Fuel 141 (2015) 136–142

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Characterization of gasoline/ethanol blends by infrared and excess infrared spectroscopy

Stella Corsetti [a,b], Florian M. Zehentbauer [a,c], David McGloin [b], Johannes Kiefer [a,c,d,*]

[a] *School of Engineering, University of Aberdeen, Fraser Noble Building, Aberdeen AB24 3UE, Scotland, United Kingdom*
[b] *SUPA, Division of Physics, School of Engineering, Physics and Mathematics, University of Dundee, Nethergate, Dundee DD1 4HN, Scotland, United Kingdom*
[c] *Technische Thermodynamik, Universität Bremen, Badgasteiner Str. 1, 28359 Bremen, Germany*
[d] *Erlangen Graduate School in Advanced Optical Technologies (SAOT), Universität Erlangen-Nürnberg, Erlangen, Germany*

HIGHLIGHTS

- Frequency-shifts and excess absorbance suggest alcohol self-association via hydrogen bonding.
- High sensitivity and accuracy can be obtained using the alcoholic CO stretching mode for quantitative measurements.
- FTIR provides a fast and straightforward tool for measuring the chemical composition of a blend.

ARTICLE INFO

Article history:
Received 8 July 2014
Received in revised form 9 October 2014
Accepted 14 October 2014
Available online 28 October 2014

Keywords:
Biofuel
Fossil fuel
Alcohol
Excess absorption
Frequency shift

ABSTRACT

Fuels for automotive propulsion are frequently blends of conventional gasoline and ethanol. However, the effects of adding an alcohol to a petrochemical fuel are yet to be fully understood. We report Fourier-transform infrared spectroscopy (FTIR) of ethanol/gasoline mixtures with systematically varied composition. Frequency shifts and excess infrared absorbance are analyzed in order to investigate the mixture behavior at the molecular level. The spectroscopic data suggest that the hydrogen bonding between ethanol molecules is weakened upon gasoline addition, but the hydrogen bonds do not disappear. This can be explained by a formation of small ethanol clusters that interact via Van der Waals forces with the surrounding gasoline molecules. Furthermore, approaches for measuring the chemical composition of ethanol/gasoline blends by FTIR are discussed. For a simplistic approach based on the Beer–Lambert relation, an optimized set of parameters for quantitative measurements are determined. The best compromise between measurement sensitivity and accuracy is found for the CO stretching mode of the alcohol. For the traditional method of calibrating the ratio of integrated band intensities of the CH and OH stretching regions it is found that narrowing the spectral window of the CH stretch can significantly improve the measurement sensitivity.

1. Introduction

The transport sector relies heavily on fossil fuels, for example in the form of gasoline, diesel, compressed natural gas (CNG) and liquefied petroleum gas (LPG). The excessive use of fossil fuels, however, is leading to the depletion of these resources (those that can be accessed easily) and is presumed to contribute to the greenhouse effect, air pollution, acid rain, ozone depletion and climate change. Pollutants generated via combustion of fossil fuels, e.g. carbon monoxide and dioxide, unburned hydrocarbons (UHC), nitrous oxides (NOx), hydrofluorocarbons (HFC), and perfluorocarbons (PFC), pose a serious problem not only for the environment but also for human health [1]. Hence, there is a strong need for alternative fuels [2].

Biofuels may provide a feasible solution to these problems due to their natural/renewable origin and their low pollutant emissions when compared to their fossil fuel counterparts. Bio-ethanol is obtained from a variety of feedstocks such as sugar cane, corn, sunflower, fruit, grain, cotton and agricultural waste material such as straw [3]. It can also be extracted from sugar produced directly from the biosynthesis process of algae, which makes use of sunlight, carbon dioxide and sea water. There are some difficulties, however, in using bio-ethanol directly as an engine fuel. The high viscosity of ethanol hinders the atomization process during fuel

---

* Corresponding author at: Technische Thermodynamik, Universität Bremen, Badgasteiner Str. 1, 28359 Bremen, Germany. Tel.: +49 421 218 64777.
E-mail address: jkiefer@uni-bremen.de (J. Kiefer).

http://dx.doi.org/10.1016/j.fuel.2014.10.025
0016-2361/© 2014 Elsevier Ltd. All rights reserved.

injection and contributes to incomplete combustion reducing the engine efficiency and lifetime [4].

At present, many commercial fuels are mixtures of conventional petrochemical fuels and a certain amount of biofuel. Ethanol/gasoline blends up to 20% can be used in constant speed engines without any modification and no significant power reduction [5]. It was observed that a mixture of bio-ethanol with gasoline leads to a reduction of up to 6% in CO emission and up to 24% in NOx emissions when compared to the use of fossil fuel alone [6]. Blending bio-ethanol with gasoline, however, can significantly alter the fuel properties and thus the evaporation and combustion characteristics of the fuel [7]. As a consequence, the past 20 years have seen significant research effort aimed at understanding the influence of ethanol on the physicochemical properties of fuel blends, for example the vapor pressure [8], the viscosity [9], and the density [10]. Other works studied the effects of ethanol addition on the fuel performance in terms of spray formation [11,12] and combustion behavior [13,14]. Understanding the fundamental nature of the changed properties and behavior, however, is highly desirable as it would help to predict the macroscopic phenomena without extensive experimental testing.

The aim of this work is to develop an understanding of the behavior of ethanol/gasoline mixtures at the molecular level. For this purpose, the ethanol blends of a gasoline surrogate with systematically varied ethanol content are studied using Fourier-transform infrared spectroscopy (FTIR). In the past, IR and near-IR spectroscopy was mainly used for determining the ethanol content in gasoline in a small number of studies [15–17]. In this paper, we analyze the IR spectra of ethanol/gasoline blends across the full composition range, i.e. from pure ethanol to pure gasoline surrogate in systematically varied concentration steps. Frequency shifts as well as excess infrared absorbance are evaluated in order to infer information about molecular interactions in the mixtures. Furthermore, methods for determining the chemical composition of the mixtures from the IR spectra are discussed.

2. Experimental section

2.1. Fuel blends

A gasoline surrogate was prepared by mixing iso-octane (2,2,4-trimethylpentane, purity > 99%) and n-heptane (purity > 95%) with a ratio of 1:1 by weight. Different ethanol/gasoline blends were prepared with systematically varied ethanol (purity > 99%) percentage (by weight) in 10% increments. The samples span the entire composition range from pure gasoline to pure ethanol. All blends were prepared gravimetrically using an analytical balance.

2.2. FTIR spectroscopy

The IR spectra of the solutions were collected over the range from 500 to 4000 cm^{-1} using a Bruker Vertex v70 spectrometer. The nominal resolution was 1 cm^{-1}. In order to increase the signal to noise ratio, for every sample 32 scans were averaged. The instrument was equipped with an attenuated total reflection (ATR) module (diamond, one reflection, 45°). During the measurements the samples on the ATR crystal were covered with a small glass cap to avoid sample evaporation. All measurements were carried out at 294 K.

3. Results and discussion

The IR spectra are analyzed in different ways reflected by the organization of this section. In a first step, the unprocessed spectra are studied with respect to peak positions and frequency shifts. Thereafter, the excess absorbance spectra are calculated and analyzed. Eventually, methods for obtaining compositional analysis are tested.

3.1. Infrared spectra

The infrared spectra of the gasoline surrogate, the pure ethanol and the blends are displayed in Fig. 1. There are no absorption peaks from gasoline in the OH stretching region between 3000 and 3600 cm^{-1} and in the CO stretching region from 1020 to 1120 cm^{-1}, while ethanol exhibits distinct bands in those regions. The peak absorbance of the OH stretching band is observed at 3319 cm^{-1}. Further characteristic features of ethanol can be found in the fingerprint region. The dominant feature is a peak doublet at 1046 and 1088 cm^{-1}, which can be assigned to the symmetric and asymmetric CO stretches, respectively. In the CH bending and stretching regions (1200–1600 cm^{-1} and 2800–3000 cm^{-1}, respectively) overlapping vibrational bands of ethanol and gasoline can be found.

Fig. 2 shows the enlarged CH stretching region where contributions from ethanol and gasoline alkyl groups overlap. However, there are sub-regions, which are dominated by either the gasoline or the ethanol. Ethanol vibrational modes are identified at 2973, 2928 and 2881 cm^{-1}. The predominant bands of the hydrocarbons in the gasoline surrogate can be found at 2956 and 2925 cm^{-1} (asymmetric CH stretching vibrations) as well as 2873 and 2861 cm^{-1} (symmetric CH stretching vibrations). The gasoline spectrum crosses the ethanol spectrum in the isosbestic points at 2966, 2896, 2876, and 2846 cm^{-1}. These points represent the wavenumbers at which the absorbance of the mixture remains invariant and ethanol and gasoline absorb the same amount of light. The range between 2966 and 2896 cm^{-1} (highlighted in Fig. 2) is dominated by gasoline but with a background from ethanol. Considering the entire CH stretching region, the integrated absorbance decreases with increasing percentage of ethanol.

The CH bending region is displayed enlarged in Fig. 3. As found in the stretching region, contributions from ethanol and gasoline methyl and methylene groups can be observed. Again, there are sub-regions, which are dominated either by the gasoline or by the ethanol bands. Peaks from ethanol appear at 1455, 1448, 1419, 1479, 1328 and 1275 cm^{-1}, peaks from the gasoline components at 1468, 1393, 1379, 1365, 1353, 1282, 1248, 1207 cm^{-1}. Isosbestic points can be found at 1480, 1459, 1368 and 1369 cm^{-1}. The range between 1480 and 1459 cm^{-1} (highlighted in Fig. 3) is dominated by gasoline but with a background from ethanol.

Fig. 4 shows the asymmetric and symmetric CO stretching modes of ethanol. They represent rather isolated lines at 1088 and 1046 cm^{-1}, respectively. Interestingly, both peaks are

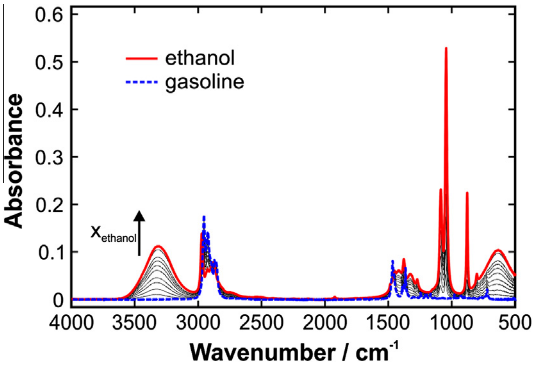

Fig. 1. FTIR spectra of the gasoline surrogate, the pure ethanol and the blends.