Trans-Esterification for Production of Biodiesel from Waste Frying Oil (WFO)

N. Akhavan Moghaddam, K. Tahvildari, and S.Taghvaie

***Abstract*—**Biodisel is a type of biofuel having similar properties of diesel fuel but lacks substances (undesirable emissions) such as sulfur, nitrogen and aromatic polycyclic. Upon filtration of waste oil, the biodiesel fuel was produced via carrying out transestrification reaction of triglycerides followed by conducting viscosity, density, flash point, cloud point, pour point and copper strip corrosion tests on the samples and comparing with EN14214 and ASTM 6751 standards and all results were found in the permitted limit. The highest yield of biodiesel production reaction was found 46.6435 g when Sodium Hydroxide catalyst in amount of 0.375g was employed, 44.2347 g when Sodium methoxide catalyst in amount of 0.5g was employed and 56.5124 g when acid sulfuric catalyst in amount of 1g was employed and 47.3290 g when two stage reaction was done.

***Keywords*—**Biodiesel, Transesterification, Basic catalyst, Acidic catalyst.

I. Introduction

DEPLETION of fossil fuel deposits, threat of supply instability, rising petroleum prices and increasing threat to the environment from exhaust emissions informed the reactivation of worldwide interest in renewable biofuels [1], [2]. The production of biofuel to replace oil and natural gas is in active development in major parts of the world and in nascent status in numerous others [3], [4], focusing on the use of cheap organic matter in the efficient production of liquid and gas biofuels which yield high net energy gain. Modern biofuels are a promising long term renewable energy source which has potential to address both environmental impacts and security concerns posed by current dependence on petroleum based fuels [1], [3] and [5].

Biofuel is a new possible substitute of regular fuel and from the natural and renewable materials such as: Biogas, Bioethanol, Biopetrol and biodiesel.

Biodiesel (fatty acid methyl ester) refers to fuel deriving from the natural and renewable materials such as vegetable oils and animal fats. The biodiesel fuel energy is comparable with diesel fuel although it is preferable as a "Clean fuel" which emits fewer pollutants owing to its natural origin in comparison with fossil fuel producing environmental pollutants such as Unburned Hydrocarbons (UHC), sulfur contained materials, CO and CO_2 which is considered as the major defects of the fossil fuels increasing the greenhouse gases in the atmosphere, depleting the ozone layer, polluting the environment and imposing respiratory disorders for inhabitants of the big cities [6], [7].

Biodiesel is produced employing one of the three following ways:

1) Pyrolysis
2) Microemulsion
3) Transesterification

Transesterification was employed in this study owing to the following advantages comparing with two other above mentioned methods:

1) The oxygen atoms remained intact and not taken out but in pyrolysis these atoms are taken out from the biodiesel.
2) This production method requires less requirements and facilities.
3) This production method enjoys high performance.
4) This production method is more acceptable and most biodiesel production plants in the world exploit this method.

The molecular structures of these compounds must be breakdown to simple compounds and become balanced in order to be employed directly as energy resources in internal combustion engines. To this end, the oil or fat based materials must involved in a chemical reaction designated as trans-esterification, after purification, with an alcohol such as methanol at the presence of an acidic or alkaline catalyst in which OH group of the employed alcohol replaces the hydrocarbon chain of oil molecule and therefore esters with new molecular structure i.e. fatty acid methylated esters are produced with great similarities with diesel No. 2. There is no need to change the engine for using this fuel but carrying out a few adjustments on amount of injected fuel, injection pressure in fuel injector, injection duration and start and ending of injection, depending on the thermal value, density, viscosity and cetane number. The studies showed that the blends comprises of 20% biodiesel and diesel are appropriate for all types of diesel engines and the blends with higher amounts of biodiesel ,i.e. by 100% of the pure biodiesel can be used for new engines [8].

Production of biodiesel from waste oil requires several

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stages and at the first step the waste oil impurities must be taken out via carrying out purification process [9], [10].

In order to avoid the problem of saponification, the two-stage method was used for synthesis of biodiesel from WFO. In the first stage, esterification of FFA (Free Fatty Acids) present in WFO was carried out using sulfuric acid as a catalyst and in the second stage transesterification of neutral WFO was performed using NaOH as a catalyst

The WFO was contaminated with water, solid particles, FFA and many other chemicals. Since water and FFA create a problem during transesterification, WFO was pretreated before the reaction. Solid portion of WFO was removed using a centrifuge. Water was removed by methods that will be described in materials and methods.

In this paper some efforts was done to increase the yield of the trans-esterification reaction by using several acidic and basic catalysts and subsequently increasing the performances of the obtained biodiesel by adjusting the reaction conditions to avoid the saponification reaction as adverse reactions, Sodium Methoxide was used, so formation of soap is reduced and the washing stage is simplified.

II. Experimental

A. Materials and Methods

Waste Frying Oil (WFO) was obtained from confectionery, Anhydrous methanol 99.8%, Sodium hydroxide, Sodium Methoxide, Sulfuric acid, diethyl ether were purchased from Merck Co, Ltd (Germany).

B. Apparatus

1) FT-IR with ATR (Attenuated Total Reflectance) cell (PerkinElmer, cat.No.58900, U.S.A.).
2) Hydrometer
3) Cannon-Fenske Viscometer (Brookfield, cat. No. RT519 14, U.S.A.)

C. Trans-Esterification reaction with basic catalyst

50 g of WFO was refluxed for two hours in a flask equipped with a condenser, thermometer and magnetic stirrer at 60°C using different amounts (0.125, 0.25, 0.375, 0.5, 0.635, 0.75, 0.875, 1g) of basic catalysts of sodium hydroxide and sodium methoxide mixed with 11g methanol (6:1 alcohol to WFO ratio) that poured to the WFO. Results are shown in tables 1, 2, 3 and 4.

D. Two stage biodiesel production

50g of WFO was refluxed for 6h using various quantities of diethyl ether (15,30 g) as a solvent for expediting the acidic reaction, were conducted using different quantities of acidic catalyst (Sulfuric acid: 1%, 2%, 5% equivalent to 0. 5, 1, 2. 5g) mixed with 22g methanol (12:1 alcohol to WFO ratio) and in second stage 25gr of produced biodiesel from first stage refluxed for 2 hours with 5.5g methanol (6:1) and highest efficiency of the basic catalyst sodium hydroxide (0.1875g) and sodium methoxide (0.25g) in separate reactions mixed with 5.5 g methanol which indicated the highest efficacy for sodium hydroxide and all results are found to be placed in the permitted range. Results are shown in tables 5, 6, 7, 8, 9, 10, 11, 12 and 13.

III. Results and discussion

In one-stage synthesis of biodiesel with basis catalysts, saponification with sodium hydroxide is more observable in comparison with sodium methoxide, but sodium hydroxide is more economical and in denuded regions of water sodium methoxide is more economical because of less saponification and costs of washing with water.

In two-stage method (first stage esterification and second stage trans-esterification) in comparison with one-stage synthesis, took long time. Considering bellow tables, at first there is increase and then there is decrease because of the saponification.

The properties of a fuel determine the fuel quality and the biodiesel properties was determined, using fuel standard tests, and compared with biodiesel standards in US (ASTM D6751) and EN (EN1421). The standard tests are acid value, viscosity, density, flash point, cloud point, pour point, copper strip corrosion, Iodine value, boiling pint, saponification value, cetane index and lubricity number.

Fuels with high densities may increase the compression rate of tiny particles and NOx gas point diesel engines and with high viscosity blunder the injection process and culminates to the improper atomization and high flash point may produce deposited carbon in combustion chamber [11], [12] and [13]. Three standards including cloud point, freezing point and pour point have not been determined in ASTM standards for biodiesel and depend on the weather situation of the zone that weather this fuel is used, it should be noticed.

According to below charts, all of the characteristics were found in the permitted limit.

According to the table 1, the highest yield of biodiesel production reaction was found 46.6435 g when Sodium Hydroxide catalyst in amount of 0.375g was employed.

According to the table 3, the highest yield of biodiesel production reaction was found 44.2347 when Sodium Methoxide catalyst in amount of 0. 5g was employed.

According to the table 5, the highest yield of biodiesel production reaction was found 44.9122 when Sodium Methoxide catalyst in amount of 1g was employed.

TABLE I
YIELD REVIEW OF BASIS CATALYST SODIUM HYDROXIDE

Sample	Sodium Hydroxide(g)	Ester (g)	Yield
1	0.125	43.5234	87.0468
2	0.25	43.6741	87.3482
3	0.375	46.6435	93.2870
4	0.5	42.1328	84.2656
5	0.635	36.6573	73.3146
6	0.75	36.5813	73.1626
7	0.875	33.2150	66.4300
8	1	-	-

TABLE II
PROPERTIES OF PRODUCED BIODIESEL OF FWO AND SODIUM HYDROXIDE

Characteristics / Catalysts	Density	Viscosity	Cloud Point (°C)	Freezing Point (°C)	Flash Point (°C)	Pour Point (°C)
Sodium Hydroxide	870	4.1	-10	-14	160	-12
ASTM D6751	N. D.	1.8-6	N. D.	N. D.	Min 130	N. D.

[a]N. D. = Not Determined

TABLE III
YIELD REVIEW OF BASIS CATALYST SODIUM METHOXIDE

Sample	Sodium Methoxide(g)	Ester (g)	Efficiency
9	0.125	41.8653	83.7306
10	0.25	42.3165	84.6330
11	0.375	43.3596	86.7192
12	0.5	44.2347	88.4694
13	0.635	42.8345	85.2542
14	0.75	42.6271	85.2542
15	0.875	41.8231	83.6462
16	1	40.7103	81.4206

According to the table 6, the highest yield of biodiesel production reaction was found 43.0762 g when Sodium Hydroxide catalyst in amount of 1g was employed.

According to the table 8, the highest yield of biodiesel production reaction was found 45.6902 g when Sodium Methoxide catalyst in amount of 1g was employed.

According to the table 9, the highest yield of biodiesel production reaction was found 43.7782 g when Sodium Hydroxide catalyst in amount of 1g was employed.

According to the table 11, the highest yield of biodiesel production reaction was found 46.2476 g when Sodium Methoxide catalyst in amount of 1g was employed.

According to the table 12, the highest yield of biodiesel production reaction was found 47.3290 g when Sodium Methoxide catalyst in amount of 1g was employed.

TABLE IV
PROPERTIES OF PRODUCED BIODIESEL OF FWO AND SODIUM METHOXIDE

Characteristics / Catalysts	Density	Viscosity	Cloud Point (°C)	Freezing Point (°C)	Flash Point (°C)	Pour Point (°C)
Sodium Hydroxide	870	4.1	-10	-15	160	-14
ASTM D6751	N. D.	1.8-6	N. D.	N. D.	Min 130	N. D.

TABLE V
YIELD REVIEW OF ACIDIC CATALYST SULFURIC ACID AND BASIS CATALYST SODIUM METHOXIDE IN TWO-STAGE

Sample	Sulfuric Acid (g)	Ester (g)	Yield	Sodium Methoxide (g)	Ester (g)	Yield
17	0.5	45.5536	91.1072	0.25	21.2831	42.5662
18	1	46.2894	92.5788	0.25	22.4561	44.9122
19	2.5	45.1153	90.2306	0.25	20.7841	41.5682

TABLE VI
YIELD REVIEW OF ACIDIC CATALYST SULFURIC ACID AND BASIS CATALYST SODIUM HYDROXIDE IN TWO-STAGE

Sample	Sulfuric Acid (g)	Ester (g)	Yield	Sodium Methoxide (g)	Ester (g)	Yield
20	0.5	45.5536	91.1072	0.1875	20.8419	41.6838
21	1	46.2894	92.5788	0.1875	21.5381	43.0762
22	2.5	45.1153	90.2306	0.1875	21.1932	42.3864

TABLE VII
PROPERTIES OF PRODUCED BIODIESEL OF FWO AND SODIUM METHOXIDE

Characteristics / Catalysts	Density	Viscosity	Cloud Point (°C)	Freezing Point (°C)	Flash Point (°C)	Pour Point (°C)
Sodium Hydroxide	870	4.1	-8	-12	160	-11
ASTM D6751	N. D.	1.8-6	N. D.	N. D.	Min 130	N. D.
Sulfuric acid Sodium Hydroxide	870	4.1	-9	-14	160	-12

TABLE VIII
YIELD REVIEW OF ACIDIC CATALYST SULFURIC ACID AND WITH 30 ML DIETHYL ETHER AND IN SECOND STAGE WITH SODIUM METHOXIDE

Sample	Sulfuric Acid (g)	Ester (g)	Yield	Sodium Methoxide (g)	Ester (g)	Yield
23	0.5	45.4515	90.9030	0.25	21.4567	42.9134
24	1	46.0589	92.1178	0.25	22.8451	45.6902
25	2.5	44.5313	89.0626	0.25	21.1784	42.3568

TABLE IX
YIELD REVIEW OF ACIDIC CATALYST SULFURIC ACID AND WITH 30 ML DIETHYL ETHER AND IN SECOND STAGE WITH SODIUM HYDROXIDE

Sample	Sulfuric Acid (g)	Ester (g)	Yield	Sodium Methoxide (g)	Ester (g)	Yield
26	0.5	45.4515	90.9030	0.25	21.3471	42.6942
27	1	46.0589	92.1178	0.25	21.8891	43.7782
28	2.5	44.5313	89.0626	0.25	20.6359	41.2718

TABLE X
PROPERTIES OF PRODUCED BIODIESEL OF FWO IN TWO-STAGE REACTION WITH SULFURIC ACID AND 30 ML DIETHYL ETHER AND SODIUM HYDROXIDE AND ONCE WITH SODIUM METHOXIDE

Characteristics / Catalysts	Density	Viscosity	Cloud Point (°C)	Freezing Point (°C)	Flash Point (°C)	Pour Point (°C)
Sulphuric acid Diethyl Ether 30 ml Sodium Methoxide	870	4.1	-10	-15	160	-12
ASTM D6751	N. D.	1.8-6	N. D.	N. D.	Min 130	N. D.
Sulphuric acid Diethyl Ether 30 ml Sodium Hydroxide	870	4.1	-9	-14	160	-12

TABLE XI
YIELD REVIEW OF ACIDIC CATALYST SULFURIC ACID AND WITH 15 ML DIETHYL ETHER AND IN SECOND STAGE WITH SODIUM METHOXIDE

Sample	Sulfuric Acid (g)	Ester (g)	Yield	Sodium Methoxide (g)	Ester (g)	Yield
29	0.5	48.4598	96.9196	0.25	22.4873	44.9746
30	1	46.5124	113.0248	0.25	23.1238	46.2476
31	2.5	49.7831	99.5662	0.25	22.1891	44.3782

TABLE XII
YIELD REVIEW OF ACIDIC CATALYST SULFURIC ACID AND WITH 15ML DIETHYL ETHER AND IN SECOND STAGE WITH SODIUM HYDROXIDE

Sample	Sulfuric Acid (g)	Ester (g)	Yield	Sodium Hydroxide (g)	Ester (g)	Yield
32	0.5	48.4598	96.9196	0.25	22.6423	45.2846
33	1	56.5124	113.0248	0.25	23.6645	47.3290
34	2.5	49.7831	99.5662	0.25	22.1124	44.2248

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