BIODIESEL PRODUCTION FROM OLIVE ACID OIL IN SUPERCRITICAL ETHANOL

Nalan A.AKGÜN
Yıldız Technical University
n_akgun@yahoo.com

Filiz ÖZDEMİR
Yıldız Technical University
filizsem@gmail.com

Abstract
The production of biodiesel derived from olive acid oil in supercritical ethanol was investigated by using a tubular reactor of 45 ml in a bench-scale. Experiments were performed based on experimental design, and operating conditions such as temperature (280-360 ℃), pressure (100-180 bar), volumetric ratio of ethanol to OAO (1:1-1:2), and flow rate of the mixture (0.3-0.9 ml/min) were selected as parameters to evaluate their effects on ester conversion. Samples collected were purified with magnesol after removing of ethanol by vacuum distillation. Ethyl ester contents were determined by gas chromatography analysis. Subsequently, accelerated oxidation stability tests of biodiesel samples were studied at a temperature of 110°C by using the Rancimat 743, and following the European standard EN 14214.

Keyword: biodiesel, olive acid oil, oxidation stability, supercritical ethano

1.Introduction

Biodiesel, an alternative diesel fuel derived from vegetable oils, animal fats or waste frying oils by transesterification, is composed of saturated and unsaturated long-chain fatty acid alkyl esters. The most common use of biodiesel is in transportation systems such as on- and off-road compression-ignition engine powered vehicles and locomotives. Since the use of biodiesel brings about a series of environmental, economical and social advantages, a number of studies on biodiesel production and technical characteristics have been reported in the literature. These studies demonstrate that biodiesel may be used in diesel engines without the need of any modification; decreases the emissions such as sulfur, carbon dioxide, unburned hydrocarbons and particulate materials; presents higher flash point which guarantees security in the handling and storage; may be produced by different catalyst-free methods such as supercritical alcohol; may be used neat or as biodiesel/diesel fuel blends in the transport sector. Despite the emphasized advantages, since refined or edible oils, water-free and containing free fatty acid (FFA) lower than 3 wt-%, are mostly employed; the biodiesel production results in high cost and energy consumption. Hence, to make biodiesel competitive in the market, less-expensive feedstock with high FFA should be used instead of refined oil, and to reduce the energy consumption different methods such as catalyst-free or acidic-transesterification or two-step process should be preferred.

Therefore, in this work, the transesterification of olive acid oil (OAO) in supercritical ethanol without any catalyst was investigated on a bench scale. The effects of reaction conditions such as temperature, pressure, flow rate and volumetric ratio of ethanol to OAO on the ester conversion were reported. The fuel properties of neat biodiesel were then analyzed.

2.Experimental Study

2.1 Materials

OAO, which is a byproduct of olive oil refining process and cheaply available, contains mainly high FFA, squalene and tocopherols in smaller quantities, and was kindly supplied by Verde A.S (www.olioverde.com.tr). Magnesol D-60 (Delfin) and all chemicals used were of analytical grades and purchased commercially.

2.2 Reaction in Supercritical Ethanol

Experiments were carried out in a reaction system consisting of a magnetic stirrer with hot plate, a high pressure pump, an electrical furnace equipped with a 45 ml flow type tubular reactor, a back pressure valve and a condenser (Fig. 1).

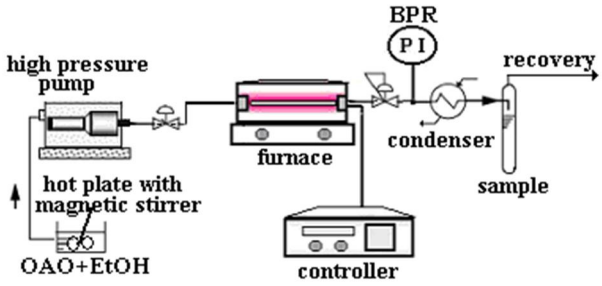

Fig. 1. Experimental set-up

Since OAO was in a pasty form at the laboratory conditions, it was heated to 30°C using by the hot plate, and mixed with ethanol before pumped into the reactor. Experiments were performed based on experimental design, and operating conditions such as temperature (280-360°C), pressure (100-180 bar), volumetric ratio of ethanol to OAO (1:1-1:2), and flow rate of the mixture (0.3-0.9 ml/min) were selected as parameters to evaluate their effects on ester conversion. Samples, collected during 1 hour, were purified with magnesol after removing of ethanol by vacuum distillation. Ethyl ester contents were determined by gas chromatography analysis.

2.3 Accelerated Oxidation Tests

A Rancimat 743 Instrument (Metrohm AG, Herisau, Switzerland, www.metrohm.com) was used to determine the oxidative stability of biodiesel samples. In this method, volatile oxidation products formed via a radical chain mechanism are transferred by the stream of air into the measuring vessel which contains deionized water. Consequently, the conductivity of water in the vessel begins to increase rapidly. At that time, the conductivity of deionized water is continuously measured and plotted by the instrument as a function of time. At the end of the induction period, induction time is determined automatically from the second derivative of the measuring curve.

In this series of experiments, biodiesel samples were analyzed at a temperature of 110°C by following the European standard EN 14214. The temperature correction factors, ΔT, were set at 0.8 and 0.67°C for heating blocks A and B, respectively. Flow rate of air stream blown through the sample was 10 Lh^{-1}. Stop criteria for conductivity was selected as 200 $\varepsilon S.cm^{-}1$.

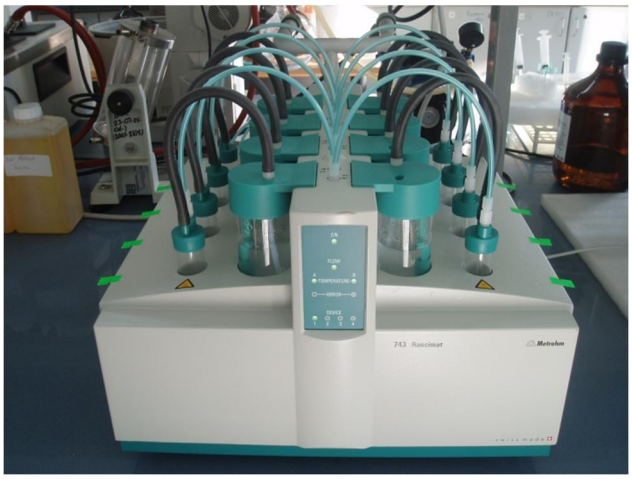

Fig. 2. Oxidation stability tests (Rancimat 743)

3. Results and discussion

In transesterification method, the molar ratio of alcohol to vegetable oil is also one of the most important variables affecting the yield of methyl esters. Especially, an excess of alcohol is used in order to shift the equilibrium in the direction of the products. Surprisingly, Saka and Kusdiana stated similar effects in their works (2001, 2004), which were performed in supercritical methanol by using batch system. However, a similar trend was not observed for conversions in ethanol in this study. An explanation for higher conversions in ethanol may be attributed to using acid oil in that flow system. Actually, in order to determine the effect of varying volumetric ratios of ethanol to OAO on the ester conversion, reactions were carried out in the ranges of 280-360°C temperatures, 0.3-1 ml/min flow rates and 100-200 bar pressures.

Experimental results showed that the reaction was incomplete for the higher ratios of ethanol to OAO due to higher FFA content in biodiesel. This phenomenon can be explained by the fact that lower flow rates probably caused hydrolysis and decomposition due to reversible character of the reaction. However, higher ester contents up to 99% were observed at the lower ratios of ethanol to OAO and higher flow rates. In addition, the response surface methodology results also indicated that most important variables affecting the ester content were residence time and volumetric ratio of ethanol to OAO.

Although better oxidation stability of vegetable oil means better biodiesel quality the biodiesel samples derived from OAO in this set did not pass the standard EN 14214. Induction period of shorter than 6 h can be explained by higher FFA content as expected. Therefore, special attention should be focused on reducing FFA content of biodiesel during the reaction or solution should be selected as addition of antioxidant in proper amounts.

Consequently, biodiesel production from even the feedstock containing FFA of 88 wt-% in supercritical ethanol was achieved within several minutes. This new process which does not need intensive pre- or post-treatments as such in transesterification, can offer an alternative instead of commercial method in an environmental friendly manner. Nevertheless, further researches have to be done to reduce FFA content of biodiesel and satisfy the EU standards

Acknowledgment

The authors gratefully wish to acknowledge the financial supports by TUBITAK (project 107M243) and BAPK (project 26-07-01-01).

References

(1) Kusdiana, D.; Saka, S., Kinetics of Trabsesterification in Rapeseed Oil to Biodiesel Fuel as Treated in Supercritical Methanol. *Fuel* 2001, 80, 693-698.
(2) Kusdiana, D.; Saka, S., Effects of Water on Biodiesel Fuel Production by Supercritical Methanol Treatment. *Bioresource Technology* 2004, 91, 289-295.
(3) Saka, S.; Kusdiana, D., Biodiesel Fuel from Rapeseed Oil as Prepared in Supercritical Methanol. *Fuel* 2001, 80, 225-231.