Kinetic studies on biodiesel production using a trace acid catalyst

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ABSTRACT

Biodiesel was produced by transesterification in the presence of trace sulfuric acid (0.02–0.1 wt% of oil mass). The kinetics for the transesterification of corn oil with ethanol was investigated between 155–195 °C. The transesterification in the pseudo-homogeneous system consisted of three consecutive steps. All steps were found to be second order reactions, with the first and the second steps being irreversible, while the third step was reversible. It was observed that the apparent rate constants of the forward reactions increased linearly with increasing acid concentration. Compared to the initial two steps of the ethanolysis reaction, the effect of the reversible transformation in the third step is significant, as the conversion of monoglyceride to glycerol is difficult. In addition, the presence of free fatty acids (<30 wt%), water (<3 wt%), and the use of stirring had little effect on the final content of biodiesel. Finally, it was observed that methanol exhibited a higher reactivity than ethanol in transesterification, while corn oil exhibited higher reactivity than Pennycress oil.

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1. Introduction

Over the past few decades, alternative and renewable energy sources have attracted a growing amount of attention. Biodiesel, for example, is a renewable fuel produced from the trans-esterification of renewable resources such as alcohols and vegetable oils/animal fats [1–4]. As these oils normally contain free fatty acids (FFAs), which can induce saponification in a traditional base-catalyzed transesterification process, a pre-esterification process is required. This process involves the esterification of such oils with alcohol to convert the FFAs to esters under acidic conditions, thus reducing the acid value of the oil below 1 mg KOH/g. Many literatures have reviewed different methods of reducing FFAs in the raw oil [1,5–7]. Both acid including homogeneous and heterogeneous acid and enzyme

can be used to catalyze esterification and transesterification simultaneously and avoid soap formation. But in commercial processes, approximately 0.5–5 wt% (based on oil weight) of a liquid acid is employed as catalyst, and the spent catalyst is removed after pre-esterification to prevent interference in the subsequent alkali-catalyzed transesterification. This process results in not only the corrosion of pipelines, but also in the production of significant quantities of wastewater. Although many solid acids have been studied to avoid soap formation and waste water, they are easy to deactivate and expensive [5,6]. The high price, slow reaction rate and deactivation of enzyme also limits its commercialization [6].

It has previously been demonstrated that liquid acids such as sulfuric acid can slowly catalyze transesterification reactions at room temperature, with accelerated rates achieved by increasing the reaction temperature [8,9]. We previously reported a subcritical production process for biodiesel using high acid value oils using trace acid catalysts (0–0.1% weight of oil) at an elevated temperature below the supercritical temperature of the alcohol. Experimental results showed that the conversion rate was reasonable at significantly lower pressures than those required for the supercritical method [10].

In the acid catalyzed subcritical process, the trace acid catalyst dissolves in the glycerol product following evaporation of excess

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alcohol, giving a residual amount of acid catalyst in the biodiesel phase which can be within acceptable biodiesel standards [11]. Transesterification between methanol and *Jatropha curcas* L. oil in the presence of trace amounts of acid was previously investigated in our group [10], where we found that both the esterification and the transesterification reactions could be carried out simultaneously.

With regard to renewable resources for such processes, ethanol can be produced by the fermentation of grain and sugarcane, and has additional advantages over methanol in that it is less toxic. Recently, the production of ethanol from lignocellulosic biomass has been investigated, to increase ethanol production from abundant renewable feedstocks [12]. In addition, it has been found that the biodiesel produced from ethanol has improved low temperature flow properties compared to that produced from methanol [13].

We herein report the use of H_2SO_4 (0–0.1 wt% based on the weight of oil) for the catalysis of the simultaneous esterification and transesterification of alcohol under subcritical conditions. Literatures relating to kinetics studies of biodiesel production with acid catalyst have been published with different oils at different reaction conditions in the past decade. Marchetti et al. investigated the kinetics of esterification of FFA in acid oils between 35–55 °C [9]. Two kinetic models were set up with and without considering the effect of transesterification. Nautiyal et al. studied the kinetics and thermodynamics on biodiesel production from algae [14]. Hexane, sulfuric acid and methanol was added to dried algae biomass to carry out extraction and transesterification in one step. It showed that transesterification followed the first order kinetics and the rate of reaction varied linearly with yield of methyl ester from 30 to 60 °C. Shuit et al. studied the kinetics of esterification of palm fatty acid distillate with solid acid catalyst [15]. But few studies have been carried out into kinetic studies of the transesterification under trace acid catalyst conditions. We therefore report investigations into the measurement of kinetic properties relating to the intermeidates of monoglyceride (MG) and diglyceride (DG) in the trace H_2SO_4-catalyzed transesterification process. In addition, a range of oils (corn oil and Pennycress oil) and alcohols (methanol and ethanol) were compared. The impact of water and FFA in the reaction system was also investigated.

2. Experimental

2.1. Materials

Corn oil was purchased from a local supermarket (Syracuse, New York, USA). Pennycress oil was supplied by Alberta Agriculture and Rural Division (Edmonton, Alberta, Canada) (see Table 1 for composition details). Methanol (99.9%; Fisher Scientific), ethanol (absolute 99%, extra dry, Fisher Scientific), and *n*-heptane (anhydrous, 99%, Sigma Aldrich), were used without further purification. Standard solutions and internal standards of triglyceride (TG), diglyceride (DG) and monoglyceride (MG) for analysis according to the ASTM method D6584 were purchased from Sigma Aldrich. *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA) (97%) was purchased from Fisher Scientific (Agawam, MA, USA). Unless otherwise stated, all other chemicals were purchased from Fisher Scientific (Agawam, MA, USA) and were of analytical grade. The components of the fatty acids in corn oil and Pennycress oil are listed in Table 1.

2.2. Biodiesel preparation

Transesterification was carried out in a 1 L stainless steel autoclave (Parr 4048), equipped with a heating jacket, an internal cooling coil, an adjustable two-blade propeller agitator, a sampling port, and a reflux condenser.

A mixture of the desired alcohol and oil with the sulfuric acid catalyst were charged to the autoclave (total volume 400 mL). After heating the closed autoclave to the desired temperature (155 °C, 165 °C, 175 °C, 185 °C, or 195 °C) over 35 min (±5 min), the agitator was switched on (at 300 rpm, unless specified otherwise), and the zero point of the reaction time taken. The reaction mixture was sampled at a range of time intervals. Each sample was washed with distilled water to give a pH of approximately 7. After drying over $MgSO_4$ overnight, the transparent golden product was analyzed by GC (see details below) to give the biodiesel components, MG, DG, and TG. All experiments were conducted in triplicate to ensure reproducibility. And the errors were within 3.5%.

2.3. Analytical methods

Analysis of the esters present in biodiesel samples was by GC, using a Thermo Scientific Focus GC system equipped with a Triplus automatic sampler and Trace TR-WaxMS (30 m × 0.25 mm × 0.25 μm) GC column. During analysis, the temperature was increased from 120 °C to 260 °C at a rate of 5 °C/min. The injector temperature was set at 250 °C. Methyl salicylate was used as internal standard.

Quantitative analysis of TG, DG, and MG was carried out using an HP 5890 Series II GC system equipped with an FID detector, in combination with a previously reported GC method [16].

For GC analysis, each sample was analyzed twice. Concentrations of ethanol and glycerol were determined using the mass balance of the reaction. The equations are as following,

$$[EtOH] = [EtOH]_0 - [FAEE] \tag{1}$$

$$[GL] = [TG]_0 - [TG] - [DG] - [MG] \tag{2}$$

where [TG], [DG], [MG], [EtOH], and [GL] are the concentrations of triglyceride, diglyceride, monoglyceride, ethanol, and glycerol, respectively. $[EtOH]_0$ and $[TG]_0$ are the initial concentrations of ethanol and triglyceride when they were added into the autoclave.

3. Results and discussion

3.1. Transesterification process

The three successive reactions, which take place during the transesterification of TG, are shown in Scheme 1.

As can be seen in Scheme 1, during the transesterification, TG initially reacts with ethanol (EtOH) to form DG and FAEE (1). DG then proceeds to react with an additional equivalent of ethanol to form MG and FAEE (2). Finally, MG reacts with ethanol to produce glycerol and FAEE (3).

Fig. 1 shows a typical concentration profile during the transesterification of corn oil with ethanol. As expected, the concentrations of TG and ethanol decreased, whereas that of FAEE and glycerol increased over time. The concentrations of the intermediates, DG and MG, increased initially, and then decreased as the reaction progressed. The presence of small quantities of FAEE, DG, and MG at $t = 0$ is due to the reaction beginning to take place during the heat ramp to the reaction temperature. It should be noted that these concentrations were taken as the initial concentrations for kinetic analysis. It can also be seen from Fig. 1 that after 141 min, the conversion of TG was complete, but after 240 min DG and MG were still present, and the FAEE yield according to the fatty acid in TG was < 100%. These factors suggest that the yield of FAEE is limited by the three equilibria.