

IMPROVEMENT OF COLD FLOW PROPERTIES OF BIODIESEL BY USING METHYL PROXYTOL (PM)

METİL PROKSİTOL (PM) KULLANIMI İLE BİYODİZEL YAKITININ SOĞUK AKIŞ ÖZELİKLERİNİN İYİLEŞTİRİLMESİ

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Abstract

Cold flow properties of biodiesel are worse compared to diesel fuel; and this may cause problems during first start in cold weather. Cold properties of biodiesel exhibit variations according to oil acid composition and alkali groups in cold climates. Biodiesel containing high amount of saturated fatty acids has high pour point, cloud point and cold filter plugging point values. Therefore, the use of fuel, with no good cold flow properties, damages the fuel supply elements of the engine and causes first movement problems. The ability to maintain the properties of fuel at low temperatures is called cold flow performance. Up to 20% of diesel fuel may consist of relatively heavy molecules (paraffin). At low temperatures, these heavy paraffin molecules decompose to form paraffin wax and precipitate, causing clogging of fuel lines and filters. This causes the engine to lose power and/or stop. Adding a heater to the fuel system immediately after the fuel filter or with a filter coupled provides a solution to the viscosity problem that occurs during the use of biodiesel in cold weather. Since biodiesel and biodiesel-diesel blends have higher pour and cloud point values than that of diesel, it is envisaged to use suitable additives (methyl proxytol, ethyl proxytol, anti-gel substances) for effective use of fuels in the cold. In this study, biodiesel fuels, 2%, 5% and 7% in the fuel mixture density (880,882,883kg (m^3) and viscosity (4.04, 3.69 and 3.48 mm²/s) values are then obtained by joining the additive methyl proksitol pour point (-51, -53 and -57°C), cloud point (-57.4, 60.2 and 63.6°C), cold filter plugging point (-54, -56 and -59°C) values were measured.

Keywords: Biodiesel, Cold flow properties, Pour point, Cloud point, CFPP, Methyl Proxytol.

Özet

Biyodizelin soğuk akış özellikleri dizel yakıtına oranla daha kötüdür ve soğuk havalarda ilk çalıştırma esnasında sorunlara neden olabilir. Biyodizelin yağ asidi kompozisyonuna ve alkil gruplarına göre soğukta akış özellikleri iklim koşullarına göre değişkenlik gösterir. Yüksek miktarda doymuş yağ asidi içeren biyodizellerin akma noktası, bulutlanma noktası ve soğuk filtre tıkanma noktası değerleri yüksektir. Dolayısıyla kış aylarında soğuk akış özelliği iyi olmayan yakıt kullanımı motorun yakıt besleme elemanlarına hasar verir ve motorda ilk hareket problemlerine neden olur. Düşük sıcaklıklarda yakıtın özelliklerini koruma yeteneği soğukta akış performansı olarak adlandırılır. Dizel yakıtın en fazla % 20si göreceli olarak ağır moleküllerden (parafin) oluşabilir. Düşük sıcaklıklarda bu ağır parafin molekülleri ayrışarak parafin mumu oluşturur ve çökelirler dolayısıyla yakıt hat ve filtrelerinin tıkanmasına neden olurlar. Bu durum motorun güç kaybetmesine ve/veya stop etmesine neden olur. Yakıt sistemine, yakıt filtresinden hemen sonra veya filtre ile akuple edilmiş bir ısıtıcı ilavesi biyodizelin soğuk havalarda kullanımı sırasında oluşan viskozite problemine çözüm sağlamaktadır. Biyodizel ve biyodizel-dizel karışımları, dizelden daha yüksek akma ve bulutlanma noktasına sahip olduklarından yakıtların soğukta efektif bir şekilde kullanılmaları için uygun katkı maddelerinin (metil proksitol, etil proksitol, anti-jel maddeleri) kullanılması öngörülmektedir. Bu çalışmada biyodizel yakıtına %2, %5 ve %7 oranlarında metil proksitol katkı maddesi katılarak elde edilen yakıt karışımlarının başta yoğunluk (880,882,883kg / m³) ve viskozite (4.04, 3.69 and 3.48



mm²/s) değerleri akabinde de akma noktası ((-51, -53 and -57°C), bulutlanma noktası (-57.4, 60.2 and 63.6°C), soğuk filtre tıkanma noktası ((-54, -56 and -59°C) değerleri ölçülmüştür.

Anahtar Kelimeler: Biyodizel, Soğuk akış özellikleri, Akma noktası, Bulutlanma noktası, CFPP.

1. INTRODUCTION

Increasing population and living standards in the world have increased energy consumption in large scales. Merely since 1950, the world population has more than doubled; and it is expected that it will increase 40% more until 2050 [1, 2]. These data make it unavoidable to find a solution to energy problem. On the one hand scientists search for how to meet the increasing energy needs; on the other hand, they try to do this by employing economically, environmentally and socially sensitive methods as well as including combating greenhouse gas emissions. People should use the energy sources in the world more carefully; hence, they should emphasis on R&D and innovation studies. In order to realize all these, the transition processes to renewable energy sources should be accelerated [3]. Renewable energy sources have gained importance because they will never run out, and there is no harm to the environment, and their cost is much less than fossil fuels. As the fact that this great energy hunger in the world cannot be met with non-renewable energy sources, namely fossil fuels (coal, oil, and natural gas), the need and interest in renewable energy sources have increased. The energy obtained from fossil fuels has started to damage our planet day by day [4]. Sustainable energy means using as much energy as needed without risking it [5]. The importance of renewable energy sources for the future of the world and Turkey is great in this respect. The importance of renewable energy sources for the future of Turkey is increasing every day. Investments in renewable energy should be increased, especially these days when we are increasingly feeling the effects of climate change. When using renewable energy sources in Turkey it can be obtained the following results.

- i. Dependence on imported fuels will decrease.
- ii. Priority will be given to domestic resources.
- iii. Employment will increase as a result of domestic production.
- iv. It will enable sustainable economic growth and development.
- v. Energy supply security will increase.
- vi. With the security provided to meet the energy demand, the sectors that use energy will be positively affected and this will encourage them to invest.
- vii. Stability will increase with the trust in environment provided in production and consumption.
- viii. Welfare and stability will increase in social and economic life.

Biomass energy is one of the primary sources to be used to provide sustainably energy without causing environmental pollution [6]. Since biomass energy is an inexhaustible source and it can be obtained everywhere, it is seen as an appropriate and important energy source, especially because it helps socio-economic developments of rural areas [7]. For biomass, specially grown plants such as corn, wheat, herbs, algae, algae at sea, animal droppings, fertilizer and industrial wastes, and all organic wastes (fruit and vegetable) from houses are sources [8]. The use of biomass is becoming increasingly important to solve the energy problem because of the limited energy resources such as oil, coal and natural gas, as well as their environmental pollution [9].

Advantages of bio-mass energy [10-12]; It is known that energy production using fossil fuel sources damages the environment. Any energy source to be used is now being evaluated together with its environmental impact. Global environmental problems are directly dependent on the energy consumed, more precisely on the use of fossil fuels containing high levels of sulfur and other harmful substances. While the energy consumption in the world has increased 17 times in the last century, harmful gases such as CO₂, SO₂ and NOx originating from fossil fuels and discharged into the



atmosphere have increased at the same rate. With the regional and modern operation of biomass, it is possible to create residential areas that are developing with self-sufficient energies, especially in remote areas. For the production of energy from biomass, as more agricultural work is required, the issue of bio-energy is an ideal option for creating business areas especially in rural areas. It is possible to prevent migration from rural areas to big cities, which is one of the biggest problems developing countries face. Biomass grows in very barren areas and is of great importance for the use of previously unavailable soils and the evaluation of rural areas in terms of cultivation.

Biodiesel, which is the sub-subject of biomass energy that is among the renewable energy sources, is an alternative fuel obtained from vegetable or animal origin oils [13]. Production of biodiesel fuel is easier than other alternative energy sources (such as wind energy and solar energy). Its production is becoming widespread day by day due to its low cost. Along with this, biodiesel, a sustainable type of energy, creates new jobs, especially in rural areas, by ensuring that industry, agriculture and environmental fields work together [14]. However, the cold flow properties of biodiesel are worse than diesel fuels and can cause problems during cold start-up [15-18]. However, while converting these oils into biodiesel, it is predicted that the cold flow properties of the fuel can be improved by using alcohols such as methanol, ethanol, isopropyl alcohol and methyl proxytol [19-24]. The cold flow behavior of biodiesel is generally characterized by the temperature in which biodiesel starts to change from fluid to solid state, resulting in performance issues. Biodiesel has start-up and operability problems during cold weather because of its poor cold flow behavior [27-30].

COLD FLOW PROPERTIES OF BIODIESEL

Crystallization of the saturated fatty acid during winters causes fuel starvation and operability problems as solidified material clogs to fuel lines and filters. With decrease in temperature, more solid is formed and material approaches the pour point which is the lowest temperature at which it will cease to flow. It has been well established that the presence of higher amount of saturated components increases the cloud point and pour point of biodiesel utilization of additives that enhance the impact of crystal morphology and blending with a fuel like kerosene which causes freezing point depression [31,32].

POUR POINT (PP):

The pour point of a liquid is the lowest temperature at which it becomes semi solid loses its flow characteristics. The oil flow is retarded due to increase in viscosity and formation of wax crystals at low temperatures [33]. Diesel fuel should not lose its flowability especially in cold weather. High pour point can clog the fuel filter in cold weather, causing the engine to stop running [34, 35]. To reduce the pour point of fuel, especially in diesel engines operating in cold regions, certain amounts of kerosene and various chemical additives are added.

CLOUD POINT (CP)

In the petroleum industry, cloud point refers to the temperature below which wax in diesel or biowax in biodiesels forms a cloudy appearance. The presence of solidified waxes thickens the oil and clogs fuel filters and injectors in engines. The wax also accumulates on cold surfaces (producing, for example, pipeline or heat exchanger fouling) and forms an emulsion with water. Therefore, cloud point indicates the tendency of the oil to plug filters or small orifices at cold operating temperatures [33, 34, 36].



COLD FILTER PLUGGING POINT (CFPP)

It is the lowest temperature expressed in degrees Celsius, where a particular type of diesel fuel passes through a standardized filtration device at a certain time when cooled under certain conditions [37, 38]. In other words, cold filter plugging point (CFPP) is the lowest temperature, expressed in degrees Celsius (°C), at which a given volume of diesel type of fuel still passes through a standardized filtration device in a specified time when cooled under certain conditions. This test gives an estimate for the lowest temperature that a fuel will give trouble free flow in certain fuel systems. This is important as in cold temperate countries, a high cold filter plugging point will clog up vehicle engines more easily [39].

2. MATERIALS AND METHODS

PHYSICAL AND CHEMICAL PROPERTIES OF THE TEST FUELS

The sunflower oil used in the study was obtained from the local commercial market. In order to produce fuel suitable for the standard, Sigma-Aldrich's 99.7% purity methyl alcohol and as a catalyst, Merck brand 99.9% purity potassium hydroxide (KOH) were purchased from commercial companies. The experiments were conducted in accordance with our previous studies and literature information, and 65°C temperature, 60min reaction time, 1% catalyst and 20% of methyl alcohol was determined as optimum conditions, and transesterification reactions of all oils were performed under these conditions. The properties of the biodiesel fuels produced were analyzed in Batman University Technical Sciences Vocational School Refinery and Petro-Chemistry Technology program laboratory. Fuel properties of methyl proxytol-biodiesel blends mixed in different proportions are given in Table 1.

Fuels	Density 15°C (kg/m³)	Kinematic Viscosity 40 °C(mm/s ²)	Pour Point (°C)	Cloud Point (°C)	CFPP* (°C)
Diesel	795	3.20	-22	-6.0	-15
Biodiesel	878	4.25	-9	-3.0	-9
MP**	922	1.32	-78	-68.0	-79
%2 MP	880	4.04	-51	-57.4	-54
%5 MP	882	3.69	-53	-60.2	-56
%7 MP	883	3.48	-57	-63.6	-59

Table 1. Fuel properties of methyl proxtyl-biodiesel blends mixed in different proportions

CFPP*: Cold filter plugging point MP**: Methyl proxytol

The fuel properties of biodiesel vary greatly depending on the fatty acid distribution [26]. The most important features are ignition ability, cold flow properties and oxidative stability. Although saturation and fatty acid distribution in lipids do not have a significant effect on the production of biodiesel by the transesterification method, it is directly associated with the properties of the fuel.

3. RESULTS AND DISCUSSION

Viscosity and density are the two physical properties of biodiesel fuels which are more responsible for the engine performance. Both of these parameters are related to combustion process, which is highly dependent on the quality of atomization. In turn, fuel atomization is dependent on fuel properties such as viscosity, surface tension and density. Two factors like pressure and temperature are dependence of physical properties that affect biodiesel fuel atomization and combustion (viscosity, surface tension, density droplet size in injector). Physical properties of biodiesel are dependent on temperature. Since density is the ratio of mass per unit volume, measuring the variation in volume of a given mass of oil as a function of temperature leads to the density at elevated temperatures. In Figure 1, density and viscosity changes of fuels and blends used in the study are seen.

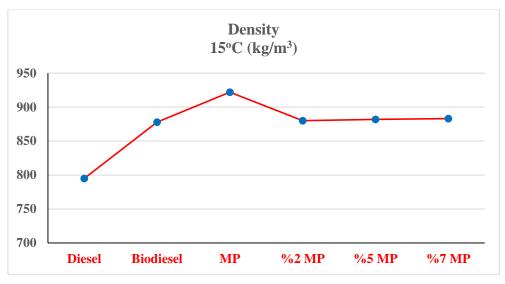


Figure 1. Density changes of fuels and blends

As can be seen in Figure 1, the density of methyl proxytol is higher than normal diesel and biodiesel. Therefore, as the percentage of weight increases in the methyl proxytol fuel mixture, it is seen that the densities formed increase. However, it was determined that all of the results obtained were in compliance with ASTM D6751-12 / EN ISO 12185 standards.

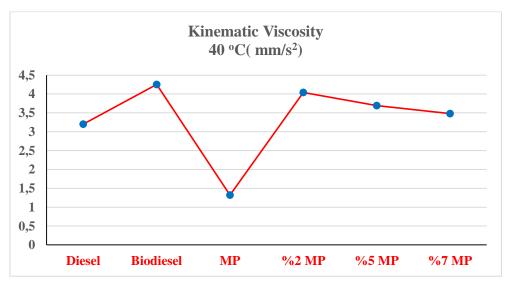


Figure 2. Viscosity changes of fuels and blends

Since the viscosity of the methyl proxytol we use in the study is quite low, it is seen in Figure 2 that the viscosity values of the mixtures decrease significantly when mixed with biodiesel. It is anticipated that fuel mixtures will be transported to the combustion chamber in the engine in a healthier manner. In this study, the main purpose is to improve the cold flow properties of the obtained fuel mixtures by adding methyl proxytol to biodiesel fuel at different rates whose freezing, flowing, clouding and



cold filter plugging points are quite low compared to diesel. In Figures 3,4 and 5, the flow, clouding and cold filter plugging points of fuels mixed with biodiesel at different rates can be seen.

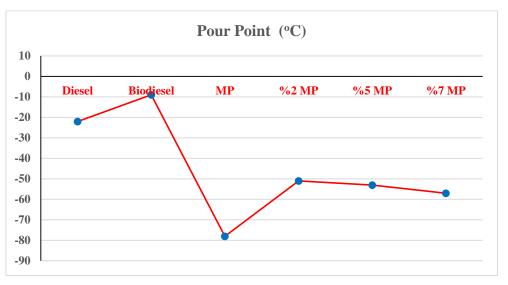


Figure 3. Pour point changes of fuels and blends

Since the pour points of biodiesel are higher than diesel fuel, vehicles running on biodiesel may experience more fuel system plugging problems than petroleum diesel fuel products [40,41]. When Figure 3 is examined, it is observed that the pour points of the fuel mixtures decreased when methyl proxytol, whose pour point is much lower than both normal diesel and biodiesel, is mixed with the biodiesel at certain rates. This is especially important in the use of such a fuel blend, especially in cold climatic conditions, and the fuel system clogging problem will be eliminated.

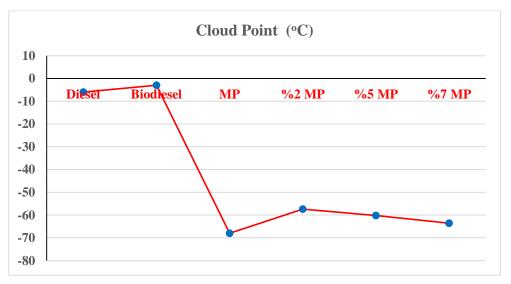


Figure 4. Cloud point changes of fuels and blends

Cloud point is the temperature at which wax (paraffin) begins to separate when oil chilled to a low temperature, and it serves as an important indicator of practical performance in automotive applications in low temperatures [42]. As seen in Figure 4, it is determined that there is a significant decrease in the clouding points of the fuel blends that are formed when the methyl proxytol biodiesel



is mixed with different rates at the cloud point compared to diesel and biodiesel. This is thought to have a positive effect on automotive performance at low temperatures.

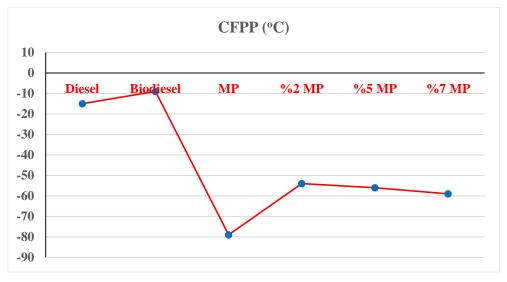


Figure 5. Cloud filter plugging point changes of fuels and blends

Biodiesel like all diesel fuels tends to gel in cold weather, resulting in clogged filters and plugged fuel lines. One of the most important properties for biodiesel is CFPP. It is absolutely undesirable for fuel to gel early in the cold, and clog the fuel filter. When Figure 5 is examined, it is evident that the CFPP values of the obtained fuel blends, whose CFPP values are quite low, decreased significantly when used with methyl proxytoel biodiesel. Therefore, it is thought that when certain amounts of methyl proxytol are added to the biodiesel in cold climatic conditions, the problem of gelling and blockage of the fuel filter will be eliminated.

4. CONCLUSIONS

The main purpose of this study is to improve the cold flow properties such as pour point, cloud point and CFPP of the fuel mixture obtained by adding 2%, 5% and 7% methyl proxytol to biodiesel fuel. The density and viscosity values of the fuel blends obtained in the study were also compared. Since the density of methyl proxytol is higher than that of normal diesel and biodiesel, it is observed that the density of the blends formed as the percentage of weight of the methyl proxytol increases in fuel mixture (880-883kg/m³). It was determined that all of the obtained results are in accordance with ASTM D6751-12 / EN ISO 12185 standards. Since the viscosity value of the methyl proxytol (1.32mm²/s) is very low compared to the biodiesel (4.25mm²/s), it is observed that the viscosity values (4.04, 3.69 and 3.48 mm²/s) the fuel blends also significantly decrease. Considering the cold flow properties of fuel mixtures, which are the main purpose of the study, both pour point (-51, -53 and -57°C), cloud point (-57.4, 60.2 and 63.6°C) and CFPP (-54, -56 and -59°C) have decreased. Therefore, when methyl proxytol is added as an additive to the biodiesel, it has been determined that there are significant improvements in viscosity as well as cold flow properties.

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