



# The effect of tetrahydrofuran on the base-catalyzed sunflower oil methanolysis in a continuous reciprocating plate reactor



Ivana B. Banković-Ilić, Zoran B. Todorović, Jelena M. Avramović, Ana V. Veličković, Vlada B. Veljković\*

Faculty of Technology, University of Niš, Bulevar oslobođenja 24, 16000 Leskovac, Serbia

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## ABSTRACT

The homogeneous base-catalyzed methanolysis of sunflower oil in the presence and absence of tetrahydrofuran (THF) as a co-solvent was studied in a continuous cocurrent upflow reciprocating plate reactor (RPR). The measurements of the dispersed phase drop size demonstrated the effects of the THF concentration on the Sauter-mean drop diameter and the drop size distribution in both non-reactive (methanol/oil) and reactive (methanol/KOH/oil) systems. The presence of THF shifted both heterogeneous systems to the stable homogeneous emulsion consisted of small dispersed phase drops. The triacylglycerol (TAG) conversion degree was measured in the reactive system. The sigmoidal kinetics was observed in the absence and presence of THF at lower THF concentrations ( $\leq 10\%$  of the oil mass). This shape was explained by the existence of the initial TAG mass transfer controlled region followed by the irreversible second-order reaction controlled region. However, at the highest THF concentration (30% of the oil mass) the irreversible and reversible second-order reaction kinetics was used to describe the variation of TAG conversion degree with time. The proposed kinetic models satisfactorily fitted the experimental data.

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## 1. Introduction

Biodiesel (a mixture of fatty acid methyl or ethyl esters) is an alternative to diesel fuels with well-known economical and environmental benefits. Transesterification is the most common reaction to produce biodiesel from a source of triacylglycerols (TAGs) and an alcohol, which is most frequently performed at commercial scale in the presence of alkaline catalysts. The two reactants are not miscible at ambient temperature and pressure, so the reaction mixture in a typical homogeneous transesterification reaction consists of at least two phases. The miscibility of the phases can be enhanced by increasing the reaction temperature, but this is an energy-consuming process. A possible solution of this problem is the use of a co-solvent in the reaction mixture to increase the solubility of alcohol in the oil phase and to minimize the induction period by overcoming the initial mass transfer resistance [1]. Furthermore, the addition of co-solvent helps to enhance the separation rate of obtained phases (biodiesel and glycerol) and to suppress the rate of soap formation [2].

When added in sufficient amounts, co-solvents make the resulting mixture monophasic [3], but they should be inert and must not react with the reactants or deactivate the catalyst. Low-molecular weight ethers (methyl *tert*-butyl ether, dimethyl ether, diethyl ether and tetrahydrofuran, THF) function as co-solvent in the reaction. Many other organic compounds have been also used as co-solvents such as propane,

heptane, *n*-hexane and carbon-dioxide. Besides the organic solvents, the use of ionic liquids as co-solvents has recently gained importance [4]. It is worth mentioning that biodiesel itself functions as a co-solvent [2].

THF is one of the most commonly used co-solvents because of several positive properties. Because of its boiling point close to that of methanol, THF can easily be recovered from the final reaction mixture and reused. Its additional advantages are small cost, non-toxicity, chemical inertness and enhancement of glycerol separation [3]. Furthermore, THF is attractive because it may increase the rate constant of transesterification reactions [5–7]. A disadvantage of THF is its tendency to form peroxide during the storage [8].

The effect of co-solvents on the conversion of various vegetable oils with an alcohol has been mainly studied in homogeneously-catalyzed transesterification processes in batch reactors [7–16]. However, there are a few studies of the continuous biodiesel production in the presence of a co-solvent (Table 1). These studies include base- [8,12,17] and enzyme-catalyzed methanolyses [24–26], as well as the transesterification under the supercritical conditions of carbon dioxide using methanol [18,21] or ethanol [19,20,22,23] as the acyl acceptor.

The controversial conclusions about the impact of co-solvents on the kinetics of base-catalyzed transesterification of vegetable oils in batch reactors have been reported. Karmee et al. [27] did not observe any dramatic increase in the reaction rate when THF was added in the reaction mixture consisting of pongamia oil and methanol, probably because the reaction mixture was homogeneous even without the addition of THF. Some other kinetic studies have clearly indicated that the

\* Corresponding author. Tel.: +381 16 247 203; fax: +381 16 242 859.  
E-mail address: [veljkovicvb@yahoo.com](mailto:veljkovicvb@yahoo.com) (V.B. Veljković).

**Table 1**

A review on continuous transesterification processes using co-solvents.

Oil	Type of reactor (volume, cm <sup>3</sup> , inner diameter, mm)	Type of acyl acceptor	Alcohol:oil molar ratio, mol/mol	Catalyst/loading, conc.	Co-solvent, % vol. to alcohol	Temperature, °C	Pressure, MPa	Optimal reaction conditions		Reference
								Reaction conditions	Yield (conversion), %/residence time, min	
Rapeseed	Tubular static mixing	Methanol	6:1	KOH/1%	THF, butanon	250–270			(90)/6–9	[17]
Sunflower	Microtube (–, 0.96)	Methanol	8:1	KOH/1%	Diethyl ether, 0.73 <sup>a</sup>	25			(92.8)/1.55	[8]
Corn	Electrolysis cell (18.6 V)	Methanol	24:1		THF, 0.25 <sup>a</sup>	25			96.8/60	[11,12]
Rapeseed	Tubular (75, –)	Methanol, sc <sup>b</sup>	24:1	Triethylamine/0.27:1 <sup>a</sup>	Ethyl acetate, 1:10	280	25		85/145	[18]
Soybean	Microtube (36.5, 0.76)	Ethanol, sc	10:1–40:1		CO <sub>2</sub> , 1:5–1:10	250–325	10–20	40:1, 1:5, 325 °C, 20 MPa	54.9/35	[19]
Soybean	Tubular (88, 3.2)	Ethanol, sc	10:1–40:1		CO <sub>2</sub> , 0:1–0.5:1 <sup>c</sup>	300–350	7.5–20	40:1, 0.05:1, 250 °C, 10 MPa	70/110	[20]
Soybean	Tubular	Methanol, sc	3:1–6:1		CO <sub>2</sub> , 4 <sup>d</sup>	350–425	100–250		(100)/2–3	[21]
Soybean	Microtube (37.9, –)	Ethanol, sc	20:1–40:1		CO <sub>2</sub> , 0.5:1–0.2:1 <sup>c</sup>	250–325	10–20	20:1, 0.2:1, 325 °C, 20 MPa	78/–	[22]
Soybean	Microtube (37.9, 0.775)	Ethanol, sc	20:1–40:1		CO <sub>2</sub> , 0.5:1–0.2:1 <sup>c</sup>	250–325	10–20	20:1, 0.2:1, 325 °C, 20 MPa	78/47	[23]
Soybean	Microtube (24.9, 0.571)	Ethanol, sc	20:1–40:1		CO <sub>2</sub> , 0.5:1–0.2:1 <sup>c</sup>	250–325	10–20	20:1, 0.2:1, 325 °C, 20 MPa	84/49	[23]
Triolein	–	Methanol, sc		<i>Candida antarctica</i> lipase B	<i>t</i> -Butanol	45	18		95/–	[24]
Cottonseed	Fixed bed (–, 60)	Methanol	6:1	<i>Candida antarctica</i> (Novozym 435)/(32.5%)	CO <sub>2</sub> <i>t</i> -Butanol, 32.5%	50			95/500	[25]
Soybean	Packed bed (–, 2.5)	Methanol	3:1–5:1	<i>Candida antarctica</i> (Novozym 435)	<i>n</i> -Hexane: <i>t</i> -Butanol, 9:1 <sup>e</sup>	45–65		4.3:1, 52 °C	(75.2)/–	[26]

<sup>a</sup> Molar ratio.<sup>b</sup> Supercritical.<sup>c</sup> Co-solvent to substrate mass ratio.<sup>d</sup> mol.%<sup>e</sup> 9:1 v/v.

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