SEDIMENTATION SUSCEPTIBILITY OF PETROLEUM DIESEL FUELS BLENDED WITH BIODIESEL COMPONENTS

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Abstract

Low sulfur diesel fuel, neat biodiesel (RME), i.e. rapeseed oil methyl ester, and blends of ON diesel fuel with 5 % (B5) and 20 % (B20) of RME were treated with two additives influencing flow and storage properties (depressants of the WAFI type). The fuels with the addition of the depressants as well as those without the depressants were tested with the use of standard methods involving the determination of cloud point (CP), cold filter plugging point (CFPP), simulated filter plugging point (SFPP), and pour point (PP). After establishing the minimal depressant concentrations at which the value of CFPP was not higher than –20 ^{o}C, the fuels were conditioned for 64 hours in the temperature of -17 ^{o}C (sedimentation test). After the completion of the test, both CP and CFPP were determined in the samples taken from the upper and lower layers of the fuels. The blends B5 and B20 treated with the additive R442 failed the low-temperature sedimentation test; after its completion, the presence of white sediment was recorded in lower layers of the fuels, the CFPP grew by 11-12 ^{o}C, and, in the case of the B20 fuel, the CP increased by 6 ^{o}C as compared to that prior to the test.

1. Interduction

The sedimentation phenomenon is connected with the growth and settling of wax crystals during a long storage of diesel fuels at temperatures lower than the cloud point [1-3]. As a result of sedimentation of wax crystals two layers are formed in the originally homogenous fuel: the clear (or clouded) upper layer and the clouded lower layer enriched with paraffin sediment. If this phenomenon takes place in the fuel tank of a car, then the wax crystals settling on the filters hinders or completely stops the fuel supply to the combustion chamber. Petroleum middle distillate diesel fuel and biodiesel derived from vegetable oils (fatty acid methyl esters, FAME) have inadequate low-temperature properties [3-5]. They can not be used in temperate climate in winter because their cold filter plugging point (CFPP) is too high. The CFPP of diesel fuels used in Poland in wintertime should not be higher than -20 ^{o}C (PN-EN 590). A reduction of CFPP and improvement of low-temperature operability can be achieved by introducing depressants to diesel fuels [3, 5-7]. Our earlier study showed that wax-anti-settling flow improvers (WAFI additives) enhance the pour point and decrease CFPP of petroleum diesel/RME blends; however, additives do not greatly affect the cloud point [8].

The paper discusses the experimentally determined low-temperature properties of petroleum diesel fuel and its blends with biodiesel (FAME, derived from the rapeseed oil), depressed with two additives. The effectiveness of depressants was evaluated by means of the sedimentation test developed by the ITN (Institute of Petroleum Processing, Kraków) [9].

2. Experimental

Materials: low sulphur ON diesel fuel (ON Ekodiesel Plus, produced by PKN Orlen), RME biodiesel (97,2 % of methyl esters, derived from rapeseed oil from Biofuels Production Department of Trzebinia Oil Refinery) as well as blends of diesel fuel with 5 % (B5) and 20 % (B20) of RME ester in base diesel oil. Preparation of blends containing 5 % (v/v) RME (B5) or 20 % (v/v) RME (B20) in diesel oil involved combining a definite amount of fuels at the temperature of 25 ^{o}C and their homogenization by continuous stirring for 30 minutes.

Depressants: ash-free additives of the WAFI type (*Wax-Anti-Settling -Flow Improvers*): (i) additive R442 recommended for conventional diesel fuels and (ii) additive R477 recommended for rapeseed methyl ester (from INFINEUM UK Limited). The additives were prepared in the form of 1 % solutions in the examined fuels. Next, definite amounts of solutions of each additive were added to the particular fuel at 40 ^{o}C, and at that temperature the sample was stirred for 15 minutes. The set of samples with the addition of the depressants prepared in order to determine low-temperature parameters was characterized in table 2. The examinations were carried out after 24 h.

Laboratory equipment: cloud point (CP), pour point (PP), and cold filter plugging point (CFPP) were determined in the ISL-apparatus while simulated filter plugging point (SFPP) was determined with the use of the NORMALAB-device. The measurements were conducted in accordance with the standards applying to conventional diesel fuels [10-13].

Laboratory sedimentation test: The test was carried out in the low-temperature test chamber produced by Vötsch. Fuel samples were cooled down in closed cylinders for 8 hours to the temperature of -17 ^{o}C and kept at that temperature for 64 hours. Next, from each fuel, the upper layer (80 % v/v) was separated from the lower one (20 % v/v). The separated fuel samples were heated up to 45 ^{o}C and that temperature was maintained for 1 hour in order that the samples became homogeneous. Subsequently, the fuels were cooled down to the ambient temperature. After 24 hours of conditioning, the cloud point and the cold filter plugging point were determined in the samples taken from the upper and lower layers.

3. Results and discussion

Characteristics of the examined fuels, i.e. ON diesel fuel, rapeseed methyl ester (RME) and blends: 5 % (B5-fuel) and 20 % (B20-fuel) of RME in diesel fuel, is shown in Table 1. The RME-biodiesel contains 97,2 % of methyl esters and, in terms of quality, meets the requirements of the PN-EN 14214-23004 Standard. Exhaustive characteristics of the RME is found in another paper delivered at this conference [14].

Data given in Table 1 suggests that the examined fuels display quite good low-temperature properties. The diesel oil and the RME, as well as well as their blends (B5 and B20) have the same cold filter plugging point (CFPP) equal to -15 ^{o}C, and similar values of the simulated filter plugging point (SFPP) equal to: -14 ^{o}C. For the diesel oil, the cloud point (CP) is equal to -11 ^{o}C and the pour point (PP) is equal to -17 ^{o}C. For the RME-ester, these parameters are: CP = -3 ^{o}C and PP = -36 ^{o}C.

The presents of 5 % or 20 % of the RME-ester in diesel oil does not influence the cloud point (CP) of the B5 and B20 blends, but it does lower the pour point (PP) of the B5 blend to -23 ^{o}C and of the B20 blend to -26 ^{o}C. Relatively low value of the cloud point for the diesel oil and its blends with the RME-fuel should facilitate the process of depressing.

Table 1. Selected properties of ON diesel fuel, neat rapeseed biodiesel (RME), and ON diesel/RME blends: B5 - 5 % and B20 – 20 % of RME in ON diesel fuel

Fuel properties	Unit	ON	B5	B20	RME
Density (15 °C)	kg/m^3	845,0	844,2	885,0	882,5
Kinematic viscosity (40 °C)	mm^2/s	3,472	3,530	3,618	4,454
Flash point	°C	67	70	75	189
Distillation:					
Initial boiling point	°C	171,9	166,3	193,3	327,2
90 % recovered	°C	334,8	331,3	335,0	347,5
95 % recovered	°C	349,1	342,3	343,6	349,0
Final boiling point	°C	358,4	353,5	352,6	353,7
Total recovered	% (V/V)	98,3	96,6	96,8	96,7
to 250 °C recovered	% (V/V)	17,0	16,6	11,9	-
to 350 °C recovered	% (V/V)	95,2	96,7	96,9	353,7
Cloud point, CP	°C	-11	-11	-11	-3
Cold Filter Plugging Point, CFPP	°C	-15	-15	-15	-15
Simulated Filter Plugging Point, SFPP	°C	-14	-14	-14	-14
Pour Point, PP	°C	-17	-23	-26	-36

The data in Table 2 suggest that, for the diesel oil the lowering of CFPP from: -15 ^{o}C down to - 20 ^{o}C was achieved with the use of 300 mg/kg of the R442 depressant. An increase in the amount of the additive to 500 mg/kg reduces CFPP by 9 ^{o}C (to - 29 ^{o}C). The R442 depressant did not cause a change in the cloud point of the diesel oil but it did bring about a slight decrease in the simulated filter plugging point (only 3 ^{o}C) and a significant reduction of the pour point. A drastic drop of the pour point (by 17 ^{o}C) was recorded with the amount of the depressant being equal to 200 mg/kg while with 500 mg/kg the value of PP decreased to -46 ^{o}C. The RME-ester required a far greater amount of the R447 additive, i.e. as much as 1800 mg/ kg, in order to obtain the value of cold filter plugging point equal to - 20 ^{o}C. An increase in the amount of the R447 additive up to 2200 mg/kg did not have a significant effect on the value of the CFPP for the ester. The impact of the R422 additive on CFPP of the B5 blend is interesting. With the proportioning level of 100 - 200 mg/kg, the CFPP decreases by 3 - 4 °C (to -19 °C), and with 300 mg/kg, a drastic decrease in CFPP occurs (to -29 ^{o}C). A further increase in the amount of the R442 additive results in a decrease of CFPP by 2 ^{o}C per each 100 mg of the depressant.

The behaviour of the B20 blend, depressed by the R442 additive is different from that of the B5 fuel. Namely, under the influence of 200 mg of the R442 additive, CFPP of the B20 blend decreases by 9 ^{o}C (down to -24 ^{o}C). The drop of the simulated filter plugging point of the B20 fuel to -22 ^{o}C required the use of 300 mg/kg of the R442 additive.

The B5 and B20 blends were also depressed with the R477 additive (1800 mg/kg) and the blends of additives at the mass ratio R442 : R477 equal to 1: 6 and R442 : R447 equal to 1: 9.

The R477 additive reduced the cold filter plugging point of the B5 blend by 2 ^{o}C and caused no change of the simulated filter plugging point. In the case of the B20 blend, CFPP and SFPP decreased by 13 ^{o}C and 8 ^{o}C, respectively. It is worth noting that the pour point (PP) of the B5 fuel, depressed with a mixture of the R422 and R477 additives at the mass ratio of 1:6, is lower by 4 ^{o}C that the pour point obtained with the use of 300 mg/kg of the R442 depressant. In the case of B20 fuel, this difference is steel higher and is equal to 18 ^{o}C (depressant (R442 + R477) = 1:6) or 15 ^{o}C (depressant (R442 + Y477) = 1: 9).

To evaluate the effectiveness of depressants for a longer period of keeping the diesel fuel and its blends with the RME ester in extremely low temperatures, selected samples of the depressed fuels were subjected to the process of winterization at the temperature of -17 ^{o}C and lasted 64 hours – the extended sedimentation test [9].

Table 2. Low temperature properties of ON diesel fuel, rapeseed biodiesel (RME) and ON/RME blends treated with additives; CP- cloud point, CFPP – cold filter plugging point, SFPP – simulated filter plugging point and PP – pour point

Additive	Additive level (mg/kg)	CP	CFPP	SFPP	PP
		(°C)			
ON diesel fuel					
R442	None	-11	-15	-14	-17
	200	-11	-19	-15	-34
	300	-11	-20	-15	-34
	400	-11	-20	-16	-39
	500	-11	-29	-17	-46
B5 (5 % RME and 95 % ON diesel)					
R442	None	-11	-15	-15	-23
	100	-11	-18	-14	-29
	200	-11	-19	-15	-30
	300	-11	-29	-15	-35
	400	-11	-31	-23	-37
	500	-11	-34	-23	-41
R447	1800	-11	-17	-14	-30
(R442 + R447)	(300 + 1800)	-11	-30	-24	-39
B20 blend (20 % RME and 80 % ON diesel)					
R442	None	-10	-15	-14	-26
	100	-10	-16	-14	-30
	200	-10	-24	-14	-30
	300	-10	-26	-22	-30
	400	-10	-28	-21	-37
	500	-10	-29	-22	-42
R447	1800	-10	-28	-22	-32
(R442 + R447)	(200 + 1800)	-10	-29	-21	-45
	(300 + 1800)	-10	-30	-23	-48
Rapeseed oil methyl ester (RME)					
R447	None	-3	-15	-14	-36
	500	-3	-15	-14	-38
	1000	-3	-15	-14	-38
	1800	-3	-20	-15	-38
	2000	-3	-21	-15	-38
	2200	-3	-22	-15	-39

The concentrations of the depressants in fuels, for which the determined value of CFPP, was not higher than -20 ^{o}C , were the basis for selecting samples for the sedimentation test. With the purpose of comparison, fuels without depressants were also subjected to the sedimentation test. The results of examinations and of the samples after the winterization process are given in Table 3.

The fuel samples without depressants were clouded (the entire volume) after the winterization process, without the visible sediment in lower layers. The analysis of the data contained in Table 3 shows that fuels without depressants subjected to winterization at the temperature -17 ^{o}C retained the stability of their low-temperature properties. This is evidenced by the values of CP and CFPP for the fuel from the upper and lower layers, determined both prior to and after the test. CP for the lower layers of fuels was higher than those of the upper layers by 1 ^{o}C and it did not differ very much from the values determined for the fuels before winterization. The corresponding differences in the value of CFPP did not exceed 2 - 4 ^{o}C.

Table 3. Cloud points (CP) and cold filter plugging points (CFPP) for the ON diesel fuel and for B5 and B20 blends before the sedimentation test and for the samples taken from upper and lower layers after the test has been completed

Additive before/after test (-17 C, 64 h)	Additive level (mg/kg)	Sample	CP (°C)	CFPP (°C)
ON diesel fuel				
Before test	None	Whole	-11	-15
R442	300	Whole	-11	-20
After test	None	Upper layer	-12	-17
		Lower layer	-11	-13
R442	300	Upper layer	-11	-20
		Lower layer	-9	-17
B5 blend (5 % of RME and 95 % of ON diesel				
Before test	None	Whole	-11	-15
R44	300	Whole	-11	-28
(R442 + R447)	(300+1800)	Whole	-11	-30
After test	None	Upper layer	-12	-17
		Lower layer	-11	-13
R442	300 mg/kg	Upper layer	-11	-20
		Lower layer	-9	-17
(R442 + R447)	(300+1800)	Upper layer	-11	-31
		Lower layer	-10	-32
B20 blend (20 % of RME and 80 % of ON diesel				
Before test	None	Whole	-10	-15
R442	200	Whole	-10	-24
	300	Whole	-10	-26
(R442 + R447)	(200 + 1800)	Whole	-10	-29
	(300 + 1800)	Whole	-10	-30
After test	None	Upper layer	-10	-18
		Lower layer	-10	-17
R442	200	Upper layer	-13	-18
		Lower layer	-4	-12
	300	Upper layer	-11	-29
		Lower layer	-8	-22
(R442+R447)	(200 + 1800)	Upper layer	-10	-30
		Lower layer	-8	-30
	(300 + 1800)	Upper layer	-11	-27
		Lower layer	-10	-28

In the ON diesel fuel depressed with the R442 additive, after the sedimentation test, a white ring of paraffin sediment was recorded. That is why, for the sample from the lower layer the obtained value of CFPP was higher by 3 ^{o}C and the value of CP was higher by 2 ^{o}C that those for the upper layer.

During the sedimentation test, the behaviour of the B5 blend, depressed with the same additive, was radically different from that of the ON diesel fuel. With the same amount (300 mg/kg) of the R442 depressant, the B5 blend displayed a significant deterioration of the low-temperature properties after winterization. With the process of winterization being over, a white ring of sediment could be observed in the lower layer of the B5 blend and the fuel became clouded. CFPP grew both, in the lower layer (by 11 ^oC) and in the upper layer (by 9 ^oC), when compared to the value prior to the test. Interestingly enough, the cold filter plugging points for the upper and lower layers of the depressed blend B5 differ only by 2 ^oC from the CFPP values obtained for the relevant layers of the B5 fuel without the depressant. What is more, they do not differ from the values obtained for the ON diesel fuel depressed with the same amount of the additive R442. It can be concluded, therefore, that the depressant loses its effectiveness due to its being kept in low temperatures.

Data in Table 3 show that the B5 fuel, depressed with a mixture of the R442 and R447 additives, retains good stability of low temperature properties after winterization.

Worth noting is the behaviour of the B20 blend during the winterization process. The B20 fuel without additives retains its low temperature properties after winterization. After that process, in the B20 blend, depressed with the R442 additive (200 mg/kg) two clearly separate layers were well visible – the clouded upper layer and the lower layer which contained considerable amounts of white sediment. The differences in the values of CP and CFPP, determined for the samples taken from both layers of the fuels after the test, were equal to 9 ^oC and 6 ^oC, respectively. However, the difference between the cloud point of the B20 fuel, depressed with 200 mg of the R422 additive, determined before winterisation test, and CP after that process in the lower layer of the fuel, was equal to 6 ^oC. The corresponding difference in the CFPP values was equal to 12 ^oC.

An increase in the amount of the R442 additive to 300 mg/kg reduces the difference between CP of the lower and the upper layer of the B20 fuel to 3^oC but, at the same time it makes the difference between CFPP of these layers grow slightly (up to 7 ^oC). Moreover, the differences between CP and CFPP of the fuels determined for the lower layer before and after the test are reduced. As in the case of the B5 fuel, the use of a blend of the R442 and R447 additives in appropriate proportions improves the stability of the B20 fuel at low temperatures.

According to the BASF criterion [9], the effectiveness of the additive is satisfactory, if the difference in the value of CP for the fuel before the test, and that determined after the sedimentation test in the sample taken from the lower layer, does not exceed 2 - 3^oC, and the difference in the CFPP value is within the range of 4 - 5 ^oC.

The examination results showed that, the B5 blend depressed with 300 mg/kg of the R442 additive and the B20 blend depressed with 200 mg/kg of the same additive, were not featured by good stability of CP and CFPP in the winterization process. An increase in the amount of the R442 depressant or the use of a mixture of the R442 and R447 additives reduces the sedimentation susceptibility of waxes and improves the stability of fuels.

4. Conclusions

1. Fuels without depressants, winterized at –17 ^oC displayed high stability of low temperature properties, i.e. the cloud point (CP) and the cold filter plugging point (CFPP).
2. The R442 depressant fulfilled its role in the ON diesel fuel very well. The depressed fuel retains its stability after winterization. In the case of the B5 and B20 blends, the effectiveness of the depressant R442 depended on its concentration in the fuel. The amounts of the X422 depressant established at the preliminary stage of the examinations turned out to be ineffective during winterization. After the winterization test, a distinctive

sediment of paraffin occurred in the lower layers of fuels and the differences in the CFPP values, as well as in the CP values, significantly exceeded the limits of the BASF test.

3. The stability of the B5 and B20 blends in winter time can be improved by increasing the amount of the R442 depressant, or by using a mixture of the R442 and R447 additives in appropriate proportion.

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