Full Length Article

Aqueous ethanol laminar burning velocity measurements using constant volume bomb methods

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ARTICLE INFO

ABSTRACT

Ethanol is attractive as a renewable fuel for spark ignition engines, and can also be used as an extender in gasoline (up to about 20% by volume) or as a major component (say above 70% by volume). There are three reasons for wanting to know the laminar burning velocity of water/ethanol/air mixtures. The first reason is that a significant fraction of the fuel calorific value is required to remove the last 10 per cent or so by volume of water from bio-ethanol, and in some applications it might not be necessary to remove all the water. The second reason is to provide extended data for model validation. The third reason is that in turbocharged engines the knock-free operating range can be extended through water addition so as to improve both output and efficiency.

Laminar burning velocity measurements with up to 40% water by volume have been made with a constant volume combustion vessel using two distinct techniques: a) imaging of the flame front during the constant pressure period and b) analyzing the pressure rise data. When the pressure rises the adiabatic core is compressed isentropically, so if a combustion model is used, a single experiment generates a sequence of measurements that include data at high temperatures (up to 600 K) and high pressures (up to 12 bar) that are relevant to spark ignition engine combustion. Data from the two methods is shown here to be consistent and in-line with published data for ethanol, and satisfactory comparisons have also been found with predictions from kinetic mechanisms for the ethanol/water/air mixtures. The constant volume combustion vessel also generates data on the Markstein length and the pressure at the onset of cellularity, with both being increased by the presence of water.

The laminar burning velocity has a direct influence on the early flame growth in a spark ignition engine, and unless the ignition timing is adjusted for slow burning mixtures there will be a significant loss of efficiency. Engine data show that even with 40% water by volume in the ethanol, combustion performance is still acceptable if the ignition timing is advanced.

1. Introduction

With environmental concern regarding the emissions of CO_2 from the transport sector, liquid biofuels are seen as a way of reducing reliance on fossil fuels whilst maintaining the high energy density provided by liquid fuels. For example, Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 [1] requires a "mandatory 10% minimum target to be achieved by all Member States for the share of biofuels in transport petrol and diesel consumption by 2020". Despite acknowledged issues regarding production and the effect of associated indirect land use change, ethanol has received much attention as a potential biofuel, and is already in use globally, either as a neat fuel (E100), or blended with a base gasoline (e.g. E85). In some

countries, such as Brazil, flex fuel engines, designed to run on any blend of gasoline and ethanol are widespread. E100 cannot easily be used in most countries as the vapour pressure is too low and this leads to difficulties in cold-starts. When gasoline is added to ethanol it increases the vapour pressure significantly because of substantial deviations from Raoult's law. Similarly, when ethanol is added to gasoline it also increases the vapour pressure significantly, and specifications for the vapour pressure of gasoline can limit the amount of ethanol that might be added.

Ethanol has been used extensively in automotive fuels primarily as a fuel extender and anti-knock agent in ethanol gasoline blends, and ethanol was considered as an alternative for reducing dependency on oil reserves as early as the 1920s [2]. The advantages of ethanol

include: higher octane number (allowing higher compression ratios) and the reduced demand on petroleum fuels. Wang et al. [3] have reported on the benefits of the higher octane rating and the separated these from the benefits associated with the higher enthalpy of evaporation. Wang et al. [3] report on tests that compare ethanol blends with hydrocarbon fuels that have matched Research Octane Number (RON) and Motor Octane Number (MON) values. At the knock-limited engine loads the ethanol fuels with a higher ethanol content allowed higher engine thermal efficiency, this is because the ignition timing need not be retarded and there was less fuel enrichment for limiting the exhaust gas temperature. This was because the higher enthalpy of vaporisation of ethanol increased the charge cooling, thereby reducing the engine knock tendency because the unburned gas temperature was lowered. Pure ethanol fuel (E100) has also been studied, for example Brewster [4] demonstrated a higher output and brake efficiency.

To minimise the impacts of ethanol production, processing routes should be examined to determine where savings in terms of energy production can be made. Some of the biggest savings are achieved by reducing the energy required for the removal of water from the bio-produced ethanol since ethanol forms an azeotropic mixture with water (95.6% by weight ethanol or 97% by volume). Fermentation will typically produce an ethanol concentration of around 12% by volume, meaning that to produce neat ethanol, extensive distillation is required. Data from Martinez-Frias et al. [5] shows that the distillation energy requirement increase almost linearly to become 10% of the Lower Heating Value (LHV) of ethanol to produce 80% by volume ethanol. There is then an asymptotic increase in energy requirements as the azeotrope is approached, so that 90% by volume ethanol requires 23% of the LHV of ethanol, with a further 14% of the energy required for dehydration beyond the azeotrope. These results are summarised in Table 1 that also defines the corresponding mass and molar compositions.

It is also important to recognise that the method of manufacturing ethanol can have a profound impact on the "Well to Tank" Greenhouse Gas (GHG) emissions. In general, advanced ethanol from residual feedstock material (e.g. waste wood, straw, bagasse from sugar cane) will give a better GHG reduction than from farmed materials. See Table 2 for selected results from the 2014 JEC/EUCAR/CONCAWE European well to wheels study [6].

Clearly the source of any external energy required for the process will strongly influence the GHG emissions. However, the way that co-products are accounted for can also have a profound impact on the GHG impact of ethanol production. Common examples of co-products are slops from sugar beet production, or Distiller's Dried Grain with Solubles (DDGS) from Maize or Wheat. These can be used for either fuel (either combusted or to produce biogas) or as animal feed (AF). A determination then needs to be made of the GHG emissions avoided through substituting the co-product of ethanol manufacture.

An additional complication is accounting for Land Use Change (LUC) to reflect the fact that the Solid Organic Content (SOC) can either decrease or increase, depending on the crop. If land is converted from cropland-pasture to maize, the SOC will decrease, and carbon will be released to the atmosphere. However, conversion of this same type of

land to miscanthus or switchgrass production is thought to sequester carbon [7,8].

In many cases, a crop going into production of biofuels comes from land which was already producing that crop, and there is no additional carbon sequestration associated with the change of use of that crop, that is no Direct LUC. However, diverting land from food to biofuel production potentially results in food crops being grown elsewhere, potentially resulting in carbon being released form an Indirect LUC. This is however extremely difficult to account for [8].

A study by Brewster et al. [9] investigated the effect of water content on the performance of a direct injection multi-cylinder turbocharged engine developed to run on E100, and found that increasing the water content resulted in reduced output and efficiency, but this can be attributed to the ignition timing not being re-optimised. The increased water content results in lower combustion temperatures and hence lower NO_x, as well as supressing knock and pre-ignition, presenting opportunity to extend the engine operating regime. Wyman and Hinman [10] report fewer volatile organic compounds (VOCs) emissions and fewer smog producing compounds. Costa and Sodré [11] compared the performance of a 1.0 litre flex-fuel engine when operated on a gasoline-anhydrous ethanol blend (22% by volume) and a hydrous ethanol fuel (6.8% water by mass), to provide a comparison with a typical ethanol blend. This study showed that it is possible to achieve a comparable power output, although advanced ignition timing is required to enable this. A further application for hydrous ethanol is in Homogeneous Charge Compression Ignition (HCCI) engines. Whilst fuel with high concentrations of water can be problematic in SI or diesel engines, HCCI is better suited to hydrous ethanol, provided the fuel can be fully vaporised before combustion. Mack et al. [12] successfully ran a HCCI engine on hydrous ethanol mixtures with up to 60% water. Hydrous ethanol also provides opportunities for steam reforming. Shimada and Ishikawa [13] tested such a system, and reported thermal efficiencies of 1.18 times that of a conventional spark ignition engine.

Whilst hydrous ethanol clearly presents opportunities for improved energy efficiency, blending with gasoline can be problematic due to the immiscibility of water and gasoline, which can lead to phase separation within the fuel blend. Ormandy and Craven [2] report on the ethanol/water/hydrocarbon phase equilibria for a number of hydocarbons, including benzene, di-methyl benzene and several alkanes (C5 to C7) and some gasolines. They show that the aromatics are more tolerant of water than the alkanes and that as the number of carbon atoms increases, then the tolerance reduces. They also report how the tolerance reduces with temperature. There have been many more recent reports on the phase equilibria of ethanol blends. French and Malone [14] consider the impact of ethanol on the vapour pressure and distillation characteristics of ethanol gasoline mixtures, and present ternary equilibrium diagrams for water and ethanol mixtures with both trimethyl pentane and toluene (methyl benzene). They include tie-lines (that can be used to identify the composition of the two phases (one being mostly ethanol and water with traces of hydrocarbons, and the other being ethanol and hydrocarbons with traces of water).

2. Measurement of burning velocity

A combustion bomb with a diameter of 160 mm was used. This has quartz windows (with a viewing diameter of 40 mm) to allow imaging of the initial stages of flame propagation using a schlieren system with a high speed camera. A pressure transducer is used to measure the pressure rise in the vessel during combustion. The premixed mixture of fuel and air is ignited using a pair of electrodes forming a spark gap at the centre of the vessel. Burning velocity measurements have been made from two methods over a range of initial temperatures (380 and 450 K), initial pressures (0.5, 1, 2 and 4 bar) and equivalence ratios in the range of 0.7–1.4, for hydrous ethanol mixtures containing up to 40% water by volume.

The two methods have been explained recently elsewhere [15], but

Table 1
The energy requirements for separating ethanol from water expressed as a percentage of the Lower Heating Value (LHV); data from (5).

Ethanol Concentration			% of LHV for Separation
%vol	%mass	%mol	
12	9.7	4.0	0
80	75.9	55.3	10
90	87.7	73.5	23
96.5	95.6	89.5	Azeotrope
100	100.0	100.0	37