DETERMINATION OF PROPERTIES OF E-B DIESEL FUELS

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Abstract— In this study, biodiesel production was realized by converting raw oil obtained from safflower seed to Safflower Oil Methyl Esther (Safflower Biodiesel) by means of raw oil extraction with heating at 90 °C and pressing after Vals process and consequently transesterification process followed raw oil extraction. Experimental fuels were obtained as in M₁₀₀, E2.5B2.5M95, E5B5M90, E5B2.5M92.5 and E2.5B5M92.5 forms by mixing biodiesel fuel obtained from safflower with diesel fuel and bioethanol additives at a ratio of 2.5% and 5% and by mixing in volumetric ratio according to inversely proportion. Fuel properties of diesel fuel and the obtained fuel mixtures were determined with following tests; Kinematic viscosity, Density, Water content, PH values, Color determination, Heating value, Flash point, Cloud, Pour and Freezing points, Copper rod corrosion test, Iodine number, CFPP (Cold Filter Plunge Point) and Cetane number tests. Finally, the fuel properties of E-B Diesel were found suitable with standards.

Keywords: Safflower, bioethanol, biodiesel, transesterification, fuels.

I. INTRODUCTION

Energy is an indispensable part of human life. Besides, energy consumption per person is among the indicators of development of a country. Supplying energy in a steady, sufficient and safe manner and increasing efficiency along with effectiveness through processes for energy procurement is a must in order to support socioeconomic growth and continue sustainable development [27].

There are three main routes for the countries in order to keep energy sources persistent. First and the primary one is detecting its own resource potential accurately and converting this resource to energy in the most appropriate way by improving it. Second one is to be able to acquire control over necessary resources and their transport routes and means for energy production via participating international resource search and exploiting activities in the abroad with national companies and having share in these resources. For the cases that the first two routes are insufficient or for the cases that need action for strategic-economic measures, third route is tending towards short, medium and long term imports. When import is deemed to be a necessity, one of the most important points is diversifying suppliers and resources [26].

Fuels that countries gather from their own herbal and animal resources are briefly called biofuels. Biofuels contains

all sorts of liquid and gas fuels originating from herbal and animal resources. Alternative fuels such as biogas, bioethanol, biomethanol and biodiesel are in the range of biofuel definition. However bioethanol is the most commonly used one among biofuels [11].

Bioethanol is a biofuel that can be produced by means of fermentation of sweet and amylaceous plants or acidic hydrolysis of cellulosic mass. Plants such as sugar beet, sugar cane, corn, wheat, potato, woody plants such as stem, straw, shell, agricultural waste and residuals and,molasses that is side product of sugar production can be used as raw material [9].

The first method utilized in the bioethanol production was acid hydrolysis. Enzyme production method took place of this method in the following years. Historical development situation is given in figure 1 [19].



Fig. 1 Historical development of bioethanol production [19]

The biggest bioethanol producers in the world are USA and Brazil. For common usage of ethanol as fuel alcohol, USA, Austria, France, Switzerland, Brazil, India and Thailand can be given as instances. 2012 World bioethanol production was determined as 22.7 billion liter/year. Bioethanol production between1975 and 2012 from all around the world is shown in figure 2.



Cetane number of the fuel is important because fuels those can be easily self ignite and those decreases the ignition delay are preferred in diesel engines [10].

Solubility of bioethanol in diesel fuels is limited. Phase separation in bioethanol – diesel mixtures and water content of the mixture are important problems. Besides, cetane number of bioethanol is very low [16].

Heat content (heating value) of the mixture is reduced when bioethanol is added to diesel fuel [12].

These negative points can be overcome by means of biodiesel additives.

Biodiesel is oil acid methyl ester mixtures as described in TS EN 14213 and/or TS EN 14214 standards and which are produced from herbal and animal oils, oil wastes and residuals [13].

Flash point of biodiesel is higher than diesel fuel. This feature makes biodiesel a safer fuel in usage, transportation and storing. Biodiesel can be mixed with petroleum originated diesel fuel in every ratio and this characteristic can be used in order to increase the quality of petroleum sourced diesel fuel. It reduces emission values of hazardous gases occurred after combustion, increases lubrication amount of the engine [15].

The raw materials that biodiesel is produced from can be listed as; Safflower, canola, soybean, palm, sunflower, olive pomace (prina), mustard, other oily seeds and fruits, waste oil after frying, seeds of the fruits and animal fats [22]. Biodiesel cycle appears in figure 3.



Fig. 3 Biodiesel cycle [3]

Although there are methods for biodiesel production, the most widespread one today is transesterification method. In the transesterification, oils from oily seeds of plants such as canola, safflower sunflower, soybean or animal fats are reformed by transesterification reaction together with a short chained alcohol (usually methanol or ethanol) with the help of a catalyst. The product is a liquid, environmentally friendly, renewable biofuel [14].

Transesterification reaction scheme is seen in figure 4.



Fig. 4 Transesterification reaction of triglyceride with methanol [21]

Rudolf Diesel (1858-1913) tested his engine designed according to herbal oils and exhibited his engine using peanut oil as fuel in Paris World Exhibition in 1900 [18].

The topic lost its popularity due to the difficulties in direct usage of herbal oils as fuels and wide spread usage of petroleum products. However scientific studies on eliminating glycerin in the herbal oils in order to use them as fuels had kept going and the first patent was secured at 31 August 1937 by G.Chavanne from Bruxelles in Belgium for the fuel that we know as "Biodiesel" today. The petroleum crises at 1970s and 1990s speeded up search for alternative fuels and "Biodiesel" was taken into consideration again. There have been many incentive studies going on for biofuels and biodiesel in EU since 2003. Member countries were asked to state their national production and usage targets in their progress reports. They are utilizing "polluting one pays" criteria in their energy and tax politics. USA, which sees "safety of energy supply as a national safety element", targeting to compensate 25% of its energy consumption from renewable energy resources in 2025 with its "25x25" motto and developing projects for these aims, established its own system in the biodiesel subject too. Primarily they prepared ASTM-6751 standard applicable to soybean oil, which can be regarded as their national herbal oil. During 5% biodiesel mixed B5 form of the fuel was sold in the fuel stations extensively, they ensured 100% utilization by providing tax privilege [5].

World biodiesel productions from 1985 to 2012 are shown in figure 5.

Safflower is a one year, long day, oil plant that can be cultivated between 130-150 days averagely, containing 30-35% oil in its seeds, having summer characteristics, exhibiting various colored flowers such as yellow, red, orange, white and it can usually grow to 80-100 cm heights, and forms with and without pricks can be found [24].

Safflower having more tolerance against cold and drought comparing to other summer time oily plants is one of the plants that should be seriously considered for compensating our herbal oil deficit as it can be an important alternative, especially in arid agricultural fields [20].



The most obvious property of safflower oil is low saturated fatty acid ratio and high unsaturated fatty acids ratio. It has very low linoleic fatty acid or no linoleic fatty acid in its fatty acid composition so no dark colors can be observed. With this feature, it is consumed as margarine, salad and mayonnaise oil in western countries. Safflower oil regarded as in half drying oil group is also utilized in varnish, paint, polish and soap production [23].

Total cultivation area of safflower of *Compositeae* family (*Carthamustinctorius* L.) is 1.121.212 ha. India comes first with its 700.000 ha area and 400.000 tons production and it supplies 70% of world safflower production. USA, Mexico and China follow India regarding their capacities [17].

Comparison of safflower types cultivated in Turkey is given in table 1.

TABLE 1. Comparison of safflower types cultivated in Turkey [25][6][7]

Safflower Species	Barbed	Flowers Color	Plant Length (cm)	Seed color	Oil Rate (%)	1000 weight (g)
Yenice	Barbless	Red	100-120	White	24-25	38-40
Dinçer	Barbless	Orange	90-110	White	25-28	45-49
Remzibey 05	Barbed	Yellow	60-80	White	35-40	46-50
Balcı	Barbed	Yellow	55-70	Cream	38-40	40-48
Linas	Barbed	Orange	85-90	Cream	39-41	38-42
Ayaz	Barbed Less	Orange	90-120	White	22-26	40-44

II. MATERIAL AND METHODS

The methyl alcohol used for biodiesel production from safflower oil in the present study has the chemical formulation of CH₃OH and it has Merck brand name. The density of the used methyl alcohol is 0.791 - 0.793 kg/l at 20° C and its molecular mass is 32.04 g/mol (Figure 6).



Fig. 6 Alcohol utilized in safflower biodiesel production [8]

In the safflower biodiesel production, sodium hydroxide (NaOH) having 40 g/mol molecular mass, a greater purity than 97% and Merck brand name was used as catalyst (Figure 7).



Fig. 7 Catalyst used in safflower biodiesel production [8]

Molasses originating bioethanol that was used in the experiments was supplied by "Konya eker Sanayi veTicaret A. ." company at 15.08.2012 date. The bioethanol was 99.8% pure. Its chemical formulation is C_2H_5OH . Breathing or swallowing the bioethanol is very dangerous. It must be avoided from contacting to eyes or skin. It should be kept in a cool environment, away from oxidizing materials. Flow scheme of bioethanol process is seen in figure 8.



Fig.8 Bioethanol productin process from molasses [1]

Biodiesel production facility in Selcuk University, Faculty of Agriculture, Biodiesel Laboratory has a capacity of 100 liter biodiesel production per hour. The facility can be operated both by manually or by automation systems. With the automation system, production can be completed without any further interference after necessary materials are placed in raw oil tank, catalyst tank and methanol tank (Figure 9).



Fig. 9 Biodiesel production and programmable logic controller (PLC)facility
[8]

Present study was performed in six steps as explained below.

- Acquisition of safflower seed,
- Safflower oil extraction from safflower seed,
- Production of safflower oil methyl ester (SOME) which will be used as an alternative fuel in engines,
- Bioethanol procurement and preparation
- Preperation of M_{100} , $E_{2.5}B_{2.5}M_{95}$, $E_5B_5M_{90}$, $E_5B_{2.5}M_{92,5}$ and $E_{2.5}B_5M_{92,5}$ fuel mixtures,
- Determination of properties of M_{100} , $E_{2.5}B_{2.5}M_{95}$, $E_5B_5M_{90}$, $E_5B_{2.5}M_{92.5}ve E_{2.5}B_5M_{92.5}fuel mixtures.$

Although there are different methods for biodiesel production, the most widespread method today is transesterification. This method is a process in which herbal oils are reacted with alcohol with the help of a catalyst and reesterification of the oils. Recently, this method is the most effective one in decreasing viscosity [23].

Samples tested during experiments were prepared according to volumetric ratio basis. Mixtures were tried to be homogenous by mixing them both in a laboratory type mixer at 1500 min⁻¹ and in a homogenizer at 24000 min⁻¹ each for 7.5 minutes, totally 15 minutes. No separation was observed after mixing process. Five different fuels were created via diesel, safflower biodiesel and bioethanol mixtures. 100% diesel is denoted as M_{100} , the fuel that was formed with 2.5% volumetric bioethanol and 2.5% volumetric safflower biodiesel along with diesel fuel was denoted as $E_{2.5}B_{2.5}M_{95}$, the fuel that was formed with 5% volumetric safflower biodiesel along with diesel along with diesel fuel was denoted as $E_{5}B_{5}M_{90}$, the fuel that was formed with 5%

volumetric bioethanol and 2.5% volumetric safflower biodiesel along with diesel fuel was denoted as $E_5B_{2.5}M_{92.5}$, the fuel that was formed with 2.5% volumetric bioethanol and 5% volumetric safflower biodiesel along with diesel fuel was denoted as $E_{2.5}B_5M_{92.5}$. Names of the fuels and their volumetric constitution percentages were given in table 2 [8].

TABLE 2. I	Names	of the	fuels	and	their	volum	etric	const	itution
		per	centa	iges	[8].				

Fuels	DieselFuel	Bioethanol	Biodiesel
M_{100}	100	0	0
$E_{2.5}B_{2.5}M_{95}$	95	2.5	2.5
$E_5B_5M_{90}$	90	5	5
$E_5B_{2.5}M_{92.5}$	92.5	5	2.5
$E_{2.5}B_5M_{92.5}$	92.5	2.5	5

Prepared fuel samples are seen in figure 10.



Fig. 10 Fuel samples [8]

Analyses results are seen in table 3. Standard values in the table are from TS EN 590 for diesel fuel and TS EN 14214 for biodiesel.

III. CONCLUSIONS

In this study, M_{100} , $E_{2.5}B_{2.5}M_{95}$, $E_5B_5M_{90}$, $E_5B_{2.5}M_{92.5}$ and $E_{2.5}B_5M_{92.5}$ fuel mixtures were used. These fuel mixtures were obtained by mixing biodiesel fuel obtained from safflower by means of transesterification with diesel fuel at a biodiesel to diesel volumetric ratio of 2.5% and 5% and bioethanol additives at a ratio of 2.5% and 5%.

Decreasing the viscosity of the biodiesel fuel and improving its convenience as a diesel fuel were achieved by mixing high viscosity biodiesel with diesel and bioethanol. Diesel fuel cetane number was increased by means of the mixture and it was seen that the fuel properties of ethanolbiodiesel-diesel mixtures are in the range of the standards.

Characteristic Properties	Unita	Raw Safflower Oil	Safflower Biodiesel	M ₁₀₀	E _{2.5} B _{2.} 5M ₉₅	E5B5 M90	E5B2.5 M92.5	E _{2.5} B ₅ M _{92.5}	Bio ethanol	Limiting Values	
	Units									Diesel Fuel	Bio diesel
Density (15 [°] C)	g/cm ³	0,92	0,88	0,83	0,83	0,83	0,83	0,83	0,79	0.82- 0.84	0.86- 0.90
Kinematic Viscosity (40°C)	mm ² /s	31,23	4,32	3,35	2,69	2,63	2,56	2,66	1,27	2-4.5	3.5-5
Flash Point	^{0}C	170	121	60						55	101
Water Content	ppm	20,18	393	33,51	78,84	75,42	89,67	83,63	372,8	200	500
pН		4,8	5	5	5	5	5	5	5		
Color Determination	ASTM	2,3	1,4	1,2	1,2	1,2	1,2	1,2	<0,5		
Calorific Value	kJ/kg	5897	40801	47628	47389	46239	47504	46718	29594		
Cloud Point	⁰ C	-1	-2	-9	-8,1	-6,4	-6	-6,2			
Pour Point	⁰ C	-15	-7,5	-20	-12,3	-11,2	-11,1	-10,5			
Freezing Point	⁰ C	<-20	-13,4	<-20	<-20	<-20	<-20	<-20	<-20		
CFPP	⁰ C		-6	-19	-18	-18	-17	-18	<-50	- 20	-15
Copper Strip Corrosion		1a	1a	1a	1a	1a	1a	1a	1a	No:1	No:1
Iodine value	giyot/ 100g	117,9	117,9								
Cetane Number		45,27	41,92	54,84	57,28	56,26	55,99	57,50		51	

TABLE 3.	Analyses	results	of the	fuels	[8]	
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