Article

Hydrotreated Vegetable Oil as a Fuel from Waste Materials

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Abstract: Biofuels have become an integral part of everyday life in modern society. Bioethanol and fatty acid methyl esters are a common part of both the production of gasoline and diesel fuels. Also, pressure on replacing fossil fuels with bio-components is constantly growing. Waste vegetable fats can be replacing biodiesel. HVO seems to be a better alternative. This fuel has a higher oxidation stability for storage purposes, a lower temperature of loss of filterability for the winter time, a lower boiling point for cold starts and other. Viscosity, density, cold filter plugging point of fuel blend, and flash point were measured to confirm that a fuel from HVO is so close to a fuel standard that it is possible to use it in engines without modification. The objective of this article is to show the properties of different fuels with and without HVO admixtures and to prove the suitability of using HVO compared to FAME. HVO can also be prepared from waste materials and no major modifications of existing refinery facilities are required. No technology in either investment or engine adaptation of fuel oils is needed in fuel processing.

Keywords: biofuel; biodiesel; hydrotreating; hydrocarbon; waste

1. Introduction

A long-term European strategy is an effort for a so-called "recycling society". With the growing volume of waste is growing industries dealing with waste management and recycling. Despite noticeable progress is still great potential in previously underutilized sources of waste. The main obstacles are the legislative problems and the small application of approved rules, the differentiation of regulations in different countries, and generally the low awareness of the professional and lay public about new possibilities and prospects. The current EU waste policy is based on the concept of the so-called waste hierarchy, which states that it is primarily necessary to prevent the generation of waste itself and, if this is not possible, it must be recycled or otherwise exploited, under condition of minimal dump disposal. As a waste could be considered everything which can be somehow reused even materials like grey water, wood chips, old clothing, kitchen scraps or diseased fruit and vegetables [1–6].

Legislative requirements are higher for double-counting materials to meet the 10% share of biofuels. This double counting applies to biofuels made from wastes and residues, as well as to biofuels made from raw materials that have been grown on so-called degraded areas and is thus another supportive step to meet the sustainability criteria [7].

Sustainability criteria in the EU are determined by Directive 2009/28/ES. Among these, we include reducing GHG (Green House Gas) emissions, optimizing land use and carbon stocks, biodiversity, environmental requirements for crop production, etc. To achieve 10% CO_2 savings between 2010 and 2020, a minimum biofuel share of 15% must be reached.

Hydrotreated vegetable oils are one of the possibilities to use the increased biofuel content in diesel fuel. This would allow another option to meet the CO_2 reduction target for the year 2020. At the same time, it will be necessary to include these advanced biofuels into legislation so as to establish clear rules for their use. In addition to these changes, changes in the composition of diesel fuel can also be expected in the future. This concerns above all the requirements for increasing the cetane number and cetane index, adjusting the course of the distillation curve (reduction of temperature by 95% of the pre-distilled volume), further reducing the content of polycyclic aromatic hydrocarbon and introducing a limit for aromatics similar to automotive gasoline and tightening requirements for lubrication and mechanical impurities for fuels for diesel engines. Introducing changes that have a positive effect on reducing harmful emissions and particulate matter pollution will entail an increase in production costs and therefore the speed of their deployment will depend on the economic situation and legislative changes adopted within the EU [8–10]. Biofuels are renewable compared to fossil fuels. As far as their technological development is concerned, the issue of biofuels is only at an early stage. The most commonly declared "first generation" of biofuels is bioethanol produced from starch and sugar, biodiesel produced from vegetable oils (rape, soy, etc.) and animal fats without chemical treatment or produced due to the transesterification process to fatty acid methyl esters (FAME – rapeseed oil) [11]. These are sophisticated technologies and, above all, commercially available [12–14].

Among the "second generation" of biofuels belongs ethanol made from lignocellulosic biomass. In addition, BtL (Biomass to Liquid) fuel produced by thermal-chemical processing of biomass to liquid synthetic fuel, as well as hydrogen produced from renewable energy sources. The production processes used to acquire "second generation" biofuels are in the state of research and development - the pilot phase. It is an extremely complex and highly investment-intensive technology. It is not yet possible to make a final assessment of the related processes in terms of energy and environmental balance and production economics. Even if the aforementioned processes were carried out on an industrial scale, it is not possible to anticipate any significant quantities of such fuel in the market by the year 2020 [15–17].

The transition stage consists of biomethane, which is biogas purified by the respective processing technology for the quality of natural gas and methane, further hydrotreated vegetable oils and animal fats as motor fuel. They are referred to as "one and a half generation" biofuels. Technological facilities for their production are commercially available and are rapidly being perfected. Fig. 1 shows a simplified difference between the production of hydrotreated oils and fatty acid methyl esters (FAME).

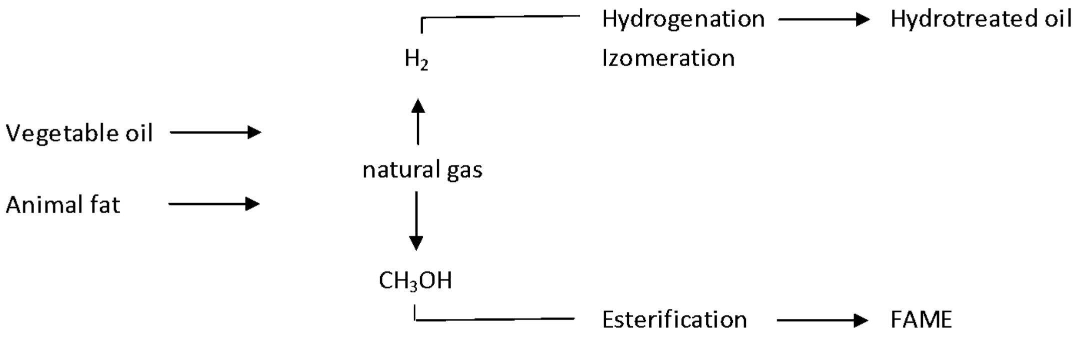

Figure 1. Simplified scheme for the production of hydrotreated oils and fatty acid methyl esters.

The production of hydrotreated vegetable oils is based on introducing hydrogen molecules into the raw fat or oil molecule. This process is associated with the reduction of the carbon compound. When hydrogen is used to react with triglycerides, different types of reactions can occur, and different resultant products are combined.

The best known is the hydrotreatment of fats for the purpose of stiffening. This is an addition reaction when the degree of unsaturation of the fatty acid chain is reduced, so the double bond changes to a simple one. This brings fat to the change in its state, when the liquid fat changes to solid.

Edible hydrotreated oils have been produced by the fat industry for over 100 years. Enrichment with hydrogen – the hydrotreatment – takes place in the reactor with the catalyst. The reactor is similar to that used to produce biogas from slurry. The reaction takes place in the presence of Ni catalyst [16].

The original oil obtained by hydrotreatment gets higher oxidation stability, which is desirable for frying fats. Partial fat stiffening is used for raw margarine production. For fuel purposes, such a final product is not suitable. In hydrotreated fuels, therefore, partial hydrotreatment is mostly omitted and overall hydrotreatment is ongoing, often with free fatty acids (Figure 2).

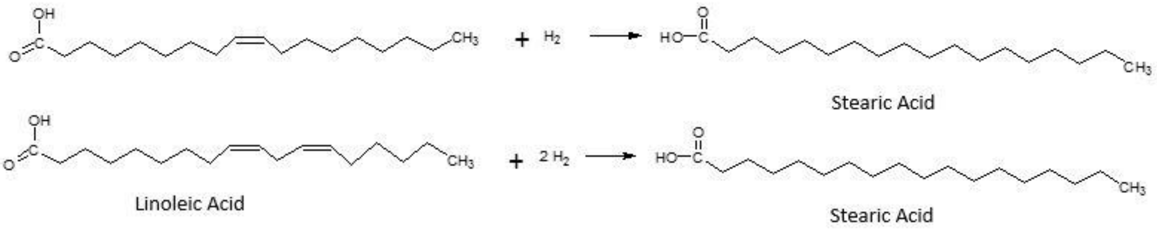

Figure 2. Hydrotreatment of fatty acids.

Another method of converting triglycerides by hydrogen is the cleavage of the ester to hydrocarbon and glycerol-derived propane and free fatty acids (Figure 3). These fatty acids (n is the number of carbons) are either:

1. by hydrodeoxygenation reduced to hydrocarbons (n) and water (Figure 4),
2. subject to decarboxylation, i.e. carbon dioxide CO_2 is cleaved to give n-1 hydrocarbons (Figure 5),
3. or decarboxylation is carried out by removing the carbon monoxide (CO) and water molecule to produce a n-1 hydrocarbon (Figure 6).

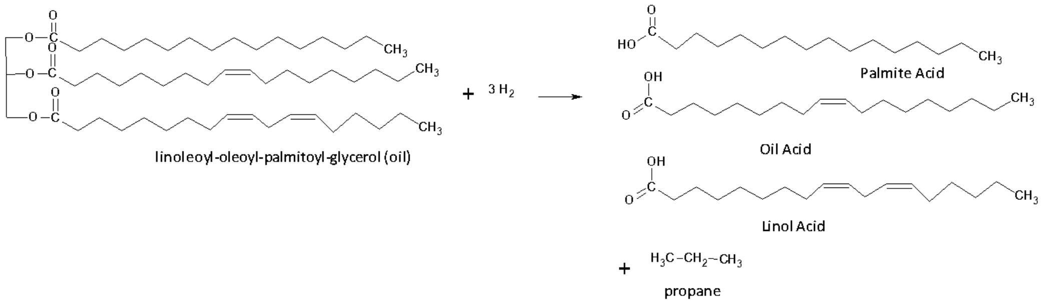

Figure 3. The release of fatty acids from fat.

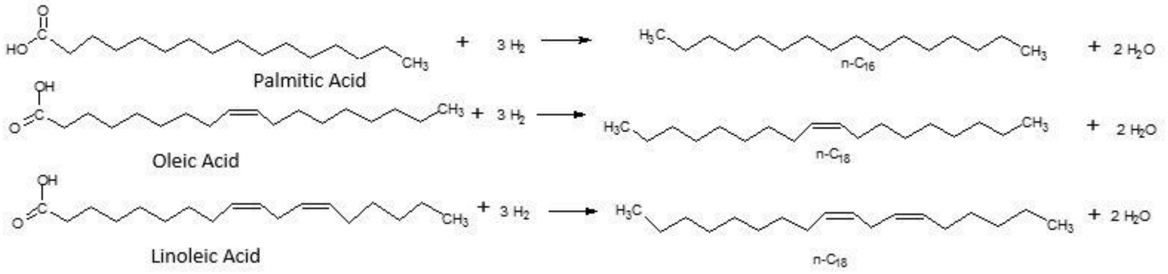

Figure 4. Hydrodeoxygenation.

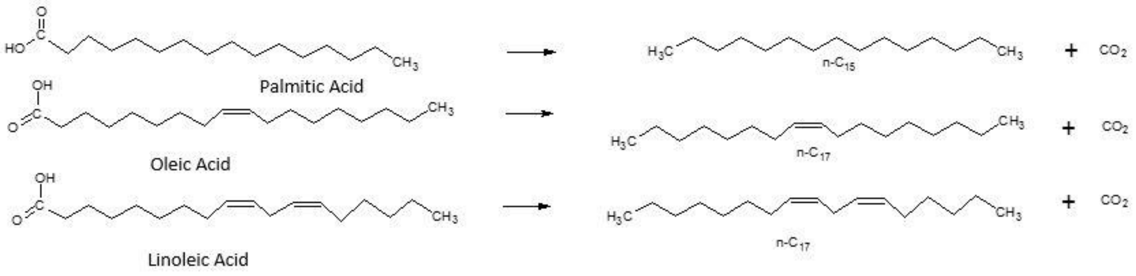

Figure 5. Decarboxylation.

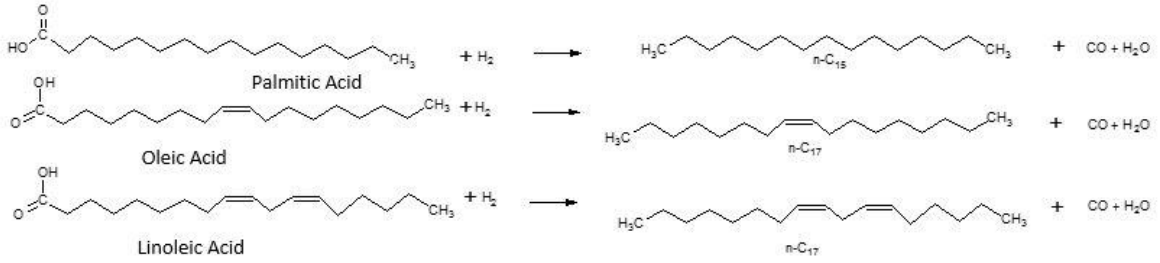

Figure 6. Decarboxylation.

These processes are used frequently and are the basis for the production of hydrotreated oils. The resulting products are almost identical to hydrocarbons in petrol and diesel oil .

The production of renewable fuels from triglycerides has been practiced in refineries 60 years ago. For the reaction of hydrogen with vegetable oils and vacuum gas oil, the same catalysts and the same types of reactors and equipment used for oil processing were used [18,19].

Vacuum gas oil is a term used to describe semi feedstock to the refinery or it is called the incomplete fuel to produce fuel compositions.

In recent decades, efforts have been made to find the best catalysts, to optimize hydrogen reaction processes and to find suitable sources of vegetable oil or fats. Indeed, the latter lack of resource availability and high hydrogen consumption have increased production costs. However, shortcomings have been managed commercially [20].

Reactions with hydrogen are important types of catalytic processes used in fuel refining and production refineries. The use of hydrogen permits the production of various products using petroleum fractions (gas oil) and vegetable oils, their preparation and conversion to obtain a motor fuel and heating oil. The use of hydrogen permits the cleavage and hence reduction of the molecular weight of carbonaceous compounds and their isomerization. These products correspond to their properties of petrol and diesel (Figure 7).

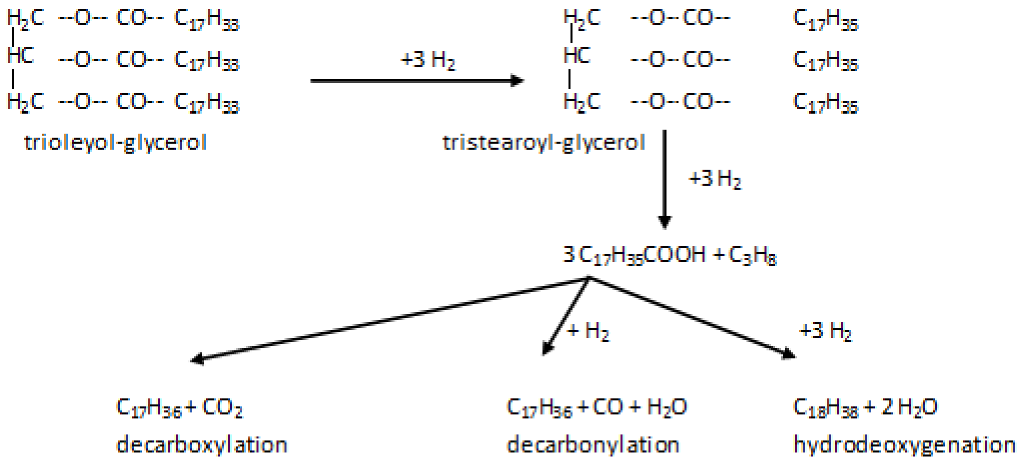

Figure 7. The production of fuel oil from fat by means of hydrogen.

The choice of a suitable catalyst depends on the type of reaction. The catalyst used, along with the reaction temperature, significantly influences the course of the reaction, the type of products and their yield. Catalysts of various types and mechanisms of action, such as metal / acid type or aluminosilicate-based catalysts, namely aluminosilicate phosphates (SAPO) and crystalline zeolites, are used herein. Furthermore, catalysts based on noble metals (e.g., Pt and Pd) or active metals, for example NiMo or CoMo in the sulfide state with the aid of gamma Al_2O_3 [18,19,21,22]. The latter catalyst is most commonly used in refineries because it works well on the entry of hydrogen into the fat molecule due to mild acidity and converts (reduces) the triglycerides to hydrocarbons [23]. As another acid catalyst, the HZSM-5 zeolite was proven. The effect of the catalyst is due to the presence of a high amount of the acid phase of the catalyst which increases the reaction of hydrogen.

Fat processing for hydrotreated oils, i.e. pure hydrocarbons, brings a number of benefits. Addition of hydrogen to double bonds and removal of oxygen from the carboxyl group using metal catalysts results in vegetable oils for the production of hydrocarbons of the C15-C18 length which form the basis of petroleum. Hydrotreated oils are therefore similar to petroleum fuels [24].

In the production of lighter hydrocarbons having the same boiling point as those for jet engines or gasoline, a catalyst with a stronger acidity (e.g., zeolites) is used. The acid part of the catalyst also increases the degree of isomerization of molecules and therefore improves the low temperature properties of the fuel and increase its cetane number.

Long chain triglycerides require higher hydrogen consumption to meet fuel standards. Reaction conditions and catalyst are also important in the processing of vegetable oils in two possible ways: a) separate processing of triglycerides and b) adding triglycerides of vegetable oils to vacuum gas oil in refineries (Figure 8).

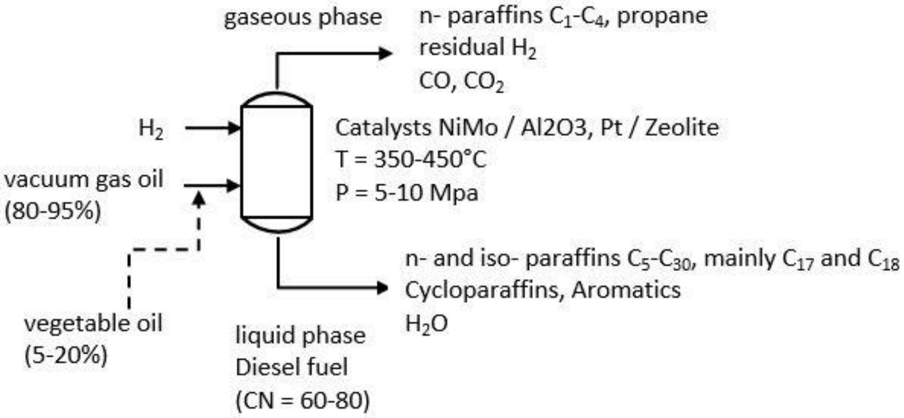

Figure 8. Hydrotreatment of vacuum gas oil and vegetable oil.

For the production of various types of renewable fuels (C_5-C_{10}), kerosene (C_{11}-C_{13}), diesel fuel (C_{14}-C_{20}) and liquid petroleum gas (LPG) the type of catalyst is very important. Catalysts with less aggressive values produce more stable biofuels, such as diesel. The yield and quality of biofuels is affected by temperature of the reaction. Biodiesel quality parameters are losing with rising temperatures, while volatile biofuels are the opposite due to thermal decomposition of hydrocarbons. For high volatile biofuels, therefore, high temperature and strongly acidic catalyst are important. The middle distillation fraction requires lower temperature and moderate acidity of the catalyst [25,26].

Two steps are used to produce bio petrol, which happen separated in two reactors. In the first one, oxygen is removed as water, the resulting heavier (C_{17}-C_{18}) fractions are transferred to the second reactor, where the fractions are cleaved by hydrocracking to lighter C_5-C_{10} hydrocarbons.

Hydroisomerization is also carried out in the first reactor in the presence of the catalyst. The output are three differently flammable liquid fuels (Figure 9).

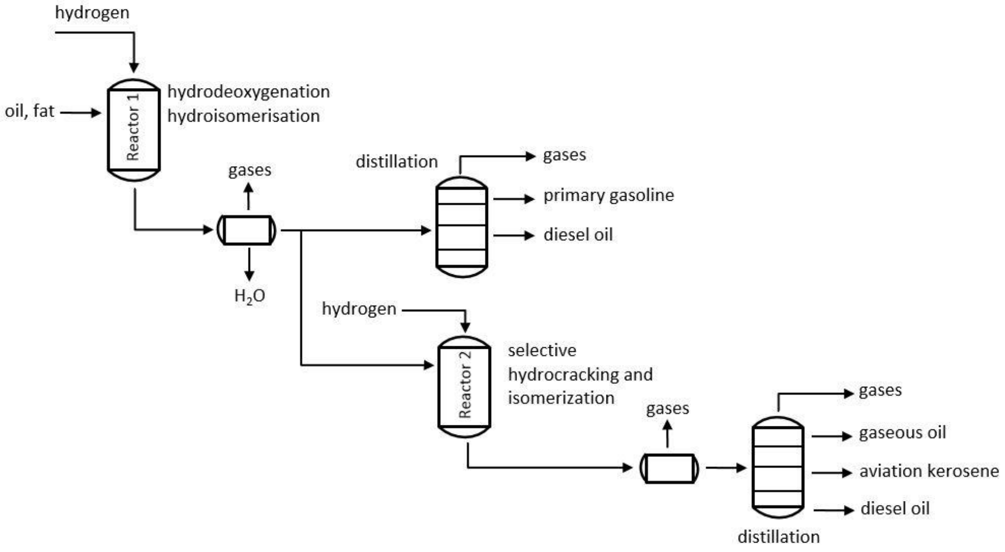

Figure 9. The process of enriching fat with hydrogen in two steps

Hydroisomerisation is a key process for obtaining branched hydrocarbons. This is a radical reaction where branching of hydrocarbon molecules is achieved by the use of form-selective catalysts such as zeolites or other acid catalysts. N-paraffins having a boiling point corresponding to diesel fuel generally have a higher cetane number than their branched isomers. In contrast, isoparaffins have lower solidification points than n-paraffins. There is, therefore, a compromise on the quality of the paraffin-rich fuel, whether the fuel has either good combustion properties or good low-temperature properties. The result of hydroisomerization is therefore a fuel with a lower solidification point and a lower cetane number. The relationship of these two properties is illustrated in Figure 10 [22].

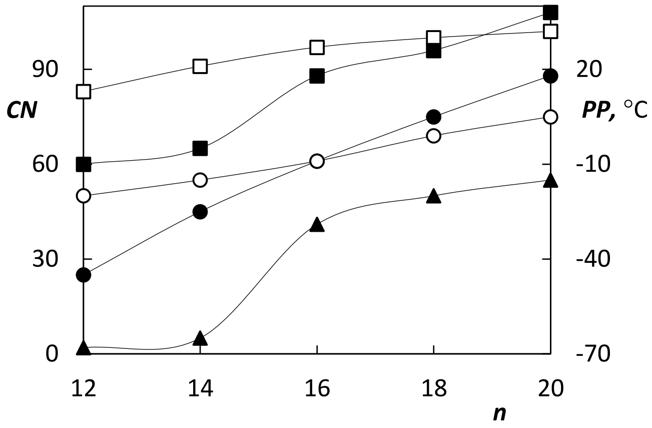

Figure 10. Cetane number and paraffin solidification points depending on carbon number

On the x-axis is number of carbons in the string (n), on the main y-axis is the value of the cetane number (CN), on the minor y-axis is the pour point (PP) in °C; ■ n-paraffins; ○ isoparaffins; ● 2-methylisoparaffin; ▲ 5-methylisoparaffin.

Hydrotreated oils are characterized by very good low temperature properties. The cloud point also occurs below -40 °C. Therefore, these fuels are suitable for the preparation of premium fuel with a high cetane number and excellent low temperature properties. The Cold Filter Plugging Point (CFPP) virtually corresponds to the cloud point value, which is why the value of the cloud point is significant in the case of hydrotreated oils.

The production process of hydrotreated oils can also produce fuel with appropriate low temperature properties also from palm oils and other oils including animal fats whose methyl esters have a very poor applicability at lower temperatures [27]. This results in the use of hydrotreated oils throughout the year, without risking loss of serviceability or fuel logistics problems. Hydrotreated vegetable oils thus find their potential usability as aviation fuels. The production process of hydrotreated oils can also produce fuel with appropriate low temperature properties also from palm oils and other oils including animal fats whose methyl esters have a very poor applicability at lower temperatures. This results in the use of hydrotreated oils throughout the year, without risking loss of serviceability or fuel logistics problems. Hydrotreated vegetable oils thus find their potential usability as aviation fuels .

Hydrotreated vegetable oils meet EN 15940: 2014 for paraffinic diesel fuels from synthesis or hydrotreatment, formerly TS 15940: 2012 for paraffinic diesel fuels (specifications with no formal standard status see Table 1). This specification also applies to Fischer-Tropsch synthesis products: GTL, BTL and CTL. Specification TS 15940: 2012 was preceded by CWA 15940: 2009 CEN Workshop Agreement, which was created in cooperation between car and fuel manufacturers. HVO is usually supplied without FAME, however, it is allowed to add up to 7% (V/V) according to EN 15940 specification, which the earlier CWA 15940 did not allow. In many cases, "XTL / HVO" is used to designate paraffinic fuels. Just XTL is the term used for GTL, BTL and CTL Fischer-Tropsch synthesis. EN 14214 for FAME for HVO does not apply, as HVO is composed only of hydrocarbons. However, HVO meets the requirements of EN 590 for diesel fuel, except for the density below the lower limit of this standard. This also applies to the US ASTM D975 and the CGSB-3.517 in Canada.

Table 1 shows differences in paraffin oil parameters from synthesis or hydrothermal treatment according to EN 15940 compared to diesel fuel according to EN 590.

Table 1. Requirements to EN 15940: 2014 "Diesel fuel - Paraffin oil from synthesis or hydrothermal treatment - Technical requirements and test methods [28].

Parameter	EN 15940	EN 590:2013

Cetane number	≥ 70.0	≥ 51.0
Density at 15 °C (kg.m^{-3})	765–800	820–845
Viscosity at 40 °C (mm^2.s^{-1})	2.00–4.50	2.00–4.50
Hydrocarbons (% weight)		
polyaromatic	-	≤ 8
aromatic	≤ 1.0	-
olefin	≤ 0.1	-
Sulfur content (mg.kg^{-1})	≤ 5.0	≤ 10.0
Flash point (°C)	> 55	> 55
Lubricity HFRR at 60 °C (μm)	≤ 460*	≤ 460
95% by volume distils at (°C)	< 360	< 360
CFPP (°C)	≥ -34	≥ -34
Ash content (% weight)	≤ 0.01	≤ 0.01
Total impurity content (mg.kg^{-1})	≤ 24	≤ 24

* Including lubricating additives for use in vehicles approved for driving on the fuel according to the standard.

2. Results

The density of the hydrotreated vegetable oil (about 780 kg.m^{-3}) is lower than the density of fossil diesel (800 to 845 kg.m^{-3}) because of their paraffinic character, and also a lower temperature distillation end. The density of the fuel has traditionally been an important factor in terms of volume of fuel consumption and maximum performance, and we can say that the reduction in volume calorific value is a function of just density. At a lower calorific value, the engine gets less energy and needs more fuel to ensure the same power output at a partial load.

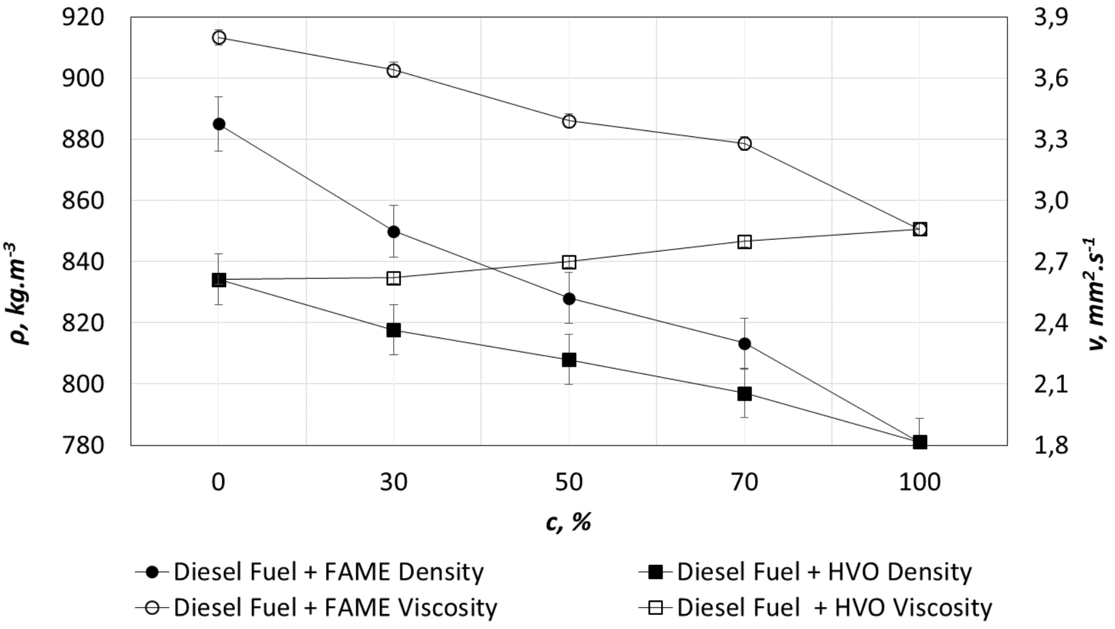

Figure 11. Density and kinematic viscosity of diesel fuel and FAME with HVO.

On x-axis of the Figure 11 is concentration (c) in % (V/V); on main y-axis is density (ϱ) in kg.m^{-3}; on secondary y-axis is viscosity in mm^2.s^{-1}: ● is density of Diesel Fuel + FAME; ■ is density of Diesel Fuel + HVO; ○ is viscosity of Diesel Fuel + FAME; □ is viscosity of Diesel Fuel + HVO.

In the case of hydrotreated oils, the effect is different, as the calorific value compensates the lower density effect (Figures 11 and 12). The higher calorific value of the hydrotreated oils is based on the fact that the amount of hydrogen in the hydrotreated oils is about 15.2% (m/m), as opposed to 13.5% (m/m) in standard diesel.

The Figure 11 shows that the density with increasing HVO concentration in the mixture is expected to decrease. This is due to the lower permissible water content and paraffinic character with a higher hydrogen content than diesel, which results in a higher energy content per kg. Mixture of diesel fuel with HVO > 30% (V/V) HVO in the mixture exceeds the EN 590 (Table 1) limit for diesel (820-845 kg.m^{-3}). High proportion mixtures did not meet the standard limits. On the contrary, low density offers the possibility of blending HVO into diesel fuels with higher contents of heavier fractions or their incorporation into less profitable products such as fuel oil. Conversely, standardized kinematic viscosity limits meet all HVO mixtures.

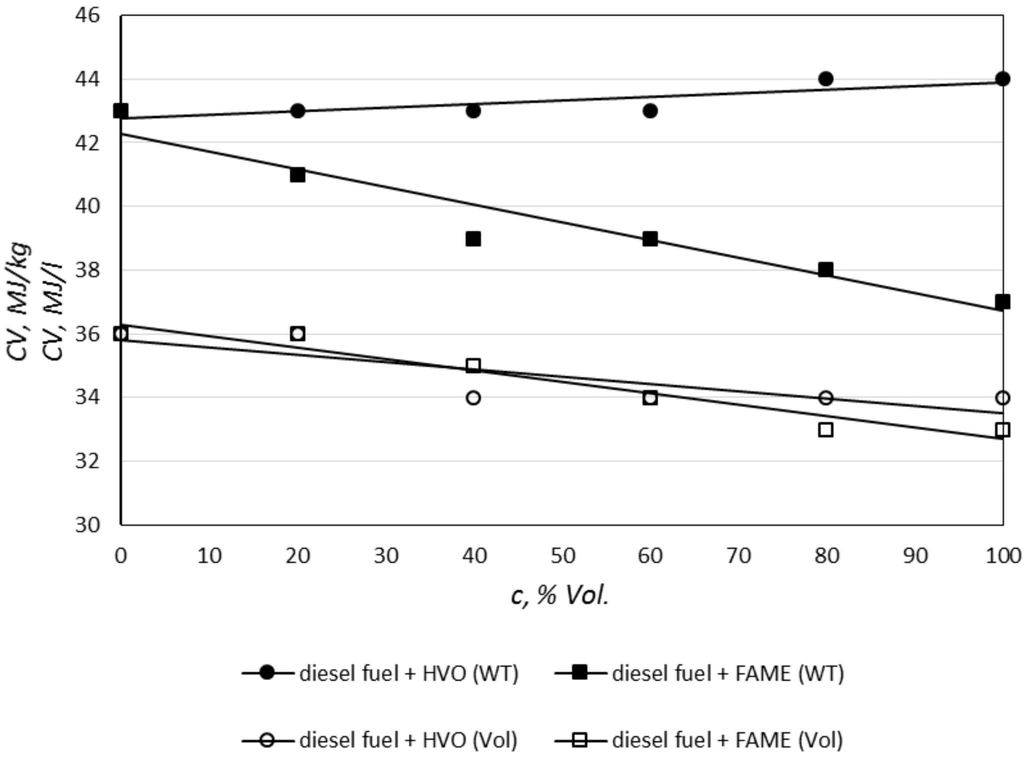

Figure 12. Calorific value of mixed fuels

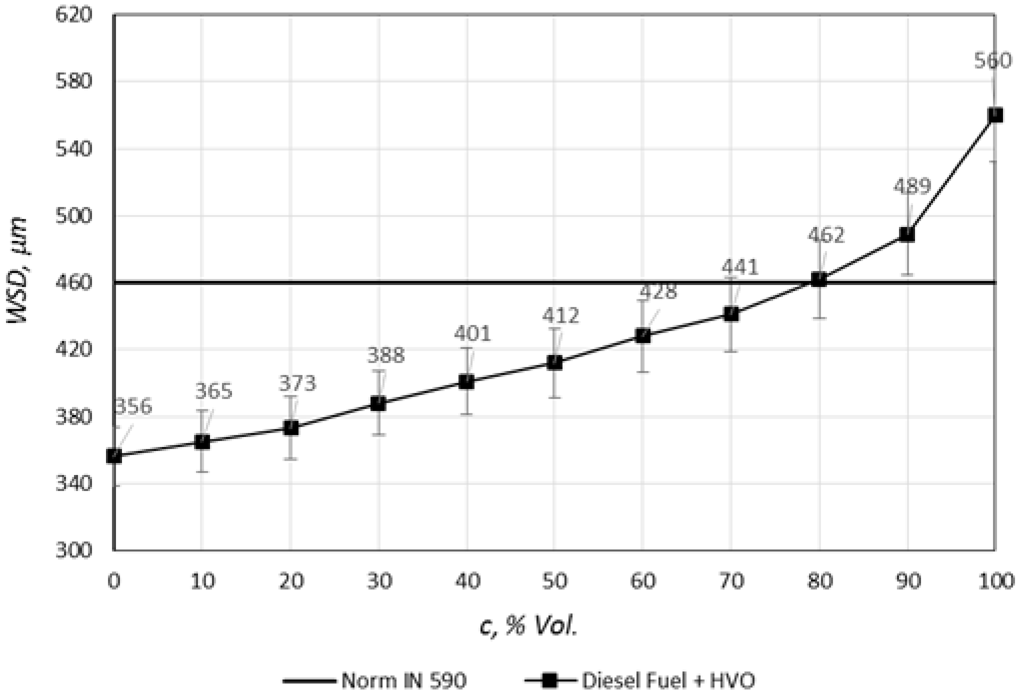

Figure 13. Lubrication of diesel with addition of HVO

On x-axis is concentration (c) in % (V/V); on y-axis is lubricity (WSD – Wear Scar Diameter) in µm: ■ is lubricity of Diesel Fuel with HVO. (European Standard for Diesel Fuel is EN 590). HVO has very low lubricity, therefore must be added up to 80% of volume as maximum. Once the concentration reaches 80% and more, the mixture of the fuel does not match the EN standard. It will lead to seizure of the fuel part of the machine.

An aromatic-free hydrocarbon composition results in a lower lubricity of the fuel. Lubrication of hydrotreated oils corresponds to sulfur-free winter grade diesel or GTL. It is essential that lubricant additives are added to these fuels to meet the requirements of EN 12156-1 (HFRR High Frequency Reciprocating Rig, corrected abrasion area diameter at 60°C < 460mm). It is possible to apply commonly used lubricants for diesel with similar dosage. When using this fuel at higher concentrations, it is assumed that a further test for lubrication verification will be added.

The hydrotreated oil can also be supplied with lubricating additives for use in pure form or as an additive. It is, however, common to supply, for example, HVO without these additives if the fuel is designated as a component of the mixture. The lubricity of the resulting fuel must then be controlled and must be increased to cover the HVO in the mixture. From the point of view of lubricity, this is the only parameter where FAME is better and in itself can replace the additive in all hydrocarbon fuels. The lubricating ability can be improved by adding the appropriate additive or a small addition of FAME content. The expanded uncertainty of the result is ± 5%.

Also, the distillation curve is different from diesel fuel and FAME. Distillation properties show how the fuel evaporates when injected into the combustion chamber of the diesel engine. Low boilers are important for the engine's start-up, and the fraction of heavier boiling points at higher temperatures can cause problems in fuel being incompletely burned and increasing the proportion of harmful emissions in the engine exhaust. Standard diesel fuel has a boiling range of approximately 180 °C to 360 °C.

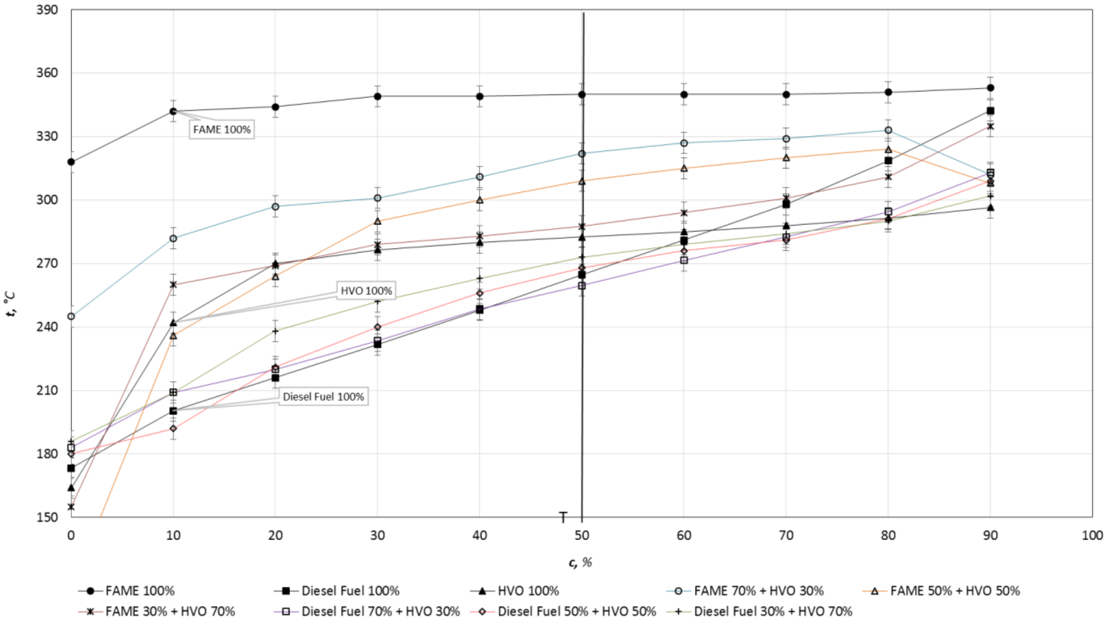

Figure 14. Distillation curves of FAME, diesel fuel, HVO and their mixtures.

On x-axis is process of distillation curve (c) in % (V/V); on y-axis is temperature (t) in °C: ● is 100% of FAME; ■ is 100% of Diesel Fuel; ▲ is 100% of HVO; ○ is 70% of FAME + 30% of HVO; Δ is 50% of FAME + 50% of HVO; x is 30% of FAME + 70% of HVO; □ is 70% of Diesel Fuel + 30% of HVO; ◊ is 50% of Diesel Fuel + 50% of HVO; + is 30% of Diesel Fuel + 70% of HVO.

Expanded measurement uncertainty is ± 4 °C and ± 2%. Changes in the mixed fuel distillation curve as compared to pure mineral diesel on the x-axis.

Determination of the distillation curve by means of a distillation test is a test that must always be carried out when assessing the quality of the fuel. The distillation curve expresses the volume percentage of the fuel that is distilled to a certain distillation temperature. T50 is the temperature at which 50% of the fuel is distilled. At this point the amount of air is bound for perfect combustion. For HVO and diesel, there is no need to worry about combustion air as the temperature in T50 has not increased significantly, the value is shown in the picture.

Figure 14 shows individual distillation curves. On the horizontal x-axis is the pre-distilled volume in % (V/V), on the vertical y-axis is the distillation temperature in °C, each mixture has its mark in the graph legend. It is clear from Figure 14 that HVO does not affect the beginning of oil distillation. The presence of "light components" is not compromised so that the moving parts of the fuel system cannot be damaged as the result is a degradation in fuel lubricity. The addition of HVO results in a flattening of the distillation curve. Distillation indicates a lower proportion of high boiling heavy fractional fractions, thereby reducing carbonization shares and reducing exhaust emissions. Higher concentrations of HVO can be expected to affect engine performance.

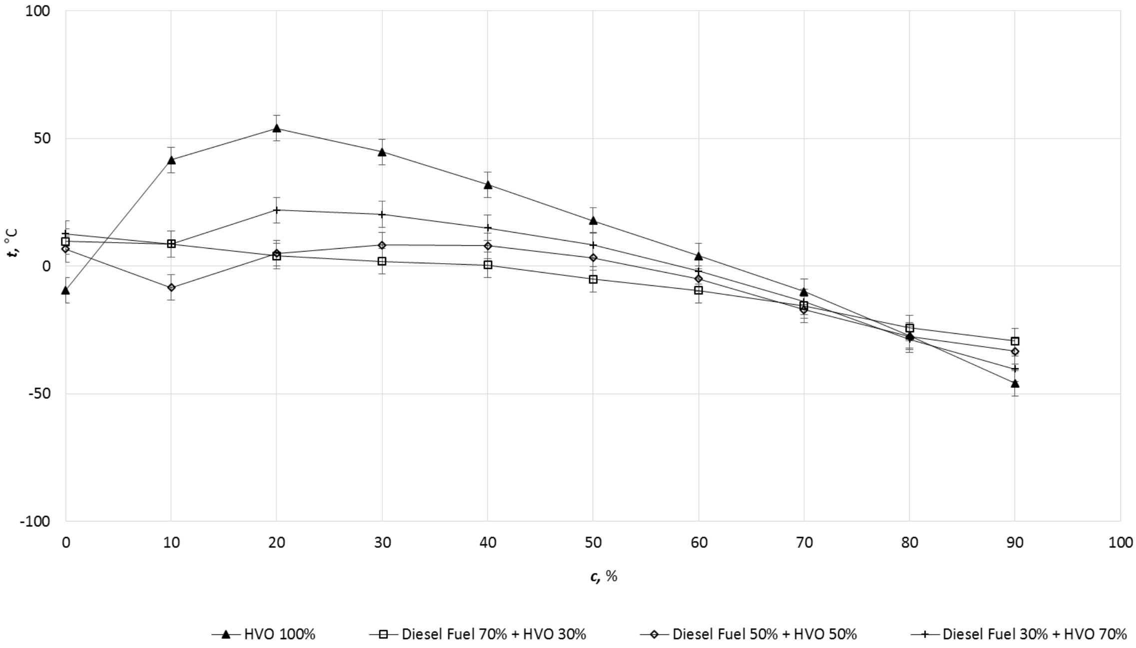

Figure 15. Changes in the mixed fuel distillation curve as compared to pure mineral diesel on the x-axis

On x-axis is process of distillation curve (c) in % (V/V); on y-axis is temperature (t) in °C: ▲ is 100% of HVO; □ is 70% of Diesel Fuel + 30% of HVO; ◊ is 50% of Diesel Fuel + 50% of HVO; + is 30% of Diesel Fuel + 70% of HVO.

Expanded measurement uncertainty is ± 4 °C and ± 2% (V/V).

Figure 15 shows the difference of values due to the HVO admixtures; on the x-axis, the course of the distillation curve is the pure mineral diesel fuel; on the y-axis the distillation temperatures are in °C.

The addition of HVO to diesel fuel positively affects the loss of filterability (CFPP – Cold Filter Plugging Point). Standard CSN EN 590 sets the temperature -20 °C as the maximum value for F-class winter diesel, 14 is marked with a thick horizontal line.

The cloud point (CP = TVP – the paraffin removal temperature) is the temperature at which it first starts to exclude paraffins from fuel, but it is not a mandatory indicator.

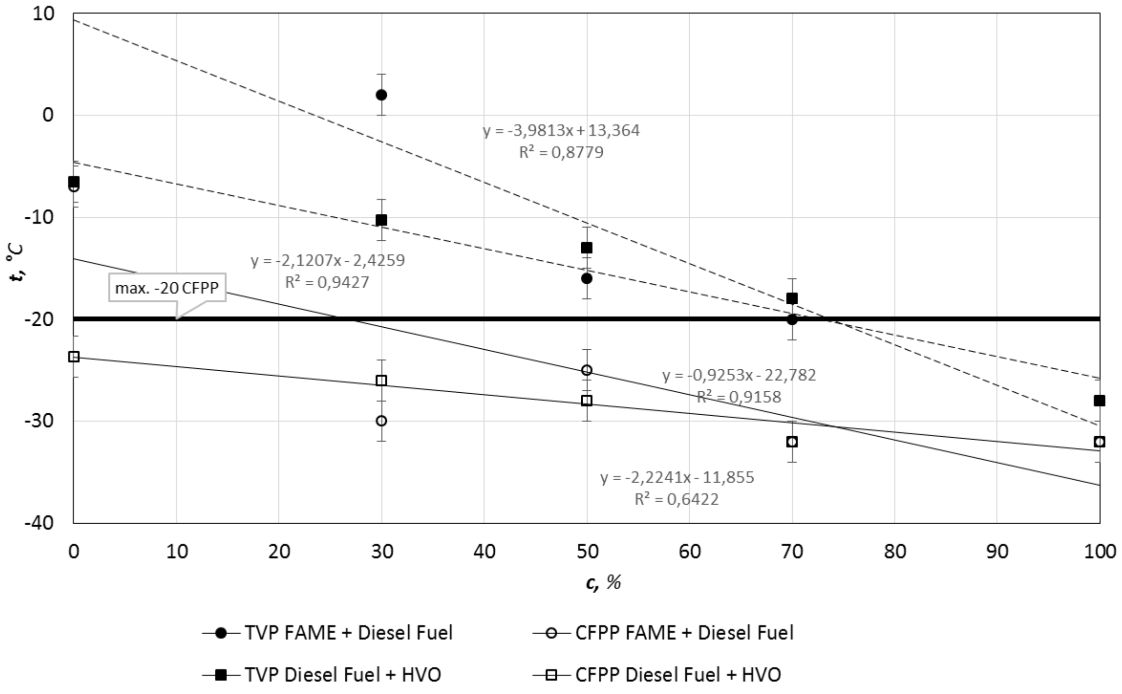

Figure 16. CFPP and TVP (= CP) of mineral diesel fuel and FAME with HVO

On x-axis is concentration (c) in %; on y-axis is temperature (t) in °C: ● is TVP of FAME + HVO; ○ is CFPP of FAME + HVO; ■ is TVP of Diesel Fuel + HVO; □ is CFPP of Diesel Fuel + HVO. The expanded uncertainty of the assay result is ±1°C.

Figure 16 illustrates the decrease of temperature with increasing addition of HVO. On the x-axis, the content of HVO is in % (V/V), on the y-axis is the temperature at °C. In the case of HVO 100, the CP value is practically the same as the CFPP value. HVO addition to diesel fuel favors low temperature properties which are even in case of a mixture HVO 30 6 degrees below the winter diesel fuel EN Class F. ČSN EN 590 also sets the CFPP for arctic climate (for 1st class to -26°C, for 2nd class it is -32°C), both of which exceed Diesel + HVO 70-100.

At temperatures above the cloud point, the hydrotreated oil is colorless, clear to water. It has no characteristic aroma typical of other fuels. It does not contain any visible dirt at temperatures above the cloud point. The cloud point causes the creation of scum characteristic for diesel.

The flash point is the lowest temperature at which the flammable substance produces so many flammable vapors at atmospheric pressure that they blend briefly with the air in a short-term approach to a precisely defined open fog, but do not continue to burn.

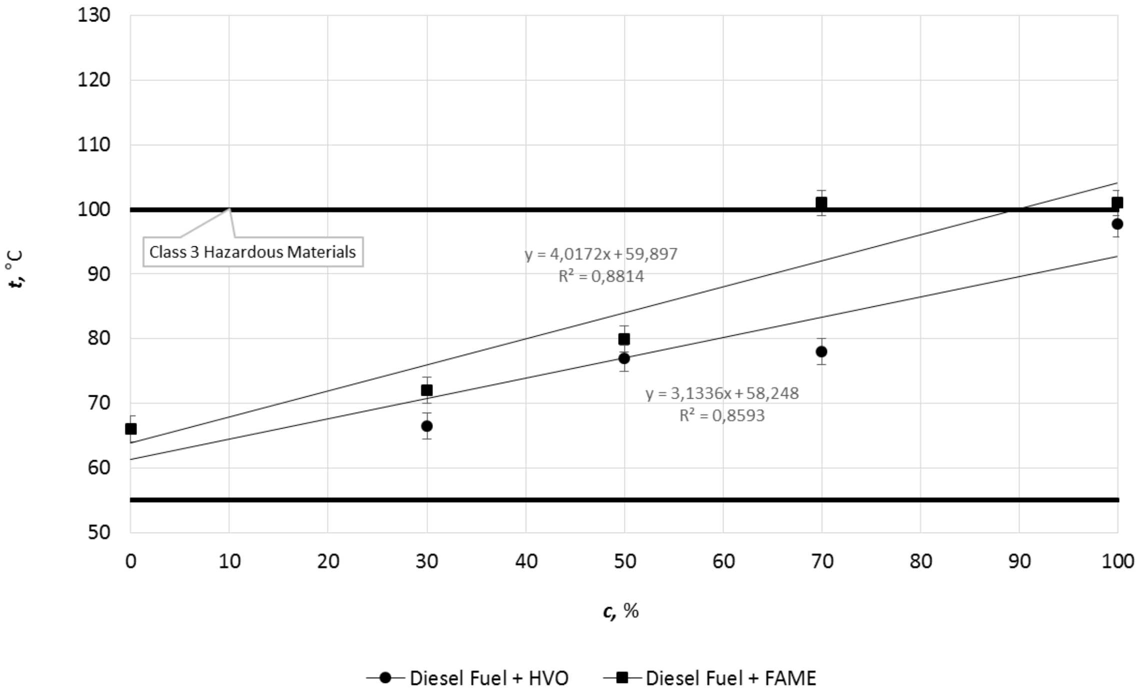

Figure 17. Flash points of diesel fuel with HVO and FAME

On x-axis is the concentration (c) in % (V/V); on y-axis is temperature (t) in °C: ● is Diesel Fuel + HVO in °C; ■ is Diesel Fuel + FAME in °C. The expanded uncertainty of the assay result is ± 1 °C.

Figure 17 shows the temperature increase of the flashpoint with increasing HVO content. On the x-axis, the content of HVO is in % (V/V), y-axis is the temperature at °C. The temperature range III of hazard class is defined here in which the measured temperatures of all HVO mixtures are located. However, in the case of a flashpoint value, these values do not affect the work of the diesel engine.

The cetane number indicates the reactivity of diesel fuel in terms of its diesel characteristics. The higher the fuel gets, the better it is, the higher the cetane number, the more regular and better its combustion, and at the same time the engine running and noise. Direct injection engines get better start, higher power, less consumption and smoke. Because of the relative difficulty of the cetane number test, the cetane index, which can be determined based on the calculation from the results of the laboratory density and distillation tests, has been introduced as a characteristic of ignition capability. According to ČSN EN 590, the cetane number is at least 51 units, the cetane index is 46 units.

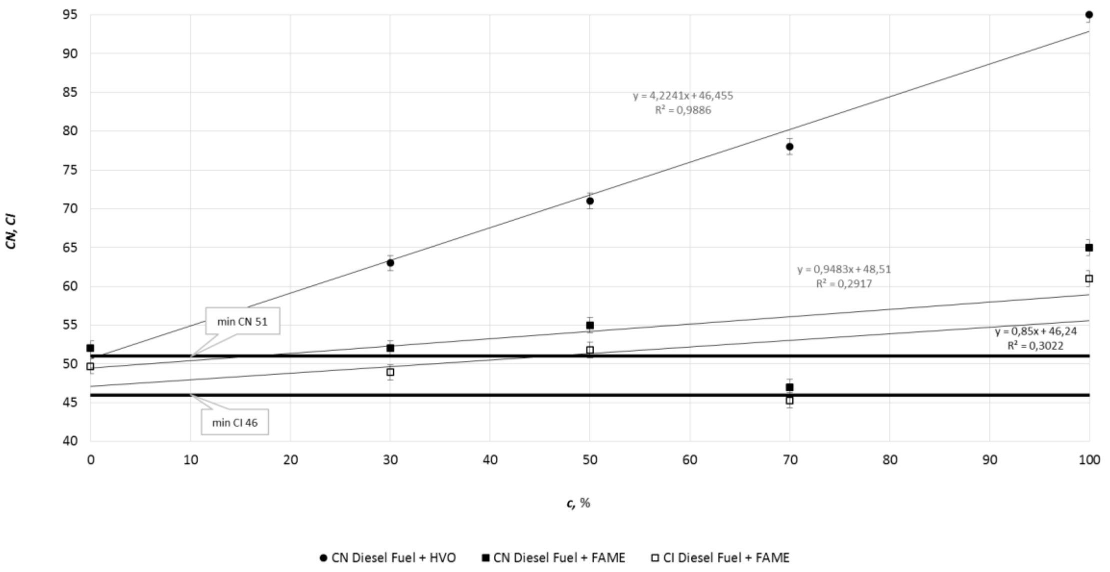

Figure 18. Cetane numbers and diesel engine indexes with HVO and FAME

On x-axis is concentration (c) in % (V/V); on y-axis is Cetane Number and Cetane Index: ● is Cetane Number of Diesel Fuel + HVO; ■ is Cetane Number of Diesel Fuel + FAME; □ is Cetane Index of Diesel Fuel + FAME. The expanded uncertainty of the assay result is ± 1 unit of cetane number.

The cetane number of hydrotreated vegetable oils ranges from 75 to 95 units due to the composition (n-paraffins and isoparaffins). In mixed fuels, there is a linear increase in the cetane number corresponding to the proportion of components. Hydrotreated oil is a suitable additive for increasing cetane number due to the nature of the fuel, where its effect is more effective than the use of conventional additives. For measuring the cetane number on the test engine, the hydrotreated oil must be mixed with a fuel with a known and low cetane number such that the cetane number of the resulting mixture is below 70 units within the measuring range. Then the cetane number of the hydrotreated vegetable oil is determined by linear extrapolation. The calculation of the cetane index is for standard diesel and its use in hydrotreated oils is not appropriate.

Figure 18 shows the increasing trend lines of cetane number and cetane index with increasing HVO content. On the horizontal x-axis, the content of HVO in % (V/V), on the vertical y-axis is the cetane number and index. The limit value according to ČSN EN 590 for the cetane number is highlighted in the graph with a horizontal line, for the cetane index 46 is also highlighted by the horizontal line. The extrapolated cetane number is high because of the very high content of n- and isoparaffins in HVO, the value of the HVO 30 mixture already means a much higher cetane number than min. value in ČSN EN 590.

In the measurement in this work were compared mineral diesel oil without bio-component, 100% pure HVO and the concentration of their mixtures prepared in ratios based on the possibility of comparison of the results of own measurements with already published results of measurements in the literature. The individual measurement procedures were performed according to applicable valid standards and were repeated three times to avoid any measurement error. The density measurement results of mixtures with increasing HVO concentration had an expected decreasing trend, which should have a negative effect on the calorific value (energy content per kg). According to the HVO manual, this drop is due to the lower permitted water content and the pure paraffinic character of HVO fuel, which mineral diesel does not have, but due to its higher hydrogen content, HVO has a higher calorific value at lower density.

Since hydrotreated oil consists only of hydrocarbons, traditional methods for fossil diesel but not FAME are also suitable for determining fuel stability. This applies especially to methods "Rancimat" according to ČSN EN 15751, which is intended for the pure diesel fuel and FAME containing 2-7 % (V/V) FAME and is not suitable for a hydrotreated oil, even if the additives in diesel.

The stability of hydrotreated oils is at the standard level of diesel fuel and there should be no risks except for long-term vehicle shutdown or storage.

The sulfur content of the hydrotreated oil is based on the production process and is < 1 mg.kg^{-1}. As the standard oil logistics system is used for hydrotreated oil, the sulfur content due to contamination may be higher, and then the normalized value is ≤ 5.0 mg.kg-1. Addition of hydrotreated oils can also positively reduce the sulfur content, for example, in diesel, where the value exceeds the relevant standard ČSN EN 590.

The ash content in hydrotreated oils is very low (< 0.001%). Also, the content of P, Ca and Mg is well below the detection limits of analytical methods (< 1 mg.kg^{-1}).

Hydrotreated oil is like fossil hydrocarbons nonpolar, while water is polar. So, water solubility is similar to traditional diesel fuel, or even less. It follows that the issue of water requires no further action in the field of logistics as well as for diesel.

The issue of microbial growth is primarily about FAME, which also promotes microbial growth in diesel fuel blends. FAME is biodegradable and tends to increase the water content of diesel fuel. Unlike FAME, the presence of hydrotreated oil mixed with diesel fuel does not require any further action. However, monitoring of the quality indicator is useful because the microbes can proliferate even in the pure fossil fuel during long term storage in the presence of free water. Higher temperatures, especially in the summer, can increase microbial growth, especially if mineral salts are present in the water phase. At lower temperatures, growth of microorganisms slows down.

The hydrocarbon composition corresponds to the hydrocarbons from which diesel fuel is composed. HVO has its composition closer to diesel oil than fatty acids, which is an advantage for the use of HVO as a substitute for FAME.

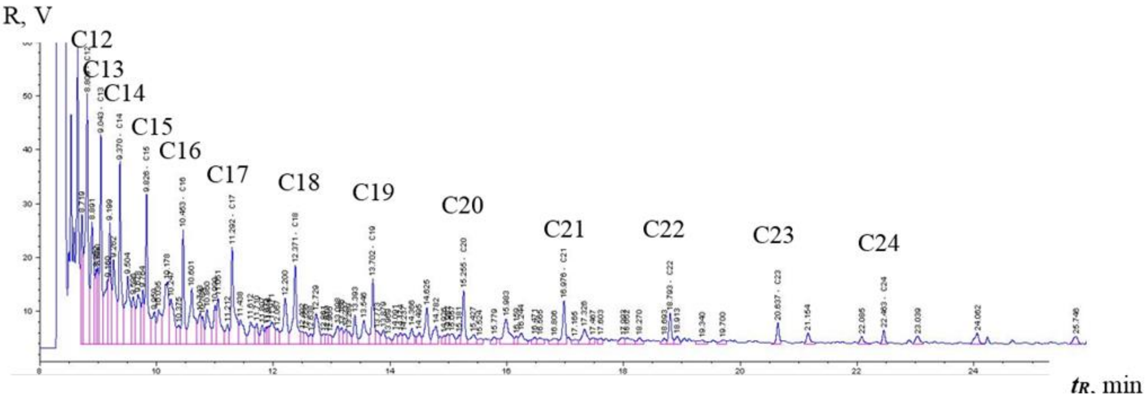

Figure 19. Chromatogram of 100% diesel fuel with identified (labeled) n-alkanes

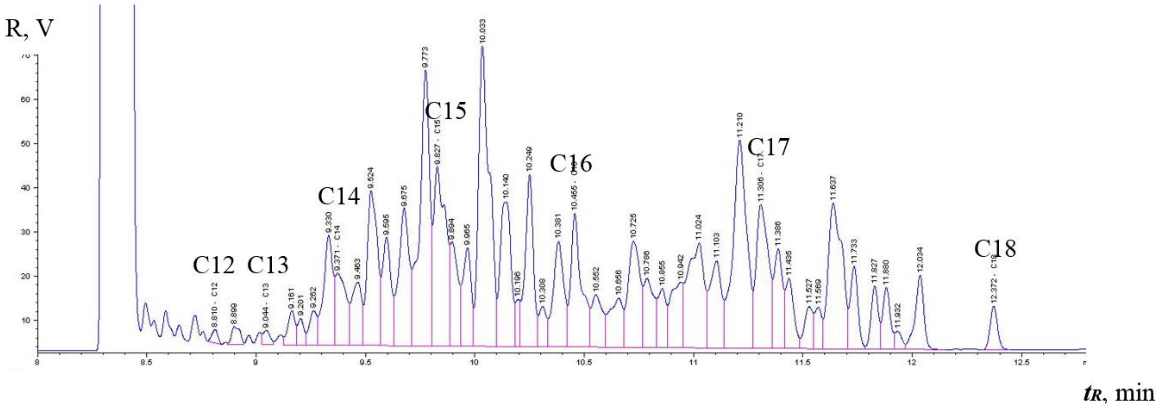

Figure 20. Chromatogram of 100% HVO with identified (labeled) n-alkanes

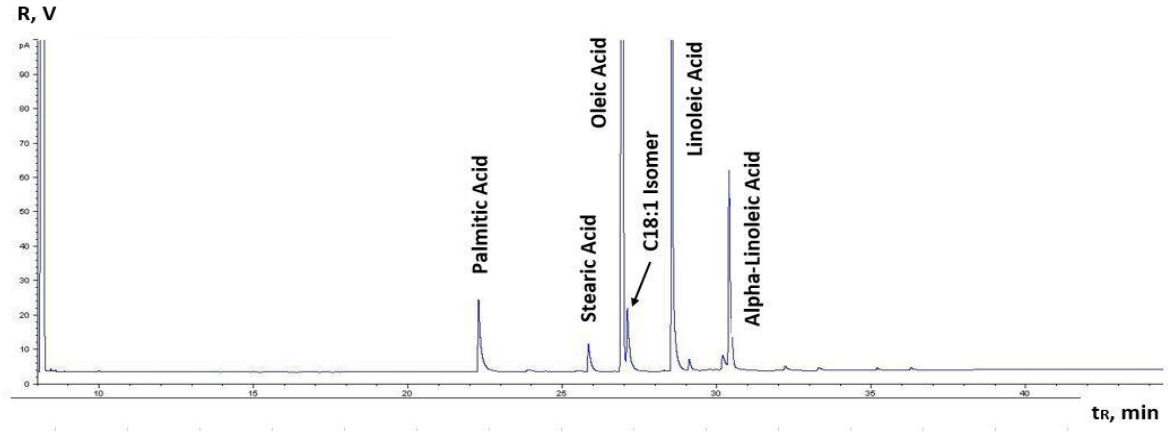

Figure 21. Chromatogram of 100% FAME

R is Detector Response in Volts; t_R is Retention Time in minutes.

The Figures 19 – 21 are chromatograms of fuel samples (Diesel Fuel, HVO and FAME). On Figure 19 we can see the representation of individual hydrocarbon chains. Figure 20 shows the percentage of hydrocarbon components in HVO. Gas chromatography on Figure 21 allowed us to specify the presence of various acids in FAME, the peaks are well separated.

Chromatographic results may vary, depending on the refinery they come from. The final composition depends on season, country of distribution, class of fuel and more.

The statistical analysis was then conducted to obtain general equation of density and viscosity for independent variable concentration. Analysis was done for mixture of diesel and HVO and mixture of FAME and HVO. For the needs of the article, statistical tool R and the built-in library lm() were used.

As a first analysis, a linear regression analysis was calculated to predict density of diesel and HVO mixture based on concentration. A significant regression equation was found (F(1, 3) = 1411, $p < 0.01$, N = 20), with R^2 of 0.9972. Model predicted density in form of equation (1). Assumptions of linear regression were verified by gvlma library. All assumptions were accepted: Global Stats ($p = 0.5704$), Heteroscedasticity ($p = 0.9905$), Skewness ($p = 0.2229$), Kurtosis ($p = 0.9911$) and Link Function ($p = 0.2302$).

$$\rho = 0.52147c + 780.97672 \tag{1}$$

Complementary linear regression was calculated to predict viscosity of diesel and HVO mixture based on concentration. A significant regression equation was found (F(1, 3) = 49.97, $p < 0.01$, N = 20), with R^2 of 0.9245. Model predicted viscosity in form of equation (2). All assumptions were accepted: Global Stats ($p = 0.5884$), Heteroscedasticity ($p = 0.8937$), Skewness ($p = 0.7208$), Kurtosis ($p = 0.4098$) and Link Function ($p = 0.1579$).

$$\upsilon = -0.0038750c + 2.89085 \tag{2}$$

As a second analysis, a linear regression analysis was calculated to predict density of FAME and HVO mixture based on concentration. A significant regression equation was found (F(1, 3) = 94.09, $p < 0.01$, N = 20), with R^2 of 0.9588. Model predicted density in form of equation (3). Assumptions of linear regression were verified by gvlma library. All assumptions were accepted: Global Stats ($p = 0.5035$), Heteroscedasticity ($p = 0.8260$), Skewness ($p = 0.4299$), Kurtosis ($p = 0.1330$) and Link Function ($p = 0.5241$).

$$\rho = 0.7478c + 785.6795 \tag{3}$$

Complementary linear regression was calculated to predict viscosity of FAME and HVO mixture based on concentration. A significant regression equation was found (F(1, 3) = 88.94, $p < 0.01$, N = 20), with R^2 of 0.9674. Model predicted viscosity in form of equation (4). All assumptions were accepted: Global Stats ($p = 0.8565$), Heteroscedasticity ($p = 0.6979$), Skewness ($p = 0.5792$), Kurtosis ($p = 0.4987$) and Link Function ($p = 0.5205$).

$$\upsilon = 0.011987c + 2.887347 \quad (4)$$

3. Discussion

The experiment shows that the hydrotreatment process is an alternative to the production of biofuels for the esterification process to eliminate the undesirable effects, as described in [12] and [15]. These include, in particular, increased NO_x content, emissions, fuel storage problems, engine oil wear, and so on. HVO are also characterized by high cetane numbers, as confirmed by the measured results [12]. The characteristics for diesel compared to HVO were practically the same, as illustrated by Sugiyama article [13]. Experiments and proven measurements show that HVO impurities have a positive effect on the characteristics of diesel engines.

Characteristics to be monitored include, above all, the lubricity to provide the lubricating ability of the moving parts of the fuel system and the cetane number. The graphs show, in accordance with [15], that the recommended HVO impurities will be around 50% in order to be consistent with the diesel fuel characteristics.

According to the article [29], low density and low sulfur content has an effect on lower lubricity, which can be improved by the application of conventional lubricating additives as is the case with today's low-grade mineral diesel fuel. The kinematic viscosity of all HVO mixtures meets the standard parameters. The distillation curve determines that by addition of HVO to mineral diesel fuel, its process is flattened. Which, according to Article [30], has a positive effect on the reduction of carbonation deposits and exhaust emissions. The HVO Manual [28] indicates CFPP up to -40 °C. This value has not been confirmed by its own measurement. The lowest measured CFPP was -36 °C in 100% HVO. This is even 11 °C less than that found in article [12]. Even with this mismatch, all blends have a positive effect on the CFPP drop and are well below the F-class for diesel fuels, the CFPP reported by ČSN EN 590 max. -20 °C. The results of the flash point measurement have an increasing tendency as well as in all the articles to compare the measured values. This has a positive effect on reducing the risk of fuel explosion during handling and storage under standard conditions. The measured high values of the cetane number and the calculated cetane index value increase with the HVO content in the mineral oil mixture. The values of the cetane number and cetane index set out in this work correspond to the already high values of these figures in Articles [12,29–31] and the HVO guidelines [28].

The properties of hydrotreated oils are much more similar to high quality sulfur-free diesel or synthetic GTL diesel fuel than to FAME.

In the production of fuels, components with n-hydrocarbons and branched hydrocarbons are suitably combined to achieve suitable fuel properties (cetane number, pour point). Biodiesel produced by hydrotreated of vegetable oil consists of C_{17} and C_{18} n-hydrocarbons with a high cetane number but has poor low temperature properties due to a melting point between 20 and 28 °C. Improvement of these parameters can be achieved by adding a second proportion of highly isomeric hydrocarbons.

During long-term storage, pure hydrotreated oils as well as mixtures containing them behave like traditional diesel fuels. Hydrotreated oils do not contain any hazardous impurities, such as saturated monoglycerides present in FAME. There is therefore no risk of clotting above the cloud point. However, as with standard diesel, this phenomenon may occur due to the presence of paraffins in the fossil fuel or hydrotreated oil during long-term storage at temperatures below the cloud point.

4. Materials and methods

The sample of tested hydrotreated vegetable oil was received from the Neste Oil Company (Finland). Simultaneously, diesel fuel free of fatty acid methyl esters compliant to EN 590 and a FAME mixture compliant to EN 14 214 were used for laboratory test.

The following tests of blends were made:

1. Density at 15 °C according to EN ISO 3675
2. Kinematic viscosity at 40 °C according to EN ISO 3104

3. Cold filter plugging point (CFPP) according to EN 116
4. Flash point according to EN 2719
5. Oxidation stability of vegetable oil according to EN 15 751
6. Cetane number according to EN ISO 5165
7. Lubricity according to EN 12156-1 (HVO lubrication 460–650 μm)
8. Calorific value according to ISO 1928 on IKA C200 Calorimeter
9. Gas Chromatography – Flame Ionization Detector GC-FID

Following samples and their mixtures were analyzed:

1. 100% FAME
2. 100% HVO (from Neste Oil Company)
3. 100% Diesel Fuel (without any FAME)

For the GC measurements, the samples were diluted 1/50 (20 μl sample + 980 μl hexane).

Analytical Standards:
1. Mixed standard: n-alkanes C10 to C30 in hexane
2. Mixed standard: Supelco 37 Components FAME Mix

For sample analysis, an Agilent Technologies 7890A gas chromatograph equipped with an autosampler, a capillary quartz column SPB-2560 and a flame ionization detector (FID) was used. The basic instrument parameters and GC analysis conditions are shown in Table 2.

Table 2. Device parameters and GC analysis conditions

Device	Type and settings
Gas Chromatograph	Agilent Technologies 7890A
Autosampler	G4513A (16 positions) with a syringe Agilent Gold Standard 10μl
Analytical column	SPB-2560, 100 m x 0.25 mm i.d., film thickness 0.2 μm
Temperature program	140 °C (5 min), increase 4 °C.min^{-1}, 245 °C (20min) → 51.25 min
Carrier gas	Helium 5.6, const. inlet pressure 50 psi (flow rate 1.58 ml.min^{-1} at 140 °C)
Injection chamber	Temperature 280 °C, injection volume 1 μl, split ratio 1 : 100
Detector	Temperature 280 °C, gas flow: hydrogen (6.0) 30 ml.min^{-1}, air (5.0) 400 ml.min^{-1}, makeup = nitrogen (6.0) 25 ml.min^{-1}
Data collection software	Agilent ChemStation (Revision B.04.02 SP1)

Lubrication was measured on a PCS instrument: HFRR (High Frequency Reciprocating Rig). The PCS instrument uses an electromagnetically vibrating moving body with low amplitude while simultaneously compressing it against a solid body. The instrument measures the frictional forces between the bodies and the electrical contact resistance between them. Settings in is Table 3.

Table 3. Technical parameters PCS: HFRR

Parameter	Value
Frequency	10-200 Hz
Shift	20 μm - 2 mm
Load	0.1 - 1 kg with supplied weights
Maximum fractional force	by amplitude, max 10 N
Temperature	From room temperature to 150 °C
Standard upper test body	Ball Ø 6 mm
Standard lower test body	Disk Ø 10 mm and thickness 3 mm
Power supply	100-230 V
Heating	Two heating cartridges 24 kW, 15 kW

5. Conclusions

Due to the pressure of the European Union to reduce the total amount of greenhouse gases produced into the atmosphere, there is a need to reduce greenhouse gas emissions even in transport, one of which is to increase the share of biofuels in mineral diesel over 7%. By using other types of biofuels than fatty acid methyl esters which are - due to their undesirable low oxidation stability necessary for long-term storage, higher temperature of cold filter plugging point (CFPP?) which prevents winter operation, high boiling point and the associated cold starts with inadequate combustion - inappropriate.

A much better biofuel is HVO, whose hydrocarbon character can be compared to high quality mineral diesel with a very high cetane number and a very low temperature of cold filter plugging point (CFPP). As confirmed by the actual measurement, HVO does not have the above-mentioned drawbacks as fatty acid methyl esters. HVO can be mixed without limitation into mineral diesel fuel. Its presence in mineral oil blends improves engine performance and reduces fuel consumption, exhaust emissions, and cold filter plugging point (CFPP) so it can also be used in aviation turbine engines.

The properties of hydrotreated oils are much more similar to high quality sulfur-free diesel or synthetic GTL diesel fuel than to FAME.

The production technology of this biofuel is intergenerational in its own way, as raw materials, both food and waste, can be used for its production without significantly changing the hydrotreatment conditions. It is also beneficial for this technology that it can be operated, after minor modifications, directly in existing refineries.

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