Research article

1-hexene autoignition control by prior reaction with ozone

Alessandro Schönborn [a,*], Paul Hellier [b], Nicos Ladommatos [b], Christian P. Hulteberg [c], Göran Carlström [d], Parisa Sayad [e], Jens Klingmann [e], Alexander A. Konnov [f]

[a] SINTEF Energy Research, Kolbjørn Hejes vei 1 A, 7034 Trondheim, Norway
[b] Department of Mechanical Engineering, University College London, Roberts Building, Torrington Place, WC1E 7JE London, UK
[c] Department of Chemical Engineering, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden
[d] Centre for Analysis and Synthesis, Department of Chemistry, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden
[e] Lund University, Division of Thermal Power Engineering, P.O. Box 118, SE-221 00, Lund, Sweden
[f] Lund University, Division of Combustion Physics, P.O. Box 118, SE-221 00 Lund, Sweden

ARTICLE INFO

ABSTRACT

The autoignition timing of 1-hexene was controlled in a Homogeneous Charge Compression Ignition (HCCI) engine by reacting the fuel with ozone-containing air prior to its combustion. The experiments were conducted in a single cylinder research engine instrumented with a cylinder pressure sensor. The fuel was chemically characterised using Nuclear Magnetic Resonance (NMR) spectroscopy before and after its reaction with ozone. The NMR analyses showed that this preliminary reaction produced several oxygenated products within the fuel, and was likely to have resulted in the formation of ozonide molecules having a peroxidic structure with several oxygen molecules in series. To understand how this would affect the ignition reactions, the ignition process was modelled numerically using a single-zone chemical kinetic reactor model. The modelling suggested that peroxide molecules decomposed during the compression of the reactants in the engine and advanced ignition timing by promoting early decomposition of the fuel through the formation of radicals.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Partially premixed combustion concepts for internal combustion engines, such as Homogeneous Charge Compression Ignition (HCCI) and Reactivity Controlled Compression Ignition (RCCI), are promising technologies for combining high fuel conversion efficiency with lower emissions of soot and nitrogen oxides (NOx) [1]. The indicated thermal efficiency of RCCI in particular, has been reported to reach 55–60% even in light-duty engines [2]. In HCCI and RCCI, the autoignition and combustion processes are entirely controlled by the chemical kinetics of the reactants. This results in a fast combustion process around the point of maximum geometrical compression of the charge i.e. at piston top-dead-centre (TDC) when the engine is operating optimally. Yet, changes in engine air charge temperature and pressure, or variations in engine load and speed, require the chemical kinetics to be controllable, in order to achieve ignition around TDC under all conditions [3]. One way to ensure that ignition takes place around TDC at varying engine operating conditions is to control the ignition quality of the fuel. This can be achieved by blending two fuels of varying ignition qualities [4], such as petrol and diesel fuel. The disadvantage of this approach is

that an engine would require two fuels to operate, which would have to be kept in separate fuel tanks.

The development of a single 'smart' fuel, the ignition quality of which can be varied, could provide a more rational approach to this concept [5,12]. This work aims to highlight the potential of developing 'smart' fuels of variable ignition quality as a practical way of achieving high-efficiency RCCI combustion.

A simplified schematic of an RCCI engine using this approach is shown in Fig. 1. Fig. 1 illustrates how a single fuel may be used to provide two fuel streams of varying ignition qualities to an engine, by reacting one of the fuel flows in a reactor prior to its combustion. Two separate injection systems may be used to stratify the reactivity of the fuel and air mixture within the cylinder. By blending unreacted fuel with reacted fuel in varying proportions during the experiments, the point of ignition of the fuel and air charge can be adjusted within the engine cycle. A buffer tank may be used to store reacted fuel, in order to de-couple the speed of reaction of the fuel with ozone, from the rapid changes in fuel quality required by the engine.

A reliable low-temperature reaction of the fuel prior to combustion can be achieved using ozone (O_3). Ozone can be produced in compact devices at efficiencies of 340 g/kWh [6], and the reaction with fuel can produce peroxide species known to advance the time of ignition [5]. The ozone required to convert 1000 ppm of fuel into a peroxide, could theoretically be achieved with less than 1% of the fuel energy. Ozone may also be used to advance ignition directly, as has been demonstrated
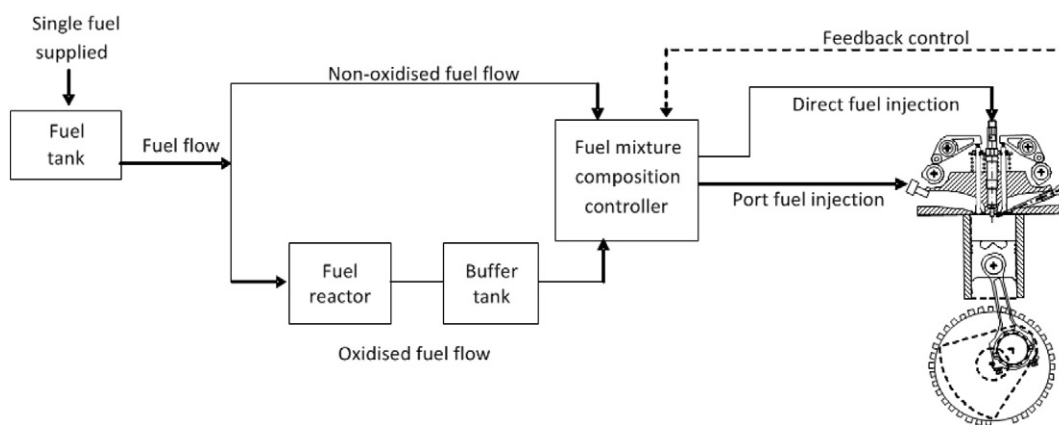
Fig. 1. Engine system using single fuel with variable ignition quality.

by Flynn et al. [7], Foucher et al. [8], and Masurier et al. [9,10]. Using an ozonised liquid fuel instead of gaseous ozone directly, may have the advantage of better cycle-to-cycle control, ease of stratification as well as limiting ozone destruction and energy losses occurring due to gaseous compression and injection of ozone.

In the present work, the ability of 1-hexene to control its ignition timing by altering its molecular structure in a reaction with ozone was investigated. Alkenes are known to be prone to reactions with ozone via cleavage of their double-bonds [11]. It was thus chosen to use 1-hexebe as an alkene of suitable size and volatility as model fuel for this work. A series of engine experiments were conducted in a single-cylinder direct injection diesel engine using a nearly homogeneous charge of fuel and air. Such HCCI combustion conditions allowed investigating the potential use of this 'smart' fuel approach in controlling combustion phasing, and allowed simple chemical kinetic modelling. It is hoped that once the fuel-and ozone reactions and the combustion chemistry of its products are better understood, this 'smart' fuel approach may be extended to stratified reactant mixtures, as applicable to RCCI combustion conditions.

2. Experimental methods

2.1. Engine characteristics

The engine was an automotive production engine (Ford Duratorq TDCi) customised to a single cylinder design using a single cylinder engine block (Ricardo Hydra). The compression ratio of the engine was 15:1, and the engine intake air was naturally aspirated at a constant temperature and absolute pressure of 300 K and 102 kPa. The head, cylinder bore, stroke, piston and injectors were identical to the original automotive engine. Fuel was injected into the air intake duct approximately 1 m upstream of the inlet valves. The engine speed was controlled to a constant speed of 1200 rpm using a direct-current dynamometer. Detailed engine specifications are given in Table 1.

Table 1
Engine specification.

Engine model	Ford Duratorq 2003
Number of cylinders	1
Cylinder bore	86 mm
Crankshaft stroke	86 mm
Swept volume	499.56 cm^3
Compression ratio	15: 1
Maximum cylinder pressure	15 MPa
Piston design	Central ω-bowl in piston
Oil type	10 W40
Water temperature	85 °C

2.2. Fuel injection system

The fuel and air mixture were premixed in the intake duct of the engine over 10 diameters upstream of the intake valves. The fuel was injected using a solenoid-actuated multihole injector (Ford), and was supplied using a sealed tank pressurised to a constant gauge pressure of 300 kPa using air. A schematic of this system has been described earlier [5].

2.3. Instrumentation

The cylinder of the engine was instrumented using a piezoelectric pressure transducer (Kistler 6056 AU38) coupled to a charge amplifier (Kistler Type 5011) to provide measurements of the cylinder pressure at 1/5° crank angle intervals. The sampling was timed using an optical shaft encoder (Encoder Technology EC85), and pegged to an absolute reference pressure at bottom-dead-centre (BDC) of every engine cycle. The reference pressure was measured using a piezo-resistive pressure transducer (Druck PTX 7517-3257) located 160 mm upstream of the inlet valves. The cylinder pressure was measured for at least 100 engine cycles for each experiment, and averaged. The composition of the exhaust gases was determined using an automotive gas analysing system (Horiba MEXA9100 HEGR), consisting of a chemiluminescence analyser for NO_x, non-dispersive infrared (NDIR) analysers for CO and CO_2, a flame ionisation detector for unburned hydrocarbons and a magneto-pneumatic gas analyser for O_2. The number and size of particulates in the exhaust gases was determined using a differential mobility particle spectrometer (Cambustion DMS500) [13]. The particulate sampling probe was heated to 65 °C and a two-stage dilution process was used having a primary dilution ratio of 1:4, and a secondary dilution ratio of 1:35.

2.4. Fuel properties and reaction with ozone

The fuel used in the engine experiments consisted of 1-hexene, 1-hexene reacted with ozone-containing air, and a 50% volumetric mixture of these two. 1-hexene was obtained from a specialist chemical supplier (Sigma-Aldrich) and had an assay of at least 97%. The ozone in the ozone-containing air was generated using a corona-discharge, and had a mole fraction of approximately 4%. The ozone-containing air was passed through a quantity of 250 g 1-hexene using a stainless-steel tube of 250 mm length, 4 mm internal diameter and 6 mm external diameter. This process was applied to the fuel for 4 h, and was carried out at a temperature of 293 K, and an absolute pressure of 102 kPa. The reaction time of fuel with ozone used in these experiments was long compared to the rapid cycle-to-cycle changes in fuel quality required by the engine. This long time was chosen to ensure ample