

Production of Bioethanol and Sunflower Methyl Ester and Investigation of Fuel Blend Properties

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ABSTRACT

Biofuels are the main substitute to fossil fuels. These fuels are less polluting in comparison to fossil fuels and can be produced from agricultural material residues for use in diesel engines. In this research work bioethanol was produced from potato waste. It was dehydrated in a vapor phase using 3A zeolite and was used in combination with sunflower methyl ester oil and diesel fuel blending which was evaluated thereafter. The sunflower methyl ester was also produced using a transesterification method. Considering the laboratory conditions and fuel stability limits to be used, the suitable blending proportion of bioethanol and diesel fuel was determined to be 12 to 88 and then, for maintaining fuel stability at temperatures lower than 15°C, the sunflower methyl ester was added to the mixture. The pour point of the fuel and different fuel blends, the viscosity, cetane number, flash point, amount of fuel ash, sulfur content and copper corrosion were determined in the laboratory. Experiments show that ethanol plays an important role on the flash point of the blends. With the addition of 3% bioethanol to diesel and sunflower methyl ester, the flash point was reduced to 16°C. The viscosity of the blends was reduced with the increase in the amount of ethanol. The sulfur content of bioethanol and sunflower methyl ester is very low compared with that of diesel fuel. The sulfur content of diesel is 500 ppm whereas that for ethanol and sunflower methyl ester is 0 and 15 ppm, respectively. The lower amount of sulfur content facilitates the use of fuel blends in diesel engines. For the ethanol and sunflower methyl ester combination, this amount is less than 20 ppm.

Keywords: Biodiesel, Bioethanol, Biofuel, Ediesel, Methyl Ester.

INTRODUCTION

The increase in the prices of petroleum based fuels, strict governmental regulations on exhaust emissions and future depletion of worldwide petroleum reserves encourage studies to search for alternative fuels (Harkin, 2000; Howard, 1994). Alcohols (ethanol and methanol) have been considered as alternative fuels for diesel engines (Ghobadian and Rahimi, 2004). Ethanol and biodiesel is a biomass based renewable fuel (Madras *et al.*, 2004), which can be produced from plants, such as corn, sugar cane, sugar beets, sorghum, barley and cassava,

(Meo, 1984; FAPRI, 2001). Although both methanol and ethanol reduce emissions in diesel engines, ethanol has the advantage of being a renewable fuel and of having a higher miscibility. Therefore, the use of ethanol in compression ignition (CI) engines has received considerable attention in recent years (Can *et al.*, 2004).

There are some difficulties encountered when attempting to use alcohols in diesel engines (Abu-Qudais *et al.*, 2000). Its limited miscibility at lower temperatures and the required minor variations in fuel delivery systems restrict the use of ethanol in diesel fuel (Gerdes and Suppes, 2001). It was determined that the aromatic contents and in-

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intermediate distillate temperatures had a significant impact on the miscibility limits (He *et al.*, 2003). Fuel viscosity and lubricity play significant roles in the lubrication of fuel injection systems, especially for rotary fuel pumps. However, fuel lubricity is not very important in line pumps and unit injectors (Hansen *et al.*, 2001).

Studies on the use of ethanol in diesel engines have been continuing since the 1970s. The initial investigations were focused on reduction of the smoke and particle levels in the exhaust. Ethanol addition to diesel fuel results in different physico-chemical changes in diesel fuel properties, particularly reductions in cetane number, viscosity and heating value (Henham *et al.*, 1991).

Potato ranks third after wheat and rice as far as its importance in the human diet is concerned in Iran. After harvesting, potatoes are stored and losses during storage reaches as much as 30% (Shamoradi, 1985; Alam, 1974). Potato losses include the losses before harvesting, during storage, packing, transportation, processing and supplying (Meyhuay, 2000; Solis, 1991). Potato losses before reaching the consumer in Asia are about 15% and, in Iran, 10% (FAO, 1995). In Iran, about 20% of the potatoes are wasted after being purchased by consumers. About 100 to 110 liters of ethanol can be obtained from every ton of potatoes. If we consider that only 10% of wastes potatoes are to be converted into bioethanol, the annual bioethanol production from wasted potatoes will be 150 million liters.

Although bioethanol fuel has been produced and evaluated according to its properties in other countries, this has not been done in Iran which is the subject matter of the present paper. Bioethanol and biodiesels have oxygen in their structure that makes them an oxygenated fuel and adding oxygenates to fossil fuel reduces HC and CO emissions dramatically. Ethanol and biodiesel have been used as additives for diesel fuel and each of them has different advantages and disadvantages. Using combined ethanol and sunflower methyl ester in conjunction with diesel fuel is better in many

cases, and examination of this is the main purpose of the present paper.

MATERIALS AND METHODS

Ethanol Production

There are two major industrial pathways to ethanol production. Ethanol is made by the petroleum synthetic and alcoholic fermentation (O'Leary, 2000). In the present investigation, bioethanol was produced via alcoholic fermentation using potato waste as a raw material. About 100 kg of raw potato waste was used for this purpose in two batches. The potato wastes were first cut into pieces by a chopper. The wastes were then mixed with about 100 liters of water and alpha-amylase, and were passed through cookers where the starch was liquefied. Heat was applied at this stage to enable liquefaction. Cookers with a high temperature stage (120-150°C) and a lower temperature holding period (95°C) were used. These high temperatures reduced bacteria levels in the mash. The mash from the cookers was cooled and the secondary enzyme (glucoamylase) was added to convert the liquefied starch to fermentable sugars (dextrose), a process called saccharification. Yeast (*Saccharomyces cerevisiae*) was then added to the mash to ferment the sugars into ethanol and carbon dioxide. Completion of the fermentation process depends on the amount of initial yeast, the temperature of the fermentation batch, the size of chopped raw material and the quantity of starch converted into fermentable sugars during saccharification. During the fermentation process, CO₂ is produced that leaves the liquid in the form of air bubbles. Depending upon the previously mentioned parameters, the whole fermentation process took 3-7 days to be completed. In this case, the optimum temperature range was found to be 25-30°C (O'Leary, 2000; Anonymous, 1980; Anonymous, 2004; Detmold, 2003). The fermented mash, now called "beer", contained about 10% alcohol, as well as all the non-

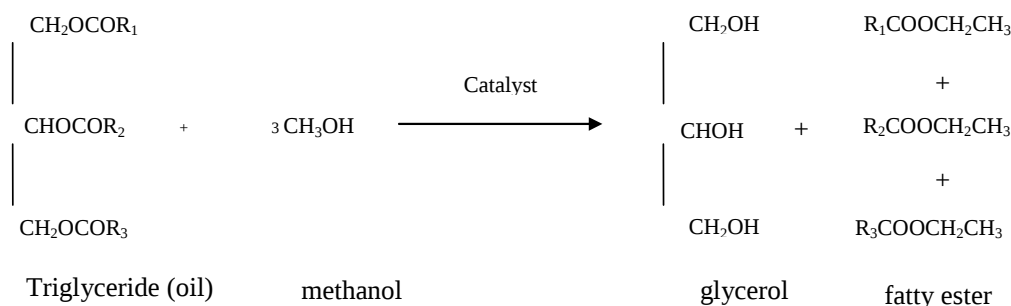


Figure 1. Transesterification reaction.

fermentable solids from the potato wastes and the yeast cells. The mash was first filtered and then it was pumped into the continuous flow, multi-column distillation system, where the alcohol was removed from the solids and the water. The alcohol left at the top of the final column had about 96% purity. The purity of the bioethanol was measured with the help of a densitometer made by Anton Paar (Model DMA 35 N). This instrument is capable of measuring the alcohol purity percentage with an accuracy of ± 0.001 .

Dehydration

Although the boiling point of ethanol, i.e. 78.3°C , is significantly lower than the boiling point of water (100°C) these materials cannot be separated completely by distillation (Kvaalen *et al.*, 2005). Instead, an azeotropic mixture (i.e. a mixture of 95% ethanol and 5% water) was obtained, and the boiling point of the azeotrope was 78.15°C . In a distillation, the most volatile material (i.e. the material that has the lowest boiling point) is the first material to distill from the distillation flask, and this material is the azeotrope of 95% ethanol which has the lowest boiling point. If an efficient fractionating column is used, the first 95% alcohol is obtained, then a small intermediate fraction of lower concentration, and then water. However no matter how efficient the fractionating column used, 95% alcohol could not be further concentrated by distillation

(O'Leary, 2000). The alcohol from the top of the column was then passed through a dehydration system where the remaining water was removed. In this work a molecular sieve (Zeolit 3A) column was used in the vapor phase to capture the last bit of water in the ethanol. The alcohol produced at this stage is called anhydrous (pure, without water) ethanol and is approximately 2000 proof.

Sunflower Methyl Ester Production

Sunflower methyl ester is a biodiesel that is typically produced through the reaction of a sunflower oil with methanol in the presence of a KOH catalyst to yield glycerine and methyl esters (Al-Widyan and Al-Shyoukh, 2002; Lee *et al.*, 2004). The reaction is depicted in Figure 1 (Al-Widyan and Al-Shyoukh, 2002; Lee *et al.*, 2004).

1.8 gr KOH (as alkali catalyst) and 33.5 cc methanol (as an alcohol) were applied to 120 gr sunflower oil in this reaction. The reaction time (with stirring and no heat), was 1 hour, separation and washing took about up to one week and the % yield was 80-85%. Several blends of diesel fuel with ethanol and biodiesel were prepared. These blends were obtained by mixing ethanol, biodiesel and diesel fuel by volume in the following proportions:

$$\begin{array}{l}
 E_P B_Q D_R = E_P B_Q D_R \longrightarrow \text{Diesel \%} \\
 \begin{array}{|c|} \hline \longrightarrow \text{Biodiesel \%} \\ \hline \longrightarrow \text{Ethanol \%} \\ \hline \end{array}
 \end{array}$$

**Table 1.** Diesel fuel properties and test methods based on ASTM D6751 standard.

Property	Standard method	Limits	Unit
Cetane number	D613	40	-
Pour point	D2500	-	°C
Viscosity	D445	1.9-6	mm ² s ⁻¹ (cSt)
Flash point (open cup)	D93	Min 47	°C
Ash content	D482	0.05	wt. %
Sulfur content	D5453	Max 0.05	wt. %
Copper strip corrosion	D130	Max number 3	-

P = Ethanol percentage; 0, 3, 6, 9 and 12

Q = Biodiesel percentage; 0, 2, 4, 6 and 8

R = Diesel percentage; 0, 80, 85, 90, 95 and 100.

$$P/Q = 3/2$$

$$P+Q+R = 100$$

Laboratory tests were then carried out using ASTM test standards to determine properties such as: fuel stability, cetane number, pour point, viscosity, flash point, ash content, sulfur content and copper strip corrosion. Table 1 shows the diesel fuel properties, test methods and limits based on the ASTM D6751 standard.

RESULTS AND DISCUSSION

Fuel Solubility

A solution is a single-phase liquid system, homogeneous at the molecular level. Some e-diesel formulations may be a solution of ethanol, plus additives, in diesel fuel. Solubility changes by ambient temperature. Low temperatures have low solubility (He *et al.*, 2003; Suppes, 2000). The presence of water in ethanol or diesel fuel can critically reduce solubility (Suppes, 2000; Li *et al.*, 2005). Lowering diesel aromatic content reduces the solubility of ethanol (McCormick and Parish, 2001; He *et al.*, 2003). The phase separation temperature up to 4-5% ethanol in Iranian diesel fuel is identical to the cloud point of the pure fuel. Thus blending of up to 4-5% ethanol places no additional temperature restrictions on these fuels. If no water is present, for example, blending ethanol with a zero aromatic diesel increased the

cloud point by nearly 25°C at 5% ethanol. Thus, diesel fuel chemical properties can have a large effect on ethanol solubility.

The most important advantage of using fuel blends in diesel engines is to be able to use ethanol without any modification of the diesel engines. Some material such as emulsifier, cosolvent or isopropanol, was added to the mixtures to satisfy homogeneity and prevent phase separation (Xing-cai *et al.*, 2004; He *et al.*, 2003; McCormick and Parish, 2001). In this paper, sunflower methyl ester was added as an additive to increase the miscibility, viscosity, lubricity and cetane number of the fuel blend.

Cetane Number

The cetane number is an important fuel property for diesel engines. It has an influence on engine start-ability, emissions, and peak cylinder pressure and combustion noise. A high cetane number ensures good cold starting ability, low noise and a long engine life. Cetane numbers of blended fuel depend on the amount and type of additive used in the blends and these can be measured through the engine CFR. Since the cetane number of ethanol is extremely low (5-8) compared with that of diesel fuel (47), the cetane number of the ethanol-diesel blend fuel is reduced significantly. Using 12% ethanol to diesel fuel reduced the fuel blend cetane number to 40. But adding sunflower methyl ester in the present case improved the ethanol-diesel cetane number due to the higher cetane number of sunflower methyl ester (54) and this made the blend an

ideal one for diesel engines.

Pour Point

Pour point is the temperature below which the fuel will not pour. The pour point obtained for diesel fuel and fuel blend is given in Table 2. The fuel blends can increase resistance of fuel at lower temperatures and may be more suitable for cold climates. During winter, many conventional diesel fuels need to be modified by blending them with No. 1 diesel, kerosene or low temperature flow improving additives, to avoid phase separation or fuel gelling. Because of the very low freezing point of ethanol relative to diesel fuel, it might be expected that e-diesel would have improved low temperature flow properties, as long as the ethanol remains soluble. Solubility of ethanol in diesel fuel is very low especially in low temperatures. Phase separation occurs when the temperature of ethanol–diesel blends is reduced. Adding sunflower methyl ester to ethanol–diesel blends solves the phase separation problem at lower temperature. Adding 10–20% of sunflower methyl ester and bioethanol to diesel fuel reduces the pour point of the mixture from -2°C to -7°C , making it more suitable for cold climates.

Viscosity

Most diesel fuel injection systems compress the fuel for injection using a simple

piston and cylinder pump called the plunger and barrel. In order to develop the high pressures needed in modern injection systems, the clearances between the plunger and barrel are approximately one ten-thousandth of an inch. In spite of this small clearance, a substantial fraction of the fuel leaks past the plunger during compression. If fuel viscosity is low, the leakage will correspond to a power loss for the engine. If fuel viscosity is high, the injection pump will be unable to supply sufficient fuel to fill the pumping chamber. Again, the effect will be a loss in power. The viscosity range for typical biodiesel fuels overlaps the diesel fuel range, with some biodiesels having viscosities above the limit. If fuel viscosity is very excessive, as is the case with vegetable oils, there will be a degradation of the spray in the cylinder causing poor atomization, contamination of the lubricating oil, and the production of black smoke. The viscosities of the used diesel fuel and obtained fuel blends measured are given in Table 2. It can be observed from this table that adding bioethanol to diesel fuel reduces the blend viscosity. Biodiesel viscosity is highest (4.22) and the pure ethanol viscosity has the lowest value (1.10). The diesel fuel viscosity is next to the biodiesel with an amount of 3.28. The bioethanol can be referred as a viscosity regulator in the blend.

Flash Point

The flash point is the lowest temperature at

Table 2. Pour point, viscosity and flash point of fuel blends and diesel fuel.

Fuel type	E ₁₂ B ₈ D ₈₀	E ₉ B ₆ D ₈₅	E ₆ B ₄ D ₉₀	E ₃ B ₂ D ₉₅	E ₁₂ B ₀ D ₈₈	E ₉ B ₀ D ₉₁	E ₆ B ₀ D ₉₄	E ₃ B ₀ D ₉₇	E ₀ B ₀ D ₁₀₀	E ₀ B ₁₀₀ D ₀	E ₆₀ B ₄₀ D ₀	E ₁₀₀ B ₀ D ₀
Pour point (°C)	7-	7-	7-	5-	5-	5-	4-	3-	2-	3-	-9	<<-50
Viscosity mm ² s ⁻¹	2.74	2.77	2.90	3.00	2.47	2.62	2.74	2.99	3.28	4.22	1.65	1.10
Flash point (°C)	14	14	14	17	14	14	14	16	64	187	14	14



which a fuel will ignite when exposed to an ignition source. The flash point of the fuel affects the shipping and storage classification of fuels and the precautions that should be used in handling and transporting the fuel. In general, flash point measurements are typically dominated by the fuel component in the blend. It can be concluded that the flash point of ethanol–sunflower oil methyl ester–diesel blends fuels is mainly dominated by ethanol. The measured flash points of diesel fuel and obtained fuel blends are given in Table 2. Adding only 3% ethanol to diesel fuel reduces the flash point of the fuel blend to very close to the flash point of pure ethanol. The flash point of pure biodiesel is the highest (187) and that of the bioethanol is the lowest (14). The flash point of pure diesel fuel lies in between at 64.

Ash Content

Ash is a measure of the amount of metals contained in the fuel. High concentrations of these materials can cause injector tip plugging, combustion deposits and injection system wear. Soluble metallic materials cause deposits, while abrasive solids will cause fuel injection equipment wear and filter plugging. The amount of diesel fuel ash content is 0.001 mass fraction and the ash content of sunflower methyl ester and bioethanol are 0.001 and 0.000, respectively. It is observed that the ash content of the blend reduces with the increase of ethanol in blend, making it beneficial.

Sulfur Content

The sulfur content of diesel fuel is another of the important fuel properties. The sulfur content of ethanol and sunflower methyl ester is 0 and 15 ppm, respectively. In contrast with the 500 ppm diesel fuel sulfur content, the ethanol and sunflower methyl ester combination has very small amount of sulfur of less than 20 ppm, bringing the blend to

level to comply with the most stringent fuel regulation.

Copper Strip Corrosion

Several parts of the engine, fuel delivery and fuel tank may be built from copper and copper alloys. The copper strip corrosion of diesel fuel and blends was determined according to ASTM D130 standard. The experimental results show that the copper strip corrosion of diesel, bioethanol and sunflower methyl ester are 1a, 1a and 1b respectively.

CONCLUSIONS

1. Addition of ethanol to diesel fuel greatly reduces the fuel blend cetane number extremely. On the other hand, biodiesel can increase the ethanol–diesel fuel cetane number.
2. Ethanol and sunflower methyl ester can improve low temperature flow properties due to the very low freezing point of ethanol and low pour point of sunflower methyl ester relative to diesel fuel, as long as the ethanol remains soluble at low temperatures due to the effect of biodiesel.
3. Sunflower methyl ester and ethanol viscosity is slightly higher and lower than diesel fuel, respectively. However, fuel blend viscosity is in the standard range and acceptable.
4. Adding only 3% ethanol to diesel and sunflower methyl ester reduces the flash point of the fuel blend very much lower than ASTM standard limits. As a result, much caution is necessary for the storage and transportation of these fuel blends.
5. The ash content of blends is reduced with the increase of ethanol in blends.
6. The sulfur content of blends is greatly reduced with the increase of ethanol and sunflower methyl ester in the blends.

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تولید بیواتانول و متیل استر روغن آفتابگردان و بررسی خواص سوختی مخلوطها

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چکیده

سوختهای گیاهی مهمترین سوختهای جایگزین سوختهای فسیلی می باشند. این سوختها آلودگیهای کمتری نسبت به سوختهای فسیلی دارند و می توان آنها را از ضایعات مواد کشاورزی برای بهره برداری در موتورهای دیزل تولید کرد. در این کار تحقیقاتی بیواتانول از ضایعات سیب زمینی تولید شد. بیواتانول بوسیله ژئولیت 3A در فاز بخار خشک و به صورت ترکیبی با متیل استر روغن آفتابگردان و سوخت دیزل استفاده شد و سپس مورد بررسی قرار گرفت. همچنین متیل استر روغن آفتابگردان به روش ترانس استریفیکاسیون تولید شد. با توجه به شرایط آزمایشگاه و محدود بودن پایداری سوخت استفاده شده، نسبت مناسب بیواتانول و سوخت دیزل ۱۲ به ۸۸ تعیین شد و سپس برای بقای پایداری سوخت در دماهای کمتر از ۱۵°C متیل استر روغن آفتابگردان به مخلوط اضافه شد. نقطه ریزش سوخت و مخلوطهای مختلف شامل ویسکوزیته، نقطه اشتعال، میزان خاکستر، میزان گوگرد و میزان خوردگی مس در آزمایشگاه اندازه گیری شد. آزمایشها نشان داد که اتانول نقش مهمی را در نقطه اشتعال مخلوطها بازی می کند. با اضافه کردن ۳٪ بیواتانول به دیزل و متیل استر روغن آفتابگردان، نقطه اشتعال تا ۱۶°C کاهش یافت. ویسکوزیته مخلوطها نیز با افزایش مقدار اتانول کاهش پیدا کرد. محتوای گوگرد بیواتانول و متیل استر روغن آفتابگردان نسبت به سوخت دیزل بسیار پایین است. میزان گوگرد سوخت دیزل ۵۰۰ ppm می باشد، درحالی که محتوای گوگرد اتانول و متیل استر روغن آفتابگردان بترتیب صفر و ۱۵ ppm می باشد. میزان گوگرد کمتر استفاده از ترکیبات را در موتور دیزل راحت تر می کند. این مقدار برای اتانول و متیل استر روغن آفتابگردان کمتر از ۲۰ ppm است.