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Biodiesel production from a non-edible oil, *Lipidium sativum* L. seed oil by optimized alcoholysis reaction

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Abstract

This study reports the exploitation of Garden cress *Lepidium sativum* L. seed as a novel non-edible raw feedstock for producing high yield and quality biodiesels vial the optimized alcoholysis reaction. The satisfactory oil content of the Garden cress seeds (28.50± 1.50 % w/w) encouraged its utilization for biodiesel (BD) creation. The garden cress seed oil (GCSO) was transesterified with ethanol and a blend of methanol and ethanol via optimized alkali-catalyzed alcoholysis reaction. The typical reaction conditions, which resulted in the maximum yield of the ethylic BD (90.45 ± 2.0 % were 1.0 wt.% KOH, 8:1 ethanol: GCSO molar ratio, 65 ℃ for a duration of 75 minutes, while 0.80 wt.% KOH, 6:1 mixed alcohols: GCSO molar ratio, 60 ℃, and a duration of 1h, were the typical experimental conditions, which produced the superlative yield of MEBD (97.50± 1.50%,). Transformation of the GCSO to its corresponding alkyl esters was certified through the FTIR, ^{1}H NMR, and thin-layer chromatography studies. Besides, fuel properties of the pristine GCSO have noticeably changed and obeyed the ASTM criteria as a result of the alcoholysis reaction of GCSO with the said alcohols. Blends prepared by blending BD samples with petro diesel at various ratios (v/v) exhibited their compatibility with the specifications fixed by the ASTM standards. The alcoholysis reaction of the GCSO obeyed the first-order kinetics with activation energy values of 30.71 kJ/mol for the ethanolysis of the GCSO, and 32.93 kJ/mol for the transesterification with mixed methanol/ethanol alcohols. This study disclosed that the GCSO possessed the potential to be utilized as a successful alternative to petroleum-based diesel.

Keywords: Garden cress *Lepidium sativum* L. seed oil ; Alcoholysis ; Biodiesels ; Diagnosis of biodiesels; Kinetics.

1. Introduction

Great industrial attention has been given to biodiesel (BD) for its suitability a substitute liquid fuel to petrodiesel (PD) in diesel engines. Sunflower, soybean, and rapeseed oils are the supreme vegetable oils exploited for BD creation with methanol in the existence of a base catalyst. Nevertheless, BD production from vegetable oils has faced several challenges being essential food sources, which in turn raised the production cost of BD. Therefore, exploring new oil sources for BD production is an energetic issue. Non-eatable oils (NEO), waste animal fats, and waste cooking oils have recently been utilized as an attractive option for BD synthesis [1, 2, 3]. In this regard, the garden cress seed oil (GCSO), was presented as a new promising alternative oil for the production of BD. The garden cress is a plant belongs to the *Brassicaceae* species, which essentially originates in Egypt and West Asia [4]. This plant matures rapidly, and widely planted in temperate climates worldwide. According to Nehdi et al. [5], the oil's level of the garden cress seeds (GCS) amounted to 26.77 wt.%, and linolenic, linoleic, gadoleic, oleic, and erucic acid, were the significant fatty acid making it. Production of methylic biodiesel (MBD) from variant oils and NEO has widely reported in the literature due to the low cost and the availability of methyl alcohol, which is a petrochemical product. Ethanol has also utilized in the production of ethylic biodiesel (EBD), which is a greener fuel than MBD because ethanol is renewable fuel as it has been derived from renewable sources, biomass. Besides, the biodegradability of EBD is greater than that of MBD. Besides, EBD emits lower greenhouse gases and particulates than MBD [6,7]. Even so, the exploitation of methanol/ ethanol blend for BD synthesis was also established in the literature, to boost the solvent properties of alcohol via provoking the solubility of the oil in the alcohol phase through the transesterification (TE) process, which causes a greater conversion rate and yield. Furthermore, exploiting a mixture of alcohols

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increased the lubricity characteristics of the resultant BD. Finally, reliance on the synthetic sources for methanol can be conducted by replacing part of methanol by ethanol [8,9].

The literature survey disclosed that only one work was reported on MBD synthesis from GCSO [5]. Nevertheless, that investigation neither provided the optimization of the TE parameters, nor the diagnosis of the BD by any analytical techniques. Moreover, the production of EBD and mixed methyl/ethyl biodiesel (MEBD) via optimized protocol with the evaluation of the physic-chemical properties of the BD and PD blends haven't included in that investigation, which in turn encouraged us to conduct this investigation.

Therefore, this investigation records for the first time the optimized alkali- catalyzed alcoholysis reaction of GCSO with ethanol and a blend of methanol and ethanol alcohols. ^{1}HNMR and FTIR spectroscopy, as well as TLC, were exploited to diagnose the obtained biofuels. Furthermore, the characterization of the EBD and MEBD has done following ASTM standards methods. Besides, various blends of the BD samples with PD have prepared and evaluated according to ASTM standards. Finally, investigating the alcoholysis kinetics of GCSO with the said alcohols was involved as well.

2. Materials and methods

2.1 Feedstock and chemicals

The GCS were collected from the fields located in Mosul city, north of Iraq in July 2018, and was implemented as a non-edible source for BD synthesis. Analytical grade chemicals and solvents, such as KOH (pellets, 85.0 – 100.5%),CH_3OH (HPLC grade, 99.90%),CH_3CH_2OH (99.90%),CH_3OCH_3 (99.0%) ,CH_3COOH (≥ 99 %), petroleum ether (40-60ºC), anhydrous Na_2SO_4 (98,5 - 101 %) were obtained from Scharlau, Spain and BDH, UK.

2.2 Oil extraction and analysis

The matured GCS was washed by distilled water (DW), sun-light dried for 48h, and next pulverized utilizing an electrical grinder to acquire the seeds powder. Oil extraction was performed in a Soxhlet extractor for 10h with petroleum ether (40-60 ºC) as a solvent. After stripping the solvent from the extracted GCSO by a rotary evaporator, anhydrous Na_2SO_4 was utilized to eliminate any traces of humidity in GCSO, followed by filtration to recover the refined oil. The exact calculation of oil content on the GCS was accomplished in triplicate using 10 g of the seeds. The content of the oil was quantified on weight bases. Assessment of the density (D) at 15.6 °C, kinematic viscosity (KV) at 40 °C, acid value (AV), saponification value (SV), refractive index (RI) at 20 °C, flash point (FP) and pour point (PP) of the GCSO has achieved following ASTM standards.

2.3 Transesterification reaction of GCSO with different alcohols

Synthesis of EBD and MEBD was accomplished in a glass reactor equipped with a magnetic stirrer with a reflux condenser. All experiments have been achieved using 100 g of GCSO. At first, a proper amount of alcohol was implemented to dissolve the required mass of KOH. Next, the KOH solution was added to the round containing the GCSO. The reaction blend was heated at the required reaction temperature with stirring at 600 rpm for a pre-determined period. By the end of the TE reaction, the products were transferred to a separating funnel and left overnight to guarantee the complete settlement of glycerol at the bottom. The upper layer (BD) was cleaned with warm DW to eliminate any remaining amounts of KOH and glycerine, followed by distillation under vacuum to discard the surplus alcohol. The purified alkyl esters were dried over anhydrous Na_2SO_4, and the calculation of the BD yield was specified using the following formula [10]:

$$\text{BD Yield (\%)} = \frac{Wt.\ of\ the\ purified\ alkyl\ esters}{\text{Wt. of GCSO used (g)}}\ X\ 100$$

2.4 Evaluation and analysis of BD samples

The fuel properties of the EBD and MEBD synthesized from the GCSO have ascertained following ASTM standard test methods. The titration method (AOCS Cc 17-95) was followed on specifying the soap content (SC) on the BD. Determination of the total glycerin (TG) content in the BD samples was achieved through exploiting the titration method proposed by Pisarello et al.[11]. The purity (ester content, EC) of biofuels was identified following the liquid chromatography method [12]. Each test was repeated three times, and the outcomes have presented as the average ± SD. The GCSO, EBD and MEBD, have been identified using Fourier transform infrared (FTIR) spectrometer (Model: A Bruker EQUINOX 55, USA) in the range of 4000-400 cm^{-1} to recognize the effective functional groups occurred in them. A Bruker Bio-Spin GmbH 400.22 Mhz ^{1}H NMR spectrometer has also employed to affirm the conversion of the GCSO into EBD and MEBD. The spectra were recorded employing $CDCl_3$ as an international reference. Progress of the alkali-alcoholysis of the GCSO was followed through thin layer chromatography (TLC) as quick and cheap analysis method on a TLC plate (Silica Gel 60 F254; Merck, Darmstadt, Germany) with using a mixture of hexane, ethyl ether, and acetic acid at the ratios 80:20:1, vol/vol/vol) as the fractionating solvent, and

the iodine vapor for the visualization of the separated spots [13].

3. Results and discussions

3.1 Physicochemical properties of the oil

The acquired yield of oil is greater than that announced for *Annona diversifolia* seeds (21.0 wt.%) [14], and Polanga (*Calophyllum inophyllum*) seeds (24.96%) [15]. The D of GCSO was analogous to that established for other NEO, while its KV was below those published for other NEO given in **Table 1**. This is due to the high polyunsaturated fatty acid (PUFA) content of GCSO in comparison to other NEO. The lower AV of GCSO than other NEO encourages the direct base-catalyzed TE without the need to pre-treatment step, which raises the production cost of BD, and produces high amounts of the pollutant water. The GCSO has a lower RI than other NEO. Besides, its RI was within the established range stated for other NEO (1.466- 1.470) [17,19]. The fatty acids composition of GCSO manifested its higher content of unsaturated fatty acids (UFA) than saturated fatty acids (SFA). Additionally, the PUFA content in GCSO is greater than those of other NEO (**Table 1**). Following the literature, oil with a higher PUFA level has lower KV because of its loosely-packed structure [20].

The GCSO was submitted to an initial examination before converting it into BD fuels by alcoholysis route. Following the Soxhlet extraction outcomes, an oil yield of 28.50 ± 1.50 wt.% oil was recovered from the GCS.

3.2 Base-catalyzed transesterification of GCSO with different alcohols

Base-catalyzed alcoholysis of GCSO is possible as a consequence of its low AV(1.01 mg KOH/g). Besides, the need for the esterification step is not required compared to other NEO (**Table 1**), suggesting a lower production cost of BD from GCSO. The impact of alcohol: GCSO molar ratio, KOH concentration, reaction time, reaction temperature, and stirring speed on the EBD and MEBD yields were thoroughly inspected.

Base-catalyzed TE of GCSO with ethanol and mixed methanol/ethanol was carried out using KOH as a catalyst. Numerous concentrations of KOH (0.2-1.40 wt.%), were inspected during the alcoholysis of GCSO with maintaining other operating conditions fixed at 65°C,6:1 alcohol: GCSO molar ratio, 600 rpm stirring speed for 60 minutes. A progressive

Table1. Properties of the GCSO compared to other NEO.

Property	***GCSO***	**SMSO** [a]	**WMSO** [b]
Oil content (wt.%)	28.50±1.0	28-30	33.02
D @ 15.6 °C, g/mL	0.9198±0.0001	0.9250	0.9118
KV @ 40 °C, mm^2/sec	18.88±0.50	45.20	24.13
FP, °C	240±1.0	236	145
AV, mg KOH / g oil	1.01±0.02	20.0	2.70
SV, mg KOH / g oil	204.11±2.0	204.0	190.0
PP, °C	-4.0±0.50	-7.0	-
RI @ 20°C	1.4606±0.0010	1.4619	1.4780

Fatty acid profile of GCSO compared to other NEO			
Fatty acid	***GCSO*** [c]	***RSO*** [d]	***WMSO*** [b]
C_{16}	9.03	6.13	2.93
$C_{16:1}$	0.22	0.05	0.14
C_{18}	3.28	1.86	1.0
$C_{18:1}$	22.51	23.87	11.61
$C_{18:2}$	11.17	13.46	11.45
$C_{18:3}$	30.11	10.34	11
C_{20}	3.92	0.68	0.85
$C_{20:1}$	12.22	8.57	10.31
C_{22}	0.99	1.64	0.95
$C_{22:1}$	4.51	31.76	45.39
Others	2.04	3.28	4.32
Total saturated FA	17.58	10.31	5.78
Total USFA	81.85	88.05	89.90
Total PUFA	42.23	23.80	22.45
Total MUFA	39.62	64.25	67.45

[a] *Silybum marianum* L. seed oil from [16]; [b] wild mustard seed oil [17];[c] Garden cress oil [5]; [d] oilseed radish [17].

increase in the BD yield was noticed with the increment of the KOH amount, as illustrated in **Fig.1**.

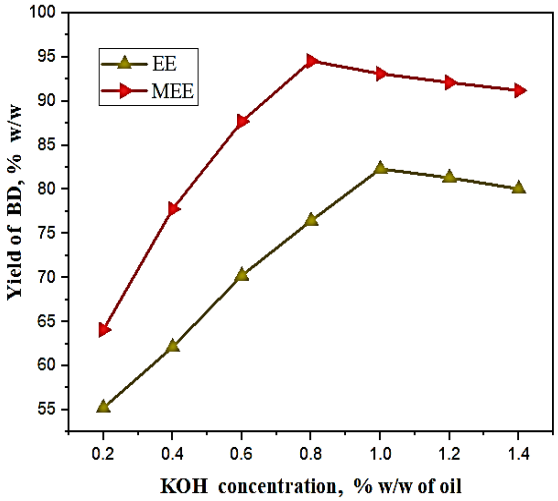


Fig.1. Effect of KOH amount (wt.%) on EBD and MEBD yield. (6:1 ROH:GCO; 65 ℃; 60 minutes; 600 rpm).

The best yield of MEBD (94.55± 1.50 %) was attained at 0.80 wt.% KOH , while1.0 wt.% KOH was typical to produce the highest yield of EBD (82.33± 2.0 %). The excess quantity of KOH contributes to a diminish in the BD yield, which was possibly due to the formation of soaps, which makes the product more viscose, and hard to be stirred in addition to consume more energy [21,22].

It is preferable to conduct the TE reaction by implementing an excess of alcohol to drive the reaction towards the products side. Investigating the effect of alcohol: GCSO molar ratio on BD yield was achieved by testing multiple molar ratios of alcohols in the range of (3:1-10:1). The BD yield increased as the molar ratio of alcohol increased, as observed in **Fig.2**.

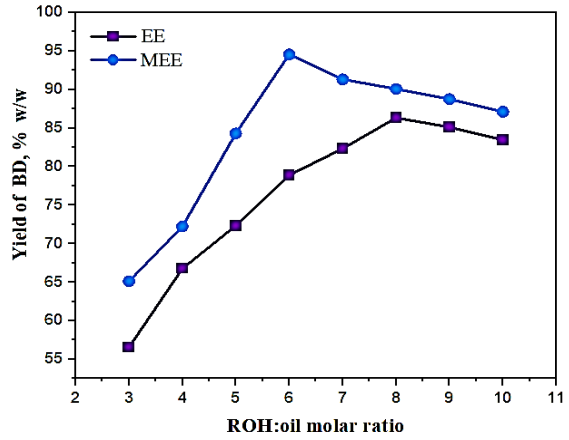


Fig.2. Effect of alcohol: GCSO molar ratio on EBD and MEBD yield. (1.0 wt.% for EBD and 0.80 wt.% KOH for MEBD; 65 ℃; 60 minutes; 600 rpm).

Ethanol: GCSO molar ratio of 8:1 supplied the best yield of EBD (86.33± 1.50 %), while 6:1 mixed alcohols: GCSO molar ratio provided the maximum yield of MEBD (94.55± 1.50 %). A considerable lessening in the BD yield occurred when the amount of alcohol exceeded the optimal ratio, as a consequence of the increase the solubility between the glycerine and alcohol, causing a reverse reaction to happen, and so declined the yield of BD [23,24].

As illustrated in **Fig.3**, the effect of temperature on the EBD and MEBD yields was examined in the range of 30–75°C, as demonstrated in Fig.3. With the increase of temperature, the BD yield raised. The viscosity of the GCSO diminishes with raising the alcoholysis reaction temperature, which in turn promotes the mass transfer between the GCSO and alcohol, resulting in faster conversion to BD [25].

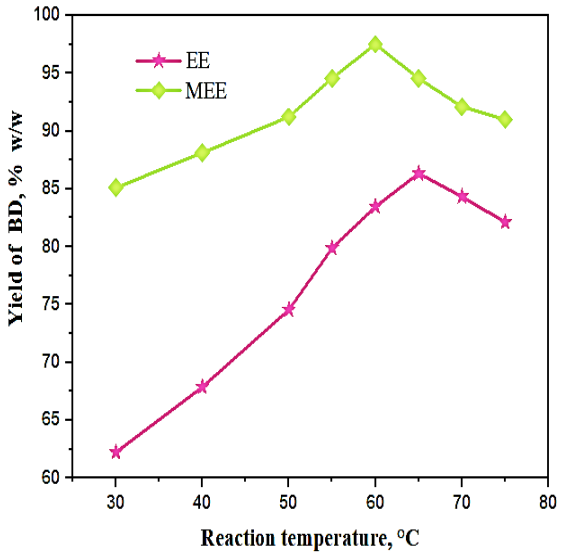


Fig.3. Effect of temperature on EBD and MEBD yield. (1.0 wt.% for EBD and 0.80 wt.% KOH for MEBD; 8:1 Ethanol: GCSO and 6:1 mixed ROH: GCSO molar ratio; 60 minutes; 600 rpm).

The maximum conversion of GCSO to EBD and MEBD happened at 65°C and 60°C, respectively. These temperatures are much below the boiling points of the alcohols exploited, referring to a lower production cost. Temperatures greater than the optimal values diminished the BD yield because of the soap formation before the completion of the TE reaction. Also, the high temperatures accelerate the evaporation of alcohol, and thus its concentration within the reaction media will be diminished, resulting in a lower conversion of the oil to BD [26,27].

The alcoholysis of GCSO was achieved at diverse reaction interval between 15 and 90 minutes as demonstrated in **Fig.4**. The BD yield was low at the shorter periods of the reaction as a consequence of inadequate period to achieve the TE completely. With increasing the TE period, the BD yield raised so that the best EBD yield achieved after 75 minutes of the TE reaction, while the best conversion of the GCSO to MEBD completed after 1h of alcoholysis reaction. Still, the BD yield dropped as the reaction period exceeded the optimal time for the TE as a consequence of the degradation of part of the obtained BD to FFA [28-30].

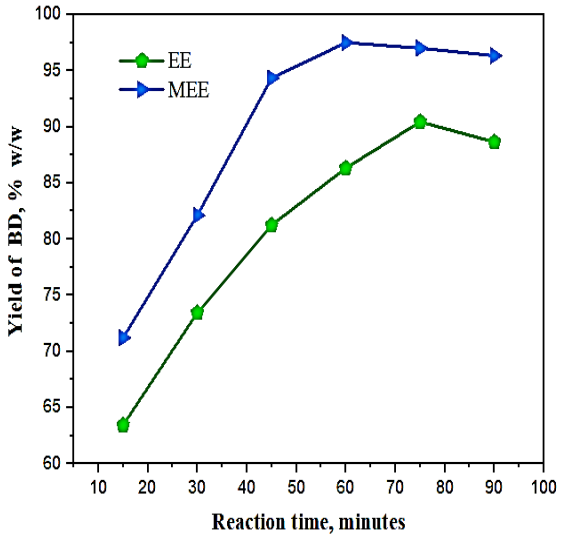


Fig.4. Effect of reaction period on EBD and MEBD yield. (1.0 wt.% for EBD and 0.80 wt.% KOH for MEBD; 8:1 Ethanol: GCSO and 6:1 mixed ROH: GCSO molar ratio; 65 ℃ for ethanolysis and 60 ℃ for alcoholysis ; 600 rpm).

Enhancing the intact area between the GCSO and alcohol-KOH solution can result in a better transformation of the oil to BD. To reach this target, the mixing intensity has to be optimized. Hence, the mixing speed was varied from 300 rpm to 900 rpm during alcoholysis reaction of GCSO, as demonstrated in **Fig.5** with fixing the other variables at their typical values. The transformation of GCSO improved as the mixing speed increased from over 300 rpm because of the homogeneity increment between the reactants species. The maximum conversion of GCSO to EBD (90.45±2.0 %) and MEBD (97.50±2.0 %) achieved at 600 rpm mixing rate. The decomposition of the BD to its corresponding FFA happened when the mixing speed surpassed the optimum rate causing a lower modification of the GCSO to its EBD and MEBD [9].

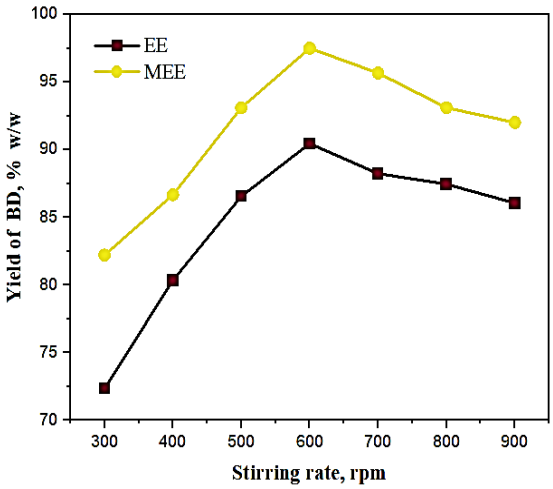


Fig.5. Effect of reaction period on EBD and MEBD yield. (1.0 wt. % for EBD and 0.80 wt. % KOH for MEBD; 8:1 Ethanol: GCSO and 6:1 mixed ROH: GCSO molar ratio; 65 ℃ for ethanolysis and 60 ℃ for alcoholysis; 75 minutes for ethanolysis and 60 minutes for alcoholysis).

The aforementioned consequences exhibited that the sort of alcohol involved in the TE reaction had a great effect on the BD. This conclusion has been drawn from the alcoholysis results, which disclosed that the GCSO conversion to MEBD has done at conditions lower than those needed to supply the supreme yield of EBD. These findings may be referenced to the higher solubility of the GCSO in mixed methanol/ethanol than ethanol, leading to a better mass transmission between the GCSO and alcohol.

Table 2 presents a comparison of the optimal conditions determined for the synthesis of the maximum yield of EBD and MEBD with those required to produce the same alkyl esters from varied oils in literature. Following the outcomes listed in **Table 2**, the yield of the EBD produced from GCSO was low and comparable in other cases to those declared for several raw oils in the literature. On the other hand, the yield of the MEBD synthesized from GCSO was greater than those reported for MEBD samples synthesized from varied oils in literature and comparable in other cases. Nonetheless, the variances in the typical conditions wanted to provide the highest yield of numerous alkyl esters prepared from varied precursors may be ascribed to many reasons, like the chemical composition of the authentic oil, its FFA content, the TE method employed, refining method applied for the purification of BD besides the heating mode utilized on the TE reaction.

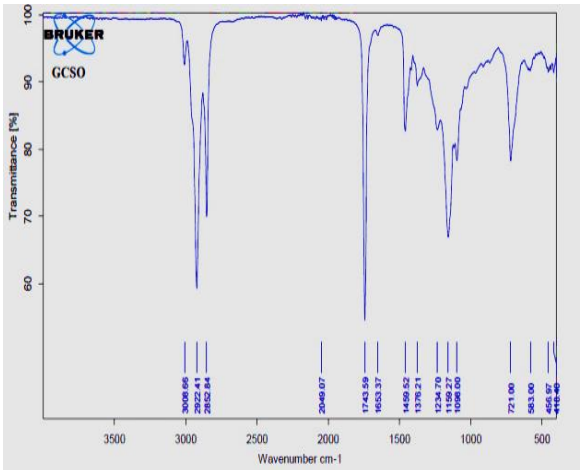
3.3 FTIR, ^{1}H NMR, and TLC analysis of EBD and MEBD

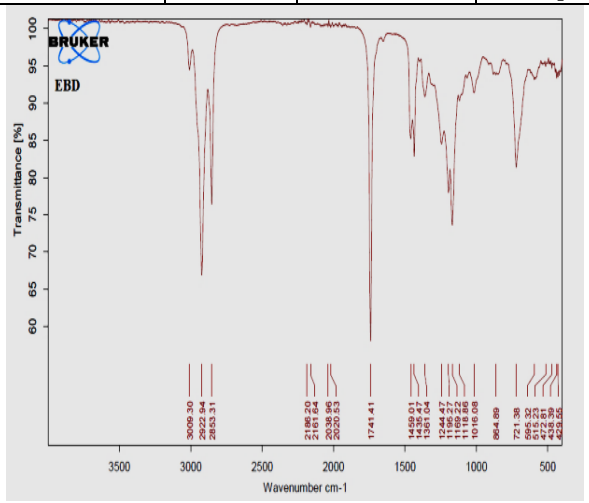
The GCSO and its derived EBD and MEBD were analyzed by FTIR in the range of 4000–400 cm^{-1} to identify the main functional groups present in them, and to recognize the alteration that occurred in the GCSO after the alcoholysis reaction, as illustrated in **Fig.6**. The asymmetrical and symmetrical stretching vibration of (–C–H) bond in both ($–CH_2$) and ($–CH_3$) groups, respectively, occurred at 2921 and 2852 cm^{-1}, while the bending vibrations of ($–CH_2$) and ($–CH_3$) aliphatic groups have seen in the region between 1600–1400 cm^{-1}. The stretching vibration of (–C=O) of carbonyl present in esters was beholden at 1741 cm^{-1}, while the stretching vibration of (–C–O) of an ester was observed at 1234 cm^{-1}. cm^{-1}.

As shown in **Fig.6**, the FTIR spectra of the GCSO and its BD samples were approximately similar because of the chemical similarity found in both the lipid and its derived esters. Still, several peaks in the GCSO, such as 1744.59 and 1159.27, and 901.8 cm^{-1} have respectively shifted to 1741.01, 1169.41, and 852.46 cm^{-1} in the BD. Also, some peaks in the parent GCSO, like those seen at 1459.52 cm^{-1} and 1098.0 cm^{-1} have vanished from the spectra and replaced by new bands at 1435.52 cm^{-1} and 1022.29 cm^{-1} in the MEBD spectra. The presence of these new bands approves the transformation of the original GCSO to its corresponding alkyl esters [43-45]

Table 2. A comparison of alcoholysis conditions of GCSO with those established for other BD samples in the literature

Feedstock	Catalyst % w/w	EtOH: Oil molar ratio	Temperature, °C	Time, minutes	FAEE Yield, % w/w	Reference
GCSO	**1.0 KOH**	**8:1**	**65**	**75**	**90.45**	**This study**
Chicken fat	1.0 KOH	8:1	70	90	90.0	[21]
Mixed Radish and apricot seed kernel oils	1.0 KOH	8:1	65	75	95.19	[25]
coconut oil	1.0 KOH	6:1	70	60	97.20	[31]
Palm oil	1.0 NaOH	6:1	70	60	96.0	[32]
Grape seed oil	2.0 CH_3CH_2ONa	6:1	70	180	90.30	[33]
Waste coconut oil	1.25 KOH	11.9:1	73	-	96.70	[34]
Arachis hypogaea oil	1.0 KOH	9:1	70	90	94.59	[35]
Feedstock	**Catalyst % w/w**	**ROH: Oil molar ratio**	**Temperature, °C**	**Time, minutes**	**Yield, % w/w**	**Reference**
GCSO	**0.80 KOH**	**6:1**	**60**	**60**	**97.50**	**This study**
Mixed Radish and apricot seed kernel oils	0.60 KOH	6:1 8	60	45	95.19	[25]
Waste fryer grease	1.0 KOH	9:1	25	30	> 90	[36]
Palm olein	1.0 KOH	6:1	50	60	98.10	[37]
Radish seed oil	1.0 KOH	6:1	60	60	93.33	[38]





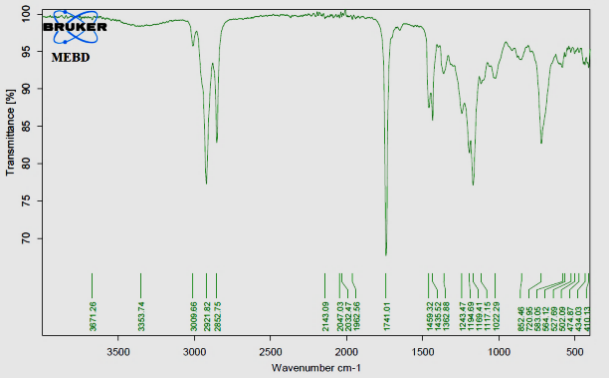


Fig.6. FTIR spectrum of GCSO and its BD samples synthesized at the typical reaction conditions.

The ^{1}HNMR spectroscopy was also implemented in analysing the so-created MEBD and EBD, as demonstrated in **Fig.7**. The NMR analysis revealed a complete loss of the intensity of the peaks referred to the triglyceride hydrogens at values of 4.0–4.3 ppm for both EBD and MEBD. On the other hand, a new peak was seen at 2.31 ppm, which belongs to the α-CH_2 protons. This peak observed in both fuels. For the EBD, the characteristic band, which assigns to the ethoxy moiety in the EBD was observed at 4.12 ppm. The appurtenance of this peak at this position assures the transformation of the GCSO to EBD[25].

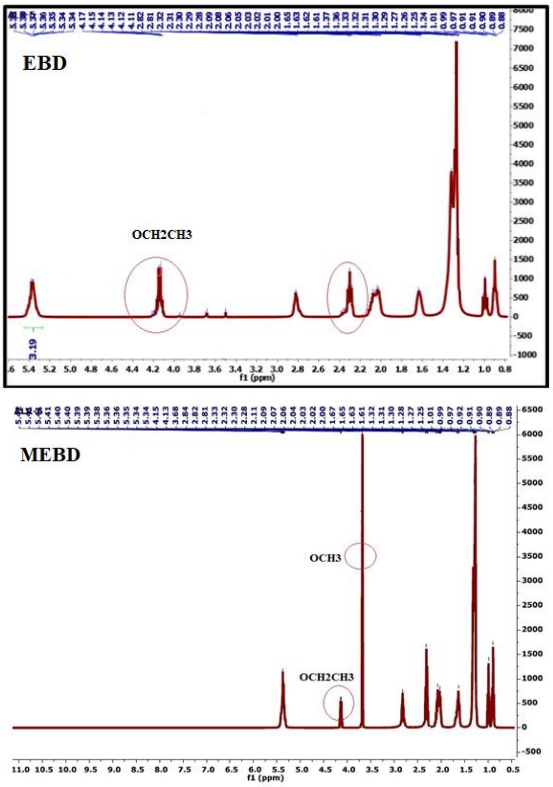


Fig. 7. ^{1}H NMR spectrum of EBD and MEBD and its BD samples synthesized at the typical reaction conditions

^{1}HNMR spectroscopy can be implemented as an easy and accurate tool to certify the best tool that
The formation of both methylic and ethylic routes in the MEBD was assured through the occurrence of strong singlet band at 3.67 ppm, which assigned to methoxy protons and a quartet peak appeared at 4.11 ppm assign to the ethylic protons in the ethoxylated fraction (-O-CH_2-CH_3)[45].

The TE action in addition to the BD purity was investigated by the TLC technique utilizing a silica gel plate. **Fig.8** illustrates that the pristine GCSO exhibited multiple spots t diverse positions. These spots belong to the mono, and di-glyceride as well as FFA and tri-glyceride. After the ethanolysis of the GCS, those spots become lighter, and a new spot at different position appeared, while in the MEBD, those spots disappeared and a new spot was also seen at new position. These consequences certified the transformation of the GCSO to its corresponding alkyl ester [21].

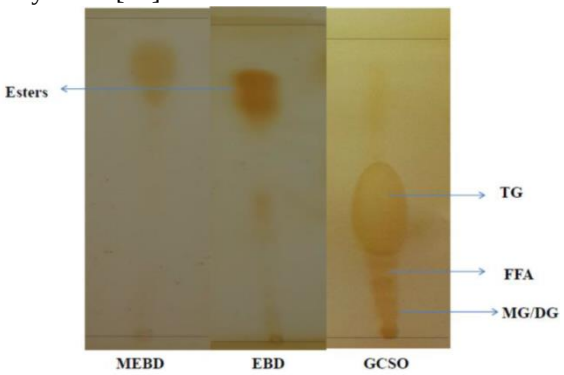


Fig.8. The TLC images of GCSC and EBD and MEBD.

3.4 Fuel properties evaluation

Table 3 summarizes the important fuel properties of EBD and MEBD derived from GCSO along with a comparison with ASTM D6751 standard BD. The D values of the produced esters ranged from 0.8587-0.8698 g/mL, which meet the specification fixed for the standard BD. The reduction in the KV of the EBD and MEBD was in the range of 81.72 and 84.53 %. Additionally, the KV values were satisfactory based on ASTM D6751. The pour point values of the resultant BD samples were low and thus affirmed their suitability for the utilization in the cold climate conditions. The FP values of the fuels ranged between 175°C and 178°C. The decrease in the FP values were between 25.85 to 27.08 %. Also, the values were greater than that of PD, and thus risks associated with transport and storage will be minor. The AV of the EBD and MEBD were below the limit given in the ASTM D6751 (0.50 max.). Moreover, the decrease in the values of both EBD and MEBD was 74.85 % and 80.19 &, respectively. The cetane

number of BD samples derived from GCSO was in the range of 49.60- 49.90, which satisfy the ASTM standard of (min. 47). These outcomes attribute to the high UFA content of the GCSO. The WC, SC, and TG of the attained BD samples reflect their high purity. It is clear from **Table 3 that** the properties of MEBD were superior to those of EBD. These remarks are due to the ester content of each BD sample, which is greater in the MEBD than that in the EBD.

Table 3. The most important fuel properties of EBD and MEBD produced from GCSO

Property	ASTM D6751	EBD	MEBD
Yield,% w/w	-	90.45±2.0	97.50±1.50
EC, (% w/w)	-	93.45±1.5	97.10±1.0
D @ 15.6°C,g/mL	0.9000	0.8689±0.0011	0.8587±0.0010
KV @ 40 °C, mm^2/sec	5.0	3.85±0.11	2.92±0.12
FP , °C	130	178 ±1.0	175±1.0
Cetane number	47 min.	49.90 ±0.50	49.60±0.50
AV, mg KOH / g oil	0.50	0.26±0.01	0.20±0.01
PP, °C	-	-4.0±0.50	-5.0 ±0.50
RI, @20°C	-	1.4505±0.0002	1.4503±0.0002
TG, wt. %	0.24	0.17 ±0.01	0.11±0.01
SC, ppm	5.0	1.72±0.11	1.12±0.12
WC, (%)	-	0.020±0.002	0.011±0.001

3.5 Properties assessment of (BD+PD) blends

The BD and PD are miscible at any percentages. This can enhance properties of both fuels. On this account, multiple blends of (MEBD+PD) in the range of (10-50 MEBD: PD) were prepared and examined for D, KV, AV, RI, and FP, as illustrated in **Fig.9**. The consequences presented in **Fig.9 (a, b, and c)**.

demonstrated that the D,KV, and FP values of PD raised with the increment of BD content in the prepared blends. These consequence attributes to the high molecular mass of BD compared to PD[48,13]. However, the D, KV, and FP values of the prepared blend still within the safe limits fixed by the ASTM standards. On the other side, the RI and AV values of PD declined with increasing ratio of BD in the prepared blends. This outcome may ascribe to the lower AV of the BD than that of PD. The higher AV in PD compared to PD may ascribe to the occurrence of some aromatic fractions in PD. The attained outcomes were in line with those announced by other authors[46]. Based on the above results, it is reasonable to use the prepared blends as fuels for diesel engines directly without the need for pre-modification of the engine.

3.6 Kinetics study

Numerous orders could be implemented to describe the kinetics of the TE reaction through the correlation between the temperature and time as well as its reliance on reaction rate. The constant of the reaction rate (k) can be attained through changing the reaction periods versus temperature, which their linear plot gives k. Various orders of the TE reaction were tested, and the model, which best fits the TE process was selected from the regression coefficient (R^2). Due the implementation of alcohol in excess, the reverse reaction can be neglected at the beginning of the reaction, where the rate of the reaction is zero. It was stated that the reversible reaction obeys many orders of the reaction based on the creation of the product. Therefore, it was presumed that pseudo first order reaction, which is expressed below is followed during the TE of lipids with an alcohol.

$$-\ln(1-X) = k\,.\,t$$

where, k, X , and t represent pseudo first order reaction rate constant, alcohol content, and the reaction time, respectively. Alcoholysis of GCSO was investigated at 323 K, 333 K, and 338 K, and the results have displayed that the rise of the temperature improved the rate constant for the forward reaction. When $-\ln(1-X)$ vs t is plotted, k will be produced from the plot's slope as illustrated in **Fig.10**, whereas values of the rate constants are listed in **Table 4**.

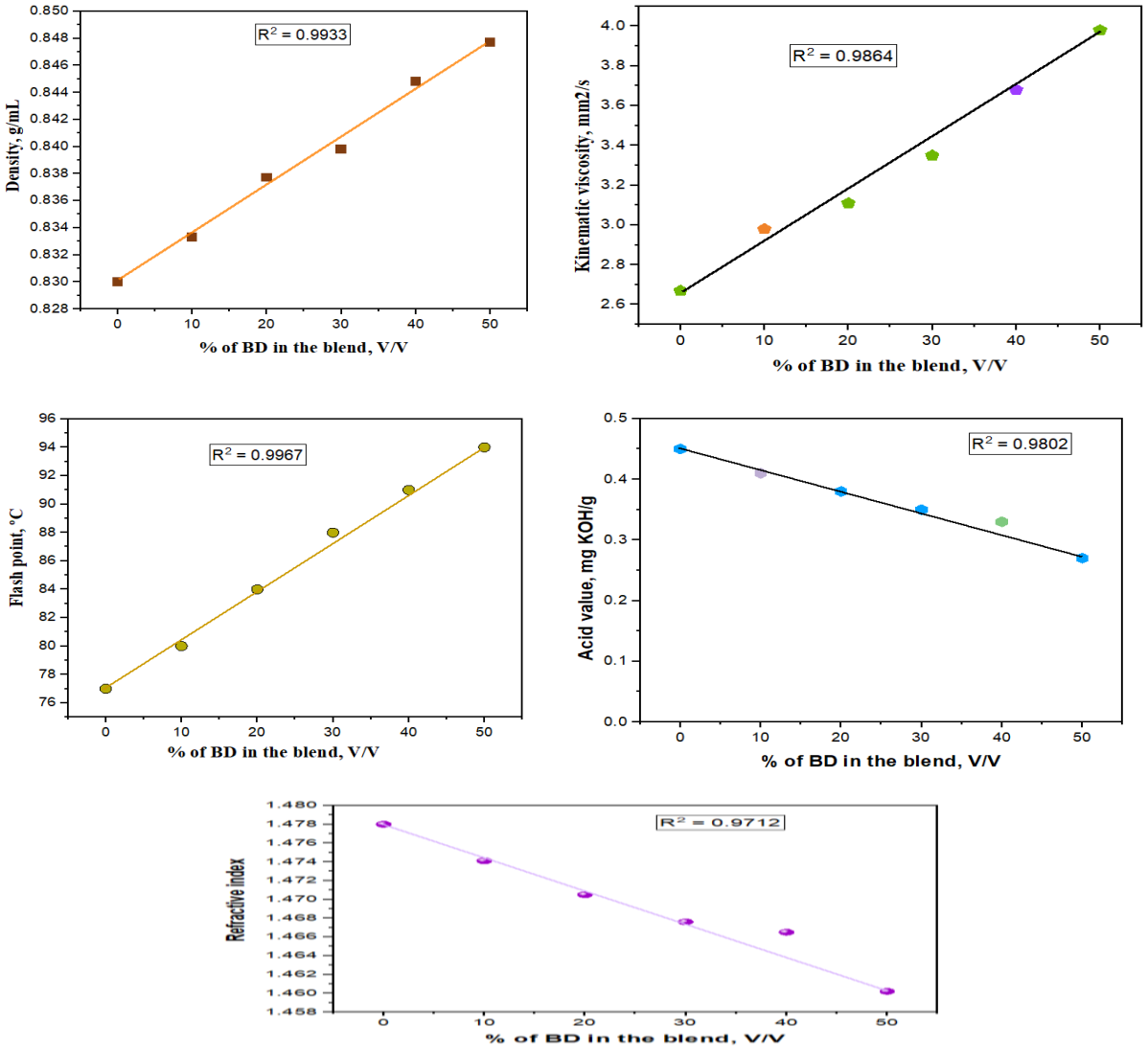
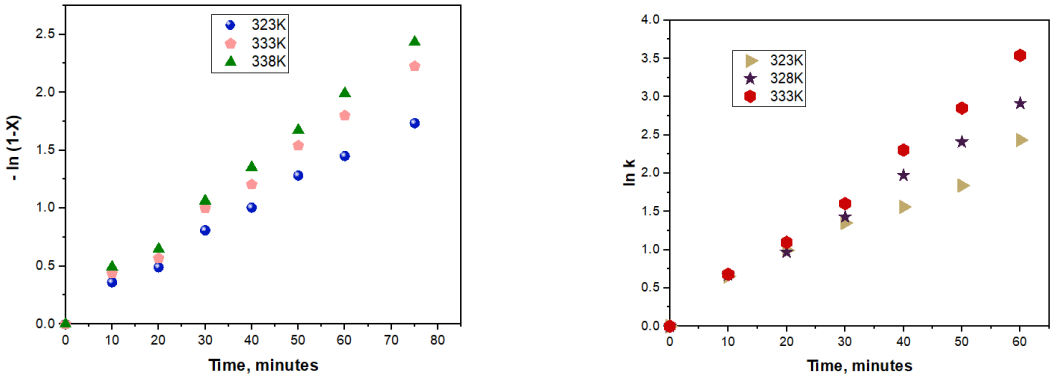


Fig.9. Effect of blending BD with PD on the properties of the latter.



1.0 wt. % KOH ; 8:1 Ethanol: GCSO molar ratio; 600 rpm **0.80 wt. % KOH ; 6:1 Alcohol: GCSO molar ratio; 600 rpm**

Figure 10. Plotting of - ln (1- X) versus time for alcoholysis of GCSO with ethanol and mixed methanol/ethanol alcohols.

Table 4. Rate constants of alcoholysis of GCSO with different alcohols at various temperature.

Transesterification with ethanol		
Temperature (°K)	***Rate constant, k (min^{-1})***	***R^2 value***
323	0.02296	0.9917
333	0.01316	0.9943
338	0.02913	0.9954
Transesterification with mixed alcohols		
Temperature (°K)	***Rate constant, k (min^{-1})***	***R^2 value***
323	0.03656	0.9755
328	0.04722	0.9956
333	0.05766	0.9960

The obtained consequences were in line with results performed by other authors [47,48]. The relationship among the reaction rate constant, temperature and activation energy can be given by the Arrhenius equation:

$k = Ae^{-Ea/RT}$ ……(4)

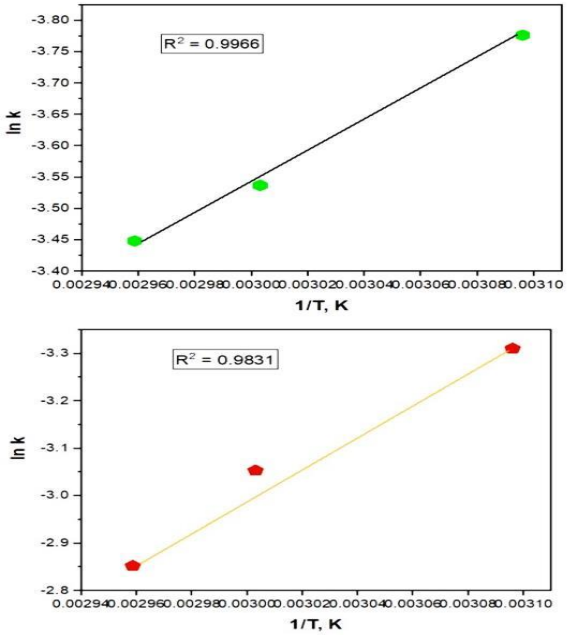
where A is the frequency factor, Ea is the activation energy, R is the universal molar gas constant, and T is the temperature (K). As the activation energy is temperature dependent, the rate constant at any temperature can be expressed using the following Eq.:

$\ln k = \ln A - Ea/RT$…….. (5)

The linear plot of *ln k* versus *1/T* has given the activation energy as depicted in **Fig.11**. The activation energy calculated for the ethanolysis of GCSO was found to be 30.71 kJ/mol, while its value was 32.93 kJ/mol for TE of GCSO with mixed methanol/ethanol alcohols. The obtained outcomes revealed the great catalytic activity of basic catalyst (KOH) and also support that reaction is chemically controlled and not by diffusion or mass transfer limitations [47,48].

4. Conclusion

The GCSO was studied as a possible raw material for the synthesis of various types of BD, namely ethylic BD and methylic/ethylic BD through alkali - catalyzed transesterification process with ethanol and mixed methanol/ethanol alcohols. The assessment of the GCSO exhibited that its physicochemical properties were comparable to those of other NEO. Besides, it possessed a very low acid value (1.01 mg KOH/g), which encouraged its alkali –catalyzed transesterification. Additionally, yields of EBD and MEBD exceeded (90.0%) at the typical reaction conditions. The fuel properties of GCSO alkyl esters, as well as (BD+PD) blends fitted well with the ASTM D6751 and ASTM D7467-17 standards, respectively. In addition, the lower KV values of the obtained alkyl esters comparing with the ASTM standards propose that their pumping will be easier. Therefore, they will be atomized easier, and will entirely be combusted in the diesel engines. The analysis of the as-produced fuels using FTIR and ^{1}H NMR spectroscopy, as well as TLC, affirmed conversion of the pristine GCSO to its alkyl esters. The alcoholysis of GCSO followed first-order kinetics. In conclusion, the produced fuels might be exploited as a potential alternative, sustainable, and environment-friendly fuels.



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Conflict of interest:

The authors declare no conflict of interest.

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