



## The importance of double bond position and *cis*–*trans* isomerisation in diesel combustion and emissions

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### HIGHLIGHTS

- ▶ Four octene isomers were tested as single component fuels in a single cylinder diesel engine.
- ▶ Engine tests were conducted using a novel low volume fuel system.
- ▶ Moving the double bond towards the centre of the molecule had a non-linear effect on ignition delay.
- ▶ Ignition delay of the *cis* isomer was shorter than the equivalent *trans* isomer.
- ▶ Emissions levels were primarily driven by duration of ignition delay.

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### ABSTRACT

Future fuels will be developed from a variety of biomass and fossil sources, and this presents an opportunity to design new fuels that carry a much reduced environmental burden. To this end, understanding how the molecular structure of a fuel impacts on the processes of combustion and emissions production is critical in selecting suitable feed-stocks and conversion methods. This paper presents experimental studies carried out on a diesel engine supplied with a range of single-molecule fuels to investigate the effect of fuel molecular structure on combustion and emissions. Four isomers of octene, 1, *trans*-2, *cis*-3 and *trans*-3, were investigated so as to ascertain the way in which the position and arrangement of a double bond within an alkene molecule affects diesel combustion and emissions. The engine tests were carried out at constant injection timing and they were repeated at constant ignition timing and at constant ignition delay, the latter being achieved through the addition of small quantities of ignition improver (2-ethylhexyl nitrate) to the various fuels. The order of ignition delay (shortest first) was found to be 1-octene, *cis*-3-octene, *trans*-3-octene and *trans*-2-octene. The higher reactivity of the *cis* isomer was attributed to the need of *trans* isomers to adopt the *cis* conformation prior to undergoing certain low temperature radical branching reactions. The longer ignition delay of *trans*-2-octene relative to *trans*-3-octene suggests a greater net reactivity of the saturated alkyl portions of the latter molecule. At constant injection and constant ignition timings, the combustion phasing and the exhaust level of NO<sub>x</sub> emitted by each fuel were dictated by the duration of ignition delay. With ignition delay equalised, an effect of increasing particulate emissions with the movement of the double bond towards the centre of the molecule was observed.

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### 1. Introduction

Efforts to develop new fuels from biomass and fossil sources are seeking to reduce the environmental impacts that arise in the use of traditional fossil fuels [1–4], whilst ensuring that new fuels remain compatible with the existing transport and power generation infrastructure. While the fossil diesel utilised for the past hundred

years has been a mixture of molecular components, defined by a range of physical properties, the fuels of tomorrow will have more distinct molecular structures, defined by the material from which they are drawn and the chemical and physical processes to which they are subjected. Understanding how specific features of molecular structure impact on energy release during combustion of a fuel, and formation of pollutants, is therefore invaluable in aiding the design of future fuels.

The impact of fuel saturation on diesel combustion and emissions has been the subject of numerous studies, the bulk of which have been concerned with the suitability of various

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## Nomenclature

NO <sub>x</sub>	nitrous oxides	O <sub>2</sub>	oxygen
CO <sub>2</sub>	carbon dioxide	SOI	start of injection
IQT	ignition quality testing	BTDC	before top-dead-centre
CFR	cooperative fuels research	TDC	top-dead-centre
DCN	derived cetane number	SOC	start of combustion
CO	carbon monoxide	2 EHN	2 ethyl hexyl nitrate
THC	total hydrocarbons	IMEP	indicated mean effective pressure
CAD	crank angle degree	PPM	parts per million
PID	proportional integral derivative	FAME	fatty acid methyl ester
DAQ	data acquisition		

saturated fatty acids for FAME production [5–9]. The presence of double bonds within non-oxygenated compounds has also been studied [10]. However, the effect of moving a single double bond within an alkyl chain and the arrangement of that bond has received less attention, and this paper is the first one to investigate the direct injection diesel combustion of octene isomers.

The first comparative study of olefin double bond position, and also *cis* versus *trans* isomerisation, was conducted in the late 1960s by Salooja [11] who investigated the combustion properties of 1-butene and also *trans*- and *cis*-2-butene. In both flow reactor and variable compression engine experiments (the latter conducted to determine knocking tendencies), 1-butene was found to be the most reactive, followed respectively by *cis*-2-butene and *trans*-2-butene. The cool flame combustion of pentene isomers was studied by Hughes and Prodhon [12] in the early 1970s. They found 1-pentene to possess the shortest ignition delay, but no difference between that of *cis*- and *trans*-2-pentene. More recently, the low temperature oxidation of 1-pentene was investigated by Prabhu et al. [13] in a pressurized flow reactor. Sampling of the reaction mixture and identification of the species present revealed that the abstraction of hydrogen atoms from the saturated portion of the alkene was far more prevalent than radical addition to the double bond. Tanaka et al. [14] and Vanhove et al. [15] studied the premixed stoichiometric combustion in rapid compression machines of heptene and hexene *trans* isomers respectively. In both instances, moving the position of the double bond progressively towards the centre of the molecule consistently resulted in an increased duration of ignition delay. Furthermore, in addition to possessing the longest ignition delay, in both studies the isomer with the double bond in the three position showed only single stage ignition in contrast to the other isomers studied which showed two stage ignition. Considering the double bond position within the alkyl chain of a fatty acid ester, Zhang et al. [16] found a similar influence. In motored premixed combustion in a CFR engine, they found the following order of ignition delay (shortest first): methyl-nonanoate, methyl-*trans*-2-nonenoate and methyl-*trans*-3-nonenoate (with the first exhibiting two stage ignition delay and the latter two single stage ignition delay).

Mehl et al. [17,18] and Bounaceur et al. [19] utilised the experimental data of Tanaka et al. [14] and Vanhove et al. [15] to develop detailed chemical models that sought to better understand the change in olefin reactivity with double bond position. Highlighted was the importance of the carbon chain length of the saturated portions of the alkenes studied [11,12,15,17] and how the properties of the C–H bonds present in these chains influence the well understood mechanisms of low temperature *n*-alkane oxidation [20]. In addition, as the chain length of the residual saturated alkyl chains decreases, reactions involving the double bond are of increasing importance [15,17]. The kinetic modelling of Bounaceur et al. [19] found that for 1, *trans*-2 and *trans*-3 hexene the total rate

of reactant consumption by reactions with an inhibiting influence on ignition was found to be 34%, 49% and 66%, respectively. In the case of fatty acid esters [16], the movement of the double bond towards the centre of fatty acid moiety was suggested to be an increasingly inhibiting influence due to the limitations that the position of the double bond placed on the formation of six and seven membered transition rings. Such transition rings are necessary for the isomerisation of alkyl peroxy radicals to peroxy alkyl structures, which is a key stage in the branching reactions that produce radicals necessary for autoignition [16,20].

This paper presents the results of engine experiments in which a series of octene isomers were tested. The isomers were chosen to investigate the effect of double bond position and *cis* versus *trans* isomerisation on diesel combustion and emissions. Relative to previous studies on this subject, this paper is the first to utilise a modern direct injection diesel engine and to consider alkenes of longer carbon chain length than heptene.

## 2. Experimental methods

### 2.1. Apparatus

All combustion experiments presented were conducted in a single cylinder direct injection diesel engine specially designed for combustion research. Several of the fuels tested were available in only small quantities at the high assay required, or had physical properties, such as low lubricity, which would have resulted in damage to the fuel pump and common rail components. So, to overcome these issues, a previously designed and manufactured [10] low volume and high injection pressure fuel system was utilised.

Based on the concept first proposed and implemented by Schönborn et al. [21], the system uses the engine common rail system as a hydraulic fluid supply so as to pressurize a small quantity of the sample fuel (100–250 ml) via two free pistons. The redesigned system used for the tests discussed in this paper features a bypass operated by high pressure needle valves that allows fossil diesel fuel from the engine pump circuit to flow at pressure through the test fuel circuit. This allows the fuel system and combustion chamber to be flushed with a reference diesel between every test run. A schematic of the system is given in Fig. 1, with further details of the engine and control apparatus given in Table 1.

The engine cylinder gas pressure was measured and logged with a PC data acquisition system (National instruments) at every 0.2 CAD using a piezoelectric pressure transducer (Kistler 6056AU38) and charge amplifier (Kistler 5011). At bottom-dead-centre of every combustion cycle the cylinder pressure was pegged by the data acquisition system using a piezoresistive pressure transducer (Druck PTX 7517-3257) located in the intake manifold, 160 mm upstream of the inlet valves. The normally aspirated

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