



Article Info

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Catalytic Conversion of Castor Seed Oil to Diesel Range Hydrocarbons Using NiO –CuO Catalyst Supported On ZSM-5

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Bio-oils are an alternative fuel that can be produced from organic resources such as vegetable oils in which castor seed oil is an example. In this research work castor seed oil was converted to diesel range hydrocarbons using NiO-CuO/ZSM-5 as catalyst. The catalyst was synthesized using wet impregnation method which was characterized using Fourier Transform Infrared (FT-IR) and Energy Dispersive X-ray Fluorescence (EDXRF). The castor seed oil was extracted by using hot water stirring method. The extracted raw oil and catalytically cracked bio-oil were also characterized by FT-IR. The optimum yield of bio-oil 80.70 % was attained at the temperature of 300 °C, reaction time 60 mins and catalyst loading of 2 wt% respectively. The Bio-oil was also characterized using GC-MS to determine the molecular compositions of the raw, thermally and catalytically cracked bio-oil. However, this makes castor seed oil a good feedstock for bio-oil production with little modifications on its properties. This indicates that the products can be used as an alternative fuel in diesel engines.

Keywords: Catalytic; conversion; Castor seed; Oil, Diesel range hydrocarbons.

1. Introduction

The major source of energy that anchored industries, transportation, agriculture as well as domestic purposes such as cooking, heating, is fossil fuels. However, the depletion of fossil fuel reserves and their environmental impact have led to the search for alternative and renewable sources of energy. The burning of large amount of fossil fuel has increased the carbon dioxide (CO₂) level in the atmosphere causing global warming (Mussatto, 2016).

With the increasing consumption of fuels around the world, the supply of non-renewable fossil fuels is diminishing rapidly, thus, high worldwide demand for energy is unstable and uncertain petroleum sources, and concern over global climate change has led to renewable in the development of alternative energy that can displace the conventional transportation fuels. Alternatively, many countries have explored extensive research and development programs in the production of biofuels, sustainable and renewable energy resources that can provide eco-friendly fuels to enhance the transportation

smoothly with clean and greener environment (Faaij, 2006).

Nowadays, attention has been focused on the production of clean biofuels from vegetable oils, due to its versatility; it can be used as either a fuel substitute or additive to fossil fuels to reduce vehicle emissions, which offers solutions for future energy and environmental challenges (Li *et al.*, 2015). Vegetable oils can be converted to biofuels using transesterification, esterification, pyrolysis, gasification and catalytic cracking reactions (Jahirul *et al.*, 2012).

Vegetable oils are suitable substrates for hydrocarbon biofuel production as they are similar to petroleum derivatives, high energy density and a simple chemical composition (Zhao *et al.*, 2017). Vegetable oils can be directly used in diesel engines, but high viscosity and low volatility may cause engine problems (Biswas *et al.*, 2017; Lestari *et al.*, 2009). On the other hand, the appropriate treatment of vegetable oils allows the production of hydrocarbon biofuels that are fully compatible with fossil fuel derivatives. Biodiesel, produced by transesterification of vegetable oils, and green diesel (or renewable

diesel), obtained by the catalytic deoxygenation of vegetable oils, are alternative fuels to mineral diesel due to their favorable eco-friendliness as compared to the conventional fuels generally (Biswas *et al.*, 2017).



Figure: 1: Castor seed plant



Figure: 2: Matured castor seeds

Catalytic cracking, involves adding catalysts along with moderate temperature and pressures, the temperature ranges between 475 to 530°C, pressure 20 (atm) and it is used to obtain biofuel with octane number 65-70 as compared to thermal cracking process (pyrolysis), where it operates usually at very high temperatures and pressure, the temperature ranges between 500-700°C, pressure 70 (atm), used for vis-breaking and delayed coking processes (Madhusa, 2017). It is an effective and simple method to produce bio-oil from vegetable oil, with advantages of low operational cost, flexibility with respect to oil source and compatibility with

available infrastructures (Yigezu *et al.*, 2014; Cheng *et al.*, 2015). Catalytic cracking process of vegetable oil takes place in two stages: Thermochemical decomposition of triglyceride molecules into fatty acids; degradation of fatty acids and the formation of hydrocarbons (Mota *et al.*, 2014; Zhao *et al.*, 2015).

Nickel (Ni) and Copper (Cu) are transition metals referred to as d-block elements in the periodic table. These two transition metals were chosen in this study for zeolite functionalization. Ni was chosen due to its properties similar with other group 10 element such as Pd and Pt (Kordulis *et al.*, 2016). On the other hand, Cu is a transition metal which is commonly used as catalyst in various cracking and treating of petroleum products. Bimetallic catalysts are more active and selective than monometallic catalysts. They present a higher conversion rate and a higher degree of deoxygenation; at the same conversion degree, they have a higher selectivity towards the formation of hydrocarbons (Simacek *et al.*, 2009).

The aim of the research is to study the performance of a series of metal functionalized zeolite in catalytic cracking of Castor Seed Oil (CSO) in order to explore for a more efficient and cheaper catalyst.

2. Materials and Methods

The materials used for this study includes: Routine laboratory apparatus and equipments, vegetable oil from castor seed kernel, copper II trioxonitrate hexahydrate $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Nickel II trioxonitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, steel autoclave reactor, distilled water (H_2O), pH meter, Thermometer, paraffin oil, n-hexane, hot plate, stirrers, and laboratory oven, commercial ZSM-5 zeolite powder was used.

2.1 Sample Collection and Treatment

The matured castor seeds popularly known as 'Zurma' in native Hausa language were obtained from Kasuwar daji market in Sokoto metropolis in December, 2022. The procured seeds sample was stored in polyethene bag under laboratory condition prior to the pretreatment. The sample seeds were de-shelled manually to obtain the seed kernel, which was grinded in order to reduce the particles size and converted into paste using pestle and mortar. The paste was extracted to obtain the oil manually by hot water stirring method.

2.2 Oil Extraction Process

The extraction of castor oil was carried out manually using hot water stirring method. In a typical method of extraction, stainless steel cooking pot containing 10 liters of water was pre-heated at temperature of 50 °C for 45 minutes using fire wood. The paste sample was then added into the pot and heated continuously at 100 °C with constant stirring for 1 hour. The pot was kept open throughout the process until oily surface begins to appear at specified boiling point, which marked the beginning of the oil collection but with some few amount of water to it. After the collection was completed which marked the end of the extraction, the Extracted oil was subjected to further treatment to remove water. The percentage yield of the oil was calculated using equation 1

$$\% \text{ yield} = \frac{\text{weight of oil extracted (g)}}{\text{weight of the sample (g)}} \times 100\% \quad \dots\dots\dots(1)$$

2.3 Determination of Molecular Compositions

GC-MS analysis for the fatty acid methyl ester of the two samples was carried out at Multi-User Science Research Laboratory, Ahmadu Bello University, Zaria on Agilent Technologies GC 7890B, MSD 5977A. The injection volume was 1 µl and the inlet temperature was maintained at 300°C. The oven temperature was programmed initially at 40°C for 2 minutes and then maintained at 300°C at the rate of 8°C per minute and held at the temperature for 7 minutes, the total runs time was 30 minutes. The MS transfer line was maintained at 300°C, the source temperature was 230°C and maintained at maximum temperature of 250°C, the MS Quad at 150°C and maintained at maximum temperature of 200°C. The sample in cubicle was inserted onto GC sample holder and injected by sample injection unit of the machine. The spectrum of the separated compounds was compared with the database of the spectrum of known compounds saved in the NIST02 Reference Spectral Library (Ahmed, 2023).

2.4 Preparation of NiO-CuO Supported on ZSM-5 Catalyst

The catalyst was prepared by wet impregnation method, the metals was loaded at 2.5 wt % on ZSM-5 zeolite. 45 wt % of zeolite support was measured and transferred into the beaker, followed by metal precursor loading (2.5 wt %), 14.865 g of Ni (NO₃)₂.6H₂O was dissolved in

10cm³ distilled water. Then, the mixture was thoroughly stirred, the mixture was then oven dried at 120°C for 16 hours. The dried material was then calcined using muffle furnace at 550 °C for 2 hours to produce fine metal oxide on ZSM-5. The formed catalyst is termed NiO/ZSM-5. The procedure was repeated by replacing nickel precursor with 13.956g of Cu (NO₃)₂.6H₂O as copper precursor at metal loading of (2.5 wt %) to obtain CuO/ZSM-5 catalyst. The catalyst prepared after calcination, was in oxide form (Mohamed and Ching, 2018).

2.5 Catalyst Characterization

(a). FT-IR Analysis

The FT-IR spectroscopic analysis of Nickel and Copper oxide on ZSM-5 (NiO-CuO/ZSM-5) was carried out at Centre for Advance Science Laboratory Complex (CasLac), Usmanu Danfodiyo University, Sokoto using Agilent technologies FT-IR spectrometer. The spectrum was acquired in the range of 4000-650 cm⁻¹ at a resolution of 4 cm⁻¹. A drop of the sample was placed on a thin film positioned in the standard sample compartment of the FT-IR and the spectral data was obtained (Sokoto *et al.*, 2022).

(b). EDXRF Analysis

The EDXRF spectroscopic analysis of Nickel and Copper oxides on ZSM-5 (NiO-CuO/ZSM-5) was conducted at Umaru Musa Yar'adua University, Katsina to ascertain the elemental composition of the metals doped on the modified ZSM-5 zeolite support. The principle involved direct excitation of the atoms in a specimen which are excited by primary photons from external sources, such as X-ray tube, radioactive source, and synchrotron beam, to produce primary fluorescence.

2.6 Catalytic Cracking Process

The cracking process was carried out by using stainless steel autoclave reactor system, exactly 10g each of the castor and waste cooking oils were placed separately into Teflon tube of the reactor. Exactly 1 wt%, 2 wt% and 3 wt% of the catalyst was weighed separately also and placed in the Teflon, the reaction temperature was set at 300°C for 1 hour, to crack the oils. After the reaction is complete, the reactor was quenched in cold water. The liquid product was collected with the use of organic solvent called n-hexane after thoroughly washing of the Teflon; the mixture was then centrifuged for 5 mins, Rpm 4500 at 30 °C and acceleration 9. The mixture was heated at 75 °C to evaporate the solvent out

of the cracked bio-oil before taken for subsequent analysis (Changzhu *et al.*, 2018).

3. Results and Discussion

3.1 Results

3.1.1 FT-IR Characterization of the Neat ZSM-5 and Synthesized Catalyst

Analysis of functional groups of the neat ZSM-5 and the doped zeolite obtained by wet impregnation method and calcination was performed using FT-IR. The differences in the functional groups before and after doping of metals were observed. The absorption bands and possible functional groups observed were presented in Table 1 and 2.

Table 1: Absorption bands of neat ZSM-5 zeolite

Absorption bands (cm ⁻¹)	Bond type (Functional group)
3605	Al-OH-Si
3438	O-H
1625	H-OH
1233	Si-O-Si
1058	AlO ₄
793	SiO ₄
682	Five membered ring

Table 2: Absorption bands of the synthesized catalyst

Absorption band (cm ⁻¹)	Bond type (Functional group)
1051	AlO ₄
1625	H-OH
801	SiO ₄
689	Five membered ring

3.1.2 Energy Dispersive X-ray Fluorescence of the Synthesized Catalyst

Table 3 shows the result of elemental composition, relative concentrations and peak areas of the bimetallic catalysts of NiO-CuO/ZSM-5 in which number of counts against Kev of each metal oxide and the support is presented above. The bulk elemental composition for transition metal oxide (TMO)-doped with ZSM-5 catalyst was studied.

Table 3: EDXRF Analysis of the Synthesized catalyst

Elemental composition	Relative concentration (%)	Peaks (cps/mA)
NiO	6.239	30214
CuO	9.365	55518
Al ₂ O ₃	7.862	124
SiO ₂	58.564	5001
MgO	1.9	2

3.1.3 FT-IR Characterization of Raw and Catalytically Cracked Castor Seed Oil

The summary of absorption bands and possible functional groups of both raw and catalytically cracked castor seed oils were presented in Table 4 and 5:

Table 4: Absorption bands of raw Castor seed oil

Absorption bands (cm ⁻¹)	Bond type (Functional group)
3625	O-H - Stretching vibration
2922-2851	-CH ₂ - Asymmetric vibration
1738-1735	C=O - Stretching vibration
725-721	=CH ₂ - Disubstituted olefins

Table 5: Absorption bands of Catalytically cracked Castor seed oil and functional groups

Absorption bands (cm ⁻¹)	Bond type (Functional group)
3424	O-H - Stretching vibration
3007	=C-H -Stretching vibration of cis double bond of unsaturation
2918-2851	-CH ₂ - Stretching vibration
1738-1735	C=O - Stretching vibration
1455	CH ₂ - Aliphatic reveals C=C double bond
725-721	=CH ₂ - Disubstituted olefins

3.1.4 Molecular Compositions of Raw and Thermally Cracked Castor Seed Oil

The raw castor seed oil has total peak percentage area of 100 % fatty acids methyl esters compositions were presented in Table 6: While that of the thermally cracked castor seed oil molecular compositions is presented in Table 7.

Table 6: Molecular compositions of raw castor seed oil

Name of Compounds	Molecular Formula	% Peak Area
12-hydroxy, 9-Octadecenoic acid	C ₁₈ H ₃₄ O ₃	9.99
9, 12-Octadecadienoic acid	C ₁₈ H ₃₂ O ₂	8.33
Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	1.85
9-Octadecenoic acid	C ₁₈ H ₃₄ O ₂	2.23
9-Oxabicyclo nonane	[6.1.0] C ₈ H ₁₄ O	3.27
-	Others	-
	74.33	25.67
Total % peak area	100%	

Table 7: Molecular compositions of thermally cracked castor seed oil

Name of Compounds	Molecular Formula	% Area	Peak
9- Octadecene	C ₁₈ H ₃₆	0.19	
(E-Z)-1, 3, 12- Nonadecatriene	C ₁₉ H ₃₄	0.89	
Cyclohexane	C ₆ H ₁₂	1.84	
Cycloheptane	C ₇ H ₁₄	1.50	
Cyclopentane	C ₅ H ₁₀	0.97	
Cyclotetradecane	C ₁₄ H ₂₈	1.16	
Dodecane	C ₁₂ H ₂₆	2.16	
5-Eicosene	C ₂₀ H ₄₀	0.94	
1-decene	C ₁₀ H ₂₀	0.77	
-	Others	-	
	89.58	10.42	
Total % peak area	100%		

3.1.5 Molecular Compositions of Catalytically Cracked Castor Seed Oil

Table 8 shows molecular compositions of catalytic cracking bio-oil to diesel range hydrocarbons using the synthesized bimetallic catalyst of NiO-CuO/ZSM-5.

Table 8: Molecular compositions of catalytically cracked castor seed oil

Name of Compounds	Molecular Formula	% Area	Peak
10 Heneicosene	C ₂₁ H ₄₂	0.97%	
18-eicosapentaene	C ₂₀ H ₃₂	1.46%	
(Z,E)- 2, 13- Octadecadien-1-ol	C ₁₈ H ₃₄ O	29.93%	
9-Octadecenal	C ₁₈ H ₃₄ O	19.73%	
10-decenol	C ₁₀ H ₂₂ O	0.64%	
12-chlorobicyclo [8 . 2 . 0] dodecan-11-one	C ₁₂ H ₁₉ ClO	0.27%	
-	Others	-	
	47%	53%	
Total % peak area	100%		

3.2 Discussion

3.2.1 FT-IR Characterization of the Neat ZSM-5 and Synthesized Catalyst

The FT-IR spectra of parent ZSM-5 zeolite shows in the range of 400-4000 cm⁻¹, the peaks at 682 cm⁻¹, could be assigned to double five membered ring tetrahedral vibrations, and typically for the crystalline ZSM-5 zeolite, the peak at 793 cm⁻¹ and 1058 cm⁻¹, are assigned to the internal vibrations of SiO₄ and AlO₄ tetrahedra and the small band near 1233 cm⁻¹, is attributed to their asymmetric stretching vibrations of Si-O-Si. The band at 1625 cm⁻¹ is the H-OH bending vibrations of the adsorbed water molecules during the preparation of the catalyst which is in good match with the observation found by Ramli *et al.*, (2010). The band at 3438 cm⁻¹ corresponds to hydroxyl groups of solid catalyst, while the

band at 3605 cm⁻¹, corresponds to characteristics of protonated form of zeolite and its intensity correlated with framework of aluminium (FAI) as observed by Isak *et al.*, (2015). However, after doping of the metals on the parent zeolite, the synthesized catalyst shows no absorption band 3605 cm⁻¹, which indicates the absence of acidic hydroxyl group (Al-OH-Si) which has been replaced by NiO/CuO-Si i.e the protonated form of zeolite was lost as a result of calcination, the band at 1051 cm⁻¹, becomes a little bit narrow which corresponds to reduction of intensity and internal vibrations of SiO₄ and AlO₄ tetrahedra, 801 cm⁻¹ and 689 cm⁻¹ tends to increase in the band areas. 1625 cm⁻¹ was observed for all the catalyst, which is similar to the observation found by Ramli *et al.*, (2010). The result obtained was also in good agreement with the findings of Zhao *et al.*, (2015). Doping of NiO and CuO on ZSM-5, had no significant influence on the framework of the parent ZSM-5 as observed by Zakari *et al.*, (2012).

3.2.2 Energy Dispersive X-ray Fluorescence of the Synthesized Catalyst

The result showed that the presence of Cu at 9.365 atomic %, Ni at 6.239%, support SiO₂ at 58.564%, Al₂O₃ at 7.862% and MgO 1.9%, Silicon (iv) oxide was found as the major composition (58.564 atomic %) and Aluminium oxide (7.862 atomic %) which constitute more than 65% of the catalyst. Thus the (TMO) constitute more than 15%. Thus the experimental ratio (TMO: ZSM-5) of synthesized catalyst is (15% of active metal oxide and 66% support) were in agreement with the intended ratio of 1.5: 6.6 atomic ratio. The rest elements were found to be insignificant as shown by Asikin-mijan *et al.*, (2017).

3.2.3 FT-IR Characterization of Raw and Catalytically Cracked Castor Seed Oil

FT-IR analysis of raw castor seed oil shows the frequency of the main absorption band at peak absorbance of 3625 cm⁻¹, 2922 cm⁻¹ and 2851 cm⁻¹, 1735 cm⁻¹, and 721 cm⁻¹ which can be attributed to O-H stretching vibrations which is clearly the presence of hydroxylated ricinolic acid, asymmetric vibration of aliphatic –CH₂ fatty acid hydrocarbon chain, the ester carbonyl (C=O) stretching band of triglycerides, –CH₂ of disubstituted olefins which is characteristics of long chain fatty acids. The result obtained was in

good agreement with the observation found by Li *et al.*, (2017). However, the catalytically cracked castor seed oil one shows a peak absorption at 3424 cm⁻¹, 3007 cm⁻¹, 2918 and 2851 cm⁻¹, 1738 cm⁻¹, 1455 cm⁻¹, 971 cm⁻¹, and 725 cm⁻¹ which represents the O-H stretching vibrations clearly shows the presence of hydroxylated ricinolic acid (prominent peak of castor seed oil), represent C-H stretching vibrations of cis-double bond of unsaturation, are characteristics of aliphatic -CH₂ fatty acid hydrocarbon chain, ester carbonyl functional group C=O of triglyceride, corresponds to CH₂ aliphatic, reveals the presence of C=C, -CH₂ of disubstituted olefins which is characteristics of long chain fatty acids, as observed by Tarique *et al.*, (2019).

3.2.4 Molecular Compositions of Raw and Thermally cracked Castor Seed Oil

The Analysis of molecular compositions of raw castor seed oil sample reveals the fatty acid methyl esters, was summarized and presented in Table 6. It shows the following fatty acids and other compounds such as 12-hydroxy, 9-Octadecenoic acid, 9, 12-Octadecadienoic acid, Hexadecanoic acid, 9-Octadecenoic acid with peak percentage area of 9.99 % (21.984 RT), 2.23 % (20.318 RT), with peak area of 8.33 % (17.818 RT), 9-Oxabicyclo [6.1.0] nonane, with peak percentage area of 3.27 % (36.533 RT) and others with peak percentage area of 74.33 % respectively. This result is similar to the result found by Foglia *et al.*, (2000). It was also reported by Uzoh and Nwabanne, (2016). While the thermally cracked castor seed oil molecular compositions reveal hydrocarbon compounds after removing the oxygen atom from fatty acid methyl esters via the process called 'Deoxygenation' most of which includes 9-Octadecene with peak area of 0.19% (14.349 RT), (E-Z)-1, 3, 12-Nonadecatriene with peak area of 0.89% (14. 656 RT), Cyclohexane 1.84% (18.077 RT), Cycloheptane 1.50% (20.045 RT), Cyclopentane 0.97% (20.315 RT), Cyclotetradecane 1.16% (21.295 RT), Dodecane 2.16% (36.765 RT), 5-Eicosene 0.94% (23.553 RT), 1-Decene 0.77% (17.726 RT) with percentage peak area of 10.42% and others constitutes a peak percentage area of 89.58% as reported by Snare *et al.*, (2006). Similar observation was reported by Morgan *et al.*, (2010).

3.2.5 Molecular Compositions of Catalytically Cracked Castor Seed Oil

Table 8, shows molecular compositions of catalytic cracking bio-oil to diesel range hydrocarbons using the synthesized bimetallic catalyst of NiO-CuO/ZSM-5, the products obtained are hydrocarbons, alcohols, aldehydes and ketones respectively as reported by Roh *et al.*, (2011). Other organic products detected by the machine could be by-products as reported by Snare *et al.*, (2008). Similar result was also reported by Kubicka and Kaluza, (2010).

4. Conclusion

Castor seed oil was successfully cracked or converted into hydrocarbons bio-oil at optimal yield of 80.70 % at the reaction temperature of 300°C, reaction time of 60 minutes, at catalyst loading of 2 wt%. The choice of this bimetallic catalyst was inexpensive and readily available to ascertain its potential for the catalytic conversion of castor seed oil to bio-oil in order to obtain the target hydrocarbons. NiO/CuO mixture was not found to be a better bimetallic catalyst for vegetable oil conversion. NiO/CuO mixture was not found to be successful bimetallic catalyst in selecting the desired range of hydrocarbons as depicted by molecular characterization but highest percentage yield was recorded.

Conflict of interest

The authors declare no conflict of interest.

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