Impact of increasing methyl branches in aromatic hydrocarbons on diesel engine combustion and emissions

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ABSTRACT

Lignocellulosic materials have been identified as potential carbon–neutral sources of sustainable power production. Catalytic conversion of lignocellulosic biomass results in liquid fuels with a variety of aromatic molecules. This paper investigates the combustion characteristics and exhaust emissions of a series of alkylbenzenes, of varying number of methyl branches on the monocyclic aromatic ring, when combusted in a direct injection, single cylinder, compression-ignition engine. In addition, benzaldehyde (an aldehyde (-CHO) branch on the monocyclic ring) was also tested. All the molecules were blended with heptane in different proportions, up to 60% wt/wt. The tests were conducted at a constant engine speed of 1200 rpm, a fixed engine load 4 bar IMEP, and at two injection modes: constant start of fuel injection at 10 CAD BTDC, and varying fuel injection timing to maintain constant start of fuel combustion at TDC.

The results showed that the ignition delay period increased with increasing number of methyl branches on the ring, due to the rapid consumption of OH radicals by the alkylbenzenes for oxidation to stable benzyl radicals. Peak heat release rates, and concurrently NOx emissions, initially increased with increasing methyl branches, but subsequently both decreased as the bulk of heat release occurred further into the expansion stroke with significant thermal energy losses. With the exception of toluene, the number of particles in the engine exhaust increased as the number of methyl branches on the aromatic ring increased, attributable to the formation of thermally stable benzyl radicals.

1. Introduction

There is international consensus on the adverse changes in global climate arising from anthropogenic emissions of carbon (CO_2, CH_4, particulates) from fossil fuel source [1,2]. This concern has resulted in legislative targets in many countries for the use of renewable alternatives in road transport fuels [3–5]. However, there is growing unease regarding the use of fuels primarily derived from food crops. For example, ethanol from of sugar fermentation and fatty acid esters (biodiesel) from vegetable oils may not offer significant reductions in GHG emissions when considering the entirety of the fuel production lifecycle and the arising changes in land-use [6–8]. At the same time, there is growing public concern about the adverse health effects of engine exhaust pollutants such as NOx and PM, reflected in the increasingly strict vehicle emissions standards and plans to ban diesel vehicles from major cities [9,10]. Therefore, there is a need to develop future fuels from sustainable non-food crop sources, which also produce lower toxic pollutant emissions.

Current renewable fuels for both spark ignition and diesel engines,

predominantly bioethanol and fatty acid methyl esters (biodiesel) respectively, are acyclic and do not contain aromatic or cyclic constituents commonly found in liquid fossil fuels. Cyclic molecules are considered to be desirable as fuels for spark ignition engines as they generally exhibit high knock resistance [11]. Additionally, the higher energy density of aromatic molecules, relative to oxygenated acyclic molecules typical of current biofuels, also encourages their utilisation in fuel blends for diesel engines. For example, toluene, which is a cyclic aromatic, has a heating value of 40.60 MJ/kg [12], while that of methyl oleate, a common component of current biodiesel, is lower at 37.42 MJ/kg [13].

An alternative to the manufacture of fuels from feedstocks which are also suitable for food production, is to derive these fuels from associated crop residue material [14,15]. Such materials, which might otherwise be considered a waste-stream, often consist primarily of lignocellulosic biomass, comprising of lignin, cellulose and hemi-cellulose. Catalytic reformation processes, such as Fisher Tropsch, require the cleaving of all carbon to carbon bonds present in the biomass through the input of additional energy [16], and can yield a range of aliphatic molecules.

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Nomenclature			
		NO_x	nitrogen oxides
ATDC	after-top-dead-centre	O_2	oxygen
BTDC	before-top-dead-centre	OH	hydroxyl
CAD	crank angle degree	PM	particulate mass
CH_4	methane	ppm	parts per million
CI	compression ignition	rpm	revolutions per minute
CO	carbon monoxide	SOC	start of combustion
CO_2	carbon dioxide	SOI	start of injection
H_2	hydrogen	TDC	top -dead -centre
IMEP	indicated mean effective pressures	THC	total hydrocarbons
NO	nitric oxide	φ_{CH4}	methane-air equivalence ratio
		φ_{H2}	hydrogen-air equivalence ratio

Alternatively, the large polymers that make up lignin, cellulose and hemi-cellulose can also be converted to monomer units through the selective cleaving of specific targeted carbon to carbon bonds and carbon to oxygen bonds, which can be relatively less energy intensive [16,17].

Thring et al. [18] reported the conversion of lignin, over a zeolite catalyst in a fixed bed reactor, to gaseous and liquid products at temperatures between 500 °C to 650 °C with total yields of between 50% wt/wt to 85% wt/wt. Of this, the liquid fraction comprised approximately 80% wt/wt aromatic molecules consisting of benzene, toluene and xylene. As reaction temperatures were increased, the proportion of xylene present in the liquid fraction decreased while that of benzene and toluene increased. More recently, Zhang et al. [19] produced a mixture of benzene, toluene and xylene from the catalytic pyrolysis of sawdust mixed with a zeolite catalyst at temperatures between 450 °C and 600 °C. Similar to the observations of Thring et al. [18], it was found that increasing temperatures resulted in a reduction in the presence of methyl branches on the aromatic molecules, reducing the proportion of xylene present with a concurrent increase in levels of both toluene and benzene. Yan et al. [20] explored the conversion of duckweed (an aquatic plant which doubles in mass through growth every 24 h) to a crude liquid bio-oil via hydrothermal liquefaction, which consisted mostly of alkyl benzenes (toluene and benzene) and alkyl naphthalenes.

While benzene exhibits a higher cetane number than toluene (14.3 versus ~ 0 [21]), it is the latter which as a primary reference fuel has been more frequently tested as a blend component in diesel engines. Hellier et al. [22] tested a range of binary mixtures of toluene and n-heptane in a direct injection compression ignition engine at toluene levels of up to 52.2% and found an increase in the duration of ignition delay with toluene level being the primary driver of NOx levels in the exhaust. The addition of further methyl branches to aromatic and cyclic molecules has not been widely considered in the context of compression ignition, however, Baumgardner et al. [23] investigated the effects of blending various phenols potentially derived from biomass at either 2% or 5% with a reference fossil diesel. It was found that the addition of a further methyl branch to p-cresol to form 2,4-dimethylphenol resulted in a later time of peak heat release rate at constant injection timing when blended at 2% with reference fossil diesel and increased PM10 emissions at 50% and 75% load conditions. In addition, several researchers have observed an increase in sooting tendency (or threshold sooting index) with the addition of methyl branches to an aromatic ring in studies including benzene, toluene and xylenes in both diffusion [24,25] and premixed flames [26].

The study presented here investigates the effect of varying the number of methyl branches on a monocyclic aromatic ring, on the combustion and emissions of a diesel engine. Each of the aromatic molecules investigated were mixed with n-heptane to form binary blends, with the results baselined against reference fossil diesel fuel. Each fuel was tested at two injection timing modes, constant start of fuel injection and constant start of combustion. In addition to the

gaseous exhaust emissions, this paper also describes the number and size distribution of the particulate emissions in the exhaust arising from combustion of the binary fuel blends.

2. Experimental setup

All experiments in the current work were conducted on a direct injection, water cooled, single cylinder compression-ignition engine, described in [27], consisting of 2.0 L, 4-cylinder Ford Duratorq cylinder head (including valves, piston and connecting rod) mounted on a Ricardo Hydra crankcase - Table 1 lists the details of the engine geometry. The in-cylinder gas pressure was measured to a resolution of 0.2 CAD using a Kistler 6056A piezoelectric pressure transducer in conjunction with a Kistler 5018 charge amplifier. Various other operational pressures and temperatures were also monitored live and logged on PCs using National Instruments (NI) data acquisition systems. An in-house developed NI LabVIEW program evaluated the in-cylinder pressure data in real-time to determine net apparent heat release rates and the indicated mean effective pressure (IMEP). A Delphi DFI 1.3 six-hole, servo-hydraulic solenoid valve fuel injector was used to inject liquid fuel directly into the combustion chamber, with an EmTronix EC-GEN500 system used to control the injection pressure, injection timing and duration of injection. The intake air flow rate was measured using a Romet G65 positive displacement volumetric air flow meter. Fig. 1 shows the schematic of the single cylinder engine facility, including the high pressure fuel delivery system described in the following paragraphs.

A bespoke high pressure fuel system, based on previous designs by Schonborn et al. [28] and Hellier et al. [29], was used to deliver liquid fuels, such as the n-alkylbenzene/heptane blends used in this study, to the fuel injector. The fuel system consisted of a stainless steel vessel with capped ends and a free moving piston. As shown in Fig. 1, the fuel system utilised the conventional common rail diesel engine system to supply hydraulic pressure to the vessel on one side of the piston. The diesel fuel could be pressurised precisely using the Emtronix control system, and the free moving piston communicated this pressure to the test fuel and, therefore, the test fuel could be injected into the engine at

Table 1
Engine specifications.

Bore	86 mm
Stroke	86 mm
Swept volume	499.56 cm^3
Compression ratio (geometric)	18.3:1
Maximum in-cylinder pressure	150 bar
Piston design	Central ω – bowl in piston
Intake/Exhaust valves	2/2
Fuel injection pump	Delphi single-cam radial-piston pump
High pressure common rail	Delphi solenoid controlled, 1600 bar max.
Diesel fuel injector	Delphi DFI 1.3 6-hole solenoid valve
Electronic fuel injection system	1 µs duration control
Crank shaft encoder	1800 ppr, 0.2 CAD resolution