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Biodiesel Production from High Free Fatty Acid-Content Oils: Experimental Investigation of the Pretreatment Step

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Abstract

Biodiesel has the potential to become a suitable substitute for diesel fuel in the future. However, the reduction of production costs and finding a permanent oil source have remained the two main concerns for this green fuel. The production of biodiesel from acid oils is one of the ways to reduce biodiesel production costs. In addition, high free fatty acid oils are almost never categorized as edible oils. Consequently, this new material has a more reliable margin in debates concerning the security of food, compared to other oils considered in biodiesel production. By considering these important aspects of biodiesel production technology, this study investigates the pretreatment step of biodiesel production from acid oils. In this work, an oil with high free fatty acid content is selected and the main parameters in the biodiesel production reaction are investigated experimentally. The effects of methanol-to-oil ratio (in the range of 0.2 to 1.2 v/v), the amount of catalyst (in the range of 0.5 to 6% v/v) and time (in the range of 20 to 120 min) on the progress of the reaction are studied.

Keywords: Biodiesel; renewable fuel; alternate fuel source; esterification; transesterification.

1. Introduction

In recent years, finding a renewable source as an alternative for regular diesel has attracted many researchers because of the drawbacks associated with using diesel fuel. Significant disadvantages of using diesel, such as global warming issues, air pollution and the security of energy are the main concerns that have directed interests to green and sustainable alternatives. Currently, biodiesel (fatty acid methyl esters) is known

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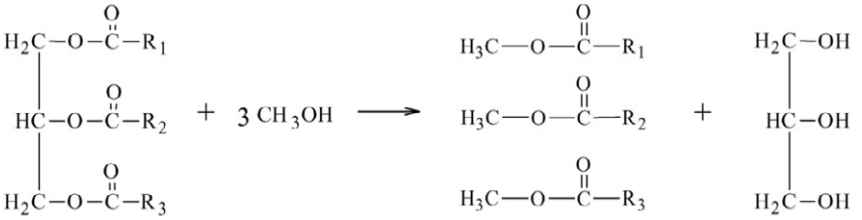
as a suitable substitute for diesel fuel because such a substitute results in great advantages. In comparison to diesel fuel, biodiesel has lower emissions of CO_2 due to better combustion, a better lubricating effect on engines, non-sulfur emissions and non-particulate matter pollutants [1, 2, 3]. Biodiesel is produced by the transestrification reaction:



Usually, the actual amount of methanol used for transestrification is higher than the stoichiometric amount in order to achieve acceptable conversions. For instance, a methanol-to-oil molar ratio of 6:1, is a good choice for achieving 95% conversion at 60 ºC with 1 gr of NaOH as catalyst. Obtaining such good results, however, requires certain precautions. First, triglyceride should be nearly pure. Studies show that the presence of water or Free Fatty Acids (FFA) acts as poison for the catalyst. Second, the price of pure triglyceride does not allow biodiesel to compete with diesel fuel in cost [4, 5]. These disadvantages are the main reasons why researchers have recently focused on other feedstock for biodiesel production. Acid oils, which have high FFA content, are well-known as a potential alternative raw material. The presence of FFA requires the addition of a pretreatment step before transestrification, in which FFAs react with methanol in the presence of acidic catalyst reacts with methanol to produce biodiesel:

The above reaction, which is known as esterification, increases the possibility of producing biodiesel at lower costs. Although pure free fatty acids are not as abundantly available as pure triglycerides, the low cost of high-acid oils is attractive enough for researchers to strive for a better understanding of this reaction [6, 7, 8, 9]. The source of an acid oil, its FFA content, the initial amount of methanol, amount of catalyst and time are important parameters which influence the final conversion of the reaction [10, 11, 12, 13, 14]. In order to achieve a better insight of the pretreatment step, this study attempts to investigate the esterification reaction with a potential feedstock for future industrial biodiesel production plants. In other words, a by-product of an operating vegetable oil refinery, containing high amounts of free fatty acids, was selected and the reaction conditions were investigated experimentally.

2. Materials and methods

To carry out this research, 98% sulfuric acid (from Merck) was used as catalyst for the esterification reaction. Anhydrous methanol (from Merck) also was used as the alcohol. A 100 ml lab-scale reactor, equipped with a reflux condenser, a constant temperature (+/- 0.1 ºC) water bath and a magnetic stirrer were used to carry out the reaction at constant temperature. A low price high-FFA oil, with 44.5% FFA content, obtained as a by-product of Shiraz Vegetable Oil Company was used as the oil source. The oil fed to the reactor was preheated before the catalyst and alcohol were added. After reaching the reaction temperature of 50 ºC, the catalyst and alcohol were added into the reactor to start the experiment. After a predetermined time, the reaction was terminated by transferring the reactor contents to a decanter. The oil rich phase was separated from the alcohol rich phase and was then washed three times with hot brine solution. To improve separation, the oil phase was centrifuged for 20 min at 6000 rpm. Finally, a weighted amount of sample was dissolved in

ethanol to measure the FFA content according to ASTM D664 [15]. The main conditions investigated were:

- Amount of catalyst
- Methanol-to-oil ratio
- Reaction time

3. Results and discussions

3.1. Effect of the amount of catalyst

The esterification reaction was investigated within a wide range of catalyst concentrations at two different methanol-to-oil ratios. 20% and 60% v/v methanol were considered as th low and high initial amounts of methanol, respectively. Reaction temperature was set to 50 ºC and reaction time was fixed at 1 hour. The conversion results displayed in Figure 1 show that when small amounts of catalyst were used, the reaction was highly dependent on the amount of catalyst. However, this dependency vanished when higher amounts of catalyst were used. This behaviour was essentially the same for both initial amounts of methanol. At low amounts of methanol, the reaction was not catalyst-dependent at catalyst concentrations higher than 2% v/v. Catalyst-dependency, in the case of high an initial amount of methanol, was not observed at concentrations higher than 1.5% v/v of sulfuric acid.

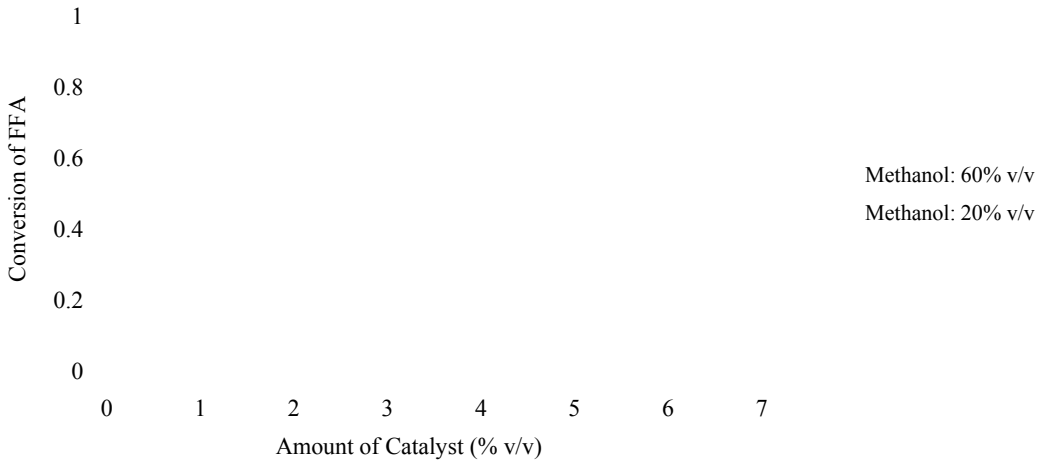


Fig. 1. Effect of the amount of catalyst on FFA conversion

3.2. Effect of the amount of initial methanol

Variation of the methanol-to-oil ratio and its effect on FFA conversion is shown in Figure 2. The temperature and time of the reaction were set to 50 ºC and 1 hour, respectively. As Figure 2 shows, a higher initial amount of methanol increases the FFA conversion. However, this relationship is not linear. The esterification reaction curve has an optimum point concerning the amount of methanol and after this point, increasing the methanol-to-oil ratio will not further affect FFA conversion because of the microscopic

equilibrium reached in the reaction.

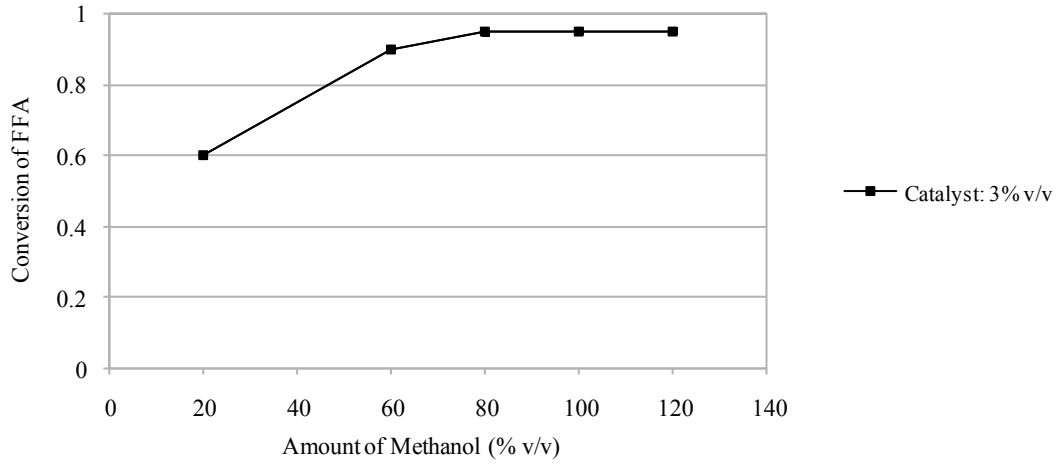


Fig. 2. Effect of the initial amount of methanol on FFA conversion

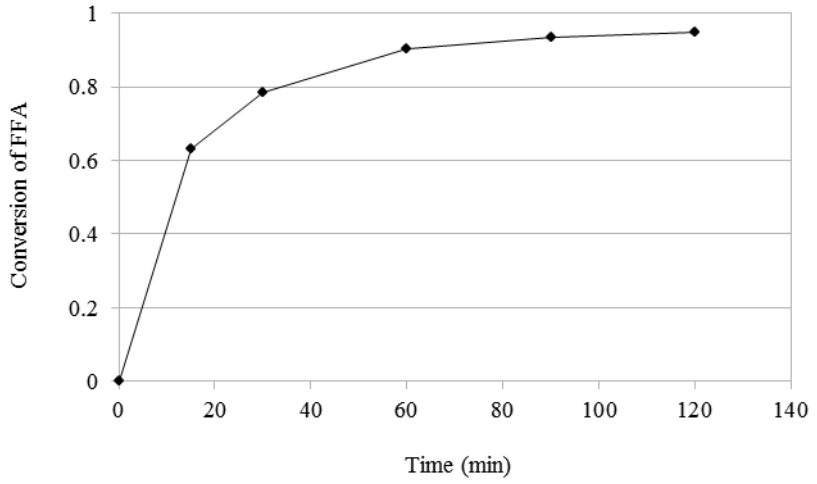


Fig. 3. Effect of time on the esterification reaction

3.3. Effect of time on FFA conversion

The time-dependency of the esterification reaction is shown in Figure 3. The initial amount of methanol,

catalyst and temperature were fixed at 60% v/v, 3% v/v and 50 ºC, respectively. Results indicate that approximately 1 hr could be an advisable time for achieving the desired FFA conversions. After 1 hour, the amount of FFA does not change significantly.

4. Conclusions

Since acid oils are readily available feedstock with lower prices, than neutral oils, their esterification is a potential method for biodiesel production at competitive costs. In this work, a real acid oil, which was a byproduct of a Vegetable Oil Company, was used for investigating the esterification reaction. The main parameters affecting esterification were studied. Results showed that regardless of the initial amounts of methanol, increasing the catalyst will not affect conversion in ranges higher than 2% v/v catalyst. Variations in methanol-to-oil ratio also could not bring conversion to one hundred percent, because the reaction is reversible. Monitoring the progress of the reaction with time also confirms the fact that equilibrium acts as the main inhibitor in completion of the esterification reaction. Finally, since even small amounts of FFA in the oil is of great importance for the operations that follow, water removal techniques during reaction, can be used to reduce the FFA to the lowest possible values.

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