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Fuel Blend Analysis using the Cary 630 Spectrometer and 5 Bounce ZnSe ATR accessory

Authors

Andreas Kerstan,

Agilent Technologies,
Waldbronn, Germany

Anja I. Lampe, Anna K. Dittmar,
Carina Heyen, Johannes Kiefer,

Universität Bremen,
Bremen, Germany

Abstract

Replacing or at least reducing environment-impairing fossil fuels by biofuels is one of the major energy topics of this century. That is why nowadays commercial fuel are already blends of petrochemicals and biofuels. Gasoline is mixed with ethanol, Diesel is mixed with biodiesel.

Another potential biofuel seems to be butanol, which can be produced by acetone-butanol-ethanol fermentation. Since petrochemical feedstock basically consists of hydrocarbons and hence adding alcohols and ester compounds may have significant impact on handling and performance, there is an urgent need for analytical methods to determine biofuel fractions and give an insight into the impact of biofuel components in fuel. FTIR is an ideal tool since it provides qualitative and quantitative information and provides accurate and fast information about the structural phenomena at the molecular level.

Introduction

The most preferred alcohol used as biofuel is ethanol up to now. The main reason is the very effective way of production via yeast-based fermentation. However, its very hygroscopic nature and its rather low energy density makes it very challenging in use and as a component in biofuel. Higher alcohols like butanol would be preferred candidates due to their lower hygroscopicity and increased energy density. Furthermore, it can be produced in acetone-butanol-ethanol fermentation from a variety of biomass resources. Another alternative is the production from whey permeate, wood hydrolysate, straw molasses and other monomer sugars, all components which are remaining as waste on a regular basis.

Chemical and physical properties like longer alkyl chain, the almost non-polar nature (despite the hydroxyl group), the higher cetane number (ignition capability), higher energy density and the lower vapour pressure are further good reasons for butanol in comparison to ethanol. Furthermore, it is less hygroscopic and less corrosive so that it can be added to commercial fuel or used in a conventional engine in its pure form. Butanol has a two-fold higher viscosity and is very close to commercial diesel fuel, which has a positive influence on atomization and spray formation in the motor.

What is not understood so far about the use of butanol as biofuel, are mixing effects and the ideal amount of butanol in the mixture. The control about mixing effects is crucial since a highly non-ideal thermodynamic and physicochemical behavior can have a huge influence on properties and engine performance. Also, de-mixing inside the tank must be avoided. The full understanding of all the underlying structure-property relationships and the inclusion into a final computational model (simulation) is the final goal of this project.

To evaluate fuel quality and optimize engine performance there is always a need for suitable analytical methods and techniques. Over the years, commercial fuels became more and more complex and efficient combustion became the main criterion (additives, content of biofuel). A full on-board analysis for the fuel before entering the engine is desirable, but too expensive. The current trend is towards robust, reliable and cheap analytics.

Fourier Transform Infrared (FT-IR) spectroscopy is a powerful tool for biofuel analysis since it provides quantitative information about the fuel composition and insights into the phenomena at the molecular level. Hence it allows studying macroscopic and molecular mixing effects in fuel blends.

The major benefits of FTIR in comparison to other techniques are:
- fast measurement times (some seconds)
- non-destructive sample analysis
- no need of consumables
- molecular finger-printing
- sensitivity to molecular interactions
- negligible sample preparation
- no interferences such as fluorescence

For this application a Cary 630 FTIR from Agilent Technologies was used since it has the smallest laboratory footprint and saves a lot of space. It is very easy to use, even for unexperienced users due to the illustrated and very intuitive Microlab Software. The compact size allows measurements in a glove box and unwanted effects of ambient moisture (absorption in butanol) could be avoided.

The 5 bounce Attenuated Total Reflectance (ATR) accessory used in this work can be easily coupled to the Cary 630 engine which is equipped with an RFID reader for automatic accessory recognition. No alignment is necessary and the use and cleaning is easy and straightforward. Due to the overall design (direct connection to the accessory, no sample compartment and no additional mirrors) the Cary 630 provides more energy throughput than any other ATR units in its class. For the 5 bounce ATR the following effective pathlengths can be obtained:

Crystal type	Effective pathlength
5 bounce ZnSe crystal	5.5 µm at 4,000 cm^{-1}
	13.0 µm at 1,700 cm^{-1}
	36.5 µm at 600 cm^{-1}

The Cary 630 + 5 bounce ATR covers a spectral range from 4000 – 650 cm-1. The multi-language software guides the user through all steps of the operation, while color coding alerts make it easy to see whether samples meet the specifications. The software also provides a feedback mechanism to advise when the accessory requires cleaning, ensuring you get the right answers every time.

Designed originally for out-of-lab use in Agilent mobile FTIR products, the Cary 630 FTIR is the most rugged FTIR on the market today. Available with ZnSe windows that are optimized for superior energy throughput, the 5 Bounce ZnSe ATR can be used in the most humid and tropical environments, providing answers you can trust, day-in/day-out.

The switch between using the 5 Bounce ZnSe ATR and DialPath/TumblIR for all your liquid measurements is extremely simple. No alignment is required, and the accessory changeover is complete within seconds. The Cary 630 FTIR allows you to measure any liquid of any concentration with any pathlength in seconds. The 5 Bounce ZnSe ATR takes up only 9.2 x 8.9 cm of bench space and weighs just 0.9 kg (2 lb). Although easy to use, single bounce ATR does have the limitation of low sensitivity compared to other ATR techniques. Many methods now require multi-bounce ATRs because of the greater sensitivity they provide. The 5 Bounce ZnSe ATR improves levels of detection while still providing the ease-of-use of a single bounce ATR.

Experimental

1-Butanol came from VWR with 99.5 % purity; N-decane was purchased from Sigma Aldrich with 99.5 %. Blends of butanol with n-decane and diesel were prepared with a microbalance. N-decane/butanol mixtures were prepared over the full range of mole fractions between 0 and 100% butanol in steps of 10 mol%. Diesel/butanol mixtures were prepared over the full range of mass fractions between 0 and 100% butanol in steps of 10 wt%. Due to the chemical complexity of commercial diesel, mass fractions had to be used instead of mole fractions.

IR spectra of the pure substances and the blends were acquired on a Cary 630 Fourier Transform Infrared (FTIR) spectrometer (Agilent Technologies). The instrument was equipped with a ZnSe attenuated total reflection (ATR) module (5 reflections at 45°). The spectra were recorded in the range between 650 and 4000 cm−1 with a nominal resolution of 2 cm−1. Before a spectrum was recorded, the ZnSe module was cleaned and a background was collected.

The Cary 630 comes as standard with the Microlab Software which allows a very easy and intuitive spectra collection and straightforward analysis.

Results and Discussion

In some prework (data not shown; [1]) spectra of diesel, n-decane and butanol were compared. Since the spectra of diesel and n-decane are remarkably similar, n-decane seems to be a perfect surrogate for diesel from a spectroscopic point of view. It also shows that the diesel contains significant amounts of medium chain hydrocarbons.

Butanol/n-decane blends show a very systematical spectrum change with composition. Since n-decane is a pure hydrocarbon, no strong polar or hydrogen bonding interactions are expectable; this result is not very surprising.

In the next step mixing effects of butanol and n-decane were investigated and some interesting observations could be made. The investigation was done by analyzing the OH-stretch band at (e.g. 3300 cm^{-1}) region. The fit of the spectra was done by a single Gaussian profile. With increasing decane concentrations there is a shift of the OH stretch band towards higher wavenumbers. The shift is strong if small amounts of decane are added and the slope becomes less steep with increasing decane concentrations. This blue-shift is a result of a strengthening of the OH bonds and a weakening of the hydrogen bonding of the butanol molecules. For butanol this effect is stronger than for ethanol due to the longer alkyl chain of butanol and enhanced interactions with decane molecules via van der Waals forces.

The most important benefit of FTIR for this study is the capability of providing quantitative data. Two different approaches were chosen: Lambert-Beer and Partial Least Squares Regression (PLSR).

This app note focusses on the second approach, PLSR, which is less straightforward than Lambert-Beer, but well established for quantifying vibrational spectra. Partial Least Squares Regression (PLSR) is commonly used for quantitative studies and could be easily supplied to mixtures of butanol and decane. The approach was also tested with real fuel.

IR Spectra of butanol and diesel blends were recorded and analyzed. Commercial diesel contains a few percent ester compounds due to blending with biodiesel. So, the main constituents are the hydrocarbons and a few percent amount of biodiesel, i.e. ester compounds. The spectra of diesel/butanol blends are shown in Figure 1 together with the spectra of pure butanol and diesel.
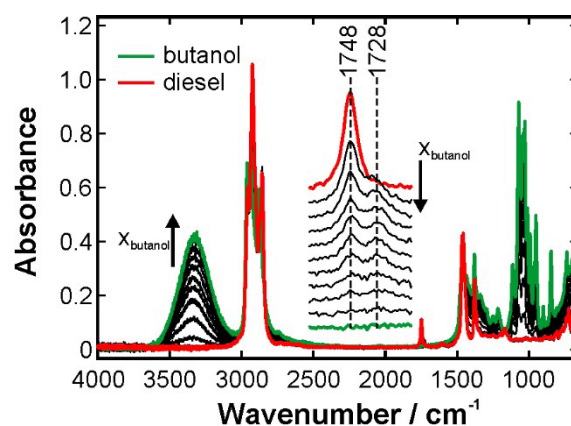
Figure 1. IR spectra of the diesel/butanol blends. The inset shows the C=O stretching region around 1750 cm−1 enlarged. Reprinted with permission from [1].

The spectra change very systematically with composition. Due to the fact that diesel contains polar ester groups exhibiting oxygen atoms with a partial negative charge, dipole-dipole or hydrogen bonding interactions between the ester groups and OH groups of butanol can be observed.

The C=O stretching vibration of the diesel has a characteristic band at 1750 cm-1. The spectra of the diesel butanol blends show another weak peak around 1730 cm^{-1}. This band is due to ester groups forming hydrogen bonds with the alcohol molecules. The strong hydrogen bond has the effect of a weakened covalent C=O bond and hence the red-shifted mode. At low diesel concentrations below 40 % both peaks at 1748 cm-1 and 1728 cm-1 exhibit similar intensity. A significant amount of ester groups, but by far not all, are hydrogen-bonded to butanol. This is possibly due to steric hindrance and because the butanol-butanol hydrogen bonds are energetically more stable and thus are favorable.
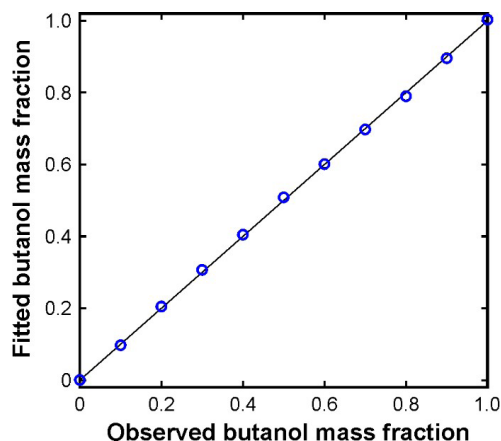
Figure 2. Results of the PLSR analysis of the IR spectra of the diesel/butanol blends. Reprinted with permission from [1].

Looking at the butanol OH stretch band, a blue-shift can be observed which is very unusual for a formation of a hydrogen bond, typically showing red-shifts. For butanol another effect seems to be dominant. Butanol already has rather strong hydrogen bonding in the neat liquid. That is why the blue shift is a result of this very strong initial bonding. This suggests that the hydrogen bonds between C=O and OH groups are weaker than those bonds between two OH groups, lending further support for our hypothesis of higher energetic stability above. Furthermore, a PLSR was applied to the butanol/ diesel spectra (figure 2).

The correlation between the butanol concentration (mass fraction) and the fitted butanol mass fraction are in excellent agreement. Therefore, it can be concluded that PLSR is capable of determining the concentration of butanol in diesel and the FTIR Cary 630 with a 5 bounce ATR show reproducible and accurate performance for this task.

Conclusion

The FTIR Cary 630 was used to determine the composition of fuel blends. The spectra provided information about quantity and mixing phenomena at the molecular level. ATR was the technique of choice since it is fast, does not need sample preparation and is non-destructive. The Cary 630 with the 5 bounce ATR shows high quality and reproducible results and has proven to be the right system for this application.

References

1.Anja I Lampe, Anna K. Dittmar, Carina Heyen, Johannes Kiefer, "Butanol as potential biofuel: A spectroscopic study of its blends with n-decane and diesel", Elsevier, Fuel, Volume 222 (312-318) 2018.