

CATALYTIC CRACKING OF USED COOKING OIL (UCO) INTO BIOFUEL USING ZINC OXIDE, ALUMINUM OXIDE AND ZIRCONIUM OXIDE CATALYSTS

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ABSTRACT

Energy problems and environmental destruction are the main issues facing today's world. The use of green energy is the perfect option for all of these issues. Edible and non-edible oils are green energy options that can be used for the production various hydrocarbons and chemical. In this research, the conversion of the used edible oil over a metal oxide catalyst into various liquid hydrocarbon compositions was analyzed and compared. In a batch reactor, reaction parameters such as metal oxides like (ZnO, Al₂O₃ and ZrO₂), catalyst quantity, temperature, residence time, heating intensity, and stirring intensity were studied. Under a controlled temperature regime, each conversion analysis was conducted. The powdered samples of the catalysts ZnO, Al₂O₃ and ZrO₂ were analyzed using XRD, EDX, and Nitrogen Adsorption Isotherms characterization techniques. Liquid hydrocarbons were studied using GC-MS. Various physical and chemical properties of liquid hydrocarbons have been tested to verify the caloric content, stiffness, flash point and kinematic viscosity of liquid hydrocarbons.

Using different percent of ZnO catalyst, catalytic cracking of used cooking oil was carried out in the batch reactor at 400 °C to 500°C. Catalytic cracking was carried out at 330°C to 430°C for Al₂O₃ and catalytic cracking was carried out at 400°C to 500°C for ZrO₂. It was funded that 81% of conversion occurs at 450°C, for 60 mints at a heating rate of 10°C/min and 4wt% of ZnO loading. 71% conversion was observed at 390°C with 8wt% of Al₂O₃ catalyst for 60 mints at a heating rate of 5°C per mint. For ZrO₂, 81% conversion Occur at 475°C using 4wt% of the ZrO₂ catalyst for 60 mints at a heating rate of 10°C per mint.

Keywords: Used cooking oil, Aluminum Oxide, Zinc Oxide, Zirconium Oxide, Catalytic creaking Bio fuel.

INTRODUCTION

Fuels are combustible hydrocarbons of varying compositions that are used mostly in the transport industry. As a whole, the mass of transportation industries is constantly growing, particularly in our region, and there

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is currently an excessive import of various liquid petro-fuels. The expense of these fuels is also rising and has a negative effect on the economy. Fuel burning, on the other hand, also emits carbon dioxide and nitrogen oxide emissions, the key explanation for global warming and climate change [1, 2]. The number of vehicles worldwide has risen considerably, consuming approximately 61 percent of the total fuel produced [3].

The world's energy demands are largely met by nonrenewable sources of energy, such as coal, oil and gas. Many non-renewable resources will be consumed in the next 50 years if production continues at the current pace and the usage of these resources will also have an effect on the atmosphere, such as pollution emissions from diesel-powered vehicles. So, the planet needs to turn to sustainable and environmentally friendly energy options.

The literature shows that bio-fuels can effectively be used in combustion engines. In contrast with petro-fuels, bio-fuels do less harm to the ecosystem. Several vegetable oils, such as soybean, palm, sunflower, rapeseed, peanut oils and recycled cooking oils, can be used to produce liquid hydrocarbons. These fuels are biodegradable, non-toxic, carbon neutral and organic [4-6].

Using cooking oil is a cheap source of hydrocarbon that can be converted into useful chemicals and fuels. However, used oil obtained from restaurants, fast food shops and other stews is still being stored or disposed of in water streams that have significant health and environmental consequences [7, 8]. A large quantity of cooking oil used is used in chemical industries for chemicals production [7-12].

In the present analysis, we will compare the catalytic activity

of many metal oxide catalysts to transform used cooking oils into various organic chemicals and fuels.

Material and Method

Used cooking oil

In my experimental work, waste cooking oil is used in the production of biofuel and other valuable chemicals in batch reactors. Used cooking oil is obtained from a variety of hotels, restaurants, fast food shops and other fried food shops. The fatty acid composition of WCO was myristic acid (C14:0): 0.5 per cent, palmitic acid (C16:0): 20.4 per cent, stearic acid (C18:0): 4.8 per cent, oleic acid (C18:1): 52.9 per cent, linoleic acid (C18:2): 13.5 per cent, linolenic acid (C18:3): 0.8 per cent and eicosanoic acid (C20:0): 0.3 per cent [12]. Various methods have been used to convert UCO into biofuel, such as fermentation, emulsification, transesterification, ultrasound-assisted catalysis, pyrolysis and catalytic cracking, etc.

Catalytic cracking of used cooking oil

The catalytic cracking technique was used in my laboratory work to transform UCO into bio fuels and high-grade chemicals. The distillation setup was used in my experimental work to convert used cooking oil into high-grade fuels and chemicals. Distillation set up consist of 250 ml two neck flat round bottom flask used as batch reactor, condenser and two neck 200 ml flat round bottom flask used for product storage . Before experimental work clean all the equipment and at take weight from all round bottom flasks. For each experimental test, 30 g of the cooking oil used was used. Reaction was carried out in the batch reactor using 2wt%, 4wt%, 8wt%, 10wt% and 12wt% of the ZnO catalyst. The mixing of oil and catalyst was achieved by a magnetic stirrer. During experimental work heaters were heated to achieve final temperatures of 400°C, 425°C, 450°C, 475°C and 500°C at heating rates of 10°C and 20°C/mint, and an isothermal condition was maintain for 60 mint. Vapors were produced and then condense in condenser. Condense liquid was collect in product collectors shown in figure (1). Fore Al₂O₃ catalyst The same 30 g of cooking oil used was used and 4 wt%, 8 wt%, 10 wt% and 12 wt% of Al₂O₃ catalyst was used. The experiment was conducted at 330°C, 370°C, 390°C, 410°C, 430°C and 450°C at heating rate of 5°C and 10°C/mint. Fore ZrO₂ used 2wt%, 4wt%, 8wt%, 10wt% and 12wt% of the Al₂O₃ catalyst. The experiment was carried out at 400°C, 425°C, 450°C, 475°C and 500°C at a heating average of 10°C and 20°C/mint.. Yield of bio fuel produce calculated using equation no:

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Yield of bio fuel produce calculated using equation no: 1

$$\text{Yield of bio fuel produced} = \frac{\text{Yield of bio fuel produced}}{\text{Mass of the UCO}}$$

Equation: 1

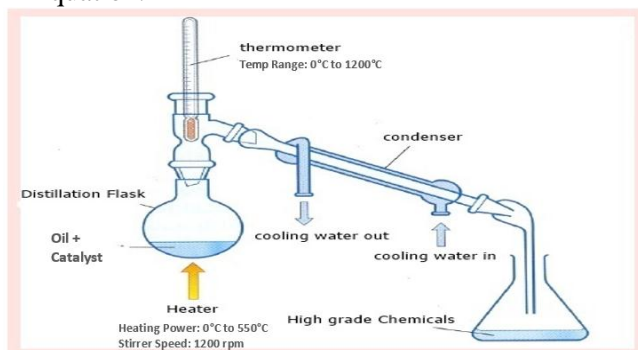
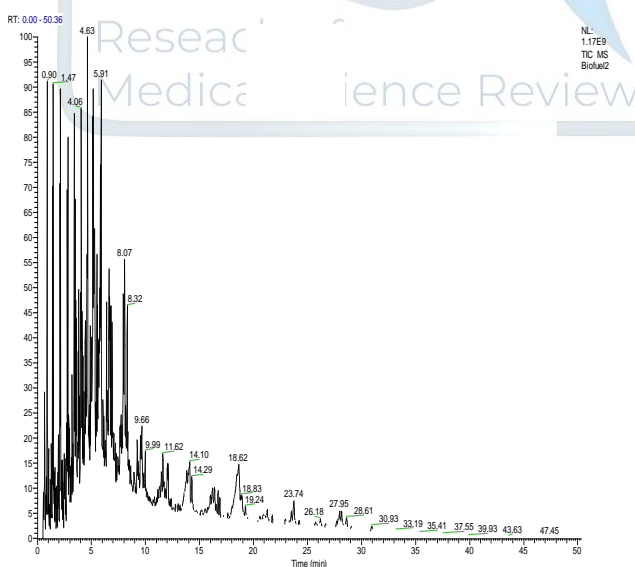


Figure 1: Schematic diagram of experimental setup.

Characterization

The reaction product species were examined in the gas chromatograph (GC) and the mass spectrometer (MS). Thermo Scientific (GC-MS), Thermo Scientific GC Focus Series and Thermo Scientific MS DSQ II, with built-in software version: 2.0.7, is used for the study of organic organisms. The oven consists of a TR-MS capillary column with an internal diameter of 0.25 μ m, a film thickness of 0.25 μ m, a size of 30 m \times 0.2 m and a length of 30 m. Helium (He) has been used as a carrier gas. In the presence of helium flow, the temperature of the oven was raised to the sample injection temperature (250 $^{\circ}$ C) by two separate ramp frequencies. Next, the oven temperature was raised from 50 $^{\circ}$ C to 150 $^{\circ}$ C at a heating rate of 25 $^{\circ}$ C/min. The



keeping time at 150 $^{\circ}$ C was around one minute. The ramp rate of 10 $^{\circ}$ C/min was sustained from 150 $^{\circ}$ C to 250 $^{\circ}$ C. Both oil samples were administered at 250 $^{\circ}$ C and 1 air pressure.

Figure (2) show GC-MS analysis of bio fuel produced using ZnO catalyst

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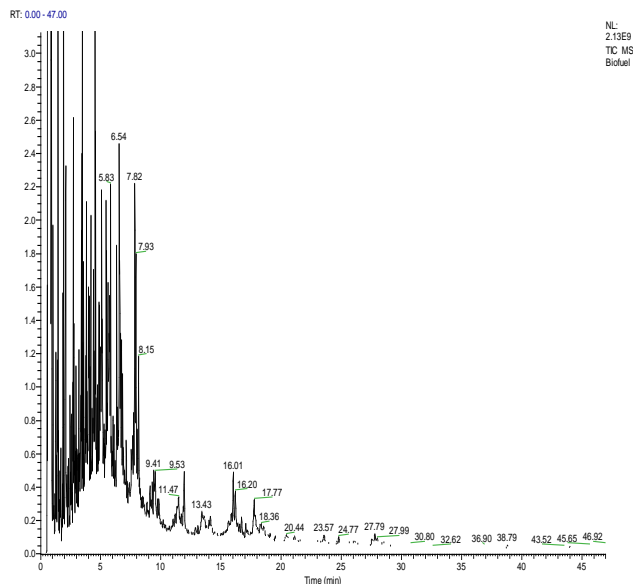
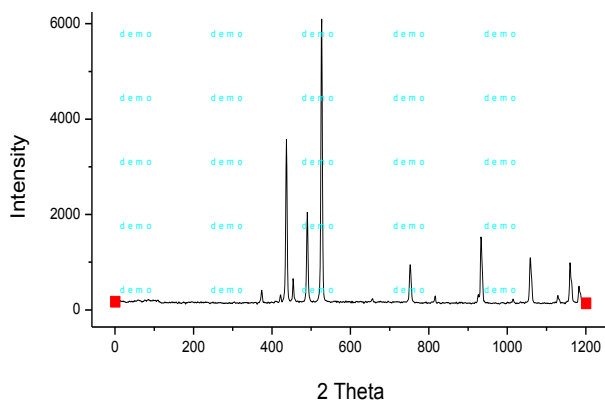


Figure (3) show GC-MS analysis of bio fuel produced using Al_2O_3 catalyst

X-Ray Diffraction, Model: JEOL (Japan) Voltage: 20-40kv, Current: 2.5-30mA, X-ray Wavelength= 1,5418Å (CuK α) 2 The range: 0 ° to 160 ° and ZnO and Al_2O_3 is used in powder form for crystal analysis seen in Figure 3.10 and Figure 3.11. During the XRD study, the analysis was conducted at room temperature, and Cupper Cu(K5-007) was used as a 20-to 55-degree radiation source for 2 θ . The Crystal Catalyst Composition of ZnO and Al_2O_3 was calculated by the X-Ray Diffraction Analyzer technique. During XRD analysis, crystal structure, chemical composition and various peaks with different intensities were studied. It is used to verify the composition of the crystal, phase recognition, atomic spacing, crystal size and crystal defects, etc. Bragg's equation is used where the gap between the crystal planes is the same, as Bragg's equation is applied as the X-ray beam strikes with equally spaced crystals, he detects the propagation of the rays with varying intensities.. After XRD analysis both catalyst have same crystalline phase along with different peaks



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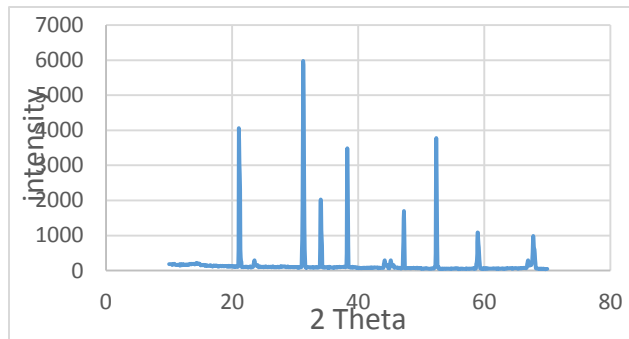


Figure (5) Show XRD graph of Al_2O_3

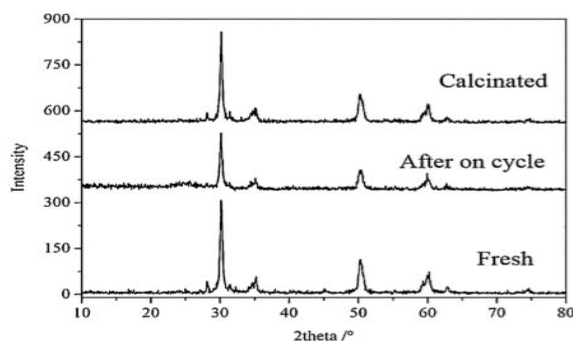


Figure (6) Show XRD graph of ZrO_2

Energy dispersive spectroscopy (EDX) Instrument JEM2100 INCA100 / Oxford, U.K. was used to analyze ZnO , Al_2O_3 and ZrO_2

Table.1

Table.1 show Energy Dispersive Spectroscopy (EDX) of ZnO

S.No	Analyte	Result	Int.(cps/uA)
1	ZnO	99.819	12920.7
2	CuO	0.079	12.22
3	Nd_2O_3	0.063	1.76
4	Cr_2O_3	0.029	2.1
5	Mno	0.01	1.1

Table.2

Table.2 show Energy Dispersive Spectroscopy (EDX) of Al_2O_3

S.No	Analyte	Result	Int.(cps/uA)
1	Al_2O_3	91.56	7.644
2	SO_3	7.7	11.46
3	TiO_2	0.392	11.05
4	CaO	0.136	1.89
5	Fe_2O_3	0.6	7.83
6	K_2O	0.57	0.49

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Table.3

Table.3 show Energy Dispersive Spectroscopy (EDX) of ZrO₂

S. No	Analyte	Result
1	ZrO ₂	99.819
2	Zn	0.059
3	Mn	0.053
4	Mo	0.020
5	Ti	0.03

Table.4

Table.4 show physicochemical properties of WCO and OLP.

S.No	Physicochemical properties	WCO	Bio Fuel (ZnO)	Bio Fuel (Al ₂ O ₃)	Bio Fuel (ZrO ₂)
1	Density (g/cm ³) @25 °C	0.94	87	84	86
2	Calorific value (MJ/Kg)	38	41.5	40.7	40.8
3	Kinematic viscosity (mm ² /s) @25 °C	42.55	3.88	3.25	1.9
4	Flash point (°C)	298.5	96	94	105

Results and discussion

Effect of reaction parameters on catalytic cracking of UCO

Effect of temperature

Temperature has a greater impact on the production of biofuel from UCO. Catalytic cracking Experimental works were carried out at 400°C, 425°C, 450°C, 475°C and 500°C for ZnO catalysts. During experimental work, conversion of UCO into biofuel start at 400°C and the maximum conversion obtained at 450°C are shown in Figure 7. The catalytic cracking of UCO into bio fuel using Al₂O₃ was carried out at 330°C, 350°C, 370°C, 390°C, 410°C and 430°C. UCO conversion to biofuel start at 330C and high conversion occur at 390°C shown in Figure 7. Similarly for ZrO₂ Biofuel conversion start at 400°C and maximum conversion occur at 475°C is shown in Figure 7. For Overall, further temperature changes result in secondary cracking that create uncondensed gases.

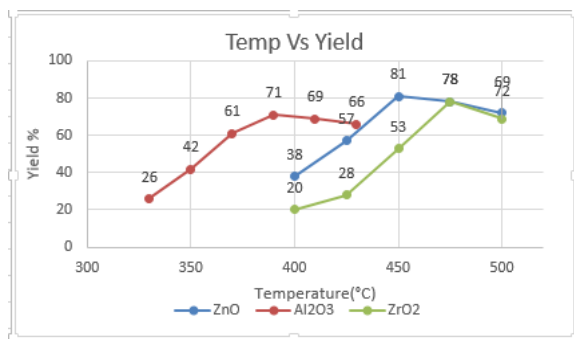


Figure (7) Show effect of temperature on bio fuel production

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Effect of catalyst loading

Effect of catalyst loading has greater effect on production of bio fuel. Selection of catalyst, surface area, pores volume, and active side of catalyst has greater effect on efficiencies of catalyst. During experimental work 30g of UCO along with 2wt%, 4wt%, 6wt%, 8wt%, and 12wt% of ZnO catalyst was loaded. It was found that at 4wt% of catalyst high conversion occur at 450°C. For Al₂O₃, 2 wt%, 4 wt%, 6 wt%, 8 wt% and 12wt% of Al₂O₃ catalyst was loaded to 30g of UCO. It was found that at 8wt% of catalyst high conversion occur at 390°C. Similarly 2wt%, 3wt%, 4wt%, 5wt%, 6wt%, 7wt%, 8wt%, and 9wt% of ZrO₂ catalyst was loaded to 30 g of UCO. It was found that maximum conversion was obtained at 4wt% when temperature was 475°C shown in figure 9. For ZnO, Al₂O₃ and ZrO₂ catalysts when we increasing catalyst loading conversion decreases because it result in segregation of catalyst which reduce active sides of catalyst.

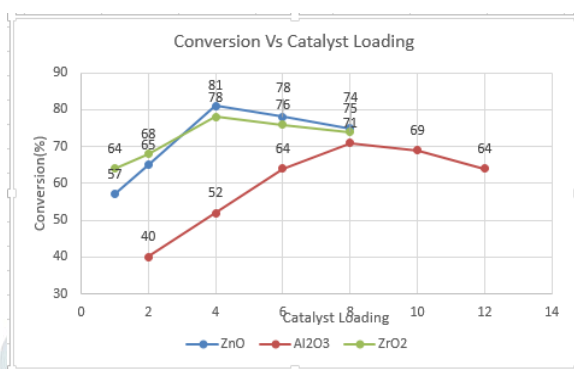


Figure (8) Show Effect of catalyst loading on bio fuel production

Effect Of heating rate

Heating rate has a greater effect on production of bio fuels. With increasing heating rate production decreases. Heating rate at 10°C/min produced more yield of bio fuel as compared to heating rate of 20°C/min when loading ZnO catalyst, heating rate at 5°C/min produced more yield of bio fuel as compared to heating rate of 10°C/min when using Al₂O₃ Catalyst and for ZrO₂ high conversion was obtain at 10°C/min as compared to 20°C/min as show in finger 10, 11 and 12 respectively. According to Nazzal in 2002 he was found that at high heating rate produced less yield as compared to low heating rate because of production high yield of gases at high temperature [13, 14]

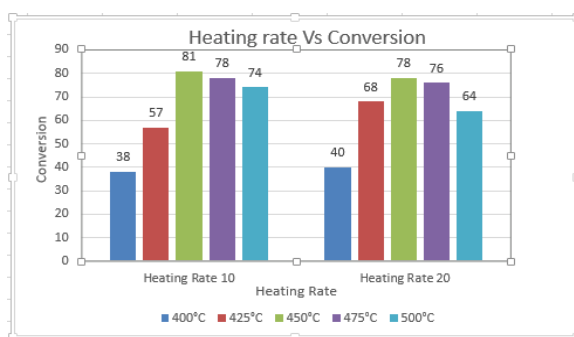


Figure (9) Show effect of heating rate on production of bio fuel at 4wt% of ZnO catalyst

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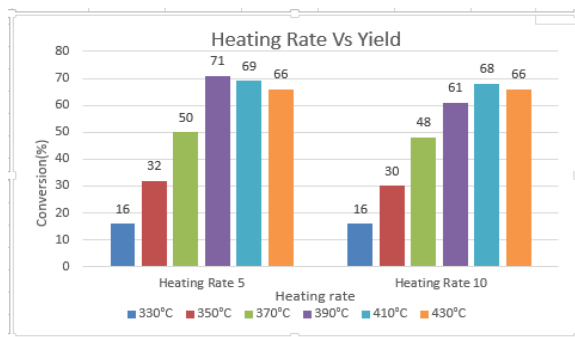


Figure (10) Show effect of heating rate on production of bio fuel at 8wt% of Al₂O₃ catalyst

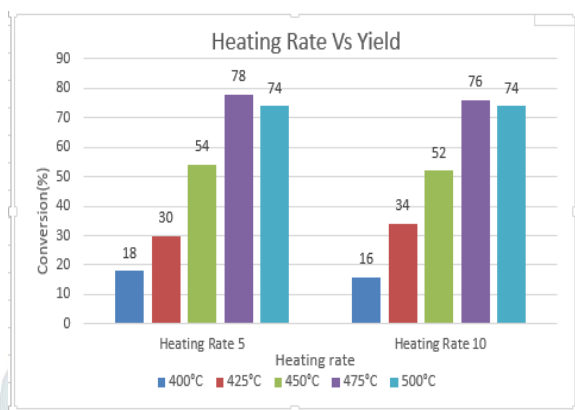


Figure (11) Show effect of heating rate on production of bio fuel at 4wt% of ZrO₂ catalyst

Conclusion

Catalytic cracking of used cooking oil using metal oxides of ZnO, Al₂O₃ and ZrO₂ was described in the report. At the appropriate reaction temperature parameter of 450°C, resident time 60mint, catalyst loading 4wt% and heating rate 10°C/min, the maximum conversion observed was 81% using ZnO as catalyst. Maximum conversion observed at low temperature 390°C was 71% using Al₂O₃ as catalyst at resident time 60min, catalyst loading 8wt% and heating rate 5°C/mint. For ZrO₂ maximum conversion was 71% at 475°C temperature, resident time of 60mint, catalyst loading 4wt percent and heating rate of 10°C/mint. Bio fuel obtained from used cooking oil using Al₂O₃ is more lighter and high octane number as compared bio fuel obtained using ZnO, ZrO₂ Catalysts. The results indicate that these metal oxides are used as catalysts for bio fuel production, but the Al₂O₃ is the most effective and economical catalyst as compared to ZnO and ZrO₂ catalysts. Since Al₂O₃ provides more conversion at low temperatures compared to ZnO and ZrO₂. Cooking oil used during catalytic cracking is converted into light compounds such as hydrocarbons, diesel, kerosene and fuel oil. The catalytic cracking process may lead to lighter hydrocarbons obtained from used cooking oil. Catalytic cracking has decreased the undesired properties of used cooking oil, such as kinematic viscosity, stiffness, flash point, and calorific strength.

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