Fuel Processing Technology 122 (2014) 30–41

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Effect of process conditions on equilibrium, reaction kinetics and mass transfer for triglyceride transesterification to biodiesel: Experimental and modeling based on fatty acid composition

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ARTICLE INFO

Article history:
Received 25 July 2013
Received in revised form 16 January 2014
Accepted 18 January 2014
Available online 6 February 2014

Keywords:
Biodiesel production process optimization/intensification
Reaction mechanism/kinetics
Mass transfer/diffusion
Renewable energy/fuels

ABSTRACT

Detailed reaction kinetics of oil transesterification were studied based on mechanism and reaction scheme of individual triglyceride, diglyceride, monoglyceride, glycerol and fatty acid methyl ester containing different combinations of gadoleic, linoleic, linolenic, oleic, palmitic and stearic acids determined by high-performance liquid chromatography. Pre-exponential factors and activation energies were correlated with molecular structure in terms of chain lengths and double bonds by response surface models. The activation energies of forward reactions were 47–61 kJ mol^{-1} with backward ones being 31–49 kJ mol^{-1}, depending on component structure. Mass transfer during initial emulsion phase was acknowledged by determining diffusivities, distribution coefficients, molar volumes, boiling points and viscosities of individual components. Model was validated for a wide range of temperatures, hydrodynamic conditions, dispersed and continuous phase ratios, and methanolysis catalyst concentrations. Rotational speed had the most profound influence on the duration of transport phenomena-limited region spanning the latter to 27 min upon use of 100 rpm. Economics of the process were finally evaluated in terms of alcoholysis cost and price breakdown. Proposed methodology may be usefully applied to transesterification syntheses employing heterogeneous catalysis and enzymes, as well as various *renewable resources* such as *microalgae lipids*, *waste oils*, *bioethanol* and *biobutanol*.

1. Introduction

Biodiesel, which is composed mainly of fatty acid methyl esters, produced by the transesterification of vegetable oils and animal fats, has become an attractive renewable substitute to the mineral petroleum-derived diesel fuel due to its environmental benefits.

Mass transfer between two organic phases (methanol and oil) plays a critical role during the transesterification (methanolysis) [1] and in this sense controls the rate at the initial stage [2]. In the studies of the transesterification process rate three regimes are well-recognized, that is an initial mass transfer-controlled regime (slow), followed by a chemically-controlled regime (fast), and a final regime, close to equilibrium (slow) [3]. Therefore, methanol is not effectively used for the reactions due to the interfacial mass transfer resistance [4]. For example, in the transesterification, performed by Sengo et al. [5] in a 30 L reactor under previously optimized conditions, a yield of only 88% fatty acid methyl esters was obtained after 90 min of reaction time, due to the mass transfer limitations. Tsuji et al. [6] noted that a homogeneous single phase was formed at the 3.9:1 molar ration of methanol to oil (triglyceride) and that the mass transfer resistance between the methanol and oil phases disappeared. Nonetheless, this is seldom reported by other researchers and is rather specific for the utilized reactor system, e.g. the resistance would probably not disappear in a continuous reactor. All three regimes should be in principle correlated into a single model, acknowledging mass transfer, kinetics, and equilibrium [7,8].

The influence of mass transfer on the production of biodiesel may be observed through mixing variation, as the use of different mixing methods (magnetic stirrers, ultrasound, dispersers, etc.) results in different conversions after the transesterification of rapeseed oil with methanol in both acidic and basic systems [9,10]. The production of biodiesel from vegetable oils may thus be assisted by ultrasound, which is a useful tool for strengthening the mass transfer of immiscible liquids [11]. Cavitation mainly affects the mass transfer rates and ensures a uniform distribution of the reactants, as one concludes from the fact that a significant effect on both the reaction rate and the equilibrium conversion is only observed in the later stages of the reactions, when heterogeneity sets in [12]. Some bubbles undergo a sudden expansion to an unstable size and collapse violently, generating the energy for chemical and mechanical effects, and may increase the mass transfer rates by disrupting the interfacial boundary layers (known as the liquid jet effect) [13]. Ultrasound in chemical processing enhances both mass transfer and chemical reactions [14], but noticeably increases the cost of the

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http://dx.doi.org/10.1016/j.fuproc.2014.01.017

produced biodiesel, rendering the use of ultrasound for liquid fuel production questionable.

Mechanical mixing is normally applied to increase contact between the reactants, resulting in an increase in the mass transfer rate [15], consequently; mixing is crucial in the biodiesel synthesis reactions in order to provide a fine dispersion of methanol in oil and therefore to favor the mass transfer rate [16]. The results indicate that under the conditions of sufficient mixing, agitation intensity influences only the initial phase of the transesterification, during which the mass transfer conditions dominate the system, but eventually it develops into a kinetics-controlled process in which agitation intensity has a minimal effect on the rate [17]. Analogously, the main goals of the research, related to continuous reactors, are to investigate the effect of the number of static mixers and of the static mixer superficial velocity on the profiles of oil conversion versus time, with particular focus on the detection of possible mass transfer limitations to the transesterification reactions; and to evaluate the specific energy requirement, associated with the static mixer utilization for biodiesel production, both in the laboratory, pilot, and at the industrial scale [18].

A proposed synthesis process mechanism consists of an initial mass transfer-controlled region, followed by a second-order kinetics-controlled region [19]. Another approach is to use iterative mass transfer and reactor design equations to model the biodiesel conversion in a batch reactor [20]. There are two general disadvantages of previous models. The first one is that mass transfer is not accounted for in the process model [2,4,5,13,15,17,19], although it plays an important role in batch reactors, e.g. at low temperatures, and a predominant one in continuous reactors. The second one is that chemical equilibrium and reaction kinetics are not accounted for [16,18] or oversimplified, i.e. the reversible or consecutive reactions are neglected [3,4,13,20], or that kinetic parameters depend on the resource, e.g. oil [2,5,15,17,19].

The present study is an attempt to develop an overall model, based on the fatty acid composition of species, acknowledging fluid mechanics (mixing), transport phenomena (mass transfer), and reaction kinetics (a single set of kinetic parameters) for an appropriate process sensitivity analysis, monitoring, regulation, optimization, or intensification, regardless of process conditions and resource origin, i.e. vegetable, algal or waste oil, and even oil mixtures.

2. Materials and methods

2.1. Materials

Commercial refined and edible-grade canola oil (Tovarna olja Gea, Slovenska Bistrica, Slovenia) was used. The acid, saponification and iodine values of the oil were 0.3 wt.%, 177 mg KOH/g, and 116 g I_2/100 g, respectively, determined according to the ISO 660:2009, ISO 3657:2008, and ISO 3961:2000 official methods. For the transesterification, a certified methanol of 99.8 wt.% purity was purchased from Sigma-Aldrich (Steinheim, Germany). KOH pellets of 88 wt.% purity were purchased from J.T. Baker (Deventer, Holland). Solvents, specifically, acetonitrile (gradient grade; 99.9 wt.%), methanol (gradient grade; 99.9 wt.%), *n*-hexane (for high-performance liquid chromatography (HPLC); 99.9 wt.%), and isopropanol (for HPLC; 99.9 wt.%), all of HPLC grade (Chromasolv) and used without purification, were obtained from Sigma-Aldrich (Steinheim, Germany). The HPLC reference standards for fatty acid methyl esters (FAME) containing methyl, ethyl, isopropyl, butyl, and *tert*-butyl esters of gadoleic (G), linoleic (L), linolenic (Ln), myristic (M), oleic (O), palmitic (P) and stearic (S) acids (different combinations of esters) and corresponding tri- (trilinolein, trilinolenin, triolein, tripalmitin, and tristearin), di- (1,2-dilinolein, 1,3-dilinolein, 1,2-dilinolenin, 1,3-dilinolenin, 1,2-diolein, 1,3-diolein, 1,2-dipalmitin, 1,3-dipalmitin, 1,2-distearin, and 1,3-distearin), and monoglycerides (1-monolinolein, 2-monolinolein, 1-monolinolenin, 2-monolinolenin, 1-monoolein, 2-monoolein, 1-monopalmitin, 2-monopalmitin, 1-monostearin, and 2-monostearin) were purchased from Sigma-Aldrich (Steinheim, Germany) and Nu-Chek Prep (Elysian, MN, USA).

2.2. Batch reactor

The reactions were carried out in a 0.6 L glass reactor equipped with the Rushton turbine (a six flat-blade disk turbine) (Fig. SD.1 and Table SD.1, Supplementary data). The impeller diameter and blade width were 25 and 6 mm, respectively. The impeller was centrally placed at 50 mm from the bottom. The reactor was equipped with glassy double jacket filled with silicone oil circulating from a thermostat bath by means of a pump. The reactor was filled with 272 mL of emulsion (the emulsion height was 75 mm).

2.3. Process conditions

The 3:1, 4:1, 5:1, 6:1, 7:1, and 8:1 molar ratios of methanol to canola oil were used in different experiments. KOH (0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 g per 100 g of oil) was dissolved into methanol before use (Table SD.2, Supplementary data). The experiments were carried out at 30, 40, 50, 60 or 70 °C, and atmospheric pressure. The impeller speeds of 100, 200, 300, 400, 500, and 600 rpm were applied to produce the dispersions of methanol into the oil of different uniformities.

2.4. Process procedure

The transesterification reactions were performed with canola oil and methanol in the proportions of 1:3, 1:4, 1:5, 1:6, 1:7, and 1:8 (mol/mol) using KOH for approximately 25–75 min (depending on process conditions) to obtain a mixture of methyl esters, glycerol, diglycerides, monoglycerides, and unreacted oil and methanol at the temperatures of 30, 40, 50, 60, and 70 °C. The reactor was initially charged with 187–222 g (depending on process conditions) of oil, placed in the reactor and heated to the desired temperature, which was then maintained at a constant value. Methanol (24–54 g; depending on process conditions) with dissolved potassium hydroxide (0.5–2.8 g; depending on process conditions), which was heated separately, was added to the reactor. The mechanical stirrer was turned on during oil heating and as soon as methanol was added to oil, the reactions were timed. For studying the equilibrium, kinetics, and mass transfer, the samples (2 mL) were removed from the reaction mixture during the progress of the reactions, immediately quenched by adding an aqueous hydrochloric acid solution (1.0:1.7 (w/w); 0.02 mL) and vigorously shaken (manually for 1 min). The heating of mixture is presented in Fig. SD.2 (Supplementary data).

2.5. Analytical methods

2.5.1. Determination of concentration of reactants, intermediates and products

The samples, removed from reaction mixtures, formed two layers, which were blended by shaking, and a part of the samples was withdrawn and dissolved in isopropanol/*n*-hexane (5:8 (v/v)) in an appropriate ratio, always obtaining the sample-to-solvent ratio of 1:30 (w/w). This procedure was used in accordance with the rule that the sample must be diluted in the solvent used for elution. The resulting mixture was used to prepare the samples for the tests that is, for HPLC analysis. The composition of the samples of the reaction mixture was determined by HPLC, as described elsewhere [21], using the optimal method, obtained by statistical analysis, setting the parameters each time according to the ones, which were calculated by the full factorial design method [21]. The analyses were conducted with a Agilent (Hewlett Packard) (Santa Clara, CA, USA) 1100 Series HPLC equipped with two G1312A solvent delivery units for binary gradient elution, a model G1315A UV–Vis detector, an automatic G1313A sample injector, a model G1316A column oven for precision temperature control above ambient temperatures, a model SCL-10AVP system controller, and ChemStation for LC 3D