



Transesterification of canola, palm, peanut, soybean and sunflower oil with methanol, ethanol, isopropanol, butanol and *tert*-butanol to biodiesel: Modelling of chemical equilibrium, reaction kinetics and mass transfer based on fatty acid composition



Blaž Likozar*, Janez Levec

^aLaboratory of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

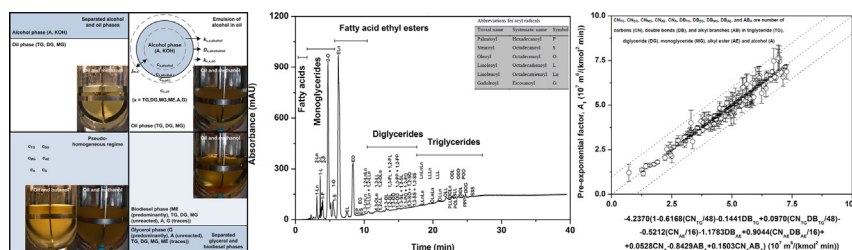
^bFaculty of Chemistry and Chemical Technology, University Ljubljana, Aškerčeva 5, 1000 Ljubljana, Slovenia

HIGHLIGHTS

- Catalysed transesterification to biodiesel with various oils, alcohols and catalysts.
- Analysis of components and reactivity based on fatty acid composition of all species.
- Simultaneous modelling of mass transfer, reaction kinetics and chemical equilibrium.
- Diffusivities, distribution and mass transfer coefficients for individual components.
- Correlation of kinetic parameters with molecular structure of reactants and products.

GRAPHICAL ABSTRACT

Modelling of chemical equilibrium, reaction kinetics and mass transfer for triglyceride transesterification with different alcohols based on fatty acid composition.



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ABSTRACT

Mechanism of alcoholysis (e.g. methanolysis) using different oils, alcohols and homogeneous base catalysts was utilized to devise chemical kinetics and thermodynamics based on fatty acid composition, differentiating among triglycerides, diglycerides, monoglycerides and fatty acid alkyl esters (e.g. fatty acid alkyl esters, FAME) with bonded gadoleic, linoleic, linolenic, oleic, palmitic and stearic acid-originating substituents. Their concentrations were measured using an optimized high-performance liquid chromatography (HPLC) method. Hydrodynamics and diffusion limitations in emulsion were considered in overall model by determining diffusivities, distribution coefficients, molar volumes, boiling points and viscosities of individual components. Pre-exponential factors and activation energies were related with structure of reactants, intermediates and products acknowledging number of carbons, double bonds and alkyl branches by linear and mixed response surface methodology. Developed model may be used with batch and continuous flow reactors, e.g. for novel micro-structured or industrial-scale process intensification, different vegetable or non-edible oils (waste cooking *Jatropha* or microalgae lipids).

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* Corresponding author at: Laboratory of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia. Tel.: +386 1 4760283; fax: +386 1 4760300.

E-mail address: blaz.likozar@ki.si (B. Likozar).

1. Introduction

The transesterification reaction of different oils and alcohols has gained much attention recently because of its use in biodiesel industry. The continuous production of algal, palm, peanut, canola, soybean, sunflower, and other oil-originating biodiesel with different alcohols in various reactor configurations demands a process model, acknowledging chemical equilibrium, reaction kinetics and mass transfer, regardless of fatty acid composition of oil.

Most of the studies investigate the biodiesel production process of a given oil and alcohol (most frequently methanol) [1–6], nonetheless; a variation in oil resource compound (e.g. waste oil mixtures), in the fatty acid composition of a single oil type (e.g. canola), or even in the alcohol, utilized for the transesterification (e.g. the partial substitution of methanol with bioethanol) may jeopardize process monitoring, regulation, optimization, or intensification.

Mass transfer is often not accounted for in the process model, although it plays an important role in batch reactors, e.g. at low temperatures and poor mixing, and a predominant one in continuous reactors. Some studies mention the process mechanism consisting of an initial mass transfer-controlled region followed by a kinetics-controlled region for the transesterification of palm [7], canola [8,9], soybean [10], and sunflower [9,11] oils with methanol, however; mass transfer is seldom incorporated into the overall process model [7,8,10,11]. When other alcohols are applied in biodiesel synthesis, the literature considering mass transfer resistances between alcohol and oil phase is even more scarce. Fluid mechanics of ethanol/oil emulsions were investigated by Duangsuwan et al. [12], nonetheless; kinetics and mass transfer during the transesterification were not studied. Mass transfer is at least qualitatively treated for the supercritical [13], acidic [14], heterogeneously-catalysed [15,16], and enzymatic [17,18] transesterification with ethanol [13,14,17], isopropanol [14,15, 18], butanol [14,16], and 2-butanol [18], however; is not directly coupled with reaction kinetics into the overall process model. Analogously may be concluded for the conventional base-catalysed homogenous transesterification with ethanol [19,20], isopropanol [20], and butanol [20]. The latter type of catalysis is the most widespread in biodiesel production process to date and should be suitably described.

Reaction kinetics were extensively studied for the transesterification of different oils with methanol, but the main disadvantage remains that the utilization of the determined kinetic parameters often remains limited to the investigated oil, as the fatty acid composition usually varies even for one oil type (e.g. canola) [9–11]. In the case of the transesterification with other alcohols (e.g. ethanol), the kinetics is often only studied in a simplified manner [17,19,20].

The aim of this study is to present a model for the transesterification of different oils and alcohols, based on fatty acid composition of tri-(TG), di-(DG) and monoglycerides (MG), and alkyl esters (AE) (biodiesel), acknowledging chemical equilibrium, reaction kinetics and mass transfer.

2. Material and methods

2.1. Materials

Commercial refined and edible-grade canola (Slovenia), palm (Slovenia), peanut (Italy), soybean (Bosnia and Herzegovina), and sunflower (Bosnia and Herzegovina) oils were used. The acid, saponification and iodine values of the oils were 0.3 wt.%, 0.6 wt.%, 0.6 wt.%, 0.8 wt.% and 0.7 wt.% (acid), 177, 220, 137, 190 and 193 mg KOH/g (saponification), and 116, 51, 95, 128 and 135 g I₂/100 g (iodine) for canola, palm, peanut, soybean, and sunflower oil, 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.% and 99.9 wt.% purity was purchased from Sigma–Aldrich (Germany) and Merck (Germany), respectively, ethanol of 99.5 wt.% purity from Sigma–Aldrich (Germany), isopropanol of 99.9 wt.% purity from Sigma–Aldrich (Germany), butanol of 99.5 wt.% purity from Merck (Germany), and *tert*-butanol of 99 wt.% purity from Merck (Germany). KOH and NaOH pellets of 88 wt.% and 99 wt.% purity were purchased from J.T. Baker (Holland) and Merck (Germany), respectively. Solvents, specifically, acetonitrile (gradient grade; 99.9 wt.%; hypergrade for LC–MS; 99.9 wt.%), methanol (gradient grade; 99.9 wt.%; for liquid chromatography; 99.8 wt.%), *n*-hexane (for high-performance liquid chromatography (HPLC); 97 wt.%; for liquid chromatography; 98 wt.%), and isopropanol (for HPLC; 99.9 wt.%; gradient grade for liquid chromatography; 99.9 wt.%), all of HPLC grade (Chromasolv; LiChrosolv) and used without purification, were obtained from Sigma–Aldrich (Germany) and Merck (Darmstadt, Germany). The HPLC reference standards for fatty acid methyl, ethyl, isopropyl, butyl, and *tert*-butyl esters (FAME, FAEE, FAiPE, FAFE, and FAtBE) 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 (not all combinations of esters), and corresponding tri-(trilinolein, trilinolenin, triolein, tripalmitin, and tristearin), di-(1,2-dilinolein, 1,3-dilinolein, 1,2-dilinenin, 1,3-dilinenin, 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 (Germany) and Nu-Chek Prep (USA).

2.2. Batch reactor

The reactions were carried out in a 0.6 L glass reactor equipped with the Rushton-type turbine (Figs. SD.1 and SD.2, 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 6:1 M ratio of alcohol to vegetable oil was used in all experiments. KOH and NaOH (0.8 g per 100 g of oil) were dissolved into alcohol before use. The experiments were carried out at 40, 50 or 60 °C, and atmospheric pressure. The impeller speed of 400 rpm (power input per unit volume was 1.5 W/m³ and 295.3 W/m³ for the canola oil mixing at 50 °C using 100 rpm or 600 rpm, respectively) was applied to produce a uniform dispersion of alcohol into oil.

2.4. Process procedure

The transesterification reactions were performed with canola, palm, peanut, soybean and sunflower oil, and methanol, ethanol, isopropanol, butanol and *tert*-butanol in the proportions of 1:6 (mol/mol) using KOH and NaOH for approximately 30 min (canola, peanut, soybean, and sunflower oil) or 40 min (palm oil) to obtain a mixture of alkyl esters, glycerol, diglycerides, monoglycerides, and unreacted oil and alcohol at the temperatures of 40, 50, and 60 °C. The reactor was initially charged with 158–206 g (depending on materials and process conditions) of oil, placed in the reactor and heated to the desired temperature, which was then maintained

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