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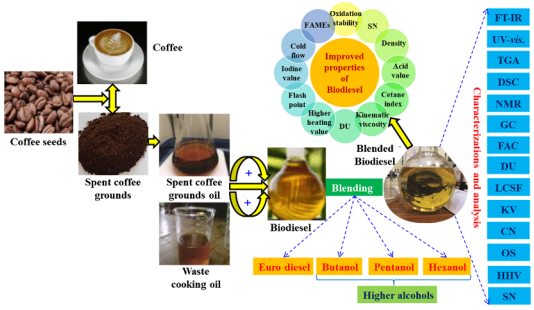
Full Length Article

Integrated valorization of waste cooking oil and spent coffee grounds for biodiesel production: Blending with higher alcohols, FT–IR, TGA, DSC and NMR characterizations

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GRAPHICAL ABSTRACT



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ABSTRACT

This work deals for the first time with recycling a binary blend of waste cooking oil (WCO) and spent coffee grounds oil (SCGO) (50/50% by volume) into biodiesel. Additionally, this work aimed at valorizing both wastes while improving fatty acids composition to obtain a stabilized product due to low degree of unsaturation of SCGO besides, reducing its high acid value. Furthermore, blending with Euro diesel and higher alcohols of butanol, pentanol and hexanol to improve some biodiesel properties was investigated. Furthermore, FT–IR, UV–*vis*., TGA, DSC and NMR analyses to assess the blends quality was examined. Results have proved the advantage of pre-blending and higher alcohols addition to improve the fuel properties. The biodiesel exhibits excellent cetane number of 56.64, oxidation stability of about 6.51 h and iodine value of 83.71 (g iodine/100 g) due to the low degree of unsaturation (89.02). Blending with higher alcohols improves density and cold flow properties while keeping acceptable level of cetane number, flash point and higher heating value (HHV) rather than lower alcohols. Consequently, this opens new gates for biodiesel research area. In conclusion, this work reinforces that blending of WCO and SCGO improves biodiesel properties and add to the economy of this

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industry. Therefore, further examination on the blends effect in compression ignition diesel engines through engine emissions and combustion characteristics is recommended.

1. Introduction

World is producing a huge amount of waste in daily basis. These include municipal, food, beverage, agricultural, and industrial wastes *etc*. Dumping these wastes directly to the landfills is very harmful if either not disposed or recycled in an appropriate manner as they are toxic and may cause serious environmental problems [1]. This is due to the existence of some organic compounds that demand excessive amounts of oxygen to degrade [2]. Creating biofuels from waste offers many environmental, social and financial benefits. Recycling of waste to energy and added-value products is an effective way to solve the problem of many countries that face a challenge in dealing with the huge amount of wastes generated daily due to their increasing population, industrial growth and human consumption. Waste recycling offers many environmental, social and financial benefits [2]. In this regard, restaurants and beverage shops generate a huge amount of wastes such as waste cooking oil (WCO), spent coffee grounds (SCG), food waste (FW), spent tea waste (STW). Among them, WCO and SCG are two valuable wastes due to their potential characteristics. Official statistics on the production and consumption of fats and vegetable oils are available, commonly. Nevertheless, the actual statistics on at least an actual level of collection of WCO oils is far more erratic and inhomogeneous [3]. This is due to the absence of appropriate collection management system in many countries. Direct disposal of WCO to the environment may cause serious problems such as polluting the rivers, drainage choking, propagations of unpleasant smell and bugs [4]. The classification of coffee tree and beverage preparation and its health benefits to reduce the risk of cancer (liver, kidney, oral, breast and colorectal), neuro degenerative disease (Parkinson, Alzheimer and Amyotrophic lateral sclerosis) and cardiovascular disease have been explained in our recent publication [2]. Due to coffee refreshing properties, millions of coffee cups are consumed every day around the world and thus, coffee is the second largest traded commodity after petroleum [1,2]. Coffee silverskin (CS) and SCG are the main coffee industry residues, obtained during the beans roasting, and the process to prepare “instant coffee”, respectively [1]. This is responsible to generate large quantities of wastes [2]. According to the literature [5,6], the coffee industry generates around 6 million tons of wastes per year. As a result, large amounts of a dark colored waste are generated as 550–670 g as SCG from 1 kg of Robusta coffee.

2. Overview of WCO and SCGO recycling potential

Both WCO and SCG wastes can be processed in different ways. For instance, WCO can be processed into biodiesel [7,8] whereby glycerin produced as a by-product during the transesterification process (10% of transesterification) which is a valuable source for cosmetics and pharmaceutical industries besides, it can be also processed further into some other types of biofuels such as biogas and biohydrogen [9,10]. Moreover, WCO is averagely five times cheaper than the refined cooking oil [4]. This remarkably cuts down the cost of biodiesel production as 75% of total biodiesel production cost comes from the price of feedstock [11]. On the other hand, SCG contains large amounts of organic compounds (*i.e.* fatty acids, amino acids, polyphenols, minerals lignin and polysaccharides [12,13] namely; galactomannans and arabinogalactans [14,15]) that remain insoluble in SCG and thus can be valorized in different ways. It can be recycled to produce biofuels such as biodiesel [2,16–22], fuel pellets [23,24], bio-oil [25–27], bioethanol [28,29], biogas [30,31], hydrocarbon fuels [32,33], biohydrogen [1,34] and biobutanol [1] or value-added products applications such a bioactive compound [35], adsorbent [5,36,37], polymers [38,39] composting [40,41], co-composting [42,43], vermicomposting [44], nanocomposites [45] and pulp-paper production [1]. Preliminary calculations conducted by the literature [34] indicated that converting the oil extracted from SCG to biodiesel besides utilizing the left over SCG, after the oil extraction as fuel pellets can yield a profit of more than $8 million/year in the United States only (considering the waste generated by Starbucks stores). Moreover, a summary on some SCG valorization pathways options has been given in our previous study [2].

SCGO compared to other waste such as brown grease, pork fat (white grease), lard, fish oil, poultry fat for biodiesel production offers many advantages due to its higher stability, well established transportation and pleasant odour. However, the oil extraction is required to process the SCG into biodiesel [2,34]. Higher alcohols such as butanol ($C_4H_{10}O$), pentanol ($C_5H_{12}O$) and hexanol ($C_6H_{14}O$) have many advantages over lower alcohols such as methanol (CH_4O) and ethanol (C_2H_6O) in compression ignition (CI) engines such as having higher flash point, density, energy density, cetane number, heating value and kinematic viscosity, lower hygroscopicity and volatility and better miscibility with diesel and biodiesel [46]. Moreover, their positive effect to reduce the high kinematic viscosity, density and cold flow properties has already been validated in the literature [47]. Butanol (But) is an organic alcohol with a four-carbon chain. Application of butanol as an oxygenated fuel in diesel engines has recently been recognized as a promising and green alternative fuel. It can be produced by petrochemical, fermentative and catalytic routes [48,49]. Pentanol (Pen) is an organic alcohol with a five-carbon chain that can be produced from renewable feedstock such as glucose or glycerol through metabolic engineering or biocatalysts [46,50]. Hexanol (Hex) is an organic alcohol with a six-carbon chain that can be produced industrially by the oligomerization of ethanol which can be produced from crops, corns, vegetables, and other feedstocks such as wastes from agricultural food and beverage processing [51].

Our previous work [2] targets the assessment of SCG before and after the lipids extraction. All samples were tested for Scanning Electron Microscopy (SEM), Differential scanning calorimetry (DSC), Thermogravimetric analysis (TGA), X-Ray diffraction (XRD), calorific value, surface analysis and porosity, Fourier transform infrared spectroscopy (FT–IR), density and elemental analysis. Oil was extracted and consequently followed by biodiesel production and blending with Euro diesel (D) at different percentages. Results showed that SCG before and after the lipids extraction can be utilized as compost, as it is rich in nitrogen (16.7%). Biodiesel exhibits excellent cetane number, higher heating and iodine values with poor cold flow properties due to the combined effect of low degree of unsaturation (DU) and high long chain saturated factor (LCSF). Furthermore, the analyses support that SCG after oil extraction is an ideal material for garden fertilizer, feedstock for ethanol, biogas production, and as fuel pellets.

This work targets to carry on our previous study where the extracted oil from SCG was blended with WCO prior to biodiesel production. This was aimed at valorizing both wastes while improving the fatty acids composition to obtain a stabilized product due to the high saturation level of SCGO. This will also reduce the high acid value of SCGO to a lesser level and thus eases the biodiesel production process (Section 3.1). The blended sample was prepared as 50/50% by volume and kept in a reagent bottle for further analyses before the biodiesel production. This was followed by blending the biodiesel with D100 and higher alcohols of But, Pen and Hex to improve the kinematic viscosity, density and cold flow properties of biodiesel. Detailed characterization of the blends using reliable, fast and cheap methods of FT–IR,

Nomenclature

B100	Biodiesel
But	Butanol
CI	Compression ignition
CN	Cetane number
CS	Coffee silverskin
DSC	Differential scanning calorimetry
D100	Euro diesel
DU	Degree of unsaturation
FAC	Fatty acid composition
FAMEs	Fatty acid methyl esters
FT–IR	Fourier transform infrared spectroscopy
GC	Gas chromatography
HHV	Higher heating value
Hex	Hexanol
IV	Iodine value
KV	Kinematic viscosity
LCSF	Long chain saturated factor
MWi	Molecular weight of fatty acid
MPn	Melting point of saturated fatty acid
N	No of double bonds in mono/poly unsaturated fatty acids
NMR	Nuclear magnetic resonance
OS	Oxidation stability
Pen	Pentanol
SCGO	Spent coffee grounds oil
SCGOME	Spent coffee grounds oil methyl ester
SN	Saponification number
TGA	Thermogravimetric analysis
UV–vis.,	Ultraviolet–visible absorption spectra
WCO	Waste cooking oil
WCOME	Waste cooking oil methyl ester
η_i	Kinematic viscosity of fatty acid at 40 °C

Ultraviolet–visible absorption spectra (UV–*vis.*), TGA, DSC and Nuclear magnetic resonance (NMR) analyses was extensively studied and presented. Moreover, some important properties of the blends were also investigated as qualitative and quantitative analyses as well that can valorize both WCO and SCGO in one pot. Consequently, such a study opens new directions for the biodiesel research area in the future. In conclusion, authors have recommended to further examining the effects of these blends in CI ignition diesel engines through engine emissions and combustion characteristics.

3. Materials and methods

3.1. Materials, equipment, oil characteristics and biodiesel production

SCG was collected from Gloria Jean coffee shop (Kayseri, Turkey) while WCO was collected from the main food Court of Erciyes University through personal communication. All the chemicals required for oil extraction, biodiesel production and blending were obtained from a local chemical supplier in Kayseri. D100 was purchased from APET petrol station. Properties of crude oil, produced biodiesel and blends were determined following the equipment list as given in the literature [52]. Table 1 also shows some main properties of the waste cooking oil methyl ester/spent coffee ground oil methyl ester (WCOME/SCGOME) besides a comparison with pure WCOME and SCGOME. Acid value of WCO/SCGO was determined and found to be 12.1 mg KOH/g oil. Therefore, two steps of acidic esterification followed by alkaline transesterification were adopted to produce biodiesel. It was observed that blending reduces the extreme high acid value of SCGO as compared to previous work [2,53] (22.3 mg KOH/ g oil and 14.65 mg KOH/ g oil). Table 2 shows the summary of biodiesel production process. This process resulted in a high quality final product with a biodiesel yield of more than 95%. It is noticeable that such blending improves density and slightly reduces cold flow properties of SCGOME.

3.2. Gas chromatography (GC) method of WCOME/SGCOME

Determination of Fatty acids composition (FAC) profile of WCOME/SGCOME has been done using Perkin Elmer Clarus 680, equipped with a flame ionization detector (FID) and a BPX70 capillary column in which 1 μL of the sample was injected following the method prescribed in our previous publications [52]. The carrier gas was Helium with column flow rate, head pressure and dimension of 1.00 mL/minute (column flow), 70 kPa (flow control made) and 60.0 mx0.25μmx0.25 mm ID respectively. The test was conducted using an optimized in-house GC method with temperature ramp details of heating to 60 °C (hold for 2 min), then to 200 °C with heating rate 10 °C/minute and finally to 240 °C with heating rate 5 °C/minute (hold for 7 min). Analyses were made as per the standard of fat and oil derivatives (TS EN 14103:2011).

DU was calculated from the proportion of monounsaturated and polyunsaturated fatty acids using the following equations [4,52,54,55]:

$$DU = (monosaturated\ \ C_n{:}\ 1,\ wt\%) + 2(polunsaturated\ \ C_n{:}\ 2,\ wt\%) + 3(polyunsaturated\ \ C_n{:}\ 3,\ wt\%) \quad (1)$$

The proportions of saturated fatty acids (wt%) and their corresponding melting points (MP_n), were used to calculate LCSF as follow [4,52,54,55]:

$$LCSF = \sum \frac{(MPn * C_n wt\%)}{100} \quad (2)$$

Kinematic viscosity at 40 °C (KV), cetane number (CN), oxidation stability (OS), higher heating value (HHV), iodine value (IV) and saponification number (SN) of WCOME/SCGOME were calculated empirically using the following formulae [4,55,56]:

$$\ln(\eta_i) = -12.503 + [2.496 \times \ln(MW_i] - (0.178 \times N) \quad (3)$$

$$CN = -0.1268(DU) - 10.805 \quad (4)$$

$$OS = -0.0518(DU) + 11.121 \quad (5)$$

$$HHV = 46.19 - \left(\frac{1794}{MW_i}\right) - (0.21 \times N) \quad (6)$$

$$IV = 1.0617(DU) - 10.805 \quad (7)$$

$$SN = Sum\left(\frac{560 \times A_i}{MW_i}\right) \quad (8)$$

where η_i represents the kinematic viscosity of the fatty acids at 40 °C

Table 1
Properties of SCGO, WCO and WCO/SCGO and its methyl esters.

Property	SCGO	WCO	WCO/SCGO	SCGOME	WCOME	WCOME/SCGOME
Density at 15 °C (kg/m^3)	932.9	915.9	923.7	891.6	883.1	885
Cloud point (°C)	−3	14	5	11	9	9
Pour point (°C)	−3	4	2	12	9	9
Cold filter plugging point (°C)	–	–	–	5	3	2

Table 2
Summary of biodiesel production process.

Esterification	Parameter	Transesterification	Parameter
Hydrochloric acid (HCL)	1% (v/v oil)	Potassium hydroxide (KOH)	1% (m/m oil)
Methanol (CH_3OH)	100% (v/v oil)	Methanol (CH_3OH)	25% (v/v oil)
Reaction time	3 h	Reaction time	1.5 h
Reaction temperature	60 °C	Reaction temperature	60 °C

MW_i represents the molecular weight of the fatty acids and N represents the number of double bonds in monounsaturated and polyunsaturated fatty acids.

3.3. Fuel modification and selection of binary and ternary blends

Blending of WCOME/SCGOME with But, Pen, Hex and D100 was adopted in this study to modify some properties of WCOME/SCGOME. Thus, two binary blends of (D80B70) and (D70B30) and three ternary blends of (D80B10But10), (D80B10Pen10) and (D80B10Hex10) were prepared and kept in reagent bottles. All the blends show good miscibility and stability over a long period. Properties such as density, kinematic viscosity, pour point, cloud point and cold filter plugging point were examined and the equipment list can be found in our previous work [52]. The densities of all the samples are predicted mathematically with a polynomial curve-fitting method, a polynomial of order k in X is expressed in the following form [57].

$$Y = C + C_1X + C_2X^2\cdots+C_kX^k \quad (9)$$

3.4. Spectral studies

3.4.1. FT–IR spectra

The infrared spectra of all the samples were obtained in a Fourier Transform Infrared Spectrometer by Perkin Elmer Spectrum Two. The supporting software was spectrum software. Each spectrum was taken within few seconds at the resolution of 4 cm^{-1} and 4 scans, in the region of 4000–650 cm^{-1} and 0.5 mL per sample. Cleaning with ethanol was employed to purify the sample crystal before the background collection. The scan results were processed with a computer software program Spectrum.

3.4.2. UV–vis. Spectra

UV–*vis*. spectra provide information about the electronic properties of the oil molecules. All organic compounds absorb light in the visible and ultraviolet region. It is possible to see various aromatic compounds in diesel fuel sources [58]. In this study, all the samples were analyzed by UV–*vis*. to obtain the spectra and the quartz cuvettes were filled with the blends. The UV absorption spectra of the biodiesel blends were obtained using Agilent Technologies Cary 60 UV–*vis*. Spectrophotometer in the wavelength range of 500–200 nm at 1 nm intervals of using standard 1 cm quartz cuvettes at room temperature.

3.4.3. Differential Scanning Calorimetric (DSC) and thermogravimetric analysis (TGA) studies

DSC is used to determine the crystallization onset temperature of the samples and can be plotted on the graph against heat flow. The DSC curves were obtained in a calorimeter model TA Q-2000 with RCS90 coupled with a cooling system. 3 ± 0.5 mg of each sample was loaded in an aluminum pan and heat flow was measured differentially by comparing the heat flow of an empty reference pan as a reference. The rate of heating/cooling was 10 °C min^{-1} between −80 °C and 20 °C under inert nitrogen atmosphere (N_2) with a flow rate of 50 mL min^{-1}. In this study, all the samples and blends were analyzed by TA Q-2000 DSC under the flow of nitrogen. Each DSC test takes about 17 mins to complete. Results were processed with the help of TA Orchestrator Version V7.2.2.1.

The thermogravimetric (TG) thermograms of WCO/SCGO, WCOME/SCGOME, D100, But100, Hex100, Pen100 and their blends were recorded in a Shimadzu DTG 60H thermogravimetric analyzer using platinum pans. 10 mg of each sample was loaded into pans. After each analysis, platinum pans were cleaned well in order to make the pans ready for the next run. In this analysis, the temperature ranges from 25 to 700 °C with a heating rate of 10 °C/min under dry air atmosphere of 100 mL /min to determine the oxidative stability. Each sample took a period of time, almost an hour. A maximum temperature of 700 °C was used as the mass remains constant until the end of the analysis and all the chemical reactions were completed at this

Table 3
FAC, DU, LCSF, KV, CN, OS, HHV, IV and SN of WCOME/SCGOME.

FAC						Analyses					
Fatty acid	MW_i	Structure	N	Systematic name	Formula	(%)	DU	MP_n	LCSF	SN	HHV
Myristic	228.37	14:00	0	Tetradecanoic	$C_{14}H_{28}O_2$	0.32		54.4	0.174	0.78	0.123
Palmitic	256.40	16:00	0	Hexadecanoic	$C_{16}H_{32}O_2$	32.56		62.9	20.480	71.11	12.761
Stearic	284.48	18:00	0	Octadecanoic	$C_{18}H_{36}O_2$	6.0		69.3	4.1580	11.81	2.393
Oleic	282.47	18:01	1	Cis-9-Octadecenoic	$C_{18}H_{34}O_2$	29.69	29.69			58.86	11.766
Linoleic	280.45	18:02	2	Cis-9-*cis*-12 Octadecadienoic	$C_{18}H_{32}O_2$	28.02	56.04			55.95	11.032
Linolenic	278.43	18:03	3	α-Linolenic acid	$C_{18}H_{30}O_2$	1.0	3.0			2.01	0.391
Arachidic	312.53	20:00	0	Eicosanoic	$C_{20}H_{40}O_2$	1.86		75.5	1.404	3.33	0.752
Gendoic	310.55	20:01	1	Cis-11-eicosenoic acid	$C_{20}H_{38}O_2$	0.29	0.29			0.52	0.117
Behenic	340.58	22:00	0	1-Docosanoic acid	$C_{22}H_{44}O_2$	0.26		80	0.208	0.43	0.106
Saturated	41.00			DU, LCSF, KV, CN, OS, HHV, IV and SN							
Monounsaturated	29.98			DU	89.02						
Polyunsaturated	29.02			LCSF	26.42						
Total	100			KV at 40 °C (mm^2/s)	3.88						
				CN	56.64						
				OS (h)	6.51						
				HHV (MJ/kg)	39.44						
				IV (g Iodine/100 g)	83.71						
				SN	204.8						

Table 4
Summary of biodiesel, biodiesel-diesel and biodiesel-diesel-higher alcohols blends properties.

Property	WCOME/SCGOME	B20	B30	D80B10But10	D80B10Pen10	D80Hex10B10	D100
Density at 15 °C (kg/m^3)	885	850.1	854.1	842.5	843.3	843.5	842.5
Cloud point (°C)	9	−3	−2	−3	−3	−2	−5
Pour point (°C)	9	−6	−3	−7	−6	−9	−14
Cold filter plugging point (°C)	2	−14	−11	−22	−20	−19	−26

B ≡ WCOME/SCGOME.

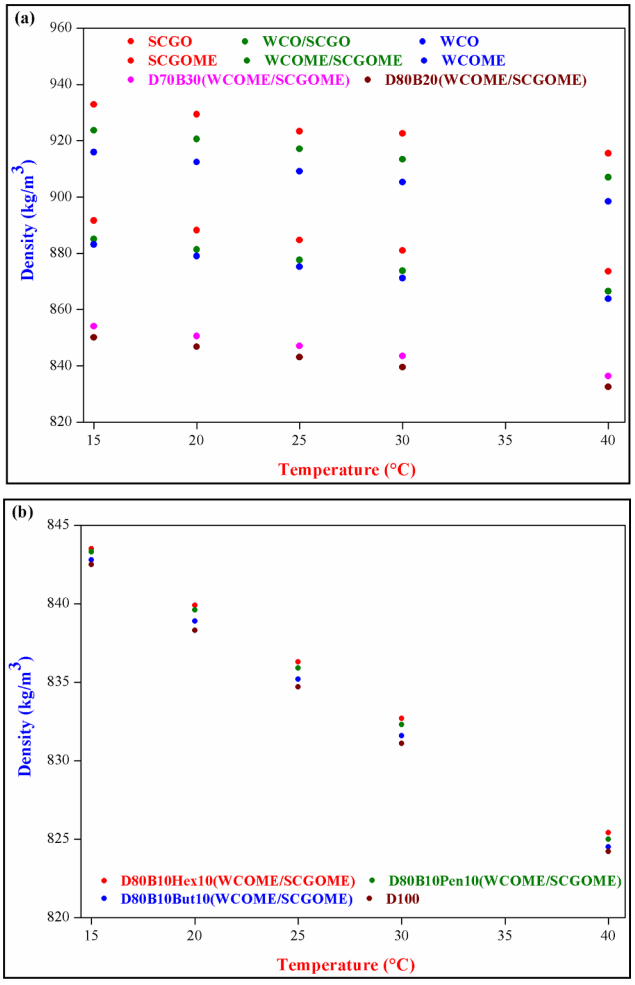


Fig. 1. Effect of temperature range (15–40 °C) on density (kg/m^3).

Table 5
Prediction of density (kg/m^3) at temperature range (15–40 °C).

Sample	Equation	R^2
WCO	−0.7016x + 926.46	0.9997
SCGO	−0.687x + 942.6	0.9684
WCO/SCGO	−0.6751x + 933.91	0.9993
WCOME	−0.7711x + 894.51	0.9996
SCGOME	−0.7219x + 902.59	0.9996
WCOME/SCGOME	−0.7411x + 896.11	1
D80B20	0.7081x + 860.81	0.9998
D70B30	−0.7086x + 864.76	1
D80B10But10	−0.7322x + 853.52	1
D80B10Pen10	−0.7314x + 854.24	1
D80B10Hex10	−0.7238x + 854.38	1
D100	−0.7265x + 853.05	0.9986

B ≡ WCOME/SCGOME.

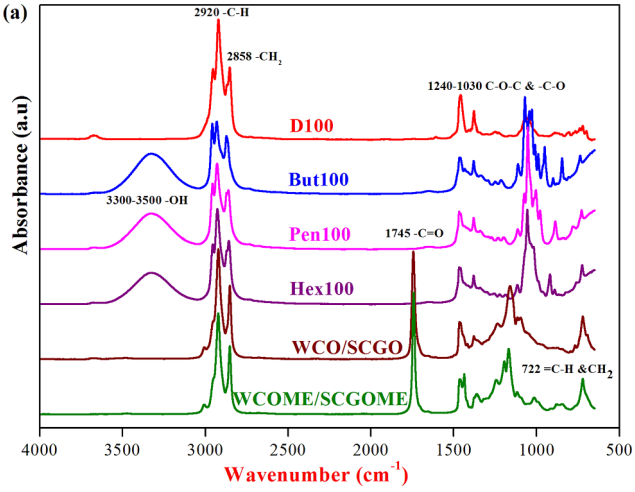


Fig. 2a. Infrared spectra of D100, But100, Pen100, Hex100, WCO/SCGO and WCOME/SCGOME.

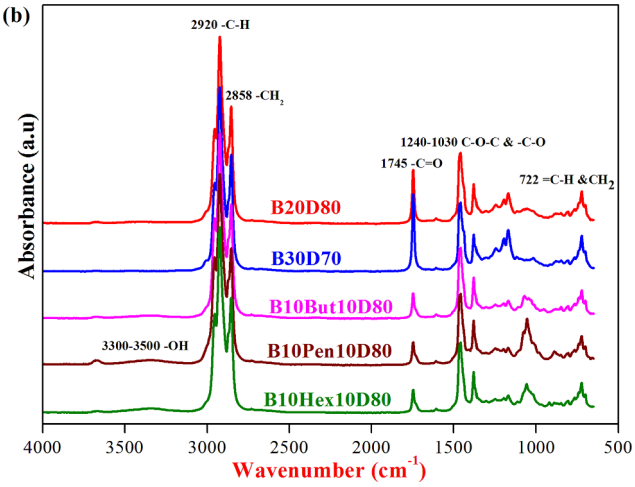


Fig. 2b. Infrared spectra of B20D80, B30D70, B10But10D80, B10Pen10D80 and B10Hex10D80.

temperature. TGA curves were used to analyze the onset temperature of WCO/SCGO, WCOME/SCGOME, D100, But100, Hex100, Pen100 and their blends.

3.4.4. *^{1}H and ^{13}C NMR studies*

The NMR analyses for all the samples were performed using Agilent Technolohies Premium Compact NMR at 600 MHz (^{1}H) and 150 MHz (^{13}C) with the residual solvent peaks as internal references. Spectrometer equipped with suitable probes for cores of ^{1}H, ^{13}C, ^{19}F, ^{31}P. MeOD was used as both the solvent as well as internal standard respectively. ^{1}H and ^{13}C spectra were recorded.

Table 6
Functional group frequencies of the fuel samples [63].

Wavenumber, cm^{-1}	Types of vibration	Functional Groups
3300–3500	Stretching	O—H of alcohols
2949	Asymmetrical stretching	=C—H of alkenes
2920	Asymmetrical stretching	C—H of alkanes
2858	Symmetrical stretching	C—H of methylene
1745	Stretching	C=O of ester carbonyl functional group in FAME
1240–1030	Stretching	C—O of alkoxy esters, ethers and C-O-C
722	Bending of alkenes and overlapping of rocking vibration of methylene	=C—H and $-(CH_2)$n methylene groups of cis disubstituted alkenes and aromatic
688	Out of plane bending	=C—H of *cis*-disubstituted alkene and aromatics

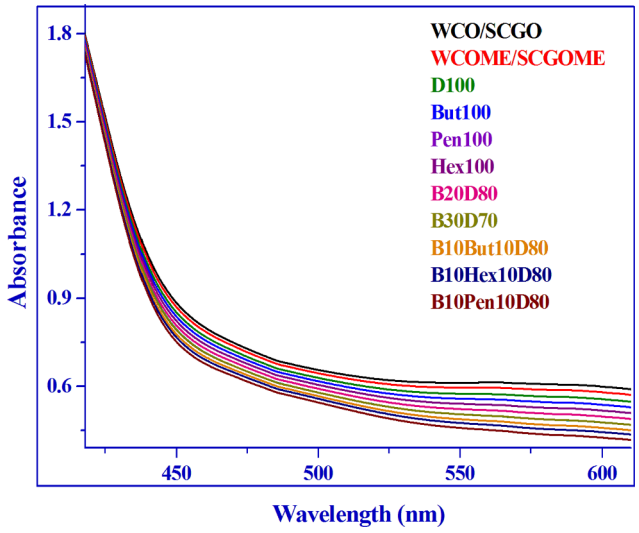


Fig. 3. UV–vis. absorbance spectra of fuel samples.

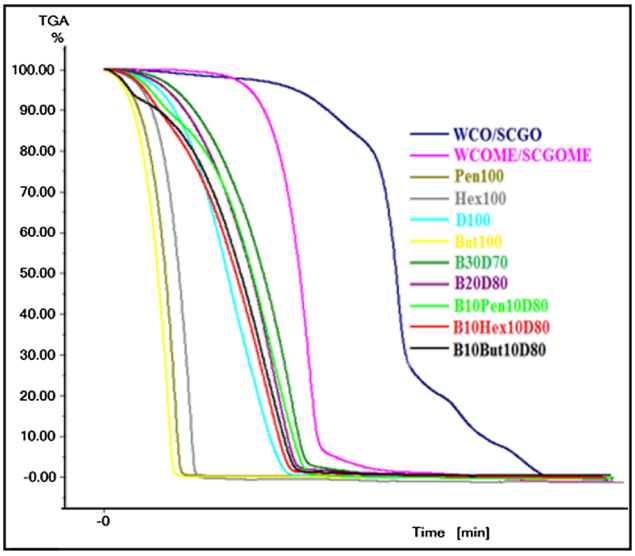


Fig. 4a. Thermogravimetric analyzes (TGA) of fuel samples.

Table 7
Crystallizations onset temperature (°C) of fuel samples.

Sample	Crystallizations onset temperature (°C)
D100	−8.02
WCOME/SCGOME	−1.43
But	−15.13
Pen	−18.09
Hex	−22.52
B10But10D80	−5.20
B10Pen10D80	−5.48
B10Hex10D80	−5.76
B20D80	−3.42
B30D70	−2.54
WCO/SCGO	−1.99

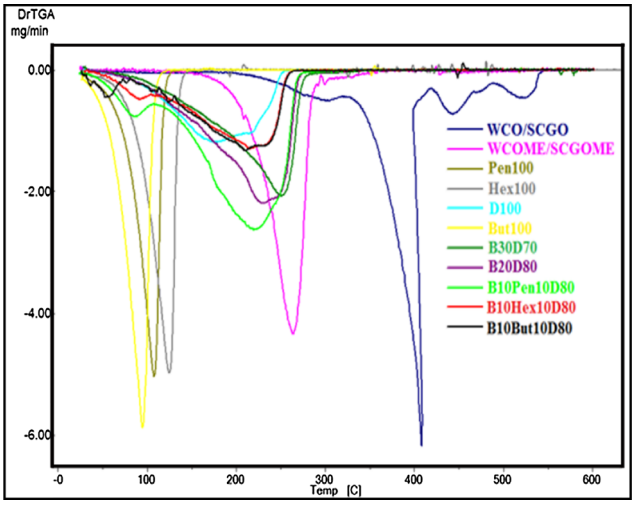


Fig. 4b. Derivative Thermogravimetric analyzes (DTGA) of fuel samples.

4. Results and discussion

4.1. FAC, DU, LCSF, KV, CN, OS, HHV, IV and SN of WCOME/SCGOME

The results of FAC (Table 3) confirmed the existence of fatty acid methyl ester with saturated fatty acids having 41% of the total fatty acid methyl ester content compared to 88.5% of SCGOME [2]. This is followed by a reasonable amount of both mono and polyunsaturated fatty acids (29.98% and 29.02% respectively) compared to 10.3% and 1.2% of SCGOME [2]. DU and LCSF of WCOME/SCGOME were 41.25 and 49.27 compared to 13.9 and 61.76 of SCGOME [2] respectively. This excellent fatty acid profile positively affects the final fuel properties and proves the advantage of feedstock pre-blending strategy. This profile resulted in a cetane number of 56.64, oxidation stability of 6.51 h, HHV of 39.44 MJ/kg and iodine value of 83.71 g iodine/100 g respectively compared to 71.2, 10.4 h and 12.4 g iodine/100 g of SCGOME [2] all of which are satisfactory according to ASTM D6751 standards.

4.2. Blends properties

Additionally, the results indicate that the advantage of higher alcohols addition to the final fuel properties (Table 4). Compared to pure biodiesel and biodiesel-diesel blends, the three biodiesel-diesel-higher

Table 8
TGA analysis of fuel samples.

Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
WCO/SCGO	10	30–400	240.2	99.7
WCOME/SCGOME	10	95–350	185.3	97.0
But100	10	40–115	78.4	98.1
Hex100	10	50–165	102.4	99.0
Pen100	10	45–165	87.9	98.0
D100	10	75–290	127.3	97.8
B30D70	10	30–345	206.5	96.4
B20D80	10	75–280	167.7	97.3
B10But10D80	10	30–300	166.4	96.3
B10Hex10D80	10	30–280	170.2	92.4
B10Pen10D80	10	70–280	162.4	96.7

B ≡ WCOME/SCGOME.

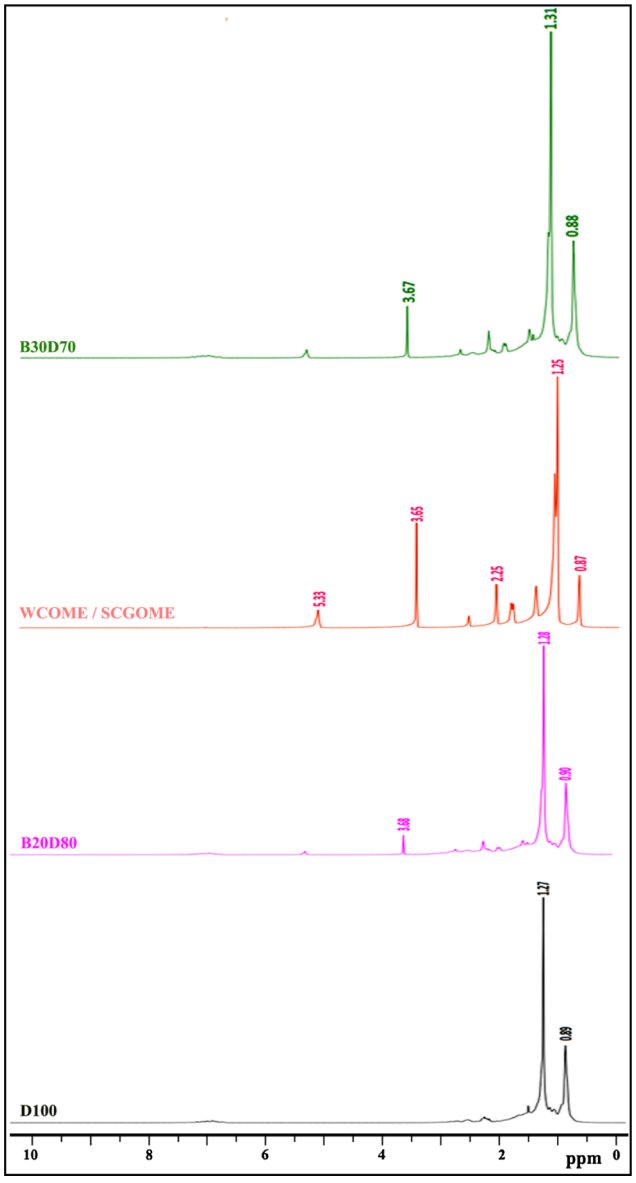


Fig. 5a. ^{1}H NMR spectra of D100, WCOME/SCGOME, B20D80 and B30D70.

alcohols blends have closer densities (842.5–843.5 kg/m^3) and cold filter plugging points (−19 to −22 °C) to D100 (842.5 kg/m^3 and −26 °C respectively). Furthermore, Fig. 1 shows the effects of temperature on densities of all samples. Table 5 summarizes the formulae to predict the density of each sample at a temperature range of about 15–40 °C.

4.3. FT–IR spectral studies

FT–IR has been employed as an easy modern analytical technique to identify the existing functionals and type of binding linkages, corresponding to various stretching and bending vibrations in the biodiesel samples. Oils and esters are noted as fairly strong absorbers in the infrared region of the electromagnetic spectrum [59]. Biodiesel is often blended with Euro diesel to make the biodiesel blends [60]. In recent years, the addition of alcohols has been investigated to improve the properties of the fuel used in diesel engines. Alcohols contain alkyl and hydroxyl functional groups. As the number of carbons in the carbon chain of alcohols increases, it is easier to blend with organic components. Thus, biodiesel can be mixed with higher alcohols more easily than with lower alcohols. Fuel with alcohol additive is called oxygenated fuel, and this type of fuel is thought to contribute positively towards the environment through engine emissions. The previous studies focused on lower alcohols such as methanol (CH_4O) and ethanol (C_2H_6O). However, some issues contribute to poor fuel properties and performance such as lower cetane number, flash point, and heat of evaporation besides corrosion and miscibility issues [61]. Recently, the higher alcohols such as propanol (C_3H_8O), butanol ($C_4H_{10}O$), and pentanol ($C_5H_{12}O$) are getting more attention in diesel engines [62]. In this study, WCOME/SCGOME and its blends with D100, But, Pen and Hex was analyzed to determine the existence of methyl ester and alcohols functionals by FT–IR spectra. The peaks of these spectrum were identified and interpreted and shown in Figs. 2a & 2b. The lists of functional groups identified were shown in Table 6 [63]. This led to the identification of functional groups in the WCOME/SCGOME and its blends with the aid of the structure correlation chart. It can be seen from Figs. 2a & 2b that the absorbance peak heights of each sample were taken at nearly 1745 cm^{-1} where strong absorption of fatty acid methyl esters exist. The strong characteristic absorption bands for ν(−O−H) occurs nearly at 3324 cm^{-1} in But, Pen and Hex and blends with higher alcohols (B10But10D80, B10Pen10D80, B10Hex10D80) in different intensities of absorbance. When the biodiesel-diesel samples were blended with different higher alcohols, the intensities of the absorbance decreased as the number of carbons increased.

The results confirmed the existence of fatty acid methyl esters (FAME) and alcohols. The FT–IR spectrum for the samples revealed the functional groups with their characteristics bands especially for ν (−C=O), ν $(-CH_2)_n$, ν(−C−O), ν(C=C) and ν(C−H) in the spectrum. The peaks for the blends show variations at nearly about 1745 and between 1240 and 1030 cm^{-1} which all are responsible to ν (−C=O) and ν (−C−O) functionals respectively. The peak intensities vary according to the biodiesel ratio. These peaks increase with the concentration of biodiesel in each blended sample. Variations in the intensities from 722 to 688 cm^{-1}indicate the existence of (=C−H) bending; *cis*-disubstituted alkenes and aromatic functionals. The intensities of peaks at 2949 cm^{-1}, 2920 cm^{-1} and 2858 cm^{-1} are attributed to ν $(C-H)_{alkyl\ \&\ alkenes}$ and are found to remain unchanged in each of the blend sample, which is an indication of the existence of D100 [64].

4.4. Uv–visible absorption studies

Fig. 3 shows a typical absorbance curves forD100, But, Pen, Hex, WCO/SCGO, WCOME/SCGOME and the blends (B30D70, B20D80, B10But10D80, B10Hex10D80 and B10Pen10D80) in the range of

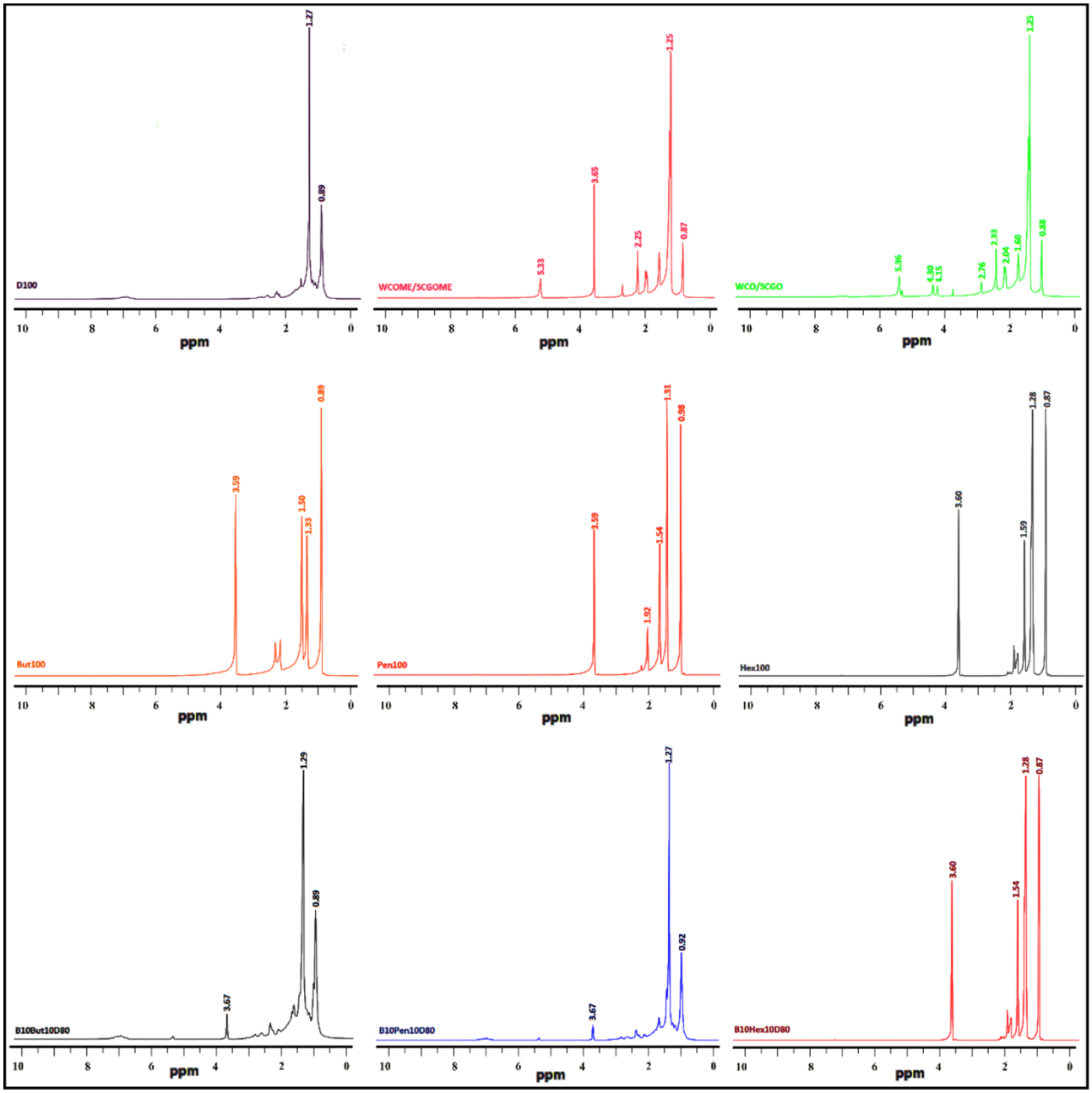


Fig. 5b. ^{1}H NMR spectra of D100, WCOME/SCGOME, WCO/SCGO, But, Pen, Hex, D80B10But10, D80B10Pen10 and D8010Hex10.

600–200 nm on account of INCT (Intra Charge Transfer) (n − π*) transitions. When the spectra were plotted, the change in suction density can be ignored. The absorbance for all samples also produced very similar absorbance, with no statistically significant differences. It is concluded that the absorbance in this band is not affected by the type of alcohol, as the blended biodiesel does not have chemical components that contribute to significant absorption in this range.

4.5. DSC and thermal studies

Both the thermal (TGA and DSC) analysis techniques are quick, sensitive and relatively inexpensive that can be utilized to determine the boiling point of methyl ester formed and also to check the chemical changes that occurs during transesterification reaction. From TGA and DTA studies, the thermograms clearly implies that the composition present in the fuel materials and the formed intermediate compounds or oxidative stabilized compounds during the decomposition pathways as well as to study the mode of decomposition of the fuel materials. In addition, the DSC studies provide the cold flow properties of the fuel materials as a function of temperature and time; however, these studies provide the crystallization phenomenon of the fuel materials.

The crystallization onset temperatures of all the samples under N_2 atmosphere were studied using DSC and presented in Table 7. The onset temperatures for WCOME/SCGOME, D100, But, Pen and Hex are −1.43, −8.02, −15.13, −18.09 and −22.52 °C respectively and hence biodiesel crystallizes faster than diesel and higher alcohols. The crystallization onset temperatures of B10But10D80, B10Pen10D80 and B10Hex10D80 are −5.20, −5.48 and −5.76 °C respectively, below WCOME/SCGOME which signifies the addition of higher alcohols lowers the crystallization temperature of biodiesel. Addition of diesel and higher alcohols reduces the crystallization of biodiesel [65]. The crystallization onset temperature of B30D70 and B20D80 are −2.54 °C and −3.42 °C respectively, below WCOME/SCGOME which represents that addition of biodiesel increases the crystallization temperature of

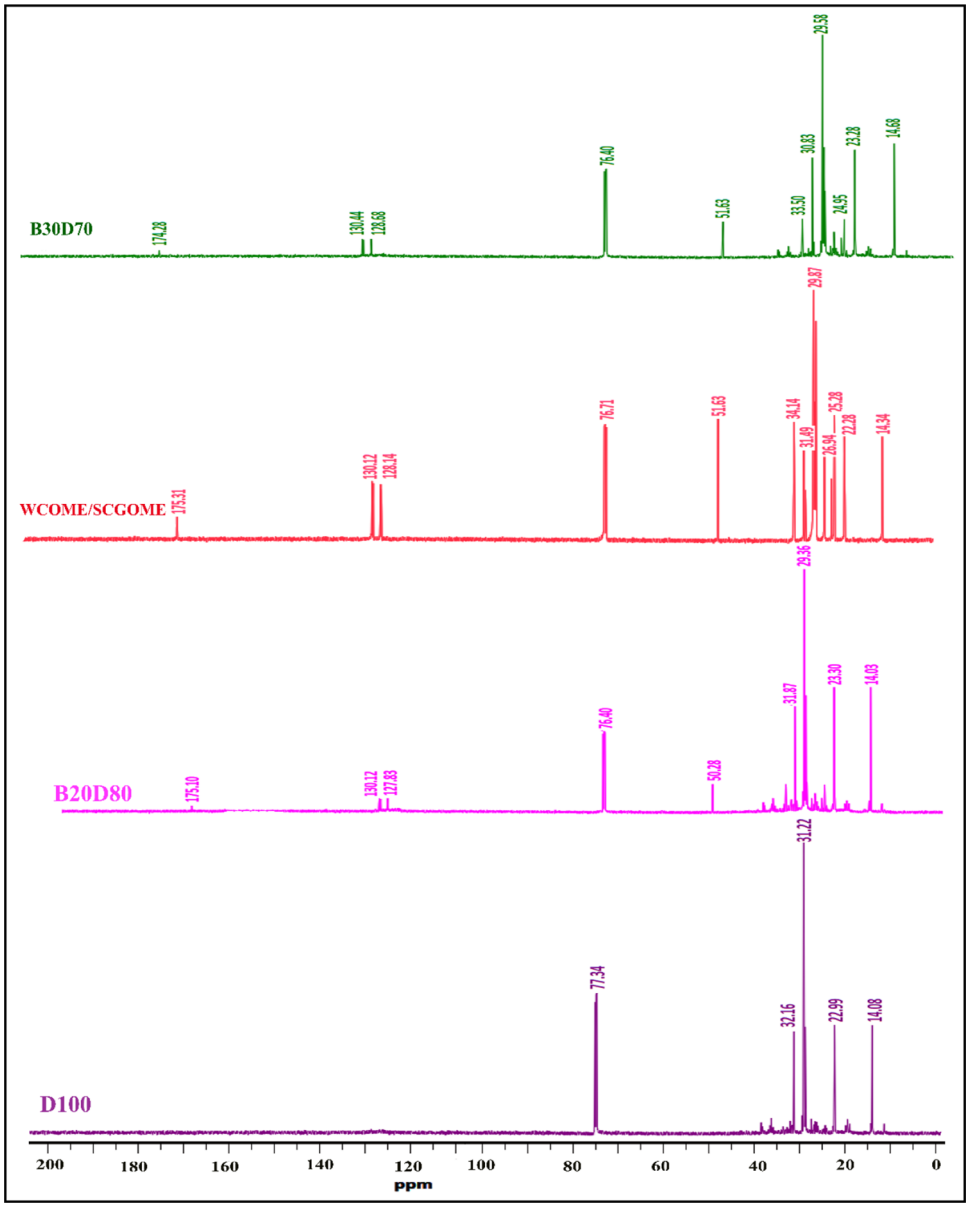


Fig. 6a. ^{13}C NMR spectra of D100, WCOME/SCGOME, B20D80 and B30D70.

diesel. The oxidative stability of all the samples was quantified by Thermogravimetric analysis (TGA), which is a technique for characterizing thermal and oxidative stability of a material (compound or mixture) by measuring changes in its physicochemical properties. These properties were expressed in terms of weight change as a function of increasing temperature. The oxidative stability is a quality indicator parameter for esters. Thermogravimetric curves (TGA) show the weight loss in different temperatures and the first derivative of the weight loss in relation to the temperature curves.

TGA/DTGA curves show that oxidative degradation occurred in a single continuous step in the temperature range 75–240 °C for WCO/SCGO ester and its blends, shown in Figs. 4a and 4b respectively. In these temperature ranges, the mass losses occur at levels of 92.4–99.7% for WCO/SCGO biodiesel and its blends. The oxidative degradation occurred at temperature of 78.4, 87.9, 102.4 and 127.3 °C, for But100, Pen100, Hex100 and D100 respectively. In this temperature range, the mass losses occur at levels of 98.198, 99and 97.8% for But100, Pen100, Hex100 and D100 respectively. The oxidation onset temperatures were represented in Table 8. It is possible to observe the great similarity between the curves, with small variations of T_{onset} between the blends.

4.6. ^{1}H and ^{13}C NMR spectral studies

In this study, all the samples were characterized by ^{1}H NMR spectroscopy and their spectra are shown in Figs. 5a and 5b. The characteristic peaks of methoxy protons δ(−O−CH_3) were observed as a singlet at around 3.65, 3.67 and 3.68 ppm for WCOME/SCGOME, B20D80 and B30D70, respectively. These the chemical shifts indicate the presence of methyl esters in biodiesel. Other observed peaks were around between 0.87 and 0.90 ppm of the terminal methyl δ (−CH_3) protons [65]. Certain charateristic signals obtained were ascribed to protons *α*- to the methylene carbonyl groups δ (−CH_2−C═O−) at 1.88–1.96 ppm, at 2.57–2.69 ppm responsible for diallylic methylene proton δ (−C═C−CH_2−C═C−) and at 4.17 ppm for the protons which are in *α*- and *β*-position in glyceryl functionals in WCOME/SCGOME, B20D80 samples.

A representative spectrum of ^{13}CNMR of all the samples are shown in Fig. 6a and 6b, which shows the characteristic peaks of ester and

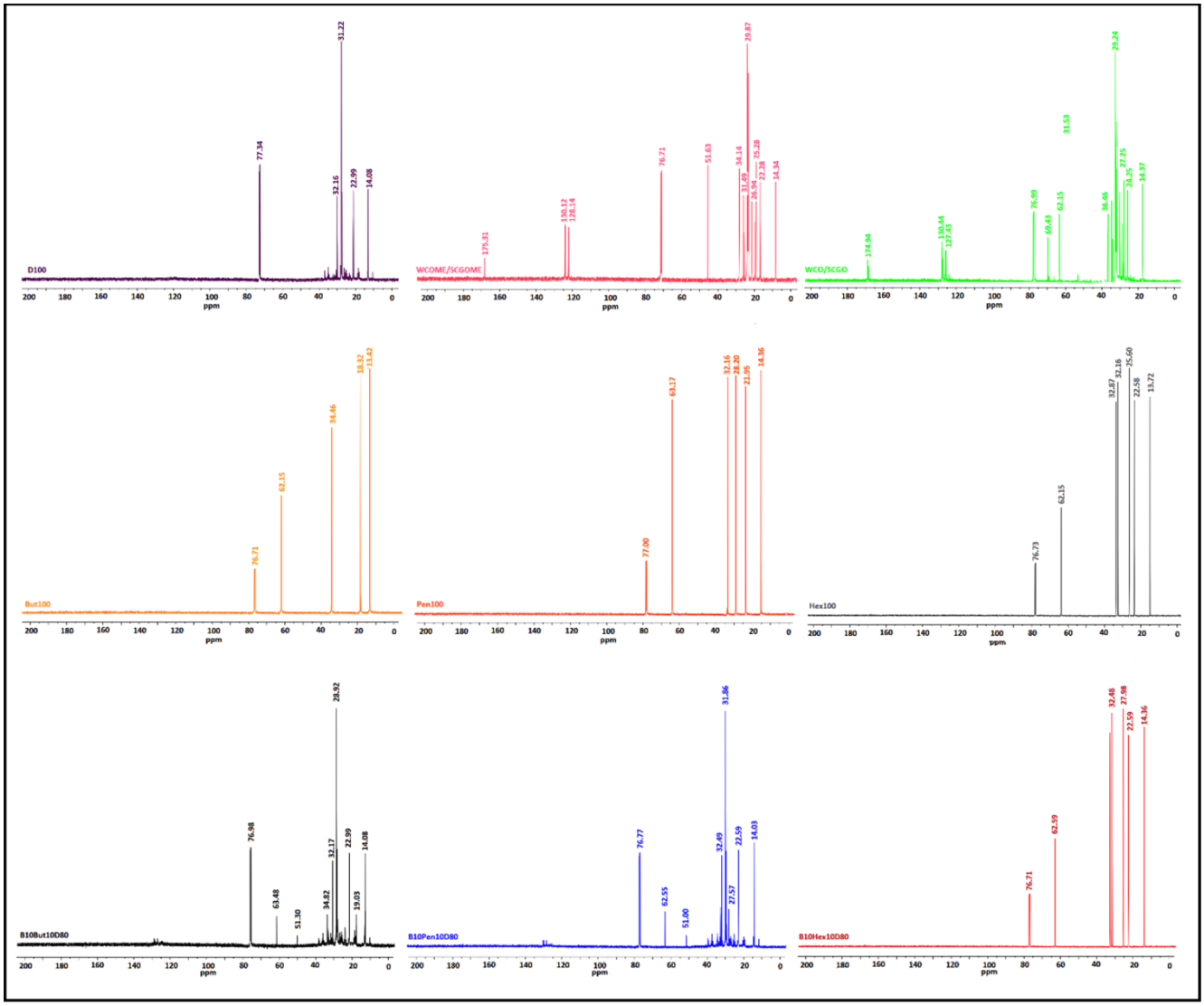


Fig. 6b. ^{13}C NMR spectra of D100, WCOME/SCGOME, WCO/SCGO, But, Pen, Hex, D80B10But10, D80B10Pen10 and D8010Hex10.

carbonyl δ (−COO−) and δ (−C═O−) at around 170 and 50 ppm, respectively. The peaks around 130 and 125 ppm indicate the unsaturation in methyl esters. Other peaks at 14 ppm are due to the terminal carbon of methyl groups δ ($-CH_3$) and signals at 10–35 ppm are related to methylene carbons δ ($-CH_2-$) of long carbon chain in FAMEs [66].

5. Conclusion

This experimental study aimed at recycling and valorizing the waste cooking oil and the oil extracted from spent coffee grounds for biodiesel synthesis. Following this strategy, the acid value of spent coffee grounds was drastically reduced. Moreover, this achieved an improvement in oxidation stability, HHV, cetane number and iodine value of the biodiesel due to the presence of modified structure in the fatty acids composition. The produced biodiesel was then blended with Euro diesel, butanol, pentanol and hexanol to improve its density, kinematic viscosity and cold flow properties. Several characteristics using FT–IR, UV–vis., TGA, DSC and NMR as cheap, fast and reliable methods were conducted to assess the quality of the binary and ternary blends. In conclusion, this work supports that the blending of waste cooking and spent coffee grounds oils improve the biodiesel properties and aid to the economics of this industry. The paper also supports the concept of recycling to save the environment. Blending with higher alcohols improves the density and cold flow properties of biodiesel while keeping acceptable level for cetane number, flash point and HHV rather than lower alcohols. Therefore, this work further shall be further carried on assessing the performance in compression ignition engines in the future study.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2019.01.169.

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