

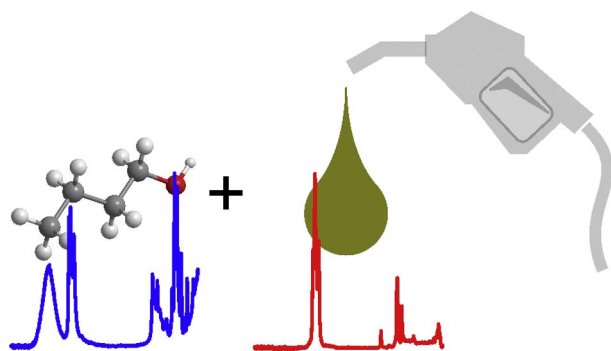


Full Length Article

Butanol as a potential biofuel: A spectroscopic study of its blends with n-decane and diesel

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GRAPHICAL ABSTRACT



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ABSTRACT

Butanol is frequently discussed as a potential biofuel as it can be produced via acetone-butanol-ethanol (ABE) fermentation. Like ethanol, it can be added to conventional petrochemical fuels in order to reduce the use of fossil fuels. However, such blending of butanol is only possible if the effects upon mixing are understood. This study makes an important step towards developing detailed knowledge of the influences butanol may exert on a hydrocarbon based fuel. Infrared (IR) spectroscopy is employed to analyze the molecular interactions in the fuel blends. In a first step, binary mixtures of butanol and n-decane, which is utilized as a single-component fuel surrogate, are studied. In the second step, blends of butanol with commercial B5 diesel fuel are analyzed. The presence of n-decane weakens the hydrogen bonding interactions between the butanol molecules. When butanol is added to diesel, strong interactions with the biodiesel components containing ester groups are found. Moreover, the potential of using IR spectroscopy for the quantitative analysis of the blends is evaluated. It is shown that the spectra allow a very accurate measurement of the butanol content.

1. Introduction

Alcohol compounds represent an important class of biofuels. Amongst them, ethanol is the most widely distributed one despite its

highly hygroscopic nature and comparatively low energy density [1]. Nevertheless, the yeast based fermentation processes to produce ethanol from sugar feedstocks are very efficient. This makes ethanol an economically viable biofuel. However, if there were ways to produce

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Table 1

Properties of ethanol, butanol, n-decane, and diesel fuel. The data are taken from the NIST Chemistry Webbook [24], the Dortmund database [25], the CRC Handbook of Chemistry and Physics [26], and the EN 590 standard for diesel fuels.

	Ethanol	Butanol	n-Decane	Diesel (EN590)
Density in g cm^{-3}	0.79	0.81	0.73	0.82–0.845
Specific energy in MJ/kg	26.8	33	44.2	42.5
Melting point in $^{\circ}\text{C}$	–115	–89	–30	
Boiling point in $^{\circ}\text{C}$	78	118	174	170–390
Vapor pressure (@20 $^{\circ}\text{C}$) in hPa	58	6.67	1.66	
Autoignition temperature in $^{\circ}\text{C}$	400	325	200	220
Flash point in $^{\circ}\text{C}$	12	35	46	> 55
Octane number	130	96	–30	
Cetane number	8	25	77	> 51

higher alcohols with the same efficiency, they would certainly be preferred as they exhibit significantly lower hygroscopicity and increased energy density. For instance, butanol is a very promising candidate. It can be produced by acetone-butanol-ethanol (ABE) fermentation from a variety of renewable biomass resources [2,3]. Besides the production from agricultural products, it can be made from whey permeate [4], wood hydrolysate [5], straw molasses [6], and other monomer sugars such as glucose [7], which promise an immense advantage as all those resources remain as waste on a regular basis. It means reducing the competition of producing biofuels with food and animal feed [8].

The chemical and physical properties of butanol are advantageous compared to ethanol. A selection of these properties is summarized in Table 1. Butanol has a longer alkyl chain, which means a higher miscibility in petrochemical fuels like diesel and gasoline [9]. Despite the polar hydroxyl group, butanol can be considered as an almost non-polar chemical. Further benefits are the higher cetane number, higher energy density, and lower vapour pressure. Additionally, it is less hygroscopic and less corrosive so that it can either be added to commercial fuels or it can even be used in its pure form in a conventional engine [10]. For example, Zhang et al. have shown that the pollutant emission from heavy duty diesel engines can be reduced by adding butanol [11]. Regarding the atomization and spray formation inside the engine, the viscosity and surface tension are further important parameters. The viscosity of butanol is about the twofold of ethanol (2.5 vs. 1.2 mPa s) and rather close to the value of commercial diesel fuels, see for instance [12]. The surface tension of butanol is also closer to that of diesel than ethanol [13].

Two important pre-requisites need to be fulfilled before butanol can be mixed with a commercial fuel like diesel: the mixing effects need to be understood and measurement techniques for quantifying the amount of butanol need to be in place. The mixing effects are important as mixtures can exhibit highly non-ideal thermodynamic and physico-chemical behavior making the prediction of the properties and engine performance difficult. In addition, de-mixing inside the tank must be avoided. The ultimate goal would be to develop a full understanding of the structure-property relationships to enable the determination of the properties from a simulation and hence eliminate the need for measurements of a series of properties. The underlying knowledge of suitable computational models must include the properties of the individual components and the molecular interactions in the mixture. These interactions represent the mixing effects at the molecular level and hence determine the microscopic and macroscopic behavior. A prominent and dramatic example for such mixing effects are the aqueous solutions of dimethyl sulfoxide (DMSO), a common solvent and anti-freeze. At the eutectic point, the freezing point is more than 70 K lower than what can be expected for the ideal mixture. This depression is attributed to the molecular interactions and dynamics in the mixture [14–16].

On the other hand, analytical methods are important to ensure a certain fuel quality and to optimize engine performance. The ever-increasing complexity of commercial fuels (additives, content of biofuels,

etc.) [17] combined with an increasing desire for efficient combustion in terms of fuel efficiency and pollutant emission call for advanced control concepts to optimize the combustion process. Such concepts could include an on-board fuel analysis or the communication between the fuel pump of the gas station equipped with analytical devices and a smart car. On-board fuel analysis could mean that the fuel is analyzed before it enters the engine. The knowledge of the detailed fuel composition would allow controlling the engine and optimizing its performance. The main obstacle for such technology is certainly the associated costs; hence, there is a need for developing robust, reliable, and cheap analytics.

Suitable analytical concepts can vary from conventional approaches such as chromatography to advanced spectroscopic methods. Santos et al. demonstrated the use of nuclear magnetic resonance (NMR) spectroscopy for the simultaneous assessment of the quality parameters in commercial diesel samples [18]. The applications of vibrational spectroscopy to fuel analysis have recently been reviewed [19]. Concerning the analysis of diesel fuels it was concluded that infrared (IR) spectroscopy is a particularly powerful tool. Basically, it can deliver information about both, the chemical composition and the mixing effects. Near-infrared spectroscopy has shown its potential as well [20,21].

In this study, IR spectroscopy is employed to analyze blends of butanol with n-decane and commercial diesel fuel. It builds on our previous work on ethanol-gasoline blends [22,23]. N-decane was chosen as a single-component model fuel for the first part of this study because it is a common constituent of gasoline and diesel. First, the IR spectra of butanol-decane blends are investigated to unravel their behavior at the molecular level and to test analytical strategies for quantifying the butanol content. Second, the butanol-diesel blends are studied.

2. Experimental

1-Butanol with a purity > 99.5% was purchased from VWR (AnalaR Normapur Butan-1-ol) and used as received. N-decane with a purity > 95% was purchased from Sigma Aldrich (Fluka Decane; purum $\geq 95.0\%$) and used as received. Diesel was purchased from a local gas station (ORLEN Deutschland GmbH, STAR petrol station) and used as received.

Blends of butanol with n-decane and diesel were prepared gravimetrically using 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.

3. Results and discussion

3.1. IR spectra of the pure substances

The spectra of the three unmixed decane, butanol, and diesel samples are displayed in Fig. 1. In the following, only a brief interpretation and analysis is provided according to Nyquist [27]. The butanol spectrum exhibits a strong and broad band between 3000 and 3600 cm^{-1} , which can be attributed to the OH stretching vibrations of the hydroxyl group. In the range 2700 – 3000 cm^{-1} , the CH stretching modes can be found. In the diesel and n-decane spectra they appear in the same

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