Fatty acid methyl ester production from waste cooking oil catalyzed by CuO-CeO2/NiO mixed oxides

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Syed Tajammul Hussain,[1,a)] Waqas Ahmed,[1,b)] Maria Saeed,[1,2]
Syed Danish Ali,[1] and Maliha Asma[2]

[1]*Nano Science and Catalysis Division, National Centre for Physics,*
Quaid-i-Azam University, Islamabad 45320, Pakistan
[2]*Department of Environmental Sciences, International Islamic University,*
Islamabad, Pakistan

The diminution of edible oils and increasing cost of edible oils and biodiesel have gained the interest of many researchers for non-edible oils as biodiesel feed stock. The major hurdle in the commercialization of biodiesel is the high cost of feedstock. Due to fast mushrooming of fast food centers, waste cooking oil is one of the most economical feedstock available for the biodiesel production. The high free fatty acid contents and moisture in the waste cooking oil hinders the homogenous transesterification for the commercial purposes. Mixed oxides of Cu with Ni and Ce were synthesized by co-precipitation method and their efficacy for the production of biodiesel from the waste cooking oil was inspected. The acid catalyzed heterogeneous transesterification of waste cooking oil was performed in the sealed container. It was also interesting to mention that no pre-treatment was executed for the waste cooking oil conversion to biodiesel. It was investigated that mixed oxide catalyst CuO-CeO₂ proved to be the potential candidate in pilot scale biodiesel production from waste cooking oil having about 92% conversion rate. Comprehensive chemical analysis of biodiesel including NMR, GC-MS, and FT-IR supports our result. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4794437]

I. INTRODUCTION

The increasing reliance of the world's energy on the fossil fuels; coal, crude oil, and natural gas for the energy stored in their carbon bonds has caused warfare, political and social instability. Rapid inflation in oil prices, uncertainty in the supply of petroleum products, and harmful exhaust emissions from engines have persistent concern over the future energy crisis. To break this energy crisis, the developing countries have created a massive demand for biomass energy such as biofuels to quick-fix petroleum supply problems and strategic tool to pre-empt the emergency.[1] In the course time of 100 years of biodiesel research and manufacture, refining process have developed, new feedstock sources have been tested, and engine technology has been continuously optimized.

At present, the high cost of biodiesel is the major obstacle to its commercialization.[2] Exploring ways to reduce the high cost of biodiesel is of much interest in recent biodiesel research, especially for those methods concentrating on minimizing the raw material cost. According to report, about 78% of the biodiesel production cost corresponds to raw vegetable oil.[3] It has been calculated that in order for a crop to yield enough oil capable of replacing diesel fuel to achieve the objectives for biofuels, a very large percentage of the land needs to be utilized.

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a)Author to whom correspondence should be addressed. Electronic mail: tajammul.hussain@ncp.edu.pk. Tel.: +92 51 2077308. Fax: +92 51 2077395.
b)Present address: Office of Research, Innovation and Commercialization, Hafiz Hayat Campus, University of Gujrat, Gujrat, Pakistan.

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With the mushrooming of fast food centers and restaurants all over the world, large quantity of waste cooking oil (WCO) is available, which is being utilized in animal feeds, soap industry or discarded into the drains.[4] The use of WCO instead of virgin oil to produce biodiesel is an effective way to reduce the raw material cost.[5] Generally, the term "used cooking oils" refers to cooking oil, which has been used in food production and which is no longer viable for its intended use.

In this context, WCO is a promising alternative for producing biodiesel because it is a cheaper raw material that also avoids the cost of waste product disposal and treatment.[6] Besides, it reduces the need to use land for biodiesel-producing crops. WCO are currently collected from large-scale food processing and service facilities. In fact, the quantities of WCO available for biodiesel production in Europe are relatively high. The amount of WCO collected for recycling in the EU is estimated to be approximately $0.7–1.0 \times 10^6$ tonnes per year.[7]

Traditionally, these WCO were used as an additive to animal feed. However, many harmful compounds are produced during the frying of vegetable oils. Most of the toxic compounds in the WCO are oxidation products from fatty acids, especially from polyunsaturated fatty acids.[4] These hydroperoxides, epoxides, and polymeric substances have shown adverse health/biological effects such as growth retardation, increase in liver and kidney size as well as cellular damage to different organs when fed to laboratory animals. An alternative to prevent inappropriate disposal of WCO is by recycling it. The main use of recycled WCO is in the production of animal feeds and in much smaller proportion in the manufacture of soaps and biodegradable lubricants. Hence, utilizing the recycled WCO in any way is not advisable from health standpoint. Besides the ill health effects of these WCO (abused oils), their disposable could also have a large environmental implication.

Waste cooking oil or abused fryer oil is a potential alternative to other feed stocks due to its low price as raw material.[8] Alkaline transesterification is never an exceptional choice for the waste cooking oil biodiesel (WCOB) production due to high sensitivity for free fatty acid (FFA) and water while combination of acid-alkali two step catalytic routes makes the process time consuming and tedious.[9] An effort was made to investigate the nanocatalyst for the conversion of WCO into biodiesel which will definitely help to achieve the target of obtaining economical and affordable biodiesel for the future.

II. MATERIALS AND METHODS

A. Reagents and materials

Cobalt nitrate hexahydrate (Fluka, 98.0%), nickel nitrate hexahydrate (Riedel, 99.99%), cerium sulphate pentahydrate (Merck, 98.5%), copper nitrate (Aldrich, 98%), sulfuric acid (H_2SO_4) and nitric acid (HNO_3) (Fluka, 96%), copper (II) nitrate dihydrate (Aldrich, 99%) were of analytical grade. WCO was collected from a cafeteria at National Center for Physics, Quaid-e-Azam University, Islamabad. Deuterated chloroform used for NMR was of spectroscopic purity and argon gas was of 99.9% pure.

B. Catalyst and methyl esters characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded on Philips X'pert PRO 3040/60 diffractometer with radiation source operated at 40 kV and 30 mA. The diffractograms were recorded in the 2θ range of 10–80. The surface area of each sample was determined by Brunauer Emmett Teller (BET), and pore volume and pore size were determined by Barrett-Joyner-Halenda (BJH).

The fatty acids methyl esters (FAMEs) obtained at the end of transesterification were tested for their physical and fuel properties (density, specific gravity, kinematic viscosity, cloud point, pour point, flash point, acid value), according to the ASTM standard test methods of analysis. FAME composition was determined by gas chromatography using GC-6890 N directly uploaded to MS 5973 MSD 01ul. The MS was set to a range of m/z 02-600 and ionization potential. The WCOB was characterized by FTIR using Excalibur Model FTS3000MX in the range of 4000–400 cm^{-1}. The scan rate was 15 scans and resolution was 8 cm^{-1}. ^1H and

^{13}C NMR was performed using Avan Ce 300 MHz spectrometer equipped with 5 mm BBO probes at 7.05 T. Deuterated chloroform CDCl$_3$ was used as solvent. [1]H (300 MHz) spectra were recorded with scan rate of 8 scans; recycle delay of 1.0 s, with pulse duration of 30°. ^{13}C NMR (75 MHz) spectra were recorded with pulse duration of 30°; recycle delay of 2 s and scan rate of 160 scans.

III. CATALYST SYNTHESIS METHODOLOGY

The CuO-NiO and CuO-CeO were prepared by co-precipitation of the metal hydroxides from their nitrate/sulphate compounds under constant stirring with alkaline sodium hydroxide media. An aqueous one molar solution of sodium hydroxide was added with constant stirring until pH > 10 to ensure complete precipitation. After filtration precipitate was washed and dried at 110 °C. The oven dried precursor was calcined at 450 °C to get desired nanomaterials.

IV. PROCEDURE FOR WCO TRANSESTERIFICATION

Crude waste cooking oil was filtered and dehydrated at 120 °C in the rotary evaporator under vacuum for 30 min. The transesterification was carried out in sealed container equipped with controlled heating system and mechanical stirrer. The mixed oxide nanoparticles of copper-nickel and copper-cerium were used for the production of biodiesel from WCO. Accurately weighed amount of catalyst 1% w/v solution was transferred to the sealed container with 30% methanol. The above reaction assembly was closed after flushing argon gas. Reaction was refluxed for 20 min at 160 °C. Argon gas was passed at 200 psi. The upper layer of biodiesel was washed with warm (50 °C) distilled water in order to remove impurities including unreacted methanol and unreacted oil. The final product, biodiesel (FAME), was dried with anhydrous sodium sulphate to get rid of water.

The practical yield was calculated by using the equation,[10]

$$\text{Biodiesel yield } (\%) = \frac{\text{weight of biodiesel}}{\text{weight of oil used}} \times 100. \tag{1}$$

V. RESULTS AND DISCUSSION

A. Catalyst characterization

The particle size of catalyst has profound effect on the catalytic efficiency of the solid catalyst. The peaks obtained for cerium-copper nanoparticles at $2\theta = 29, 33, 48, 57, 70, 77$ correspond to CeO$_2$ while $2\theta = 39, 62, 66$ correspond to CuO as shown in Figure 1. The peak appeared at $2\theta = 35$ corresponds to the Cu$_4$O$_3$ which appeared as an impurity.

The peaks obtained for copper-nickel nanoparticles at $2\theta = 36, 43, 48, 62, 68, 74, 78$ correspond to NiO while $2\theta = 35, 39$ correspond to CuO as shown in Figure 2.

The particle size calculated by Scherrer's formula by utilizing XRD data of the CuO-CeO and CuO-NiO are 17 nm and 8 nm, respectively. The SEM micrograph of copper cerium nanoparticles is shown in Figure 3 and SEM micrograph of copper nickel nanoparticles is shown in Figure 4.

These nanocatalysts are different from microsized catalyst due to presence of nanocrystalline structures, surface area, pore size and creation of meso and macropores in the presence of inter-crystalline voids as a consequence of aggregation of nanoparticles.[11] The nanocatalyst must be designed keeping in view the diameter of typical glyceride molecule which is of 58 Å. So, the nanocomposites, Cu-Ce composite and Cu-Ni composite, have average surface area of 130 m^2 g^{-1} and 110 m^2 g^{-1}, which can easily accommodate the triglyceride molecules. As the reaction take place on the surface of the catalyst, an increase in the surface area will give maximum opportunity for molecules to interact with catalyst and as a result will increase the reaction rate; hence a catalyst having large surface area show good catalytic activity.[12] Another requirement of catalyst for production of FAME is large pore volume that would minimize
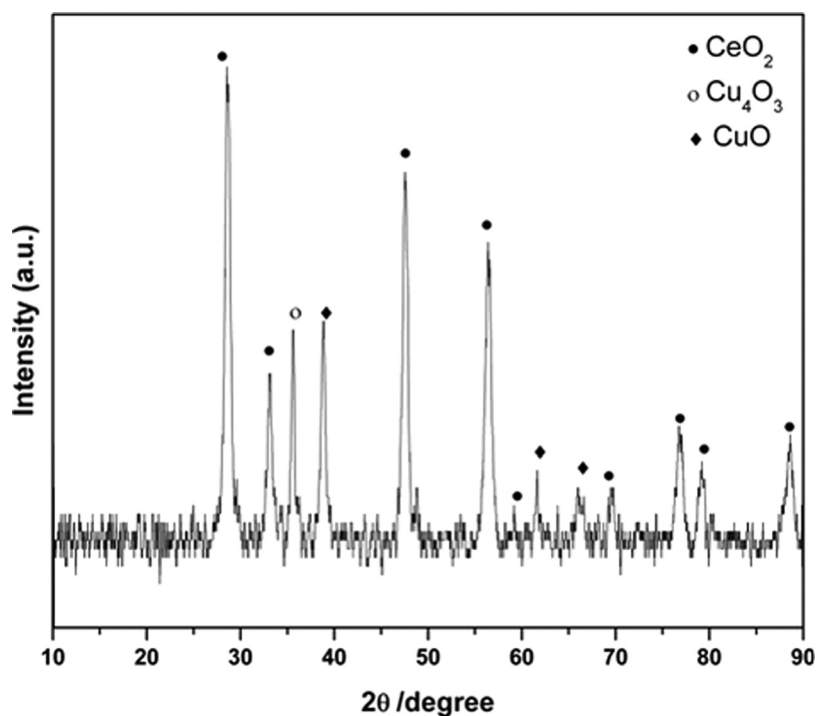
FIG. 1. XRD of cerium copper nanocomposites.

diffusion limitations of molecules having long alkyl chain. The small particle size has a large surface to volume ratio and has large pore volume.[12,13] The prepared Cu-Ce composite and Cu-Ni composite have a pore volume of 0.12 cc/g and 0.07 cc/g, and a pore size of 35.16 Å and 34.97 Å, respectively. Our synthesized nanocatalysts have high surface area, pore volume, and
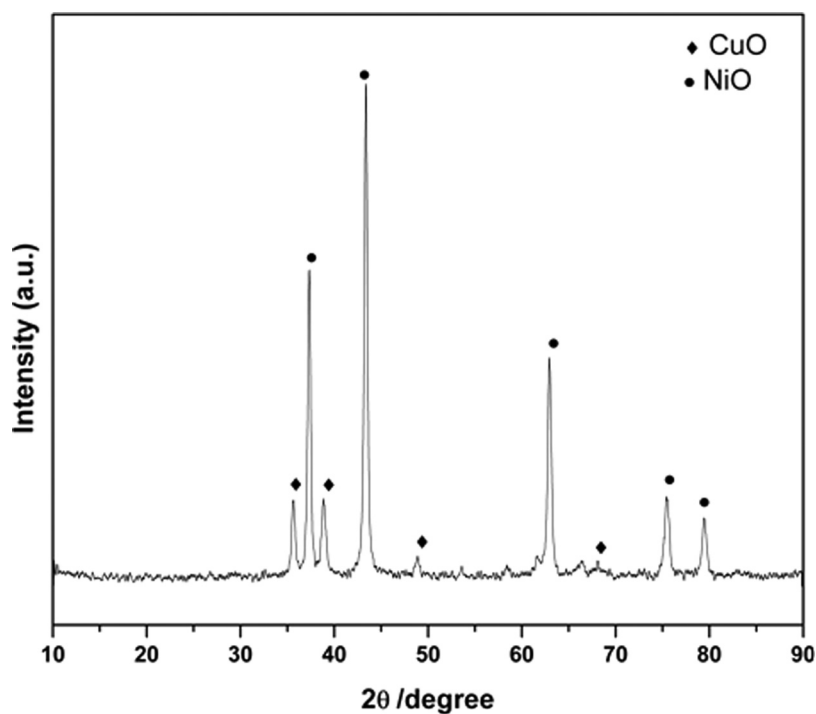

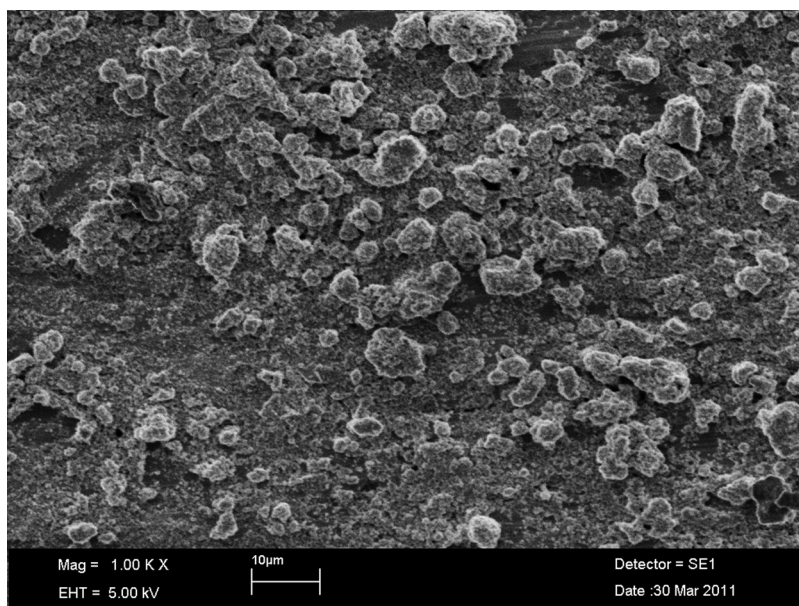FIG. 2. XRD of copper nickel nanocomposites.

FIG. 3. SEM micrograph of copper cerium nanocomposites.

pore size, which is suitable for the conversion of waste cooking oil into fatty acid methyl esters.

B. Fuel properties of biodiesel

The fuel properties of biodiesel synthesized from WCO were measured using the ASTM standard methods. Table I shows the comparison of fuel properties of prepared biodiesel to petrodiesel standards and biodiesel standards. The results show that prepared biodiesel has fuel properties within the standards range and has many advantages over the petrodiesel.

C. FT-IR results

The structure of fatty acids methyl esters (biodiesel) was elucidated by recording IR spectra of their respective peaks, various absorption bands are presented in Table II. The bands at the
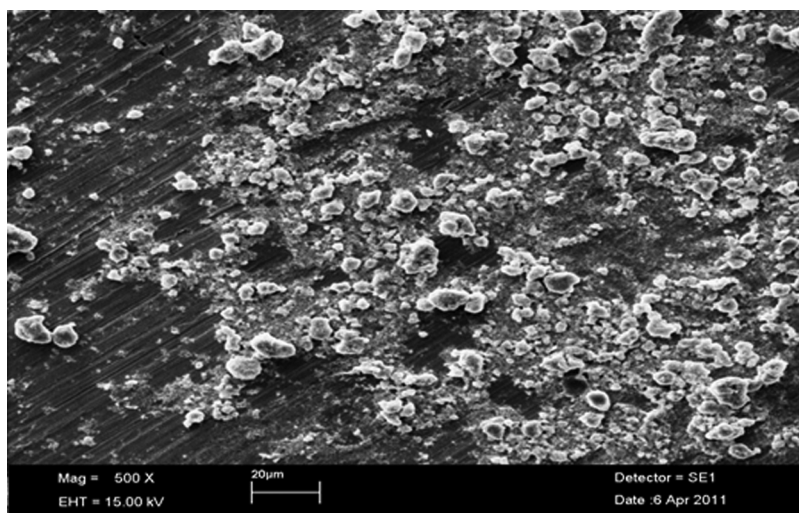

FIG. 4. SEM micrograph of copper nickel nanocomposites.

TABLE I. Comparison of fuel properties of petrodiesel, biodiesel standards, and waste cooking oil biodiesel.

Property	ASTM method	Petrodiesel (D975)	Biodiesel standard (D6751)	Waste cooking oil biodiesel
Flash point ($°C$)	D 93	60–80	100–170	127
Ash contents (wt. %)	D 482	0.01	0.01	0.002
Kinematic viscosity ($40°C$, mm^2/s)	D 445	1.9–4.1	1.9–6.0	3.579
Sulphur contents (wt. %)	D 4294	0.05	0.05	0.007
Cloud point ($°C$)	D 2500	−15 to 5	−3 to 12	9
Pour point ($°C$)	D 97	−35 to −15	−15 to 16	2
Cetane number	D 613	>46	47 min	51.26
Density ($40°C$, g/cm^3)	D 5002	0.834	0.86–0.90	0.859
Acid value (mg KOH/g)	D 664	0.50	0.80 max	0.354

range of 1750–1730 can be associated to C=O, and bands at the range of 1300–1000 can be attributed to C-O (asymmetric axial stretching).[14,15] The bands at the range of 2980–2950 represents the CH_3(s), while closely related bands at 2950–2850 are due to CH_2 (s) and bands at 3050–3000 relates to CH (s). The band set 1475–1350 attributes to CH_3 bending, bands at 1350–1150 ascribed as CH_2 bending and closely related band at 722 confirms CH bending.[16–18] The FT-IR spectra of both WCO and biodiesel were same but the various differences should be observed for identification purposes. The shifting of absorption peaks of the oil is from 1748, 1377, 1157 and 856 to 1742, 1361, 1168, 1015, and 878 in the biodiesel, respectively. The disappearance of the peaks at 1465, 1095, and 964.4 from the spectra and appearance of new bands at 1435 and 1195 confirms the synthesis of biodiesel.

D. NMR studies

1. ^1H NMR studies

^1H and ^{13}C NMR spectroscopy are useful tools for the confirmation of methyl esters and also to calculate the percentage conversion of triglycerides to corresponding FAMEs. The ^1H NMR spectrum of prepared biodiesel from WCO is shown in Figure 5. The characteristic singlet peak of methoxy protons was observed at 3.595 ppm and a doublet of α CH_2 proton at 2.207 ppm. These two peaks are the distinct peaks for the confirmation of methyl esters present in biodiesel. Terminal methyl proton peak at 0.810 ppm and intense signal of methylene protons of long chain of esters at 1.212 ppm were observed. A signal at 1.56 ppm corresponds to β-carbonyl methylene protons and at 5.254 ppm due to olefinic protons.[19,20] To compute the percentage conversion of triglycerides to corresponding methyl esters, the following equation was used:[21,22]

TABLE II. FT-IR data of copper cerium catalyzed and copper nickel catalyzed biodiesel.

Peaks no.	Functional group	Type of vibration	Characteristic absorption range (cm^{-1})	CuO-CeO catalyzed biodiesel (cm^{-1})	CuO-NiO catalyzed biodiesel (cm^{-1})
1	CH_3	Stretching	2980–2950	2934.12	2934.12
2	CH_2	Stretching	2950–2850	2924.14	2924.14
3	CH	Stretching	3050–3000	3028.16	3028.16
4	CH_3	Bending	1475–1350	1459.31	1469.59
5	CH_2	Bending	1350–1150	1161.38	1169.10
6	CH	Bending	720–740	714.48	722.76
7	C=O	Stretching	1750–1730	1740.69	1740.69
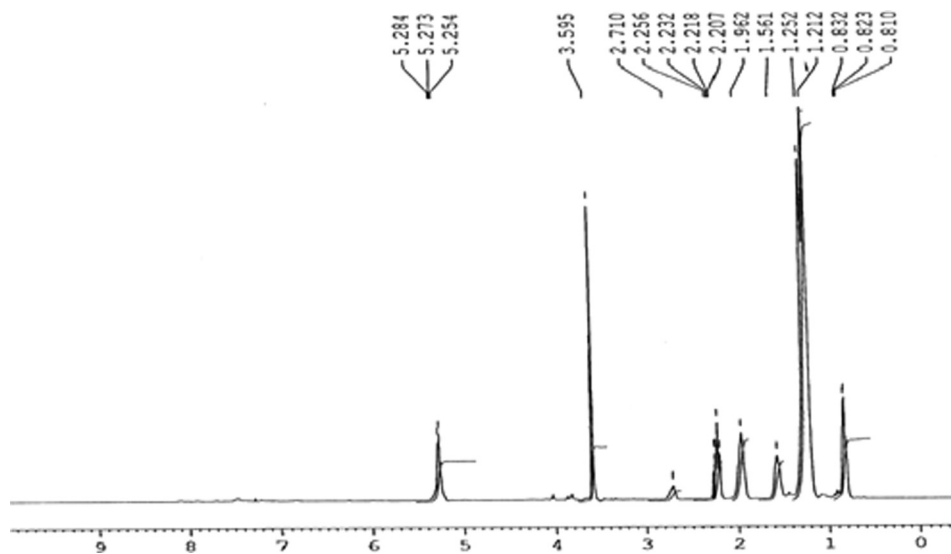
FIG. 5. ^{1}H NMR spectrum of WCOB.

$$C = 100 \times (2A_{Me}/3A_{CH2}), \qquad (2)$$

$$C = 100 \times [2(2.50)/3(1.80)], \qquad (3)$$

where

C = percentage conversion of triglycerides to corresponding methyl esters,
A_{Me} = integration value of the methoxy protons of the methyl esters, and
A_{CH2} = integration value of α-methylene protons.

By using the above equation, the percentage conversion of triglycerides to corresponding esters was found to be 92.59%.
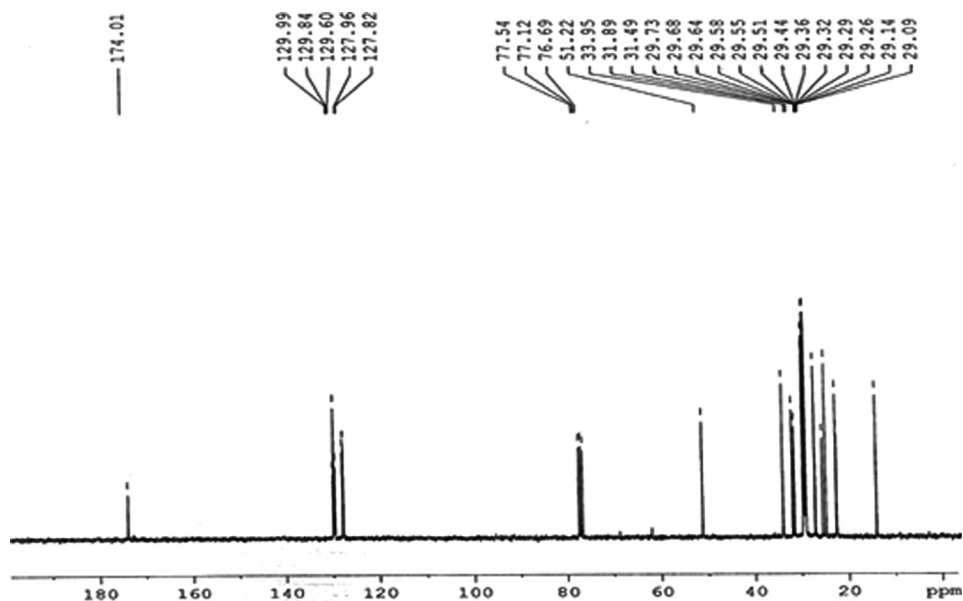

FIG. 6. ^{13}C NMR spectrum of WCOB.

TABLE III. GC data of copper cerium catalyzed waste cooking oil biodiesel.

Peak no.	Retention time (min)	Identified waste cooking oil methyl esters	Formulae	Corresponding fatty acids	Composition (%)
1	8.797	Tetradecanoic acid methyl ester	$CH_3(CH_2)_{12}COOCH_3$	C14:0	6.5
2	9.763	9-Tetradecenoic acid methyl ester	$CH_3(CH_2)_5CH=CH(CH_2)_5COOCH_3$	C14:1	3.2
3	9.878	Hexadecanoic acid methyl ester	$CH_3(CH_2)_{14}COOCH_3$	C16:0	15.4
4	10.729	10, 13-Octadecadienoic acid methyl ester	$CH_3(CH_2)_3CH=CHCH_2CH=CH(CH_2)_8 COOCH_3$	C18:2	8.1
5	10.925	9-Octadecenoic acid methyl ester	$CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3$	C18:1	26.3
6	11.635	11-Eicosenoic acid methyl ester	$CH_2(CH_2)_7CH=CH(CH_2)_9COOCH_3$	C20:1	12.1
7	11.723	Eicosenoic acid methyl ester	$CH_3(CH_2)_{18}COOCH_3$	C20:0	11.3
8	12.452	13-Docosanoic acid methyl ester	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOCH_3$	C22:1	7.5
9	12.527	Docosanoic acid methyl ester	$CH_3(CH_2)_{20}COOCH_3$	C22:0	4.6
10	13.324	15-Tetracosenoic acid methyl esters	$CH_3(CH_2)_7CH=CH(CH_2)_{13}COOCH_3$	C24:1	3.1

2. ^{13}C NMR studies

The characteristic peaks of ester carbonyl (-COO-) and C-O at 174.01 ppm and 51.22 ppm, respectively, were observed in the ^{13}C NMR spectrum of the WCOB as shown in Figure 6. The peak around 127.82 ppm and 129.99 ppm confirms the olefinic bond in the methyl esters. The

TABLE IV. GC data of copper nickel catalyzed waste cooking oil biodiesel.

Peak no.	Retention time (min)	Identified waste cooking oil methyl esters	Formulae	Corresponding fatty acids	Composition (%)
1	9.790	Tetradecanoic acid methyl ester	$CH_3(CH_2)_{12}COOCH_3$	C14:0	4.7
2	9.732	9-Tetradecenoic acid methyl ester	$CH_3(CH_2)_5CH=CH(CH_2)_5COOCH_3$	C14:1	3.6
3	9.973	Hexadecanoic acid methyl ester	$CH_3(CH_2)_{14}COOCH_3$	C16:0	18.1
4	10.800	9-Octadecenoic acid methyl ester	$CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3$	C18:1	27.2
5	11.716	10, 13-Octadecadienoic acid methyl ester	$CH_3(CH_2)_3CH=CHCH_2CH=CH(CH_2)_8 COOCH_3$	C18:2	13.8
6	11.765	Eicosenoic acid methyl ester	$CH_3(CH_2)_{18}COOCH_3$	C20:0	10.6
7	12.635	11-Eicosenoic acid methyl ester	$CH_2(CH_2)_7CH=CH(CH_2)_9COOCH_3$	C20:1	9.2
8	13.219	13-Docosanoic acid methyl ester	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOCH_3$	C22:1	7.4
9	13.878	Docosanoic acid methyl ester	$CH_3(CH_2)_{20}COOCH_3$	C22:0	3.7
10	14.152	15-Tetracosenoic acid methyl esters	$CH_3(CH_2)_7CH=CH(CH_2)_{13}COOCH_3$	C24:1	1.5

peaks in the range of 29.09–33.95 ppm are due to the methylene carbons of long carbon chain in fatty acid methyl esters.

E. Gas chromatography/mass spectrometry (GC/MS)

Gas chromatography was used to determine the chemical composition of the obtained product, the WCOB by obtaining the retention time of various components and then it was confirmed by the mass spectrometric analysis by Mass Spectrometer coupled with the Gas Chromatograph. The major peaks found in the total ion chromatogram are shown in Tables III and IV. Each peak corresponds to fatty acid methyl ester contents of the WCOB and was identified from the library match software of National Institute of Standards and Technology (NIST 05. L). The identified FAMEs were confirmed by running the standards under identical experimental conditions and the results are shown in Tables III and IV.

1. Investigation of saturated compounds

Distinguished peaks of higher saturated esters at $[M-31]^+$ due to α-cleavage (loss of methoxy group) and $[M-43]^+$ due to the removal of C2-4 propyl group were observed at all spectra of waste cooking oil methyl esters (WCOMEs) mass spectrum. Base peak of saturated WCOME's was observed at m/z = 74, which correspond to the McLafferty rearrangement.[23] As a result of β-cleavage, the first member of carbomethoxy $[CH_3OOC\,(CH_2)_n]^+$ is obtained at m/z = 87, where n = 2, 3, 4, 5, 6…., m/z 87, 101, 115, 129, 143…, with difference of 14 a.m.u. due to the CH_2 unit, a hydrocarbon series of alkyl ions. McLafferty peak at m/z = 74, β-cleavage, and alkyl series support our argument of saturated waste cooking oil methyl esters
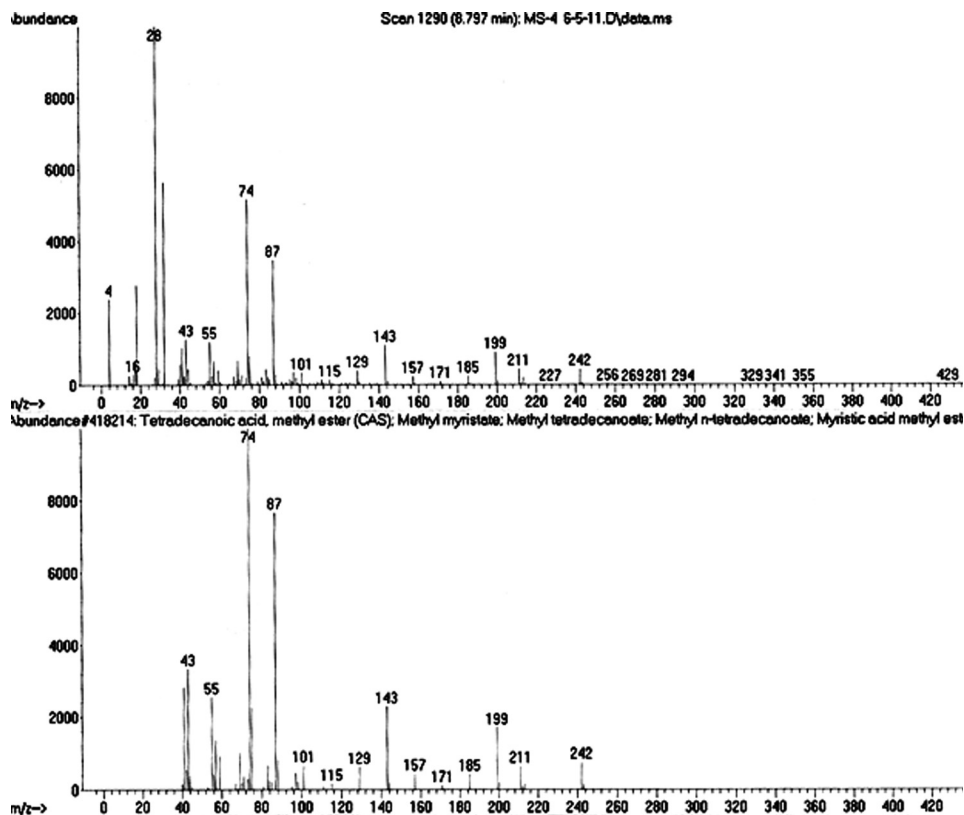

FIG. 7. Mass spectrum of tetradecanoic acid methyl ester.

(WCOMEs). A representative mass spectrum of tetradecanoic acid methyl ester prepared using with mass fragmentation ions is shown in Figure 7.

2. Investigation of mono-unsaturated compounds

[M-32]$^+$ due to loss of methanol and [M-74]$^+$ due to loss of McLafferty ion and base peak at m/z = 55 are the characteristic and distinguishable fragmentation peaks of three major mono-saturated esters present in WCOMEs. The characteristic peaks $[C_nH_{2n-1}]^+$, $[C_nH_{2n}]^+$ appear due to the cleavage at the unsaturation and then the successive loss of 14 a.m.u. (CH_2 unit) leads to the appearance of base peak at m/z = 55 for monosaturated esters in waste cooking oil methyl esters. A representative mass spectrum of 9-octadecenoic acid methyl ester with mass fragmentation ions is shown in Figure 8.

3. Investigation of di-unsaturated compounds

10, 13-Octadecadienoic acid methyl ester is the three diunsaturated methyl esters observed in the GC of the waste cooking oil biodiesel. 10, 13-octadecadienoate methyl ester (C18:2) fragmentation showed a characteristic base peak at m/z 41, [M-31]$^+$ due to loss of methoxy group and McLafferty rearrangement peak at m/z = 74. Hydrocarbon ions $[C_nH_{2n-3}]^+$ were seen in the lower mass range at m/z 67, 81, 95, 109, 123,137, etc. A representative mass spectrum of 10, 13-Octadecadienoic acid methyl ester with mass fragmentation ions is shown in Figure 9.
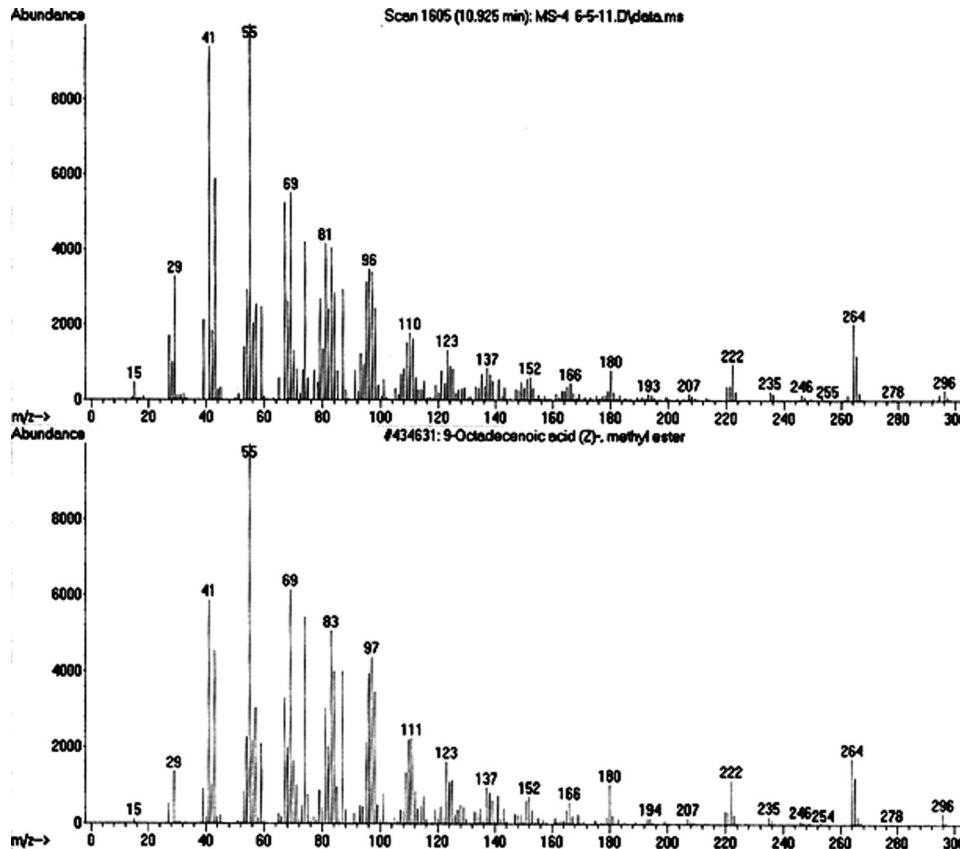

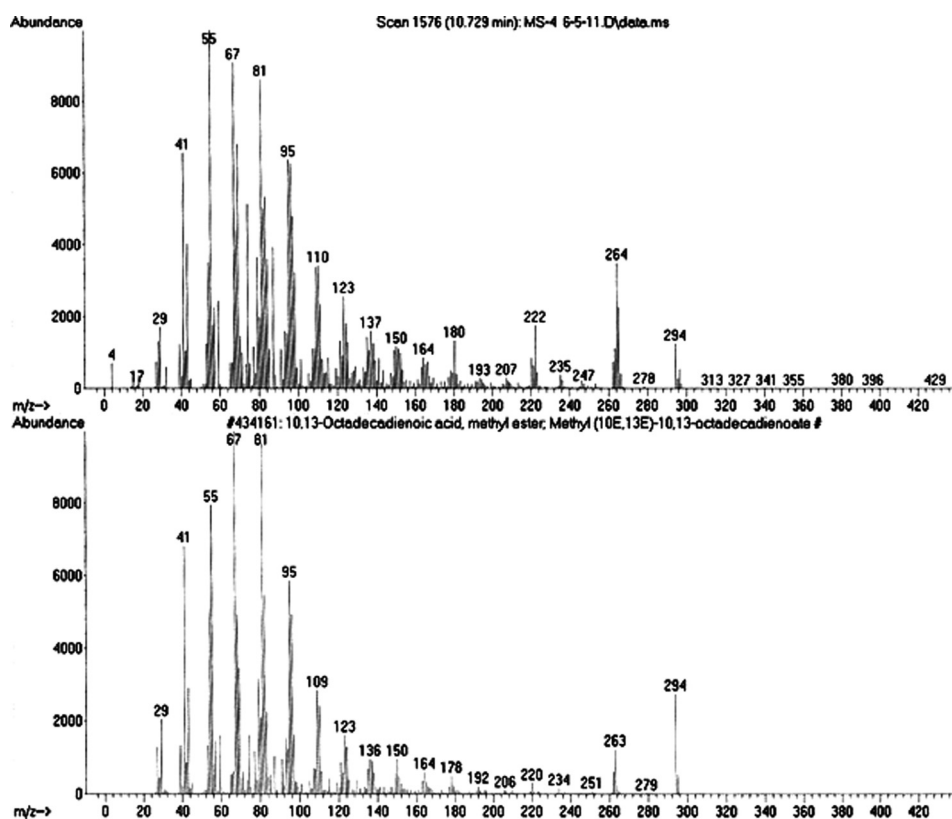FIG. 8. Mass spectrum of 9-octadecenoic acid methyl ester.

FIG. 9. Mass spectrum of 10, 13-octadecadienoic acid methyl ester.

VI. CONCLUSION

The CuO–CeO$_2$ and CuO-NiO mixed oxide catalysts prepared by the co-precipitation method were successfully used for biodiesel production. The addition of CeO$_2$ in the mixed oxide lattice resulted in the better conversion of waste cooking oil. This improves the stability while maintaining an acceptable catalytic activity. The percentage conversion calculated by ^{1}H NMR was found to be 92.59%. The physical and fuel properties were also found to be within range of ASTM (D6751) of biodiesel. The ten methyl esters have been recognized in the GC/MS analysis of the waste cooking oil biodiesel. Fatty acid methyl esters identified by their retention time are tetradecanoic acid methyl ester, 9-tetradecenoic acid methyl ester, hexadecanoic acid methyl ester, 10, 13-octadecadienoic acid methyl ester, 9-octadecenoic acid methyl ester, 11-eicosenoic acid methyl ester, eicosenoic acid methyl ester, 13-docosanoic acid methyl ester, docosanoic acid methyl ester, 15-tetracosenoic acid methyl esters and further confirmed by their mass fragmentation factor. These results were also supported by the FT-IR and ^{1}H and ^{13}C NMR data. The mixed oxides catalyst, CuO–CeO$_2$, showed tremendous potential in large-scale biodiesel production from waste cooking oil.

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