Direct analysis of conjugated diolefins in hydrotreated pyrolysis gasolines by NIR spectroscopy

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Introduction

Pyrolysis gasoline (Pygas) is a by-product of the ethylene manufacturing process. Pygas cannot be directly used as a motor fuel due to the presence of small amounts of conjugated diolefins (1–30 mg.g⁻¹) which cause gum formation in engine parts. These diolefins are converted to olefins in a Selective Hydrogenation Unit (SHU) to reduce their levels to approximately 1 mg.g⁻¹ while leaving all the other components in the Pygas almost completely unaffected. A wet chemical method is routinely used to indirectly determine the amount of conjugated diolefin as "maleic anhydride value" or MAV, and takes several hours for a single analysis. Near infrared (NIR) spectroscopic methods for this determination have been difficult largely due to the changes of the composition of feedstocks of the ethylene process from ethane, liquid petroleum gas (LPG) or naphtha. This affects the composition in the rest of the Pygas matrix (alkenes, olefins, aromatics, and non-conjugated diolefins) which make up the bulk of the Pygas sample.

Materials and methods

A NIR method was developed for Pygas samples using an XDS Rapid Liquid Analyser (RLA; Foss-NIRSystems, Silver Springs, MD, USA). Pygas samples were poured into disposable 8 mm diameter vials, and were placed in the RLA sample holder which kept the temperature of the sample at 30°C. A 60 second equilibration time preceded the NIR scan which was complete in approximately 60 seconds. 32 scans of the sample and reference were used for each sample,.

The MAV values for the calibration and validation samples were provided by placing a fixed amount of the Pygas in a fixed volume of toluene saturated with maleic anhydride. This solution was heated to boiling and refluxed for 1 hour. The conjugated diolefins react with the maleic anhydride and the unreacted maleic anhydride is hydrolysed to maleic acid, which is then titrated with a NaOH solution. The MAV result is the number of milligrams of maleic anhydride that react with 1 gram of sample.

Results and Discussion

The conjugated dienes are spectrally distinct from the other compounds in the Pygas (aromatics, alkenes, non-conjugated diolefins and alkanes; Figure 1). It should also be noted that the various conjugated diolefins present in Pygas do not have exactly the same features in the same positions as shown in Figure 2 and this provides a challenge for developing a robust calibration for MAV in Pygas.



Figure 1. Absorbance and second derivative spectra of Pygas components.





Figure 2. Second derivative spectra of several conjugated diolefins present in Pygas.

Pygas calibration samples consisted of samples directly from the SHU with a conjugated diolefin concentration range of 0-2 mg.g⁻¹. It is desirable to be able to measure up to 9 mg.g⁻¹ which would indicate upset conditions in the SHU. To accomplish this, samples from the SHU were spiked with various levels of pre-SHU material (from a number of production runs, covering differences in feedstocks).

The NIR spectra of the 100 calibration samples are shown in Figure 3. Samples were clear, colourless liquids: spectra exhibited only small baseline differences. The baseline differences that did manifest were due to slight changes in the glass vials (i.e. vials were not optically flat), and hence a second derivative pretreatment was performed prior to the calibration development. The second derivative spectra are shown in Figure 4. There were some notable differences in the calibration spectra, especially around 2200–2400 nm. These were due to differences in some of the major components, which vary with changes in the feedstocks. The levels of conjugated diolefins in these samples were all below 1% and were not likely to be the cause of these spectral changes. Such variations need to be characterised in the calibration models in order to develop accurate predictions for conjugated diolefin levels (as MAV), which are present in very small concentrations $(0-9 \text{ mg.g}^{-1}).$



1100 1150 1200 1250 1300 1350 1400 1450 1500 1550 1600 1650 1700 1750 1800 1850 1900 1950 2000 2050 2100 2150 2200 2250 2300 2350 2400 2450 2500 Wavelength

Figure 3. Absorbance spectra of the Pygas calibration samples.

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Figure 4. Second derivative spectra of the Pygas calibration samples.

A NIR calibration for MAV was developed using 100 samples (collected during dozens of production runs and including some samples spiked with pre-SHU liquid as discussed above); results are shown in Figure 5. The entire NIR spectral region was used in the PLS calibration (except those areas above 1.5 absorbance units) to adequately characterise the variations in the different conjugated diolefins present as well as all of the interferences from other non-conjugated diolefins and the rest of the matrix (alkanes, olefins and aromatic compounds). Samples (n = 20) from new production runs were then tested (covering also several changes in feedstocks) and the results are also shown in Figure 5. The SEP compares well to SEC for the calibration (SEC = 0.251 mg.g^{-1} , SEP = 0.244 mg.g^{-1}).



Figure 5. Calibration and validation results for MAV.

Conclusion

Previous studies¹ have developed calibrations by doing spectral subtractions of material before and after the Selective Hydrogenation Unit (to reduce the effects of the different feedstocks). In contrast, the work presented here used the spectra of the final Pygas without spectral subtraction in the development of a calibration for MAV. It was found that samples from a wide variety of feedstocks were needed in the calibration set to develop a model that would give accurate results in all situations in the Pygas plant.

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References

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