

**FUEL RANGE HYDROCARBON SYNTHESIZED BY
HYDROCRACKING OF WASTE COOKING OIL VIA
Co/Zn-Al₂O₄ NANO PARTICLES**

**Mohamed A. Ibrahim^a ; Reham. El-Araby^b ; Elham Abdelkader^b ;
A.M. Abdelsalam^c and Eman H. Ismail^d**

^a Egyptian projects operation & maintenance – Egyptian Refining Company, Cairo,13753, Egypt

^b Chemical Engineering and pilot plant Department, National Research Centre, Cairo,12622, Egypt

^c Ghamra research center, Misr Petroleum Company, Cairo,11674, Egypt

^d Ain Shams University Chemistry Faculty of Science, Chemistry Department, Cairo,11566, Egypt.

^a E-mail -maboubakr@eprom.ercegypt.com

ABSTRACT

The development of biofuels resources has received great attention because of the global environmental concern and the exhaustion of the fossil fuel resources. Hydrocracking of waste cooking oils to obtain biofuel is a potential processing route. This study was investigated the preparation of catalyst Co/Zn-Al₂O₄ Nano particles and then use it in biodiesel fuel synthesis by hydro catalytic cracking of waste cooking oil (WCO). The hydrocracking was done in a high-pressure catalyst activity testing unit. This catalyst was characterized by X-ray diffraction (XRD), the Brunauer-Emmett-Teller (BET), Fourier transform infrared (FTIR), High-resolution transmission electron microscopy (HRTEM) analysis. The parameters affecting the cracking process, such as temperature, hydrogen pressure and feed rate of WCO, were optimized. The cracked products were characterized by fractional distillation. The results of fractional distillation show good catalyst higher selective activity to bio hydrocarbon in rang of naphtha, kerosene and diesel compared to fractional distillation of WCO. Blend of 50% biodiesel was done with fossil diesel fuel and characterized as a drop in B50 biodiesel fuel then characterized according to the different ASTM methods.

Key Words: Biodiesel, Nano catalyst, hydrocracking, waste cooking oil.

1-INTRODUCTION

The continuous increase in the world's population, urbanization, rapid industrialization, and economic growth lead to a continuously increase in fossil fuel consumption to meet the growing energy demand. Continuous emissions from burning of fossil fuel will create the need to find the appropriate and sustainable replacement for fossil fuels (Singh, et al., 2020). In order to meet the increasing needs for energy, most of the developing countries import crude oil. For this reason, a very large amount of money is spent on purchasing crude oil and petroleum products.

Realization of the severe lack of crude oil commenced through the worldwide fuel crisis in the 1970s. So that, great attention was given to the improvement and utilization of another fuel sources. Besides this awareness towards the energy problem, also great attention for us is the degradation of environment due to large amount of emissions resulted of fossil fuel combustion. The responsible of the greenhouse gas effect in the around atmosphere is the exhaust gases such as carbon monoxide (CO), and nitrogen oxides (NOX) and sulphur dioxide (SO₂). Which has an impact lead to a global warming. Hence, it is important to improve alternative fuels with low limit of emissions to mitigate the above-mentioned energy related problems. Efficient sourcing of fuels from renewable sources is an option for meeting these challenges. Some of the renewable energy sources include traditional biomass, hydropower, solar, wind, and biofuels (**Yah, et al., 2017 and Oumer, et al., 2018**). It was founded that biofuel leads to greenhouse gas reductions, on a well-to-wheel basis, of 40–60% when compared with fossil fuel and petroleum cuts (**Singh, et al., 2020**). In the USA alone, more than 1.5 billion gallons of biofuel was produced from vegetable oils in year 2016 (**Banković-Ilić, et al., 2012**). And after the fulfillment of current biofuel policies in several countries, the global biodiesel manufacture and consumption is predicted to rise. At the meantime, the waste-based production of biodiesel was expected to grow to 4.4 billion liters (**Singh, et al., 2020**).

There are generally two ways to produce diesel from waste cooking oil; where either esterification used to convert triglycerides to methyl-esters with the help of methanol or by using of thermal treatment which includes thermal cracking, catalysts, and hydrotreating. The hydrotreating is take into considerations as one of the most effective method in waste cooking oil cracking process. This is because the presence of hydrogen minimizes the cock formation and consumes less heat energy (**Oumer, et al., 2018**). It includes the hydrogenation and cracking of the double bonds of the hydrocarbon chain and removes oxygen with metal as the catalyst. The hydrotreating of waste cooking oil leads to C15-C18 hydrocarbons production as green diesel (**Yah, et al., 2017**). Catalytic hydro processing technology is an alternate technology for biofuels manufacture process which uses the existing infrastructure base of petroleum refineries (**Stumborg, et al.,1996 and Huber, & Corma 2007**), and has already sundry (**Sivasamy, et al., 2009**). The hydrotreating technology has a great power as the resulted hydrotreated vegetable oils have better hydrocarbon fuel properties than the biodiesel fuel produced via transesterification process, and their use enhance engine fuel economy (**Shaban, 2012**). Hydro processing of raw vegetable oil heavy vacuum gas oil mixtures has been explored by employing hydrotreating (**Huber, et al., 2007**) and hydrocracking (**Bezergianni, et al.,2009**) catalysts at normal little operating

conditions and parameter. Though, this process technology has only been utilized to raw vegetable oil feedstocks (Stella, and Aggeliki 2009).

During the frying process, oil diligently degraded when exposed to elevated temperature, oxygen, and moisture so it leads to physical and chemical changes including the compose of hydrolysis products such as free fatty acids (FFAs) (Bazina, and He 2018). To convert FFA into biofuel compounds, meso-sized material is required as a great adsorption medium. The mesoporous materials have attracted the attention of numerous researchers in different application fields (Trisunaryanti, et al., 2018). The choice of basic mesoporous material is critical because it acts as a building block. One of the main ingredients that are superior is silica since it has properties that are thermally stable, safe, and inexpensive (Trisunaryanti, et al., 2020). Pure silica materials are MCM, SBA, HMS, whereas the non-silica mesoporous materials incorporate transition metal oxides (Kumar, et al., 2017).

2. EXPERIMENTAL

2.1. Material and Methods

Waste cooking was oil collected from local fast-food restaurants. Zn (NO₃)₂·6H₂O, Co (NO₃)₂ · 6H₂O, Al (NO₃)₃·9H₂O and ammonia solution (25 Wt %) were obtained from Sigma Aldrich. Distilled water was also obtained from the laboratory through a distillation apparatus.

2.1.1. Catalyst Preparation

Co-precipitation method has been used to prepare Zinc cobalt aluminate nanoparticles in an aqueous solution from metal nitrates using ammonia as a precipitating agent as follows. Firstly, 10 mmol of Zn (NO₃)₂·6H₂O and 10 mmol of Co (NO₃)₂·6H₂O were placed in dry and clean 100 ml glass beaker. Then dissolve the mixture in 10 ml of fresh distilled water, then added to a solution of Al (NO₃)₃·9H₂O (40 mmol) in 10 ml of fresh distilled distilled water. Secondly, suitable amount of precipitating agent aqueous ammonia solution (25 Wt %) was added to the above solution. Then, the mixture was well stirred and keep a pH between 8 and 9 until getting a complete precipitation. The resulted product was filtered, washed with adequate amount of distilled water, and dried. Finally, the dry precipitate was calcined in an oven at 600 °C for 5 h to get the Co/Zn- Al₂O₄ nanoparticles.

2.1.2. Waste Cooking Oil Preparation

Waste cooking oil was collected from local fast-food restaurants. The stage of preparing the oil begins with filtering through two steps: First, through a coarse sieve to get rid of the solid content. Then the filtration process is carried out through filter paper to ensure the removal of solid impurities. Then the waste cooking oil was kept in a container at room temperature. Prior to analysis and treatment, the oil is heated and stirred for two hours at 110 °C to remove any moisture.

2.1.3. Catalytic Cracking Test

A series of experiments were conducted to explore the influence of the various operating factors on the qualities and quantities of the obtained products. The reactions have been performed using a continuous high-pressure micro- reactor (cata- test unit). The apparatus consists mainly of 50 cm length stainless steel reactor, with internal and external diameter of 19 and 27 mm, respectively. It divided into three zones, each of them has its individual heating element and temperature controller. 30 mg (equivalent to 46 ml) of the catalyst mixed with the same volume of ceramic, has been charged in the middle zone of the reactor.

Hydrogen gas was supplied to the unit from a H₂ cylinder, while liquid feed was pumped to the top of the reactor by means of a piston pump having an adjusting knob.

The hydrotreating and hydrocracking reaction for the investigated oil, have been carried out at different operating conditions. The effect of each variable on the process is assessed while keeping other variable constant. The applied experimental conditions include:

Temperature: 350, 400, and 450 °C

Hydrogen pressure: 30, 50, 70 bar

Liquid hourly Space Velocity (LHSV): 1, 1.5, and 2 ml/min.

2.1.4. Fractional Distillation

The atmospheric distillation method ASTM D-86 of petroleum products and middle distillates. This method detects the boiling rang for lots of different hydrocarbon distillates such as gasoline with or without oxygenates, diesel, and other light and middle distillates (ASTM, 2017 and Stedile, et al., 2019). The product mixtures obtained from catalytic thermal cracking were separated by fractional distillation, and the percentage of the volumes obtained were calculated over a different boiling points temperature range of IBP from about 50 °C to about 360 °C.

2.1.5. Catalytic Activity

The conversion of the WCO into lighter liquid products during the reaction was expressed as a catalytic activity dependent on the adsorption of the reactants on the surface of the catalyst. Chemical adsorption is the main factor controlling the activity of catalysts. The percentage yield of the WCO into (x) product during the reaction was calculated by the following equation (Singh, et al., 2020):

$$\%Yield = \frac{\text{Product of (x)}}{\text{Feed}} * 100 \quad \text{Eq. (1)}$$

Moreover, to evaluate and measure the hydrocracking efficiency towards the production of a special kind of product instead of other products, the measure of selectivity was employed. The selectivity of the products such as diesel kerosene and naphtha can be determined according

boiling rang. For example, for a product with initial and final boiling points A and B, respectively, selectivity A-B is defined as: Feed A-B

$$\text{Product selectivity \%} = \text{\%Yield} = \frac{\text{Product (A-B)} - \text{feed (A-B)}}{\text{Feed } 360 - \text{product } 360} \times 100 \text{ Eq. (2)}$$

where Feed 360°C and Product 360°C were the Wt% of the feed and product, respectively, which have a boiling point higher than 360°C (*i.e.*, heavy molecules of feed and product) and Feed A-B and Product A-B are the Wt% of the feed and product, respectively, which have a boiling point range between A and B degrees Celsius. From Eq. (2) selectivity can be defined for diesel (180–360 °C), kerosene/jet (170-270 °C) and naphtha (40-200°C).

2.1.6. Characterization of WCO

The main physical and chemical characteristics of the raw waste cooking oil are analyzed by GC with capillary column DB-5(60 m: ID 0.33mm). Helium was used as a carrier gas at flow rate 1 ml/min, column temperature was kept at 240- 143 °C for 30 min.

2.1.7. Characterization of Catalyst

The results of X-ray diffraction (XRD) patterns have been measured on Smart Lab Guidance and MDI Jade 8 device by using a Rigaku RU2000 rotating anode power diffract meter (Rigaku Americas Corporation, TX) at a scan rate of 4°C min⁻¹.

The prepared Co/Zn-AL₂O₄ catalyst in the cracking process of the WCO was characterized by using BET surface area, Barrett–Joyner–Halenda (BJH) pore size and pore volume have been analyzed using a Micromeritics model ASAP 2010 surface area analyzer with 99.9% purity nitrogen gas. The results were collected on a Tristar 3020 instrument. The measuring conditions of degassing were at 400 °C with ramping heat of 10 °C min⁻¹ for 2 h before measuring.

FT-IR was used to reveal the chemistry of surface functional groups by a Perkin- Elmer FT-IR. The sample was firstly dried at 373 K and then was grinded to fine powder in order to increase the homogeneity of the sample. In addition, KBr is regarded as the background during FT-IR analysis. Transmission spectra is measured in the range of 4000 ~ 400 cm⁻¹ with 128 scan times for both background and samples.

Transmission electron microscopy (TEM) images have been gotten with a JEM 2010 HR TEM instrument, which is equipped with a digital camera system allowing the capture of both high-resolution images and electron diffraction patterns.

2.1.8. Diesel 50% Blend Characterization

The biofuel products of the diesel fractions that attained at the operating conditions of this study were blended in weight percentage (50%) with fossil diesel fuel then characterized according to the different ASTM methods.

3. RESULTS AND DISCUSSION

3.1. Characterization of prepared catalyst,

3.1.1. Powder X-ray Diffraction (XRD) Analysis

The powder X-ray diffraction patterns of prepared catalyst is shown in Figure 1. It can be seen that sample have crystallized in a single phase with a spinel structure and with space group $O7h$ and contains small amounts of ZnO (JCPDS card No. 36–1451) impurities in addition to the major phase of spinel $ZnAl_2O_4$ structure (JCPDS card No. 05–0669). According to the literature (Ianoş, et al., 2014 and Stedile, et al., 2019). The observed diffraction peaks at 2θ are 31.22, 36.77, 44.69, 48.98, 55.52, 59.27, 65.06, 73.97, and 77.12 and can be ascribed, respectively, to the (220), (311), (400), (331), (422), (511), (440), (620), and (533) planes of $ZnAl_2O_4$. The mean grain size of sample was quantitatively evaluated based on the line broadening of the (220), (311), (511), and (440) peaks using the Scherrer formula, to be 13, 16, and 24 nm, respectively. XRD results indicate that the choice of the aluminum salts also has an influence on the phase purity of the final product.

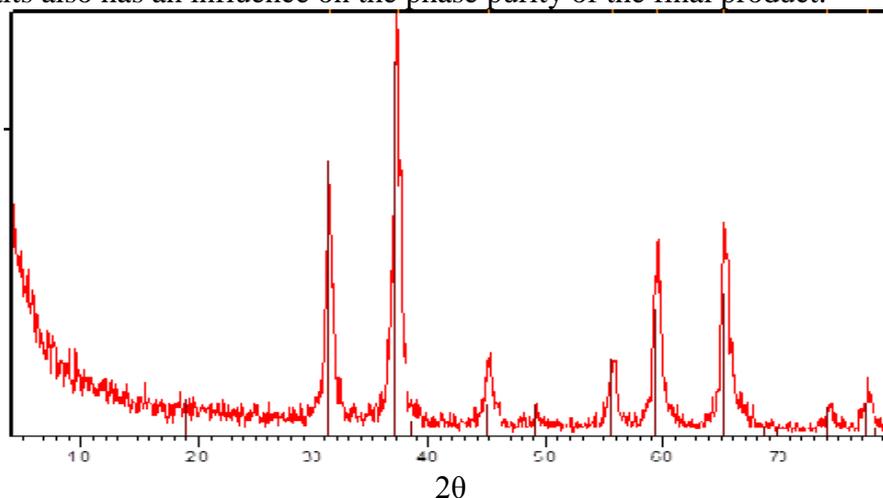


Figure 1. X-Ray Diffraction of Co/Zn- Al_2O_4 Catalyst

3.1.2. N₂ Adsorption Desorption Isotherm

The nitrogen adsorption/desorption isotherms and pore size distributions of the various prepared samples are shown in Figure 2. Three well distinguished regions of the adsorption isotherm are evident: (i) monolayer-multilayer adsorption, (ii) capillary condensation, and (iii) multilayer adsorption on the outer particle surfaces. Apparently, the prepared sample have the type IV isotherm according to the classification of the International Union of Pure and Application Chemistry (IUPAC). Based on data in Table 1, it can be found that Co/Zn- Al_2O_4 catalyst have

BET surface areas 65.51 m²/g-1, pore diameter 8.76 nm and pore volumes 0.26 cm³/g.

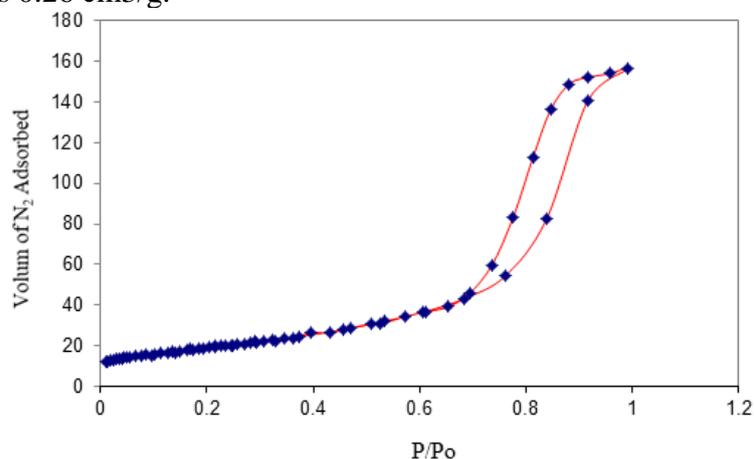


Figure 2. N₂ Adsorption Desorption Isotherm of Co/Zn-Al₂O₄ Catalyst

Table 1. Texture Properties of Co/Zn-Al₂O₄ Catalyst

Catalyst	SSA/m ² /g	Pore Diameter/nm	Pore Size Distribution/ccg
Co/Zn-Al ₂ O ₄	65.51	8.76	0.26

Fourier transform infrared (FT-IR) spectra of the Co/Zn-Al₂O₄ nanoparticles is shown in Figure 3. The FT-IR spectra shows a series of absorption peaks in the range of 400–4000 cm⁻¹. According to the specific frequencies of the absorption peaks, the functional groups existing in the samples can be deduced. Peaks at 1633, 656, 552, and 493 cm⁻¹ are present in prepared sample, and were assigned to the H-O-H bending vibration of adsorbed water (Ge, et al., 2013), Al-O symmetric stretching vibration (ν₁) Al-O symmetric bending vibration (ν₂) and Al-O asymmetric stretching vibration (ν₃ respectively) (Da Silva, et al., 2009 and Anand, et al., 2015).

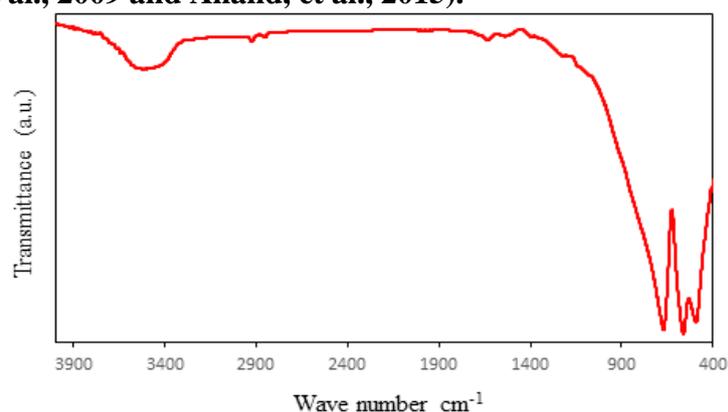


Figure 3. FT-IR of Prepared Co/Zn-Al₂O₄ Catalyst

3.1.3. High Resolution Transition Electron Microscopy (HRTEM)

Figure 4 shows the transmission micrographs for the Co/Zn-Al₂O₄ sample. The image shows that the zinc, cobalt aluminate particles are uniform and nanoaggregate; the zinc metal ions using Co²⁺ showed no significant changes in material morphology.

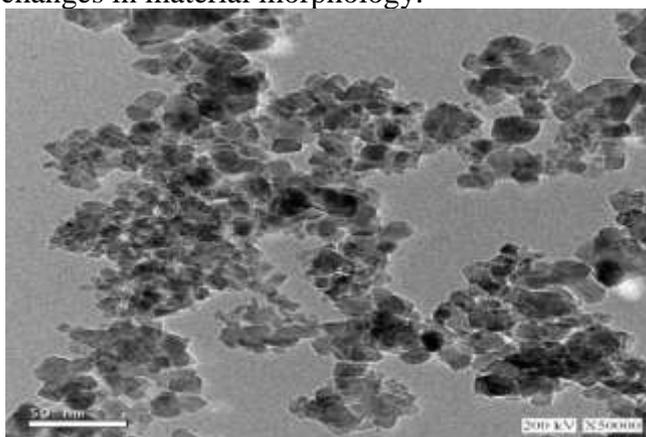


Figure 4. HRTEM of Co/Zn-Al₂O₄ Catalyst

3.2. Catalytic Activity

One of the most interesting topics in catalysis concerns the nature of the active sites on a catalyst surface. Various spectroscopic methods and test reactions have been used to search for answers. Here, however, we use the distribution of primary products in a test reaction to study and investigate the nature of the active sites responsible for their activity. One of the most common reaction is catalytic cracking of waste cooking oil by prepared catalyst under several conditions.

3.2.1. Effect of Temperature and hydrogen pressure

Temperature and pressure have been considered as a vital parameter for catalyst activity and catalyst life. Increasing temperature and pressure increases catalyst activity and increasing catalyst activity causes a faster decay of catalyst life (Shaban, 2012). This study on product yields and quality was performed on hydrocracking of used cooking oil over Co/Zn-Al₂O₄ at different reactor temperatures 350,400,450 °C pressure 30,50 & 70 bar and feed rate 1, 1.5,2 ml/min. The diesel product yield is considered as the 70 vol % of the total volume liquid product that has a boiling range between 170 and 360 °C, while the gasoline product yield is defined as 30 vol% of the total liquid product with a fraction boiling range between 40 and 200°C. Lighter products (with boiling point < 40°C) are gaseous molecules and were not considered in this analysis as liquid biofuel product. Moreover, heavier molecules (with boiling point > 360°C) compose the unconverted part of the feed that cannot be utilized as liquid biofuels. The product yields

increase as reactor temperature and hydrogen pressure increases, the produced liquid biofuels (gasoline, kerosene, and diesel) increase. This is expected as hydrocracking activity rises with increasing temperature. Diesel yield is nearly more than three times higher than the gasoline yield at all temperatures, indicating that this technology is more suitable for diesel production rather than gasoline production. The minimum diesel yield observed at 350 °C is attributed to the fact that increasing temperature causes not only heavy molecules but also diesel ones are cracked into lighter molecules. The conversion as well as the diesel, kerosene/jet and naphtha selectivity's for the different hydrocracking temperatures. The conversion and selectivity's are calculated from the fraction distillation data (Table 2) of the total liquid product of each hydrocracking temperature, using Eq. (1) and (2), respectively, as temperature increases, the conversion increases, this is an expected outcome as hydrocracking activity is favored with temperature.

3.2.2 Effect of LHSV

It was noted that the products yield percentage have been decreased as the LHSV increased, which was expected. Increasing feed LHSV, resulted in smaller residence time at in the catalyst section (reactor) and therefore smaller contact and reaction time. Diesel yield was significantly higher than gasoline yield at all LHSVs.

Table 2. Fractional distillation results of cracked WCO over Co/ZnAl₂O₄ at different temperature 350, 400, 450 – pressure 30, 50, 70 bar- Rate 1, 1.5, 2 mi/min

	T 350 °C , H ₂ P 50 b, R 1ml/min	T 400 °C , H ₂ P 50 b, R 1ml/min	T 450 °C , H ₂ P 50 b, R 1ml/min	T 400 °C , H ₂ P 70 b, R 1ml/min	T 400 °C , H ₂ P 30 b, R 1ml/min	T 400 °C , H ₂ P 50 b, R 1.5ml/min	T 400 °C , H ₂ P 50 b, R 2 ml/min
Recovery % V	T (°C)	T (°C)					
initial	70	50	55	55	64	55	88
5%	98	150	75	110	130	80	150
10%	200	230	90	160	220	155	230
20%	305	275	150	240	265	250	275
30%	>350	290	194	275	280	275	287
40%		330	235	290	285	290	295
50%		340	270	297	298	305	305
60%		> 350	290	310	308	320	319
70%			310	325	320	340	335
80%			340	345	345	>350	>350
90%			390	365	>360		
95%			>400	380			
End point				>400			

3.2.3 Results of Biodiesel Fraction Range Blends with 50% fossil diesel fuel

Blend sample of biofuel products were withdrawn after a fractional distillation stage in the range (180-360 °C) and then the sample was

blended with 50% of fossil diesel fuel. After that, tests were performed to verify that the properties of these B50 blend conform the ASTM diesel fuel specifications. Table (3) shows the results of the properties of this blend.

Table (3): Results of Physical Properties Biodiesel Fraction Range Blends with 50% fossil Diesel fuel

Property	B10* (50% Biofuel* + 50% Gas Oil Fuel)	Gas Oil Fuel	Specification Limits	Standard Test Method
Density at 15 °C; (g/cm ³)	0.8230	0.8206	Reported	ASTM D-4052
Flash point (P.M.C.C); (°C)	84	109	52 (min.)	ASTM D-93
Pour point; (°C)	-3	-9	15 (max.)	ASTM D-97
Cloud point; (°C)	15	3	Reported	ASTM D-2500
Kinematic viscosity at 40 °C; (cSt)	4.836	3.96	1.6 - 7	ASTM D-445
Distilled at 350 °C; (%vol)	94	90	85 (min.)	ASTM D-86
Water and sediment content; (%vol)	Nil	Nil	0.1 (max.)	ASTM D-2709
Sulfur content; (%wt)	0.008	0.006	1 (max.)	ASTM D-4294
Copper corrosion strip at 50 °C/3 hrs	1A	1A	1 (max.)	ASTM D-130
Carbon residue; (%wt)	0.05	0.07	0.1 (max.)	ASTM D-4530
Ash content; (%wt)	Nil	Nil	0.01 (max.)	ASTM D-482
Colour	1	0.5	4 (max.)	ASTM D-6045
Cetane index		55	46 (min.)	ASTM D-4737
Calorific value; (Mj/Kg)	43.2	43.8	Reported	ASTM D-4868
Aniline point; (°C)	69	70	Reported	ASTM D-611

4. CONCLUSION

Hydrocracking of used cooking oil is a promising process for the production of biofuels. This work considers hydrocracking of WCO over Co/Zn-Al₂O₄ at several parameters for evaluating the effectiveness of this technology, mainly hydrocracking temperature and liquid hourly space velocity (LHSV). Conversion and overall biofuels' yield is favored with increasing temperature and decreasing LHSV, as cracking activity is increased. However, moderate reaction temperatures and LHSVs are more attractive if diesel production is targeted, whereas higher temperatures and smaller LHSVs should be employed if gasoline production is also important. Renewable biodiesel hydrocarbon fuel fraction rang (C15 – C18) was obtained by fraction distillation from thermo-cracking yield at temperature (170 – 360 °C) which has an acceptable physical and chemical properties according to standard methods compared to petroleum-based fuel. WCO oil is a good source

and raw materials for producing Bio-fuel, this is because of its low cost and its contribution for environmental pollution.

5. REFERENCES

- Anand, G. T. ; L.J. Kennedy ; J.J. Vijaya ; K. Kaviyaran and M. Sukumar (2015).** Structural, optical and magnetic characterization of $Zn_{1-x}Ni_xAl_2O_4$ ($0 \leq x \leq 5$) spinel nanostructures synthesized by microwave combustion technique. *Ceramics Int.*, 41(1): 603-615.
- ASTM, (2017):** Standard Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure. Designation: D86 – 17
- Banković-Ilić, I.B. ; O.S. Stamenković, and V.B. Veljković (2012).** Biodiesel production from non-edible plant oils. *Renewable and Sustainable Energy Rev.*, 16(6): 3621-3647.
- Bazina, N. and J. He (2018):** Analysis of fatty acid profiles of free fatty acids generated in deep-frying process. *J. of Food Sci. and Technol.*, 55(8): 3085-3092.
- Bezergianni, S. ; A. Kalogianni and I.A. Vasalos (2009):** Hydrocracking of vacuum gas oil vegetable oil mixtures for biofuels production. *Bioresource Technol.*, 100 (12): 3036-3042.
- Da Silva, A. A. ; A. de Souza Gonçalves and M.R. Davolos (2009).** Characterization of nanosized $ZnAl_2O_4$ spinel synthesized by the sol-gel method. *J. of Sol-Gel Sci. and Technol.*, 49(1): 101-105.
- Ge, D.L. ; Y.J. Fan ; C.L. Qi and Z.X. Sun (2013).** Facile synthesis of highly thermostable mesoporous $ZnAl_2O_4$ with adjustable pore size. *J. of Materials Chem. A*, 1(5): 1651-1658.
- Huber, G.W. ; P. O'Connor and A. Corma (2007):** Processing biomass in conventional oil refineries: production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures. *Appl. Catalysis A: General*, 329: 120-129
- Huber, G.W. and A. Corma (2007):** Synergies between bio- and oil refineries for the production of fuels from biomass. *Angewandte Chemie Int. Edition*, 46: 7184-7201.
- Ianoş, R. ; S. Borcănescu and R. Lazău (2014).** Large surface area $ZnAl_2O_4$ powders prepared by a modified combustion technique. *Chem. Eng. J.*, 240: 260-263.
- Kumar, S. ; M.M. Malik and R. Purohit (2017):** Synthesis Methods of Mesoporous Silica Materials. *Materials Today: Proceedings*, 4(2): 350.

- Oumer, A.N. ; M.M. Hasan ; A.T. Baheta ; R. Mamat and A.A. Abdullah (2018).** Bio-based liquid fuels as a source of renewable energy: A review. *Renewable and Sustainable Energy Rev.*, 88: 82-98.
- Shaban, S.A. (2012).** Biodiesel production from waste cooking oil. *Egyptian J. of Chem.*, 55(5): 437-452.
- Shaban, S.A.(2012):** Biodiesel production from waste cooking oil. *Egypt. J. Chem.*, 55: 437–452.
- Singh, D. ; D. Sharma ; S.L. Soni; S Sharma ; P.K. Sharma and A. Jhalani (2020).** Review on feedstocks, production processes, and yield for different generations of biodiesel. *Fuel*, 262, 116553
- Sivasamy, A. ; K.Y. Cheah ; P. Fornasiero ; F. Kemausuor ; S. Zinoviev and S. Miertus (2009):** Catalytic applications in the production of biodiesel from vegetable oils. *Chem. Sus. Chem.*, 2: 278-300.
- Stedile, T. ; R.F. Beims; L. Ender ; D.R. Scharf ; E.L. Simionatto ; H.F. Meier and V.R. Wiggers (2019).** Evaluation of distillation curves for bio-oil obtained from thermal cracking of waste cooking oil. *Brazilian J. of Chem. Eng.*, 36: 573-585.
- Stedile, T. R. ; F. Beims ; L. Ender ; D. R. Scharf ; E. L. Simionatto ; H. F. Meier and V. R. Wiggers (2019):** Evaluation of distillation curves for bio-oil obtained from thermal cracking of waste cooking oil. *Braz. J. Chem. Eng.*, 36 (1): 573-585.
- Stella, B. and K. Aggeliki (2009):** Hydrocracking of used cooking oil for biofuels production. *Bioresource Technol.*, 100: 3927-3932.
- Stumborg, M. ; A. Wong and E. Hogan (1996):** Hydroprocessed vegetable oils for diesel fuel improvement. *Bioresource Technol.*, 56 (1): 13-18.
- Trisunaryanti, W. ; I.I. Triyono ; A.D. Falah ; Siagian, and M.F. Marsuki (2018):** Synthesis of Ce-mesoporous silica catalyst and its lifetime determination for the hydrocracking of waste lubricant. *Indonesian J. Chem.*, 18(3): 441-447.
- Trisunaryanti, W. ; T. Triyono and D.A. Fatmawati (2020):** Synthesis of Co-NH₂/mesoporous silica bifunctional catalyst using sidoarjo mud and bovine bone gelatin template for conversion of used cooking oil into biofuel. *Rasayan J. of Chem.*, 13: 723-732.
- Yah, N.F. ; A.N. Oumer and M.S. Idris (2017).** Small scale hydro-power as a source of renewable energy in Malaysia: A review. *Renewable and Sustainable Energy Rev.*, 72: 228-239.

انتاج وقود الديزل الحيوي عن طريق التكسير الحرارى الحفاز لزيوت الطعام المستعمل باستخدام $Co/Zn-Al_2O_4$ كعامل حفاز نانومتري.

محمد أبوبكر ابراهيم⁽¹⁾ ، ريهام العرابي⁽²⁾ ، الهام عبد القادر⁽²⁾ ، أشرف عبد السلام⁽³⁾
، ايمان اسماعيل⁽⁴⁾

1 - ادارة وصيانة المشروعات المصرية - الشركة المصرية للتكرير ، القاهرة ، 13753 ، مصر

2- قسم الهندسة الكيميائية ، المركز القومي للبحوث ، القاهرة ، 12622 ، مصر

3- معهد بحوث البترول ، غمرة ، القاهرة ، 11674 ، مصر

3- قسم الكيمياء - كلية العلوم - جامعة عين شمس ، القاهرة ، 11566 ، مصر.

حظي تطوير موارد الوقود الحيوي باهتمام كبير بسبب القلق البيئي العالمي و بسبب عوادم الوقود واستنفاد موارد الوقود الأحفوري. التكسير الهيدروجيني لنفايات زيوت الطهي للحصول على الوقود الحيوي هو احد الطرق الواعدة. استهدفت هذه الدراسة تحضير $Co / Zn-Al_2O_4$ كعامل حفاز نانومتري ثم استخدامه كعامل مساعد في تصنيع وقود الديزل الحيوي عن طريق التكسير التحفيزي الهيدروجيني لبقايا زيت الطهي (WCO). تم إجراء التكسير الهيدروجيني في وحدة اختبار نشاط محفز عالي الضغط. تم اختبار خواص العامل الحفاز باستخدام الأشعة السينية (XRD) ، و (Brunauer-Emmett-Teller (BET) ، الأشعة تحت الحمراء (FTIR) ، والتحليل المجهر الإلكتروني عالي الدقة (HRTEM). تم تحديد الظروف المثالية التي تؤثر على عملية التكسير مثل درجة الحرارة وضغط الهيدروجين ومعدل التغذية المنتظمة لبقايا زيت الطعام. وقد استخدمت طريقة التقطير التجزيئي لتحديد مدى غليان نواتج التكسير الحفازي. وقد أظهرت نتائج التقطير التجزيئي نشاطاً انتقائياً عالياً للعامل الحفاز للهيدروكربون الحيوي في نطاق النافثا والكيروسين والديزل مقارنةً بالتقطير الجزئي لزيوت الطعام المستعمل. تم عمل مزيج من وقود الديزل الحيوي بنسبة 50% (B50) مع وقود الديزل الأحفوري وتم اختبار خواص الوقود الناتج وفقاً للطرق القياسية ASTM المختلفة.