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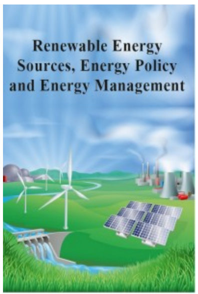

Original Review Article

Improvement Of Cold Flow Properties In Biofuels Used In Aviation

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ABSTRACT

This study includes investigations on the determination and development of cold flow properties of biofuels used in aviation. Cold flow properties of biodiesel are weaker according to petroleum sourced fuels, but it is possible to improve these properties. For this, the results were evaluated by adding additives in different ratios to biodiesel obtained from various oils. Acetone, Diethyl Ether, Ethyl Acetoacetate, Ethylene Vinyl Acetate Copolymer, Lubrizol, Olefin Ester Copolymer, Poly Alpha Olefin, Poly Lauryl Methacrylate, Poly Methyl Acrylate, Viscoplex 10-305, Wintron Synergy additives were positive effects on cold flow properties. However, the proportion of additives added to fuels and the raw material of oil also change the results significantly.

Keywords: Biodiesel, environment, aviation, cold flow properties, additives

1. Introduction

With the continuous development of aircraft engines from the past to the present, the types of fuel used in aviation have also improved according to engines. Aircraft engines mostly consist of light piston engines or gas turbine engines. In aviation, gasoline and diesel fuels used in piston engines were replaced by jet engines and kerosene-type fuels were introduced. Nowadays, kerosene type fuels used in civil aviation are mainly Jet A-1 and Jet A fuels, as well as Jet B and TS-1 fuels are used. Fuel used in military aviation nowadays is JP-8 fuel. In the aviation sector, where the majority of cargo transfers, primarily airline passenger transportation, are made, mostly oil-derived fuel is used. The use of petroleum-derived fuels causes both high fuel costs in transportation and an increase in polluting emissions in the atmosphere resulting from these fuels. Therefore, the use of alternative fuels in the aviation sector will provide a significant improvement for the environment by reducing the effect of greenhouse gas emissions and for the national economy by reducing dependence on oil.

With the widespread use of biofuels in the world, these fuels have also started to be used in the aviation industry, where fuel consumption is high. These fuels can be used by mixing with jet fuel at certain mixing ratios. Properties such as cold flow feature, oxidation stability, viscosity are very important in terms of weather conditions, storage and flight safety in aviation fuels. Biodiesel has a high saturated fat ratio as it is obtained from vegetable or animal origin oils. This situation causes the cold flow properties of the fuel to be high. The cold flow properties and oxidation stability of biodiesel can be improved by various methods and these properties are brought closer to the appropriate fuel standards. In this study, the method of developing cold flow properties with additives is examined.

2.Cold Flow Improvement Additives Used in Biodiesel Fuels

Pour Point Depressant (PPD): PPD is typically the formation of low molecular weight, n-alkane paraffin molecules whose melting point and structure are similar copolymers. It has been first developed in the 1950s. They are additives used to improve the pumping ability of pure oils [1].

Wax Crystal Modifier (WCM): It is suitable for after sales applications. Improvers in this group can generally be classified as cold filter plugging point improvers, cloud point depressors and wax precipitation inhibitors. In general, WCMs are categorized as cold filter plugging point improver, cloud point lowering, wax settling inhibitor. WCMs provide a bi-directional function by reducing the cloud point. CFPP developers reduce their reduction capacity by 10-20 ºC. Although some additions report reducing LTFT, most CFPP reducers do not affect cloud point [1].

In this research, different experiments conducted by adding additives to fuels to improve the cold flow properties of biodiesel at low temperatures were investigated.

The cold flow properties of the fuel were examined by adding EVAC, PAO, PMA, EAA and MgO nanoparticles to the biodiesel obtained from waste cooking oil [2, 3].

The cold flow properties of biodiesel with 20 % by weight of waste cooking oil biodiesel are significantly improved with EVAC, PAO and PMA additives. By reducing the pour point, cloud point and cold filter plugging point between 8 and 10 ° C, EVAC has been the additive with the best effect. As a result, PAO and PMA additives have also been proven to be good cold flow improvers for waste frying oil biodiesel. Other additives showed minimal effect on cold flow properties.

While the EVAC additive had a significant effect on the properties of waste cooking oil biodiesel, it did not show a good effect for biodiesel derived from tobacco seed oil. However, the cold filter plugging point of biodiesel obtained from tobacco seed oil had lowered to 7 °C with 0.5 % octadecene-1-maleic anhydride copolymer addition and improved.

The cold flow properties of the fuel were examined by adding PLMA, Wintron Synergy, EL, Viscoplex 10-305 and Viscoplex 10-330 additives to biodiesel obtained from canola oil [4, 5].

Wintron Synergy and EL additives added to canola oil biodiesel exhibited behaviour well at cloud point, PLMA additive at pour point, and Viscoplex 10-305 additive at cold filter plugging point. PLMA additive of 1 % by weight provided a 30 °C reduction in pour point, proving to be an important cold flow improver. Viscoplex 10-305 additive, providing a decrease of 11 ºC, showed that it is a better cold flow improver for canola-based biodiesel than Viscoplex 10-330.

The cold flow properties of the fuel were investigated by adding OECP, EACP, PMA, Lubrizol, Viscoplex 10-305 and Viscoplex 10-330 additives to the biodiesel obtained from soybean oil [4, 6].

With the 0.03 % OECP additive added to soybean biodiesel, a better result was obtained compared to other additives by reducing filter clogging and pour point 6-8 ºC in the cold. While the addition of Lubrizol showed minimal effect on the cloud point, it showed a better effect on the pour point. The Viscoplex 10-305 contribution was found to be a better cold flow developer for the filter clogging point in cold than the Viscoplex 10-330 contribution. EACP and PMA additives had showed almost no effect on the cold flow properties of soybean biodiesel.

The cold flow properties of the fuel were investigated by adding PGE, EVA, DEP, PA and Viscoplex 10-330 additives to the biodiesel obtained from palm oil [7, 8].

The addition of EVA, PGE, DEP and PA additives to palm oil biodiesel was reduced cold filter plugging point by 3 to 5 ºC. Adding EVA and PGE additives together has shown a better effect on the cold flow properties of palm oil. When DEP, PGE and PA additives were added to the palm oil biodiesel at a ratio of 3: 1: 1 or 2: 2: 1, the cold filter plugging point had been reduced by 7 °C and the best performance was achieved. The Viscoplex 10-330 contribution had a minimal effect on the cold filter plugging point. The Viscoplex 10-330 additive by a minimal has affected on the filter plugging point in cold.

The cold flow properties of the fuel were investigated by adding EAA, EL, ACE and DEE additives to the biodiesel obtained from dairy waste [9, 10].

The EAA contribution to biodiesel obtained from dairy waste showed an average effect by reducing the cloud point 3-6 ºC, the cold filter plugging point 3-10 ºC and the pour point 2-4 ºC. The hand contribution had showed a similar effect to the EAA contribution by reducing the cloud point by 3-7 ºC, the cold filter plugging point by 4-6 ºC, and the pour point by 1-4 ºC. ACE and DEE contributions have shown a better effect than other contributions by reducing the pour, cloud and cold filter plugging points by 7-12-13 ºC.

When the ozonized sunflower oil additive was added to the biodiesel obtained from sunflower and soybean oil at a rate of 1.5 % by weight, respectively, it reduced the pour point by 20 ºC and 8 ºC. When added to biodiesel obtained from palm and canola oil, it decreased the cloud point by 5 ºC and 17 ºC and showed an important performance on cold flow properties.

3. Results

The effects of additives on the cold flow properties of fuels are listed in Table 1.

Table 1. Effect of additives on cold flow properties

Fuel	Additive	Effects on Cold Flow Properties	Ref.
Waste Cooking Oil Biodiesel	PAO	**1.** The addition of PAO up to 400 ppm had reduced the CP, CFPP and PP of B20 by 8, 9 and 7 °C, respectively. **2.** B20 treate with PAO provided low viscosity at a low temperature, thus exhibiting the best cold flow properties. **3.** PAO effectively had delayed the aggregation of wax crystals, restricting the formation of large wax crystals, thus improving the cold flow properties of biodiesel blends.	**[11]**
	PMA	**1.** By adding 0.04 % of PMA, the PP and CFPP of waste cooking oil biodiesel were reduced by 8 and 6 °C respectively.	**[2]**
	EVAC	**1.** EVAC has been shown to significantly affect CP, CFPP and PP in B0, B20 and B40 fuels. **2.** The values of CP, CFPP and PP of B0 and B20 without additives had measured as -4, -5 and -8 °C, respectively. **3.** When the EVAC additive is added to B0 and B20 at the rates of 0.02 %, 0.04 % and 0.08 %, CP, CFPP and PP values are respectively; It had measured at -9, -11, -14 °C, -12, -15, -18 °C and -12, -16, -18 °C. **4.** The CP, CFPP and PP values of the unadulterated B40 fuel were measured as 0, -1 and -3 °C, respectively. When EVAC additive is added to B40 fuel at the rates of 0.02 %, 0.04 % and 0.08 %, CP, CFPP and PP values are respectively; It had measured at -6, -6, -6 °C; -6, -7, -8 °C and -6, -7, -8 °C. **5.** EVAC has been observed to have a minimal effect on CP, CFPP and PP in B60, B80 and B100 fuels.	**[3]**
	MgO Nanoparticles	**1.** The CP, PP and CFPP values of the pure B100 fuel had measured as -6, -3 and -2 °C, respectively. **2.** When 20 ppm and 30 ppm MgO nanoparticles were added to B100 fuel respectively, CP, PP and CFPP values had measured as 3, -9, -7 °C and 4, -11, -8 °C, respectively.	**[12]**

		3. The CP, PP and CFPP values of the pure B20 fuel had measured as 2, -7 and -5 °C, respectively. **4.** When 20 ppm and 30 ppm MgO nanoparticles were added to B20, respectively, the CP, PP and CFPP values had measured as -2, -11, -9 °C and 5, -16, -12 °C, respectively. **5.** The CP, PP and CFPP values of the pure B10 fuel had measured as 1, -9 and -6 °C, respectively. **6.** When 20 ppm and 30 ppm MgO nanoparticles were added to B10, respectively, CP, PP and CFPP values had measured as -1, -16, -11 °C and -3, -20, -15 °C, respectively. **7.** The CP, CFPP and PP of biodiesel had been significantly improved by the addition of MgO nanoparticles. MgO nanoparticle concentration of 30 ppm had been optimum for improvement in CFPP and PP. Increasing the MgO nanoparticle concentration above 30 ppm in biodiesel blends had been a negative effected on CFPP and PP.	
	EAA	**1.** The pure PP, CP and CFPP values of waste cooking oil biodiesel had measured as -4, 2 and 2 °C, respectively. **2.** By adding different amounts of EAA additive to the waste cooking oil biodiesel, the CP, PP and CFPP values of the fuel had measured. With the addition of 2.5 % by weight of EAA, the CP, PP and CFPP values were reduced to 6, 1 and 1 °C, respectively. With the addition of 5 % by weight of EAA, the CP, PP and CFPP values were reduced to -7, -1 and 0 °C, respectively. With the addition of 10 % by weight of EAA, the CP, PP and CFPP values were reduced to -7, -2 and -1 °C, respectively. With the addition of 20 % by weight of EAA, the CP, PP and CFPP values were reduced to -8, -2 and -2 °C, respectively. **3.** As a result, it was found that the addition of EAA improved the low temperature properties of biodiesel which would encourage the use of biodiesel in cold weather.	**[13]**
Sunflower Oil, Soybean Oil, Palm Oil, Canola Oil Biodiesel	Ozonized Sunflower Oil	**1.** Cloud and pour points of pure sunflower oil biodiesel had measured as 1 and -5 °C, respectively. When 1 % by weight ozonated sunflower oil biodiesel was added to pure sunflower oil biodiesel, cloud and pour points are reduced to 0 and -24 °C, respectively. When 1.5 % by weight of ozonized sunflower oil biodiesel was added, the cloud point remained the same, while the pour point was reduced to -25 °C.	**[14]**

		2. Cloud and pour points of pure soybean oil biodiesel had measured as 1 and -2 °C, respectively. When 1 % ozonated sunflower oil biodiesel was added to the pure soybean oil biodiesel by weight, the cloud point remained the same, while the pour point was reduced to -9 °C. When 1.5 % by weight ozonized sunflower oil biodiesel was added, the cloud and pour points were reduced to -1 and -10 °C, respectively. **3.** Cloud and pour points of pure palm oil biodiesel had measured as 18 and 12 °C, respectively. When 1 % and 1.5 % ozonated sunflower oil biodiesel was added to pure palm oil biodiesel, the cloud and pour points had been reduced to 13 and 11 °C, respectively. **4.** Cloud and pour points of pure canola oil biodiesel had measured as -4 and -13 °C, respectively. When 1 % ozonized sunflower oil biodiesel was added to pure canola oil biodiesel, the cloud and pour points were reduced to -6 and -30 °C, respectively. When 1.5 % ozonized sunflower oil biodiesel was added by weight, the cloud point and pour point were reduced to -4 and -30 °C, respectively.	
Calophyllum, Coconut Oil Biodiesel	PMA	**1.** The PMA additive improved the cold flow properties of blended biodiesel and the best results were obtained for CB20 with 0.03 % PMA. The PP, CP and CFPP of CB20 had decreased by 9 °C, 6 °C and 12 °C, respectively. Similarly, PP, CP and CFPP of CIB20 had decreased by 5 °C, 6 °C and 6 °C, respectively. **2.** The results showed that it can be used without any problem in terms of physicochemical quality of the fuel in cold climates by mixing with 0.03 % PMA.	**[15]**
Coconut Oil Biodiesel	PMA	**1.** The CP, PP and CFPP values of CB20 without additives had measured as -9 °C, -17 °C and -15 °C, respectively. **2.** By adding 0.03 % PMA to CB20, the CP, PP and CFPP values were reduced to -12 °C, -26 °C and -23 °C, respectively. **3.** With the addition of 0.03 % PMA additive to CB20, the CP, PP and CFPP values decreased by 3 °C, 9 °C and 8 °C, respectively, and as a result, PMA was found to be an effective cold flow improver.	**[16]**
Jatropha Oil Biodiesel	ZnO	**1.** Cloud and pour points of pure Jatropha oil biodiesel had measured as -2.9 and -13.1 °C, respectively.	**[17]**

		2. With the addition of 100 ppm concentration and 20 nm size ZnO nanoparticles to B10 fuel, clouding and pour point were reduced to -9.8 and -25.9 °C, respectively. **3.** With the addition of 100 ppm concentration and 40 nm size ZnO nanoparticles to B10 fuel, clouding and pour point were reduced to -9.4 and -29.1 °C, respectively.	
	Viscoplex 10-330	**1.** The CFPP value of Jatropha seed oil biodiesel without additives was measured as 0 °C. **2.** With the addition of 0.5 % and 1 % Viscoplex 10-330 by weight to Jatropha seed oil biodiesel, CFPP values were measured as -3 and -4 °C, respectively.	**[4]**
Canola Oil Biodiesel	PLMA	**1.** The cloud and pour point of canola oil biodiesel without additive had measured as -12 and -16 °C, respectively. **2.** With the addition of 1 wt % PLMA of canola oil biodiesel, the cloud point was unchanged and the pour point had been lowered to -46 °C.	**[5]**
	Wintron Synergy	**1.** The cloud point of the undoped B100 fuel was measured as -2.6 °C, by adding 2 % Synergy additive by weight to this fuel, the cloud point was reduced to -7.9 °C. **2.** The cloud point of the undoped B50 fuel was measured as -13.2 °C, by adding 2 % Synergy additive by weight to this fuel, the cloud point was reduced to -21 °C. **3.** The cloud point of the undoped B20 fuel was measured as -21.2 °C, by adding 2 % Synergy additive by weight to this fuel, the cloud point was reduced to -34.8 °C.	**[18]**
	EL	**1.** The PP and CP values of pure canola oil biodiesel had measured as -15 and 9 °C, respectively. **2.** By adding up to 20 % by weight of EL additive for canola oil biodiesel, the pour point was measured as -12 °C while the cloud point was lowered to -6 °C.	**[19]**
	Viscoplex 10-305 Viscoplex 10-330	**1.** The CFPP value of canola oil biodiesel without additive had measured as -14 °C. **2.** By adding 0.5 % and 1 % Viscoplex 10-330 by weight to canola oil biodiesel, CFPP values had measured as -15 and -16 °C, respectively. **3.** By adding 0.5 % and 1 % Viscoplex 10-305 by weight to the canola oil biodiesel, CFPP values had measured as -25 and -26 °C, respectively. **4.** With Viscoplex 10-305, a better result has been achieved than with Viscoplex 10-330 with a 12 °C reduction of CFPP.	**[4]**

	PLMA PVL Poly (n-decyl methacrylate) Poly (hexadecyl methacrylate) Poly (octadecyl vinyl ether-co-maleic anhydride)	**1.** The pour point of canola oil biodiesel without additive had measured to be -16 °C. **2.** Among the additives added, at 1 % loading, PLMA has been shown to most effectively improve the cold flow properties of biodiesel by reducing the pour point by 30 °C.	**[20]**
Palm Oil, Waste Cooking Oil, Canola Oil, Soybean Oil, Calophyllum Oil, Coconut Oil, Jatropha Oil Biodiesel	PMA EVAC OECP PAO HPMA IbE IpE Wintron XC30	**1.** In this study, it was concluded that the most effective cold flow improver was PMA followed by EVAC and OECP. **2.** PAO and HPMA have been found to be less effective in the literature. **3.** However, polymeric additives have been found to be more effective than other additives such as IbE, IpE, ethanol and methanol.	**[21]**
Palm Oil Biodiesel	Viscoplex 10-330	**1.** The cold filter plugging point of pure Palm oil biodiesel in had measured as 11 °C. **2.** With the addition of 0.5 % and 1 % Viscoplex 10-330 by weight to palm oil biodiesel, the filter plugging point values in cold were measured as 9 and 9 °C, respectively.	**[4]**
	PGE EVA	**1.** The cold filter plugging point of pure Palm oil biodiesel in had measured as 13 °C. **2.** The cold filter plugging point of palm oil biodiesel was reduced to 10 °C with the addition of 2 % EVA, and 8 °C with the addition of 2 % PGE additive. **3.** When EVA and PGE together additives were added to palm oil biodiesel at a ratio of 1 % by weight, the cold filter plugging point in has been reduced to 7 °C.	**[7]**
	DEP PGE PA	**1.** The CFPP value of the undoped Palm oil biodiesel had measured as 16 °C. **2.** With the addition of 0.1 %, 0.5 % and 1 % DEP by weight to palm oil biodiesel, CFPP values were measured as 16, 16 and 12 °C, respectively.	**[8]**

		3. With the addition of 0.1 %, 0.5 % and 1 % PGE by weight to palm oil biodiesel, CFPP values were measured as 15, 14 and 11.5 °C, respectively. **4.** With the addition of 0.1 %, 0.5 % and 1 % PA by weight to palm oil biodiesel, CFPP values had measured as 16, 14.5 and 11 °C, respectively. **5.** Tek bileşenli bir CFI veya iki bileşenden formüle edilmiş bir CFI ile karşılaştırıldığında, belirli bir formülasyon oranında üç bileşenden formüle edilmiş bir CFI en iyi performansı gösterir. When the DEP: PGE: PA ratio was 3: 1: 1 or 2: 2: 1, the CFPP of PME decreased by 7 °C, showed the best performance.	
Olive Oil Biodiesel	Manganese	**1.** An organic-based Manganese additive was added to biodiesel at a rate of 12 µmol / l oil methyl ester, reducing the pour point from 0 °C to -15 °C.	**[22]**
Soybean Oil Biodiesel	OECP EACP PMA	**1.** Pour point and cold filter plugging point of soybean oil biodiesel without additive were measured as -1 and 0 °C, respectively. **2.** The pour point and cold filter plugging point were measured as -4, -2 °C, -9 and -6, -2, -1 °C, respectively, by adding 0.01 %, 0.03 % and 0.05 % OECP additive to the soybean oil biodiesel. As a result, the OECP contribution of 0.03 % had a significant effected on the cold flow properties. **3.** Other additives, such as EACP and PMA, have had virtually no effect on the cold-flow properties of soybean oil biodiesel.	**[6]**
	Lubrizol	**1.** The cloud and pour points of soybean oil biodiesel without additives had measured as -4.4 and -6.7 °C, respectively. **2.** With the addition of 2 % lubrizol by weight to soybean oil biodiesel, the cloud and pour points were reduced to -6,6 and -17.7 °C, respectively. **3.** Cloud and pour points of the undoped B40 had measured as -12.2 and -15 °C, respectively. **4.** By adding 2 % by weight of lubrizol to B40, the cloud and pour points had lowered to -15 and -17.7 °C, respectively. **5.** Cloud and pour points of the undoped B30 had measured as -12.2 and -15 °C, respectively. **6.** By adding 2 % by weight of lubrizol to B30, the cloud and pour points were lowered to -15 and -28.8 °C, respectively.	**[5]**

		7. Cloud and pour points of the undoped B20 had measured as -15 and -20 °C, respectively. **8.** With the addition of 2 % by weight of lubrizol to B20, the cloud point was not change, while the pour point was lowered to -31.1 °C.	
	Viscoplex 10-305 Viscoplex 10-330	**1.** The cold filter plugging point of pure soybean oil biodiesel in had measured as 4 °C. **2.** With the addition of 0.5 % and 1 % Viscoplex 10-330 by weight to soybean oil biodiesel, the cold filter plugging point values were measured as -6 and -6 °C, respectively. **3.** With the addition of 0.5 % and 1 % Viscoplex 10-305 by weight to soybean oil biodiesel, the cold filter plugging point values were measured as -7 and -9 °C, respectively. **4.** The 5 °C reduction of cold filter plugging point with 1 % additive was showed that Viscoplex 10-305 is a better cold flow improver than Viscoplex 10-330.	**[4]**
Biodiesel Derived From Dairy Waste	EAA EL	**1.** With the addition of 5 %, 10 % and 15 % EAA to biodiesel derived from dairy waste, the cloud point of biodiesel was reduced from 17 °C to 14, 13 and 9 °C, the pour point from 10 °C to 8, 7 and 6 °C and cold filter plugging point from 17 ° C to 14, 12, 7 °C respectively. **2.** With the addition of 5 %, 10 % and 15 % EAA to biodiesel derived from dairy waste, the cloud point of biodiesel was reduced from 17 °C to 14, 13 and 10 °C, the pour point from 10 °C to 9, 7 and 6 °C and cold filter plugging point from 17 °C to 13, 13, 9 °C respectively.	**[9]**
	ACE DEE	**1.** The increase in the volume of ACE and DEE in the mixtures led to a decrease in the biodiesel PP, CP and CFPP. **2.** The addition of 20 % by volume ACE significantly reduced the PP, CP and CFPP of biodiesel derived from dairy waste by 7 ° C, 12 ° C and 12 °C, respectively. **3.** The addition of 20 % by volume DEE significantly reduced the PP, CP and CFPP of biodiesel derived from dairy waste by 7 °C, 12 °C and 13 °C, respectively.	**[10]**
Tobacco Seed Oil Biodiesel	EVAC Oktadesen-1-maleik anhidrit kopolimer	**1.** The CFPP value of the pure tobacco seed oil biodiesel had measured as -5 °C. **2.** The CFPP values has been measured as -12 and -9 °C with the addition of 0.5 % and 1 % octadecene-1-maleic anhydride copolymer by weight to the tobacco seed oil biodiesel.	**[23]**

		3. The CFPP values has been measured as -7 and -6 °C, with the addition of 0.5 % and 1 % EVAC by weight to the tobacco seed oil biodiesel. **4.** Octadecene-1-maleic anhydride copolymer has been found to be a more effective cold flow developer for tobacco seed oil than the EVAC additive.	

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