Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

A Competent, Humble Cost Catalyst from Biowaste: High Performance and Combustion Characteristics of Alternative Diesel Fuel

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Abstract

This current work displays experimental results obtained from assessing the methyl esters from the local waste cooking oil as an alternative fuel for diesel engines using a heterogeneous catalyst based on agricultural waste. The performance of the diesel engines and their exhaust emissions have been experimentally investigated using the produced biodiesel from waste cooking oil as a blend with fossil fuel (B10, B15, and B20) compared to the diesel. The reusability of the catalyst confirmed a high conversion efficiency after 8 cycles of the production. The highest conversion efficiency of the converting waste cooking oil extended to 90.38% with 92.5% maximum mass yield and methyl ester content of 97.7% wt. at the optimized conditions. According to the results, the effective blend for thermal efficiency and specific fuel usage is B15. Also, all emission concentrations decrease with increasing the engine load, especially for B15 fuels compared to diesel oil.

Keywords: Alternative fuel; Diminish contamination; Eco friendly catalyst; Performance and combustion characteristics; Waste cooking oil

1. Introduction

Biodiesel is an alternative energy resource, that is environmentally friendly. It is an up -and- coming clean-burning fuel with environmental values, it is a substitute for diesel fuel. In comparison to petroleum-diesel fuels, it is oxygenated, low in emissions, sulfur-free, non-toxic, and biodegradable [1]. The biodiesel is produced from renewable non-edible oil as waste cooking oil, which reduces the biodiesel production price three times more than virgin oils [2-3]. Despite the effectiveness of the uniform acid catalyst, it will cause absolute contamination issues that will require good separation and product purification processes that will result in a higher cost. Unlike the heterogeneous acid catalyst, which is made from agricultural wastes reducing, the environmental costs. It is not affected during the conduction of esterification and transesterification processes. The benefits of the production of biodiesel are the reduction of the gas emission problems and the saving of about 90 tons of the energy used compared to the traditional fuel [3-5]. Biodiesel is mixed with the diesel fuel to be suitable for the compression ignition engine, and no modifications are required to be made to the engine. The disposal of agricultural waste needs more financial or environmental costs. That means it is important to convert agricultural waste into useful materials to reduce its effect on the environment. The

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Receive Date: 22 January 2022, **Revise Date:** 05 March 2022, **Accept Date:** 27 April 2022, **First Publish Date:** 27 April 2022
DOI: 10.21608/EJCHEM.2022.117718.5306

conversion of this agricultural waste into a useful catalyst is considered one of the aims of this paper [8-10]. This paper is interested in the protection of the environment from the pollution caused by agricultural waste and diesel engine emissions. In addition to lowering the rate of petroleum resources. It is done by producing biodiesel from harmful environmental waste and assessing the likelihood of applying this biodiesel as an alternative fuel to the diesel engine. It is performed by the comparison between the efficiency of the performance parameters and the exhaust gas emissions from diesel fuel.

2. MATERIALS AND METHODS

2.1 Material used

Rice straw was collected from the municipal Egyptian farmers (Qalyubia governorate). It contains about 65% holocellulose (cellulose and all of the hemicellulose), 18 % lignin and Ash 11.5 %. Its moisture content 5-6%. They were calculated related to TAPPI T257 om-85, TAPPI T222 om-88 and TAPPI om-85 [2]. WCO was derived from home activities. Its moisture content was 2.3%. It was determined by gravimetric analysis. Acid value 2.8 (mg KOH/g) and saponification value 156.8 (mg KOH/g) were calculated related to ASTM D664 and ASTM D94, respectively. Sulfuric acid, Methanol have been used in our experimental work, from sigma Aldrich of purity 99% . For all the experiments, distilled water was used.

2.2 Catalyst Synthesis

As pointed out in our previous literature study [10], the novel catalyst of the polycyclic aromatic sulfonates RS-SO3H was created from agricultural waste (rice straw). The chemical process was described in the chemical reaction equation in figure (1) [10, 11, 12, 13]. First, it was prepared from the fast pyrolysis for the Egyptian rice straw at the conditions of temperature at 510 ± 5ºC for 8 ± 2 s. The resulting brown, black matter was ground to a powder. For 15 hours at 150oC, a 10 gm was sulfonated with 100 mL of 95% sulfuric acid. After cooling, the prepared catalyst was washed by using hot distilled water to remove the excess of the sulfonate ions. Finally, the prepared catalyst was dried at a temperature of 80ºC for 24 h in an electrical oven [10-14].

2.3 Biodiesel Production

As pointed out [10], the biodiesel production was achieved by transesterification process. RS-SO3H has used as a catalyst. First, the organic residue of WCO was removed by the settling and filtration process through the fiber filter. The filtrate was dried at 90-110°C in the electrical oven to evaporate the moisture content from the oil. Methanol and RS-SO3H catalyst were mixed with each other then it was added to the preheating oil which charged into the three necks flask with a magnetic stirrer and a reflux system. After achieving the transesterification process, Two layers were appear the upper one is FAME and the lower one contains glycerol and traces of methanol. FAME layer separated and washed several times with hot water at 60oC to remove any impurities of methanol and sulfates ions. Then it dried in an oven at 100oC. As discussed in our previous literature report [10], the transesterification process was carried under the different conditions of the temperature, time, the catalyst concentrations, and the molar ratio between solvent (methanol) and WCO to get the highest conversion efficiency % of changing raw material with the maximum mass yield (%) of the acidic methyl ester (biodiesel).Biodiesel produced was then described by chromatography analysis (GC) analysis to identify biodiesel production yield and determine oil conversion%.

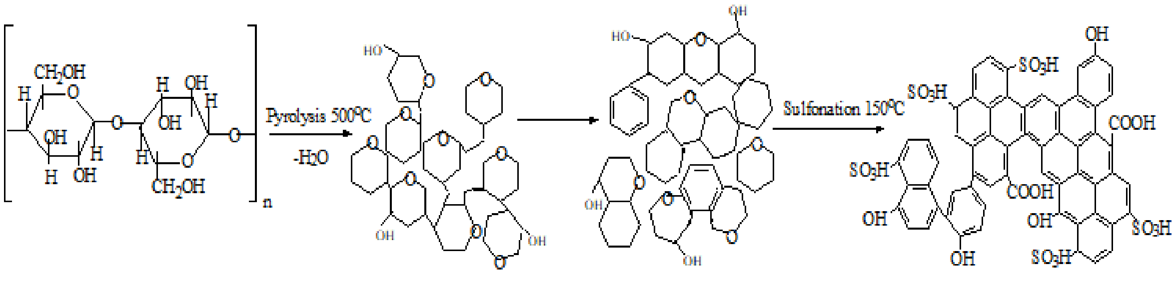


Fig. 1 The chemical process equation of the prepared catalyst.

From the equation (1), The maximum mass yield% of the biodiesel produced was calculated at the optimized conditions as discussed in our previous work [10][14-19].

Mass yield%=(weight of biodiesel)/(weight of oil used)×100 (1)

Equation (2) was used to estimate the highest conversion efficiency% of converting raw material to biodiesel. This equation depends on the gas chromatography analysis technique

Conversion efficiency % =ester content% ×mass yield% (2)

2.4 Biodiesel Fuel for Diesel Engine

The present investigation measures the performance and exhaust emissions of the diesel engine using biodiesel prepared. The tests were conducted by using diesel fuel as the origin line data. The biodiesel prepared was burned in a diesel engine at different load conditions in steps of 25%. The results achieved from the experimental investigations are used to study the performance parameters and the exhaust emissions [3].

2.4.1 Experimental Test Procedure

Figure (2) shows the experimental test engine rig using the DEUTZ F1L511 diesel engine. The technical descriptions of the engine are: single cylinder, rated speed of 1500 rpm, direct injection, and air cooling. The sequence of events that were performed to hold out the experiments is:

- Check out all the measuring instruments and make sure of zero reading adjustments.
- Run the engine.
- Warm up the engine for 15 minutes under no load condition using diesel fuel.
- Wait a period for the engine to reach steady state operation conditions.
- Change to a tried-and-true fuel, such as diesel-biodiesel blends.
- Record all instrument readings.
- Measure the airflow and the fuel flow rates at these conditions.
- Measure the exhaust emissions concentrations (CO, CO2, HC, O2) at different engine loads.
- Repeat these steps for each fuel level of 0, 25, 50, 75, and 100% at full engine load [4][5].

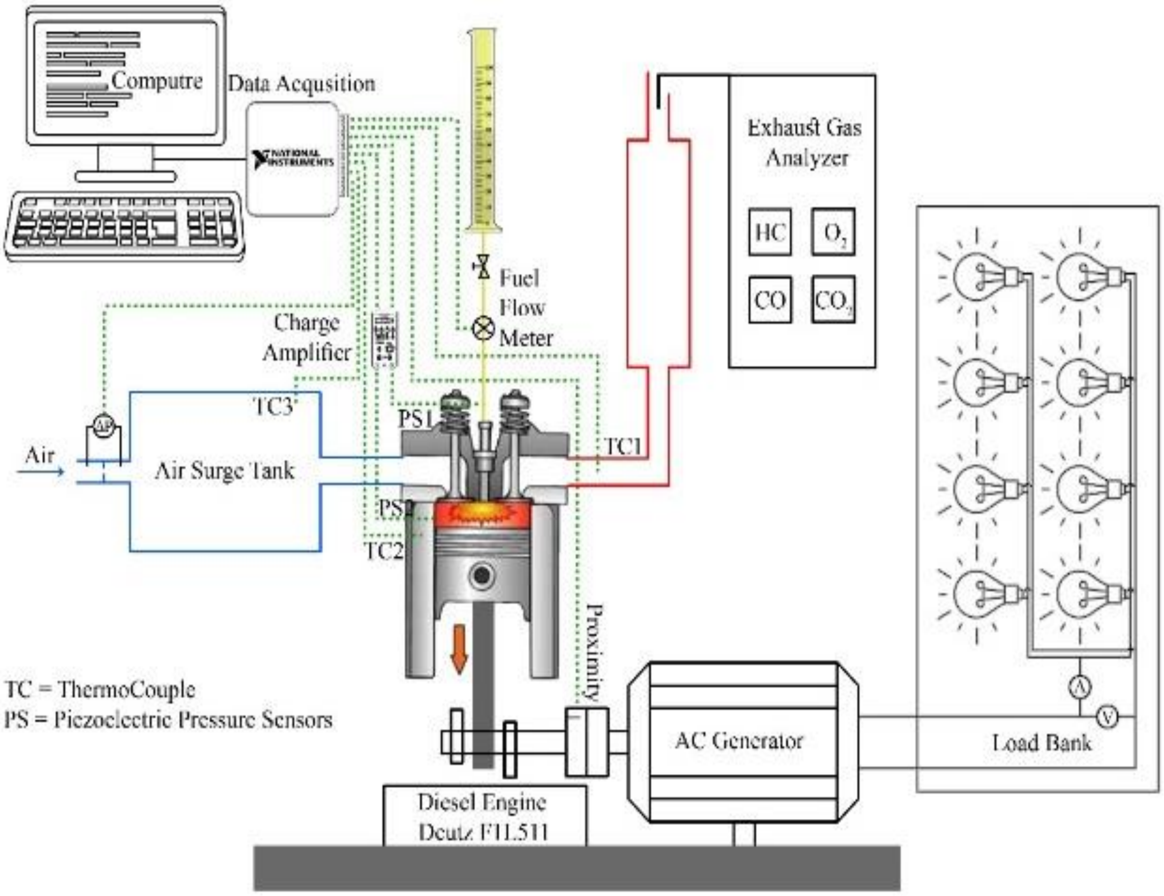


Fig. 2 Schematic diagram of the experimental test engine rig

RESULT AND DISCUSSION

Catalyst Characterization

The polycyclic aromatic sulfonate catalyst structure (RS-SO_3H) was confirmed through the FT-IR spectrum in figure (3), where the SO_3H group was present at 1180.46 cm-1. The SEM in figure (4) showed rough particles with irregular surfaces contained many holes on the surface. The average surface area of RS–SO_3H was 39.11 m^2/g, and the average size of the hole was 9.19 nm. For the decomposition of-SO_3H, the thermal stability of RS–SO_3H was 280ºC [10].

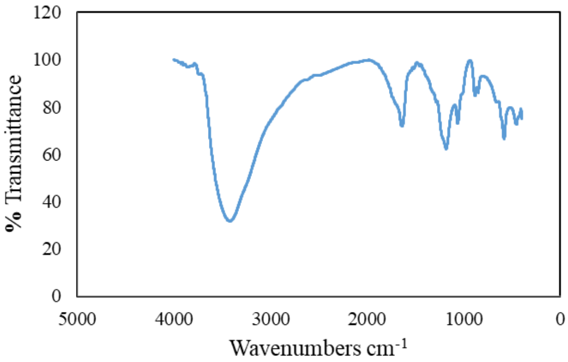


Fig. 3 The sulfonated catalyst

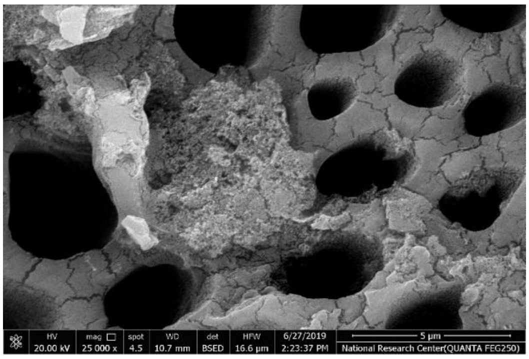


Fig. 4 SEM of sulfonated catalyst

Biodiesel Production

The highest conversion efficiency of converting WCO into biodiesel was extended to 90.38% using the equations (1) and (2) and the Gas Chromatograph technique in Table (1), with 92.5% maximum mass yield and 97.7% wt. methyl ester content at the optimized conditions (50 g oil used at 70 °C and methanol: oil molar ratio (20: 1) at 10% wt. catalyst for 6 h).

The reusability of the acidic catalyst was studied in Fig.5 (a). At the optimized condition, the conversion efficiency% decreased from 90.37 to 88.56% after 8 cycles since the number of catalytic active sites on the catalyst reduced after 8 cycles. while the percent FFA conversion remained constant around 91.1 percent, as shown in Fig 5 (b). Then it started to fall. The catalyst's reusability has demonstrated to be quite stable. After eight runs, the SO_3H level of fresh catalyst reduced from 10 mmole/gm to 8.18 mmole/g (approximately 18.2%), indicating that the catalyst's activity had decreased slightly as a result of SO_3H leaching. [10].

The aspen plus program was used in the description of the biodiesel production process starting from catalyst synthesis and depending on the lab scale as shown in (figures 6,7).

Figure (6) described the heterogeneous catalyst synthesis process, while figure (7) shows the process scheme commencing with the biodiesel synthesis and followed by the downstream processing steps to obtain the pure biodiesel and glycerol products. Table (2) shows the feed and product material flow details for the process.

Fuel Sample Characterization

The properties of the pure biodiesel prepared (B100), the commercial diesel fuel (D100), and the ASTM standards biodiesel D6751 are given in the table (3).

It is explained that the diesel oil viscosity is lower than the biodiesel fuel. The biodiesel density is around 6.09% greater than the diesel oil. The heating value is nearly 14% lower than that of diesel oil. Therefore, it's essential to increase the injected fuel quantity in the combustion chamber to supply the same quantity of power. Fuels having a flash point exceeding 63°C are considered nonviolent. Thus, biodiesel with a high flash point (90oC) is a very secure fuel to handle and store. The flashpoint of biodiesel blends (B10, B15, B20) is much higher than the diesel oil, which makes the biodiesel a desirable choice as concerns safety. According to the diesel oil, the WCO methyl ester can be used as an elegant diesel fuel in cold weather due to its high pour point [17]

Table (1): The methyl ester content% for the optimum produced biodiesel

Peak	Retention time	FAME	GC yield%	Common name
1	20.927	C16:0	10.29851	Palmitic acid ME
2	25.541	C18:0	18.59634	Stearic acid ME
3	25.872	C18:1	17.70973	Oleic acid ME
4	26.535	C18:2	48.72631	Linoleic acid ME
5	27.179	C18:3	2.37877	Linolenic acid ME
		Total	**97.70965**	

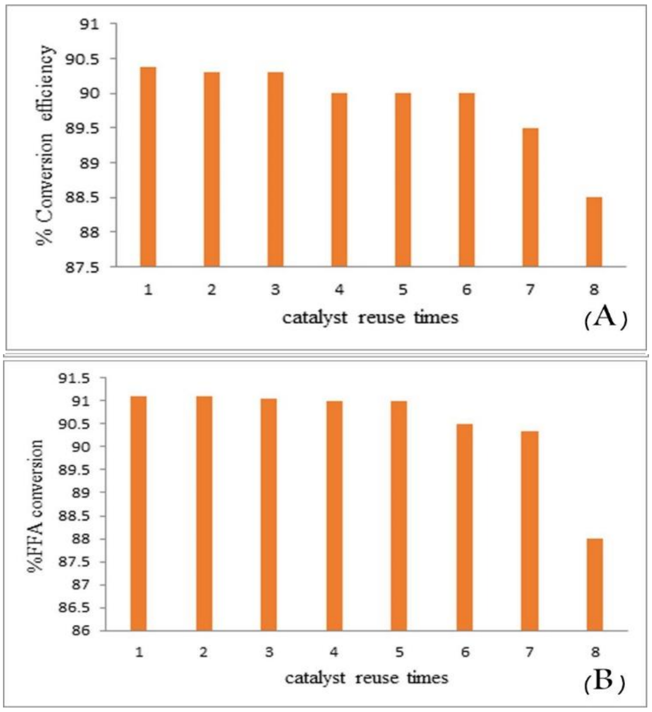
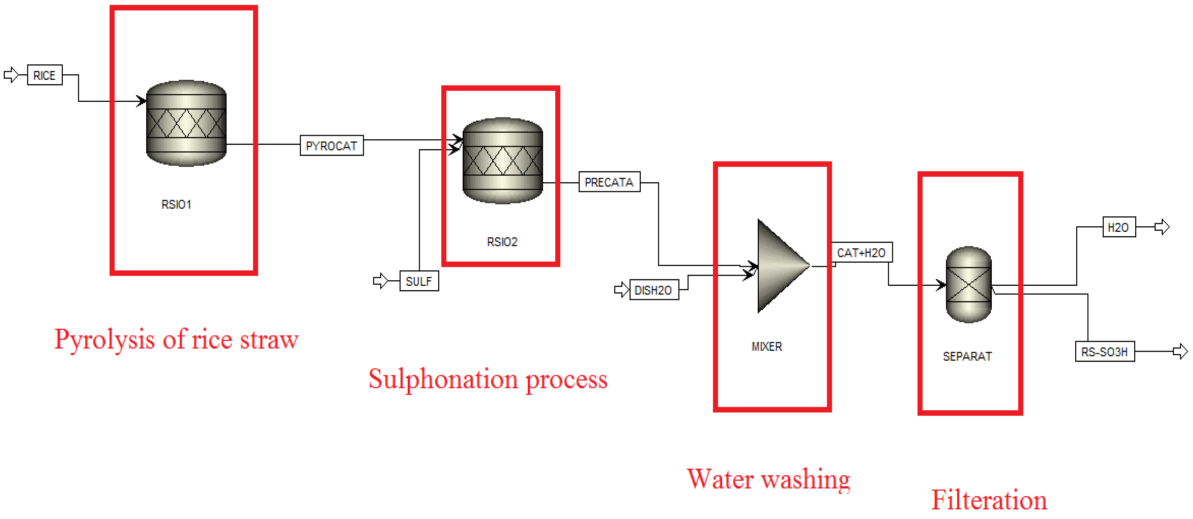


Fig.5. a. Influence of catalyst reuse on % conversion efficiency of raw oil under optimum condition. b. Influence of catalyst reuse on %FFA conversion under optimum condition



.Fig. 6 ASPEN PLUS model for catalyst preparation

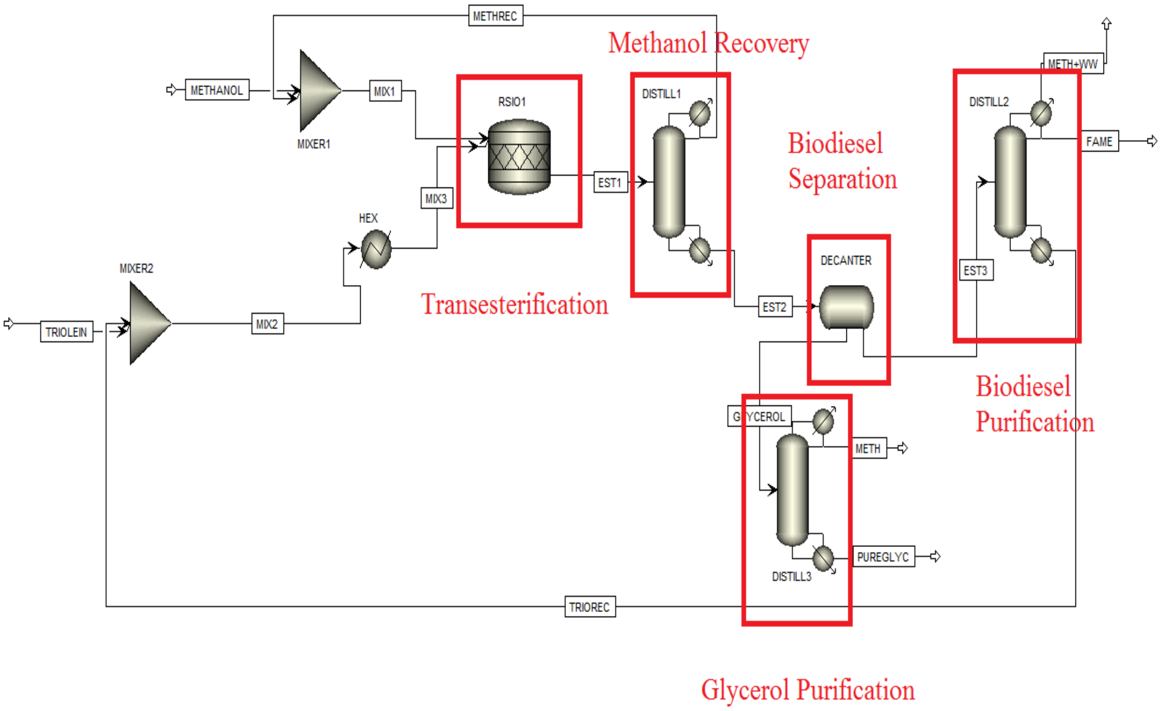


Fig. 7 ASPEN PLUS model for biodiesel production from WCO

Table (2): Full description for material balance of input streams and output streams

Units	**Temperature**	**Mass Flows**	**TRIOL-01**	**METHA-01**	**GLYCE-01**	**METHY-01**	**WATER**	**Volume Flow**
	ºC	Kg/h	Kg/h	Kg/h	Kg/h	Kg/h	Kg/h	L/Min
TRIOLEIN	25	945	945	0	0	0	0	17.313
METHANOL	25	103	0	103	0	0	0	2.165
MIX1	52.098	315	0	315	0	0	0	6.909
MIX2	94.931	1055	1050	0	0.051	4.949	0	20.774
MIX3	50	1055	1050	0	0.051	4.949	0	20.02
EST1	70	1370	105	212.409	98.341	954.252	0	239.938
EST2	366.577	1158	105	0.409	98.341	954.252	0	37.184
EST3	25	1059.40	105	0.107	0.051	954.251	0	22.932
GLYCEROL	25	98.591	0	0.302	98.288	0.001	0	1.292
METH	109.046	1	0	0.125	0.875	0	0	0.015
PUREGLYC	286.616	97.591	0	0.177	97.413	0.001	0	1.565
FAME	341.894	949.349	0	0.107	0	949.243	0	25.716
METH+WW	341.894	0.061	0	0	0	0.06	0	0.167

Performance of The Diesel Engine Fueled By The Biodiesel Blend From The Produced Methyl Esters of WCO

Performing the diesel engine has been experimentally examined with the produced methyl esters of WCO as biodiesel blends (B10, B15, and B20) compared to the diesel oil. Engine performance parameters such as the thermal efficiency, specific fuel consumption, air-fuel ratio, and the exhaust gas temperature were assessed for several engine loading conditions and at 1500 rpm steady rotation speed.

Specific Fuel Consumption

Brake specific fuel consumption is expressed as the proportion of mass fuel consumption to brake power. Figure (8) points out the variation of specific fuel consumption at several loads for the WCO biodiesel blends (B10, B15, and B20) and diesel oil. Because of an increase in load, the specific fuel consumption decreases with a rise in load [4][18-20]. Most investigators agree that a small increase in the biodiesel fuel is required by the engine to achieve the identical output power as a compensation for the lower calorific value of the biodiesel. B15 is the best blend compared with the other proportions.

Thermal Efficiency

Figure (9) illustrates the thermal efficiency for the biodiesel blends with varied engine loads as related to diesel oil. For all engine loads, the biodiesel blends thermal efficiencies are elevated compared to diesel oil. The rise in the thermal efficiency for the biodiesel blends was because of the deficient combustion characteristics and the volatility of WCO biodiesel related to the diesel oil. The WCO biodiesel density exceeds that of diesel oil. Higher viscosity results in a decrease in thermal efficiency, lower calorific value, and lower volatility of biodiesel may cause deficient atomization and vaporization [21-24]. Because its calorific value is close to that of diesel oil, B15 has a higher thermal efficiency than the other blend proportions.

Exhaust Gas Temperature

The exhaust gas temperature at several engine loads for the biodiesel blends (B10, B15, B20, and D100) is given in Figure (10). Decreasing the exhaust gas temperature refers to high thermal efficiency. The exhaust gas temperature increases by the rise of the load. This increase could also be because of the higher interior temperature of the engine chamber, which requires more fuel to satisfy the higher load needs. Relating to fossil diesel, the exhaust gas temperatures are recorded for the biodiesel blends for all engine loads. B20 is the preferred blend compared with the other proportions at the different loads [25-27].

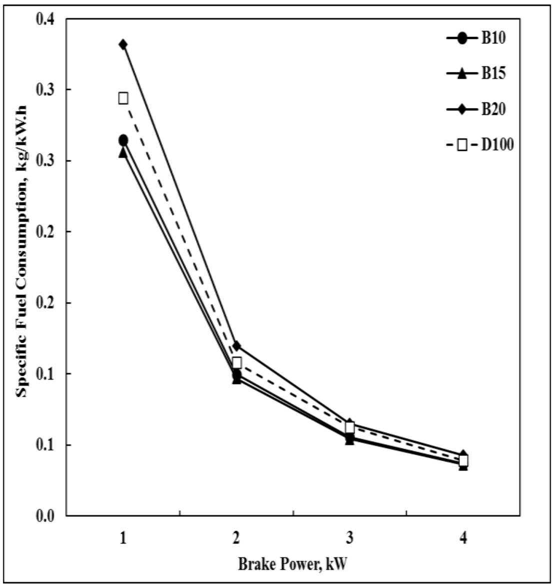


Fig. 8 Variation of specific fuel consumption with engine loads for diesel, WCO biodiesel blends (B10, B15 and B20).

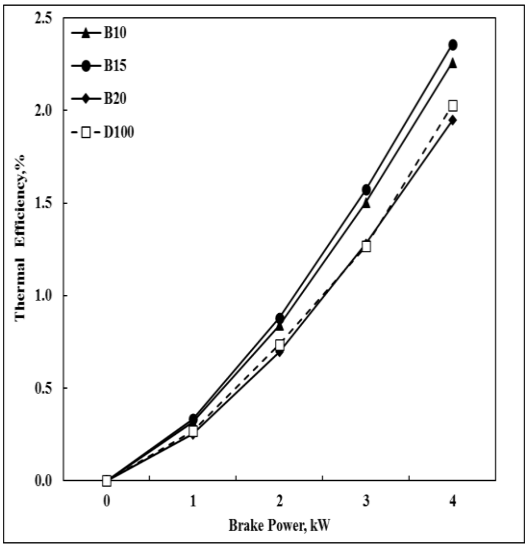


Fig.9 Effect of engine brake power on thermal efficiency for different engine loads for biodiesel blended (B10, B15, B20 and D100)

Volumetric Efficiency

Figure (11) presents the effect of volumetric efficiency with the engine load for the different biodiesel blends (B10, B15, B20, and D100). This higher interior temperature the engine chamber may be the reason for this increase, which leads to extra fuel burning to meet the high load needs. The volumetric efficiency decreases by increasing the load for tested fuels and increases for the biodiesel blend proportions. B20 is the suitable one which has high efficiency compared with the other blends. Since the diesel oil has a lower exhaust temperature, the volumetric efficiency is high [28-31] [6].

Air-Fuel Ratio

The impacts of air to fuel ratio for different engine loads for the biodiesel blended (B10, B15, B20, and D100) are noted in Figure (12). Comparing with the diesel fuel (D100), the Air to fuel ratio for B10 is approximately the best of the other blends as a result of the complete combustion [14-16].

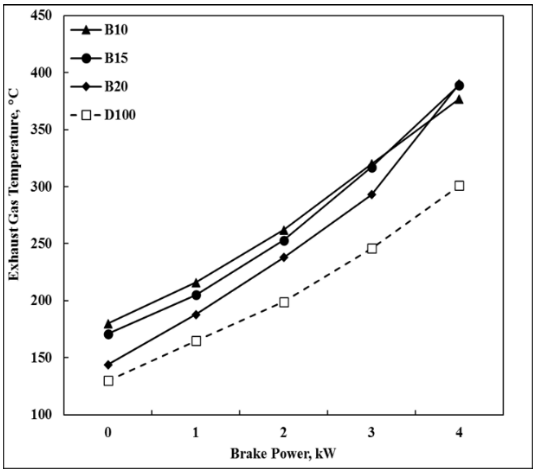


Fig.10 Effect of engine brake power on exhaust gas temperature for different engine loads for biodiesel blended (B10, B15, B20 and D100).

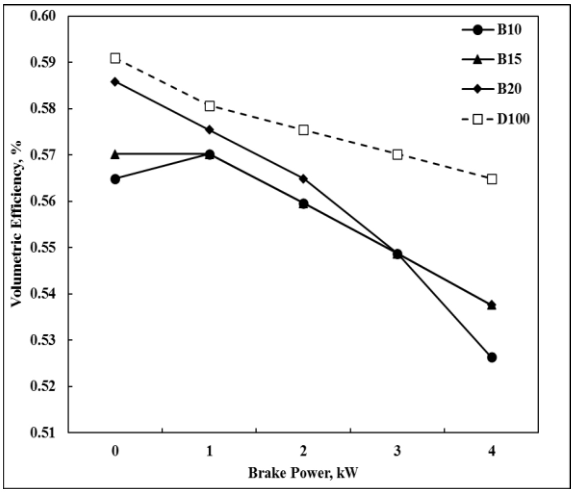


Fig. 11 Effect of engine brake power on volumetric efficiency for different engine loads for biodiesel blended (B10, B15, B20 and D100).

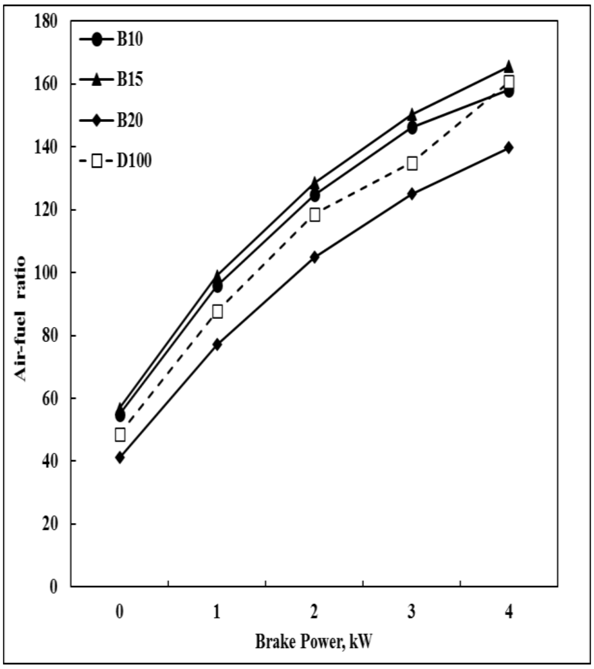


Fig. 12 Effect of engine brake power on air-fuel ratio for different engine loads for biodiesel blended (B10, B15, B20 and D100).

Comparison of Diesel Engine Performance Fueled With (Diesel- Biodiesel) Blended (B10, B15, B20)

The following Table (4) shows a comparison of the diesel engine performance during burning of the biodiesel blends at 100% of the engine load compared to the performance during burning of the diesel oil. Specific fuel consumption for B15 decreased by nearly 7.6% compared to diesel oil. When compared to diesel fuel, the thermal efficiency of B15 increased by up to 16%. The exhaust gas temperature increased for B10 by about 25% and for B15 by 29% compared to the diesel oil. Volumetric efficiency decreases for B15 by about 4% compared with diesel oil. Air to fuel ratio for B10 decreased by 1.6% compared to diesel fuel and for B15 increased by 3%. Applying the Multi-criteria technique by using equation (3), B15 gives the best engine performance, as shown in table (5).

$$\boldsymbol{x = \frac{f - f*}{f** - f*}} \qquad \textbf{(3)}$$

Where; f: performance value , x: value after normalization

f*: unfavorable value f**: favorable value.

Table (4): Comparison of engine performance for different fuels.

Performance	B10	B15	B20
Specific Fuel Consumption	-5%	-7.60%	9%
Thermal Efficiency	11.30%	16%	-4.00%
Exhaust Gas Temperature	25%	29%	30%
Volumetric Efficiency	-6.80%	-4%	-4.80%
Air- Fuel Ratio	-1.60%	3.00%	-13%

Table (5): Normalization of engine performance results using multi-criteria technique

Performance	B10	B15	B20
Specific fuel consumption	0.84	1	0
Thermal efficiency	0.76	1	0
Exhaust gas temperature	1	0.21	0
Volumetric efficiency	0	1	0.71
Air: fuel ratio	0.71	1	0
SUM	0.66	0.84	0.14

Exhaust Emissions and Oxygen Concentration

The exhaust emissions of the diesel engine have been experimentally investigated with the produced WCO methyl esters as biodiesel blends (B10, B15, and B20) compared to diesel oil. The engine emissions, like CO_2, CO, HC, and oxygen concentration, were measured at the engine under various loading conditions and at a constant rotation speed of 1500 rpm.

CO2 Emissions

The variance of CO_2 emissions with the engine load for the biodiesel blended proportions (B10, B15, B20, and D100) is shown in Figure (13). The increases in engine load increase CO_2 emissions due to the greater fuel entry during the load increase. The CO_2 emissions from B15 are lower than those from B10, B20, and diesel fuel [17,18].

CO Emissions

The variance of carbon monoxide emissions with the engine load for the biodiesel blended proportions (B10, B15, B20, and D100) is depicted in Figure (14). For all examined fuels, there is an increase in CO emissions with the increase of engine loads. The CO emissions from B15 are lower than the CO emissions from B10 and B20. The CO emissions from B15 are lower than the CO emissions from D100. Carbon monoxide is a product of partial combustion due to the deficient amount of air in the air to fuel mixture. The reduction in carbon monoxide emissions for biodiesel is due to the oxygen molecules present in the fuel and the lower carbon content as compared to that of diesel fuel, which leads to the better combustion [31-33].

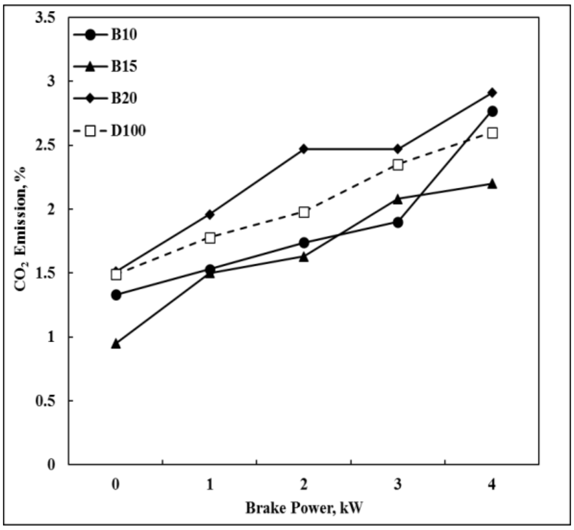


Fig. 13 Effect of engine brake power on CO_2 Emission for biodiesel blended proportions (B10, B15, B20 and D100)

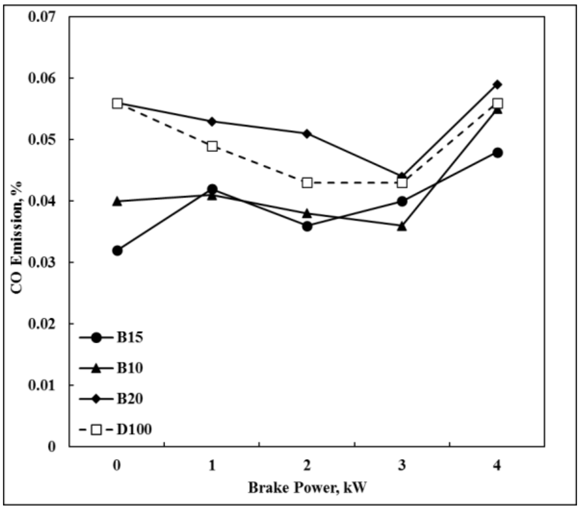


Fig. 14 Effect of engine brake power on CO Emission for biodiesel blended proportions (B10, B15, B20 and D100)

HC Emission

As shown in figure (15), at low engine load, the HC emissions decrease and increase with the increase in the engine load. This is often because of the presence of the fuel-rich mixture and the lack of oxygen resulting from the engine operation. The biodiesel blends with the diesel oil produced lower HC emissions with the least engine loads compared to the diesel oil. HC emissions decrease when the biodiesel percentage increases in its blends because of the better cetane number and oxygen content. It can be perceived that B15 has the least value of the hydrocarbons thanks to the oxygenated nature of the biodiesel, where more oxygen is accessible for the burning and thus reduces the hydrocarbon emissions within the exhaust [24][34,35].

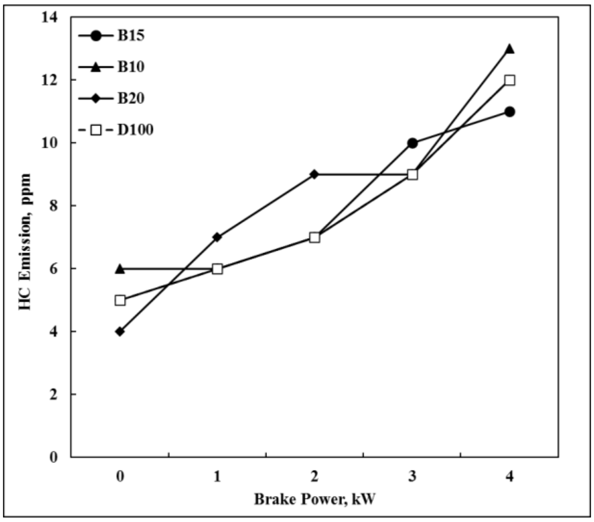


Fig. 15 Effect of engine brake power on HC emission for biodiesel blended proportions (B10, B15, B20 and D100)

Oxygen Concentration

The effect of the oxygen concentration on the engine load for the biodiesel blends (B10, B15, B20, and D100) is indicated in figure (16). The O_2 content decreases in the exhaust gas with the increase in load because of the fuller mixture being burnt in the interior of the engine chamber. The higher exhaust temperature leads to the largest portion of the oxygen available in the cylinder additionally reacting with the carbon to form CO and CO_2 at the higher loads. Therefore, a lesser amount of O_2 is liberated into the atmosphere. In the case of B20 is the best blend compared to the other blends and the diesel fuel [36-41].

Comparison Between (Diesel- Biodiesel) Blends (B10, B15, B20) For Diesel Engine Exhaust Emissions

Table (6) presents the comparison of the diesel engine exhaust emissions fed with the WCO biodiesel blends at 100% of the engine load with the results for the diesel fuel. The CO_2 emissions for B15 decreased by up to 15% compared to diesel fuel, but for the other blends, it is increasing. The CO emissions decreased for B15 by about 14% compared to diesel fuel. When compared to diesel fuel, B15 reduced HC emissions by up to 8%. Applying the Multi-criteria technique by using the equation (3), B15 gives the best exhaust emissions, as shown in table (7).

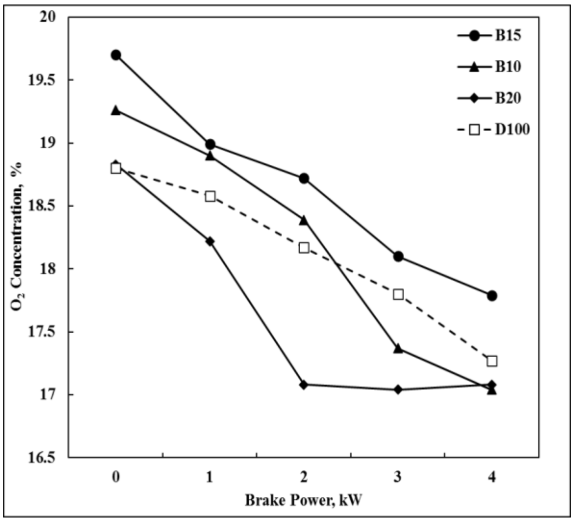


Fig. 16 Effect of engine brake power on O_2 Emission for biodiesel blended proportions (B10, B15, B20 and D100)

Table (6): Comparison of the emissions for different fuels

Emissions	B10	B15	B20
CO	-1.7%	-14%	5.3%
CO2	7%	-15%	12%
HC	8%	-8%	0%
O2	-1.3%	3. %	-1.1%

Table (7): Normalization of the emission results using multi-criteria technique

Emissions	B10	B15	B20
CO	0.36	1	0
CO_2	0.18	1	0
HC	0	1	0.5
O_2	0.58	0.31	0.56
SUM	0.28	0.82	0.265

Conclusions

- An environmentally friendly, inexpensive, heterogeneous sulfonated (RS-SO3H), catalyst showed a highly effective convert (WCO) into biodiesel. The maximum mass yield of the biodiesel was extended to 92.5% and the conversion efficiency% reached 90.38 wt.%.
- The engine performance and the exhaust emissions of the direct injection diesel engine

fueled with the biodiesel from the WCO as elegant biodiesel and its blends with diesel are studied and compared with the elegant diesel fuel, which indicates to:

- As engine loads increase, all emission concentrations decrease. The emissions concentrations of CO, CO_2, and HC are reduced for B15 fuels, but the O_2 content reduced for B20 compared to diesel fuel.
- As engine load increases, specific fuel consumption decreases. is the best blend compared with the other proportions due to the slight increase in the biodiesel fuel needed by the engine to accomplish the same output power as recompense.
- As engine loads are increased, thermal efficiency increases. Because B15's calorific value is close to that of diesel fuel, its thermal efficiency increased when compared to the other blend proportions.
- The volumetric efficiency of the tested fuels decreases with increasing load and increases with increasing biodiesel blend proportions.B20 is the best one which has high efficiency compared with the other blends.
- The increase in exhaust gas temperature is caused by an increase in loads. Elevated exhaust gas temperatures are noted for the biodiesel blends related to fossil diesel for the engine loads. B20 is the best blend compared with the other proportions at the different loads.

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Table (8): list of Symbols

Symbols	Name
RICE	Rice Straw
RSIO	Stochiometric Reactor
PYROCAT	Pyrolyze Catalyst
PRECAT	Pre-Catalyst
CAT+H2O	Catalyst + Water
MIX	Mixer
METHREC	Methanol Recovery
HEX	Heat Exchanger
EST	Ester
DISTILL	Distilled Water
PURE GLY	Pure Glycerol
FAME	Fatty Acid Methyl Ester
WCO	Waste cooking oil
B100	Pure biodiesel
B10	10% biodiesel + 90% diesel fuel
B15	15% biodiesel+ 85% diesel fuel
B20	20% biodiesel + 80% diesel fuel
RS-SO_3H	polycyclic aromatic sulfonate catalyst