Energy Conversion and Management 124 (2016) 377–388

Contents lists available at ScienceDirect

Energy Conversion and Management

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

Comparative analysis of single-step and two-step biodiesel production using supercritical methanol on laboratory-scale

Radoslav D. Micic [a], Milan D. Tomić [b], Ferenc E. Kiss [c,*], Ferenc L. Martinovic [c], Mirko Đ. Simikić [b], Tibor T. Molnar [b]

[a] Scientific-Technological Centre, NIS-Naftagas, Put Sajkaskog Odreda 9, Novi Sad, Serbia
[b] Faculty of Agriculture, University of Novi Sad, Trg Dositeja Obradovica 8, Novi Sad, Serbia
[c] Faculty of Technology, University of Novi Sad, Bul. cara Lazara 1, Novi Sad, Serbia

ARTICLE INFO

Article history:
Received 9 May 2016
Received in revised form 14 July 2016
Accepted 16 July 2016
Available online 21 July 2016

Keywords:
Biodiesel
Hydrolysis
Methyl esterification
Supercritical conditions
Waste oil
Costs

ABSTRACT

Single-step supercritical transesterification and two-step biodiesel production process consisting of oil hydrolysis and subsequent supercritical methyl esterification were studied and compared. For this purpose, comparative experiments were conducted in a laboratory-scale batch reactor and optimal reaction conditions (temperature, pressure, molar ratio and time) were determined. Results indicate that in comparison to a single-step transesterification, methyl esterification (second step of the two-step process) produces higher biodiesel yields (95 wt% vs. 91 wt%) at lower temperatures (270 °C vs. 350 °C), pressures (8 MPa vs. 12 MPa) and methanol to oil molar ratios (1:20 vs. 1:42). This can be explained by the fact that the reaction system consisting of free fatty acid (FFA) and methanol achieves supercritical condition at milder reaction conditions. Furthermore, the dissolved FFA increases the acidity of supercritical methanol and acts as an acid catalyst that increases the reaction rate. There is a direct correlation between FFA content of the product obtained in hydrolysis and biodiesel yields in methyl esterification. Therefore, the reaction parameters of hydrolysis were optimized to yield the highest FFA content at 12 MPa, 250 °C and 1:20 oil to water molar ratio. Results of direct material and energy costs comparison suggest that the process based on the two-step reaction has the potential to be cost-competitive with the process based on single-step supercritical transesterification. Higher biodiesel yields, similar or lower energy and methanol consumption per unit of biodiesel, and higher market value of the glycerol obtained in the two-step process explain this observation.

1. Introduction

Price variations on the global market, uneven regional distribution, and significant ecological footprint represent some of the fundamental issues associated with fossil hydrocarbon use and processing. Compliance of fossil fuels to strict standards requires complex and expensive treatments (e.g. hydrotreating) which further increase the price of final oil products. Biodiesel is a renewable and more environmentally friendly alternative to fossil derived diesel. However, biodiesel still struggles to become an economically viable substitute on the global market [1]. Previous research papers indicate that the production costs of biodiesel are mainly determined by the price of oil feedstock [2–4]. The origin and quality of oil feedstock also determine the choice of the processing technology. Significant research is directed towards improving the economics of biodiesel production by using low quality cheap oil feedstock, primarily waste oils [2–4]. The main problem with this type of feedstock is its high free fatty acid (FFA) and water contents. The presence of water and FFA in feedstock has negative impact on the effectiveness of conventional base-catalysed homogeneous and heterogeneous transesterification processes [5–8]. Although acid-catalysed transesterification is less sensitive to the presence of FFA in the oil feedstock, its commercial application is limited by slow reaction rate and low conversion [9,10].

One of the alternatives to conventional base- and acid-catalysed biodiesel production processes is the non-catalytic transesterification in supercritical conditions [11–16]. Advantages and disadvantages of supercritical transesterification have been extensively discussed in literature [17,18]. The main advantages of supercritical transesterification are high conversion, rapid reaction rate and the possibility to use feedstock with high FFA (up to 36%) and water (up to 30%) content [11,19,20] which allows using low-cost feedstocks such as waste and non-edible oils [21]. In supercritical conditions the contact between reactants is good; therefore,

* Corresponding author.
E-mail address: fkiss@tf.uns.ac.rs (F.E. Kiss).

http://dx.doi.org/10.1016/j.enconman.2016.07.043
0196-8904/

intensive mixing is not required. Other advantage of the process is the high purity grade of the obtained glycerol [22]. Disadvantages of the supercritical transesterification are high investment and operational costs. The reaction is conducted at high temperatures and pressures (for methanol >239 °C, >8.09 MPa; for ethanol >243 °C, >6.4 MPa; for propanol >264 °C, >5.1 MPa); thus, it is energy intensive and requires specialized equipment. The process requires additional pumps and heat exchangers because of the high methanol to oil molar ratio (usually 42:1) which further increase the costs [7,8,22–24]. An alternative to the single-step transesterification in supercritical conditions is the two-step supercritical process. In the two-step process, first the oil is hydrolysed into FFA and glycerol in subcritical conditions, then, in the second step, the resulting FFA is esterified with supercritical alcohol [20].

1.1. Influence of reaction parameters on hydrolysis

In subcritical conditions oil hydrolysis is a pseudo homogenous reversible first order reaction with one of the reactants (usually water) in excess [25]. Three steps can be identified in the reaction. In the first step, triglycerides hydrolyse to diglycerides, diglycerides to monoglycerides in the second step, and in the final step, monoglycerides hydrolyse to glycerol (Eqs. (1)–(3)). In each step, one FFA is formed and their total yield determines the efficiency of hydrolysis.

Hydrolysis:

$$\text{Step I}\quad C_3H_5(OOCR)_3 + H_2O \leftrightarrow C_3H_5(OH)(OOCR)_2 + RCOOH$$
$$\text{triglyceride} + \text{water} \leftrightarrow \text{diglyceride} + \text{fatty acid} \tag{1}$$

$$\text{Step II}\quad C_3H_5(OH)(OOCR)_2 + H_2O \leftrightarrow C_3H_5(OH)_2(OOCR) + RCOOH$$
$$\text{diglyceride} + \text{water} \leftrightarrow \text{monoglyceride} + \text{fatty acid} \tag{2}$$

$$\text{Step III}\quad C_3H_5(OH)_2(OOCR) + H_2O \leftrightarrow C_3H_5(OH)_3 + RCOOH$$
$$\text{monoglyceride} + \text{water} \leftrightarrow \text{glycerol} + \text{fatty acid} \tag{3}$$

$$\text{Overall}\quad C_3H_5(OOCR)_3 + 3H_2O \leftrightarrow C_3H_5(OH)_3 + 3RCOOH$$
$$\text{triglyceride} + 3\ \text{water} \leftrightarrow \text{glycerol} + 3\ \text{fatty acid} \tag{4}$$

Reaction parameters for hydrolysis should be set to achieve the highest FFA content in the product (i.e. the highest acid number), as the previous investigations had confirmed positive correlation between the FFA content in the feedstock and fatty acid methyl ester (FAME) content in the product of methyl esterification [26]. The highest FFA yield can be achieved by setting the reaction parameters (temperature and pressure) for hydrolysis so that the dielectric constant of water is small and the ionic product of water is high [27,28]. These attributes enable water to dissolve in oil and act like an acidic solvent by donating protons. Best results can be achieved when the difference between the polarity of water and oil is the smallest. Even in the conditions of enhanced solubility, there are still two separate water and oil phases present. This allows glycerol, one of the reaction products, to diffuse into the water phase. Removal of one of the products slows the reversible reaction and drives the reactions Eqs. (1)–(3) to the right.

1.2. Comparison of transesterification and methyl esterification reactions

Single-step transesterification has three stages: tri-, di- and monoglycerides are transesterified with methanol and in each reaction FAME and a glyceride with a fatty acid chain substituted with OH group are produced, until the final stage when glycerol is formed (Eqs. (5)–(8)). In the second step of the two-step process reaction between FFA and methanol results in the production of methyl esters and water (Eq. (9)).

Transesterification:

$$\text{Step I}\quad C_3H_5(OOCR)_3 + CH_3OH \leftrightarrow C_3H_5(OH)(OOCR)_2 + CH_3OOCR$$
$$\text{triglyceride} + \text{methanol} \leftrightarrow \text{diglyceride} + \text{methyl ester} \tag{5}$$

$$\text{Step II}\quad C_3H_5(OH)(OOCR)_2 + CH_3OH \leftrightarrow C_3H_5(OH)_2(OOCR) + CH_3OOCR$$
$$\text{diglyceride} + \text{methanol} \leftrightarrow \text{monoglyceride} + \text{methyl ester} \tag{6}$$

$$\text{Step III}\quad C_3H_5(OH)_2(OOCR) + CH_3OH \leftrightarrow C_3H_5(OH)_3 + CH_3OOCR$$
$$\text{monoglyceride} + \text{methanol} \leftrightarrow \text{glycerol} + \text{methyl ester} \tag{7}$$

$$\text{Overall}\quad C_3H_5(OOCR)_3 + 3CH_3OH \leftrightarrow C_3H_5(OH)_3 + 3CH_3OOCR$$
$$\text{triglyceride} + 3\ \text{methanol} \leftrightarrow \text{glycerol} + 3\ \text{methyl ester} \tag{8}$$

Methyl esterification:

$$RCOOH + CH_3OH \leftrightarrow CH_3OOCR + H_2O$$
$$\text{fatty acid} + \text{methanol} \leftrightarrow \text{methyl ester} + \text{water} \tag{9}$$

1.3. Aims of the research

Previous research has shown that the two-step process has the potential to reduce operating and investment costs of supercritical transesterification as the hydrolysis and esterification of FFA are performed at milder reaction conditions compared to the single-step transesterification process while the reaction rates are higher [26]. Milder reaction conditions are preferable since higher reaction temperatures intensify the thermal decomposition of FAME [29]. Glycerol obtained in the two-step process has higher market value as it is produced via hydrolysis, and it is not contaminated with alcohol.

Only a few studies have provided comparative analysis of the single-step and the two-step supercritical processes [20,26,30] and data regarding process economics is very limited. The goal of this research was to provide a comparative analysis of reaction parameters and their influence on yields in the single-step and two-step processes, and to provide a comparative cost analysis focusing on direct material and energy costs of biodiesel production.

2. Materials and methods

2.1. Description of the experiment

The experiment was conducted by measuring the reaction parameters (temperature, pressure, and methanol to oil molar ratio) and their influence on FAME yields during the single-step transesterification and the two-step process consisting of hydrolysis and esterification reactions. The process flow and equipment used in the research is presented in Fig. 1. Single-step transesterification was conducted by heating the oil and methanol mixture in the reactor to the desired temperature. After reaching the reaction temperature, the pressure was increased to the required value by introducing nitrogen (99.8% purity, Messer). As the starting point of the reaction it was considered the moment when methanol transitioned to a supercritical phase. After the desired reaction time passed, the mixture in the reactor was cooled down to 150 °C and the unreacted methanol in the vapour phase was flushed with nitrogen and condensed in a condensing column. The biodiesel and glycerol mixture was transferred to a gravity separator where they were separated. Detailed description of the experimental procedure of the single-step transesterification was presented in a previous report [31].

The two-step process involved two reactions. The first reaction was the hydrolysis of mono-, di- and triglycerides in subcritical