Energy Conversion and Management 99 (2015) 8–19

Contents lists available at ScienceDirect

Energy Conversion and Management

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

Economic and environmental performance of oil transesterification in supercritical methanol at different reaction conditions: Experimental study with a batch reactor

Milan Tomic [a], Radoslav Micic [b], Ferenc Kiss [c,*], Nebojsa Dedovic [a], Mirko Simikic [a]

[a] University of Novi Sad, Faculty of Agriculture, 21000 Novi Sad, Trg Dositeja Obradovića 8, Serbia
[b] Scientific-Technological Center, NIS-Naftagas, Put Šajkaškog Odreda 9, Novi Sad, Serbia
[c] Faculty of Technology, University of Novi Sad, Bul. cara Lazara 1, Novi Sad, Serbia

ARTICLE INFO

Article history:
Received 26 February 2015
Accepted 5 April 2015
Available online 20 April 2015

Keywords:
Rapeseed oil
Biodiesel
Supercritical methanol
Transesterification
Economics
Life cycle assessment

ABSTRACT

This study aims to investigate the influence of various reaction parameters (temperatures, working pressures and reaction time) on biodiesel yields and environmental and economic performance of rapeseed oil transesterification in supercritical methanol. Experiments were carried out in a laboratory-scale batch reactor. Results were statistically analysed and multiple regression models which describe and predict biodiesel yields with high certainty at different reaction conditions were provided. The highest biodiesel yield (93 wt%) was achieved at 350 °C and 12 MPa after 15 min of reaction. The lowest direct costs and life cycle environmental impacts (in terms of GHG emissions and fossil energy demand) are achieved at the highest yield due to the lowest oil consumption per unit of biodiesel produced. The results of sensitivity analysis showed that even at significantly lower oil feedstock prices this observation stands firm.

1. Introduction

Biodiesel is non-toxic, biodegradable alternative for fossil diesel fuel produced from renewable sources such as vegetable oils or animal fats typically by transesterification of triglycerides with methanol. In its composition biodiesel is a fatty acid methyl ester (FAME) [1,2]. At industrial-scale, transesterification is generally performed in the presence of homogenous or heterogeneous catalysts [3]. However, due to a number of problems, which are reflected in the limited application of catalyst in the case of feedstock with higher water and free fatty acid (FFA) contents, as well as the large number of expensive and complex procedures of neutralization, rinsing and separation [4], non-catalytic transesterification processes have been investigated recently as alternative. One of the alternatives to the catalysed process is transesterification in supercritical methanol.

In supercritical condition methanol becomes more chemically reactive and its viscosity and surface tension are reduced, which directly affects enhancement of mass transfer. Namely, molecules of a substance in supercritical state have high kinetic energy when they are in gaseous form and high density when they are in liquid form. Furthermore, the ionic product of alcohol is increased with increased pressure which is the basis for assumption that in supercritical conditions alcohol is not only a reagent but acid catalyst as well [5]. Researches with different alcohols in supercritical conditions (methanol [6], ethanol [7], propanol [5], 1-butanol, 1-octanol [8], and ethyl acetate [9]) have been conducted recently.

Results of the latest research have shown that transesterification in supercritical methanol requires shorter reaction time and simpler refining process [10,11]; also, the processes occurring under supercritical methanol can process raw materials with high water and FFA content in order to produce biodiesel [12,13]. According to Pinnarat et al. [14] this could be explained with the simultaneous occurrence of hydrolysis and methanolysis in the processes of supercritical methanol transesterification. Although the stoichiometric methanol to oil molar ratio for the transesterification reaction is 3:1, in supercritical methanol the transesterification is performed at significantly higher alcohol to oil ratios, usually between 6:1 and 60:1. However, most of the researches suggested around 42:1 as the optimal alcohol to oil molar ratio [15]. Large excess of methanol has a favourable impact on the formation of fatty acid esters and also slows down their thermal decomposition (primarily polyunsaturated fatty acids esters) [16].

In order to reduce the required temperature and pressure, as well as to reduce the alcohol to oil molar ratio and eliminate the

* Corresponding author. Tel.: +381 21 485 3641.
E-mail address: ferenc1980@gmail.com (F. Kiss).

http://dx.doi.org/10.1016/j.enconman.2015.04.010
0196-8904/

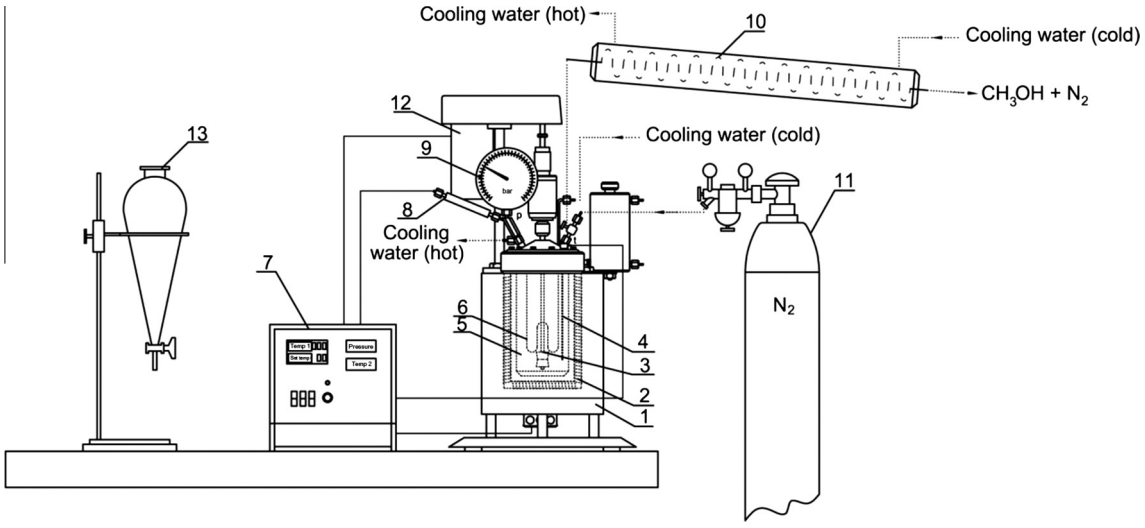

Fig. 1. Equipment used for oil transesterification. Notes: (1) Reactor Parr 4520, (2) heater, (3) stirrer, (4) thermocouple, (5) reaction vessel, (6) mass cooler, (7) control unit Parr 4842, (8) piezo reader, (9) manometer, (10) condenser, (11) nitrogen bottle, (12) electro-motor for stirrer, (13) separation vessel.

Table 1
Operation conditions for gas chromatography.

Item	Description/condition
Column flow	0.54 mL min^{-1}
Split ratio	40:1
Sample volume	1 μl
Oven program initial temp	200 °C
Hold time 1	5 min
Rate 1	4 °C min^{-1}
Oven program final temp	240 °C
Hold time 2	5 min
Equilibration time	1 min
Carrier gas	Helium
Gas flow	3 mL min^{-1}
FID temperatures	260 °C
H_2 flow	40 mL min^{-1}
Air flow	400 mL min^{-1}
Makeup flow	30 mL min^{-1}

thermal decomposition of FAME some researchers suggested the introduction of a third component or co-solvents (CO_2, methane, ethane, propane, n-butane [17], hexane [18], cyclohexane, dimethyl ether, ether and toluene [19]). A two-step procedure, comprising of oil hydrolysis in subcritical water followed by transesterification of the resulted FFAs into FAME in the second step [20] was also proposed. Alenzi et al. [21] have concluded that the esterification of FFA in supercritical methanol is performed at milder conditions compared to the transesterification of triglycerides.

There are number of research papers available on the reactivity and kinetics of supercritical transesterification [22–25]. Although these studies provided some useful information concerning the effect of reaction parameters on biodiesel yield they did not consider the economic and environmental feasibility of the process which is also of great importance to access process viability. The economic [26–28] and environmental [24,29,30] viability of the process has been investigated by several researchers with varying and often contradictory results. Furthermore, these estimations are typically derived by process simulator software and do not necessarily coincide with empirical results.

The primary aim of this research was to investigate the economic and environmental performance of rapeseed oil transesterification in supercritical methanol depending on the reaction conditions in a batch reactor. The secondary aim was to create a mathematical model based on the experimental results which would precisely describe the effects of reaction parameters on FAME yields and predict the reaction progress under reaction conditions that are different from the conditions used in the experiment.

2. Material and methods

2.1. Experimental research

A cold-pressed oil of oilseed rape was used in the experiment. The oil consists of ca. 91 wt% unsaturated fatty acids (66.96 wt% oleic, 16.79 wt% linoleic and 7.80 wt% linolenic) and 8.45 wt% saturated fatty acids (4.75 wt% palmetic, 1.49 wt% stearic, 0.49 wt% arachidic and 1.72 wt% others). The oil has the following characteristics: acid value of 2.91 mg KOH g^{-1}, molar mass of 881.48 g mol^{-1}, and iodine number of 107.9 gI_2 100 g^{-1}.

Methanol used in the experiments was supplied by the Methanol & Acetic Acid Complex from Kikinda, Serbia with the following characteristics declared by the producer (in wt%): water 0.05, free acids 0.003, formic acid 0.0023, free alkali 0.0003 and a sum of aldehydes and ketones 0.003. Density of methanol was 0.791 g cm^{-3}.

Experiments were carried out in a batch-type reactor (Anton Parr 4520) (Fig. 1). Detailed description of the experimental procedure was presented in our previous report [5].

The experiment was carried out at different temperatures (250, 270, 300, 320 and 350 °C), pressures (8.1, 10 and 12 MPa) and reaction times. The reaction was conducted until the time needed to achieve the equilibrium state of the process, i.e. until a decrease in FAME yield was observed. All experiments were performed in three replications, and the calculations are based on the average values. Rapeseed oil was mixed in the reactor with methanol at alcohol to oil molar ratio of 42:1.

In all experiments the methyl esters yield (ME_{Yield}) was obtained as a function of purity of ester layer by involving the values of the ester amount and the amount of oil feedstock (Eq. (1)):

$$ME_{Yield} = \frac{\text{Amount of ME layer } (g) \cdot \text{ Purity of ME layer } (\%)}{\text{Amount of oil, feedstock } (g)} \ (wt\%) \quad (1)$$

Content of FAME in the resulting product was determined with gas chromatograph Shimadzu GC-210 Plus (according to EN 14103) which is equipped with autosampler AOC-20i, Capyllary