

USE OF BLEND OF HYDROTREATED VEGETABLE OIL WITH BIOBUTANOL FOR APPLICATIONS IN DIESEL ENGINES

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Abstract. Hydrogenation of vegetable oils (HVO) or animal fats is an alternative process to the esterification. HVOs have straight chain of paraffinic hydrocarbons that are free of aromatics, oxygen and sulphur having high cetane number. Hydrotreating of vegetable oils produces very high-quality biobased diesel fuels without compromising fuel logistics, engines, exhaust after treatment devices, or exhaust emissions. The article deals with the fuel properties of blends of HVO and biobutanol. Biobutanol is an alternative to bioethanol with more favourable combustion parameters in diesel engines. Biobutanol is produced from the same raw materials as bioethanol. The experimental part measures the influence of biobutanol on HVO parameters for engines and the nature because biobutanol and HVO can be produced from waste biomass as one and half generation biofuel. Model fuel blends were tested according to the standard EN 590. The article raises a number of advantages of HVO compared to the standard fatty acid methyl esters (FAME) and also the possibility of adding larger volume of biobutanol than it is possible with diesel or FAME. Development of renewable energy sources and applications of hydrotreated oils and biobutanol can also reduce dependence on import of fossil fuels besides increased employment in agriculture and in the region.

Keywords: hydrotreated vegetable oil, biobutanol, diesel engine, distillation curve, density.

Introduction

Biofuels are renewable opposed to fossil fuels. But development of the quality of biofuels is still in the introductory phase of the life cycle curve.

First Generation Biofuels

Biofuels produced of agricultural products compose the so called first generation. They are composed of bioethanol and fatty acid methyl ester (FAME), which is also called biodiesel. Bioethanol is produced either from starch or sugar. Biodiesel is produced of vegetable oils from soy and oilseed rape for market competitive price. Also animal fats or palm oils can be used, but more expensive processing is needed [1].

Second Generation Biofuels

Biofuels produced of lingo-cellulosic part of biomass are called BtL (biomass to liquid). Hydrogen is added during BtL thermo-chemical treatment of biomass. This technology of second generation biofuels is still under development. Especially, financing of investment, by-product and co-product commercialisation and ecological sustainability need to be clarified. Industrial processes could be solved until 2020 but the market share will still stay marginal [2].

One and Half Generation of Biofuels

Biomethan as purified biogas by technology into the quality of ground gas is an example of biofuel transiting between the first and second generation of biofuels, also hydrogenated biofuels, vegetable oils (HVO) and animal fats. The technology is available and progressing fast. The market is developing. HVO have approximately equal distillation distances as diesel. But, composition of its carbohydrates is different. Almost no aromatic or olefin carbohydrates, zero content of sulphur, excellent cetane number, very good properties under low temperatures, minimum particles and unburned carbohydrates in emissions are the principal advantages of HVO according to the CWA 15940 norm for this kind of fuels [3]. Therefore, HVO has no disadvantages of biodiesel. Still, a limited amount of this product is added to diesel recently. The CEN Workshop agreement (CWA 15940) distinguishes fuels on a level with over 70 and B level between 51-66 cetane number [4]. Alcohols have very low cetane number, which is compensated by HVO in blends.

The maximum volume of this biofuel to add to diesel is 30 % in regions with temperate climate. Composition of carbohydrate without aromatics causes worsened lubricity of fuel. HVO concentration above 30 % in diesel must be tested. Lubricity can be improved by additive or by blend with FAME [5]. This is the way how to produce premium fuel with high cetane number performing well during low temperatures. HVO licences are offered by Neste Oil (NexBTL), UOP, UOP/ENI, PetroBras,

Axens, ConocoPhillips, CLG-ARA and others. HVO are one of the options how to decrease carbon emissions on the EU 2020 target level by increasing the content of biofuel in diesel [6]. The EU also targets the bio refinery concept, which is applicable through the sector of biofuels and mineral fuels as well.

Sustainability and economics of HVO as part of diesel (Table 1) depend on:

- choice, accessibility and GHG saving parameters of vegetable oil;
- availability of the processing technology for waste vegetable oils and its double counting;
- 12.9 % of bio component saving 50 % or 10.8 % of bio-component saving 60 % of GHG should be reached in 2020;
- production units opened after 1.1.2017 should produce bio-components saving min. 60 % [7].

Table 1

Sustainability criteria of fuels saving GHG

Fuel	Fuel origin	Sustainability criterion %
Oilseed Rape Oil as Fuel	Oilseed rape oil as fuel	58
Fatty Acid Methyl Ester	Biodiesel from oilseed rape	45
	Biodiesel from palm oil	36
	Biodiesel from palm oil, process absorbing methane	62
	Biodiesel from soy	40
	Biodiesel from sunflower	58
	Biodiesel from waste UCO* and animal fats	88
Hydrotreated Vegetable Oil	HVO from oilseed rape	51
	HVO from sunflower	65
	HVO from palm oil	40
Synthetic Diesel	From wood waste by FT** technology	95
	From purposely grown wood by FT** technology	93

* used cooking oil

**Fisher-Tropsch synthesis

This paper searches the opportunities of HVO and biobutanol blends. Biobutanol (n-butanol, butan-1-ol) is an alternative to bioethanol, which is currently commercially produced and used as a component of motor gasoline or as E85 [8]. Biobutanol can replace bioethanol having far better combustion parameters for diesel engines. Especially, the calorific value (Table 2) and higher cetane number allow higher content of biobutanol than the blend of HVO with bioethanol. It is important that biobutanol is less hygroscopic opposed to bioethanol [9].

Table 2

Calorific values of selected fuels

Parameter	Diesel	FAME	HVO	Bioethanol	Biobutanol
Calorific value, MJ·kg ⁻¹	43	37	44	29	33
Calorific value, MJ·dm ⁻³	36	33	34	21	27
Oxygen content, % wt.	-	-	-	34.7	21.6

Materials and methods

Raw materials for biobutanol production are the same as for bioethanol:

1. Starchy (potatoes, corn, wheat, rice);
2. Sugary (sugar beet molasses, whey);
3. Lignocellulose (straw, wood).

Production of biobutanol from waste biomass as it is known from the second generation bioethanol would improve sustainability of biobutanol fuel blends.

HVO from Neste Oil was used for laboratory experiments. The tested n-butanol had p.a. LachNer 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.

Model fuel blends were tested according to the standard EN 590. The following experiments were performed and evaluated:

1. Density at 15 °C according to EN ISO 3675,
2. Kinematic viscosity at 40 °C according to EN ISO 3104,
3. Distillation examination according to EN 3405,
4. Flash point according to EN ISO 2719,
5. Cold Filter Plugging Point according to EN 116.

HVO and n-butanol blends for evaluation purposes were marked as follows:

1. BUT 10: blend of 5 % n-butanol and 95 % HVO,
2. BUT 30: blend of 30 % n-butanol and 70 % HVO,
3. BUT 50: blend of 50 % n-butanol and 50 % HVO,
4. BUT 60: blend of 60 % n-butanol and 40 % HVO.

The value of viscosity and the flash point were assessed by three analyses. Final value was calculated as the average of the three measurements. The three measurements were of separate samples for assessment of distillation curve, where the difference of temperature was below 1 °C. The value of the second sample was taken for further processing. Other values were measured directly without any statistical processing according to the standard EN 590.

Results and discussion

Assessment of the distillation curve, leading to the boiling point, is necessary for evaluation of the fuel quality. Biobutanol significantly influences the introductory part of the distillation curve (Fig. 1).

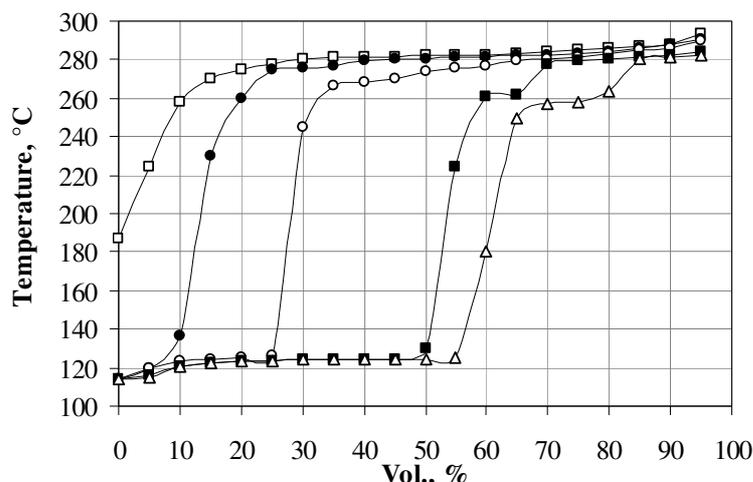


Fig. 1. Distillation curve of HVO and blends of HVO with n-butanol:
 □ HVO, ● BUT 10, ○ BUT 30, ■ BUT 50, △ BUT 60

The shape of the distillation curve allows us to guess that the blends of n-butanol and HVO let emerge azeotropic mixtures because the interval of the boiling points of pure biobutanol is 116 – 118 °C. The curve has a typical HVO shape after distillation exceeds the boiling point of n-butanol.

Fig. 2 shows changes of distillation curves of different fuel blends. The distillation curve of pure HVO is shown as horizontal axis x. Fuel blends are light enough to allow evaporation and simultaneously contain heavier parts needed for cooling down the walls of the combustion chamber.

N-Butanol is increasing the density of HVO (Fig.3). Increase of the density corresponds with differences of densities of diesel and n-butanol. In the case of kinematic viscosity at 40 °C a different course of decline has appeared. It is assumed that the more pronounced curvature of viscosity is caused by hydrocarbon chain.

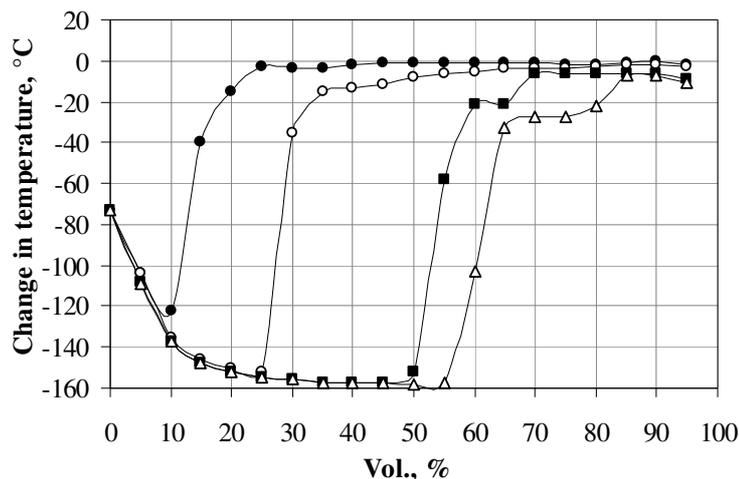


Fig. 2. Influence of n-butanol to HVO distillation curve:
 ● BUT 10, ○ BUT 30, ■ BUT 50, △ BUT 60

It is known that bioethanol significantly influences the density and kinematic viscosity of fuels for diesel engines. Therefore, low density and kinematic viscosity may damage the moving parts of the fuel system [8]. Opposed to bioethanol, biobutanol does not increase significantly the density and kinematic viscosity of HVO. Kinematic viscosity in the tested interval from 0 to 60 % of n-butanol complies still with the standard EN 590 for diesel fuel. Blend of HVO and biobutanol is stable under low temperatures. Separation of layers does not occur as is common for blends with bioethanol [7].

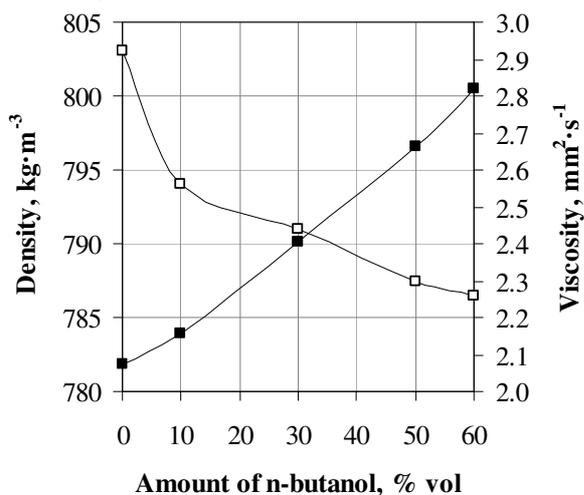


Fig. 3. Effect of n-butanol in HVO blend on density at 15 °C and kinematic viscosity at 40 °C:
 ■ Density, □ Kinematic viscosity

Also the flashpoint significantly changes with increased biobutanol content in HVO. Figure 4 shows that from about 5 % of biobutanol in HVO is decreasing combustibility to the second class level. This value is not changing from 20 % vol. to 100 % vol. of n-butanol. But the value of the flash point has no impact on the performance of the vehicle.

Pure HVO performs well under low temperatures. The CFPP value of the tested sample is -28 °C. The CFPP value is decreasing if the n-butanol content is increased (Fig.4). The maximal measurable value of CFPP occurs if n-butanol reaches 10 % vol. No separation of n-butanol and HVO fuel blend phases occurs under low temperatures. Therefore, no stabilisers are needed.

Bioethanol is currently commercially produced and used as a component of motor gasoline or as E85 [8]. Further, we have shown that biobutanol can replace bioethanol. Also, the calorific value (Table 2) and higher cetane number allow higher content of n-butanol than the blend of HVO with bioethanol. It is important that n-butanol is less hygroscopic opposed to bioethanol and the blend of HVO and biobutanol is stable under low temperatures [9].

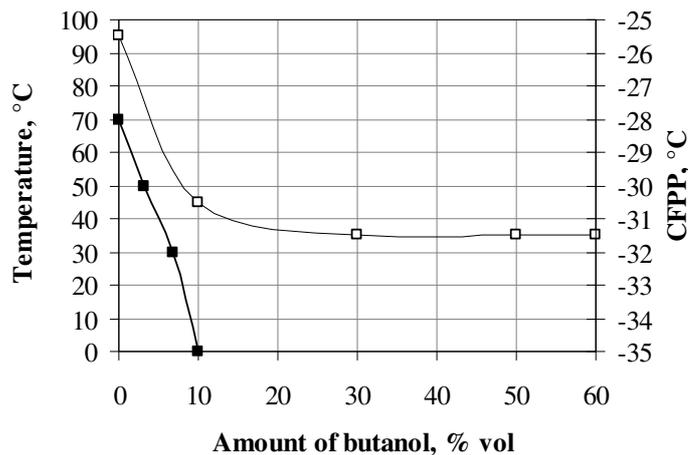


Fig. 4. Effect of n-butanol in HVO blend on flash point

Conclusions

HVO has excellent combustion properties, especially high cetane number, excellent properties during low temperatures, low emissions of HC, CO and particles. Already 5 % of biobutanol in HVO is decreasing combustibility to the second class level. Fuel blends allow evaporation and due to the content of heavier parts cool down the walls of the combustion chamber. Both effects are decreasing emissions. Therefore, we may recommend HVO to be part of premium fuels. Its higher price can be compensated by CO₂ emissions savings. These properties of HVO further improve if waste is used as raw material for fuel production. Consumption tax is decreased if 100 % HVO is used.

HVO and biobutanol blend is an example of 1.5 generation of biofuels, eventually the second generation biofuels if waste is used as raw material. Content of HVO with alcohol in blends may be much higher than blends with diesel allow. High cetane number of HVO can compensate low cetane number of biobutanol into a certain level.

Opposed to bioethanol, biobutanol does not increase significantly the density and kinematic viscosity of HVO. Kinematic viscosity in the tested interval from 0 to 60 % of n-butanol complies still with the standard EN 590 for diesel fuel. Blend of HVO and biobutanol is stable under low temperatures. Separation of layers does not occur as is common for blends with bioethanol. CFPP value of pure HVO was -28 °C. If n-butanol is added, further decline of CFPP occurs due to the low melting point of this alcohol at -89 °C.

The higher content of biobutanol in HVO blend, the lower the performance and higher consumption because biobutanol has lower calorific value than pure HVO. We consider the tested blends with biobutanol as very perspective biofuels due to the advantageous composition of emissions of diesel engines.

References

1. Anastopoulos G., Zannikou Y., Stournas S., Kalligeros S. Transesterification of Vegetable Oils with Ethanol and Characterization of the Key Fuel Properties of Ethyl Esters. *Energies*, No. 2, 2009, pp. 362-376.
2. Mosier N., Wyman C., Dale B., Elander R., Lee Y.Y., Holtzapple M., Ladisch, M. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology*, 2005, vol. 96, No. 6, pp. 673-686.
3. Šimáček P., Kubička D., Šebor G., Pospíšil M. Fuel properties of hydroprocessed rapeseed oil. *Fuel*, No. 89, 2010, pp. 611-615.
4. Kim D., Kim S., Oh S., No S.-Y. Engine performance and emission characteristics of hydrotreated vegetable oil in light duty diesel engines. *Fuel*, No. 125, 2014, pp. 36-43.
5. Arvidsson R., Persson S., Fröling M., Svanström M. Life cycle assessment of hydrotreated vegetable oil from rape, oil palm and Jatropha. *Journal of Cleaner Production*, No. 19, 2011, pp. 129-137.

6. Pinto F., Martins S., Gonçalves M., Costa P., Gulyurtlu I., Alves A., Mendes B. Hydrogenation of rapeseed oil for production of liquid biochemicals. *Applied Energy*, No. 102, 2013, pp. 272-282.
7. Hromádko J., Hromádko J., Miler P., Hönig V., Štěrbá P. The lifecycle assessment of fossil fuels and bioethanol. *Listy cukrovarnické a řepařské*, No. 125, 2009, pp. 320-323 (in Czech).
8. Mužíkova Z., Pospíšil M., Šebor G. The use of bioethanol as a fuel in the form of E85 fuel. *Chemické listy*, 2010, vol 104, No. 7, pp. 678-683 (in Czech).
9. Hönig V., Kotek M., Mařík J. Use of butanol as a fuel for internal combustion engines. *Agronomy Research*, 2014, vol. 12, No. 2, pp. 333-340.