Methyl-ester bio-fuel characteristics as a substitute renewable I.C.E. fuel: 1- Fuel perparation and performance tests of waste vegetable oil as bio-diesel

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The production of the Methyl Ester of Waste Vegetable Oil [MEWVO] for use as a bio-diesel fuel has been studied. The essential part of the process is the transesterification of waste vegetable oil with methanol alcohol in the presence of an alkyl sodium hydroxyl-catalyst, to yield the methyl ester bio-diesel of waste vegetable oil as a product and glycerin as a by-product. Bio-diesel production unit has been built to produce about 200 liters of bio-diesel fuel and 40 liters of glycerin daily. Experiments have been performed for the purpose of determining the optimum conditions for the production of MEWVO. It was found that the room temperature of 25 °C; sodium hydroxide catalyst percentage by weight of waste vegetable oil 0.5-0.6 %; stirring time 60 minutes and 50% excess of methanol with $NaOCH_3$ were optimum conditions. In addition, agitation was not necessary after the reaction mixture became homogeneous. Density, viscosity, calorific value, and Cetane No. of the MEWVO were measured. To test the produced Bio-diesel as a fuel, engine performance tests were performed using tractor diesel engine, 2cylinder,Helwan 35-IMT of maximum power 26.12 kW at 2200 rpm at B20 (20% bio-diesel+80% pure-diesel).

اجريت دراسة انتاج وأختبار الأداء للوقود الحيوى المستخلص من الزيوت النباتية المستعملة . كان الجزّ ء الرئيسى فى عملية الانتاج هو الخاص باسترة الوقود النباتى المستعمل باستخدام الكحول المثيلى فى وجود محفز لأنتاج وقود الديزل الحيوى اساسا وأنتاج الجلسرين كأحد روافد الأنتاج الثانوية. الوحدة التى صممت لذلك أنتجت 200 لتر وقود حيوى و 40 لتر جلسرين يوميا بالمعمل. التجارب التى أجريت لاستخلاص الوقود الحيوى كانت بهدف الحصول على أفضل السبل لانتاج هذا الوقود من حيث أفضل درجة حرارة غرفة لاستخلاص الوقود ، افضل نسبة وزنية للمحفز {هيدوكسيد الصوديوم % 6.0 لتر جلسرين يوميا الخط المكونات اللازمة لأنتاج الوقود (60 دقيقة)؛ أفضل نسبة وزنية للمحفز {هيدوكسيد الصوديوم % 6.0 ÷0.0 } الفضل زمن الخواص الفيزيائية و القيمة الحرارية للوقود الحيوى بمعامل مصر للبترول. تم اجراء تجارب لدراسة اداء محرك زراعى عند استخدام الوقود الحيوى الماستملة المستعملة المؤسترة حيث تم تعذية المحرك بالوقود الحيوى بمعامل معال استخدام الوقود الحيوى الماستعمان المالية المستعملة المؤسترة من معال العمل واليوقود الحيوى المالين المؤلول التى تعطى و 20 أنه معرك إلى الحيوى عالم العالين و من استخدام الوقود الحيوى المصنع من الزيوت النباتية المستعملة المؤسترة حيث تم تعذية المحرك بالوقود الحيوى المالي النع

Keywords: Bio-diesel, Trans esterification, Waste vegetable oil, Edible and non edible oils

1. Introduction

Biomass fuel- created by synthesis and obtained from recycled, plants or plants to be used again, is the fourth energy carrier in the world after oil, natural gas and coal. This fuel includes wood, straw, sugarcane residue, rice husks, municipal solid waste as well as edible and non-edible oil derived from seeds of vegetable plants. Biomass accounts for 3.2% of the primary energy consumption in the US and 18% in Sweden, [1]. Globally, the usage of environment friendly fuel is being encouraged. Energy extracted from biomass is perhaps the oldest source of renewable energy. The most important bio-fuels generated from biomass are bio-diesel, bio-gasoline and bio-ethanol.

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Bio-diesel is produced from virgin or used vegetable oil (both edible and non edible) and animal fats through various chemical processes. The most common is the transesterification process. These are generally methyl, ethyl or higher alcohol ester produced triglycerides which is from the main constituents of all natural oils and fats. Triglycerides react with alcohols in presence of a catalyst to form fatty acid esters. The physical and chemical properties of fatty esters are similar or even better than petroleum- based diesel, [3]. Accordingly, these fatty acid esters are generally called biodiesel.

Vegetable oil can be directly used in a diesel engine but only for short periods. It contains mixture of molecules with differing degrees of saturation that polymerize the engine oil. Engine performance problems encountered by using raw vegetable oil include poor atomization, chocking of nozzles, thermally unstable, higher viscosity, high amount of gum and wax, low heating value and make knocking and starting problems, [2]. Usta et al, [3] showed that tobacco seed oil methyl ester can be partially substituted for the diesel fuel at most engine operating conditions without any engine modification or preheating of the bio-diesel blended fuel. In Egypt, scientists are devoting good deal of research effort to produce economical biodiesel fuel from non edible vegetable plants as Jojoba, [4] and Jatrophia Curcas, [5], besides the source of waste vegetable oils.

The viscosity difference between triacylglycerols of vegetable oils and their corresponding methyl esters resulting from transesterification is approximately one order of magnitude as mentioned in Refs. [5-9]. Research on methyl ester as an alternative diesel fuel has been going on for last ten years but intensified in last five years. The main causes for the attention paid to bio-diesel are recent higher petroleum price, the reduction of the reserved crude oil allover the world as well as the advantages of bio-diesel than that of pure diesel from view point of emissions reduction in combustion, besides free from sulfur [6-10]. Moussa et al, [7-8] found that sunflower, soybean and corn oil blends had similar CO and NO_x emission trends showing lower CO emission and higher NO_x emission than diesel oil. In case of cotton oil, there was a more marked reduction in both CO and NO_x emission than that of diesel oil. Soot emission was lower for all bio-diesel tested fuels.

Corinna WU. [11] stated that ordinary diesel fuel is a mixture of hydrocarbon molecules of differing lengths and structures. These molecules contain no oxygen atoms. They may have double-bonded carbons that cause the chains to bend. The characteristics of the hydrocarbons affect how they burn. Vegetable oils, on the other hand, are mixtures of fatty acids molecules that contain carbon, hydrogen, and oxygen atoms. The fatty acids may be saturated, monounsaturated, or polyunsaturated. Length of carbon chains and number of double bonds in the fuel molecules produce low temperature suitability. spray formation and carbon residue.

The present work deals with the production of bio-diesel from the most available waste vegetable oil as an example of edible oil. Physical and chemical properties of oil are measured and compared with that of diesel fuel. The waste oil is taken from cafeterias and restaurants that used the oil derived from cotton seeds. Field performance tests using tractor engine 2-cylinder,Helwan 35-IMT of maximum power 26.12 kW at 2200 rpm at B20 (20% bio-diesel+80% pure-diesel) were carried out.

2. Seting up for trans-esterification process

Bio-diesel is made by the transvegetable oil with alcohol, esterification of namely methanol, in the presence of a catalyst, namely sodium hydroxyl, NaOH. The vegetable oil molecules are composed of fatty acids held together by a glycerin back one. The catalyst is added to the vegetable oil along with the alcohol. The catalyst helps the separation of vegetable oil molecules and the separation of glycerin back bone. The fatty acids then combine with the alcohol molecules to form alky-ester, the chemical name of which is the bio-diesel or methyl ester biodiesel as shown in fig. 1, [7]:

An experimental set-up shown in fig. 2 is used for production of bio-diesel from waste vegetable oils. The yield of this unit is to produce 200 lit of bio-diesel and 40 lit of glycerin daily.

The set-up contains five stainless steel tanks, namely, waste vegetable oil tank, catalyst tank, premix tank, processor tank and the washing tank. Two electric heaters are installed. One in the raw vegetable tank and the other in the processor tank. Two pumps are associated with four control valves for pumping and circulating for the purpose of stirring. The above components are fixed on metal frame. Procedures of trans-esterefication include the following steps:

1- Pouring the waste vegetable oil into the first tank where the screen filter is installed at the entrance of the tank preventing any impurities as seeds particles or food residue to be found in the mixture. The oil is then preheated to a prescribed temperature so as the water content in the raw oil is evaporated.

2- In the catalyst premix tank, the sodium hydroxyle is added to methanol and then stirred well by the closed circulation pump. Methoxide is then formed as shown in the following equation:

$$Na OH + CH_3 OH \rightarrow Na CH_3 O + H_2 O$$
(1)



Fig. 1. Chemical reaction structure of esterefication process.



Fig. 2. Schematic diagram for bio-diesel trans-esterefication unit.

It is necessary to obtain the exact amount of NaOH needed to neutralize the fatty acids because adding higher or lower quantity reduces the quantity of produced bio-diesel.

3- The waste vegetable oil and sodium methoxide,NaCH3O, were pumped to the processor tank with stirring softly during circulation for prescribed time and temperature. During this time, trans-esterification process takes place.

4- The circulation is terminated and the mixture is allowed to make phase separation over night. The ester phase is then decanted from the mixture where ester methyl bio-diesel is separated from glycerin.

5- Excess alcohol and residual catalyst are washed out from ester with water in a separate tank prepared for this purpose. Water is sprayed into the top of the tank at low velocity. When water falls down it washes the soaps and surplus methanol out of the bio-diesel.

6- As an example of one experimental time schedule is that:

- a. Heating and filtering time is 40 mins
- b. Mixing of constituents' time is 20 mins.
- c. Blending of chemicals with oil time is 60 mins.
- d. Settling time is 8 hrs.
- e. Water washing time is 12 hrs.
- f. Drying time is 1.0 hrs

Table 2

g. Total process time for one batch of 200 lit bio-diesel and 40 lit of glycerin is 23 hrs, approximately.

h. Set of experiments is carried out to study the effect of catalyst quantity, oil temperature, time of stirring and water content, methanol quantity on the ester conversion percent.

7- Physical and chemical properties of yielded bio-diesel derived from waste vegetable oils are

measured in Miser Petroleum labs, as shown in tables 1 and 2. The given properties of biodiesel is matched with that given for bio-diesel in ASTM D6751-07b (March 2007) Table. The flow diagram of trans-esterefication process is shown in fig. 3.

One may observe that when waste oil is heated it becomes hydrogenated and produces free fatty acids that lead to higher gelling temperature. As a consequence, many waste oils are existed as solid at room temperature. Therefore, on processing this waste oil source must be neutralized and the free fatty acids must be eliminated, [10-12].

3. Results and discussion

Experiments are carried out to study the effect of catalyst quantity, reaction temperature, stirring time, and quantity of water content on the oil ester conversion percentage. The ester conversion percentage equals the ratio of mass of vielded bio-diesel to the total mass of raw vegetable oil participating in the process.

Table 1 Free fatty acid composition of waste vegetable oil

Componens	Wt,%	
Mystric (C ₁₆ :O)	1.4	
Menstotic (C ₁₄ :1)	0.1	
Palmitic (C ₁₆ :0)	23	
Palmitic (C ₁₆ :1)	2	
Stearic (C18:0)	1.1	
Oleic (C ₁₈ :1)	22.9	
Linolenic (C ₁₈ :2)	47.8	
Linolenic (C ₁₈ :3)	0.3	
Erucic (C ₂₂ :1)	1.3	

Properties of methyl-ester waste vegetable oil and diesel fuels

parameter	Waste oil bio diesel	Diesel fuel
Density at 15 C ⁰	0.8978	0.846
Viscosity,mm ² /s at 40C ⁰	6.0	3.3
Cetane number	51.2	47
Pour point, C ⁰	-3	3
Heating value MJL ⁻¹	38.3	40
Water and sediments, vol%	0.0	0.075
Viscosity index,mm ² /s, at 40 °C	205	97
Flash point, min	141	134
Ash content,%	0.001	0.4



Fig.3. Flow diagram of Esterefication process.

3.1. Effect of reaction temperature

Fig. 4 shows the effect of variation of reaction temperature on the yielded bio-diesel. The increase of reaction temperature causes the increase of the bio-diesel yield (ester conversion, %) up to the maximum value and then starts to decline. The variation seems to be linear except at the end where the trend turns over down wards. The maximum temperature gives maximum yield as 55 °C. It is the boiling temperature, the methyl alcohol. At this temperature, the methanol begins to evaporate. For this reason, the bio-diesel begins decreasing. One may conclude that the optimum temperature for ester process is $55 \,^{\circ}$ C.

3.2. Effect of catalyst quantity

Fig. 5 depicts the effect of catalyst amount variation on the yield of bio-diesel. The ester formation increases as the mass of catalyst mass increases. The rate of ester conversion is high at first and then lowers with the mass of the catalyst. The reaction is carried out at temperature of $55 \, ^{\circ}$ C with oil to methanol ratio equals 5:1.



Fig. 4. Effect of oil temperature on ester conversion (yield,%) at the oil to methanol ratio of 5:1.

3.3. Effect of stirring time

The effect of stirring time is illustrated in fig.6, where the bio-diesel yield increases with the increase of stirring time. A high degree of conversion could be obtained only if alcohol phases have been blended into one homogeneous phase of the oil.

This requires extremely vigorous stirring at the start of the reaction. When the reaction mixture is homogeneous, the conversion and time to reach maximum conversion are independent of agitation. There is a significant effect of stirring time on the yield percentage.



Fig. 5. Effect of amount of catalyst on ester CONVERSION at temperature of 55°C and ratio of 5:1.



Fig. 6. Effect of stirring time on ester conversion at temperature of 55°C and ratio of 5:1.

3.4 . Effect of water content percentage increase

Fig. 7 shows the bad effect of water content increase on the ester conversion percentage. Therefore, it can be observed that the increase of water content reduces the biodiesel yield. It is fruitful to reduce the water content in the waste vegetable oil as low as zero value to maximize the yield of bio-diesel as shown in fig. 7.

It is worth-mentioning that the importance of washing is the removal of residual catalyst from ester. Complete removal of sodium in the glycerin phase and the total sodium removal from the ester phase are needed.

4. Performance field tests

Bio-diesel derived from waste vegetable oil and pure diesel fuels individually are used to operate an agriculture tractor. The tractor is coupled with dynamometer to apply varying loads to traction engine at rated speed. The dynamometer is equipped with measurement facility of engine speed and brake torque. The tractor engine is a 2-cylinder, Helwan 35-IMT of maximum power 26.12 kW at 2200 rpm. The bore x stroke is 105 mm x 125 mm, where the compression ratio is 16:1, engine rated speed 1800 rpm. The experiments are carried out in the Agriculture Research Institute, in Alexandria.

A set of experiments are performed to determine the effect of engine power on exhaust temperature, brake specific fuel consumption, pollutant emission and brake thermal efficiency. Pure diesel fuel, BO, and the blend B20 (20% bio-diesel plus 80% diesel) fuels are used in this tests. Fig. 8 depicts the variation of brake torque and power with engine speed in case of bio-diesel and diesel fuels individually. The two fuels give the same behavior trends. At the same time the torque and power given by diesel are slightly higher than that of bio-diesel. Fortunately, the increase in torque of diesel than bio-diesel is not greater than 8%, while the increase in power is not greater than 5%, approximately. These results give proper engine performance of bio-diesel comparable to diesel fuel.



Fig.7. Effect of water content on ester conversion at temperature of 55°C and ratio of 5:1.



Fig. 8. Variations of torque and power for bio-diesel and diesel fuels with engine speed.

The results obtained at constant-speed operation showed that the diesel fuel operation recorded higher exhaust temperatures than B20 at all loads as shown in fig 9. This was due to the higher relative density and lower energy content of B20. The net calorific value of the bio-diesel used is about 12.22% lower than that of diesel fuel. The exhaust temperature served as an indicator of the combustion temperature.

As shown in fig. 10 the bsfc values decrease gradually with the load to levels that depend on the engine speed, remaining at higher level for B20 than pure diesel. The higher fuel consumption of bio-diesel can be related primarily to the lower-in average by 12.22%-net calorific value of biodiesel. However, this is probably not the only reason that leads to the higher bio-fuels consumption, bsfc. The lower bsfc can be related, reasonably, to the higher amounts of oxygen present in the considered blends. Fuel based oxygen, because of its indigenous property, accelerates reactions from within the extremely fuel rich spray patterns themselves, leading to more complete combustion.

As seen in fig. 11, the brake thermal efficiency of the engine increases with the load due to the bsfc decrease. It will be lower for biodiesel than that of diesel at low loads, and will be higher at slightly higher loads. It should be noted that their calorific values decrease with the increase of biodiesel and also that the calorific value is lower than conventional diesel. The bsfc will be higher for biodiesel for that reason. Brake thermal efficiency would be higher for biodiesel blend at higher loads. We think that the causes of decrease of brake thermal efficiency of biodiesel blend than diesel at low loads may be related to the atomization of the blends during injection and/or with the stability of the mixtures of fuels during storage, pumping and injection.

Since bio-diesel is free from sulfur, less sulfate emissions and particulate reduction is reported in the exhaust due to nearly absence of sulfur in biodiesel as shown in fig. 12. Bio diesel is an oxygenated fuel which leads to more complete combustion; hence CO emissions reduce in the exhaust as shown in fig. 13.



Fig. 9. Variation of exhaust temperature with engine brake power at rated speed.



Fig. 10. Variation of brake specific fuel consumption of diesel and bio-diesel fuels with engine power.

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Fig. 11. Comparison between diesel and bio-diesel brake thermal efficiency.



Fig. 12. Comparison between diesel and bio-diesel SO₂ emission.



Fig. 13. Comparison between diesel and bio-diesel CO emission.

The mechanism of NO_x formation from nitrogen been atmospheric has studied extensively and it is accepted that it is highly dependent upon temperature, due to the high activation energy needed for the reactions involved. Hence the most significant factor that causes NOx formation is high combustion temperatures. As shown in figs. 14 and 15, the emissions of NO and NO₂ firstly increase until the (air/fuel) ratio reach the theoretical value, and then decrease at higher loads. This is probably due to the increase in turbulence inside the cylinder, which may contribute to a faster combustion and to lower residence time of the species in the high temperature zones. every bio-fuel produced Almost higher amounts of NO_x than conventional diesel. It has been proposed that certain injection systems suffer from an unexpected advance of fuel injection timing caused by the higher bulk modulus of compressibility in the fuel blends containing bio-diesel. This increases the speed of sound, causing a faster transference of the pressure wave from the injection pump to the nozzle, thereby advancing the needle lift. It is well known that advancing injection timing causes an increase in NO_x emissions. But in this experiment we tested the only most optimum blend of biodiesel (B20), so the emissions of NO_x for biodiesel will be lower than that of diesel fuel.



Fig. 14. Comparison Between Diesel and Bio-Diesel NO Emission.



Fig. 15. Comparison between diesel and bio-diesel NO_2 emission.

5. Economic study

The cost of one liter of bio-diesel from waste vegetable oil is calculated and compared with the price cost of one liter of pure diesel fuel. The study is summarized in table 3.

One may conclude that the production of bio-diesel as an alternative to pure diesel is better for the national income by about 2.38 LE/lit.

6. Parametric study

A parametric and statistical study is performed for the factors affecting the methylester conversion yield. The resultant parametric equation that contains the effect of water content, reaction temperature, stirring time and catalyst mass is presented for waste vegetable oil as follows in empirical formula:

Table 3

Cost of one liter of bio-diesel

material	Price,
	LE/Liter
Waste vegetable oil	0.5
methanol	2
Catalyst (6 gm/lit)	0.06
Washing water(2 lit)	0.01
Electric consumption	0.1
Wages (2.5 LE/hr)	0.1
Total cost for 1.0 lit	2.77
Price of produced glycerin(200 ml)	5.0
Price of 1.0 lit of yielded bio-diesel if	0.75
sold as price of diesel	
Total gain for each lit of bio-diesel	5.77
The national income benefit for each	5.75-
litre	2.77=2.38

Yield,
$$\% = -66.9 + 10.77 \text{ W}^* + 24.25 \text{ C}^* + 0.2 \text{ T}^* - 0.34 \text{ St}^*.$$
 (2)

Inspection of the previous equation shows that water content of alcohol is the most important independent factor affecting the degree of conversion and that increasing water content decreases degree of conversion.

7. Conclusions

• Methyl ester derived from waste vegetable oil proved to have similar properties to diesel oil and is consequently suitable to be blended with diesel fuel in different percents.

• The use of a bio-diesel fuel as a blending stock for diesel fuels did not reveal any operating problems in the engine, besides showing many positive attributes.

• Transesterified oils give better performance, lubricity enhancers and consequently would have a positive synergism with fuel system components and serves as an additional oxygen source.

Nomenclature

BDF:	the bio-diesel fuel
C^* :	the normalized catalyst mass,
	(C _{catalyst} /C _{total mass of ingredients})
DF:	the diesel fuel
MEVO:	the Methyl Ester Vegetable Oil
<i>N</i> :	is the RPM
P:	is the horse power, kW
St^* :	is the normalized stirring time; (ST/t
	total experiment time)
St:	is the stirring time, s.
TOR:	is the torque, N.m.
Т	is the temperature, ^o C
T^* :	normalized reaction temperature,
	(T/T _{ambient})
t	is the time, s.
W^* :	the normalized water content of
	alcohol, (W/W total mass of ingredients)
W:	the mass, kg.
Yield,%:	is the percentage conversion of oil to
	ester mass.

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