



Ain Shams University



Faculty of Science

# **Biojet Fuel: Production and Characterization using Catalytic cracking of natural oils**

A Thesis submitted for  
The Award of the Ph.D. Degree of Science in Chemistry  
By

**Haytham Nabil Mohamed Aziz Abu-Zied**

M.Sc. in Organic Chemistry - Zagazig University (2014)

## **Thesis Supervisors**

**Prof. Dr. Galal Hosni Sayed**

*Prof. of Organic Chemistry, Faculty of Science, Ain Shams University*

**Prof. Dr. Nabel Abdel Moneem Negm**

*Prof. of Petrochemicals, Petrochemicals Department  
Egyptian Petroleum Research Institute*

**Dr. Ghada Ishaq Amer**

*Researcher of Organic Chemistry, Petrochemicals Department  
Egyptian Petroleum Research Institute*

**2020**



Ain Shams University



Faculty of Science

## Approval Sheet

**Title: - Biojet Fuel: Production and Characterization  
using Catalytic cracking of natural oils**

**Name of Candidate:** Haytham Nabil Mohamed Aziz Abu-Zied

This Thesis has been approved for submission by supervisor:-

**Thesis Supervisors**

**Thesis approved**

**Prof. Dr. Galal Hosni Sayed**

*Prof. of Organic Chemistry*

*Faculty of Science Ain Shams University*

.....

**Prof. Dr. Nabel Abdel Moneem Negm**

*Prof. of Petrochemicals*

*Petrochemicals Department*

*Egyptian Petroleum Research Institute*

.....

**Dr. Ghada Ishaq Amer**

*Researcher of Organic Chemistry*

*Petrochemicals Department*

*Egyptian Petroleum Research Institute*

.....

*Head of Chemistry Department*  
*Faculty of Science Ain Shams University*  
**Prof. Dr. Ayman Ayoub Abdel-Shafi**



Ain Shams University  
Faculty of Science  
Chemistry Department

**"Biojet Fuel: Production and Characterization using Catalytic  
cracking of natural oils"**

**A Thesis submitted by  
Haytham Nabil Mohamed Aziz Abu-Zied**

**For the degree of Ph.D. in Chemistry**

**Prof. Dr. Galal Hosni Sayed** .....

**Prof. Dr. Nabel Abdel Moneem Negm** .....

**Dr. Ghada Ishaq Amer** .....

*Head of Chemistry Department*

**Prof. Dr. Ayman Ayoub Abdel-Shafi**



Ain Shams University



Faculty of Science

## Researcher Data

**Name:** Haytham Nabil Mohamed Aziz Abu-Zied

**Date of Birth:** 25/05/1986

**Academic Degree:** Ph.D. Degree of Science

**Field of specification:** Chemistry

**University issued the Degree:** Ain shams University - Faculty of  
Science- Chemistry Department

**Graduation year:** - 2007

**Date of issued Degree:** 2020

## **ACKNOWLEDGMENT**

Before all and above, I thank and pray to **ALLAH** for unlimited help and uncounted reasons.

I am greatly indebted to ***Prof. Dr. Galal Hosni Sayed***  
Prof. of Organic Chemistry, Faculty of Science, Ain Shams University, for his fruitful discussion, effective participation and deep concern of this work.

I am immensely grateful and highly indebted to my revered guide  
of ***Prof. Dr. Nabel Abdel Moneem Negm***  
Professor of Petrochemical, Petrochemicals Department, Egyptian Petroleum Research Institute, for suggesting the topic of this thesis, planning of experimental work, continuous following and enormous time spent in careful revision.

I am thankful to ***Dr. Ghada Ishaq Amer***  
Researcher of Organic Chemistry, Petrochemicals Department, Egyptian Petroleum Research Institute.

Finally, I cannot forget complete assistance and encouragement of my Family.

---



---

## Contents

<b>Introduction</b>	<b>1</b>
Diesel and Biodiesel	<b>5</b>
Chemical composition	<b>5</b>
Types of biofuels	<b>6</b>
Green diesel	<b>6</b>
Bioethers	<b>6</b>
Biogas	<b>6</b>
Syngas	<b>7</b>
Solid biofuels	<b>7</b>
Resources of biodiesel production	<b>8</b>
Edible oils	<b>8</b>
Non-edible plant oils	<b>8</b>
Used edible oils	<b>10</b>
Microalgae	<b>10</b>
Animal fats	<b>11</b>
Physical and chemical properties of biodiesel	<b>13</b>
Cloud point (CP) and pour point (PP)	<b>13</b>
Cold filter plugging point (CFPP)	<b>13</b>
Flash point (FP)	<b>14</b>
Kinematic viscosity	<b>14</b>
Cetane number (CN)	<b>15</b>
Density	<b>15</b>
Acid number	<b>16</b>
Carbon residue	<b>16</b>
Iodine number	<b>16</b>
Calorific value	<b>17</b>
Sulfur content	<b>17</b>
Sulfate ash content	<b>17</b>
Water and sediment content	<b>18</b>
Free and total glycerin	<b>18</b>
Phosphorus, calcium and magnesium content	<b>19</b>
Moisture impurities and unsaponifiables (MIU) content	<b>19</b>
Fuel Properties	<b>20</b>

Advantages and Disadvantages of Biodiesel Fuel	29
Advantages of Biodiesel	29
Disadvantages of Biodiesel	31
Biodiesel quality from different sources as compared to conventional petroleum diesel fuel	34
Catalyst	39
Process	65
Thermal cracking (pyrolysis) and catalytic cracking	78
<b>Experimental Section</b>	<b>92</b>
Materials and Methods	92
Materials	92
Preparation of activated carbon derived from date palm leaves	92
Preparation of $\text{SO}_4^{2-}/\text{CuO-ZnO}$ catalyst	93
Methods	94
Catalytic cracking of Castor oil	94
Biofuel specification	94
Reusability test of catalysts	101
<b>Results and Discussion</b>	<b>102</b>
Chemical structure of castor oil	102
Characterization of the castor oil	102
Catalytic cracking mechanism	107
Chromatographic analysis of produced biofuel	109
Catalysts	113
Activated carbon catalyst	113
$\text{SO}_4^{2-}/\text{CuO-ZnO}$ catalyst	120
Properties of the obtained biofuel	131
Distillation characteristics of the obtained biofuel	146
Catalysts reactivity	149
Catalyst reusability	151
Engine performance of petroleum diesel/castor oil biofuel mixtures	154
<b>Summary and conclusions</b>	<b>156</b>
<b>References</b>	<b>160</b>

### List of Figures

<b>Figure No.</b>	<b>Title</b>	<b>Page</b>
<b>Figure.1.1</b>	The Ca/Al composite oxide which contains Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub> and CaO.	<b>57</b>
<b>Figure 2.1</b>	Ubbelhood suspended level kinematic viscosity apparatus.	<b>97</b>
<b>Figure 2.2</b>	Density/Specific Gravity Meter (KEM, DA-640 model).	<b>98</b>
<b>Figure 2.3</b>	Digital Electric Pensky-Martens Apparatus (S.D.M. Apparatchik Scientific Srl model).	<b>100</b>
<b>Figure 3.1</b>	Chromatographic analysis of castor oil and castor oil biofuel.	<b>111</b>
<b>Figure 3.2</b>	FTIR spectrum of activated carbon sample of date palm leaves.	<b>114</b>
<b>Figure 3.3</b>	(a) N <sub>2</sub> adsorption-desorption isotherm of AC samples (b) Pore size distribution of AC samples.	<b>116</b>
<b>Figure 3.4</b>	SEM image of activated carbon sample derived from date palm leaves.	<b>119</b>
<b>Figure 3.5</b>	N <sub>2</sub> adsorption-desorption isotherm of SO <sub>4</sub> <sup>2-</sup> /CuO-ZnO.	<b>122</b>
<b>Figure 3.6.a</b>	TEM image of SO <sub>4</sub> <sup>2-</sup> /CuO-ZnO.	<b>124</b>
<b>Figure 3.6.b</b>	SEM image of SO <sub>4</sub> <sup>2-</sup> /CuO-ZnO.	<b>125</b>
<b>Figure 3.7</b>	XRD pattern of SO <sub>4</sub> <sup>2-</sup> /CuO-ZnO.	<b>126</b>
<b>Figure 3.8</b>	Raman spectrum of SO <sub>4</sub> <sup>2-</sup> /CuO-ZnO.	<b>128</b>
<b>Figure 3.9</b>	TGA curve of SO <sub>4</sub> <sup>2-</sup> /CuO-ZnO.	<b>130</b>
<b>Figure 3.10</b>	Variation of density of the obtained biofuel by changing the catalysts ratio.	<b>133</b>
<b>Figure 3.11</b>	Variation of kinematic viscosity of the obtained biofuels by changing the catalysts ratio.	<b>135</b>
<b>Figure 3.12</b>	Variation of pour points and cloud points of the obtained biofuels by changing the catalysts ratio.	<b>139</b>



<b>Figure 3.13</b>	Variation of flash points of the obtained biofuels by changing the catalysts ratio.	<b>141</b>
<b>Figure 3.14</b>	Catalytic activity of activated carbon and $\text{SO}_4^{2-}$ /CuO-ZnO in the cracking of castor Oil.	<b>149</b>
<b>Figure 3.15</b>	Reusability of: activated carbon and $\text{SO}_4^{2-}$ /CuO-ZnO salts in catalytic cracking reaction of castor oil.	<b>153</b>

---

---

### List of Tables

<b>Table No.</b>	<b>Title</b>	<b>Page</b>
<b>Table 2.1</b>	Chemicals used in the study	<b>92</b>
<b>Table 3.1</b>	Fatty acid profile of castor oil	<b>104</b>
<b>Table 3.2</b>	Physicochemical properties of castor oil	<b>106</b>
<b>Table 3.3</b>	Texture data for activated carbon samples derived from date palm leaves	<b>117</b>
<b>Table 3.4</b>	Texture data for $\text{SO}_4^{2-}/\text{CuO-ZnO}$	<b>121</b>
<b>Table 3.5</b>	Reaction products of catalytic cracking of castor oil using activated carbon and $\text{SO}_4^{2-}/\text{CuO-ZnO}$	<b>131</b>
<b>Table 3.6</b>	Properties of biofuel obtained from castor oil cracking	<b>136</b>
<b>Table 3.7</b>	ASTM distillation of biofuel from catalytic cracking of castor oil	<b>148</b>
<b>Table 3.8</b>	Engine test results for petroleum diesel/castor oil biofuels blends	<b>155</b>

---

---

### Abstract

In this study, two catalysts which are activated carbon and  $\text{SO}_4^{2-}/\text{CuO-ZnO}$  were prepared from palm leaves and according to the procedure reported in [Minli *et al.*, 2012] respectively. The prepared two catalysts were characterized using different spectroscopic and surface analysis to determine their chemical and morphological structures. The prepared activated carbon was characterized using FTIR spectroscopy, surface analysis and SEM spectroscopy. While,  $\text{SO}_4^{2-}/\text{CuO-ZnO}$  catalyst was characterized using surface analysis, TEM and SEM spectroscopy, XRD, Raman spectroscopy and TGA analysis.

The prepared activated carbon and  $\text{SO}_4^{2-}/\text{CuO-ZnO}$  were used as heterogeneous catalysts at different ratios in catalytic cracking of castor oil to produce biofuel. The parameters controlling the production of the biofuel were determined and the reaction condition was optimized.

The fuel properties of the produced biofuel were determined including: density, viscosity at 40 °C, flash point, cloud point, pour point, cetane number, sulfur content, ash content, and carbon residue. The ASTM distillation of biofuel from catalytic cracking of castor oil in the presence of activated carbon and  $\text{SO}_4^{2-}/\text{CuO-ZnO}$  salts at different ratios used to calculate the cetane number as a property of the biofuels.

The measurements of the reactivity of the used two catalysts were determined by the amount of the distillates that obtained after 1 h of the catalytic cracking reaction.

The chromatographic analyses for both of castor oil and produced biofuel were represented. The reusability of the different catalysts was determined by repeating the cracking reaction using one catalyst sample for several rounds and the properties of the obtained biofuel after each round were determined.

Engine test has been done for the mixture of petroleum diesel/castor oil biofuel using three blends of the obtained biofuels (B10, B20, and B40) from catalytic cracking of castor oil.

**Keywords:** activated carbon; biofuel; castor oil; catalytic cracking; heterogeneous catalyst;  $\text{SO}_4^{2-}/\text{CuO-ZnO}$ .

### **Aim of the Work**

1. Synthesis of activated carbon and  $\text{SO}_4^{2-}/\text{CuO-ZnO}$  catalysts.
2. Catalytic cracking of the castor oil using the synthesized two catalysts.
3. Determination the suitable conditions to obtain the maximum biofuel product including: time of reaction, temperature and amount of catalyst.
4. Determination the properties of the produced biofuel according to density, viscosity, flash point, cloud point, pour point, cetane number, sulfur content, ash content, and carbon residue.

---

**I. INTRODUCTION**

In recent years, many researchers are concentrating on developing biofuels from alternative and renewable sources to replace commercial petroleum products. The suitable properties of plant oils and animal fats (renewable and low sulfur, nitrogen and heavy metal content), which are made up of triglycerides with long chained fatty acid groups 16 to 24 carbon atoms in length, makes them ideal sources for the production of synthetic fuels and useful chemicals. At present, the most successful class of biofuels is biodiesel, which is produced from plant oils or animals fats by a liquid-phase catalyzed transesterification process at low temperature or a solid catalyzed catalytic cracking process at high temperature. However, the process requires large investments for the production units in order to ensure high efficiency. Also biodiesel product is not stable compared with the petroleum fuel because of its low oxidation stability and poor cold flow properties. Recently, an alternative method of converting plant oils and animal fats into biofuel products has been studied by using a catalytic hydrotreating process similar to what is found in the oil and gas industry. Two important chemical steps occur during the conversion of oils into biofuel products: oxygen removal (hydrodeoxygenation, hydrodecarbonylation, and hydrodecarboxylation) and hydrocracking. Both of these chemical processes are included in a larger group of processes generally

---

referred to as hydroprocessing. During the process, a dual function catalyst composed of a metallic part and amorphous mixed oxides of acidic nature or proton exchanged crystalline zeolites is required, where metallic sites are required for hydrogenation and dehydrogenation reactions and the acid sites are necessary for isomerization and cracking activities. Therefore, it is very important to design the acidic sites and metal components as well as tailor the balance between the metal and acid for the product selectivity, catalyst activity and stability.

At present, two types of catalysts have been reported as effective hydrotreating catalysts in converting vegetable oils to biofuels, especially green diesel: supported noble metal catalysts (Pd and Pt) and sulfided bimetallic catalysts (usually Mo- or W-based sulfides promoted with Ni or Co). However, there are disadvantages of using these catalysts. On one hand, the rarity and high price of noble metal catalysts has made the process economically unfeasible. Furthermore, since noble metal catalysts are very sensitive to catalyst poisons, impurities (such as sulfur, heavy metals and oxygenated compounds) in feedstock can cause significant deactivation of the catalysts. Therefore, it is necessary to remove impurities from the biomass feedstock before the reaction. On the other hand, conventional  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported sulfide bimetallic catalysts (usually Mo or W based sulfides promoted with Ni or Co) as presently used for desulphurization of