COLD FLOW PROPERTIES OF FATTY ESTERS

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Abstract: This article is devoted to the study of cold flow properties of neat esters of branched chain alcohols with fatty acids and blends of these esters with fossil diesel fuel. According to determined CFPP values the influence of alcohol branching on the fuel filterability is negligible. Fossil fuel blending with fatty esters of branched alcohols up to 10 vol % does not substantially change the cold flow properties of fossil fuel. The low-temperature properties of fossil diesel and fatty acid methyl/ethyl ester (FAME/FAEE) blends with low ester content (up to 10 vol %), prepared mainly from oils/fats with higher share of saturated fatty acids namely palm oil, tallow and lard, were also measured. The obtained results show that studied esters do not change low-temperature properties of fossil fuel in the blends with the low esters content of 3–5 vol %, although their own CFPP is over the value permissible by the standard EN 14 214. However, current standard EN 590 specifies to meet all parameters of the standard EN 14 214 also for FAME assigned for blended fuels entirely. The proposal to repeal the CFPP limit for esters assigned for blending is fully justified, without any negative effects on fuel quality.

Keywords: methyl esters; ethyl esters; blended fuels; cold flow properties; cold filter plugging point; branched alcohols.

INTRODUCTION

Alkyl esters of higher fatty acids, especially methyl esters (FAME) and ethyl esters (FAEE) are at present considered as real alternative fuels for diesel engines. They are produced by transesterification of natural triacylglycerols—vegetable oils, but also animal fats—with methanol in the presence of alkali catalysts. The main advantage of this alternative fuel is that its properties are similar to those of fossil diesel fuel (DF). They are miscible with DF in any ratio, and they can be used in standard diesel engines without adjustment of the engine. The most pronounced advantages include favourable emission profile in comparison with standard fuel, the fact they originate from domestic renewable sources, they do not increase the amount of CO_2 in the atmosphere, and so on. There are, however, also disadvantages in comparison with standard fossil fuels, especially limited resources for their production, three to five times higher production price and less favourable low temperature properties.

The behaviour at low temperatures is one of the few research problems of FAME/FAEE. Unlike DF, the esters have relatively high cloud point CP, and the pour point PP as well. While the CP and PP of diesel fuel are around -15°C and -27°C respectively, the respective values for FAME are about 15–25°C higher. The use of alkyl esters in our geographical latitudes can be seriously limited by seasonal drop of external temperatures, especially in winter period. If the temperature drop is large enough to achieve the saturation temperature of any of the FAME/FAEE components, these precipitate in the liquid mixture in the form of microscopic crystals, invisible by the naked eye. At further decrease of temperature the submicrometer crystals grow further; as soon as they achieve the size of about 0.5 μm, they become visible. This temperature is then denoted as the cloud point. With further decrease of temperature the saturation temperatures of other components are achieved, the crystals gradually grow until they achieve the dimensions of about 0.5–1 mm, and they start to coalesce into sizeable agglomerates. Gradually the whole system ceases to be liquid, which is referred to as the pour point. Agglomeration of crystals occluded by the liquid phase hinders the flow of fuel through the fuel pipe and blocks the fuel filter.

Except of CP and PP, also other parameters are used in order to evaluate the low temperature properties of fuels, e.g., LTFT (Low Temperature Flow Test ASTM D4539) in the North America and CFPP (Cold Filter Plugging Point EN 116) in Europe. These values are more relevant than CP and PP regarding the applicability of fuels at lower temperatures. Some correlation between CP and CFPP was found (Dunn and Bagby, 1995). The filterability

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CFPP defines the lowest temperature at which at least 20 ml of fuel passes through a 45 μm mesh sieve filter with the diameter of 15 mm under defined conditions (time 1 min, vacuum 200 mm H_2O). CFPP is defined by melting points of individual components of blended FAME/FAEE. The melting points are influenced by lengths of acyl chains, by the number of double bonds, by isomeric state of unsaturated groups, and by the location of double bonds. The melting point increases with increasing length of the acyl, and decreases with the number of double bonds at the same number of carbon atoms. Conjugated double bonds increase the melting point. Cis-isomers have lower melting points than the trans-isomers. Generally, the double bond represents a defect in the structure of tightly ordered layers, and therefore decreases the melting point.

In order to overcome the problems with fatty esters at low temperatures, five solutions have been proposed:

(1) blending of FAME/FAEE with conventional DF;
(2) use of additives—flow improvers;
(3) preparation of fatty esters with branched chains;
(4) preparation of esters with bulky substituents in the chain;
(5) winterization.

Blending of FAME with fossil DF is at present the preferred and most widely used method of improvement of low temperature properties of FAME. Fossil fuel in blended fuels acts at low temperatures as a solvent of precipitated crystals, which is reflected in improved low temperature characteristics of the fuel. Published data (Dunn and Bagby, 1995) indicate that blended fuels do not exhibit significantly inferior low temperature properties in comparison with neat fossil fuel up to the content of FAME 20 vol%. The attention is paid especially to CP and CFPP. The usual blending rates FAME : DF in the North America are 20 : 80, and in Europe were 30 : 70, respectively. At the ratio of 30 : 70, a significant reduction of emission in the faultlessly operating engine was achieved, accompanied by slight increase of consumption (2–5%) in comparison with neat DF. The advantage is preparation of the mixture by simple blending of the components. According to (Purcell *et al.*, 1996) the properties of soybean oil-based FAME were as follows: cetane number (CN) 54.7, viscosity at 40°C 3.05 $mm^2 s^{-1}$, and CP − 2°C. The CN of DF was 43.2, the viscosity at 40°C was 2.37 $mm^2 s^{-1}$, and CP −17°C. The blend FAME : DF 30 : 70 had CN 49.1, viscosity at 40°C was 2.84 $mm^2 s^{-1}$. However, parameters of blended fuel can vary significantly according to the parameters of actual used DF which naturally are not constant. The output power of the blend was by about 4% lower than that of DF, while the output power of the neat ester was by about 9% lower. The emissions of CO and of polycondensed aromatic compounds (PAH) were significantly lower in comparison with DF, the NO_x emissions were comparable. According to our measurements of low temperature properties of blended fuels containing 30% FAME from rapeseed oil, and 70% of diesel fuel of the class F (Slovnaft Bratislava), the CP, and CFPP of neat FAME were both −8°C, while the CP and CFPP of fossil fuel were −11°C, and −10°C, respectively. The CP of the blended fuel was −9°C, CFPP −10°C (Cvengroš, 2000). The addition of biogenic component did not improve the low temperature properties, but it did not impair them either.

A range of additives has been synthesised, which decrease CP, but especially PP. The choice includes the viscosity modifying polymers, e.g., inter-polymers containing carboxyls, copolymers styrene-malein anhydride, polymetacrylates, polyacrylates, copolymers ethylene-vinylacetate, polyoxyalkene compounds, and so on. These additives influence especially PP, CP in smaller extent. However, from the point of view of cold flow properties of the fuel, especially CP is important. Some additives improving the low temperature flow properties (PP-depressants) developed for fossil fuel are effective also for FAME-based alternative fuels. They are applied at low concentrations between 0.05 and 0.2 wt%. The flow improvers influence the saturation temperature at low temperature at which the nucleation of the respective component takes place neither in fossil fuel nor in FAME, but they influence the size and morphology of crystals, and the rate of their growth. The CP value is therefore altered only slightly, but the PP decreases significantly. These additives crystallise together with that component of the fuel, which is first to nucleate. The molecules of additives contain function groups, which prevent the crystal growth and agglomeration. This leads to formation of a large number of small compact needle-like particles, which form a porous filtration cake on the filter, and do not hinder the passage of the liquid phase through the filter (Dunn *et al.*, 1996).

In the case of blended fuels with flow improvers our measurements yielded interesting results. The CP of fossil fuel was −11°C, CFPP −10°C; the addition of 0.05% of the flow improver DF-4598 from the company LUBRIZOL decreased the CFPP to −29°C while the CP value did not change. The addition of the flow improver to FAME produced from rapeseed oil and with the CP and CFPP values of −8°C, and −8°C, respectively, resulted in no change. The addition of 0.05% of the additive LUBRIZOL DF-4598 to the blend of 30% of FAME and 70 vol% DF with the CP, and CFPP values of −10°C, and −11°C, respectively resulted in decrease of the CP and CFPP values of −10°C and −127°C, respectively (Cvengroš, 2000). In another set of measurements (Bírová *et al.*, 2003) with flow improvers of the company LUBOCONS Stupava, SR, the CFPP value of studied FAME from used fritting oils was +1°C. The CFPP of diesel fuel was −5°C, and the CFPP of the blend of 31.8 vol% FAME, 67.5% DF, and 0.7% of LUBOFLOW 3101 was −16°C. The addition of 0.3% of LUBOFLOW 3111, the flow improver developed specially for the use with FAME from rapeseed oil, decreased the CFPP from the original value −10°C down to −21°C (Cvengroš *et al.*, 2004).

Another possibility of influencing the low temperature properties of fatty esters is the synthesis, which builds a bulky substituent into the chain, on a double bond of an acyl, for example. A hypothesis exists that the bulky substituent disrupts the harmony during the solid phase formation, and the orientation in one direction.

Similar effect is observed also with the use of secondary isopropyl- and isobutyl alcohols for the preparation of esters. According to Lee *et al.* (1995) the esters based on these alcohols and soybean oil-based FFA exhibit the onset temperatures from DSC (differential scanning calorimetry) measurements by 7–11°C and 12–14°C lower for isopropyl- and 2-butyl esters, respectively. Simultaneously, decreased values of CP and PP were recorded. However, due to economic reasons (higher price of isoalcohols), the possibilities in this respect are rather limited.

Winterization removes by filtration the solid fraction formed by cooling of esters, and the liquid fraction of predominantly