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Calcined Petroleum Scale- CaO a Cost-Effective Catalyst for Used Cooking Oil Methanolysis

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THE OBJECTIVE of the research aim to study biodiesel production from used cooking oil using calcium oxide derived from petroleum scale (PS) as catalyst in transesterification process. Calcium oxide based catalyst was obtained by calcinations of petroleum scale at 850ºC for 4 h. Calcined Petroleum scale catalyst (CPS-CaO) was characterized by different techniques such as: XRD, EDAX, N2-Adsorption /desorption and basic strength by Hammett method. Response surface methodology (RSM) was used for optimizing transesterification process depending on Independent variables, i.e. methanol to oil molar ratio (M:O), catalyst concentration and reaction time. The Optimal parametric values lead to maximum biodiesel yield (~97%) were obtained at Methanol:Oil molar ratio of 12:1; catalyst loading of 2.0 %w/v and reaction time of 2 h at constant temperature 65ºC. The results of this study showed a high performance, and the proposed experiment could be used as a new and innovative way to produce biodiesel in the future using cost-effective heterogeneous catalyst based on petroleum scale as a waste materials.

Keywords: Biodiesel, Heterogeneous catalyst, Petroleum scale, Used cooking oil.

Introduction

The persisting global energy crisis and the escalating greenhouse gas emissions at global levels from fossil fuel consumption have provided impetus for research and development in the areas of renewable energy and fuels production. Several renewable energy sources such as solar, nuclear, geothermal, wind and biomass have been explored and appropriate technologies have been developed in the past few decades to serve as carbon–neutral energy sources.

Among these renewable energy sources, energy production from biomass and its derived feedstock (i.e., oil) appears to be a very attractive option since the energy/fuel derivatives from these sources possess high energy content/ density with minimum environmental emissions. Biodiesel produced from biomass derived oils is also an excellent example of carbon–neutral transportation fuel. As such, it is critical to develop energy-efficient technologies for biodiesel production to enhance the environmental benefits, as well as the net energy benefits of the overall process [1].

On the biodiesel production, the homogeneous and heterogeneous catalysts can be used. The most homogenous catalysts such as NaOH, KOH and NaOCH$_3$ for examples are used in the biodiesel production [1, 2]. Due to decide to use homogeneous or heterogeneous, some critical factors should be considered such as production cost, environmental effect, catalysts reuse ability.

On the biodiesel production, the heterogeneous catalysts are easily removed from the reaction and often reused several times. Moreover, the production does not require the step of cleaning process [2]. Heterogeneous catalytic system can produce high quality esters and glycerol. This approach eliminates the need for an aqueous quench and also simplifying downstream separation steps of preparation, [2,3]. Further, the reusability and eco-friendly nature of heterogeneous catalyst make the biodiesel synthesis process to be more economical [3-6].

The major obstacle to biodiesel commercialization is its high cost, which is approximately 1.5 times higher than petroleum diesel fuel due to the reaction processes and catalyst used [7, 8].

The fabricating cost of catalyst could be a important factor in its industrial applications. Thus, the production of biodiesel calls for an efficient and cheap catalyst to make the process economic and fully ecologically friendly, accordingly reducing its price and making it competitive with petroleum diesel [9, 10]. To address this issue, the interest of using waste material (calcium carbonate) from several natural calcium sources such as raw materials for catalyst synthesis could eliminate the wastes and simultaneously produced an efficiency heterogeneous catalyst for transesterification. The discovery of inexpensive catalysts with high catalytic activity from the abandoned waste materials makes the biodiesel production process highly capable of competing on a cost and quality basis with the diesel fuel produced from petroleum, [11-13].

Scale formation is a severe problem encountering many industries including oil or gas production, water transport and power generation [14-16]. Scales are sparingly soluble salts formed in steam generators, boilers, pipes, cooling towers and other equipments related to water processes. Carbonate and sulfate scales of alkaline earth metals, especially calcium, have a particular concern because these salts are crystalline in most cases and demonstrate inverse solubility, i.e. their solubility decreases as temperature increases [17].

Calcite is the most common form of insoluble $CaCO_3$ [18]. The oxygen reduction reaction additionally leads to calcite scaling in the presence of Ca^{2+} and HCO_3 ions in the same medium according to Eq. (1) and Eq. (2) [19, 20]:

$$O_2 + 2H_2O + 4e \rightarrow 4OH \qquad (1)$$

$$Ca^{2+} + HCO_3 + OH \rightarrow CaCO_3 + H_2O \qquad (2)$$
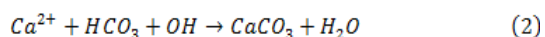
The non-productive expenses related to scaling were estimated at 1.5 billion Euros per year in France [21]. The same expenses were about 0.8 billion $US in Great Britain, 3 billion $US in Japan and 9 billion $ in the USA [22].

The use of such wastes for catalyst preparation has a significant potential for biodiesel synthesis: (1) the Ca-based catalysts have moderate catalytic activity in the transesterification reaction; (2) the use of those catalysts can partly prevent the environmental impact and disposal problem; (3) the catalysts can be prepared at low cost, which can reduce the high synthesis cost of biodiesel and make it an increased competitiveness; (4)

the utilization of those catalysts would produce a higher value applications for the recycled wastes. Particularly, in recent years, the use of Ca-based heterogeneous catalyst from a variety of calcium rich waste materials for biodiesel synthesis has been the subject of enormous investigations, [23].

Experimental

Materials and catalyst preparation

Petroleum Scale was collected from the local petroleum refining company in the east desert and gulf Area. Both methanol and sodium hydroxide were purchase from merck (Germany). All the experimental work was executed using analytical/ research grade chemicals. The petroleum scale derived CaO was synthesized from the petroleum scale via high temperature calcination process. Breifly, petroleum scale derived CaO was prepared by collection of petroleum scale formed in pipe line, crushing and drying in a hot air oven at 105ºC for 24 h. then the petroleum scale- CaO was calcined in a muffle furnace under static air conditions at temperatures of 850ºC for 4 h. Calcined scale was grinding to fine powder, screening through a stainless steel sieve 60 mesh, stored in a closed bottle to avoid the carbonation and water adsorption.

Catalyst characterization

X-ray diffraction (XRD) patterns were recorded by Panalytical X'Pert PRO system with the powdered samples less than 100 μm. The target was Cu Kα radiation in the diffraction angle (2θ) range of 5–70◦ at a sweep rate of 3◦ min⁻¹. Nitrogen adsorption-desorption isotherms were obtained using a conventional volumetric apparatus (Autosorb-1- MP) at 77K. The linear BET plots (SBET) was used to determine the equivalent surface area and the pore size distribution of samples was calculated by BJH method. The composition analysis of Calcined Petroleum Scale-850 was carried out with Environmental scanning electron microscope equipped with electron dispersive X-ray (EDX) (Philips XL30, Holland). The total basicity and base strength of the basic calcined petroleum scale derived CaO was determined using Hammett indicators method as reported by [24, 25]

Transesterification reaction

Used cooking oil (UCO) was dried in hot air oven at 110°C for 2 h to eliminate its moisture content. Transesterification was performed in a 250 ml three neck flask equipped with Magnetic stirrer, condenser and thermometer on

a hot water bath. This dried UCO was used for transesterification by using Calcined Petroleum scale derived CaO (CPS-CaO) as a heterogeneous catalyst. CPS-CaO was dispersed in methanol at 40°C for 30 min with constant stirring. After that UCO was added in this mixture and reaction was continued for 2 h at 65°C. After complete reaction, the catalyst was separate from the mixture, by catalyst settled at bottom with centrifuged at 2500 rpm for 15 min. Excess of methanol and traces of water were eradicated by rotary evaporator and anhydrous Na_2SO_4, respectively.

^{1}H-NMR spectra were used to identify and calculate the percent conversion of Used cooking oil methyl ester by using equation:

$$FAME\ content\ (\%) = \left(\frac{2A_{ME}}{3A\alpha_{CH_2}}\right) \cdot 100 \quad (3)$$

Where, A_{ME} indicates integration value of methyl ester proton and $A_{\alpha CH2}$ specifies integration value of methylene proton.

Optimization of FAME conversion using response surface methodology (RSM)

Response surface methodology (RSM) through Central Composite design (CCD) was used for optimization of FAME conversion in transesterification reaction by using Design Expert software version. Operating parameters i.e., methanol:oil molar ratio (A), catalyst concentration (B) and reaction time (C) were varied in order to maximize the FAME conversion (y). Table 1 indicated the coded and un-coded levels of Central Composite design (CCD) independent variables used for optimization of reaction parameters in transesterification of Used cooking oil. Experimental design consisting 20 experiments runs were shown in Table 2.

TABLE 1. Central Composite design (CCD) independent variables (coded and uncoded) for optimization of reaction variables in transesterification process.

Factors	Unit	Levels				
		-1.682	-1	0	1	1.682
Methanol/Oil MR		3:1	6:1	9:1	12:1	15:1
Catalyst conc.	%	0.5	1.0	1.5	2.0	2.5
Time	min.	30	60	90	120	150

TABLE 2. Experimental design for optimization of various reaction variables in transesterification reaction.

No	Methanol/ oil MR		Catalyst concentration (%)		Time (h)		Yield (%)
	Coded	Actual	Coded	Actual	Coded	Actual	
1	-1	6:1	-1	1	-1	60	30
2	1	12:1	-1	1	-1	60	52
3	-1	6:1	1	2	-1	60	44
4	1	12:1	1	2	-1	60	75
5	-1	6:1	-1	1	1	120	44
6	1	12:1	-1	1	1	120	86
7	-1	6:1	1	2	1	120	70
8	1	12:1	1	2	1	120	97
9	-1.682	3:1	0	1.5	0	90	55
10	1.682	15:1	0	1.5	0	90	92
11	0	9:1	-1.682	0.5	0	90	78
12	0	9:1	1.682	2.5	0	90	91
13	0	9:1	0	1.5	-1.682	30	60
14	0	9:1	0	1.5	1.682	150	95
15	0	9:1	0	1.5	0	90	90
16	0	9:1	0	1.5	0	90	88
17	0	9:1	0	1.5	0	90	91
18	0	9:1	0	1.5	0	90	90
19	0	9:1	0	1.5	0	90	89
20	0	9:1	0	1.5	0	90	91

These experiments facilitated to study the influence of each independent variable (methanol:oil molar ratio, catalyst concentration and reaction time) and relations between these variables on the FAME conversion i.e., dependent variable [26].

Biodiesel properties

The research studied properties of biodiesel products from each condition. They were analyzed by acid value (ASTM D664), density (ASTM D1298), flash point (ASTM D93), heat of combustion (ASTM D4809) [27].

Results and Discussion

Catalyst characterization
XRD patterns of catalyst

The crystallinity of the catalyst was characterized by XRD ray diffractograms were used to identify the crystallographic phase of scale before and after calcination as described in Fig. 1. Scale before calcination exhibits a diffractogram with several diffraction peaks. The main diffraction lines located at 26.24°, 27.23°, 38.39°, 42.93° and 45.86° are described to aragonite phase. After the calcinations step, the diffraction lines attributed to carbonate species disappear due to its liberation in the form of CO_2, arising new diffraction lines with a lower intensity than catalyst before calcination which suggests a decrease of the particle size for calcined catalyst. Thus, the diffraction lines located at peaks were obtained at 32.2°, 37.3°, 53.8°, 64.1° and 67.3°, have been assigned to quicklime, CaO.
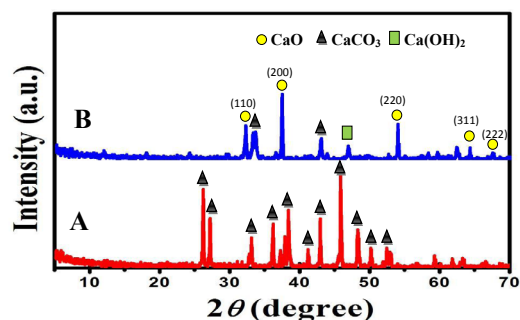

Fig. 1. XRD patterns of catalyst; a) before and b) after calcinations.

As shown in Fig. 1 small and low intensity diffraction peaks which are identical to $CaCO_3$ were detected for the calcined scale. Meanwhile, weak diffraction peaks were detectable for the present of $Ca(OH)_2$ and thus in order to prevent deterioration of the catalyst, it must be keep in desiccator to avoid any long exposure of the CaO with air.

Surface analysis (BET)

From the result, it can be seen that the calcined CaO possess a higher surface area (46.446 m^2/g) as a result of surface exfoliation. On the other hand, large pores daimeter (45.875 nm) CaO indicate that there are pores located established as carbon liberation during the catalyst calcinations. These properties of catalyst are favorable to be used in the liquid solid heterogeneous phase reactions due to the enough large reaction area in stirred reactor.

N_2 adsorption–desorption isotherms and pore size distributions of calcined scale CaO are shown in Fig. 2. The adsorption–desorption of unimodal catalyst is typical IV-type pattern with H2-type hysteresis loop (Fig. 2), which is a dominant characteristic of mesoporous structure with ink-bottle shape. The pore size distribution of the catalyst reveals a very narrow and unimodal pore size distribution in the range of mesoporous region with mean pore diameter of 45.87 nm (Table 3).

EDAX

The energy dispersive spectroscope (EDAX) spectra of 850°C calcined Petroleum scale catalyst was investigated (Fig. 3). EDAX displayed in Figure 3 showed that some elements (O, Ca, P, Cl) could be found by the result of EDAX analysis and these strong and sharp peaks at E = 0.6 corresponds to O, while the two at E = 3.8 and 4.0 keV were correspond to Ca elements.

Basicity of catalyst

Due to base sites over the heterogeneous catalysts are the active centers for transesterification, therefore it is important to determine the total basicity and base strength of the basic heterogeneous catalysts obtained from the calcination of the scale. As a result, it can be concluded that the basic strength of the CaO catalysts obtained after calcination of petroleum scale lie in the range of 9.8<H<17.2, which is in good agreement with the literature [28]. Therefore, the surface basicity of these catalysts could be attributed to the strong basicity of the metal–O groups (Lewis base) which is considered as a strong base site for transesterification reaction [29]. The total basicity of the catalysts which was evaluated by the Hammett indicator method is summarized in Table 4. It was found that basicity of the catalysts is increased with the increasing calcination temperature from 400 to 850°C, which is resulted the transformation of $CaCO_3$ to CaO.
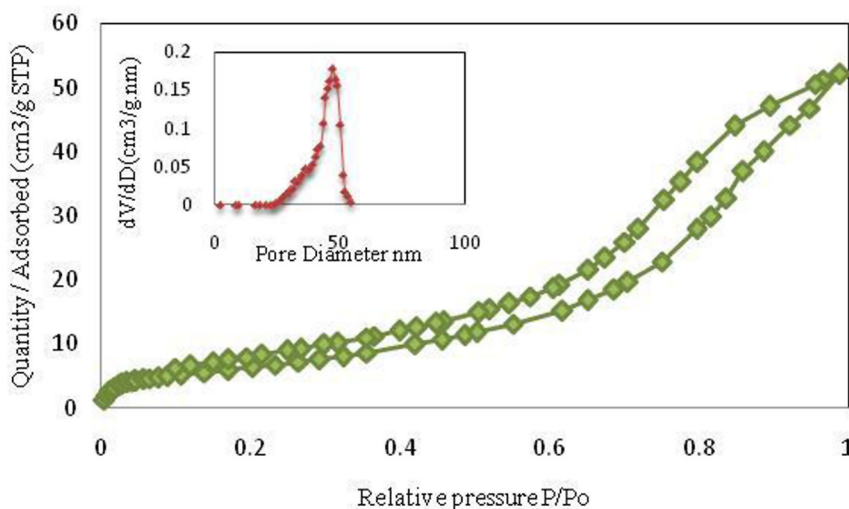
Fig. 2. BET of petroleum scale-850 catalyst

TABLE 3. The BET specific surface area, average pore diameter and pore volume of calcined petroleum scale.

Sample	BET surface area (m²/g)	Pore diameter (nm)	Pore volume (cm³/g)
Scale-850	46.446	45.875	0.087

Element	Wt%	At%
O k	18.74	36.30
Ca k	77.11	59.63
Si k	0.99	0.95
P k	0.94	0.95
S k	0.96	0.92
Cl k	1.26	1.10
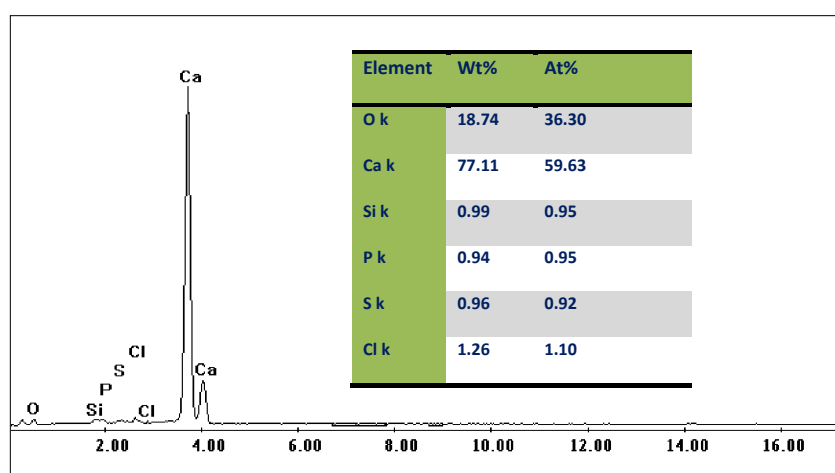
Fig. 3. EDAX of CaO based scale.

TABLE 4. Basicity and basic strength of the calcined scale catalyst.

Samples name	Basic strength of the samples (H)	Total basicity (mmol/g)
Scale-400	7.2<H<9.8	2.28
Scale-600	9.8<H<17.2	3.74
Scale-850	9.8<H<17.2	6.15

According to Table 4, the stronger basicity of the scale-850 catalyst was found, with high total basicity (6.15 mmol/g) which was regarded as the strong alkaline sites of basic CaO. The other scale-calcined (scale-400 and scale-600) proved lower bascity more than scale-850, where the basicity may be due to the calcinations temperature. The difference of catalytic activity in biodiesel production of the basic catalyst was attributed to the different basicity [30].

Transesterification reaction

The response surface plot of %FAME from various combinations of catalyst concentration, methanol-to-oil molar ratio, and reaction time is shown in Fig. 4 and represents the graphical three-dimensional surface plot of Eq. (4) [31].

$FAME\ Yield\ (\%)$
$$= 90.50 + 13.56A + 7.09B + 11.41C - 0.62AB + 2.13AC + 0.13BC - 9.09A^2$$
$$- 5.20B^2 - 7.67C^2 (4)$$

Response surface plots indicate the interactions between the variables and FAME conversion. Based on these results, maximum FAME conversion of 97.98% was predicted through software which is close to experimentally obtained results. The optimized reaction conditions obtained were, molar ratio of 12:1 (methanol:oil), 1wt% catalyst and 120 min of reaction time.

Methanol:oil molar ratio was varied at 3:1 to 15:1 in order to study the influence of methanol:oil molar ratio on FAME conversion. Figure 4.1 shows surface plots of combined effect of molar ratio and catalyst concentration on FAME conversion respectively. It has been observed that rise in methanol amount more than 12:1 M ratio reduced the FAME conversion and this shows difficulty in separation of methyl ester and glycerol due to emulsion formation [32].
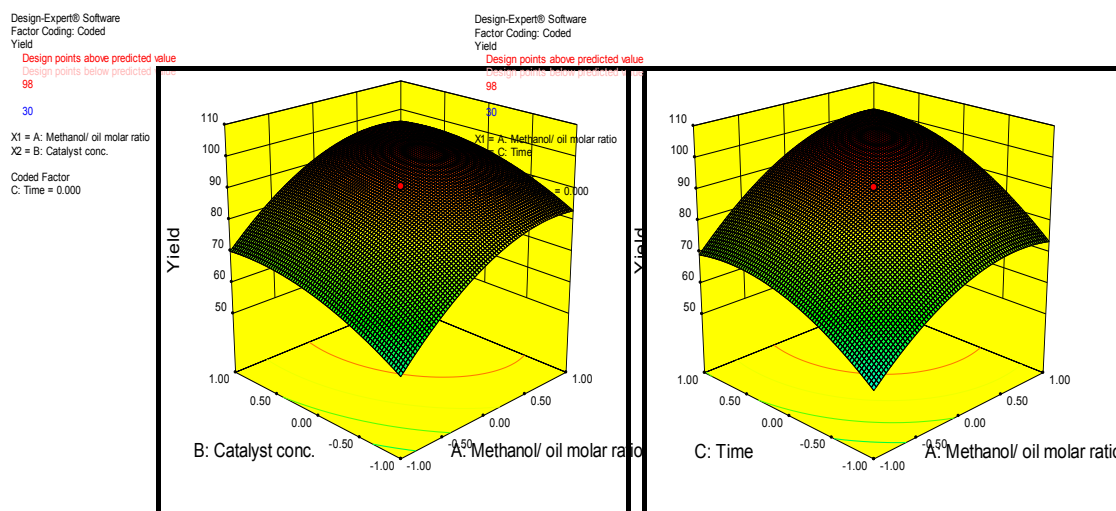

Fig. 4.1. Effect of molar ratio and catalyst concentration on yield

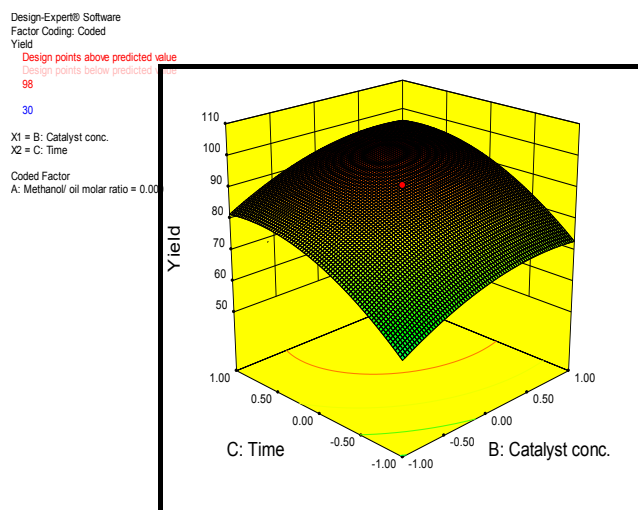**Fig. 4.2. effect of molar ratio and time on yield**

Fig. 4.3. Effect of catalyst concentration and time on yield

Fig. 4. The response surface plots and variables interactions.

FAME conversion was obtained maximum for 12:1 M ratio (methanol:oil), 2wt% catalyst and 120 min of reaction time condition as shown in Table 2 and this confirms that these are the optimum reaction parameters for transesterification reaction. This data displays that excess amount of methanol in transesterification reaction will results into the rise of product, whereas other side of excessive methanol will assist to increase glycerol solubility which results in lower conversion [33].

Figure.4.2 represents surface plots of combined effect of catalyst concentration and reaction time on FAME conversion correspondingly. Catalyst concentration was varied from 0.5 wt% to 2.5 wt% in order to distinguish the effect of catalyst concentration on FAME conversion. From Fig. 4, it has been observed that for a fixed reaction time, increment in catalyst concentration results in decrement of FAME conversion.

In addition to this, Table 2 also shows FAME conversion decrement with increase in catalyst concentration up to 2.5 wt%. FAME conversion was maximum for the optimum reaction condition 2.0 wt% catalyst. The decrement observed in the FAME conversion with rise in CPS-CaO concentration was due to saponification through excessive catalyst amount [34]. In addition to this, excessive catalytic amount can lead to emulsion formation, which results with viscosity increment of methyl ester with inducing gel formation [35].

Surface plot of combined effect of reaction time and molar ratio (methanol:oil) is shown in Fig. 4.2. Reaction time was varied from 30 min to 150 min to study the influence of reaction time on FAME conversion. From Fig. 4.3, it has been clear that for fixed molar ratio, increase in reaction time increases FAME conversion and in addition to this Table 2 also displays that maximum FAME conversion was observed for the reaction condition of 12:1 M ratio (methanol: oil), 2.0 wt% catalyst concentration and 120 min of reaction time. Hence this condition was optimum reaction condition observed for transesterification reaction.

Characterization of product biodiesel by FTIR analysis.

The FTIR spectra of used cooking oil and methyl biodiesel are shown in Fig. 5. Because the UCO and Biodiesel compounds contain nearly identical chemical groups. As can shown, these spectra (1,850–950 cm^{-1} interval) are very similar; however, differences were very clear between 1,500 and 1,000 cm^{-1}. Where the C–O stretching vibrations in UCO produce a peak at 1,163 cm^{-1} and two peaks in biodiesel at 1,169 and 1,195 cm^{-1}. The peak at 1,195 cm^{-1} is related to the presence of CH$_3$ groups near the carbonyl groups in Fatty acid methyl ester [36]. Also, The peak located at 1,375 cm^{-1} which correspond to CH$_2$ in UCO and 1,436 cm^{-1} in biodiesel, which correspond to CH$_3$ bending vibrations, and show clearly evident of used cooking oil conversion
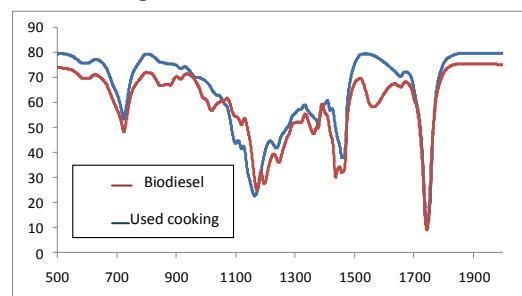

Fig. 5. FTIR of used cooking oil and biodiesel.

H-NMR

Figure 6 Represents the ^{1}H-NMR spectrum of the waste cooked oil and the conversion of triglycerides to fatty acid methyl esters catalyzed by calcined scale was analyzed using 1H NMR and it is shown in Fig. 7. The characteristic peaks of methoxy protons as a singlet at 3.667 ppm and a-methylene protons as a triplet at 2.306 ppm were observed. These two peaks are the distinct peaks for the confirmation of methyl esters.

The other peaks observed were at 0.871 ppm due to terminal methyl protons, a strong signal at 1.308 ppm arises from the methylene proton of the carbon chain, a multiplet at 1.6 ppm related to b carbonyl methylene protons, and a signal at 5.354 ppm due to olefinic hydrogen. Biodiesel purity can be seen from the large percentage of the methyl ester. Perfect formation of methyl ester will happen if it does not appear peak around proton cluster glycerides.^{1}H-NMR spectra of biodiesel, does not show peak at 4 ppm, this means that it does not appear proton groups glycerides in the biodiesel product [37].

Physicochemical properties of FAME derived from used cooking oil

Physicochemical properties of FAME derived from used cooking oil was studied as per ASTM D-6751 and EN 14214 standard as shown in Table 5. The acid value of used Cooking oil was obtained to be 1.31 mg of KOH per gm while that of methyl ester was 0.30 which was within ASTM limit. Density of used cooking oil was 0.897 g/cm^3

and of methyl ester 0.87 g/ cm³ whereas kinematic viscosity of Used Cooking oil and its methyl ester was 35.4 cSt and 4.5 cSt respectively and were within ASTM standard range. Cetane number and calorific value of Used Cooking oil and that of methyl ester were 45, 48, 36.6, 42.87 MJ/Kg respectively and were within ASTM limit. Flash point of Used Cooking oil and its methyl ester were 225 °C, 130 °C, respectively and was as per ASTM standard. Ash content of used cooking oilwas 0.08% whereas that of methyl ester was 0.02%. As shown in table all these physicochemical properties were compared with petro-diesel. From these results it has been observed that CPS-CaO utilized as a heterogeneous catalyst in this work has stupendous potential for FAME production on large scale and also has capability to substitute petrodiesel as displayed in Table 5.
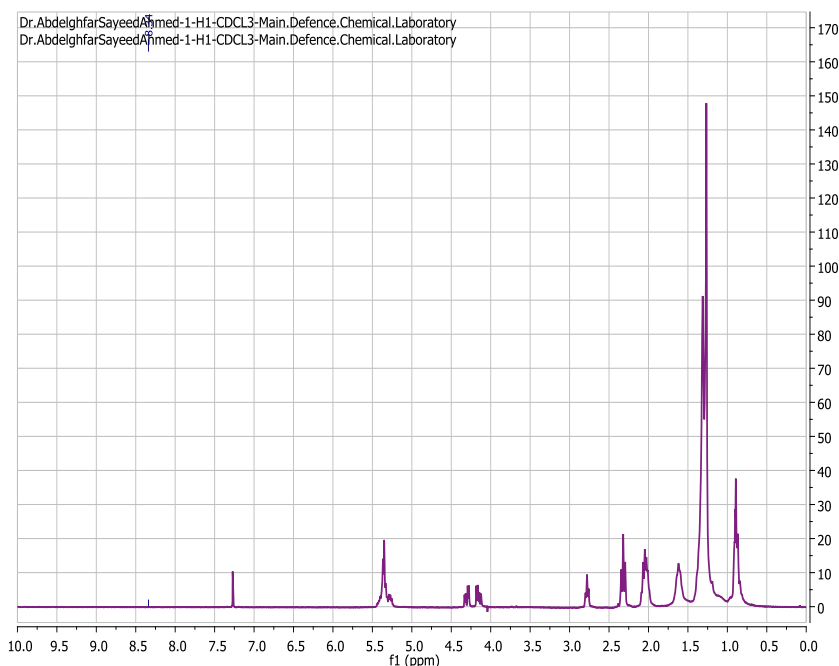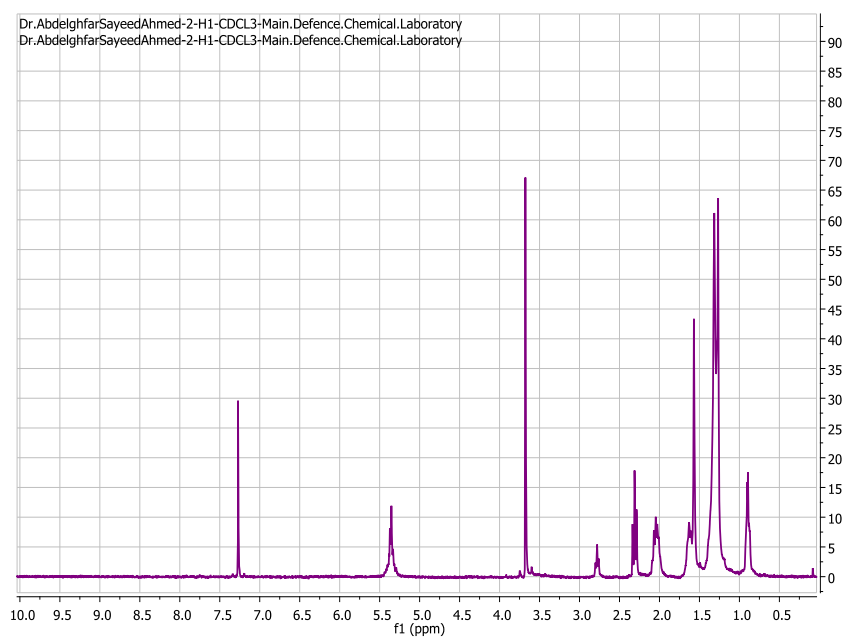

Fig. 6. H NMR of used cooking oil.


Fig. 7. H NMR of Biodiesel

TABLE 5. Physicochemical properties of the used cooking oil and produced biodiesel according to international biodiesel standard.

| Content	Unit	UCO	ASTM D-6751	EN 14214	Prepared biodiesel
Viscosity	mm³/s	35.1	1.9-6	3.5-5	4.5
Moisture content	Wt (%)	1.2	< 5.05	< 5.05	0.2
Flash point	ºC	225	< 120	< 120	130
Cloud point	ºC	3	-3 to 15	-	-1
Pour point	ºC	0	-5 to 10	-	-2
Cetane number		45	47-65	51-120	48
Density	g/cm³	0.897	0.82-0.9	0.86-0.9	0.87
Calorific value	MJ/Kg	36.6	35 min.		42.82
Acid value	mg KOH/g	1.31	< 0.8		0.31
Ash content	%	0.08	< 0.02		0.02

Mechanism of CaO catalyzed reaction

As talked about in past segments, the scale is essentially made out of calcium carbonate and obtaining CaO by various impetus planning strategies as the main driving force behind the production biodiesel. Examinations have additionally been done by taking fabricated CaO for biodiesel creation. More investigations on the role of fabricated CaO was completed by [38, 39] and the proposed mechanism for CaO amid transesterification is as per the following:

Step 1: Dissociation of CaO and methanol while activation of the catalyst (Eqs. 5 and 6).

$$CaO = Ca^{2+} + O^{2-} \quad (5)$$

$$O^{2-} + CH_3OH = OH^- + CH_3O^- \quad (6)$$
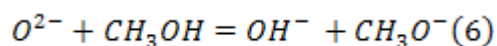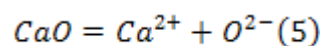
Step 2: Methanol and hydroxide ion reacts to form methoxide anion (Eq. 7)

$$OH^- + CH_3OH \leftrightarrow H_2O + CH_3O^- \quad (7)$$
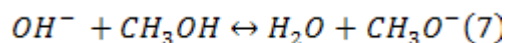
Step 3: Carbonyl carbon of triglyceride is attacked by the methoxide anion formed in the previous reaction to form tetrahedral intermediate. This is followed by the rearrangement of the intermediate molecule to form methyl ester and diglyceride (Eq. 8) (**Scheme 1**).
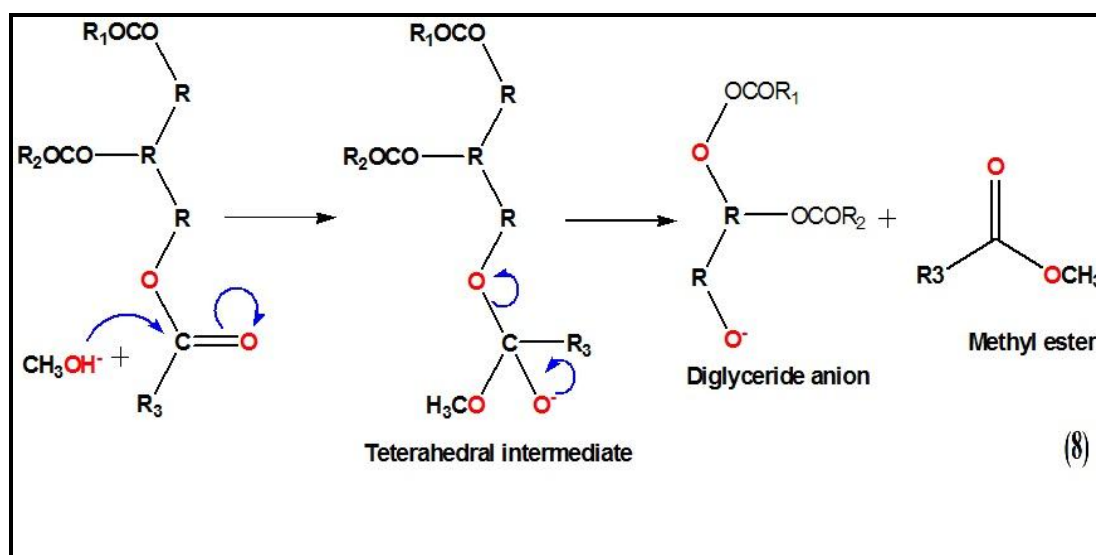
Scheme 1. Transesterification reaction of waste cooking oil and methanol with Calcined Petroleum Scale- CaO catalyst.

Step 4: The methoxide anion attack on another carbonyl carbon atom in diglyceride, forming another mole of methyl ester and monoglyceride. This continues till a total of three moles of methyl esters and a mole of glycerol is formed during the reaction [39].

Calcined Petroleum Scale- CaO catalyst recyclability

The Calcined Petroleum Scale- CaO catalyst reusability and stability in the biodiesel production is the most important parameter for economical stability of biodiesel. The Calcined Petroleum Scale- CaO catalyst was collected washed with n-hexane and calcinated at 800ºC, After completion of the each transesterification reaction process. then Catalyst recyclability was investigated by repeating the transesterification reaction with the same sample.

Five successive catalytic cycles was utilized to test catalyst recyclability under the same experimental (1:12 oil to methanol ratio, 2% catalyst amount, 90°C and 2 h) and regeneration methods. As could be seen from Fig. 8, partial loss in catalytic activity was observed during first three runs, however, a reduction in biodiesel yield was observed in fourth and fifth cycle. The loss of the catalytic activity could be due to the blockage of active sites because of the absorbed organic molecules moisture, CO_2 and another reason was partial leaching of the active species from the catalyst [40].
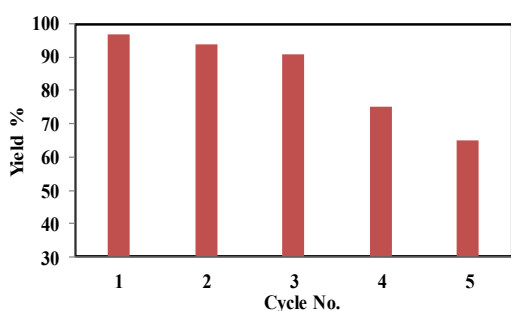

Fig. 8. Stability of Calcined Petroleum Scale- CaO catalyst for five runs of transesterification of waste cooking oil into biodiesel.

Conclusions

The CaO derived from calcined scale at 850ºC and it was a good heterogeneous base catalyst for transesterification of used cooking oil as raw material. Therefore calcination–hydration–dehydration treatment is a sufficient method to increase the catalytic activity of the

scale possessing calcium carbonate as their main constituent. From the study, it was found that the optimal conditions were catalyst loading amount of 2 wt.%, methanol/oil molar ratio of 12:1, reaction temperature of 65 ºC, reaction time 120 min. ME yield of 97.0%. They were compared with standard properties such as density, acid value, flash point, heat of combustion.

Interestingly, it has been found that the scale formed in pipe line contains large amount of calcium carbonate ($CaCO_3$) which can be directly transformed into calcium oxide (CaO) by a simple calcination under air at high temperatures without any additional chemical treatment, making the overall process more cost-effective and eco-friendly, as compared to the previous works.

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