



Full length article

When 2nd generation biofuel meets water – The water solubility and phase stability issue



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ARTICLE INFO

Keywords:

Biofuels

Water

Phase stability

Liquid–liquid equilibria

ABSTRACT

Greenhouse gas emissions from the transportation sector could be reduced by using biofuels. To avoid competition with the food chain, second generation biofuels produced from lignocellulosic biomass are of major interest. The interaction of second generation biofuels and water needs to be studied since water is known to have major impacts for first generation biofuels. In this work, we explore the water solubility and phase stability for second generation biofuels from catalytic conversion of biomass. Tetrahydrofurans are potential biofuels for compression ignition engines. We find that the water solubility in tetrahydrofurans is increased by a factor 200 compared to Diesel. In furans, suitable as fuels for spark ignition engines, the water solubility is 4 orders of magnitude larger than in gasoline. In blends of biofuels, water solubility can either be increased or decreased depending on the blend component. Water can strongly influence the miscibility of biofuel-blends: adding small amounts of water to a γ -valerolactone – di-*n*-butyl ether blend leads to phase separation resulting in two organic phases with different combustion behavior. At the same time, the biofuels studied dissolve much better in water, which is relevant for potential environmental impacts. The phase behavior with water is thus shown to be an important key performance indicator for the development of biofuels.

1. Introduction

Depleting fossil fuel resources as well as rising greenhouse gas emissions have generated the need to find ways to produce transportation fuels from renewable sources. The transportation sector is responsible for around 70% of the CO emissions as well as around 20% of the CO₂ emissions [1]. Moreover, it consumes around 60% of the world's oil [2]. A potential renewable energy source for transportation are biofuels. Currently, the most produced biofuel is ethanol: in 2014, around 90 billion litres were produced worldwide [3]. However, a large fraction of this ethanol is still a “first generation” biofuel, *i.e.*, it is produced from edible feedstock. Bioethanol is produced by fermentation of sugars derived from corn starch or sugar cane. With a rising world population, producing fuel from edible feedstock is not a sustainable solution to the world's energy needs.

This is why much effort is devoted to the production of biofuels from lignocellulosic biomass, which is not an edible feedstock, such that these so-called “second generation biofuels” do not compete with the food chain. One option of using lignocellulosic biomass for the production of biofuels is the acidic or enzymatic hydrolysis of biomass into sugar and its subsequent fermentation to lignocellulosic ethanol [4–6]. The advantage of this method is that ethanol is a well established fuel

blend component in the transportation sector, and no infrastructural changes have to be made. Another option is the gasification of the biomass to syngas, and the subsequent production of hydrocarbons by the Fischer–Tropsch process. The hydrocarbons can directly be used as fuels. These approaches, however, do not exploit the “rich molecular structure of biorenewables synthesized by nature”, as pointed out by Marquardt et al. [7]. The molecular structure of lignocellulose (*i.e.* cyclic pentoses and hexoses, and aromatic alcohols) can be maintained by catalytic conversion of lignocellulosic biomass. The catalytic conversion approach leads to a very rich portfolio of chemical compounds explored in many recent studies [8–20].

For first generation biofuels and conventional fuels it has been shown that water can lead to several problems: reduced energy density, phase separation resulting in gelling and pipe plugging [21,22], and accelerated biodegradation of biodiesel [23]. In some cases, the presence of water in the fuel may even be beneficial to the combustion process, as it decreases the combustion temperature leading to a reduction in nitrogen oxide and particulate emissions [24,25]. Water solubility and blend stability has therefore been extensively studied for conventional fuels and first generation biofuels [26–34]. Moreover, fuel solubility in water needs to be considered for environmental purposes. The solubility of gasoline and Diesel in water is fortunately very low

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and already well described [35–38], as is the influence of ethanol and other blending agents on the solubility of gasoline in water [39–49] and gasoline biodegradation [50,51].

In addition to the same water-related problems that occur to conventional fuels, the presence of an aqueous phase next to a biofuel blend can lead to the extraction of the oxygenates from the fuel phase, such that the properties of the biofuel blend leave the specification range. This suggests that mutual solubility with water should be addressed during the development of novel biofuels and not only thereafter. Still, mutual solubility with water and blend stability are not always listed as key performance indicator for second generation biofuels [52].

Blending biofuels with conventional fuels also impacts various fuel properties. However, most of the studies on this topic only blend a small percentage of oxygenates with conventional fuels. Moreover, most studies concentrate directly or indirectly on the combustion behavior of the biofuel blends by measuring ignition properties or vapour pressures [53–57]. Studies on biofuel solubility with water either investigate the amount of water that the biofuel is able to take up [53], or are of ecotoxicological nature and thus concentrate on the solubility of oxygenates in groundwater as well as on solubilizing effects of oxygenates on conventional fuel components [55]. However, a few recent studies investigate the phase behavior of biofuel blends and water [58,59,53,34,60–62]. They mainly concentrate on alcohols, and investigate the LLE from a process engineering point of view as a means for solvent selection during biofuel production.

In this work, the water solubility and blend stability are explored for second generation biofuels. Thereby, we identify water-related key performance indicators for novel biofuels. We study a set of promising second generation biofuels obtained from the catalytic conversion of biomass. These structures are often oxygen-rich compared to conventional fuels such that stronger interactions with water have to be expected. In particular, we study biomass-derived furanic compounds as well as γ -valerolactone (GVL) and 2-butanone.

Despite a research octane number of 85 [63] and a low cetane number, 2-methyltetrahydrofuran (2-MTHF) has been shown to have combustion properties suitable for compression ignition (Diesel) engines when blended with di-*n*-butyl ether (DNBE) [64]. DNBE cannot yet be produced from lignocellulosic biomass. However, an isomer of DNBE, 1-octanol, has been successfully produced from lignocellulosic biomass [65]. 1-octanol can be added to Diesel fuel, and the combustion of Diesel – 1-octanol blends shows reduced particulate matter emissions compared to Diesel [66,67]. Alternative biofuels with promising combustion properties in Diesel engines are 3-methyltetrahydrofuran (3-MTHF), 2,5-dimethyltetrahydrofuran (2,5-DMTHF), 2-butanone, and γ -valerolactone, which can also be synthesized from lignocellulosic biomass [68–74].

In spark ignition (gasoline) engines, 2-methylfuran (2-MF) [75–77] and 2,5-dimethylfuran (2,5-DMF) [78,79] have shown promising results. They can also be derived from lignocellulosic biomass [69]. Today, ethanol can also be produced from lignocellulosic biomass. As it is often added to gasoline, we investigate the influence of ethanol on the mutual solubility of biofuel-blends for spark ignition engines and water.

The studied biofuels are summarized in Table 1. The mutual solubilities of the biofuels with water were measured at 283.15 K, 293.15 K, and 303.15 K. Moreover, the liquid–liquid equilibria of the biofuel-blends listed in Table 1 with water were investigated.

The experimental workflow is given in Section 2. The results of this work are presented in Section 3. First, biofuels for compression engines are discussed. Mutual solubilities of the tetrahydrofurans (THFs) with water are reported, and the phase behavior of the THFs, γ -valerolactone, and 2-butanone blended with DNBE or 1-octanol, respectively, with water is presented. Then, the biofuels for spark ignition engines are discussed. Conclusions are given in Section 4.

Table 1

List of the biofuel-blends investigated in this work.

Compression ignition	Spark ignition
2-MTHF – DNBE	2-MF – heptane
2-MTHF – 1-octanol	2,5-DMF – heptane
3-MTHF – DNBE	2-MF – ethanol
3-MTHF – 1-octanol	2,5-DMF – ethanol
2,5-DMTHF – DNBE	
2,5-DMTHF – 1-octanol	
γ -valerolactone – DNBE	
γ -valerolactone – 1-octanol	
2-butanone – DNBE	
2-butanone – 1-octanol	

2. Materials and Methods

Liquid–liquid phase equilibria (LLE) of biofuels and biofuel blends and water were measured. The LLE measurements are performed in a highly automated workflow. The automated platform consists of a liquid-handling autosampler, a gas chromatograph (GC), a temperature controlled tray, and a thermostat. The autosampler prepares the LLE. Chemicals from reservoirs are transported into 1.5 mL GC-vials according to the overall composition of the LLE. The prepared LLE have a total volume of 1 mL. After equilibration, samples are taken from the upper and the lower phase, and are injected into the GC without dilution nor addition of a standard. A full description of the automated setup can be found in Dechambre et al. [80]. The list of chemicals and the gas chromatography parameters used to quantify the components can be found in the [Supplementary Material](#).

3. Results and discussion

3.1. Biofuels for compression ignition engines

3.1.1. Partially miscible binary subsystems

First, the water solubility has been determined in 2-MTHF, 3-MTHF, 2,5-DMTHF, and 2-butanone at 283.15 K, 293.15 K, and 303.15 K (Table 2). Water is slightly more soluble in 3-MTHF than in 2-MTHF. The water solubilities in 2-MTHF and in 3-MTHF range between 15 mol-% at 283.15 K, and 19 mol-% at 303.15 K. The values agree with data from the literature: Stephenson reports a water solubility in 2-MTHF of 16.9 mol-% at 292.45 K [41]. The water solubility in 2,5-DMTHF is decreased by almost a factor 2 compared to 2- and 3-MTHF. There is a slight temperature dependence of the water solubility, and it is much more pronounced in 2,5-DMTHF than in 2- or 3-MTHF. Most importantly, the water solubility in the THFs is up to 30 times higher than the water solubility in biodiesel [81,82]. The increase in water solubility is even higher when compared to regular Diesel fuel: At room temperature, Diesel fuel absorbs around 100 mg water per kilogram [83]. When an average molar mass of 200 g mol⁻¹ is assumed for Diesel, the water solubility corresponds to around $x(\text{H}_2\text{O}) = 0.001$. Thus, the water solubility in pure THFs is increased by up to a factor 200 compared to Diesel. The water solubility in 2-butanone ranges between 35 mol-% at 283.15 K, and 37 mol-% at 303.15 K, and is thus even about 2 times higher than in 2- and 3-MTHF.

The solubility of pure biofuels in water is shown in Table 3 for 2-MTHF, 3-MTHF, 2,5-DMTHF, and 2-butanone at 283.15 K, 293.15 K, and 303.15 K. Our measurements correspond again well to the literature data: Stephenson reports a 2-MTHF solubility in water of 3.4 mol-% at 292.45 K, and a 2,5-DMTHF solubility in water of 0.8 mol-% at 292.65 K [41]. All biofuels exhibit inverse solubility, *i.e.* mole fractions in water decrease strongly with increasing temperature. The 2- and 3-MTHF solubilities do not differ, and range between 6 mol-% at 283.15 K, and 3 mol-% at 303.15 K. The solubility of 2,5-DMTHF in water is much lower than for 2- and 3-MTHF, with values between

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