



The combustion kinetics of the lignocellulosic biofuel, ethyl levulinate

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ABSTRACT

Ethyl levulinate (Ethyl 4-oxopentanoate) is a liquid molecule at ambient temperature, comprising of ketone and ethyl ester functionalities and is one of the prominent liquid fuel candidates that may be easily obtained from lignocellulosic biomass. The combustion kinetics of ethyl levulinate have been investigated. Shock tube and rapid compression machine apparatuses are utilised to acquire gas phase ignition delay measurements of 0.5% ethyl levulinate/O₂ mixtures at $\phi = 1.0$ and $\phi = 0.5$ at ~ 10 atm over the temperature range 1000–1400 K. Ethyl levulinate is observed not to ignite at temperatures lower than ~ 1040 K in the rapid compression machine. The shock tube and rapid compression machine data are closely consistent and show ethyl levulinate ignition delay to exhibit an Arrhenius dependence to temperature. These measurements are explained by the construction and analysis of a detailed chemical kinetic model. The kinetic model is completed by establishing thermochemical-kinetic analogies to 2-butanone, for the ethyl levulinate ketone functionality, and to ethyl propanoate for the ethyl ester functionality. The so constructed model is observed to describe the shock tube data very accurately, but computes the rapid compression machine data set to a lesser but still applicable fidelity. Analysis of the model suggests the autooxidation mechanism of ethyl levulinate to be entirely dominated by the propensity for the ethyl ester functionality to unimolecularly decompose to form levulinic acid and ethylene. The subsequent reaction kinetics of these species is shown to dictate the overall rate of the global combustion reaction. This model is then used to estimate the Research and Motored Octane Numbers of ethyl levulinate to be ≥ 97.7 and ≥ 93 , respectively. With this analysis ethyl levulinate would be best suited as a gasoline fuel component, rather than as a diesel fuel as suggested in the literature. Indeed it may be considered to be useful as an octane booster. The ethyl levulinate kinetic model is constructed within a state-of-the-art gasoline surrogate combustion kinetic model and is thus available as a tool with which to investigate the use of ethyl levulinate as a gasoline additive.

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1. Introduction

The catalytic conversion of biomass derived cellulose, hemicellulose and lignin to platform chemicals and fuels has been widely recognised as an opportunity to produce sustainable economies. Ethyl levulinate (EL) (Fig. 1) is one of many liquid phase molecules that may be easily produced by the acid hydrolysis of cellulose. It may be produced at the high yields that are essential for potential economic viability, either by reaction of ethanol (the biorefinery platform chemical) and levulinic acid, or by the *in situ* acid-catalysed reaction of cellulosic sugars with ethanol [1]. The

synthetic processes that produce ethyl levulinate from cellulose use ethanol (both as a solvent and reacting partner) as a means of functionalising the levulinic acid precursor [2]. This alkylation also improves the energy density of the cellulose derived functionalities, and their solubility in conventional petroleum derived liquid hydrocarbon fuels. One can also think of the cellulose as improving the fuel properties of ethanol, notably the energy density. Ethyl levulinate has an energy density of 31.2 MJ/L (energy density of gasoline is 44.4 MJ/kg), much superior to that of ethanol (24 MJ/L). The sustainability benefits of co-reacting cellulose with ethanol are obvious when one realises that 71% of the ethyl levulinate carbon, and 58% of the ethyl levulinate hydrogen are contributed by the cellulose.

Ethyl levulinate (EL) has a high flash point of 90 °C, attributable to its low volatility as prescribed by a boiling point of 206 °C. Due

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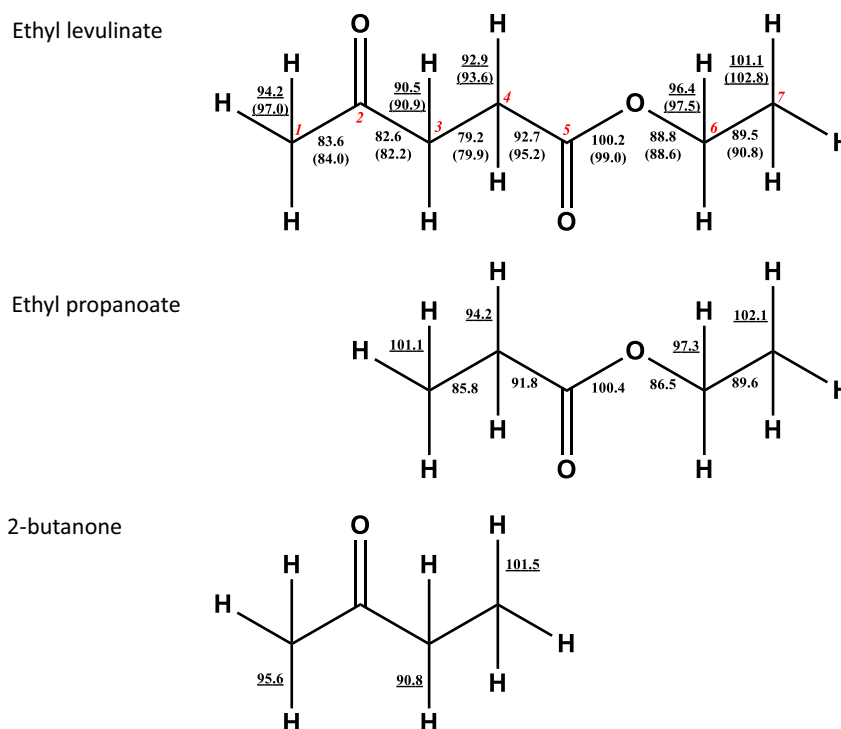


Fig. 1. Chemical structures and bond dissociation energies (kcal/mol) of ethyl Levulinate. Carbon-hydrogen bond dissociation energies are underlined. Values without parentheses are average of data produced by isodesmic work reactions calculated at CBS-QB3, CBS APNO and G4MP2 levels of theory [3]. Values in parentheses are group additivity estimates. Ethyl propanoate from [4] and 2-butanone from [5].

to its high oxygen content and high boiling point, ethyl levulinate has been originally espoused as a suitable oxygenate additive for diesel fuels to reduce soot formation. Lei et al. [6] have reported successful engine tests of various blends of ethyl levulinate, and ethyl levulinate/n-butanol with a diesel fuel, showing marginal increases in brake specific fuel consumption and also marginal effect on the emission of unburned hydrocarbons for 10 vol% ethyl levulinate mixtures with a road diesel. Koivisto et al. [7] in a direct injection compression ignition engine, studied a series of oxygenated fuel components both as neat fuels, and as 30 vol% blends with n-heptane. They noted a reduction in overall particulate mass when using ethyl levulinate as a fuel component, but also noted an increase in the overall number of particulate particles. Windom et al. [8] have determined the volatility behaviour of (1–20 vol%) ethyl levulinate blends with Ultra Low Sulphur Diesel (ULSD) and with biodiesel. They show that, while ethyl levulinate is more volatile than either fuel, modest additions of ethyl levulinate to diesel will not significantly affect the overall volatility of the fuel.

The majority of existing literature proposes the use of ethyl levulinate as a sustainable blend-stock for use with diesel fuel, however, the combustion reactivity of ethyl levulinate may present itself as a limiting factor in this regard. Koivisto et al. [7] reported that ethyl levulinate does not ignite at the typical configuration of a tested diesel engine, also noting that ethyl levulinate/n-heptane mixtures showed the longest ignition delays of a large series of fuels tested. Similarly, Murphy et al. [9] corroborate this reactivity indicator when quoting a Derived Cetane Number for ethyl levulinate of “< 5”, as deduced by an ignition quality tester. Christensen et al. [10] note that this low cetane number will limit the quantity of ethyl levulinate that might be blended with diesel fuel. The miscibility of ethyl levulinate may also be another constraining factor. Christensen et al. [10] purposely investigated the miscibility of ethyl levulinate with conventional Ultra-Low Sulphur Diesel (ULSD) showing the addition of 10 vol% ethyl levulinate to result in a significantly higher cloud point in comparison to unblended

diesel. Moreover, in the range of -10 °C to $+10$ °C, Christensen et al. [10] report a propensity for a significant fraction of ethyl levulinate to phase separate from the blended diesel. They indicate that this may lead to operational difficulties in vehicle fuel storage tanks and with engine fuel injectors under cold operating conditions. However, both Lake and Burton [11] and Joshi et al. [12] show that such miscibility restrictions are less confining when using biodiesel as the blend component, or as a co-solvent for ethyl levulinate with conventional ultra-low sulphur diesel.

The low cetane number and reactivity of ethyl levulinate may favour its use as a gasoline additive. It is also important to note that ethyl levulinate appears to be more miscible in tested gasolines than the diesels. Christensen et al. [13] show that at 10 vol% ethyl levulinate did not separate from the gasoline until -40 °C. Christensen et al. [13] also noted that the use of ethyl levulinate (at 3.7 wt% oxygen, ~ 5.9 mol% ethyl levulinate) as a gasoline extender gives favourable attributes over other possible oxygenated additives, including ethanol and propanols, by; lowering the volatility of the fuel; increasing blended octane numbers by ~ 15 . Similarly, Tian et al. [14] found in both engine and ignition quality tests that ethyl levulinate has a higher anti knock propensity than EURO95 gasoline (RON = 95). This further suggests that ethyl levulinate would be better placed as a gasoline additive. Tian et al. through analogy to ethyl butanoate, espouse that the ethyl levulinate combustion kinetics is dominated by the decomposition pathway to ethylene and levulinic acid, which results in the low reactivity of the molecule. However, a detailed study on the reaction kinetics of ethyl levulinate is needed to test this theory.

The position of the fuel and combustion literature on the prospective uses of ethyl levulinate may thus be summarised as suggesting ethyl levulinate to be intermediate in physical property between gasoline and diesel distillate, but of a kinetic reactivity much lower than conventional diesel, and even lower than conventional gasoline. We note that the to-date reactivity indicators are all derived from engine like configurations, where

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