



Key properties and blending strategies of hydrotreated vegetable oil as biofuel for diesel engines

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ABSTRACT

Hydrotreating catalysis is becoming a promising alternative to transesterification for the production of biofuels derived from vegetable oils. They have potential advantages with respect to both biodiesel fuels and petroleum-derived diesel fuels in terms of production costs, engine emissions and adaptability to current engine designs, but they have also some limitations which may restrict their capability to replace diesel fuels. Those fuel properties considered the most restrictive ones were measured on different blends of HVO (selected among the variety of names given to these fuels) with a winter ultra low sulfur diesel fuel (in 10, 20, 25, 30, 35, 40, 45, 50, 55, and 75 vol.%) in order to propose some blending strategies to optimize engine performance and emissions, to protect the engine components and to keep the vehicle operability. The results obtained show that the main restrictions are imposed by lubricity and cetane number, and, in case of cold regions, also by cold flow properties. A compromise between lubricity and derived cetane number would lead to a recommendation for low or medium HVO concentrations, and blends with concentrations above 50% would not be recommended. Density and viscosity would not impose direct blending restrictions, although the reductions in density could provide some economic savings and some flexibility to refineries. The loss of heating value per unit volume (and consequently the expected increase in fuel consumption) would be lower than 3% in blends up to 50% in volume. Finally, the sooting tendency of the blends is sharply reduced, indicating lower engine PM emissions and reduced need for regeneration of diesel particulate filters.

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1. Introduction

Depletion of the reserves of crude oil and increasing concern on greenhouse gas emissions have encouraged legislative and regulatory proposals to replace petroleum fuels with a diversity of fuels obtained from domestic renewable sources. In the case of diesel automotive engines, among the alternatives for petroleum-diesel fuels, three options are currently considered realistic, based on their capability to replace petroleum-diesel in significant proportions with no engine modifications or substantial re-design: biodiesel fuels, hydrotreated oils (both derived from vegetable oils or animal fats) and Fischer-Tropsch (FT) diesel fuels derived from lignocellulosic biomass. However, the only commercially available FT fuels are produced from fossil sources so far.

Biodiesel (and its blends) perform quite similarly to petroleum-diesel, but their properties are slightly different [1]. Much of the sulfur and oxygen containing species are removed during the diesel refining process. This removal lowers the lubricity of fuel which is

compensated by additives. This is not necessary in the case of biodiesel fuels, since they have good lubricity, being maintained by its oxygen functional groups [2]. Also, cetane numbers of biodiesel fuels are similar or even higher than those of diesel fuels [3]. All these different properties lead to significant benefits on carbon monoxide, total hydrocarbon and particulate engine emissions [4]. In contrast, biodiesel generally has higher cloud and cold filter plugging points, and thus it has more potential to clog the fuel filter than regular diesel fuel [5].

Another way to process vegetable oil is to remove the oxygen from the structure and hydrogenate the double bonds in the triglyceride chain. This is done through conventional hydrotreating catalysis. In the first step of this reaction pathway, the triglyceride is hydrogenated and broken down into various intermediates, mainly monoglycerides, diglycerides and carboxylic acids. These intermediates are then converted into alkanes (both n-alkanes and iso-alkanes) by three different pathways: decarboxylation, decarbonylation (both removing a carbon atom from the initial intermediate) and hydrodeoxygenation (with no carbon removal) [6]. Propane, water, carbon monoxide and carbon dioxide are produced as byproducts [6]. If the hydrogen partial pressure is high enough (which is necessary to reach a high reaction efficiency and to avoid aromatic formation [7]), carbon monoxide and carbon dioxide may partially be methanized, yielding methane

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as another byproduct [8]. This reaction is performed at temperatures between 300 and 360 °C and a pressure between 50 and 180 bar [9] in the presence of a zeolite catalyst (generally molybdenum-based [6, 8, 10], although other less conventional catalysts also have been successfully used [11, 12]). In the mentioned range of conditions, higher temperature leads to higher ratio between the contribution of the former reactions (decarboxylation and decarbonylation) and that of the latter reaction (dehydrodeoxygenation) [11]. Additionally, as the reaction temperature is increased (until the temperature at which deactivation of the catalyst may take place), the ratio of iso-alkanes/n-alkanes in the final product has been observed to increase [9, 11, 13], and the remaining unreacted triglycerides, to decrease [13, 14]. Finally, increasing the reaction pressure also leads to increases in the iso-alkanes/n-alkanes (this effect being less significant than that of temperature) and to decreases in the amount of unreacted triglycerides [14].

This process is attractive, on the one hand, because it can be integrated in conventional refinery hydroprocessing installations, therefore lowering capital costs for the process [15], and on the other hand, because it produces a fuel that approximates the physical properties of petroleum-diesel better than biodiesel does. Moreover, some experimental studies have shown that paraffinic fuels have a significant potential for reducing smoke opacity, particulate matter emissions [16–18], particle number, PAH and their mutagenic effects [16, 17].

Some companies are currently producing hydrotreated triglycerides and advertising their advantages as a fuel [19–22]. The production process or technologies are commercially differentiated with trademark names such as Ecofining [19], Bio-Synfining [22] or H-bio [23]. The product is referred to with different names: hydrotreated vegetable oil (HVO) [27] (it should not be confused with heavy vacuum oil –also termed HVO– which is a petroleum-derived feedstock that can also be used, together with vegetable oils, for hydrotreatment in refineries [6, 24]), hydrodeoxygenated vegetable oil (HDO-oil) [25], hydrobiodiesel, renewable diesel [10, 21, 26, 27], hydrogenation-derived renewable diesel (HDRD) [28], renewable synthetic fuel [22], green diesel [19, 21], bio-cetane [29] or H-bio [23]. The first term is used here since it is the one used in the European Normalization Committee (CEN), which has recently developed a CEN Workshop Agreement (CWA 15940) specifying requirements and test methods for marketed and delivered paraffinic diesel fuels for use in diesel engine vehicles, either coming from FT synthesis or from hydrotreating [30]. This document is the first step before moving towards an official standard, although this movement will depend on whether paraffinic diesel fuels become widely available as an automotive fuel.

There are some properties of HVO that may limit its capability to replace diesel fuels:

- Its cetane number, or propensity to autoignite, is very high. Although cetane number is considered a quality indicator of diesel fuels, the high difference between the cetane numbers of diesel and HVO would require adjustments in the electronic control of the engine to compensate for the fuel igniting earlier in the cycle.
- The lubricity is very low due to the absence of sulfur and oxygen compounds in the fuel [31]. The feedstock is mostly free of sulfur already and the hydrodeoxygenation process removes all the oxygen and all the remaining sulfur.
- The energy density of HVO is also lower due to the aliphatic nature of the compounds [26].
- The cold flow properties, such as cloud point (CP) and cold filter plugging point (CFPP), may also be worse than those of a winter diesel fuel due to the higher paraffinic character, although this depends highly on the oil feedstock [9, 14] and on the reaction conditions which may lead to a certain yield of triglycerides [14].

These problems can be addressed by blending with regular diesel fuel. This is expected to depress the cetane number and cold flow

temperatures, as well as to raise the lubricity of the HVO enough so that it is usable with no engine modifications.

2. Experimental equipment

The HVO was manufactured from pure soybean oil (considered today as the most widely used feedstock among vegetable oils) by UOP (Universal Oil Products) and the conventional ultra-low sulfur diesel (ULSD) is a winter reference diesel supplied by Chevron Phillips Chemical.

The fuel compositions were identified by gas chromatography with mass spectrometry detection (GC-MS) and quantified by GC-FID (flame ionization detection). GC-MS was performed on a Shimadzu GC-17A equipped with a QP-5000 mass selective detector with an ion source of electron impact at 70 eV. Compounds were identified by comparing their mass spectra with the NIST library. The quantification was performed on a Varian CP-3800 GC with FID. The column was a Restek Rxi-5SilMS, 30 m × 0.25 mm i.d. × 0.25 μm film thickness. The injector temperature and interface temperature was 290 °C. The oven temperature was programmed to hold at 40 °C for 4 min; ramp at 4 °C/min to 220 °C; and hold at 220 °C for 10 min. The split ratio was set to 20:1. The flow rate of helium carrier gas was 1 mL/min. Standard solutions with different range of concentrations were prepared using several normal paraffins and branched paraffins and the response factors were determined. Twenty milligrams of the sample was dissolved in 1 mL of dichloromethane and 1 μL of this solution was injected into the GC.

The derived cetane number (DCN) was measured in accordance with the ASTM D6890-08 standard, in an Ignition Quality Tester. This method uses a constant volume combustion chamber. It measures the time from when fuel enters the chamber (determined by fuel injector needle lift) to a pressure spike from the resulting combustion process. This value is measured in milliseconds and is called ignition delay (ID). From the ID value, the software calculates the cetane number which is referred to as the derived cetane number, or DCN. DCN is related to ID by the following couple of equations:

$$DCN = 4.46 + \frac{186.6}{ID} \quad \text{if } DCN \leq 61; \quad (1)$$

$$DCN = 83.99(ID - 1.512)^{-0.658} + 3.547 \quad \text{if } DCN > 61$$

Each run consists of 15 pre-injections to prepare the combustion chamber. The value from each run is the average ID and DCN of the following 32 injections. The final value for each fuel is the average of 3 runs. By this method, the reported value is the average of 96 injections for each fuel. The calibration of the system was made with n-heptane, whose DCN is 53.8.

The lubricity tests were carried out in a High Frequency Reciprocating Rig (HFRR) from PCS Instruments. These tests provide the wear scar in μm for a particular fuel, following either the European EN ISO 12156-1:2006 standard or the ASTM D 6079 standard. Prior to each test, all the components of the HFRR being in contact with the tested fuels were subjected to a cleaning procedure composed of three 10-minute immersions in an ultrasonic bath with toluene (the first and the second) and with acetone (the third). All tests were replicated twice and if differences in the wear scar were higher than 20 μm then they were repeated once more. Afterwards, the size of the wear scar was measured with a digital microdurometer from Future-Techelectronic, series FM-7, equipped with a 100 magnification lens. The mean diameter of the scar observed in the HFRR ball (MWSD) was obtained from maximum and minimum values as prescribed in the standards. Tests were made at 60 °C, as required by EN ISO 12156-1 standard, and the resulting scar size was corrected to normalize the humidity vapor pressure to 1.4 kPa (WS 1.4).

Distillation curves were obtained following standard EN 3405 with a distillation system equipped with a 0.5 L heated flask,

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