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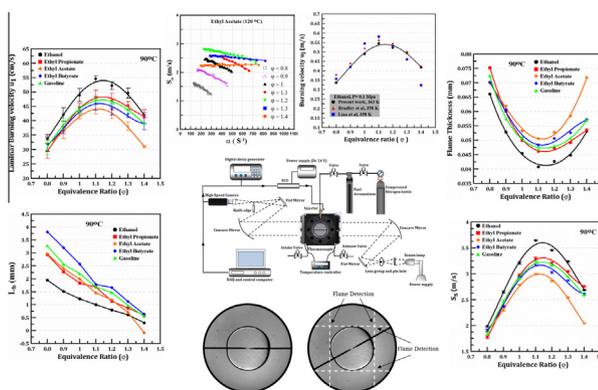
Laminar burning characteristics of ethyl propionate, ethyl butyrate, ethyl acetate, gasoline and ethanol fuels

Tawfik Badawy^a, Jake Williamson^a, Hongming Xu^{a,b,*}^a University of Birmingham, Birmingham, UK^b State Key Laboratory of Automotive Safety and Energy, Tsinghua University, Beijing, China

HIGHLIGHTS

- Effect of the initial temperature on the laminar flame speed of ester fuels in comparison with gasoline and ethanol.
- Effect of the ethyl propionate, ethyl butyrate, ethyl acetate on the flame stability.
- The highest un-stretched flame speeds occur in a range of $\phi = 1.1$ –1.2.
- Markstein number and burning velocities of ester fuels.

GRAPHICAL ABSTRACT



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ABSTRACT

Ethyl esters have been considered as promising second-generation biofuel candidates, due to the available production from low grade biomass waste. Furthermore, with desirable energy densities, emissions performance, low solubility and higher Research Octane Number (RON), ethyl esters have proven attractive as fuel additives or alternatives for gasoline. In this study, high-speed schlieren photography was used to investigate the laminar burning characteristics of three ethyl ester fuels: ethyl acetate, ethyl propionate, and ethyl butyrate, in comparison with gasoline and ethanol at different initial temperatures and a variety of equivalence ratios, with an initial pressure of 0.1 MPa in a constant-volume vessel. For the five fuels, the stretched flame speeds, the un-stretched flame speeds, Markstein lengths, Markstein number, laminar burning velocities and laminar burning flux were calculated and analysed using the outwardly spherical flame method. The results show that for all examined initial temperatures (60 °C, 90 °C and 120 °C) and equivalence ratios; ethanol had the highest un-stretched flame propagation speeds, whilst ethyl acetate (EA) had the lowest. At high initial temperatures (120 °C), it was observed that the un-stretched flame speed trends of ethyl propionate (EP) and ethyl butyrate (EB) proved faster compared to gasoline, especially for rich conditions. The EB and EA flames demonstrated greater stability when compared to ethanol, EP, and gasoline. Analysis showed that ethanol yielded the fastest flame velocities, whilst EA consistently had the lowest among all the five fuels. The laminar burning velocities of the EP fuel were faster compared to EB and EA, whilst slower than ethanol and gasoline at 60 °C.

Abbreviations: RON, Research Octane Number; EP, ethyl propionate; 2MF, 2-methylfuran; DFB, dual fermentation bio-refinery; CI, compression ignition; PRF95, Primary Reference Fuels; r_u , instantaneous flame radius; L_b , Markstein length; ρ_b , burned mixture densities; n_u , number of reactant moles; T_u , initial temperature; ν , kinematic viscosity; LHV, lower heating value; Ma, Markstein number; ϕ , fuel-air equivalence ratio; EA, ethyl acetate; EB, ethyl butyrate; 2,5DMF, 2,5-dimethylfuran; SI, spark ignition; HCCI, Homogeneous Charge Compression Ignition; S_n , stretched laminar flame speed; α , stretch rate; S_u , unstretched laminar flame speed; ρ_u , unburned mixture densities; n_p , number of product moles; T_b , adiabatic flame temperature; u_l , laminar burning velocity; δ_L , flame thickness; f , laminar burning flux.

* Corresponding author at: University of Birmingham, Birmingham, UK.

E-mail address: h.m.xu@bham.ac.uk (H. Xu).

Further increase of the initial temperature, up to 120 °C, showed the laminar flame speed of EP and EB to be faster than gasoline, indicating a fast-burning property, and potential of improving engine thermal efficiency.

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1. Introduction

With an ever present demand for energy worldwide combined with a growing population and reliance on fuel powered applications (expected to grow by 57% until 2030) [1], the dependency on the finite and diminishing supply of fossil derived fuels alongside the requirement for enhanced environmental consciousness had resulted in vast investment, interest and continuous investigation into the future generation of alternative fuels [2]. The prevalent interest in recent years considered the derivation, functionality and potential of biological fuels, i.e. biofuels, sourced from biomass, with only 3% currently being economically exploited [2]. As such, research efforts have been focussed towards achieving performance characteristics of equal measure to the current market (ethanol, gasoline and isoctane).

Bio-ethanol has been established as the prominent alternative to gasoline, being mass produced via alcohol fermentation, cementing its matured status (relative to other alternatives) within the bioenergy market [3,4]. However, whilst bio-ethanol afforded a high volume of production, it resulted in a large energy consumption during processing, negating the benefits of its use as a primary fuel or component blend additive [1,5]. This was supported by unfavourable physical attributes, including: a low energy density (high gravimetric oxygen content), high volatility, and high solubility (fuel quality affected by atmospheric water content, affecting its long term stability) [6].

More recently, breakthroughs in mass production technologies broadened the spectrum of alternative fuels sourced from biomass, with research into the flame and spray characteristics of fructose derived 2-methylfuran (MF) and 2,5-dimethylfuran (DMF) yielding favourable results, with the fuels also exhibiting desirable properties such as: high energy density (close to gasoline and between 30 and 40% greater than ethanol), insolubility (high stability), high boiling point (less volatile), high Research Octane Number (RON) (increased efficiency and resistance to auto-ignition), and low energy consumption during production [5–8]. Furthermore, investigations into second generation ester biofuels showed a reduction in production complexity, thereby improving the efficiency of the necessary conversion steps (dictated by the engine specific fuel characteristics), yielding high grade fuels without detriment to the net energy balance [9–12].

Due to the lower production cost for esters in the dual fermentation bio-refinery (DFB) process, a series of ester oxygenates was evaluated recently for use as gasoline octane providers. It was found that EP, EB and EA as gasoline additives provided a significant increase in the mean octane rating without a drastic change in vapor pressure [13]. Ethyl ester fuels had several advantages over ethanol and ethers. First, they were not toxic. Second, they had pleasant odor. Third, lower exhaust emissions of carbon monoxide, aldehydes and ketones were expected because of the higher oxidation state of the esters [14]. Jenkins et al. [10] concluded that the ester fuels were completely miscible with gasoline, enabling 50:50 blends, i.e. fuel integration instead of replacement, with EA best suited to SI applications (low melting and flash point).

As an extension of the ester fuels application in spark ignition/compression ignition (SI/CI), research into Homogeneous Charge Compression Ignition (HCCI) was conducted by Contino et al. [11,12] which concluded that EA, EP and EB had a slower ignition

rate than ethanol (agreed by Jenkins et al.) [10]. Furthermore, it was shown that the esters offered no loss of power (energy content of stoichiometric mixtures were similar to ethanol), with an improved mixture preparation (greater enthalpies of vaporisation), and good overall stability at various equivalence ratios. Contino et al. [9] also investigated the engine performance and emissions of methyl and ethyl valerates in SI and found that the esters had a higher flame speed compared to Primary Reference Fuels (PRF95). Moreover, no significant difference was observed for emissions and performance when the engine was running with pure esters compared to PRF95.

Table 1 shows the general properties of the proposed fuels for baseline evaluation with ethanol and gasoline. It was noticed that the three fuels demonstrated a reduction in LHV relative to gasoline (20–30% less, due to their oxygen content which itself offered reduced soot formation), but an increase compared with ethanol (10–20% for EP and EB). Furthermore, EP and EB exhibited similar boiling properties (98.89–120 °C) and solubility (low) to that of gasoline, benefitting from reduced volatility and high stability, whereas EA demonstrated properties akin to ethanol, displaying an elevated RON (116) to accommodate higher compression ratios and cycle efficiencies. Collectively, the fuels displayed latent heat of vaporisation similar to gasoline, with flash points indicating potential diversity in application: EA (–2.78 °C) in SI; EP and EB (12.22–18.89 °C) in HCCI, thereby cementing their combustion credentials [10].

The present paper aims to analyse and evaluate the laminar flame speed of three ester biofuels, namely: ethyl acetate (EA), ethyl propionate (EP), and ethyl butyrate (EB), against gasoline and ethanol. Laminar flame propagation characteristics are important fundamental physicochemical properties of a fuel–air mixture for validating the chemical reaction mechanisms and gaining a better understanding of the combustion process in engines [15,16]. This study forms part of a series of experiments to explore the use of ethyl esters as additive or surrogate fuel for gasoline in SI, utilising schlieren photography to investigate the laminar flame speed, Markstein length, Markstein number, laminar burning velocity and burning flux at different initial temperatures.

2. Experimental setup

2.1. Schlieren optical method

The laboratory setup for experimentation was a replication of the approach as detailed by Tian et al. [5] and Ma et al. [7] with Fig. 1 providing a detailed schematic of the arrangement. As shown, a constant volume combustion vessel with two circular quartz observation windows (100 mm diameter) was utilised, alongside eight heating elements, installed at each corner. Temperature modulation of the vessel was implemented via closed loop control, to monitor the heating elements described and allow continuous observation of the fuel–air mixture condition within the chamber. The fuel injection strategy was fulfilled through a Gasoline Direct Injection (GDI) nozzle, which was mounted in the top cover of the vessel, and was driven by an ECU-computer system. Finally, to achieve the necessary spark for ignition, a pair of tungsten electrodes was positioned in the centre of the vessel, with a

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