Production of Ultra Low Sulfur Biodiesel From Waste Frying Oils and Its Mechanical Testing

Sadeq Emeish
Al-Balqa' Applied University
Faculty of Engineering Technology
Department of Chemical Engineering
Email: s.emish@fet.edu.jo

Aiman Al-Alawin
Al-Balqa' Applied University
Faculty of Engineering Tech.
Department of Mechanical Eng.
aalawin@yahoo.com

***Abstract*— The climate changes occurring due to increased carbon dioxide emissions and global warming, increasing air pollution and rapid depletion of conventional fossil fuels resources and the rising in their prices are the major problems in now a day.**

There are many projects under study such as solar power, wind power, nuclear power, oil shale, and biodiesel. Bio fuels are receiving increasing attention during the last few years.

Biodiesel was prepared from waste frying oils (WFO's) by transesterification reaction in the presence of ethoxide catalyst, which is prepared by heating ethanol and potassium hydroxide at 60˚C, and then added to the oil where the reaction will occur inside the reactor with uniform mixing.

The produced biodiesel was purified by kaolin, and the by-product during transesterification process was glycerine, which may be used in several industries such as cosmetics. A diesel engine performance tests using the produced biodiesel before and after purification were carried out. Torque, work and brake power were measured in addition to the thermal efficiency which was calculated from the measured variables.

Purified biodiesel can be used as an alternative source for petroleum diesel, where it has good specifications such as high cetane number, ultra low sulphur content, good viscosity, high net and gross energy and high thermal efficiency.

So it can be used in the diesel engines without any modifications for those engines, and without pollution problems.

Keywords—Biodiesel, Esterification, Waste Frying Oils, Ethoxide catalyst, Kaolin.

1.INTRODUCTION

1.1Definition:

The American society for testing and materials (ASTM), define biodiesel fuel as amonoalkyl ester of a long chain fatty acids derived from a renewable lipid feed stock such as vegetable oil or animal fat.

A mono alkly ester is the product of the reaction of straight chain alcohol, such as methanol or alcohol, with fat or oil (triglyceride) to form glycerol and the ester of long chain fatty acid.

"Bio" represent its renewable and biological source in contrast to traditional petroleum_based diesel fuel; "Diesel" refers to its use in diesel engine. Fatty acid alkly ester (FAAE) can be used as biodiesel fuel or can be used as an additive or extender to diesel fuel [1], [2], [3].

1.2 Description

Biodiesel is light to dark yellow liquid. It is practically immiscible with water, has a high boiling point and low vapor pressure. Typically ethyl ester biodiesel has a flash point of ~ 144 oC, making it rather non-flammable. Biodiesel has a density of ~ 0.872 g/cm3, less than of water. Biodiesel uncontaminated with starting material can be regarded as non-toxic.

It can be used as an additive in formulations of diesel to increase the lubricity of pure Ultra-Low Sulfur Diesel (ULSD) fuel. Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix.

For example, fuel containing 20% biodiesel is labeled B20. Pure biodiesel is referred to as B100. [4], [5], [6], [7].

1.3 Esterification and Transestrification:

Vegetable oils are not suitable direct replacement for diesel fuel engines due to their in appropriate physical properties such as longer molecular chains, lower pour points, lower vapor pressures, higher viscosities and higher flash point. These characteristics lead to problems in atomization an vapor air mixing which in its role causes incomplete combustion. However, physical properties of vegetable oil can be improved through dilution, pyrolysis, micro emulsion and esterification [7a]

Esterification is the general name for a chemical reaction in which two chemicals (typically an alcohol and acid) form an ester as the reaction product. These are commonly used as fragrance or flavor agents. The name ester is derived from the German Essig-Äther, an old name for acetic acid ethyl ester (ethyl acetate). [8,], [9], [10],[11].

. Biodiesel and its blends with conventional diesel are environment friendly and their use in diesel engine results in reduced exhaust pollutants as compared to conventional diesel fuel. As a result, biodiesel produces 78% less CO2 that diesel fuel. [12], [13], [14]. [15], [15a]. [15b], [15c].

2. PURIFICATION BY ADSORPTION

Using of adsorption technique instead of washing by water as a purification step will be more effective. According to the experiments, a high quantity of water still dissolved in the biodiesel after the purification step, which needs to be distilled again, so, adsorption will be more valuable.

The major types of adsorbents now days:

a) Kaolin b) Magnesium Silicate, (Mg (SiO) 2).

Kaolin is cheaper than (Mg (SiO) 2) and available in Jordan with high quality. [16]

2.1 Kaolin

A method of purifying a biodiesel fuel is by contacting with an adsorbent material such as kaolin. This method removes impurities, such as:

a) Soap b) Colors c) Odors d) unreacted catalyst

e) Glycerides f) sulfur g) Light fractions.

Kaolin is white –firing natural clay, which in its beneficial condition, is made up chiefly of minerals of the kaolin type. Kaolin clay is naturally occurring soft white clay. Also know as china clay, the name kaolin is derived from the Chinese word kaolin, which means "high ridge", and was the name of the hill where it was first discovered. Two minerals comprise the bulk of material found in kaolin, and they are: Kaolinite, dickite.

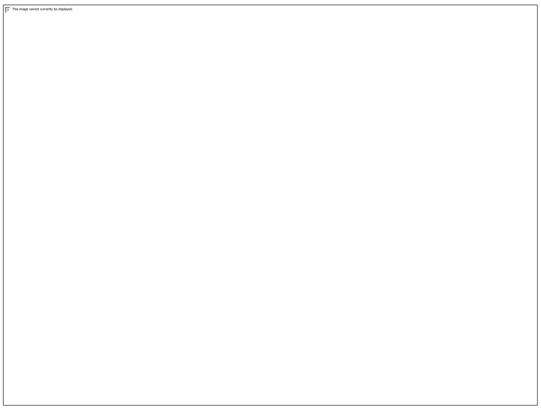

Fig. (2.1) Hydrogen's are colored in white, oxygen's in red (kaolin)

Fig. (2.2) Different view (001 plane) of kaolin

2.2 Fuel property measurements

Many fuel properties may be measured using different equipments in order to determine the produced biodiesel specifications and to compare it with the standard values given by the ASTM. These properties are the followings:

1) Specific gravity 2) Kinematic viscosity 3) Flash point

4) Boiling point (Distillation test) 5) Cetane number 6) Cloud point

7) Pour point 8) Heating values (gross & net)

3.METHODOLOGY

3.1 Experimental

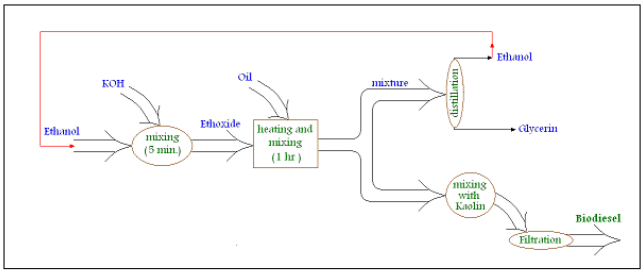

Fig. (3.1) Biodiesel process

3.1.1 Filtration

At first it's preferable to remove any food particles from waste frying oil (WFO), by warming it up, and passing it through filter paper.

3.1.2 Removing of water

Waste oil probably contain water , which can slow down the reaction and cause saponification, so that water was removed from the oil by raising the oil temperature to 100oC, to any water to boil off , then it was mixed it to avoid steam pockets forming below the oil.

3.1.3 Titration

Waste oil needs more catalyst than new oil to neutralize the free fatty acids (FFAs) formed in cooking oil, which interfere with transesterification process.

Oil must be titrated to determine the FFA content and how much catalyst will be required to neutralize it. Fig. (3.2) shows the biodiesel pilot plant.

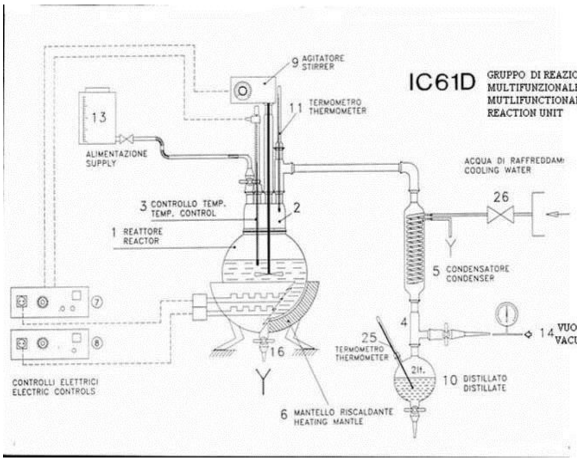

Fig. (3.2} Pilot plant

3.3 Procedure

In this work, the oil used was free of any solid particles, and the FFA's contents was acceptable, so that there was no needs to filter or titrate it, and it was started directly using the previous pilot plant (Fig. 3.2) for producing biodiesel, as follows:

- 1000ml(1Lit) of WFO was measured and then heated it to reach 60°C.
- The catalyst ethoxide was prepared by: taking 8g of KOH (catalyst),-dissolved it in 5Lit ethanol (96%con).
- The ethoxide was mixed and heated to 60°C, in order to ensure that the whole amount of catalyst is totally dissolved.
- Then ethoxide was added (gradually) to the oil, and mixed under the temperature range (55 to 65°C), and a uniform speed of 55rpm.
- The mixing processes must go on for one hour.
- As the mixing was finished, the formation of two layers was noted, and the mixture was left for 10 hour's at least to allow layers separation.
- After that and by using a separatory funnel the mixture was separated and the volume of each layer was measured
- Then the experiment was repeated for several times, in each trial the volume of each layer was measured.
- The upper layer, which was a mixture of glycerin and excess ethanol, was distilled using a simple distillation column to get pure ethanol as a recycle stream.
- And the lower layer was the biodiesel, which must be purified to get the final product.

3.4 Biodiesel purification

A lot of impurities may be contained in the biodiesel, such as, excess ethanol, residual lye, free glycerin, and other contaminants. These residuals must be removed.

-The common way used for this purpose is washing with water, where a small amount of acetic acid is added before adding the water. the acetic acid brings the pH of the solution closer to neutral , because it neutralizes and drops out any lye suspended in biodiesel . This process might be repeated two or three times .-Another way used, is bubble washing, this process needs longer time, but uses less water. It was found that's its very effective, giving a clean, polished product.

The bubbles are formed by compressed air, passing through an air stone, the air stones sink to the bottom of the tank.

When you switch on the aerator, the air bubbles rise through the biodiesel, carrying a film of water which washes the biodiesel as it passes through.

In the experiments which were carried out, another purification process was tried, using kaolin as adsorbents, where the kaolin was crushed and screened at different mesh numbers (65, 100, 150), and the amount of kaolin used was (1.1Kg). So (2.5L) of biodiesel was contacted with kaolin, then 2Lit purified biodiesel as a final product was obtained.

The reaction was carried out at the following conditions:

- Temp. = 55 °C.
- Mixing speed = 60 rpm.
- Mixing duration = 1 hr.
- Settling duration = 10 hr.

The performance tests for a diesel engine using the produced biodiesel before and after purification were carried out in one of the laboratories of the faculty of engineering technology at Al-Balqa' Applied University.

4.RESULTS AND DISCUSSIONS

Table 1: experimental data for the production of biodiesel .

Test NO	Vol.of Oil (Lit)	Weight of KOH	Vol. Of ethanol (Lit)	Vol.of Biodiesel (Lit)	Vol.of glycerin (Lit)	Vol.of ethanol (Lit)
1	1	8	5	0.910	4.95	0.14
2	1	8	5	0.915	4.90	0.185
3	1	8	5	0.915	4.95	0.135
4	1	8	5	0.950	4.85	0.2
5	1	8	5	0.920	4.92	0.16
6	1	8	5	0.930	4.88	0.19

Table 2: experimental data for distillation glycerin ethanol mixture.

Test No.	Vol.of mixture (l)	Vol.of glycerin (l)	Vol.of ethanol (l)
1	5	2.1	2.9
2	10	3.2	6.8
3	5	2.25	2.75

Table 3 : comparison data for the petroleum diesel, others biodiesel ,& the produced biodiesel .

Test	Petroleum diesel	Others biodiesel	Produced biodiesel	
Density @ 15°C (g\ml)	4.67	0.771	Before purification	After purification
Distillation: (°C)				
Initial boiling point	-	254.3	70	72
05% of volume dist.	250	-	75	76
10%	265	262.4	77	78
20%	269	264.4	320	323
30%	275	266.4	325	328
40%	282	268.4	328	330
50%	296	270.4	338	339
60%	300	272.4	343	342
70%	309	275.6	348	348
80%	319	279.6	353	354
90%	330	287.6	365	366
95%	343	294.6	____	-----
Final point	355	303.9	>370	>370
Recovery %vol.	-	-	95	94
Residue %vol.	-	-	5	6
Specific gravity	-	-	0.9071	0.9146
Viscosity @ 40°C (cst)	1.3 to 4.1	-	5.2	5.5
Total sulfur %wt	1.0	-	0.014	0.006
Pour point (°C)	-35 to -15	+9	-7	-6
Cloud point (°C)	-15 to 5	-	0	0
Gross (Kcal/Kg)	9037	10774.28	10800	10680
Net (Kcal/Kg)	8901	10146.4	10171	10090
Flash point (°C)	60 to 80	127	155	153
Cetane number	40 to 55	48 to 65	41.7	41.4

Table 4 : Mechanical tests for biodiesel

a. Before purification:

N (rpm)	F (N)	Tin °C	Tout °C	P mH2O	Tex °C	V volt	I (amp)	t (s)	mw	Torque T=F*0.22 (N.m)	Work W=2*∏*N/60(J)	Brake power=Torque*W (Wat)
1500	119	34	36	6.5	200	100	4	174	10	26.18	157	4110.26
1400	117	35	38	8	198	95	4	188	10	25.74	146.53	3771.77
1200	115	38	40	7	180	82	4	271	9	25.3	133.97	3389.52
1000	113	40	42	4.5	155	70	3	318	8.5	24.86	104.7	2602.01

b. After purification:

N (rpm)	F (N)	Tin °C	Tout °C	P mmH2O	Tex ºC	V (volt)	I (amp)	t (s)	mw	Torque T=F*0.229 (N.M)	Work W=2*∏*N/60(J)	Brake power=Torque*W	Thermal efficiency
1500	119	33	35	10	225	100	4.5	165	11	26.18	157	4110.26	0.292353
1400	117	29.5	32	8.5	200	98	4.2	186	11	25.74	146.53	3771.77	0.272643
1200	115	27	29	6.5	170	80	4	210	11	25.3	125.6	3177.68	0.286631
1000	113	25	27	5	140	70	3	275	11	24.86	104.7	2602.013	0.277089

Charts:

a. before purification:

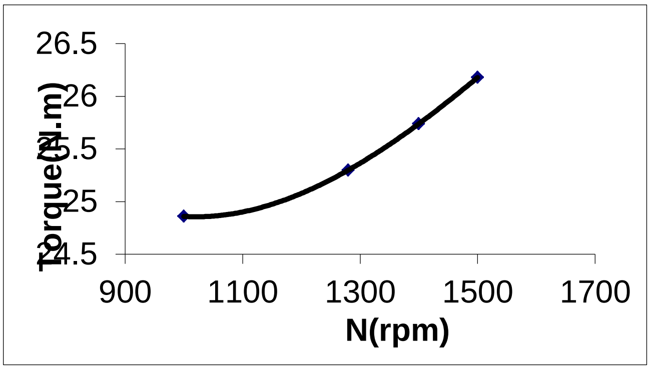

Fig.(4.1)The relation between torque and N(rpm) of the motor .

- As can be seen from Figure 4.1, as the N(rpm) of the motor increases the torque of the motor increases.

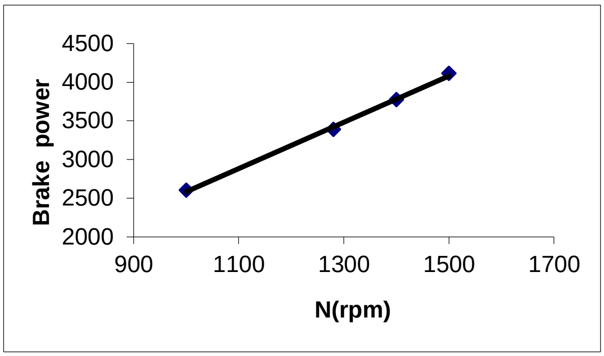

Figure 4.2 The relation between brake power and (rpm).

- As can be seen from Figure 4.2 as the N(rpm) of the motor increases the brake power increases linearly.

After purification:

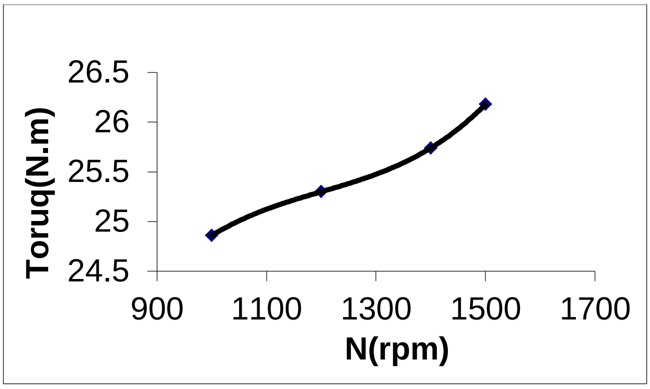

Fig. 4.3 The relation between Torque and N(rpm)of the motor after purification.

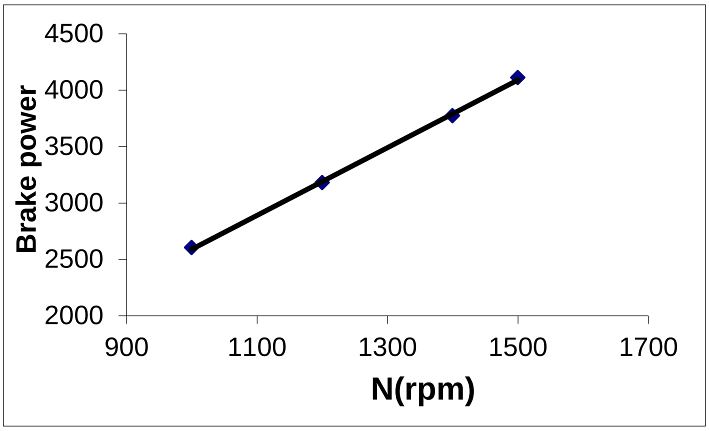

Figure 4.4 The relation between brake power and N(rpm) after purification.

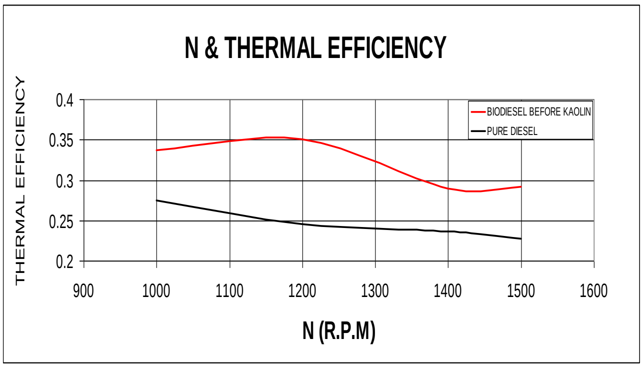

Fig. 4.5 The relation between N(rpm) and thermal efficiency after purification.

As can been seen from the figure 4.5 the thermal efficiency of biodiesel after purification was higher than that of petroleum diesel with about 20% and this may be due to the relatively higher calorific value of the produced biodiesel.

Discussion:

From the previous section it was noticed that Kaolin purification has no effect on the torque and brake power yielded by the engine.

As can be seen from the previous figures the relation between N(rpm) and torque ,and N(rpm) and brake power where identical before and after kaolin purification .

But from table 3 after purification the sulfur content in biodiesel was decreased from 140 ppm to 60ppm, which is very much lower than the sulfur content in the petroleum diesel (less than 1% compared with diesel fuel), which was 10000ppm, this means that the produced biodiesel was with ultra low sulfur content .

On the other hand the gross and net energies of the produced biodiesel were higher than that of petroleum diesel.

The produced biodiesel has 14% more net energy compared with petroleum diesel.

The produced biodiesel has 19.5% more gross energy compared to petroleum diesel.

As can been seen from figure 4.5 the thermal efficiency of biodiesel after purification was higher than that for petroleum diesel with about 20%.

On the other hand the viscosity of the produced biodiesel was increased from (5.2 cts) before purification to (5.5 cts) after purification, which will reflect itself in less biodiesel consumption in the engine.

5.CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions:

1. It can be said that the produced biodiesel has 20% more gross energy than petroleum diesel, and 14% more net energy.
2. Ultra low sulfur biodiesel was produced.
3. The benefits of the purification of biodiesel are to decrease the sulfur content, increase the viscosity, and to decrease the pollutants in the emissions to the atmosphere.
4. Thermal efficiency of biodiesel at 1200, 1500(rpm) was 22.5% more than the thermal efficiency of petroleum diesel.

5.2 Recommendations:

ACKNOWLEDGMENT:

1. Using high frequency magnetic impulse cavitations and nanotechnology to produce biodiesel.
2. Design and build up of a mobile biodiesel pilot plant.

Many thanks for the technical people in the mechanical engineering department at faculty of engineering technology who assisted performing the motor experiments with patience and skill.

REFERENCES

[1] http://www.biodiesel.org/resources/definitions/default.shtm (available on July 2014)

[2] http://en.wikipedia.org/wiki/Biodiesel production(available on 24/4/07).

[3] http://en.wikipedia.org/wiki/Esterification(availabe on 24/4/07).

[4] http://en.wikipedia.org/wiki/Transesterification(available on 24/4/07).

[5] Bioprocess Engineering Basic Concepts , 2nd edition , for Michael L. Shuler & Fikret Kargi

[6] J. Van Gerpen, B. Shanks, and R. pruszlco, low state university, D.Clements, Renewable product development laboratory, G. khotte. USDA/NCAUR, Biodiesel Analytical methods, Aug. 2002-Jaun 2004.

[7] Graduation project. June _2006 (Production of biodiesel from waste frying oils).Al-Balqa' Applied University.

[7a] T. Pushparay, and S. Ramabalan. Influence of CNSL biodiesel with ethanol additives on diesel engine performance and exhaust emissions. Int. Journal of Engineering and Technology. Vol. 3, issue (2) (2012), pages:665-674.

[8] http://www.bentlybiofuels.com/about/safety.php.(available on 29/10/07).

[9] http://www.nabfc.com/news.html(available ont 29/10/07).

[10] http://www.renewableenergypartners.org/biodiesel.html (available on 2/11/07).

[11] http://www.cpcb.nic.in/diesel/ch60902.htm(available on 7/9/07).

[12] Mittelbach, M., remschmidt, C., biodiesel handbook, 1st edition, 2004, Austria.

[13] http://www.wikipedia.com/biodiesel production/ Ultra- and high shear in-line reactors.html(available on 20/12/07).

[14] http//:www.Hislecher/ultrasound Technology.html(available on 20/10/07) .

[15] http://www.pacfuel.com/FAQs.htm(available on 20/7/07).

[15a] A.N. Shah,, G. E. Yun-Shan, He. Chao, and A. H. Baluch. Effect of biodiesel on the performance and combustion parameters of a turbocharged compression –Ignition Engine. Pak. Journal Engineering and Application science, Vol. (4) (2009). Pages:34-42.

[15b] A. Sithta, A. Kumar, and S. Mahla. Utilization of argemone oil biodiesel in commercial DI-CI engines. Int. J. Of Emerging Tecnologies Vol. 3, (2). (2012). Pages: 19-23.

[15c] M. Eswarn. Performance analysis of single cylinder diesel engine by varying injection timing using mustard oil mythyl ester. Global Journal of Engineering science and researches. Vol 1 (8) (2014).

[16] Borini etal , Kaolin project , Al-Balqa Applied University , 2005 .