NEW TECHNIQUES FOR BIODIESEL PRODUCTION

By

Marwa Mohamed Naeem Ahmed Romih

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE
in
Chemical Engineering

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Title of Thesis:

New Techniques for biodiesel production

Key Words:
Biodiesel; Waste cooking oil; Factorial design; Response surface methodology

Summary:

In this study, an activated carbon-supported heterogeneous catalyst was used for biodiesel production through conventional mechanical stirring and sonication. Waste vegetable oil with high free fatty acids was used as feedstock. Main factors affecting reaction extent were investigated with the assistance of full factorial design in combination with response surface methodology. Linear model with two-factor interactions was found to be very adequate to represent the experimental data in both techniques. In addition, representative samples were produced at optimum conditions and characterized according to ASTM standards where they were found matching these standards. Leaching and reusability tests were conducted and the catalyst was found to be leachable. Finally, a comparison was held between different techniques used.

Disclaimer

I hereby declare that this thesis is my own original work and that no part of it has been submitted for a degree qualification at any other university or institute.

I further declare that I have appropriately acknowledged all sources used and have cited them in the references section.

Name: Marwa Mohamed Date:

Signature:

Dedication

Dedicated to the memory of my sister, Mai, who always believed in my ability to be successful in life. You are gone but your belief in me has made this journey possible.

Acknowledgments

I am grateful to many people who have influenced and inspired me in my thesis; their enthusiasm, help, and support have ultimately led to the completion of this Dissertation. I would like to extend my gratitude and sincerer appreciation to my research supervisors professor Fatma Ashour and professor Mamdouh Gadalla for all of their help, support and guidance; without them this research would not have been possible. I extend my genuine and profound thankfulness to Eng. Eslam for his tremendous and endless support throughout the accomplishment of this thesis.

I would also like to thank the chemical engineering department in Cairo university for providing me with all necessary resources. Furthermore, I dedicate my deep appreciation to all who helped me throughout my thesis.

Last but not least, I would like to thank my family especially my parents, and my friends Amgad, Radwa Mahmoud, Radwa Amr, Sarah, Elias, Balaha and Jeo for all the support, courage motivation and love they nourished me with throughout this thesis.

Marwa Mohamed, July 2019

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NOMENCLATURE

KOH	Potassium Hydroxide
NaOH	Sodium Hydroxide
ASTM	American society for Testing and Materials
GWH	Giga Watt Hour
BOD	Biological Oxygen demand
WCO	Waste Cooking Oil
FFA	Free Fatty Acid
FAME	Fatty Acid Methyl Ester
CSM	Conventional Mechanical Stirring
SHTC	Sonication with Heterogeneous Catalyst
SHOC	Sonication with Homogenous Catalyst
GC	Gas Chromatography

ABSTRACT

Recently, Global focus is concentrated on finding new and renewable sources for energy production. One of these sources is biofuels that are produced from a renewable biomass source. Biodiesel is one of these new fuels which replaces petro-diesel. Heterogeneously catalyzed transesterification became an attractive option for biodiesel production due to its advantages over homogenous catalysis. In addition, using biomass gains a great attention to produce heterogeneous catalyst for the purpose of catalyzing biodiesel production.

In this study, an activated carbon-supported heterogeneous catalyst was used for biodiesel production through different techniques i.e. conventional mechanical stirring and sonication. The main characteristics of the catalyst used were tested through standard methods and analyses such as TGA, FTIR, XRD, and BET for surface area determination. Waste vegetable oil with high free fatty acids was used as feedstock for the whole study. The main factors affecting reaction extent were investigated with the assistance of full factorial design in combination with response surface methodology via central composite design. In the case of conventional mechanical stirring, the selected factors were time (0.5-1 h), methanol to oil molar ratio (6:1-18:1), catalyst loading (1-3 wt%) and temperature (45-65 ^{o}C); while in the case of sonication, the factors were catalyst loading (1-3 wt%), time (1-5 min) and methanol to oil ratio (6:1-18:1). Upon utilizing ultra-sonic waves, two types of catalyst were used; the first one was homogeneous catalyst (KOH) whereas, the other one was the heterogeneous catalyst as previously mentioned.

Linear model with two factors interactions was found to be very adequate and superior over the quadratic model to represent the experimental data in both techniques where, R^2 took the values of (99.99, 99.99 and 99.88%) in the cases of mechanical, sonication with homogenous catalysis and sonication with heterogeneous catalysis, respectively. Moreover, F-test was conducted for further testing of model validity. After performing this test for the liner model in each case, F-calculated values were found to be (6.33E-6, 5.47E-6 and 0.65) whereas the critical values were (5.05, 9.28 and 9.28). The results reveal that the developed linear model is very adequate as in all the cases F-critical is higher than F-calculated.

Furthermore, the developed model was satisfactory to predict the optimum conditions in all cases. It was found that the optimum conditions in the case of mechanical stirring were time 1 h, methanol to oil molar ratio 18:1, 1 wt% catalyst loading and temperature 45 ^{o}C at which the predicted yield was 97.76% while the observed yield was 97.77% with an error percentage of 1.56E-5. Moreover, in the case of homogeneous sonication catalysis were 1 wt% catalyst loading, 5 min time and methanol to oil molar ratio of 18:1 at which the predicted yield was 97.45% while the observed yield 97.45% with a zero error percentage; additionally, in the case of heterogeneous sonication catalysis were catalyst loading of 3 wt%, time of 5 min and methanol to oil molar ratio of 18:1 at which the predicted yield was 89.31% while the observed yield 88.36% with an error percentage of 1.08. Two representative samples were produced at previously obtained optimum conditions and characterized

according to ASTM standards. It was found that both two samples matched these standards.

Leaching and reusability tests were conducted and the catalyst was found to be leachable. In addition, the synthesized catalyst was not very good with respect to reusability as its catalytic activity dropped significantly upon using it twice. It was observed that total oil conversion decreased from almost complete conversion in the first use to about 10% and 35% in the second use in the cases of sonication and mechanical stirring, respectively.

A comparison was held between different techniques used. The heterogeneously catalyzed process assisted with sonication was found to be superior over the homogeneous one in decreasing or eliminating saponification which improves the process productivity. On comparing mechanical stirring to ultra-sonically assisted process using heterogeneous catalyst, sonication has the superiority with respect to reaction time; on the other hand, mechanical stirring produces more stable biodiesel, with respect to oxidation stability, due to excessive oxidation and polymerization of produced biodiesel from sonication process. Leaching rate is higher during using sonication and this observation was confirmed by reusability test.

CHAPTER 1: INTRODUCTION

The consumption of primary energy is increased on a daily basis with the increase of population and modern industries. In 2015, it was reported that the energy consumption was over 150,000,000 GWH and it is predicted that by the year 2050 that consumption will increase by 57% [1]. This drastic growth in energy consumption will ultimately result in more greenhouse emissions hence more environmental problems that directly threatening the survival of humans. Currently, over 80% of total energy usage is generated by fossil fuels, which directly leads to further negative effects on the environment and health of the population globally [2]. Hence, to tackle these issues, huge efforts have been underway to find suitable alternatives to fossil fuels, such as biofuels, to limit their negative effects economically and environmentally due to rapid consumption. The emergence of biofuels has proved a potential substitute to the current growing demand in energy market and reduces the threat to the environment. Among the wide array of biofuels, biodiesel has received a great amount of focus due to being an environmentally friendly biofuel as it is bio-degradable and renewable having almost no emissions. In addition, it can be used in diesel engines without any modification [3].

The biodiesel production increased over the last years due to the increase concern about the environmental impact of fossil fuels. For instance, from 2014 to 2017, it increased by almost 30% (i.e. from 27.84 to 35.82 million tons per year). The below figure shows the biodiesel production share of different countries all over the world in 2017. As illustrated, EU, USA, Brazil and Argentina produced about 13.55,6.1, 3.75 and 2.87 million tons per year, respectively. This represents about 75% of the total global biodiesel production. In addition, it is obvious that Indonesia has the highest Asian share of biodiesel production with about 2.92 million tons per year. Surprisingly, this rate is greater than the summation of production rates of both China and India which produce 0.44 and 0.15 million tons per year, respectively [4].

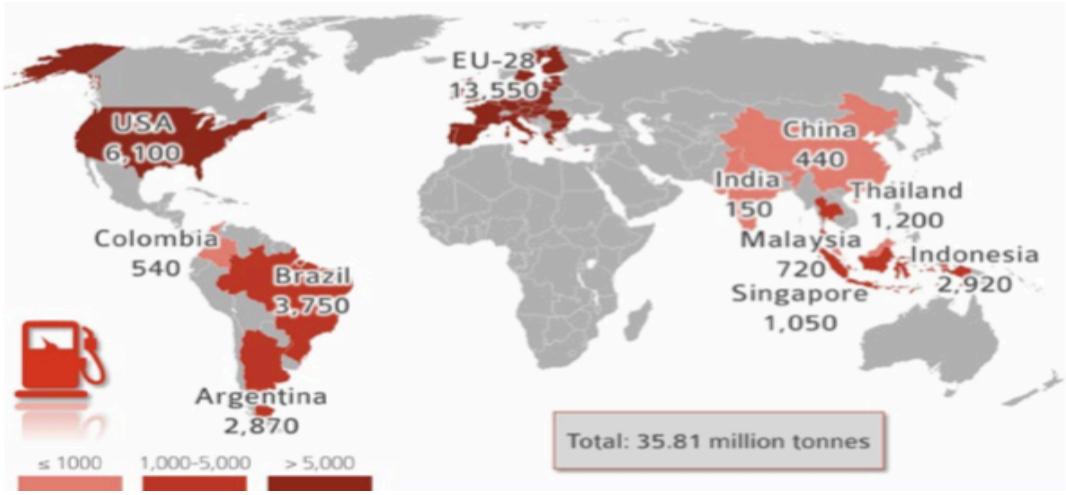

Figure 1.1: Biodiesel production in key countries in 2017