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Biodiesel production from olive pomace

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Abstract

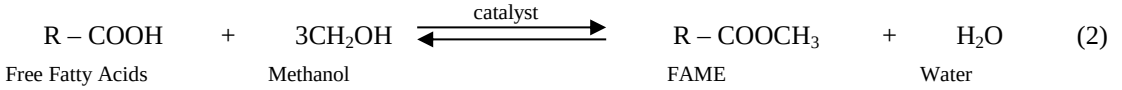
Within the scope of this research, biodiesel production from olive pomace oil (OPO) was investigated. Esterification and transesterification reactions were carried out using a microwave synthesis unit in the presence of H_2SO_4 and KOH as a catalyst, respectively. The acidity index (AI) of the oil was reduced from 20 to 0.78 mg KOH/g oil by an esterification reaction to avoid saponification during the transesterification process. Suitable esterification reaction parameters were determined as 65 ℃, for 40 minutes with a methanol:oil molar ratio of 8:1 in the presence of 2.5% (wt. %) catalyst (H_2SO_4). The highest fatty acid methyl ester (FAME) content of the biodiesel (98.56%) was determined by the transesterification at 65 ℃ for 5 min, using a 7:1 methanol:oil molar ratio, and 1.5 wt. % KOH catalyst. Found results are consistent with the EN14214 standard.

Keywords: Olive pomace, olive pomace oil, esterification, transesterification, biodiesel, microwave synthesis unit

1. Introduction

Energy requirement arises day by day because of the increasing population and developing industry. Currently, the energy requirement is fulfilled by fossil fuels, which cause climate change and environmental pollution. The greenhouse gas emissions, especially CO_2, caused a search to start for renewable energy sources [1]. Biodiesel is one of the renewable energy sources. There are a number of methods to synthesize biodiesel: pyrolysis, dilution, microemulsion, and transesterification [2]. Transesterification process is an old and well-known technology for synthesis of biodiesel from animal, vegetable and waste oils [3]. Esterification reaction (Eq. 2) is carried out prior to the transesterification reaction (Eq. 1) in order to reach the desired acidity value which is lower than 1 mg KOH/g [4].

(1)



(2)

Turkey has a big potential of olive oil production and around 250 thousand tons olive pomace per year [5]. Approximately 30 thousand tons of OPO are extracted annually. There are several published papers about the utilization of OPO for biodiesel. Diógenes Hernández et al. obtained biodiesel with the yield of 94.7% from pomace oil by a transesterification reaction, which was performed using methanol:oil ratio of

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2:1, for 60 min, and with 0.54% KOH catalyst (wt.catalyst/wt.oil%) [6]. Antonio Lama-Muñoz et al. determined the optimum esterification reaction conditions as 6:1 methanol:oil molar ratio in the presence of 1% H_2SO_4 catalyst (wt.%), for 60 min then carried out transesterification reaction using 6:1 methanol:oil volumetric ratio, 1% NaOH catalyst (wt.%) for 80 min with the FAME content of 95% [7]. In the study of Sinem Caynak et al., biodiesel from OPO with the FAME value of 75.67% was obtained [8]. In this study, biodiesel was obtained using a microwave synthesis unit to determine suitable reaction conditions.

2. Materials and Methods

2.1. Materials

OPO was supplied by an olive oil factory located in Turkey. Hexane, potassium hydroxide (KOH), methanol, sulfuric acid (H_2SO_4), phenolphthalein solution, anhydrous sodium sulfate (Na_2SO_4), diethyl ether ($(C_2H_5)_2O$) and ethanol (C_2H_6O) were purchased from Sigma Aldrich and they were used without any pre-treatment.

2.2. Equipment

A microwave synthesis unit (Milestone Smart S) was used for esterification and transesterification reactions. In order to carry out the reactions homogeneously at a constant temperature; a magnetic stirrer and an infrared thermometer were used. The methyl ester content of the biodiesel was determined using an Agilent 6890N Gas Chromatography apparatus (GC). Pour point, cloud point and flash point measuring devices were used to determine the properties of the biofuel.

2.3. Experimental Procedure

2.3.1. Properties of OPO

Relative density and AI of the OPO were determined using standard methods [9].

2.3.2. Esterification

Esterification reactions were performed using a microwave synthesis unit in the presence of H_2SO_4 catalyst (1.5 - 3% wt.catalyst/wt.oil) at various reaction temperatures (60, 65, 75 ℃), and reaction time (30, 40 min).

2.3.3. Transesterification

Transesterification reactions of esterified (0.78 mg KOH/g) oil were carried out using a microwave synthesis unit, in the presence of KOH catalyst (1-2%), at 65°C constant temperature, 3-7 minutes reaction time and using different methanol:oil molar ratio of 6:1, 7:1, 8:1.

2.3.4. Determining Properties of Biodiesel

The density of biodiesel was determined by using a 25 mL pycnometer. In order to find out the FAME content of the biodiesel, it was firstly derivatized using *N*-methyl-*N*-trimethylsilyl-trifluoroacetamide at 25 ℃, for 15 min. This process is called silylation. After silylation, the FAMEs content was identified by GC equipped with a DB-5HT column (15 m, 0.32 mm ID 3 0.10 lm film thickness) with a flame ionization detector. The temperature program was set to heat the device from 50 ℃ to 180 ℃ at 15 ℃/min. After that, the temperature was increased to 230 ℃ at 7 ℃/min. Finally, it was heated to 370 ℃ at 10 ℃/min, and remained at this temperature for 20 min [4]. Pour point, cloud point and flash point of biodiesel were measured according to standard methods [9].

3. Results and Discussion

3.1. Properties of OPO and Biodiesel

Properties of OPO and biodiesel are given in Table 1.

Table 1. Properties of Olive Pomace Oil and Biodiesel

	Olive Pomace Oil	
Density (g/cm^3)	0.96	
AI (mg KOH/g sample)	20	
	Biodiesel	**Reference Values**
Relative density at 25 ℃	0.886	0.86 - 0.9
FAMEs (%)	98.56	>96.5
Flash Point	177 ℃	>120
Cloud Point	-5 ℃	(-5) – (17)
Pour Point	-10 ℃	(-15) – (16)

Properties of biodiesel are in line with the standard of EN14214 [10, 11].

3.2. Effect of Reaction Parameters on The Esterification

AIs of the oil are plotted against catalyst ratio, temperature and reaction time (Fig.1) in order to avoid saponification during transesterification.

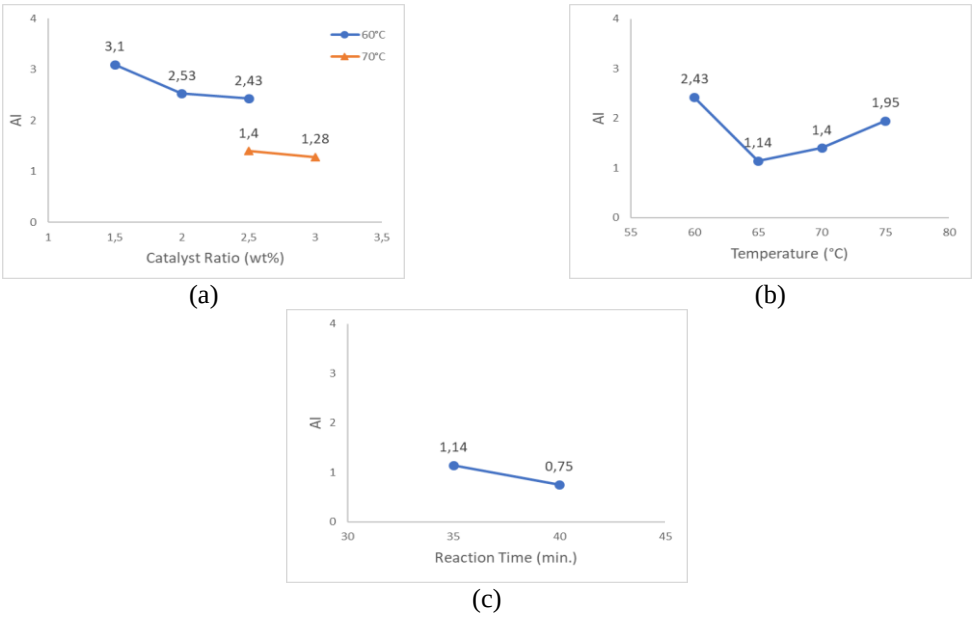

Fig. 1. Effect of (a) catalyst ratio @ 8:1 methanol:oil, 35 min, 60-70 ^{o}C, (b) temperature @ 8:1 methanol:oil, 2.5% H_2SO_4, 35 min, (c) reaction time on AI mg KOH/g sample @ 8:1 methanol:oil, 2.5% H_2SO_4, 65 ℃

Fig.1a. illustrates that AI decreases with the catalyst ratio and temperature. The lowest AI (2.43) value was achieved at 60 ^{O}C which is extremely higher than the desired value. There is no significant difference between the AIs achieved at 70^{o}C using 2.5% (AI: 1.4) and 3% (AI: 1.28) catalyst ratios. Therefore, further experiments were carried out using a catalyst ratio of 2.5%.

According to Fig. 1b. AI decreases with temperature until 65 ℃. With further increments in temperature, AI values started to increase because of the boiling point of methanol. As a consequence, subsequent experiments were carried out at 65 ℃.

Effect of reaction time on the AI was presented in Fig. 1c. The AI decreases from 1.14 to 0.75 when the time increased from 35 to 40 minutes. The aim of this reaction is having an AI less than 1 mg KOH/g, so 40 minutes was determined to be the most suitable reaction time.

3.3. Effect of Reaction Parameters on Transesterification Reaction

FAME content of biodiesel was determined according to catalyst ratio, reaction time and methanol:oil ratio (Fig. 2).

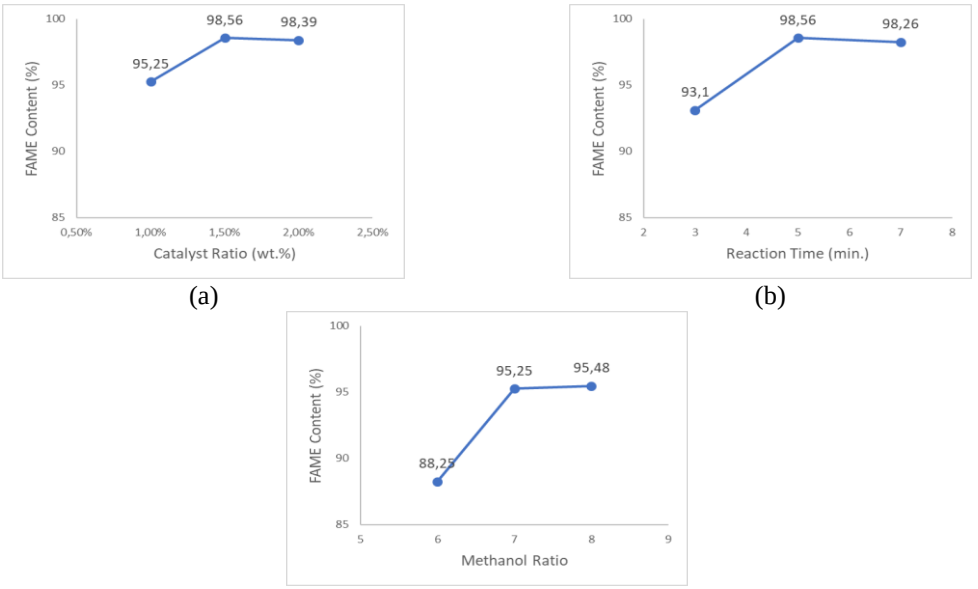

Fig. 2. Effect of (a) catalyst ratio @ 65 ℃, 7:1 methanol:oil, 5 min, (b) Reaction time @ 65 ℃, 7:1 methanol:oil, 1.5% KOH, (c) methanol:oil ratio on FAME content of biodiesel @ 65 ℃, 1% KOH, 5 minutes reaction time

Fig. 2a. illustrates that the maximum FAME content of biodiesel (98.56%) is achieved when 1.5% KOH is used.

As it is seen in Fig. 2b the FAME content of biodiesel decreases after 5 min since the transesterification reaction is reversible. As a result, the highest value of FAME (98.56%) was achieved in 5 min.

According to Fig. 2c FAME content of the biodiesel increases with the methanol:oil ratio. There is no significant difference between the FAME contents of 7:1 and 8:1 methanol:oil ratios. The most suitable value of methanol:oil ratio was found as 7:1 because of the cost of the methanol.

4. Conclusion

OPO with a high free fatty acid content was used as a promising feedstock for biodiesel production by applying esterification and then transesterification reactions. Because of the high AI of the OPO, the esterification reaction was carried out to lower its AI in order to avoid saponification occur during transesterification reaction. The suitable esterification parameters were determined as 2.5 % H_2SO_4, 65 ℃, for 40 min, with an 8:1 methanol:oil molar ratio with the result of 0.75 mg KOH/g oil of AI. In order to obtain biodiesel, the esterification reaction was followed by transesterification at 65 ℃, for 5 min with 7:1 methanol:oil ratio in the presence of 1.5% KOH catalyst. FAME content, density, flash point, cloud point and pour point of the biodiesel were found to be as 98.56%, 0.886 g/cm^3, 177, -10, -5 ℃ which are in good agreement with the EN14214. Even though there are a number of studies on OPO in the literature, none of them are in line with the standard values.

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