The importance of endothermic pyrolysis reactions in the understanding of diesel spray combustion

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ABSTRACT

The significance of pyrolysis reactions in the early stages of diesel combustion has received little attention in the literature, which warrants a mechanistic investigation of the controlling chemistry along with its potential impacts on the overall combustion process in engines. Experiments were performed in a constant volume vessel to probe these pyrolytic reactions, where diesel fuel sprays were injected into air at varied pressures and temperatures chosen to represent an engine operating at various loads. The pressure inside the vessel was found to decrease immediately following the start of injection before increasing as the exothermic heat release occurs. The initial pressure decrease has been conventionally attributed to an evaporative cooling effect of the diesel spray, but the objective of this paper is to test the hypothesis that endothermic pyrolysis reactions can make a significant contribution to the observed pressure decrease.

The addition of 1% of the cetane booster, 2-ethylhexylnitrate (2-EHN), to the fuel was found to shorten the measured ignition delay time, as expected. However the presence of 2-EHN can also increase the magnitude of the initial pressure decrease compared to conventional diesel fuel. Detailed chemical kinetic modeling shows that the effects observed in the constant volume vessel can plausibly be attributed to pyrolysis reactions, and that the addition of 2-EHN to the base fuel enhances their influence. The modelling results also imply that the influence of these pyrolysis reactions increases with increasing temperature, pressure, the alkyl chain length of the base fuel, and the amount of any radical initiator in the fuel.

1. Introduction

Solid, liquid, and gaseous fuels are known to pyrolyse, altering their molecular structure without significant oxidation, even though oxygen-containing species may be present. Such pyrolysis reactions are generally endothermic as a result of the energy required to break chemical bonds, resulting in their rate constants and hence rates being highly temperature dependent. The pyrolysis and rich oxidative combustion of fuels have been widely investigated in shock tubes [1,2], jet-stirred reactors [3–5] and flow reactors [6,7]. MacDonald et al. [1] report that test gas mixture temperatures in a shock tube can be lower than the initial temperatures immediately behind the reflected shock because of endothermic reaction. However the implications of endothermicity for practical combustion systems have been largely confined to the study of aviation fuels, where it has been suggested that endothermicity can help scramjet cooling [8] and thermal protection in general [9].

Constant-volume combustion vessels have been employed to study

the physical and chemical properties associated with liquid fuel combustion under conditions relevant to spark and compression ignition engines. When a liquid fuel is injected into such a vessel under conditions relevant to diesel fuels and engines, there is typically an initial decrease in the measured gas pressure owing to fuel vaporisation, followed by an increase in pressure due to the occurrence of exothermic chemical reactions which lead to autoignition, Fig. 1. The overall ignition delay time is usually defined as the period between the start of injection, to the point at which the pressure has recovered to its original value, and this is the protocol adopted in the measurement of derived cetane number using the Ignition Quality Tester device [10].

Various attempts have been made to separate the physical and chemical processes which control the overall ignition behaviour into a physical delay which represents the fuel evaporation and fuel-oxidiser mixing processes, and a chemical delay which accounts for the gas-phase chemical reactions which ultimately lead to combustion. Experiments are often repeated in an atmosphere of nitrogen, so that
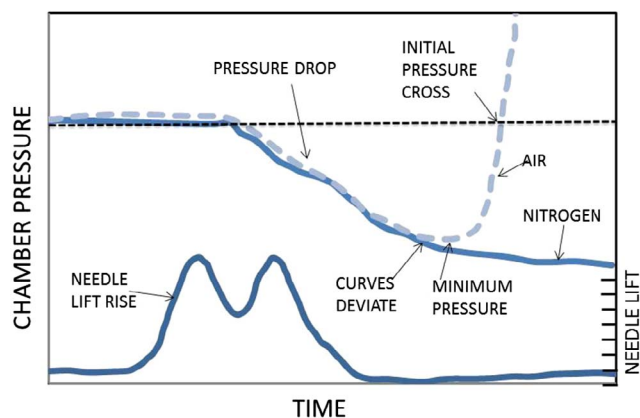
Fig. 1. Pressure-Time records and injection-nozzle needle-lift trace with identification of the various points of interest. Adapted and redrawn based on Fig. 2 of [14].

the exothermic oxidation reactions cannot take place and the divergence of the nitrogen pressure trace from the combusting pressure trace is used as the demarcation between the end of the physical delay and the start of the chemical delay [11,12].

Other studies [13–16] have defined the post-injection time step at which pressure reaches a minimum as being the point where the measured pressure signal transitions from being purely evaporation/mixing controlled to being purely chemically controlled. Although, the example in Fig. 1 shows the minimum in the pressure trace occurring at approximately the same point as the divergence of the nitrogen and air curves, more recent work for *n*-heptane has shown that the pressure minimum can occur considerably later than the point at which the nitrogen and air curves diverge [17].

Usually the initial pressure decrease is attributed only to the evaporation of the fuel [15,16] but Zheng et al. [17] acknowledge the additional possibility of endothermic reactions, in experiments in both air and nitrogen. It is already clear from the previous discussion that any attempted demarcation between physical and chemical ignition delay times is somewhat arbitrary but the existence of chemical reactions during the so-called physical delay may undermine the interpretation of such experimental data unless differences arising from variation in chemical structure are accounted for.

The objective of *this work* is to understand the influence of the addition of 2-EHN and its associated reactions on the combustion of diesel fuels and their components. Results are presented for 9 different conditions in a constant-volume vessel with varying bulk-gas pressure and temperature in which a standard diesel fuel is compared against a diesel fuel containing 1% of the cetane booster 2-ethylhexylnitrate (2-EHN). In all instances the addition of 2-EHN to the base-fuel leads to shorter total ignition delay times being measured, but in some cases a greater initial pressure decrease is observed during the so-called physical-delay stage. A greater pressure decrease due to enhanced fuel vaporisation is argued to be implausible due to the 2-EHN concentrations in the base-fuel, and so the phenomenon can only be interpreted in terms of endothermic pyrolysis reactions, which are explored using detailed chemical kinetic models from the literature.

2. Experimental setup and results in a constant volume combustion chamber

The Combustion Research Unit (CRU) in Shell Global Solutions is a constant-volume vessel, manufactured by Fueltech that can mimic combustion conditions in modern diesel engines [18,19]. A schematic diagram of the CRU is shown in Fig. 2. The unit is supplied with a common rail injection system of type Bosch CRIP2 (Part No: 0445110157) and a 7 hole nozzle. Fuel is injected into the pressurized heated chamber where it mixes with hot air and ignites.

The combustion process is monitored with a pressure sensor inside the chamber whilst a needle lift sensor inside the injector monitors the injection event. The chamber pressure, temperature, fuel pressure, gas composition and injector pulse width can all be varied by the operator. Before the fuel is injected, the chamber is filled with high-pressure air (or another gas) from an external air cylinder and heated to a pre-set temperature via two electric heaters. Some technical parameters of the CRU are listed in Table 1.

The needle lift sensor and the two dynamic pressure sensors in the combustion chamber and fuel line all sample at a rate of 50 kHz (intervals of 0.02 ms), giving outputs including needle lift, chamber pressure and fuel pressure. The needle lift enables the measurement of the start of injection (SOI) and the end of injection (EOI). The fuels used were a standard EN590 diesel and the EN590 diesel with 1% by mass of 2-EHN added. The CRU was operated at the conditions listed in Table 2, and the diesel fuel properties are provided in ESI.

The global equivalence ratio (φ) is very lean, around $\varphi = 0.075$ for the 30 bar cases and leaner still for the higher pressure cases.

Fig. 3 shows that addition of 1% 2-EHN shortens the ignition delay of the diesel for all of the conditions investigated. Increasing both the pressure and temperature also leads to a decrease in ignition delay for diesel fuels with and without 2-EHN – this is again fully expected and in line with previous findings on diesel primary reference fuels in the CRU [18,19].

In addition to the expected trends in ignition delay time, Fig. 3 also shows a divergence of the measured pressure during the pressure decrease phase, and in particular one can observe that the pressure decrease occurs faster for the fuels containing 2-EHN as the temperature and pressure of the initial gas mixture is increased. Different rates of vaporisation cannot be ruled out as an explanation for the trends observed in *this work*, but the latent heat of vaporisation of 2-EHN [20] is very similar to that of a hydrocarbon of similar carbon number, and it is present in the fuel in relatively small quantities. Higgins et al. [21] used a constant volume vessel with optical access to study ignition, evaporation and mixing effects upon the addition of 2-EHN to diesel fuels. They found that the addition of 4000 ppm of 2-EHN to a ternary *n*-hexadecane/decalin/1-methylnaphthalene diesel surrogate had a limited influence on physical processes such as atomisation, fuel vaporisation, and turbulent mixing, but it did lead to shorter ignition delay times, as found herein. Endothermic pyrolysis reactions therefore seem a plausible explanation for the experimental observations given that past studies imply no pronounced physical effect of 2-EHN addition to diesel fuels. It cannot be stated *a priori* that endothermic reactions involving both 2-EHN and the base diesel, or 2-EHN alone, are the cause of the observed effect but this will be explored later below.

3. Chemical kinetic modeling

Given the complex turbulence/chemistry interactions (spray formation and break-up, evaporation, mixing, ignition and flame chemistry) which are occurring simultaneously in our experiment, any attempt to model the results on a truly comparative basis would require a correspondingly complex computational approach. Here, the focus is on gas-phase chemical kinetic aspects of the experiment, and whilst the conditions of temperature, pressure, and fuel composition are imprecisely known in our experiment due to spatial inhomogeneity within the reactor, idealised chemical kinetic modeling can still be used to elucidate aspects of the fuel's combustion chemistry which may influence our experimental results. In order to study these effects and to interpret and inform the experimental observations at a more fundamental level, 0-D homogeneous batch reactor simulations have been carried out, under representative conditions of temperature (T), pressure (p), fuel mole fraction (χ_F), and fuel composition (n-C_7H_{16}/n-$C_{16}H_{34}$/2-EHN/O_2/N_2).

In order to account for different hydrocarbon species which may preferentially evaporate during the course of our experiment, both *n*-