

USE OF BLEND OF FAME FROM ANIMAL FATS WITH BIOBUTANOL AS FUEL IN DIESEL ENGINES

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Abstract. Biodiesel and bioethanol are currently the only fuel replacer. Its high cost opposed to crude oil should be compensated by other advantages in production mainly from waste materials that are searched for. Therefore, we discuss the blend of biobutanol with biodiesel produced from animal fat and other waste biomass as a fuel for use in diesel engines from the point of view of density, kinematic viscosity, CFPP and oxidation stability improving the properties of FAME in this article. Also the blend of bioethanol and biobutanol can be produced from waste products. Biobutanol and bioethanol are compared. The properties of biodiesel from waste fats are influenced by this raw material, but they are available in large quantities. Therefore, the ability of biobutanol to improve the parameters of biodiesel is tested and described in the experimental part of the article. Animal by-products from processing of pork were subject to thermal pressure sterilization and further processed. The next step is then followed by a classical method for producing fatty acid methyl ester and adding biobutanol. The standard EN 590 for diesel and EN 14 214 for FAME were used for evaluation of the fuel parameters. Limited quantity of biobutanol in biofuel improves its parameters minimizing the negative effects of methyl esters from waste animal fats.

Keywords: biodiesel, animal fat, waste, biobutanol, bioethanol.

Introduction

Waste and non-edible fats are motivation for producers due to their low price. Otherwise, raw material exceeds 80 % of total costs of biofuel. The public opinion is usually not aware of this value of waste fats. Soy, palm or rice hulls oils are converted to biofuel by transesterification. The public opinion is sorry of abundant edible fats, which are processed to biofuels [1]. Rare and geographically dispersed non-food raw materials as non-standard coffee beans or used frying oil from restaurants are welcome by the public opinion. Due to favourable climatic conditions refined oilseed rape oil is used for biodiesel production in Europe predominantly. Biodiesel from animal fats (AFME – animal fat methyl ester) is only about 2 % of all biodiesel produced [2].

Animal fat is produced in cañilerias, mostly from processing of pork and beef by-products and partly from poultry and fish. Content of free fatty acids must be minimised before trans-esterification with alkaline catalyst begins. Otherwise undesirable soupy emulsions would increase the consumption of the catalyst and decrease separation of fractions due to reaction of free fatty acids with alkaline catalysers. Conversion of oils to methyl esters would decrease in this case. Acid catalyst applied to methanol esterification removes free fatty acids and produces methyl ester and water [3]. The traditional processing of methyl ester from waste animal fats is composed of following steps [4]:

1. acid catalysed esterification of free fatty acids;
2. alkaline catalysed transesterification of fats;
3. purification of raw methyl ester;
4. drying;
5. distillation of methyl ester.

Concentrated mineral acids as H_2SO_4 are used as catalysers [5]. Waste animal fats are in large volumes for transesterification without legal restrictions accessible in few cañilerias for market price, which allows to produce biofuel for competitive price with fossil fuel. Waste animal fat has two disadvantages opposed to food raw materials for biofuels. Waste animal fats have a high content of free fatty acids with high acid number and have high solidification point, which is eventually higher than other animal fats. Opposite to oils from plants with a high content of triglycerides of unsaturated fatty acids, especially oleic, linoleic and linoleic fatty acids the animal fats have a high content of saturated fatty acids, especially palmitic and stearic fatty acids.

Thermo-oxidative stability influences deterioration of methyl ester fuel due to oxidation. Oxygen, higher temperatures and the contact of fuel with metals speed up its physically-chemical changes called aging. Oxidation in storage causes fuel degradation slowly due to low temperatures (5-20 °C).

Fast oxidation is occurring in the engine due to high temperature (60-80 °C). But the EN 14214 (FAME) prohibits any difference between different methyl esters (Table 1).

Table 1
Comparison of selected parameters of rapeseed oil methyl ester (RME) and animal fats (AFME) with norm EN 14214 for fatty acid methyl ester (FAME)

Parameter	FAME (EN 14214)	RME	AFME
Content of methylesters (% wt.)	min 96.5	98	> 99.5
Content of monoglycerids (% wt.)	max 0.8	0.6	0.01
Content of water ($\text{mg} \cdot \text{kg}^{-1}$)	max 500	300	100
Total content of impurities ($\text{mg} \cdot \text{kg}^{-1}$)	max 24	10	4
Content of phosphorus ($\text{mg} \cdot \text{kg}^{-1}$)	max 4.0	< 0.5	< 0.5
Content of sulphur ($\text{mg} \cdot \text{kg}^{-1}$)	max 10	4	8
Content of Na/K ($\text{mg} \cdot \text{kg}^{-1}$)	max 5.0	< 0.5	< 0.5

Differences between the fuels due to the raw materials used have different impact on the engine [6]. Oxidation caused by high temperatures creates insoluble deposits, which can cause clogging with consequent failure of different parts of the fuel system [7].

Alcohols have more favourable emissions opposed to diesel or FAME because it is simple hydrocarbon. It is generally known that blends of alcohols with diesel or FAME have more favourable composition of emissions.

Materials and methods

Processing of pork fat was comprised of drying, separation under high pressure and temperature, which was concluded by cooling. Fat tissue was cut in parts with the size of 5 cm and warmed up to 135 °C during 20 minutes under pressure 3 $\text{kg} \cdot \text{cm}^{-2}$. The pressure was decreased gradually to dry all moisture from the sample. The dried sample was warmed to 80 °C and put under pressure of 300 $\text{kg} \cdot \text{cm}^{-2}$. Liquid fat appears after releasing the pressure, but it becomes solid again with 40-50 °C. Especially, a higher acidity number differentiates the fat obtained by this procedure from the properties of homogeneous fats.

Methanol : fat 10 : 1 % wt. with 2-3 % wt. of sulphur acid was blended under temperature of 90-95 °C for transesterification during 6-7 hours to reach 90 % of methyl esters. Esterification was performed by warming in balloons with feedback water cooler. The total composition of methyl esters was monitored, not part of fatty acids only. Gas chromatography (GC-FID) was used at chromatograph Varian 3300. Methanol, diethyl ether, hexan and sulphur acid from LachNer, s.r.o., company from the Czech Republic were used. Sigma standards for methyl esters of fatty acids were applied. The resulting methyl ester was enriched by n-butanol (butan-1-ol). The tested butanol was in p.a. (LachNer, s.r.o.) quality. Guaranteed Reagent is the ideal quality for laboratory purposes. Batch to batch reproducibility is specially controlled to guarantee consistent analytical results. The grade is equivalent to Analytical grade (A.R.) Reagent grade (R.G.) or p.a. nomenclature of other manufacturers. The parameters of the resulting blend were evaluated. Model blends of FAME fuel were tested by methods compliant to the standard EN 14214.

- Density at 15 °C by EN ISO 3675.
- Kinematic viscosity at 40 °C by EN ISO 3104.
- CFPP – Cold filter plugging point by EN 116.
- Cetane number by EN ISO 5165.
- Flash point by EN 2719.
- Oxidation stability of butanol by EN ISO 7536.

It is expected that traditional acidity catalysed esterification of free fatty acids in waste animal fat can run similarly to the conditions of the transesterification process. Excess of simple alcohol, mostly methanol, which was also used in our case, is a decisive factor of transesterification. Concentration of acid can be relatively low in this case. Esterification of free fatty acids occurs similarly. Only higher concentration of acid is needed as it also removes water from the environment. Esterification of free fatty acids as all organic reactions does not run under alkaline environment. Therefore, catalyzed

alkaline transesterification applies only to part of fatty acids in glycerides. The trend was calculated by statistical software for extrapolation of the measured values of the cetane number. The value of kinematic viscosity and flash point was assessed by three analyses. The final value was calculated as the average of the three measurements. Density, CFPP and oxidation stability were measured directly without any statistic processing according to the standard EN 590.

Oxidation stability of biobutanol was set in the sample of 50 ml under the pressure of oxygen 700 kPa according to the EN ISO 7536. This standard is valid for assessment of oxidation stability of gasoline according to the standard EN 228. The measurement was done under 100 °C in high pressure reactor, which was filled with oxygen.

Results and discussion

The higher the content of saturated fatty acids, the higher the cetane number of fuel. The higher the cetane number, the easier start of the engine, which also runs smoother, is more silent with lower consumption and emissions (NO_x and particles) [6].

The cetane number of butanol is very low compared to diesel. The EN ISO 5165 allows to measure up to 19.3 cetane units. Therefore, extrapolated data for 65 % vol. and 85 % vol. in Figure 1 are calculated as it was not possible to verify them experimentally. Therefore, butanol fuel blends for diesel engines need to increase the cetane number by dinitropropan, for example. The EN 14214 sets the minimal dosage on 51 units.

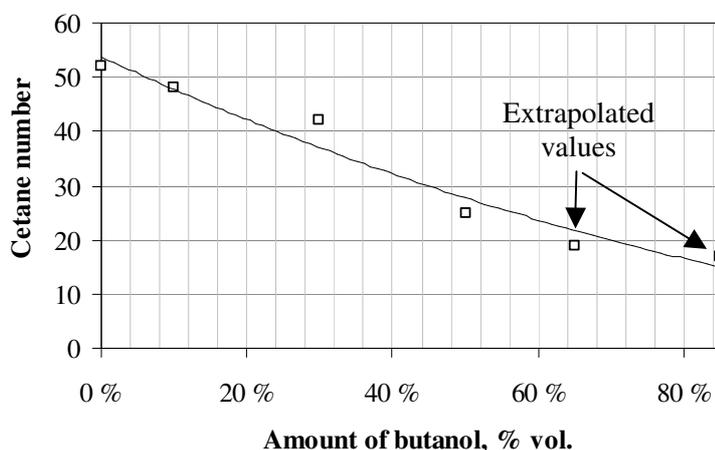


Fig. 1. Effect of n-butanol in FAME fuel blend on the cetane number

Decrease of the density corresponds with the differences of densities of diesel and butanol. In the case of kinematic viscosity a different course of decline has appeared (Figure 2). The lower density and viscosity of FAME from animal fats, the lower damage of the fuel system occurs, especially during low temperatures [2]. Minimal density according to the EN 14214 is 860-900 kg·m⁻³ with 15 °C and kinematic viscosity 3.5-5.00 mm²·s⁻¹ at 40 °C. Below the standard values cause damage of the moving parts of the fuel system. FAME has significantly better lubricity opposed to diesel. Values of lubricity of blends are outside of the range of measurement methods according to the EN ISO 12156-1 for diesel. Therefore, EN 14214 for all methods of measuring does not measure lubricity. This is true also for blends of diesel with n-butanol. Therefore, higher content of butanol than bioethanol can be used in diesel blends.

Excess of saturated fatty acids increases the filtration index. It is the lowest temperature in °C allowing to get predefined volume of fuel in predefined time through standardised filtration facility [4]. Therefore, use of methyl esters from animal fats (AFME) in winter is limited. This problem can be solved by use of additives, by blends AFME and diesel or biodiesel from selected vegetable oils. The proposed method of butanol blends positively improves the CFPP value as crystallisation of pure butanol is -88.6 and the tested samples with volume above 65 % vol. were behind the threshold of measurability. To maintain the stability of the mixture the cosolvents are used, especially alcohols and ethers. It is not needed to use cosolvents as no separation of alcohol and methyl ester layers in fuel has occurred during the tests under low temperatures [1]. The blend of AFME and biobutanol is stable

even at very low temperatures. No stabilizing additives are necessary to be used compared to bioethanol blends [1; 7].

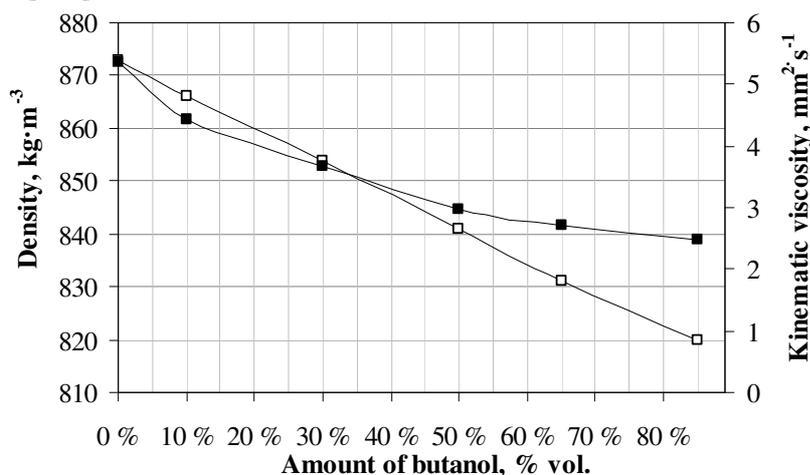


Fig. 2. Effect of n-butanol in FAME blend on density at 15 °C and kinematic viscosity at 40 °C:
 □ Density, ■ Kinematic viscosity

For oxidation stability the pressure in the reactor was measured until the beginning of the oxidation reaction occurred and consequently the decrease of oxygen pressure. The time until the beginning of the oxidation reaction and decrease of pressure is called the induction period (IP). Butanol with 99.83 % wt. concentration has IP over 25 hours. The method for measuring the oxidative stability of methyl ester with alcohols does not exist. Still, biobutanol can be admixed to increase the oxidative stability.

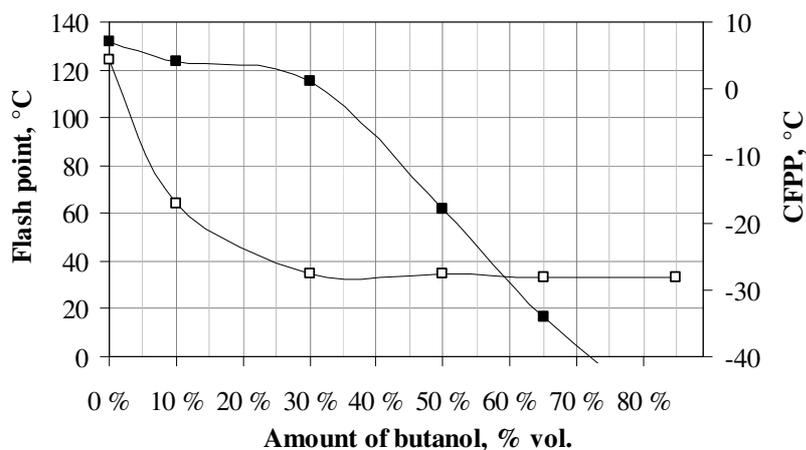


Fig. 3. Effect of n-butanol in FAME blend on flash point and cold filter plugging point:
 □ Flash point, ■ CFPP

The higher the content of biobutanol in the blend, the higher the cost of fuel. Nevertheless, the decreased emissions and risk of damage of the engine and especially its fuel system may contribute to compensation of increased costs of fuel. The costs of biobutanol should decrease due to its planned large scale production according to the rule of economy of scale. AFME, which is produced from waste fats significantly reduces the price of the resulting blends.

Conclusions

It was confirmed that animal fat from cafilerias is a useful material for transesterification. Longer stored fat from slaughter house waste contains a high amount of free fatty acids. This fact has confirmed both regular analysis from cafilerias and acid catalysed transesterification. The found differences of vegetable oils and animal fats, eventually methyl esters made out of them, are caused by different content of fatty acids in glycerids. Therefore, we may conclude that animal fats from cafilerias are a useful source for production of biofuels, but many problems must be solved during

transesterification. Waste animal fat cannot be used as food, high volumes are concentrated at few places. These are essential advantages for biofuel production.

The tested biobutanol in this article has improved properties of the produced methyl ester. The blend of methyl ester with biobutanol from waste fats or animal fats had improved oxidation stability. Performance of fuel under low temperatures, what is an especially dangerous problem of fuels from animal fats, was also improved. No separated layers of alcohol and methyl ester were observed during the tests under low temperatures. Such stable blend needs no cosolvents known from bioethanol fuel blends. Decrease of the density and viscosity by adding butanol is desirable according to the standard EN 14214 for FAME (AFME) or according to the EN 590 for diesel. Methyl esters from animal fats have much higher lubricity than diesel. Therefore, the moving parts of the fuel system of the engine are not under such danger if the biobutanol content in the blend is high. Still, it is necessary to increase the cetane number by dinitropane additive, for example. The flash-point of FAME is min 101 °C according to the standard 14214. It shows flammable IV hazard class. The higher the content of butanol, the higher flammable hazard up to class II. Even such decrease of the flash-point has negative impact on the performance of the engine. No standard of oxidation stability for blends of alcohol with methyl ester are approved yet. The EN 14214 would set minimum of 8.0 hours for oxidation stability. It is known that it is tricky to keep up with such limit with methyl esters. This problem would be solved by a blend with fuel or additive with high oxidation stability.

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