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HVO100 identification on-site with FTIR spectroscopy

In order to reduce greenhouse gas- and particulate emissions from diesel engines, all major fuel specifications mandate addition of biofuels. In most cases, this requirement is met by addition of biodiesel, or fatty acid methyl esters (FAME) in concentrations from 3 % to 30 %, depending on the country. The concentration of FAME can be measured using FTIR spectroscopy as outlined in the standards ASTM D7806, ASTM D7371 and EN14078. As FAME deteriorates the low temperature properties of diesel fuel, its use is limited in colder countries and for winter applications.

An alternative biofuel gaining in popularity is Hydrotreated Vegetable Oil (HVO). This fuel is manufactured by full hydrotreatment of vegetable oil and can also be produced from a variety of waste streams. The hydrotreatment removes all oxygen and sulfur and produces a fuel which is free from aromatics and has a hydrocarbon distribution which is very narrow. In the case of a pure product consisting of close to 100 % HVO, this is referred to as HVO100.

Due to its biological origin, HVO100 has a CO_2 footprint that is up to 90 % lower than conventional diesel. The lack of aromatics leads to a reduction of particulate emissions. The narrow hydrocarbon distribution results in excellent low temperature properties and produces fuels with a very high cetane number and cetane index. Due to these advantages, HVO100 has become considered “premium diesel” and is sold at a higher price at the gas station.

While biodiesel (FAME) is routinely measured by FTIR spectroscopy, the screening of HVO100 is difficult due to the chemical similarities between HVO100 and the hydrocarbons present in conventional diesel. In this paper we present a new method involving eralytics era**spec** FTIR fuel analyzer to distinguish HVO100 from traditional diesel. This method, available as an optional module, enables the verification of HVO100 fuel to be tested on-site and distinguished from conventional diesel fuel.

Experimental

For the validation of the FTIR method for HVO100 detection, 443 diesel samples were collected from gas stations across 80 countries. The sample set contained 174 samples containing up to 36 % biodiesel (FAME). The sample set contained 17 HVO100 samples and 6 (fossil) paraffinic diesels with low aromatic content. The complete chemical composition of the samples was determined with GC according to EN12916 and the samples were measured on an era**spec** fuel analyzer.

Discussion

HVO100 differs from conventional diesel in that it lacks aromatic compounds. Furthermore, due to the narrow distribution of hydrocarbons, the HVO exhibits a flat distillation curve. Paraffinic diesels that are not produced from biogenic sources generally exhibit a broader hydrocarbon distribution and have distillation curves more similar to conventional diesels.

This flat distillation curve translates into a very high cetane index. A plot of the total aromatic content (via GC) vs cetane index (calculated from the distillation curve) thus singles out the HVOs from the paraffinic and conventional diesels as shown in Figure 1.

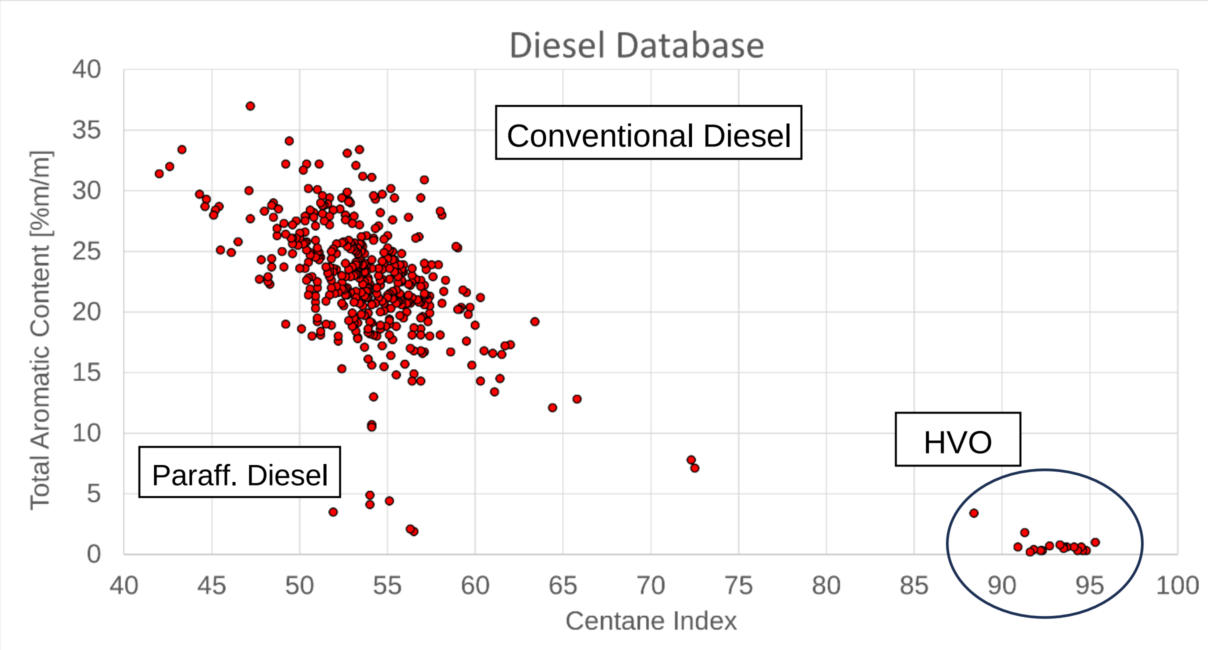

Figure 1: Total Aromatic Content (ARO) vs. Cetane Index of the diesel database

Note that a low aromatic content alone is not sufficient to distinguish HVO100 from other paraffinic diesels. Only substances with high cetane index and low total aromatic content fulfill the requirements of an HVO100.

FTIR is a suitable technique to measure the total aromatic content of a fuel and the results correlated very well with alternative methods like GC. However, the cetane index cannot be measured directly. The difference in the cetane index of HVO100 and other fuels relates to differences in the hydrocarbon chain length distribution. The difference in the hydrocarbon chain length distribution can be assessed via the CH_2 bending vibration around 1465 [cm^{-1}] as shown in Figure 2.

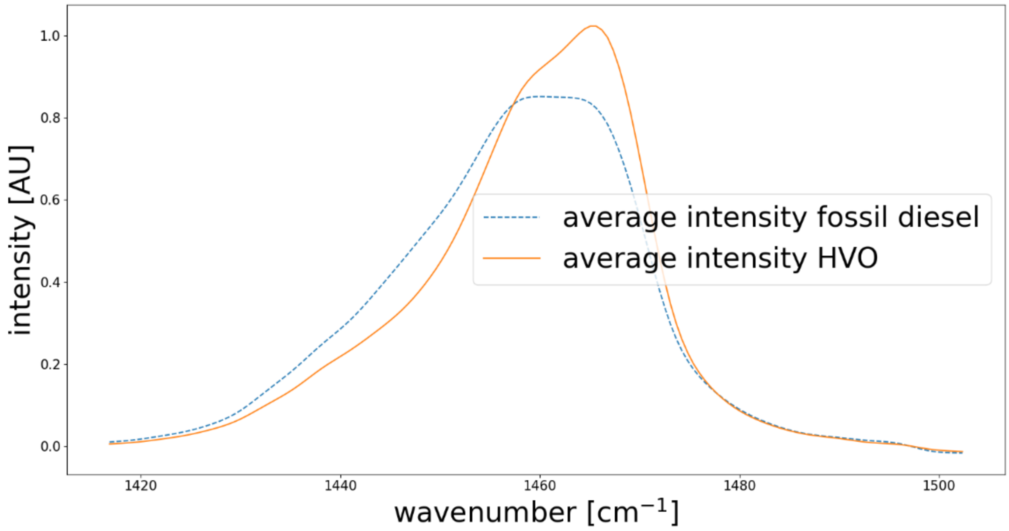

Figure 2: CH_2 bending vibration for HVO100 (red) and conventional diesel (blue)

This peak is generally too strong to be measured accurately in a 100 µm cell, which is the standard measurement cell for diesel measurements in era**spec**. Hence, an additional measurement in a 20 µm cell is required to accurately determine this peak. To quantitatively describe the difference in the shape of this peak for different fuels, a new parameter called HVO_indicator was developed.

Figure 3 shows the HVO indicator vs aromatic content, both determined directly from the FTIR spectrum. Using the results for aromatic content and the HVO indicator in combination makes it possible to single out the HVO100s from all other fuels.

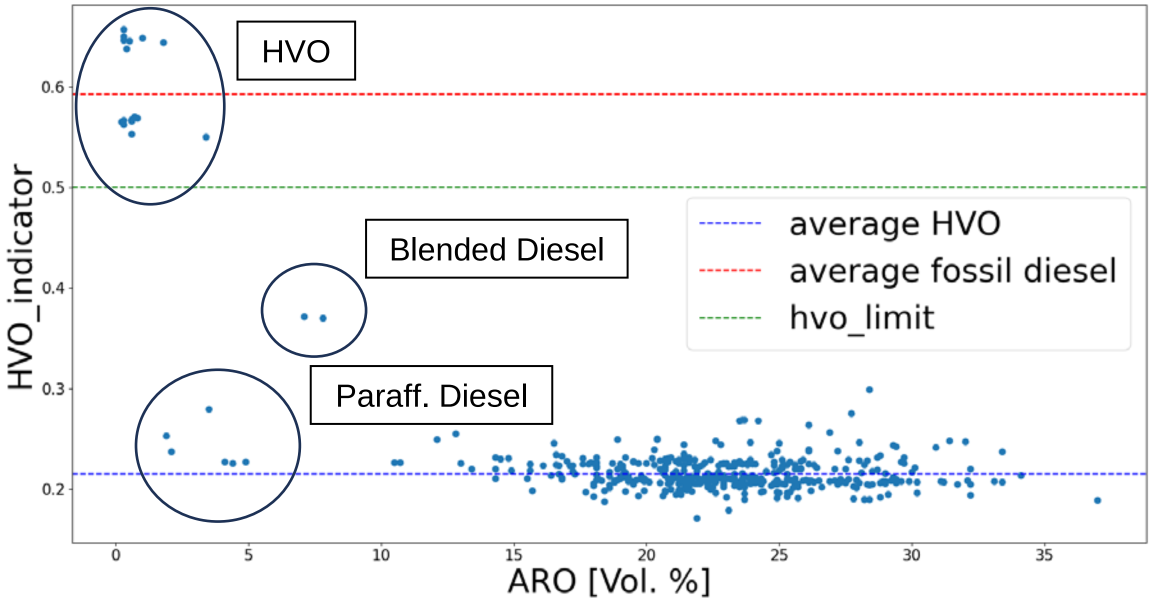

Figure 3: Calculated HVO_indicator vs. total aromatic content (ARO) [%] of the diesel database

Based on the FTIR measurement, the HVO concentration is calculated with the formula,

$$C_{HVO}[\%] = 100\% - C_{ARO}[\%] - C_{PNA}[\%] - C_{Cetaneimprover}[\%] - C_{FAME}[\%]$$

where C_{ARO} is the MLR predicted total aromatic content (ARO), C_{PNA} is the MLR predicted polycyclic aromatic content (PNA), $C_{Cetane\ improver}$ is the concentration of cetane improver and $C\__{FAME}$ is the FAME concentration.

For the HVO100 samples, the HVO concentration was determined in the range from 99.9 % to 97.0 %.

Limitations

While the method is suitable for distinguishing HVO100 from conventional diesel, it does have limitations for mixtures of HVO with conventional diesels as shown in Figure 3. The addition of 10 % to 20 % of conventional diesel to a HVO100 sample would not lower the HVO_indicator below the threshold value and these samples are therefore detected as HVO100. If 30 % or more diesel is added, these samples are detected as conventional diesel and are no longer reported as HVO100.

At this point, it also must be explained that, chemically speaking, HVO belongs to the group of isoparaffins, which also includes representatives from fossil raw materials. A well-known example is gas-to-liquid products (GTL), which are produced based on the Fischer-Tropsch process with the use of natural (fossil) gas. Only analyzing the ^{14}C content allows a distinction to be made between biogenic and fossil origins. This is done using accelerator mass spectroscopy (AMS) or liquid scintillation (LCS) as described in ASTM D6866, both of which are lab methods requiring very expensive equipment, making routine screening of fuel at gas stations or terminals impossible.

Conclusion

A new method for detection of HVO100 using the era**spec** FTIR fuel analyzer has been developed. The presented data clearly demonstrates the capability to distinguish HVO100 from conventional diesels and even from paraffinic diesels with moderate cetane index. This paves the way for on-site measurement of “premium diesel” to prevent accidental or deliberate mix-up.

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