



Highly Crystalline Heterogeneous Catalyst Synthesis from Industrial Waste for Sustainable Biodiesel Production



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IRON and steel factories in Egypt have been suffering from fine calcium oxide (CaO) emission which is considered as a waste and leads to many health hazards. An alternative, this waste (fine CaO) has been utilized as a low-cost, sustainable source of calcium sulfate impregnated sulfated silica (CSISS) nano-catalyst production. This hybrid catalyst has been utilized as a heterogeneous catalyst for biodiesel production from waste frying oil (WFO). In this study, the linear, quadratic and interaction effects of the main four factors that affect the biodiesel yield were investigated. An empirical model has correlated the experimental results and used to optimize and predict the biodiesel production yield. The model showed good agreement of about 93% with the experimental results and revealed that the optimum operating condition is: 50% SiO₂ content, 20 min reaction time, 8:1 methanol to oil molar ratio and 3% catalyst weight at 55°C and 300 rpm stirring speed to produce 99% biodiesel yield. The physicochemical properties of the produced biodiesel were analyzed. The combustion exhaust emissions of the produced biodiesel /petrodiesel blends have been evaluated. The techno-economic analysis elucidated that, the produced biodiesel is a strong competitor to petrodiesel with a cost of US\$0.488/L.

Keywords: Biodiesel production, Multivariate regression analysis, Techno-economic analysis, Waste frying oil, Heterogeneous catalyst, Exhaust emissions.

Introduction

The energy demand has been expanded to a greater extent due to industrial growth and the accelerated population rise. Energy diversification is considered as an insurance

policy against geopolitical risks and government insecurity about fossil fuel securing and costs [1,2]. Over the past twenty-five years, biodiesel has gained great international attention as an alternative source of fuel to address the fossil

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Received 1/8/2019; Accepted 17/9/2019

DOI: 10.21608/ejchem.2019.15471.1943

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fuels drawbacks such as fast diminishing, price hike, environmental and human health hazards. In addition, biodiesel has many merits like non-toxicity, high degradability and low emission of carbon monoxide, unburned hydrocarbons, and particulate matter[3-7]. Biodiesel is a mixture of fatty acid alkyl esters that can be blended with petrodiesel fuel in different proportions and directly used in existing compression ignitions diesel engines without any modifications[8-10]. Any fatty acid source, animal fats and vegetable oils can be used as a feedstock for biodiesel production [11,12]. Using of WFO as a biodiesel production feedstock has many advantages as it provides a market for the waste oils that disposed incorrectly and lead to sewage clogging, avoid the competition between food and fuel and reduce the biodiesel production cost[13-15]. Biodiesel has been successfully produced from animal fats and vegetable oils using acidic and/or basic homogeneous catalysts, mainly sulfuric acid and potassium or sodium hydroxide[16, 17]. Traditional homogeneous catalysts possess advantages including high conversion values with mild reaction conditions. However, their use leads to several disadvantages such as corrosion, separation and purification difficulties and the catalyst inability to be reused[18-20]. Thus, the total cost of the biodiesel production based on homogeneous catalysis is not yet sufficiently competitive as compared to the cost of petrodiesel[21]. One of the means to address the hurdle of the higher priced is to develop low-cost heterogeneous catalysts that could eliminate the additional running costs associated with the aforementioned separation and purification stages. Another option for cost reduction is to reduce the cost of processing through optimizing the process variables that affect the biodiesel yield and purity. Calcium oxide (CaO) is a candidate for the heterogeneous catalysts. From the literature survey, many researchers utilized CaO in biodiesel production. Some of them utilized analytical grade CaO and the other synthesized CaO from wastes calcination such as; eggshell, bones, mollusk shell, oyster shell, and mud crab shell to reduce the CaO cost[22, 23].

Calcium oxide CaO is essential in the iron and steel industry, where it is used in two important stages; slag formation and product refining. The desired grain size of CaO in this industry is 80 – 40 mm and grain size < 40 mm is considered as a waste. Alexandria iron and steel Co. produces about 250 ton CaO/day using twin shaft parallel

flow regenerative kilns as shown in Fig.1. About 30 ton of them has grain size <40 mm and considered as a waste because it pollutes the working area and leads to many health hazards such as; eyes, nose, throat and skin irritation and cause bronchitis and pneumonia. Whereas, the permissible exposure limit of CaO is 5 mg/m³ of air averaged over an eight-hour work shift according to current OSHA standards.

According to the previous studies and the literature, CaO leads to high biodiesel production yield due to its high activity. Nevertheless, CaO dissociation during the reaction with methanol is responsible for leaching out the soluble active Ca component which affects the catalytic activity and the product quality. The leached out Ca²⁺ will react with the remaining FFAs and lead to soap formation and catalyst deactivation[24]. Hence, some researchers tend to convert CaO to CaSO₄ to be used as a heterogeneous catalyst for biodiesel production and avoid the CaO drawbacks[25]. On the other side, some researchers tend to impregnate CaO on high surface area materials such as zeolite[26], alumina[27], and silica[28-30] to avoid CaO leaching and accelerate its catalytic activity. Among these catalyst supports, silica has attracted much attention due to its excellent properties such as high surface area, good thermal stability and its unique large pore structure characteristic, which reduce mass transfer limitations and allow a high concentration of active sites per mass of material[31].

This work aims to offer binary environmental protection by utilizing the fine CaO as a sustainable raw material for heterogeneous catalyst synthesis to be used for biodiesel production to reap the benefits of the high catalytic activity of CaO and avoid its environmental drawbacks. In addition to making benefit from WFO that leads to several problems in the environment and the sewage system due to its incorrect disposal and use it as a sustainable biodiesel feedstock. Hence this work presents a treble facet solution 1) environmental protection, 2) reduce the biodiesel production cost and 3) sustainable biodiesel production. The catalyst has been synthesized with different CaO to SiO₂ weight ratios to investigate the effect of SiO₂ content on biodiesel production yield.

Multivariate regression analysis and correlation analysis are used as tools to assess the effects of the independent factors on the dependent variables. The main advantage of this statistical

technique is to reduce the number of experimental runs required to generate sufficient information for a statistically acceptable result [32, 33]. The effect of different operating conditions on the biodiesel production yield has been investigated experimentally by manipulating their values over considerable range, such as; reaction time (from 30 to 180 min), methanol to oil molar ratio (from 3:1 to 15:1), catalyst loading (from 1 to 9% w Catalyst / w Oil). The experimental results have been used as the input data to perform a multivariate analysis.

Multivariate regression model and ANOVA have been used to optimize the reaction parameters and predict the biodiesel yield. The proposed model has been used to reveal which variable is much more important than the others and to which extent, and vice versa. It also was used to explore the hidden relation between the different operating variables to get maximum biodiesel production yield even with the shortage of one of the operating variables regarding an economic study. The optimum catalyst has been characterized by FTIR, XRD, SEM, EDX and particle size analysis. The catalyst ability for reusing has been tested. Furthermore, the produced biodiesel yield is evaluated and the chemical and physical properties are determined to be compared with the universal standards. Then the biodiesel is blended with petrodiesel and these blends have been subjected to a diesel engine to evaluate the blends performance and measure the exhaust gas emissions resulting from their combustion and compare them with petrodiesel.

Materials and Methods

Reagents and chemicals

Low-quality WFO with high free fatty acids (FFA) content was supplied from Chipsey Company. The oil acid value is 6.4 mg KOH/g oil, its physical properties and fatty acid composition are summarized in **Table 1**. Calcium oxide was supplied from Alexandria iron and steel company, where the twin shaft parallel flow regenerative kilns are used for CaO production from limestone calcinations. Calcium oxide with grain size 80 – 40 mm has directed to the electric arc furnace and ladle furnace. Calcium oxide with grain size < 40 mm is considered as a waste and a pollutant as shown in **Fig. 1**. This fine CaO has been utilized in the catalyst synthesis. Silica and H₂SO₄ were supplied in the commercial grade.

Catalyst synthesis

The catalyst has been synthesized with different weight ratios of SiO₂ to CaO (87.5, 75, 62.5, 50, 37.5, 25, 12.5) using the impregnation method. Calcium oxide and silica were slowly added to 1 M H₂SO₄ solutions to make a paste. The mixture was vigorously stirred for 6 h and 600 rpm at ambient temperature. The white produced precipitate was filtered, washed and calcined at 300°C for 3 h.

Biodiesel production

Anhydrous methanol was added to the esterified WFO in presence of CSISS composite as a heterogeneous catalyst. The reaction was carried out in a 250 ml three-neck round bottom flask equipped with a water-cooled reflux condenser and a magnetic stirrer. The reaction temperature was adjusted at 55°C by a water bath.

TABLE 1. Physical properties and fatty acid composition of WFO.

Physical properties	
Kinematic viscosity at 40°C, cSt ^a	41.107
Density, kg/m ³ ^b	0.9168
Flash point, °C ^c	218
Pour point, °C ^d	6
Fatty acid composition, wt. % ^e	
Palmitic	29.75
Stearic	3.08
Oleic	34.01
Linoleic	11.16
Linolenic	8.12
Arachidic	10.98
Behenic	2.06

^aASTM method: D -445.

^bASTM method: D -1298.

^cASTM method: D -93.

^dASTM method: D -97.

^eDetermined by GC.

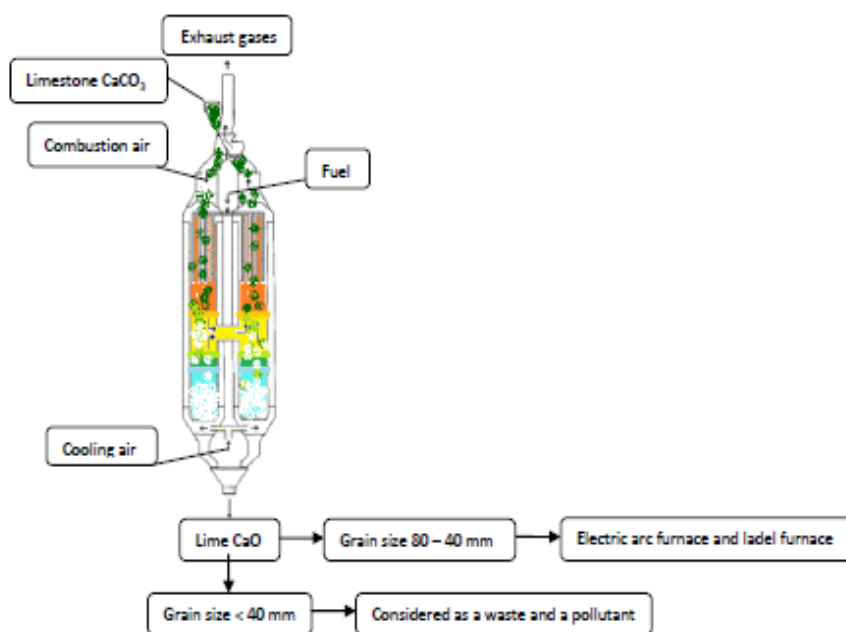


Fig. 1. Calcium oxide production cycle in Alexandria iron and steel Co.

Statistical analysis

The silica content percentage, reaction time, methanol to oil molar ratio and catalyst loading were the independent variables selected to optimize the biodiesel production operating conditions. The ranges of variables are chosen around the typical value used in industrial production. The collected 21 experiments were replicated twice and data were statistically analyzed using ANOVA to find the suitable model for the % biodiesel production yield as a function of the aforementioned four variables and evaluate the significance of the investigated factors effects and interactions. The significance of the variables and their interactions was assessed by the F-test method with a confidence level of 95% and *P*-Values of less than 0.05[34]. Significant values were assessed with Duncan's multiple range tests. The coded values of the independent variables were determined by the following equation:

$$X_i = \frac{X_i - X_0}{\Delta X} \quad (1)$$

where X_i is the coded value of the i^{th} variable, x_i is the encoded value of the i^{th} test variable and x_0 is the encoded value of the i^{th} test variable at the center point[35].

The experimental data were analyzed by a first-order model, but a curvature structure was

detected. A second-order polynomial is used in this study, with a general equation:

$$Y = a_0 + \sum_{i=1}^n a_i x_i + \sum_{i < j}^n \sum_{j}^n a_{ij} x_i x_j + \sum_{i=1}^n a_{ii} x_i^2 \quad (2)$$

where Y is the % biodiesel production yield, a_0 is the equation intercept, n is the number of variables studied and optimized in the experiments, x_i and x_j are the coded independent variables and a_i , a_{ij} and a_{ii} are the linear, interaction and quadratic constant regression coefficients respectively[36].

The regression analysis was used to build a quantitative model, in which only the significant variables were taken into account. This model was built in order to produce maximum % biodiesel production yield in the most economical even with the absence of one of these significant variables. It should be known that the use of these models outside the investigated variables is not allowed since it would lead to wrong results.

Catalyst characterization

Fourier transform infrared spectroscopy (FTIR) was recorded to identify the catalyst chemical bonds, chemical structure, and functional groups. FTIR was carried out using (Shimadzu-8400S, Japan). About 2 mg of the catalyst was mixed with 100 mg of KBr and ground to uniform particle size and then pressed as a pellet using a hydraulic press to be analyzed. Measurements

were performed using a wave number range of 4400–350 cm⁻¹, with 4 cm⁻¹ resolution.

The catalyst was characterized using X-ray diffraction (XRD) to figure out the catalyst crystallinity. The XRD patterns were recorded by (Schimadzu-7000, Japan), using Cu K α radiation ($\lambda=1.5418 \text{ \AA}$) and step-scan mode (range: 5–100° 2 θ , step-time: 0.5 s, step-width: 0.1°).

To determine the surface morphology and the major features of the physical structure of the catalyst, scanning electronic microscopy (SEM) analysis was performed using (JEOL-6360LA, Japan) at accelerating voltage 20 kV, at room temperature. The elemental composition was detected by energy dispersive x-ray spectroscopy (EDX) detector that is equipped with the SEM instrument. Also, the catalyst particle size distribution and particles surface area have been determined as well to predict the CSISS physical performance. The particle size distribution was measured by photon correlation spectroscopy techniques (N5 submicron particle-size analyzer, Beckman).

Product evaluation

Quantitative analysis of biodiesel production yield

Biodiesel production yields were quantified using a GC device; HP (Hewlett Packard) 6890 GC, (Agilent Technologies / Hewlett-Packard Company, U.S.A.). Nitrogen was used as the carrier gas, with flow 1ml/min, using flame ionization detector (FID) at temperature 250°C. The injector temperature was 220°C, injection volume 2 μ l, splitless mode. The temperature program of the GC was as follows: 2 min isothermal at 150°C, 150–200 °C with 10 °C/min, 9 min held at 200°C, 200–250°C with 5°C/min. The used column was HP-5 (5% diphenyl, 95% dimethylpolysiloxane), 30 m, 0.32 mm ID, and 0.25 μ m film thickness at temperature 200–250°C with 5°C/min.

$$Y = 101.1 - 10.6 C - 7.49 T + 6.933 M - 17.7 TW - 13.5 C^2 - 22.5 W^2 \quad (3)$$

Equation 3 represents the significant parameters of the predicted quadratic model, obtained by applying the coded levels of the factors. It can be observed that both catalyst weight and catalyst composition demonstrate quadratic coefficients. In addition to an interaction between the reaction time and methanol to oil molar ratio. The proposed polynomial model of the biodiesel production reaction is significant

Physicochemical properties of produced biodiesel

Physico chemical properties such as viscosity, density, cold flow properties, and flash point of the biodiesel which is produced using the optimum operating condition have been measured in Alexandria Petroleum Company using the standard methods according to ASTM.

Diesel engine performance

The produced biodiesel was blended with petrodiesel by ratios of 10 and 20% v biodiesel/ v petrodiesel which are known as B10 and B20 respectively to investigate the engine performance, combustion characteristics. Tecquipment TD43, a four-stroke, single cylinder, and directinjection variable compression ratio diesel engine has been used. The engine has a bore of 95 mm stroke of 82 mm, displacement of 582 cm³. The tests were carried out at engine speeds ranging from 1000 to 2000 rpm, incrementally increased by 250 rpm at full load and fully opened throttle conditions.

Combustion emission

The emissions including CO, CO₂, NO_x, and HC that exhausted from B10 and B20 combustion were analyzed using (Montronoy Techno-Test emission analyzer model 488) and compared with the combustion exhaust emissions of petrodiesel.

Results and Discussion

Multivariate regression analysis and ANOVA

The % biodiesel production yield obtained at the actual values and the coded levels of the independent variables are given in Table 2. Data were analyzed for obtaining the significant coefficients of the proposed relation, concerning the % biodiesel production yield and the factors under study. According to the analysis, equation 2 can be written in the following form :

with $P < 0.00002$ as indicate the p-value of the significant F. Also, the R^2 suggests that the obtained equation represents the data by about 93% and confirms the good correlations between the independent variables.

Equation 3 is then used to predict the % biodiesel yield in terms of the coded factors and represented in **Table 2** to be compared with the actual % biodiesel yield. A scatter diagram of

the actual % biodiesel yield versus the values of predicted % biodiesel yield calculated by equation 3 is plotted in **Figure 2**. The data in the Figure evidenced a good agreement between the two sets of data, confirming that the model interprets the experimental range studied adequately.

Applying contour plots for the effects of the SiO₂ content in the catalyst, methanol to oil molar ratio, time and amount of catalyst on the biodiesel production yield can give an overview on their effects, show the interaction between these tested variables, allow obtaining the optimum operating conditions and explore their effects in a wider range than that studied. **Fig. 6a** shows the interaction between SiO₂ content and time. It was found that there are two areas for the highest biodiesel yield; one of them can be implemented using the catalyst with SiO₂ content from 0 to 50% with a reaction time does not exceed 60 min. While the other areas appeared at SiO₂ content higher than 50% but with longer reaction time,

starts from 70 min as minimum reaction time in this case. The interaction between SiO₂ content and methanol to oil molar ratio is shown in **Fig. 6b**, it was observed that the area of the highest biodiesel yield can be produced by using the CSISS with SiO₂ content in the range from 10 to 65% and methanol to oil molar ratio in the range from 9:1 to 16:1. **Fig. 3c** shows a big area of high biodiesel production yield. This area starts from 3:1 methanol to oil molar ratio and about 3% catalyst weight and continue to 16:1 methanol to oil molar ratio and 10% catalyst weight. **Fig. 3d** shows a rapid biodiesel production at the first 20 min with methanol to oil molar ratio does not exceed 8:1. By increasing the reaction time than 30 min, the biodiesel production yield is decreased. The long time may permit the reversible reaction to occur, while the biodiesel production yield can be increased again by increasing methanol to oil molar ratio than 10:1 which acts as a driving force to hinder the reversible reaction and increase the biodiesel production yield.

TABLE 2. Actual and coded levels of independent variables for different trails.

Treatment	Independent variables				Coded levels				Biodiesel Yield, %	Predicted biodiesel yield %
	SiO ₂ content Percentage in the catalyst, % (C)	Time, min (T)	Methanol to oil molar ratio (M)	Catalyst weight (%w catalyst/w oil) (W)	C	T	M	W		
1	100	60	9.01	3	1	-0.6	0	-0.5	67.6	70.6
2	87.5	60	9.01	3	0.75	-0.6	0	-0.5	80.13	79.1
3	75	60	9.01	3	0.5	-0.6	0	-0.5	87.68	86
4	62.5	60	9.01	3	0.25	-0.6	0	-0.5	92.2	91.2
5	50	60	9.01	3	0	-0.6	0	-0.5	95.34	94.6
6	37.5	60	9.01	3	-0.25	-0.6	0	-0.5	93.91	95.4
7	25	60	9.01	3	-0.5	-0.6	0	-0.5	90.74	92.5
8	12.5	60	9.01	3	-0.75	-0.6	0	-0.5	88.62	90
9	0	60	9.01	3	-1	-0.6	0	-0.5	98.87	95.7
10	50	30	9.01	3	0	-1	0	-0.5	94.27	94.1
11	50	90	9.01	3	0	-0.2	0	-0.5	95.8	95.2
12	50	120	9.01	3	0	0.2	0	-0.5	96.63	95.7
13	50	180	9.01	3	0	1	0	-0.5	97.21	96.8
14	50	30	3.01	3	0	-1	-1	-0.5	94.27	92.4
15	50	30	6.01	3	0	-1	-0.5	-0.5	97.41	93.6
16	50	30	12.01	3	0	-1	0.5	-0.5	99.54	97.6
17	50	30	15.01	3	0	-1	1	-0.5	99.8	100
18	50	30	3.01	1	0	-1	-1	-1	56.83	60.5
19	50	30	3.01	5	0	-1	-1	0	97.19	100
20	50	30	3.01	7	0	-1	-1	0.5	100	100
21	50	30	3.01	9	0	-1	-1	1	100	96.8

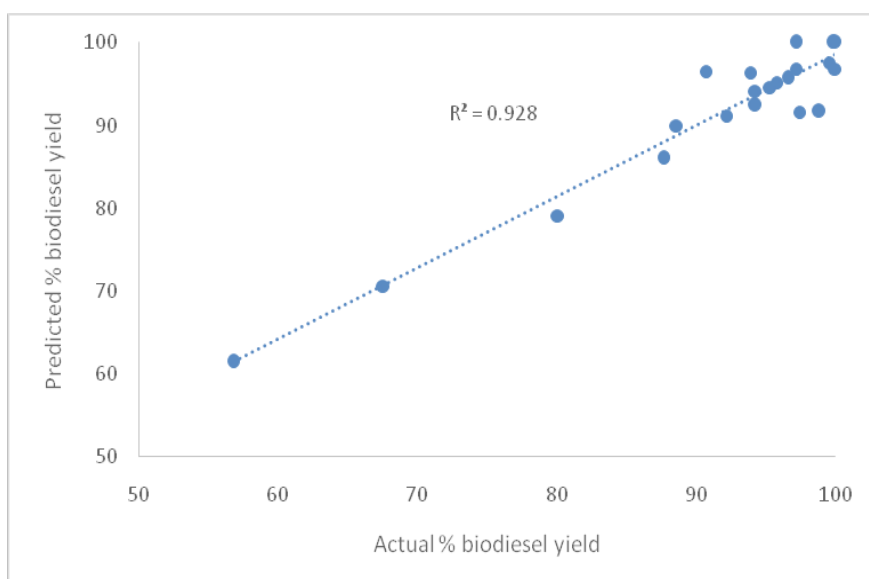


Fig. 2. Scatter diagram of actual percentage biodiesel yield vs. predicted percentage biodiesel yield calculated from equation 3.

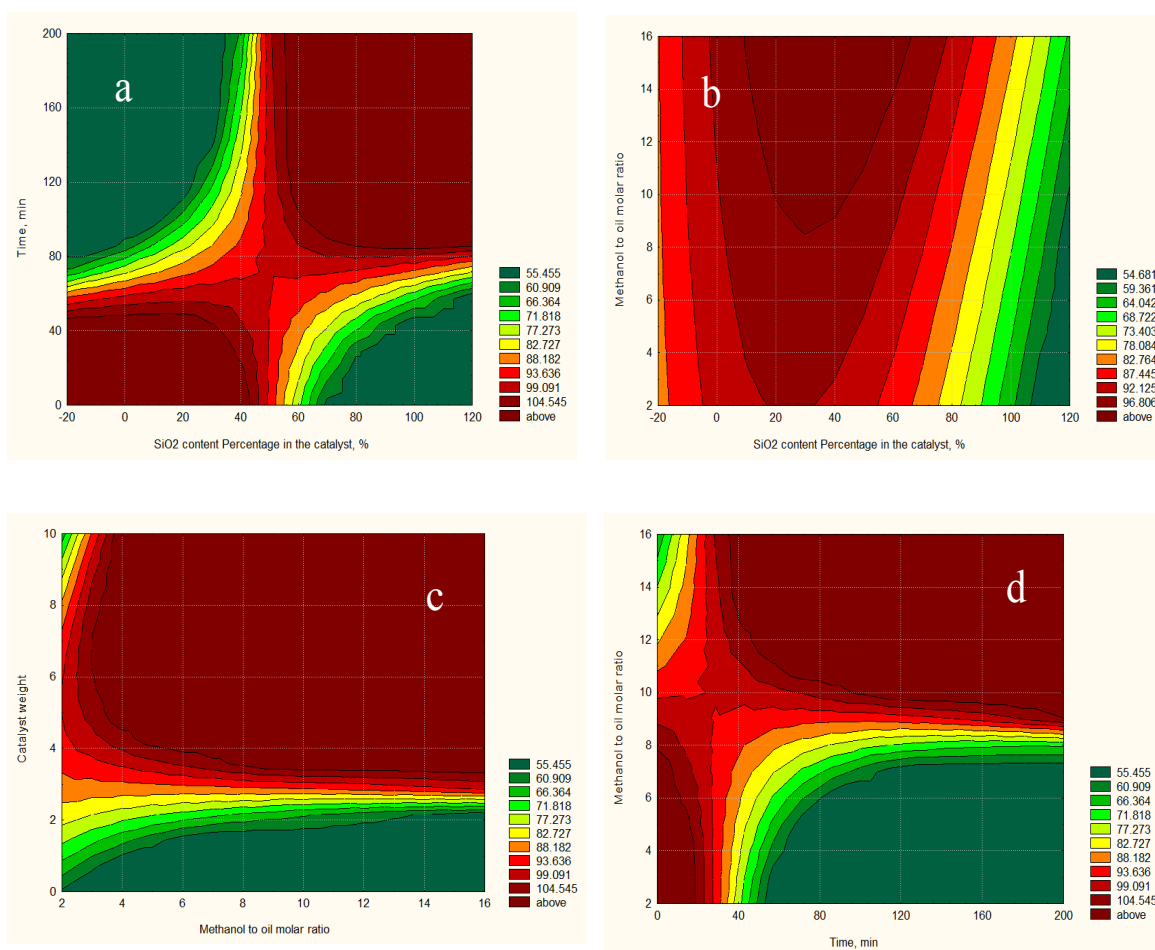


Fig. 3. The contour plots for the effects of the SiO_2 content in the catalyst, methanol to oil molar ratio, time and amount of catalyst on the biodiesel production yield.

Therefore, applying contour plots explore milder operating condition than those studied. These operating conditions are; 50% SiO₂ content, 20 min reaction time, 8:1 methanol to oil molar ratio and 3% w Catalyst/ w Oil which are more economic than the studied operating conditions as the half of the used methanol to oil molar ratio is reduced and one-third of the reaction time is reduced as well. By utilizing these operating conditions experimentally, the biodiesel production yield was about 99%. Hence these new explored operating conditions are effective and more economic.

Catalyst characterization

Fourier transform infrared spectroscopy

The FTIR spectra in the range of 4400–350 cm⁻¹ was studied as shown in **Fig.4** in order to explore the qualitative catalytic characteristics of the surface functional groups of the CSISS catalyst. The broad band at 596cm⁻¹ is due to the stretching vibration of S=O and interaction of SiO₂ on the CaO surface which lead to weaker bonding of Ca–O[37]. The small bands at 674 and 1124 cm⁻¹ represents Ca–O bonds and SiO₂ respectively [38, 39]. The bands present at the wavenumber 1158 cm⁻¹ are related to SO₄[40]. Brønsted acid sites referring to the presence of sulfuric acid has been detected as the strong band at the wave number 1620 cm⁻¹[41]. Calcium sulfate has been deduced by the band at wave number 1638 cm⁻¹[42]. The broad band present at 3463 cm⁻¹ is attributed to physisorbed water

molecules (–OH bond) on the CSISS catalyst surface which is essential to improve the CSISS catalytic activity[43].

X-ray diffraction

The crystallinity of the produced catalyst CSISS is shown in **Fig.5**. The XRD pattern shows a typical spectrum of highly crystalline composite although the amorphous nature of its components (CaO and SiO₂) which are used in the catalyst synthesis. The peaks at $2\theta = 25.5, 31.5, 36.34, 38.72, 40.92$ and 43.42° are related to presence of CaSO₄ (according to the PDF Card paper -00-001-0578, the International Centre for Diffraction Data/ICDD 2014) which is produced due to the strong interaction between sulfate ions and the calcium oxide surface due to the electron infinity of the sulfate preserved the textual properties of the metal oxides[44]. As a result of the amorphous nature of the used silica, there are no peaks appeared in the XRD pattern related to it.

Scanning electron microscopy

Figure 6 shows a typical morphology for CSISS catalyst analyzed by SEM with two magnification levels. Figure 6a shows that the CSISS particles are mostly irregular in shape, well-defined with some particles elongation and seem to be nonporous. The image with high magnification level reveals the accumulation of particles with different gray shades as shown in Fig. 6b which may be attributed to calcium sulfate particles and sulfated silica particles as proved in the FTIR and XRD analysis.

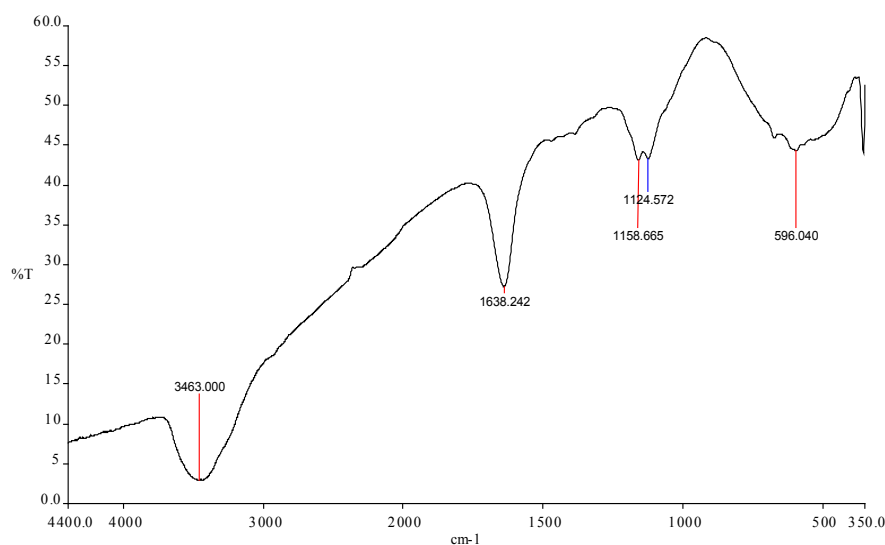


Fig. 4. FTIR spectra of CSISS.

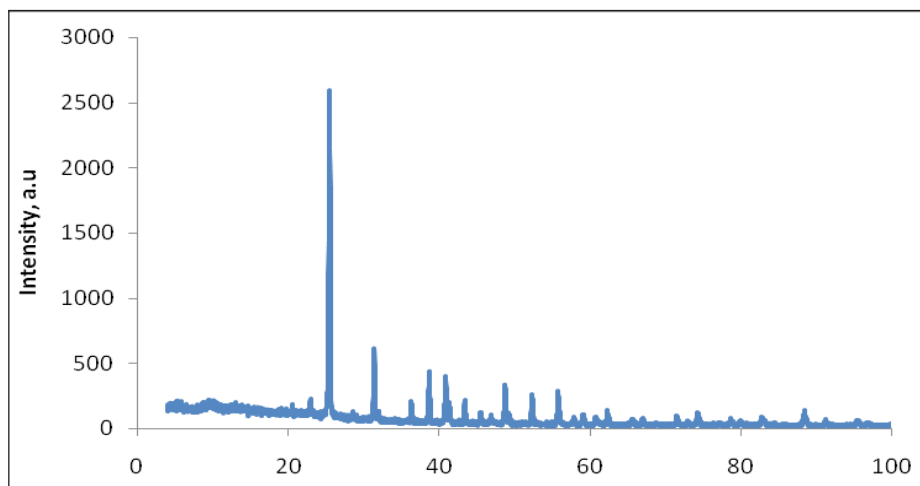


Fig. 5. XRD pattern of CSISS.

Energy dispersive x-ray spectroscopy

The elemental composition and ratio of the CSISS major constituents were determined using EDX spectrometer. The analysis revealed that CSISS is composed of Ca 35.5%, Si 33.9%, and S 30.6%. The results proved that the CSISS composite is synthesized correctly with an actual elements ratio very close to the theoretical ratio.

Particle size analysis

Catalysis is a complex process, therefore, there are many factors affect it. Among these factors the catalyst particle size, which has a great impact on the catalysis process. Particle size analysis was carried out using two diffraction angles 10.9 and 90°. It was observed that the particle size distribution is not continuous and consist of a mixture of fine particles of 11.73 ± 5.85 nm, represent about 68% of the total particles, mixed with larger particles of 638 ± 317.63 nm, represent about 32% of the total particles. As a result of the high existence of nano-particles, it is expected that it may enhance the surface chemistry and increase the catalyst functional groups interaction with the alcohol and the oil and therefore increase the catalytic activity.

Reusability test of CSISS catalysts

Regarding the economic point of view, reusability of the CSISS catalyst should be investigated. After the reaction completion under the optimum operating condition, the biodiesel and glycerol layers were discharged and CSISS was washed with acetone twice and dried at 60°C for 3h. Then, other amounts of esterified oil, methanol, and the catalyst were added to the flask for carrying out the reaction again. Eight reusing

runs were carried out and the biodiesel production yield of each run is displayed in Fig.6. The reusing experiments resulted in six successive reactions with high biodiesel production yield exceeding 90%. In all about 6% of total biodiesel yield reduced at the end of the sixth run, suggesting that the catalyst is stable and no linking of the active species is observed till the sixth run. After the sixth run, the biodiesel production yield has been reduced to be 82.2 and 71.4% which may be related to an oil layer accumulation on the catalyst surface and lead to CSISS functional groups deactivation.

Product evaluation

Table 3 summarizes the optimum operating condition, biodiesel production yield and produced biodiesel physicochemical properties of the present work and creates a comparison between these outcomes with previous similar studies. The comparison declares that the present work has :

- 1- One of the highest biodiesel production yields.
- 2- Mild operating conditions in comparison with the other studies that produce similar yields.
- 3- Physicochemical properties of the product lie within the ASTM standards and are competitive to the other biodiesel that is produced by the other studies.

Diesel engine performance

At first, the single cylinder diesel engine was fueled with petrodiesel to test its effects on the engine performance. Then the same experimental combustion analysis was carried out using B10 and B20 to compare them with petrodiesel.

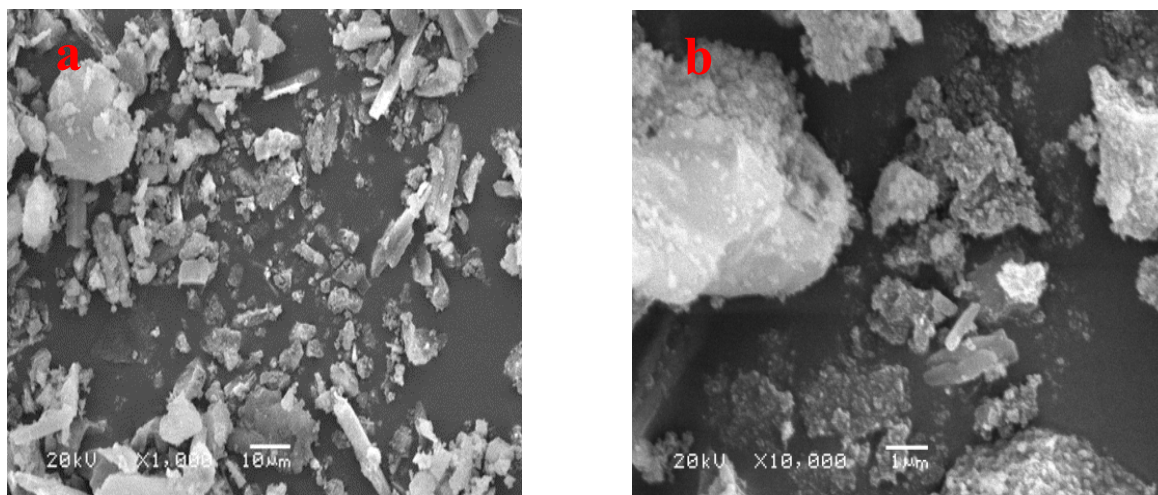


Fig. 6. SEM of CSISS with two different magnification factors; a. 1000 and b. 10000.

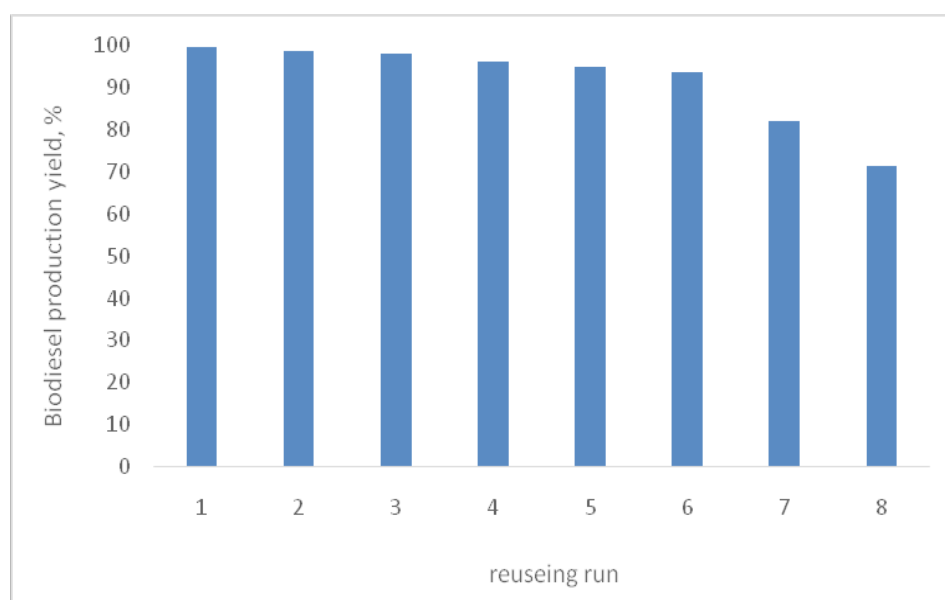


Fig. 7. Effect of CSISS reusability on biodiesel production yield under the optimum operating condition; 50% SiO₂ content, 30 min reaction time, 15:1 methanol to oil molar ratio and 3% catalyst weight at 55°C and 300 rpm.

Engine torque

The results of the engine's torque, at full load, are shown in Fig. 8a. It can be observed that by raising the engine speed, the engine torque increases for all used oil types. The B20 fuel has the lowest torque compared to petrodiesel and B10. This result may be due to the B20 low heat of combustion and low fuel delivery at full load due to the high mass flow rate required from the fixed nozzle area [54, 55].

Fuel consumption per hour (mf)

By increasing the engine speed, the fuel consumption per hour is increased as shown Egypt. J. Chem. Vol. 63, No. 4 (2020)

in Fig. 8b. Petrodiesel has the highest fuel consumption for all engine speeds. At low engine speeds, 1000 and 1250 rpm, the fuel consumption amounts are very close for all fuel types. In case of higher speeds, biodiesel blends have lower fuel consumption than petrodiesel. Hence, using biodiesel blends is more economical than using petrodiesel. B 10 and B 20 have the same trend of their consumption but the fuel consumption in case of B 20 is lower than B 10.

TABLE 3. Biodiesel production yield and physicochemical properties for several experimental studies under different operation conditions.

Oil feedstock	Catalyst type	Optimum operating conditions					Biodiesel production yield	Physicochemical properties							Refs.	
		methanol: oil molar ratio	Temperature °C	reaction time min	catalyst amount % w/w	agitation speed		Flash point °C	Cloud point °C	Pour point °C	Ash content wt%	Viscosity 40 °C mm ² s ⁻¹	Density 20 °C g cm ⁻³	Water content %		Biodiesel standards
Waste frying oil	CSISS 50% silica content	15:1	55	30	3	300	97.19	170	12	9	0.001	3.2	0.91	0.05	ASTM biodiesel standards	Present work
sunflower	CaO derived from quail egg shell	10.5:1	60	120	2	1000	99	NS*	NS*	NS*	4.49	0.882	101		[12]	
castor oil	NaOH	6:1	55	120	1	NS*	NS*	151	0	NS*	0.025	4.65	0.878	NS*	[37]	
waste cooking oil	Activated carbon	6:1	NS*	120	1	400	93.95	180	-3	-6	NS*	5.5	0.91	NS*	[38]	
Jatropha oil	Activated carbon	6:1	NS*	120	1	400	93.27	182	-2	-5	NS*	5.8	0.915	NS*	[38]	
Moringa oleifera oil	KOH	6:1	60	120	1	600	NS*	150.5	10	19	NS*	5.05	0.898	NS*	[39]	
waste cooking oil	sea sand	12:1	NS*	360	7.5	NS*	95.4	NS*	NS*	NS*	NS*	5	NS*	NS*	[40]	
Palm oil	KOH	6:1	60	60	1	NS*	88	170	13	17	NS*	4.6	0.876	NS*	[41]	
waste cooking oil	ZnAl ₂ O ₄	40:1	60-200	120	1-10	700	> 95	NS*	NS*	NS*	NS*	4.61	NS*	NS*	[42]	
jatropha oil	MgZnAlO	11:1	182	360	8.68	NS*	94	140-180	6-10	11	NS*	3.2-4.6	NS*	0.01-0.31	[43]	
rapeseed oil	KOH	NS*	50	90	0.6	600	99.5	NS*	-3.8	NS*	NS*	77.5	0.92	<0.10	[44]	
Apricot kernel oil	NaOH	6:1	NS*	NS*	NS*	NS*	93	105	-5	-15	NS*	4.26	0.855	NS*	[45]	

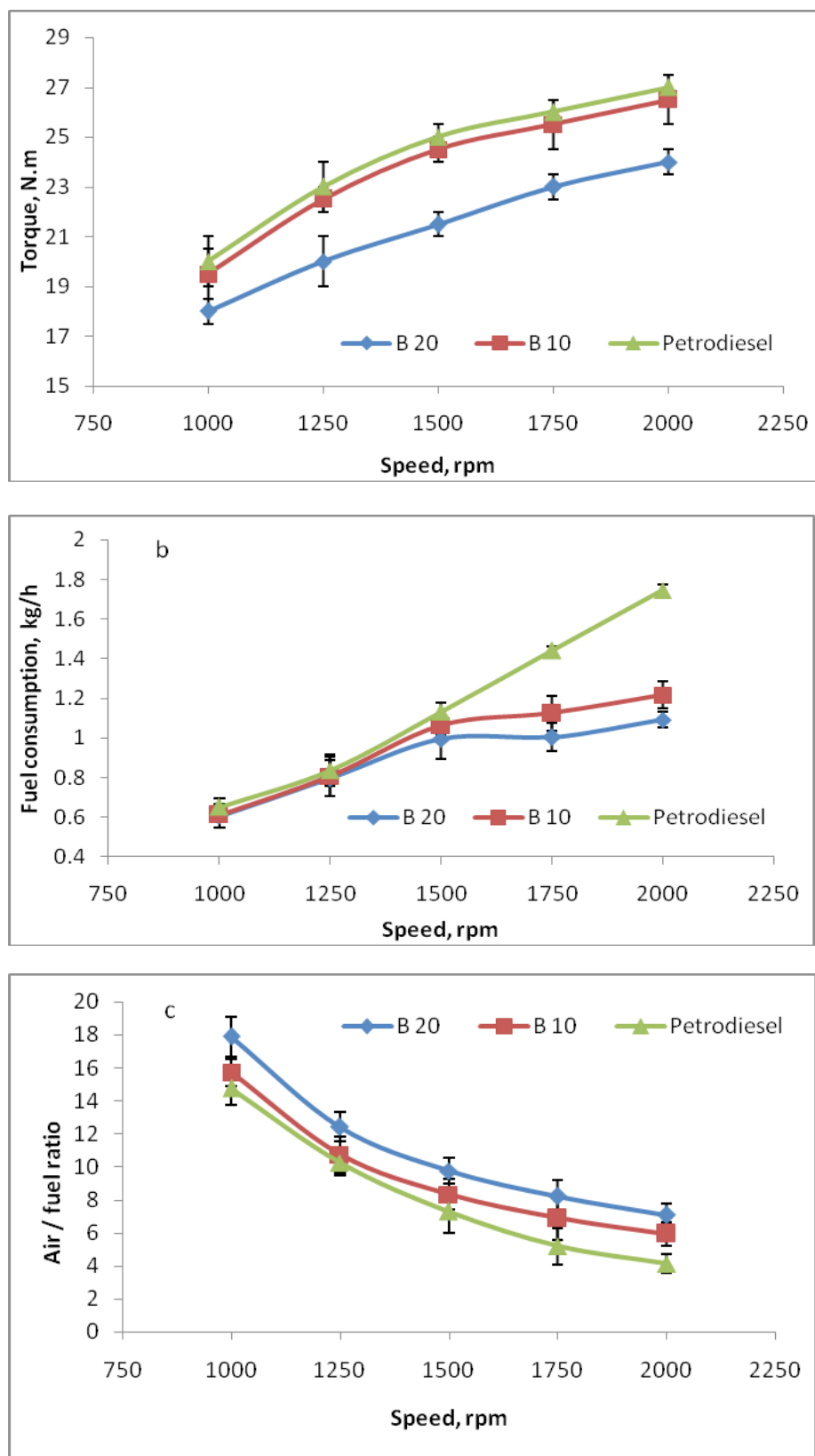


Fig. 8. B10, B20 and petrodiesel performance in diesel engine a. torque b. fuel consumption c. air/fuel ratio at the engine full load.

Exhaust emission measurements

The variation of CO, CO₂ and HC emissions for B10 and B20 than petrodiesel is shown in **Fig. 9**. Petrodiesel has the highest emission of CO as shown in **Fig. 9a**. By increasing the volume of biodiesel to the petrodiesel, the CO amounts are reduced and CO₂ amounts are increased. This phenomenon may be due to the high oxygen content in the vegetable oils that leads to complete combustion and enhances the combustion process. **Figure 9b** shows that the HC hazardous emissions exhausted from B10 and B20 combustion are 37 and 35 ppm respectively which are lower than 47 ppm HC that exhausted from petrodiesel combustion. From **Fig. 9c** it can be observed that the exhaust NO_x emissions of B10 and B20 are slightly higher than petrodiesel. This may be due to the molecular structure of biodiesel which contains more double bonded molecules than petrodiesel. These double bonds have a slightly higher adiabatic flame temperature, which leads to increase the NO_x emissions. In addition to the biodiesel oxygenated nature which leads to more complete combustion with higher adiabatic flame temperature which increases the NO_x emission [54,55].

Cost analysis

Blending the biodiesel with petrodiesel or biodiesel petrodiesel replacement can reduce the fuel cost as well as the cost involvement in dumping the WFO and waste CaO in an environment-friendly way.

In this connection, an estimated cost of 1 L biodiesel production using the optimum operating condition has been illustrated as follows :

- 1- Price of raw material, (esterified WFO, methanol and CSISS) which are needed for the transesterification process, is US\$ 0.41 + 0.051 + 0.155 /kg = US\$0.616 / kg if the catalyst is used once. By taking the catalyst recycling into consideration, the price of the raw material will be reduced to be US\$ 0.487.
- 2- Price of energy which can be calculated using the following equation:

$$Q = m \times C_p \times \Delta T \quad (4)$$

where Q is the thermal energy, kW, m is the mass flow of the reactants, kg/s, C_p is the specific heat capacity, kJ/kg.°C and ΔT is the temperature

difference, °C. By applying this equation on the biodiesel production process at 55°C and 300 rpm stirring speed for 20 min, the power consumption will be 0.0458 kW which costs US \$0.00092. Hence, the one-liter biodiesel production cost will be US\$0.488.

Conclusion

The merit of this study is utilizing wastes (WFO and waste CaO) to produce valuable, low cost and highly profitable product (biodiesel). Multivariate regression analysis was successfully applied for the reaction of WFO and methanol in the presence of CSISS composite as a low-cost heterogeneous catalyst. The model was developed using the experimental results. The second-order polynomial model was well fitted to the experimental results with high regression coefficients. This model can be used for % biodiesel yield prediction when utilizing any other operating conditions. The ANOVA implied that linear term of the catalyst composition, time and methanol to oil molar ratio and the interaction between catalyst composition and catalyst weight and the quadratic terms of catalyst composition and catalyst weight have the great significant factor affecting the % biodiesel production yield. The catalyst was promising as it leads to produce 99% biodiesel with mild operating conditions and can be reused successfully for 6 runs. The produced biodiesel has physicochemical properties compatible with the ASTM biodiesel standards. Using biodiesel petrodiesel blends is more environmentally friendly as they produce lower hazardous exhaust emissions such as CO and HC.

Funding

This research received no external funding.

This work has been accessed in City of Scientific Research and Technological Applications (SRTA City)

Conflicts of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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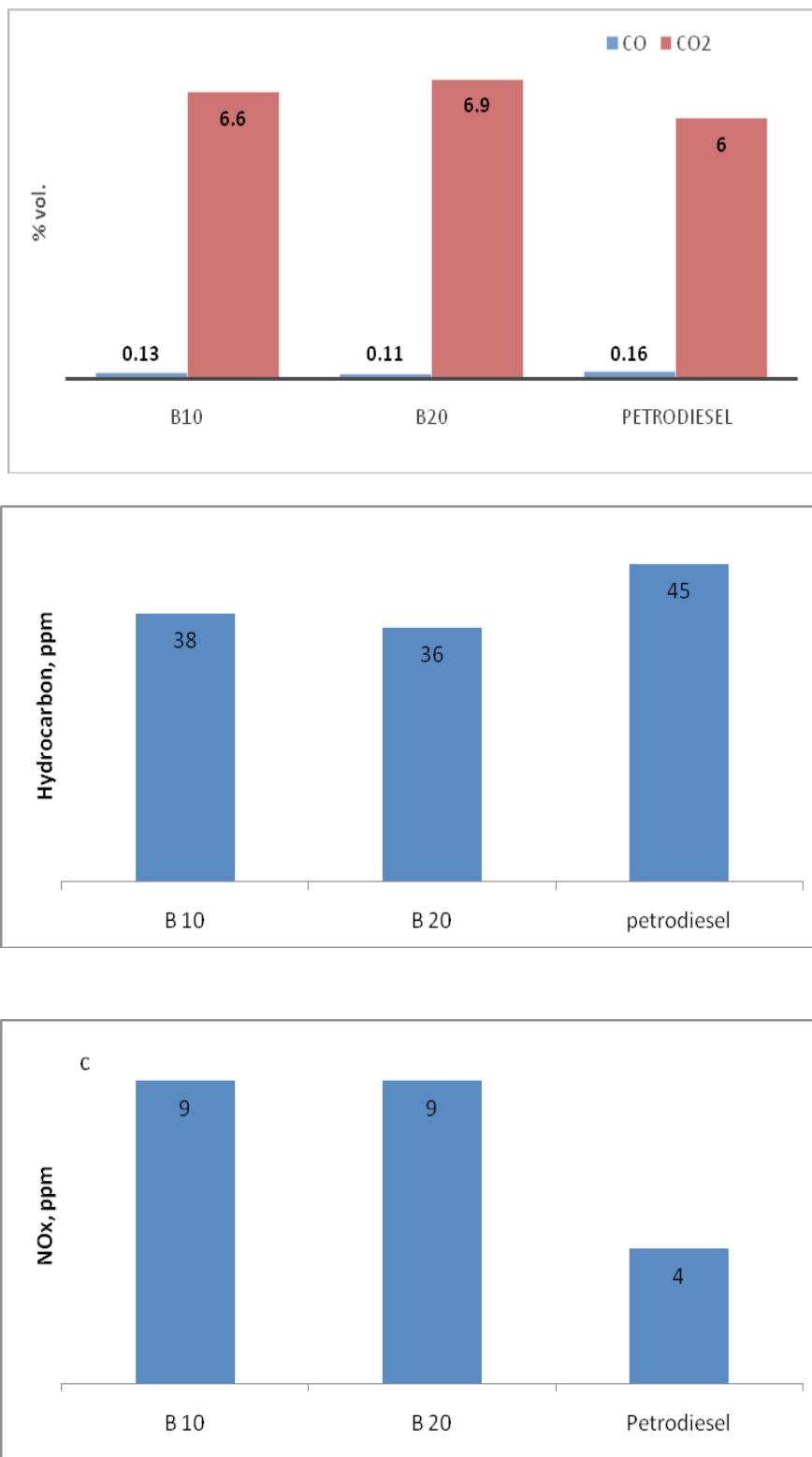


Fig. 9. B10, B20 and petrodiesel combustion exhaust emissions a. CO and CO₂ b. HC c. NO_x.

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تصنيع عامل حفاز عالي البلورية من المخلفات الصناعية لاستخدامه في الإنتاج المستدام للديزل الحيوي

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تعاني مصانع الحديد والصلب في مصر من انبعاث أكسيد الكالسيوم الناعم والذي يصنف كنفائيات ويؤدي إلى العديد من المخاطر الصحية. كحل لهذه المشكلة، تم استخدام هذه النفائيات (الناعم CaO) كمصدر مستدام منخفض التكلفة لإنتاج كبريتات الكالسيوم المخصبة بسلفات السيليكات (CSISS). تم استخدام هذا المحفز الهجين كعامل حفاز غير متجانس لإنتاج وقود الديزل الحيوي من زيت القلي (WFO). في هذه الدراسة، تمت دراسة الآثار الخطية والتربيعية والتفاعلية للعوامل الأربعة الرئيسية التي تؤثر على إنتاجية الديزل الحيوي. تم توقيع النتائج العملية على نموذج إحصائي تجريبي للوصول إلى أعلى إنتاجية للديزل الحيوي بأقل ظروف تشغيل و توافق النموذج الموضوع مع النتائج العملية بنسبة ٩٣٪ و أظهر أن أفضل ظروف التشغيل هي: ٥٠٪ سيليكات، ٢٠ دقيقة، ١:٨ نسبة مولية للميثانول إلى الزيت، ٣٪ وزن العامل الحفاز عند ٥٥ درجة سيليزية و ٣٠٠ لفة في الدقيقة و أنتجت ٩٩٪ ديزل حيوي. تم تحليل الخواص الفيزيائية والكيميائية للديزل الحيوي المنتج. تم تقييم انبعاثات عادم الاحتراق لمزيج الديزل الحيوي / السولار. أوضح التحليل التقني والاقتصادي أن الديزل الحيوي المنتج منافس قوي للديزل النفطي بتكلفة ٠,٤٨٨ دولار أمريكي / لتر.