left[(C_E \times V_p)/1000/M_E \right]/(W_i/M_L) \times 100 \quad (1)$$

$$\text{Conversion (\%)} = \left[W_i - ((C_L \times V_p)/1000) \right]/W_i \times 100 \quad (2)$$

where, C_E and C_L are the final product concentrations of ethyl levulinate and levulinic acid (mg/L), respectively, V_p is the final volume of product (L), W_i is the weight of levulinic acid (g), and M_E and M_L are the molecular weight of ethyl levulinate and levulinic acid (g/mol), respectively.

2.5. Mathematical model for kinetic and thermodynamic studies

The esterification reaction of the levulinic acid and ethanol is shown in eq. (3), while the rate of the reaction is derived in eq. (4).

$$\underset{C_A}{\text{Levulinic acid}} + \underset{C_B}{\text{Ethanol}} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{C_c}{\text{Ethyl Levulinate}} + \underset{C_D}{\text{water}} \quad (3)$$