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# Diffusion- and Homogeneous-Charge Combustion of Volatile Ethers in a Compression Ignition Engine

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The combustion characteristics of several volatile ether molecules were studied under diffusion and homogeneous charge combustion modes in a compression ignition engine. Volatile ethers of low molecular mass are organic molecules that could be used as fuel for compression ignition engines. The physical and chemical characteristics of such ethers comprise high oxygen content, high volatility, and low viscosity, all of which are conducive to high thermal efficiencies and low pollutant emission during engine operation. It is thought that sootless combustion may be achieved in diffusion flames of high-speed direct injection diesel engines with some volatile ethers, due to their high oxygen content. The formation of oxides of nitrogen from the combustion of ethers may be almost eliminated by the use of lean, homogeneous charge compression ignition combustion, for which these fuel molecules are particularly suitable due to their high volatility. The first part of the experiments examines the combustion characteristics of dimethyl ether under diesel engine diffusion combustion conditions. Heat release of combustion, engine efficiency, gaseous pollutant, and nanoparticle emissions were measured and results were compared with those of conventional diesel fuel at comparable engine operating conditions. It was observed that within the accuracy of the instruments, soot-free combustion could be achieved with pure dimethyl ether in diffusion combustion. The addition of an alkyl ester lubricity-improving additive to dimethyl ether was observed to result in the emission of small nucleation mode nanoparticles (5–40 nm diameter) in the exhaust gas under certain conditions. The experiments suggested that these particles may consist of droplets of the fuel lubricity additive and engine oil forming through condensation. The second part of the experiments investigates the potential of using volatile ethers in direct-injected homogeneous charge compression ignition combustion. The molecular structure of the fuel was observed to have an important influence on the ignition process and heat release characteristics combustion. Several straight-chained and branched ether molecules were used for homogeneous charge compression ignition combustion. The experiments showed that intentional blending of the fuel molecules could be used to achieve homogeneous charge compression ignition combustion at high thermal efficiency, and that the ignition timing of the homogeneous ether–air charge within the cycle could be controlled via the molecular composition of the fuel.

## 1. Introduction

Ethers are organic molecules consisting of two alkyl groups bound by a common oxygen atom. Their synthesis may be achieved by the dehydration of alcohols<sup>1</sup> or through direct synthesis from synthesis gas.<sup>2–4</sup> In either case, the reactant may be derived from biomass, allowing the synthesis of ethers to be achieved from renewable resources.<sup>5,6</sup> Ethers particularly

commend themselves as calorific fuel in compression ignition engines due to their favorable physical and chemical properties.<sup>7,8</sup> As a result of their inability to form hydrogen bonds among their molecules, ethers are characterized by low boiling points, low enthalpies of vaporisation, and high vapor pressures.<sup>9</sup> The high volatility of ethers is conducive to fast vaporisation of the fuel and rapid mixing with air. The high oxygen content of ethers can support the oxidation of soot and its precursors within fuel-rich gases in diesel combustion, thereby suppressing the emission of soot via the exhaust gases.<sup>10,11</sup> Sootless combustion has been reported by a number

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of researchers employing the simplest ether, dimethyl ether (DME), as fuel in a diesel engine.<sup>12–14</sup> The low ignition temperature of this ether has been reported to result in particularly smooth heat release and low combustion noise during diesel engine operation in diffusion combustion mode.<sup>15</sup> In addition to diffusion combustion employed in conventional diesel engines, ethers may also be used for lean homogeneous charge compression ignition (HCCI) combustion,<sup>16–18</sup> in which not only the formation of soot can be avoided, but also the formation of NO<sub>x</sub>. This may be achieved by reducing the occurrence of high flame temperatures through the combustion of a lean, premixed, charge of fuel and air.<sup>10,19</sup> Volatile ethers are particularly conducive to this type of combustion mode due to their high volatility, which allows adequate vaporisation of the fuel and appropriate mixing of the fuel with air to take place during charge preparation. In HCCI combustion, a suitable autoignition temperature of the charge is of principal importance to engine efficiency, since it is crucial to the ignition timing of the fuel–air charge, and thus to the phasing of combustion within the thermodynamic cycle. The autoignition temperature of ethers in air is highly variable, which provides high flexibility in matching the autoignition temperature of the fuel to the engine operating conditions. The autoignition temperature of the fuel depends significantly on the structure of the alkyl groups of the molecules. Alkyl groups of high mass and straight-chained structure cause the ether molecules to have a low ignition temperature, whereas alkyl groups of lower mass and branched structure are conducive to high ignition temperatures and strong resistance to autoignition.<sup>20</sup> A suitable choice of ether fuel molecules may be used to adjust the time of ignition toward the point of peak geometric compression, as shall be described in the ensuing experimental results. Ethers may thus achieve a reasonably high thermal efficiency not only in diesel diffusion combustion mode, but also in HCCI combustion mode, yielding limited emissions of carbon dioxide (CO<sub>2</sub>) under either condition. A drawback of the use of ethers as fuels is their low lubricity, which may cause excessive wear in the fuel injection equipment. As possible solutions to this, either the lubricity of the fuel needs to be raised by the addition of a lubricity-improving additive, or the fuel system needs to be suitably designed to operate on a fuel of such low lubricity.

The aim of the experiments described herein is the study of conventional diesel diffusion combustion and HCCI combustion of volatile ethers in a diesel engine. The diffusion combustion experiments were carried out with the molecule DME, which was tested at varying injection timings and injection

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 cc
compression ratio	15:1
maximum cylinder pressure	15 MPa
piston design	central $\omega$ -bowl in piston
oil type	10W40
water temperature	85 °C

pressures. The combustion chamber pressure, heat release rate of combustion, and emissions of gaseous pollutants were measured. Nanoparticle emissions were recorded in terms of mass and size distribution. The experimental results were compared with those obtained for conventional petroleum-derived diesel fuel. In some of the experiments, an alkyl-ester based lubricity-improving additive was added to the DME in order to provide adequate lubrication of the fuel-injection equipment for long-term engine operation. It was observed that the addition of this lubricity-improving additive can influence the formation of nucleation-mode nanoparticles (5–40 nm diameter) in the exhaust gas. These did not appear to consist of soot, but rather of volatile organic substances. Combustion without the lubricity additive was observed to result in almost particleless exhaust gases. The HCCI combustion experiments were conducted with a variety of ethers of different molecular structures: DME, diethyl ether (DEE), diisopropyl ether (DIPE), and methyl tert-butyl ether (MTBE). The HCCI combustion behavior of these ethers and the possibilities of controlling the ignition timing through various methods were studied. Control of ignition timing was achieved through varying rates of cooled exhaust gas recirculation (EGR), and variations in the molecular composition of the fuel. Adjustments in the molecular composition of the fuel were observed to provide an efficient way of controlling the ignition timing of HCCI combustion. The experimental results were compared with those obtained for the combustion of conventional diesel fuel.

## 2. Experimental Methods

**2.1. Engine Characteristics.** The engine used for the experiments was a single-cylinder direct injection diesel engine with a central  $\omega$ -bowl embedded in the piston. Fuel delivery occurred through a 6-hole direct injection nozzle, and optionally via an additional port fuel injector. The engine head, cylinder bore, stroke, piston, and injectors were those of an automotive production engine (Ford Duratorq) customized to a single cylinder design using a single cylinder engine block (Ricardo Hydra). The air was naturally aspirated into the cylinder at atmospheric pressure. Cooled EGR was used in some experiments to control the time of ignition of HCCI combustion. The compression ratio of the engine was 15:1, and the engine speed was controlled via a direct-current dynamometer. Detailed engine specifications are given in Table 1.

**2.2. Fuel Injection System.** The fuel injection system comprised two independently controllable injectors, one for direct injection of fuel into the combustion chamber and one for fuel injection in the air intake port. The direct injection nozzle was used in all experiments described herein and consisted of a solenoid-controlled and hydraulically actuated injector with 6 radially arranged valve covering orifice holes of 154  $\mu$ m diameter (Delphi DFI 1.3). It was capable of operating at injection pressures between 14.5 and 210 MPa and was used for the injection of fuel in diffusion combustion as well as for the preparation of fuel–air mixtures in homogeneous combustion.

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Table 2. Fuel Injection System Specification

high pressure diesel fuel pump  
dme fuel injection pumps  
common rail  
injector  
fuel-injection controller

single-cam actuation of 3 radial pistons (BOSCH CP3)  
pneumatic actuation of differential-area piston (Haskel MS-188)  
closed-loop solenoid control up to 160 MPa pressure (Bosch CRS2)  
solenoid-controlled with 6-hole valve-covered orifice nozzle (Delphi DFI 1.3)  
12 V digital control with 1  $\mu$ s accuracy (Emtronix EC-GEN500)

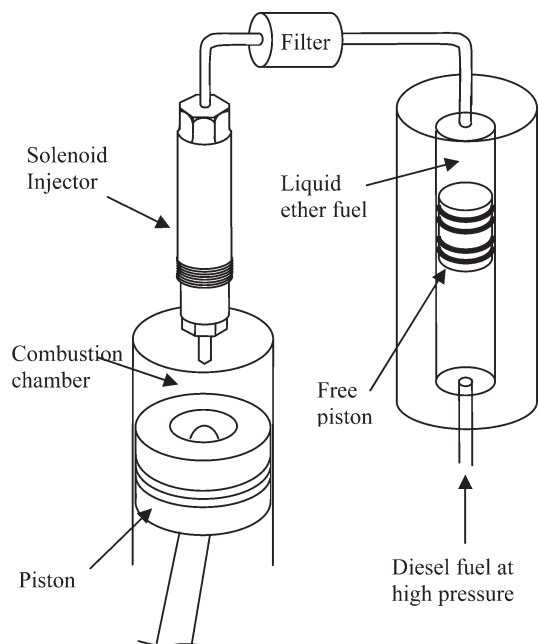


Figure 1. Liquid ethers injection system.

The port-fuel injector consisted of a solenoid-actuated multi-hole injector (Ford) operating at a constant 300 kPa injection pressure and was located 1.2 m upstream of the air intake valves. This injector was only used in specific experiments (Section 3.2.2), in addition to the direct injection nozzle.

Three different systems were used to pressurize the fuel delivered to the direct injection nozzle, and one system was used to pressurize the fuel delivered to the port fuel injector. For the direct-injection of conventional diesel fuel, a standard common rail fuel system was used to deliver the diesel fuel directly into the combustion chamber. The system used a single-cam actuated high-pressure pump with 3 pistons (Bosch CP3), a solenoid controlled common rail (Bosch CRS2), and the solenoid controlled direct injection nozzle described previously (Delphi DFI 1.3). For the injection of liquid ether fuels, this fuel system was adapted by inserting a free-piston cylinder in the fuel delivery line between the common rail and the direct injection nozzle. The free-piston cylinder was filled with a sample of the liquid ether fuel onto which the required injection pressure was transmitted from the common rail fuel pressure via the free piston. This allowed injecting ether fuels into the combustion chamber for several minutes until the free-piston system was emptied. The system allowed liquid ethers to be injected into the engine without damaging the high-pressure fuel pump by their low lubricity, and without the requirement for a lubricity-improving additive. A schematic of this system is shown in Figure 1, and a more detailed description of the system is provided in a separate paper.<sup>21</sup> For the liquid injection of DME into the combustion chamber, a further fuel system was necessary. This is because under standard conditions the vapor pressure of DME exceeds that of atmospheric pressure, causing the fuel to boil spontaneously. In order to contain the fuel and allow delivery of the fuel to the engine in liquid form, the

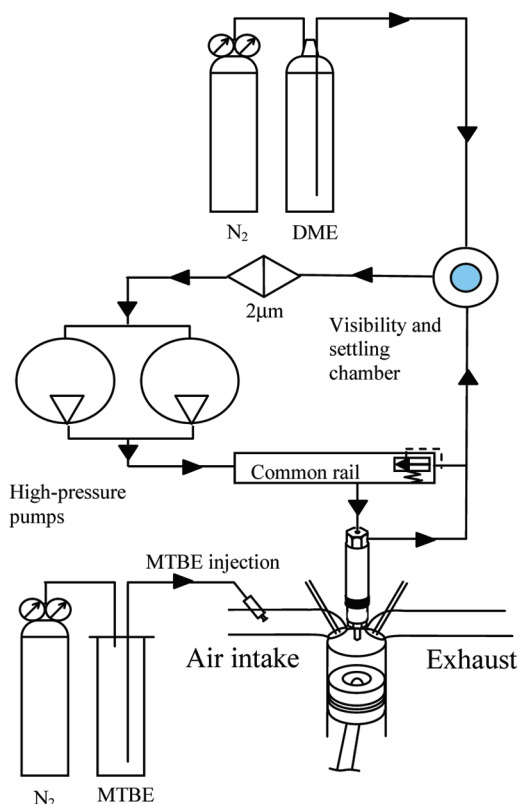


Figure 2. DME fuel system schematic with option of MTBE injection through intake air port.

common rail system was customized for pressurized fuel delivery at 1.5 MPa from a pressurized tank. The system used the same injector and common rail as that used for diesel fuel, but comprised pneumatic pumps to generate the fuel pressure and a settling chamber with optical access to check that the fuel maintained its liquid-phase. The pneumatic pumps were used instead of the original diesel fuel pump due to their better suitability for the low lubricity of DME. In the experiments described in Section 3.2.2, this DME fuel system was augmented by a port-fuel injector. This port-fuel injector allowed injection of fuel into the intake air duct at a constant pressure of 300 kPa. The fuel delivery to this injector occurred via a sealed tank that was pressurized by nitrogen gas. A schematic of this system is shown in Figure 2.

**2.3. Instrumentation.** The combustion pressure within the cylinder was measured using a piezoelectric pressure transducer (Kistler 6056AU38) and electronic charge amplifier (Kistler type 5011). The samples were recorded at intervals of 1/5° crank angle, timed using an optical shaft encoder (Encoder Technology EC85) coupled to the crank-shaft. A reference pressure was measured in the intake manifold using a piezoresistive pressure transducer (Druck PTX 7517–3257) located 160 mm upstream of the inlet valves, to which the cylinder pressure was pegged at bottom-dead-center (BDC) of each intake stroke. Exhaust gas emissions were measured using an automotive gas analyzing system (Signal Instruments), which comprises a chemiluminescence analyzer for NO<sub>x</sub>, NDIR analysers for CO and CO<sub>2</sub>, a FID for unburned hydrocarbons, and a paramagnetic oxygen analyzer. The particulate size distribution, number, and mass were measured 150 mm downstream of the exhaust valve using

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Table 3. Fuel Properties

	diesel fuel	dimethyl ether (DME)	diethyl ether (DEE)	diisopropyl ether (DIPE)	methyl-tertiary butyl ether (MTBE)
molecular formula		C <sub>2</sub> H <sub>6</sub> O	C <sub>4</sub> H <sub>10</sub> O	C <sub>6</sub> H <sub>14</sub> O	C <sub>5</sub> H <sub>12</sub> O
cetane number	54.3	65	150		
autoignition temperature (°C)		235 <sup>23</sup>	160	441	374
lower heating value (kJ/kg)	43 040	28 430 <sup>a</sup>	33 900 <sup>b</sup>	29 104 <sup>c</sup>	34 903 <sup>d</sup>
carbon proportion (% mass)	86.3	52.14	64.82	70.53	68.13
hydrogen proportion (% mass)	13.7	13.13	13.60	13.81	13.72
oxygen proportion (% mass)		34.73	21.59	15.66	18.15
density (kg/m <sup>3</sup> )	833	660	706	724	740
viscosity (mPas)	2.17 @ 40 °C	0.12	0.23 @ 20 °C	0.32	0.67 @ 20 °C
sulfur content (ppm)	3				
initial boiling point (°C)	178	−25	35	68	55
final boiling point (°C)	351	−25	35	69	55
monoaromatics	15.5				
diaromatics	1.5				
triaromatics	0.3				

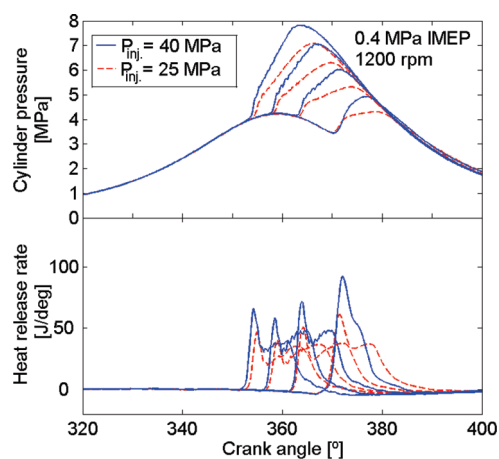
<sup>a</sup> Reference 14. <sup>b</sup> Reference 22. <sup>c</sup> Reference 23. <sup>d</sup> Reference 24.

a differential mobility particle spectrometer (Cambustion DMS500).<sup>25</sup> The particulate sampling tube used between the differential particulate mobility spectrometer and the sampling point was heated to 65 °C. Within the particulate spectrometer, a primary dilution ratio of 1:4 and a secondary dilution ratio of 1:35 (total dilution of 140) were applied to the sample flow before impaction of the particulates upon the classification electrometers. Samples of particles of specific sizes were collected using a micro-orifice uniform distribution (MOUDI) aerodynamic cascade impactor.

**2.4. Fuel Properties.** The DME was supplied by a gas supplier (BOC special gases) and had an assay of at least 95%.<sup>26</sup> DME had a vapor pressure of 510 kPa at the standard temperature of 293.15 K, and a boiling point of 248 K, meaning that DME is gaseous under standard atmospheric conditions. The lubricity-improving additive added to the DME in certain experiments consisted of a straight-chain alkyl ester mixture of an average molecular weight of 250 g/mol.<sup>27</sup> The three liquid ethers (DEE, DIPE and MTBE) were obtained from a chemical supplier (Sigma-Aldrich) and had an assay of at least 99%. The diesel fuel was an ultra low sulfur fossil refinery diesel fuel oil conforming to EN590 standard. Details of the fuel properties are given Table 3.

### 3. Experimental Results

**3.1. Diffusion Combustion of Dimethyl Ether.** *3.1.1. Effect of Injection Timing and Injection Pressure.* The diesel diffusion combustion of the simplest ether, DME, was studied at various injection pressures and injection timings, and its combustion was compared with that of diesel fuel. The injection pressures used were 25 and 40 MPa, while the injection timing was varied between 20° crank angle (CA) before top-dead-center (BTDC) to 4° CA after top-dead-center (ATDC) in incremental steps. The DME used in this series of experiments was additised with the alkyl ester lubricity additive in a concentration of 1000 ppm to protect the fuel injection system from excessive wear. All experiments were carried out at the same indicated mean effective pressure (IMEP) of 400 kPa and at the same engine speed of



**Figure 3.** Cylinder pressure and heat release rates for diffusion combustion of DME in a diesel engine. Injection pressures were 25 and 40 MPa, and injection timings 15°, 10°, 5°, and 0° BTDC.

1200 rpm. For each experiment, the injected fuel quantity was adjusted so that the engine would develop constant power.

The cylinder pressure traces for the combustion of DME and their corresponding heat release rates for injection pressures of 25 and 40 MPa and injection timings at 15°, 10°, 5° and 0° BTDC are shown in Figure 3.

The fuel injection pressure significantly influenced the heat release rates for the combustion of DME and consequently the cylinder pressure traces, as is shown in Figure 3. An increase in the injection pressure from 25 to 40 MPa resulted in distinctly higher heat release rates of combustion and higher peak cylinder pressures and temperatures. The higher injection pressure resulted in an increase in fuel flow-rate through the injector nozzle, shorter injection duration, and more rapid introduction of the DME into the combustion chamber. This is thought to have allowed more rapid mixing of the DME with air, leading to higher rates of combustion. It has been reported that increased fuel injection pressure results in increased spray tip penetration and thus better mixing of the fuel with air.<sup>28</sup> A similar trend was observed for the combustion of diesel fuel, as is shown in Figure 4. Evidence for the higher global gas temperatures occurring for both fuels under higher injection pressures is provided by the higher emission of NO<sub>x</sub> from the engine, shown in Figure 7.

Figure 3 shows that the effect which injection timing exerted on the cylinder pressure and heat release was principally one of combustion phasing. The earlier the fuel was injected, the earlier

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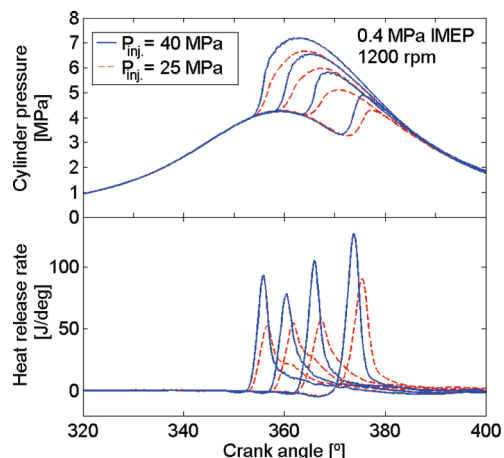
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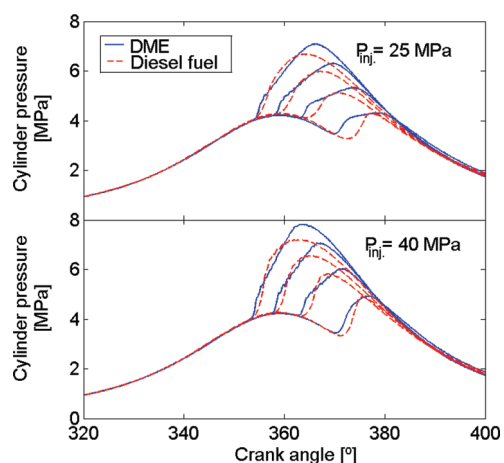
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**Figure 4.** Cylinder pressure and heat release rates for diffusion combustion of diesel fuel in a diesel engine. Injection pressures were 25 and 40 MPa, and injection timings 15°, 10°, 5°, and 0° BTDC.



**Figure 5.** Comparison between cylinder pressure traces for the diffusion combustion of DME and diesel fuel. Injection pressures were 25 and 40 MPa, and injection timings 15°, 10°, 5°, and 0° BTDC.

the combustion process took place. Under the present conditions this resulted in a larger proportion of total heat release occurring in the vicinity of TDC, which represents the point of peak mechanical compression of the cylinder charge. The coincidence of mechanical compression from the piston with heat release from the combustion process increased the peak cylinder temperatures and pressures of the cylinder charge at earlier injection timings (Figures 3 and 4). The higher gas temperatures, which are thought to occur for earlier fuel injection timings, are reflected by higher formation of  $\text{NO}_x$  from the combustion of DME or diesel fuel, as is visible in Figure 7.

A direct comparison of the cylinder pressure traces for the combustion of DME and diesel fuel for injection pressures of 25 and 40 MPa and injection timings at 15°, 10°, 5°, and 0° BTDC is presented in Figure 5. The direct comparison shows that the combustion of DME results in higher peak cylinder pressures than diesel fuel under comparable conditions. These peak temperatures occur toward the end of the combustion process. A tentative explanation for this observation may be provided as follows: First, the DME spray is likely to undergo faster vaporisation and mixing with the combustion chamber air than diesel fuel. This is likely to be attributable to higher amount of air entrainment into the fuel spray for DME as a result of the higher vapor pressure of DME and its lower boiling point, in

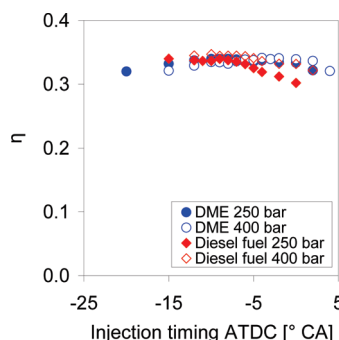
conjunction with its low enthalpy of vaporisation. Second, the heat release from the combustion of DME occurred more completely during the earlier stages of combustion during the fuel injection period, while the combustion of diesel fuel showed a higher amount of slow heat released during the burnout combustion phase which occurs after fuel injection has ceased. It is possible that this higher heat release during the final burnout stages for the combustion of diesel fuel may be a result of a higher amount of incomplete combustion products having formed as a result of pyrolysis within the fuel-rich core of the diesel flame. Such combustion products comprising of carbon monoxide, soot, and unburned hydrocarbons may contain a significant amount of the total combustion energy. This energy may be released when these combustion products are allowed to mix with sufficient amounts of air under high temperature conditions present during the burnout stages of the diffusion flame. The formation of such intermediate combustion products in the fuel-rich core of the DME spray is thought to have been much lower than for diesel fuel due the high oxygen content and better ignition quality of DME.

Figure 5 shows that cylinder pressure traces recorded for DME and for diesel fuel exhibit distinct patterns in their shape. The heat release rates of combustion (Figure 3) indicated that DME tended to burn in two distinct phases: the premixed combustion phase ensuing the ignition delay, and the later diffusion-controlled combustion phase, while the diesel fuel burned predominately in premixed combustion mode at this particular load (Figure 4). The two heat release phases of DME are reflected by the two discrete peaks in the heat-release rate, representing the premixed and diffusion combustion phases respectively. The transition between the two combustion phases was marked by a local minimum in the heat release rate. DME displayed a more pronounced diffusion combustion mode than diesel fuel. It is thought that this may be attributed to two main reasons. First, the ignition quality of DME is significantly higher than that of diesel fuel, in that its cetane number is 65, compared to 54 for the diesel fuel as shown in Table 3. Its higher cetane number reduces the ignition delay, so that for similar mixing rate of fuel with air, less fuel has premixed with air at the time of ignition. This allows less fuel to burn during the premixed combustion phase and forces fuel to burn in diffusion-controlled combustion mode. A second reason for the more pronounced diffusion-controlled combustion phase of DME with respect to diesel fuel is its lower calorific value per unit volume of fuel. In order to operate the engine at the same load, it was necessary to introduce a similar amount of calorific energy into the combustion chamber for diesel fuel and DME. Due to the lower calorific value of DME per unit volume, the injection duration for DME was around 50% longer than that for diesel fuel. Thus, at the time of ignition, a smaller proportion of the overall fuel energy had been introduced into the combustion chamber for DME than it had for diesel fuel. A smaller proportion of fuel energy was thus available for combustion during the premixed combustion phase, and consequently a larger proportion of the total heat release was forced to occur in the diffusion-controlled combustion mode.

A plot of the indicated thermal efficiency of the engine for DME and diesel fuel can be seen in Figure 6. The thermal efficiency ( $\eta$ ) of the engine was calculated for all experiments on the basis of the net indicated engine work per cycle ( $W_c$ ), the fuel mass injected per cycle ( $m_f$ ), and the lower heating value ( $Q_{HV}$ ) of the fuel, according to the relation below.

$$\eta = W_c / (m_f Q_{HV})$$

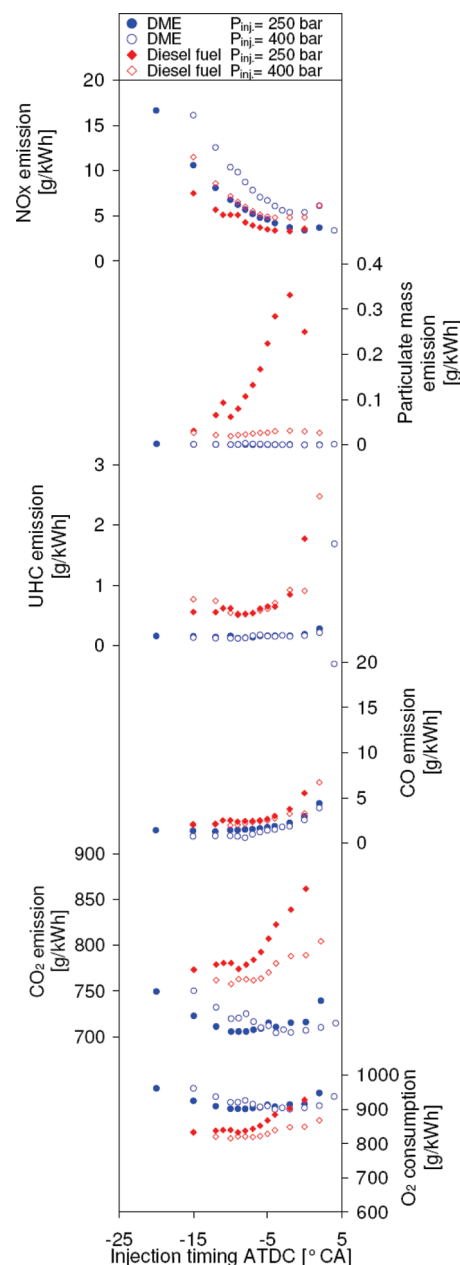
The absolute values of indicated thermal efficiency were relatively low, which could be a result of high levels of heat transfer from the charge to the combustion chamber walls and high levels of blow-by in the research engine. It can be seen that the indicated thermal efficiencies were relatively similar for



**Figure 6.** Indicated engine efficiency for diffusion combustion mode operation of DME and diesel fuel under different injection pressures in a diesel engine.

DME and diesel fuel. The highest indicated thermal efficiency for DME was recorded at an injection timing of 8° BTDC and an injection pressure of 25 MPa, whereas for an injection pressure of 40 MPa the highest indicated thermal efficiency was recorded for an injection timing of 4° BTDC. For diesel fuel, the optimum injection timings for highest indicated thermal efficiency were slightly earlier, at 9° BTDC for 25 MPa injection pressure and 10° BTDC for an injection pressure of 40 MPa. An increase in injection pressure resulted in a slight increase of thermal efficiency for both DME and diesel fuel. This increase in efficiency was more pronounced in the case of diesel fuel than it was in the case of DME.

The pollutant emissions recorded for the diffusion combustion of DME and diesel fuel are shown in Figure 7. The emission of  $\text{NO}_x$  showed clear trends with respect to injection pressure of and injection timing of both fuels. In both cases an advance in injection timing and an increase in injection pressure tend to result in an increase in  $\text{NO}_x$  emission. Detailed examination of the  $\text{NO}_x$  emissions in Figure 7 reveals that DME produces slightly higher emissions of  $\text{NO}_x$  at the same injection pressure and injection timing. Similar observations have previously been reported in the literature.<sup>14,29</sup> The theoretical adiabatic flame temperature for stoichiometric conditions at constant pressure combustion without any dissociation was calculated for initial combustion conditions of 881 K and 4.5 MPa. The calculations were performed using the thermochemical data presented in Table 3 for each fuel, and the procedure outlined by Turns.<sup>30</sup> The adiabatic flame temperatures yielded values of 2354 K for DME and 2363 K for the fossil diesel fuel. The DME was thus calculated to have a 9 K lower adiabatic flame temperature than the fossil diesel fuel, which can therefore not explain the higher  $\text{NO}_x$  emission from the combustion of DME with respect to diesel fuel. Direct comparison of the cylinder pressure traces for the combustion of DME and diesel fuel for injection pressures of 25 and 40 MPa and injection timings at 15°, 10°, 5°, and 0° BTDC in Figure 5 shows that, for the same injection timing, the combustion of DME resulted in higher peak combustion pressures. The higher combustion chamber pressures are indicative of higher gas temperatures, which in turn are conducive to higher amounts of thermal  $\text{NO}_x$  formation.<sup>31</sup> The likely reason for the higher emission of  $\text{NO}_x$  from the combustion of DME in comparison to diesel fuel is thus the higher peak gas temperature suggested by Figure 5. It is also possible that in addition to the higher cylinder pressure, differences in soot radiative heat transfer may have an effect on the relative amounts of  $\text{NO}_x$  formation between diesel fuel and DME. A higher soot loading



**Figure 7.** Exhaust gas emissions for DME and diesel oil as a function of injection timing in diffusion combustion.

in the flames of fossil diesel fuel may contribute to a reduction of the actual flame temperature of the diesel fuel. This theory is tentatively supported by the measurements of total particulate mass concentration in the exhaust gas of DME and diesel fuel. Figure 7 shows that fossil diesel fuel produced a significantly higher soot mass concentration in the exhaust gas than DME. It must be stressed that exhaust gas measurements of soot are clearly not direct measurements of the soot loading of the flames, but they may provide at least a cautious indication of the comparative soot loading within the respective flames.

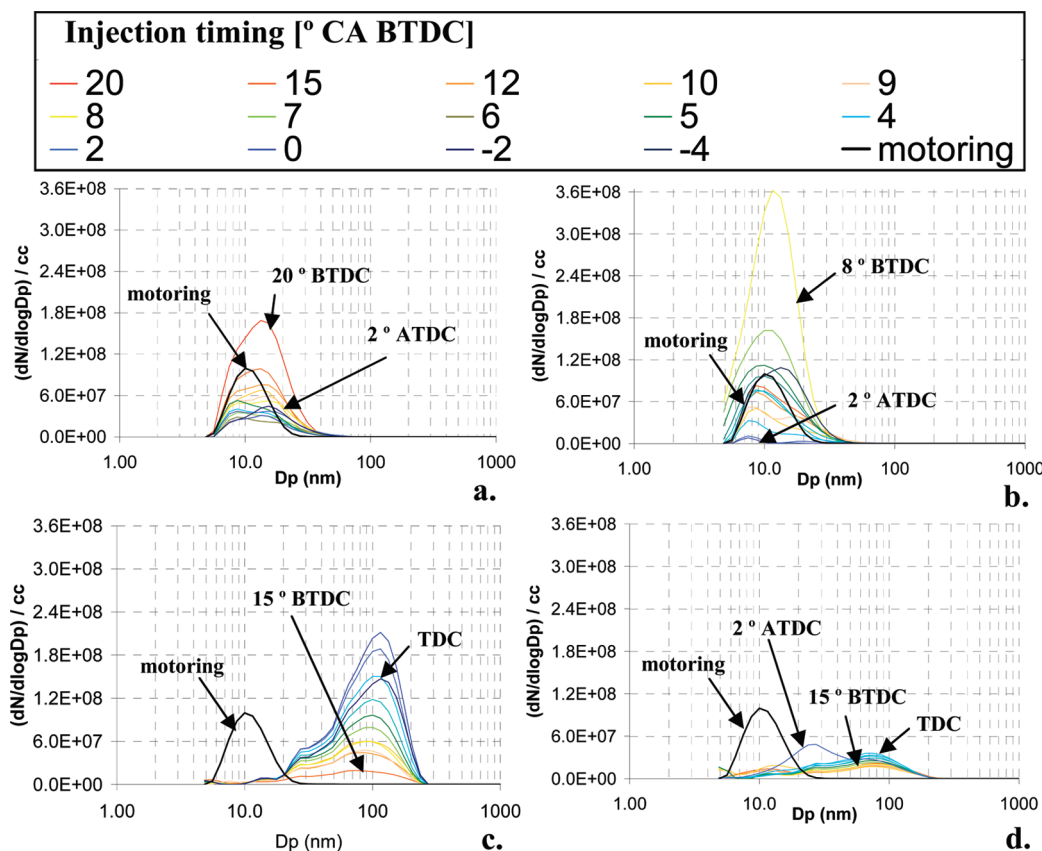
The emission of particulate mass for the combustion of DME and diesel fuel is presented in Figure 7. Figure 7 shows that the combustion of DME resulted in almost negligible emissions of particulate mass, whereas the combustion of diesel fuel resulted in particulate mass emissions that were several orders of magnitude higher than those from the combustion of DME, under similar conditions. This may be attributed to the formation of soot and its precursors within the fuel rich core of the combust-ing diesel fuel spray, whereas the high oxygen content of DME

(29) Konno, M.; Kajitani, S.; Oguma, M.; Iwase, T.; Shima, K.-I. *SAE Paper 1999-01-1116*; 1999.

(30) Turns, S. R. *An Introduction to Combustion: Concepts and Applications*; Cambridge University Press: Cambridge, UK, 2006; pp 32–35.

(31) Miller, J. A.; Bowman, C. T. *Prog. Energy Combust. Sci.* **1989**, *15*, 287–338.





**Figure 8.** Size spectral density of particulate matter for combustion of DME (a and b) and diesel fuel (c and d) at injection pressures of 25 MPa (a and c) and 40 MPa (b and d). The injection timings ranged from 20° BTDC to 4° ATDC.

allowed full oxidation of soot and its precursors to take place, due to its high oxygen content. The low emission of particulate mass from DME was independent of injection timings and injection pressures. The emission of particulate mass from the combustion of diesel fuel on the contrary showed significant correlation with injection timing and injection pressure. An increase in injection pressure of diesel fuel from 25 to 40 MPa resulted in reduction in particulate mass emissions of approximately 1 order of magnitude. This reduction in particulate mass emissions is thought to be attributable to better fuel atomization, improved air entrainment into the fuel spray, and an increase in premixed burn fraction, resulting in an improved oxidation of soot and its precursors within the fuel-rich core of the spray. An advance in injection timing of diesel fuel tended to result in a reduction of particulate mass emissions emitted from the combustion of diesel fuel at both injection pressures. This reduction in particulate mass is thought to be a result of the higher cylinder gas temperatures that occur in the postflame gases under conditions of advanced injection timing. Higher cylinder gas temperatures during the later combustion stages, in which the soot carrying postflame gases undergo dilution with sufficient oxygen in the lean cylinder charge, are known to support increased oxidation of soot.<sup>32</sup>

The size spectral density of the particulate mass emissions between 5 and 100 nm are shown in Figure 8 (a–d). Figure 8 (a and b) show the size spectral density of particulates for the combustion of DME at 25 and 40 MPa injection pressure respectively. Figure 8 (c and d) show the size spectral density of particulates for the combustion of diesel fuel at 25 and 40 MPa injection pressure respectively. It should be noted that a concentration of about 1000 ppm of alkyl-ester lubricity

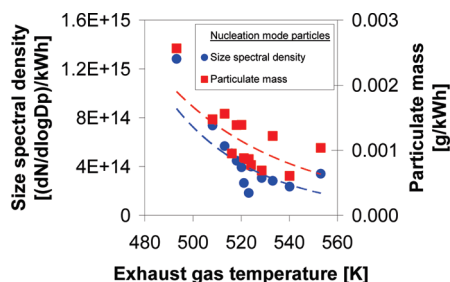
additive was present in the DME used for these experiments. The most important result shown in Figure 8 is that the combustion of DME only produced small nucleation mode particles on the order of 5–40 nm in diameter, whereas the combustion of diesel fuel produced considerable amounts of accumulation mode particles of 40–200 nm in diameter. It has been reported that the smaller nucleation mode particles (5–40 nm) typically consist of volatile organic compounds, sulphites, and water, but may contain some carbon soot and ash, whereas the larger accumulation mode particles (40–200 nm) consists predominantly of carbonaceous soot, with possible adsorbed organic compounds, sulphites, and water.<sup>33</sup> Nucleation mode particles (5–40 nm) carry considerably less mass than accumulation mode particles (40–200 nm) for a given size spectral density, due to their smaller volume. The differences in particle size shown in Figure 8 explain why the emission of particle mass from the combustion of DME were only a small fraction (0.2–10%) of the total particulate mass emitted by diesel fuel. The total level of particulate mass emitted from the combustion of DME was close to the level of particulate matter recorded for mere motoring of the engine at that particular engine speed, without any fuel injection occurring. The injection pressure did not appear to significantly influence the emission of nucleation mode particles (5–40 nm) emitted from DME, as can be seen by comparison of Figure 8 (a and b).

The effects that the fuel injection pressure and injection timing had on the size spectral density of nucleation mode particles (5–40 nm) emitted from engine operation on DME, and the accumulation mode particles (40–200 nm) formed by the combustion of diesel fuel, appeared to be fundamentally different. An advance in the fuel injection timing for DME resulted in a minor increase in the size spectral density of

(32) Tree, D. R.; Svensson, K. I. *Prog. Energy Combust. Sci.* **2007**, *33*, 272–309.

(33) Kittelson, D. B. *J. Aerosol Sci.* **1998**, *29*, 575–588.





**Figure 9.** Effect of exhaust gas temperature on nucleation mode particles from the combustion of DME with 1000 ppm straight-chained alkyl-ester lubricity additive.

nucleation mode particles, as shown in Figure 8 (a and b). An advance in fuel injection timing of diesel fuel resulted in a notable reduction of accumulation mode particle emission from the engine, as shown in Figure 8 (c and d). An increase in the fuel injection pressure for the combustion of DME resulted in a marginal increase of particulate mass emission. For diesel fuel, an increase in the fuel injection pressure resulted in a strong reduction of the accumulation mode particle emissions, as can be seen by comparison of Figure 8 (c and d). This indicates that the formation mechanisms for these two types of particle emissions are fundamentally different.

The mechanisms by which the combustion of diesel fuel leads to the emission of carbonaceous soot particles has been well documented.<sup>32</sup> The reasons for the emissions of the nucleation mode particles (5–40 nm) from the combustion of DME are less apparent, especially since DME is gaseous under the conditions encountered in the exhaust gas. It has been suggested that, due to the high oxygen content of DME, smokeless combustion may be expected in a diesel engine, which may imply that no carbonaceous soot is formed.<sup>11</sup> If the nucleation mode particles do not consist of carbonaceous soot, it is likely that they may consist of organic compounds, sulphites, water, or ash. Considering that the DME did not contain any sulfur, the formation of these particles from sulphites appears unlikely, leaving only organic compounds, water, or ash as likely constituents. Figure 9 shows that the emission of the nucleation mode particles (5–40 nm) from engine operation on DME showed some correlation with the exhaust gas temperature. A lower exhaust gas temperature results in a higher size-spectral density and mass emission of nucleation mode particles. This is an indication that the formation of these particles may result from condensation of gases within the combustion chamber or exhaust. If these particles formed through condensation, they are likely to consist predominantly of organic compounds or of water. The source of potential organic compounds was not entirely clear. DME is gaseous under the conditions encountered in the exhaust gas. Unburned DME is thus unlikely to be the cause of these particulates. It is possible that the engine lubricating oil or the alkyl-ester fuel lubricity additive present in the DME may be responsible for the formation of condensates within the exhaust gases. Further investigations were necessary to investigate the potential sources of these nucleation mode particles. The emission of nanoparticles was measured when the engine was motored without any fuel injection taking place. Figure 8 shows that mere motoring of the engine produced a similar emission of nucleation mode particles (5–40 nm) as that recorded during fuelling of the engine with DME. The particles recorded during motoring of the engine cannot derive from any component of the fuel, due to its absence. It is thought that the nucleation mode particles emitted during motoring of the engine consist of a mist of engine lubricating oil, forming within the combustion chamber as a result of the cylinder bore lubrication and the rapid reciprocating movement of the piston. When the engine was fired on diesel fuel, these nucleation mode particles were almost entirely removed, as can be seen in Figure 8 (c and d). The

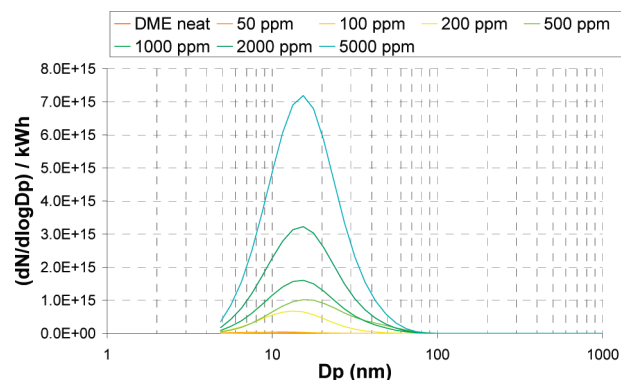
mechanism by which this removal occurs is not clear. It is possible that the oil droplets are oxidized by the combustion process, or that they may be adsorbed onto the larger accumulation mode soot particles (40–200 nm), which form under these conditions. If oxidation was the principal mechanism by which the oil particles were removed, the question arises as to why the combustion of DME did not have a similar effect. It is possible that these small particles may have been replaced by droplets forming in the exhaust gases as a result of condensation of the lubricity-improving additive. It will be shown in Section 3.1.3 that the engine lubrication oil and the fuel lubricity-improving additive can both contribute to the formation of liquid nucleation mode particles in the exhaust gases and that no visible carbonaceous soot was produced by the combustion of DME.

The emission of unburned hydrocarbons from the combustion of DME in the engine was significantly lower than that of diesel fuel under all operating conditions, as shown in Figure 7. This is likely to be mainly due to the higher ignition quality and shorter ignition delay of the DME, which reduces overdilution of the fuel spray prior to combustion. The shorter ignition delay is known to reduce the amount of fuel forming an excessively lean fuel–air mixture at the fringes of the fuel spray, which may fail to ignite.<sup>34,35</sup> For the combustion of DME, the minimum emission of UHC was recorded for fuel injection at 9° BTDC. For this injection timing, the lowest peak heat release rate was measured, suggesting that the fuel underwent the shortest ignition delay under these conditions. Figure 7 also shows that the concentration of CO in the exhaust gas is lower for the combustion of DME than it is for that of fossil diesel fuel. This is likely to be due to the higher oxygen content of DME (see Table 3), which may have reduced the local equivalence ratio in fuel-rich areas of the fuel spray, in which CO is likely to form. The emission of UHC and CO increased for both fuels if the injection timing was retarded toward the point of misfire. This indicated a deterioration of combustion efficiency of the fuels, due to insufficient time for combustion, lower temperatures, and quenching of the flames that was induced by the expansion and cooling of the cylinder charge during the later stages of the expansion stroke. Figure 8d shows that the only operating point for which any significant amount of nucleation mode particles (5–40 nm) occurred for the combustion of diesel fuel was that for fuel injection at 2° ATDC, which is the most retarded injection timing to allow reasonable combustion stability for this fuel. These nucleation mode of particles around 5–40 nm in size are likely to have formed as a result of the high concentration of UHC present in the exhaust gases under these conditions, as shown in Figure 7. This supports the hypothesis that the nucleation mode particles may predominantly consist of condensed droplets of unburned fuel.

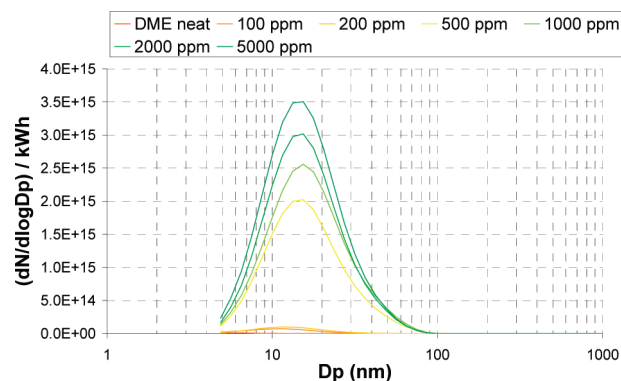
**3.1.2. Effect of Straight-Chain Alkyl Ester Fuel Lubricity-Improving Additive.** During the experiments presented so far, it had been observed that the operation of the engine on DME that had an added concentration of 1000 ppm alkyl ester lubricity additive resulted in the emission of a large number of nucleation mode particles of approximately 5–40 nm in diameter. The origin and formation mechanism of these particles remained unclear. One possibility is that these particulates consist of droplets of the alkyl ester lubricity-improving additive that may have condensed into liquid droplets due to cooling of the combustion chamber gases during expansion. A further possibility is that these particles consisted of droplets of engine lubrication oil that had formed as oil splash as a result of the rapid reciprocating movement of the piston. To establish whether the emission of nucleation mode particles was caused by the lubricity additive, a series of experiments were conducted in which the engine was operated with DME containing

(34) Heywood, J. B. *Internal Combustion Engine Fundamentals*, Int. ed.; McGraw-Hill: New York, USA, 1988; pp 622–623.

(35) Ladommatos, N.; Parsi, M.; Knowles, A. *Fuel* **1996**, 75, 8–14.



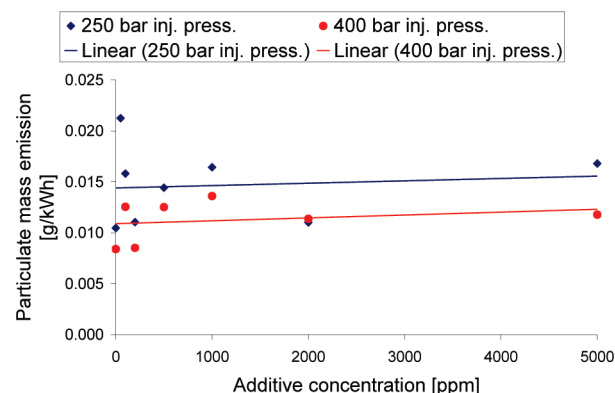
**Figure 10.** Size spectral density of particulates for DME containing different concentrations of a straight-chain alkyl ester-lubricity-improving additive injected at 25 MPa pressure.



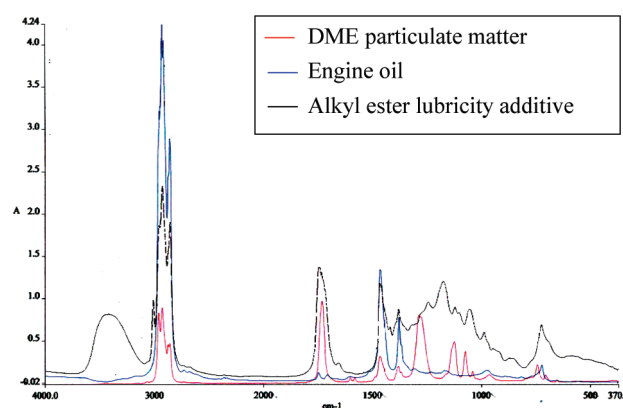
**Figure 11.** Size spectral density of particulates for DME containing different concentrations of a straight-chain alkyl ester lubricity-improving additive injected at 40 MPa pressure.

different concentrations of this additive. Neat DME and DME with progressively increasing concentrations of alkyl ester additive were injected into the combustion chamber at 25 MPa injection pressure and an injection timing of 8° BTDC, which was the optimum injection timing for minimum fuel consumption at this condition. The experiments showed that if no lubricity-improving additive was present in the DME, virtually particle-free combustion could be achieved under diffusion-combustion conditions, as can be seen in Figure 10. This provided an indication that under these conditions the engine lubrication oil droplets that were visible during motoring of the engine were oxidized to a large extent by the combustion of DME. As the alkyl ester lubricity additive was introduced into the fuel, and its concentration was gradually increased from 50 to 5000 ppm, the number of small particles increased progressively. This result suggested that the lubricity-improving additive was involved in the formation of nucleation mode particles. The experiments were also carried out for a higher injection pressure of 40 MPa. Figure 11 shows that similar results were obtained at this higher injection pressure. Despite the observed increase in number density of the nucleation mode particles due to an increased concentration of lubricity additive, only a relatively moderate increase in particulate mass from the combustion was recorded, as is illustrated in Figure 12.

**3.1.3. Fourier Transform Infrared Spectrum of Particulate Matter from DME-Fuelled Engine.** A sample of the particulate mass that had been formed during engine operation with 1000 ppm concentration in diffusion combustion mode at 25 and 40 MPa injection pressure was collected using the MOUDI aerodynamic cascade impactor. The optical appearance of the particulate mass was not that of carbonaceous particles typical of diesel combustion, but rather that of a viscous yellow liquid



**Figure 12.** Total particulate mass emissions from DME injected at different pressures with different lubricity-improving additive concentrations.



**Figure 13.** FTIR absorbance spectrum comparison of DME particulate matter formed with 1000 ppm lubricity-improving additive concentration with engine oil and straight-chain alkyl ester lubricity-improving additive.

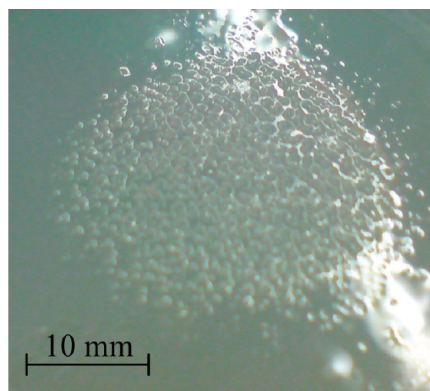
resembling engine oil or the alkyl-ester lubricity-improving additive. This liquid was analyzed for its FTIR spectrum, which was compared with that of the engine lubrication oil and that of the lubricity-improving additive. Figure 13 shows a comparison of the three FTIR traces. The FTIR analysis was not conclusive in that it did not identify either of the two liquids as the sole source of the particulates. The FTIR trace of the particulate mass showed some resemblance with both the lubricity-improving additive and with the engine lubrication oil. The visual appearance of the particulate matter on a polycarbonate membrane after being collected using a micro-orifice uniform distribution aerodynamic cascade impactor is shown in the photograph that is Figure 14.

**3.2. Homogeneous Charge Combustion of Volatile Ethers.** It is known that by reducing the occurrence of high temperatures, the formation of NO<sub>x</sub> can be reduced, and even completely suppressed.<sup>10</sup> The absence of fuel-rich gases beyond a certain stoichiometry and temperature suppresses the formation of soot during combustion.<sup>10</sup> It has thus been proposed to operate compression ignition engines on the combustion heat of a lean, homogeneous mixture of fuel and air.<sup>36–38</sup> The ignition and combustion of homogeneous mixtures of hydrocarbons and air is achieved through increasing the charge temperature by adiabatic compression of the charge, which may result in a

(36) Onishi, S.; Jo, S. H.; Shoda, K.; Jo, P. D.; Kato, S. *SAE Paper 790501*; 1979.

(37) Najt, P. M.; Foster, D. E. *SAE Paper 830264*; 1983.

(38) Thring, R. H. *SAE Paper 892068*; 1989.



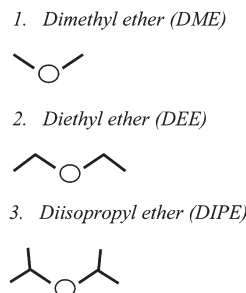
**Figure 14.** Optical appearance of the particulate matter emitted by the diesel engine during operation on DME on a polycarbonate membrane.

**Table 4.** HCCI Running Conditions for Effect of Molecular Structure

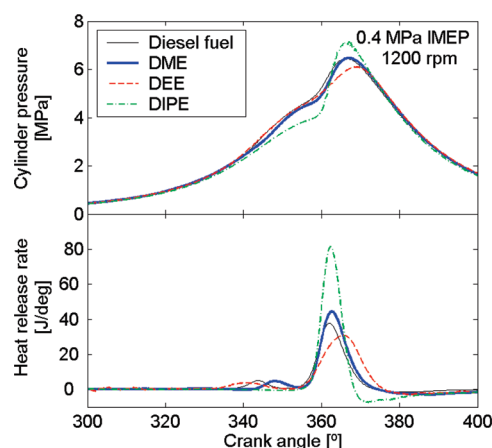
combustion type	HCCI	
compression ratio	15:1	
IMEP	400 kPa	
engine speed	2000 rpm	
injection pressure	45 MPa	
injection timing	120 ° BTDC	
coolant temperature	84 ± 3 °C	
	EGR rate	intake air temperature
diesel fuel	43%	25 °C
DME	61%	23 °C
DEE	78%	21 °C
DIPE	0%	165 °C

multistage ignition process of the hydrocarbon and air mixture, depending on the fuel chemistry.<sup>19</sup> The potential of achieving HCCI combustion with a low emission of NO<sub>x</sub> and soot, at high thermal efficiency, was examined for various volatile ethers and diesel fuel. The results were compared with those obtained under diffusion combustion mode in Section 3.1. To obtain high thermal efficiency of the engine under HCCI conditions, it is desirable to obtain ignition of the charge when the piston is situated around TDC. The experiments presented in the following sections examine various methods of controlling the ignition timing, with particular attention given to the ability of the molecular structure and composition of the fuel in achieving this.

**3.2.1. Effect of the Molecular Structure of the Fuel on HCCI.** A brief study was conducted on the effect of molecular structure of three volatile ethers in direct injection HCCI combustion, and the results were compared with those of fossil diesel fuel. The ignition timing of all fuels was controlled using cooled EGR or intake air heating so that the ignition of the high-temperature combustion phase occurred around TDC for all fuels. All experiments were conducted at the same geometric compression ratio of 15:1, the same engine speed of 2000 rpm, and under the development of the same engine load of 400 kPa. Details of the engine operating condition are given in Table 4. The three ether molecules consisted of DME, DEE, and DIPE. The molecular structure of the ethers is shown in Figure 15. Depending on their molecular structure, the fuel molecules had different ignition characteristics. Fuel molecules with alkyl groups of high mass and straight-chained structure had higher ignition qualities than fuel molecules with alkyl groups of lower mass and branched structure. Thus, DEE with its straight alkyl groups and longest alkyl chains had the highest ignition quality, followed by DME with its shorter alkyl chains, and finally DIPE with its branched alkyl groups. Cetane numbers and autoignition temperatures for the individual fuels are presented in Table 3. To obtain constant ignition around TDC during the experiments, DME



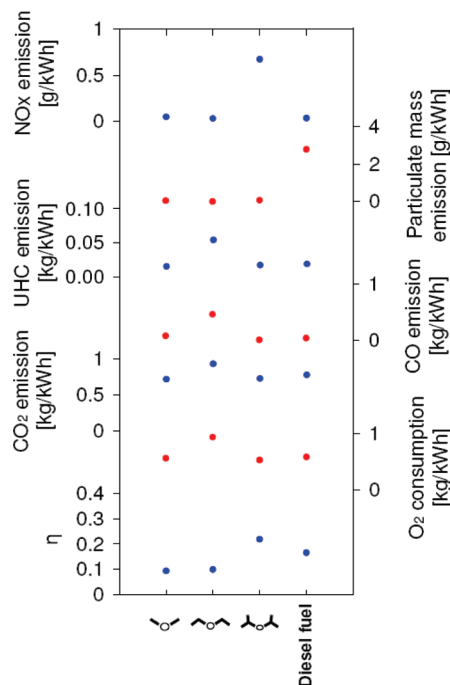
**Figure 15.** Molecular structure of the ethers.



**Figure 16.** Cylinder pressure and heat release rate for volatile ethers and diesel fuel in direct injection HCCI combustion mode.

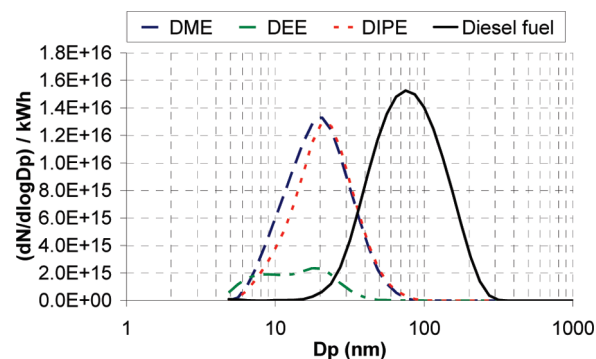
and DEE were subjected to different rates of cooled EGR to retard their ignition timing, whereas DIPE, which had a significantly lower ignition quality, was subjected to intake-charge heating to advance its ignition timing. Details about the EGR rates and intake charge temperatures are presented in Table 4. The combustion chamber pressure and heat release rates of combustion from the experiments are shown in Figure 16. The pressure traces show that the highest peak pressure among the ethers was recorded for the combustion of DIPE, followed by DME, and that the lowest peak pressure trace was recorded for DEE. The combustion of diesel fuel produced a similar pressure trace to that of DME. The heat release rates in Figure 16 illustrate that these variations in combustion chamber pressure were due to strong variations in the velocity of combustion among the fuels. DIPE clearly produced the fastest combustion process with the highest heat release rates and the shortest combustion duration. The slowest combustion was recorded for DEE, which produced the lowest heat release rates and had the longest combustion duration in Table 4, which suggests that the reduction in heat release rates is correlated with an increase in EGR rate, indicating that the combustion reactions were slowed down as a result of a dilution of the reactants through recirculated exhaust gas. In the experiment using DIPE as fuel, the higher intake air temperature may also have contributed toward the faster rate of combustion. The heat release rates in Figure 16 show that fuels released significantly different proportions of heat during the low-temperature combustion phase, depending on their molecular structure. The two ethers with straight alkyl groups (DME and DEE) showed significant heat release during the low temperature combustion phase, whereas the branched ether (DIPE) only displayed a single high-temperature combustion phase. Figure 16 suggests that the apparent heat release rate for the combustion of DIPE becomes negative for a short period of time after TDC. This may be attributed to heat transfer from the combustion chamber charge



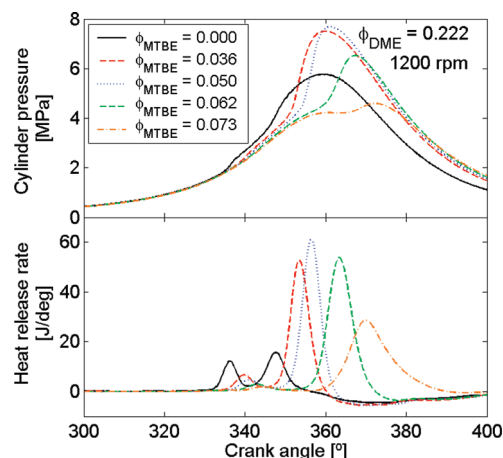


**Figure 17.** Gaseous exhaust emissions for three volatile ethers and diesel fuel for direct injection HCCI combustion.

to the walls and piston, which was accounted for in the heat release analysis, and should not be interpreted as a combustion phenomenon. Figure 17 shows the emission of gaseous pollutants and the indicated thermal efficiency of the engine. All fuels exhibited extremely low emissions of  $\text{NO}_x$  in comparison with diffusion combustion operation of the engine (Section 3.2.1), confirming the advantages of HCCI combustion for low  $\text{NO}_x$  emission. DIPE was the only fuel to produce a notable amount of  $\text{NO}_x$  among the fuels. This may be explained by the higher intake air temperature and lower EGR rate applied to its combustion process, both of which would have resulted in higher combustion temperatures. Figure 17 shows that all ethers produced low levels of particulate mass emissions in HCCI combustion. The HCCI combustion of diesel fuel produced a very high level of particulate mass under these conditions, which exceeded that of engine operation under diffusion combustion mode. It is thought that the high particulate mass emission from diesel fuel may be attributed to high levels of fuel impingement on the combustion chamber walls, as a result of its low volatility. It should be noted that the injection system and combustion chamber were not purposely adapted for operation of direct injection HCCI combustion. The low cylinder pressures and temperatures into which the fuel was injected during the early compression stroke are thought to have resulted in a long liquid length of the fuel spray, slow evaporation of the fuel droplets, and fuel impingement on the cylinder walls and piston. Although this phenomenon may be reduced by better design and operating strategies of the engine, it highlights the significance of fuel volatility when injecting diesel fuel early during the compression stroke to obtain HCCI combustion. The effect that EGR had on the pollutant emissions is clearly distinguishable for the combustion of DEE and DME in comparison to DIPE. These two straight-chained ethers clearly showed the highest emissions of carbon monoxide and unburned hydrocarbons, while also exhibiting the lowest emission of  $\text{NO}_x$ . This is likely to be a result of the high EGR rate that was applied to these fuels in order to obtain constant ignition of the fuel around TDC. A high EGR rate would be expected to reduce the flame temperatures, thereby causing lower emission of  $\text{NO}_x$  and higher emission of CO and UHC. The highest thermal efficiencies were measured for those fuels with the lowest EGR rates in these



**Figure 18.** Size spectral density of particulate emissions between 5 and 1000 nm for ethers in HCCI combustion.



**Figure 19.** Cylinder pressure and heat release rate for HCCI combustion of DME with varying concentration of MTBE in the intake air.

experiments. It is thought that this may be a result of the higher combustion efficiency of these fuels due to their lower emission of UHC and CO and due to the increased combustion temperatures.

**3.2.2. HCCI of DME with Vapor of Methyl-tert-butyl Ether As Ignition Suppressing Additive.** The experiments on the molecular structure shown in the preceding section demonstrated that the structure of the ether molecules had a strong effect on their ignition quality, which strongly affected the HCCI combustion conditions. It was observed that the straight-chained ethers DME and DEE had excessively high ignition qualities for these engine operating conditions, requiring large amounts of cooled EGR to retard their ignition timing toward TDC. High rates of EGR may have detrimental effects on combustion efficiency, resulting in reduced thermal efficiency of the engine. The branched ether on the contrary had a low ignition quality and required additional heating of the intake air to achieve ignition. In the following experiment, a mixture of varying proportions of a straight-chained ether and a branched ether were used to adjust the ignition quality of the ether fuel so that ignition of the charge could be obtained around TDC without the need for cooled EGR or intake air heating. A homogeneous mixture of DME and methyl-tertiary butyl ether (MTBE) were premixed with air in the combustion chamber using the experimental arrangement shown in Figure 2. DME was injected at 25 MPa directly into the combustion chamber at the start of the intake stroke, while MTBE was injected at 0.3 MPa into the aspirated intake air at a position 1.2 m upstream of the intake air valves. The engine speed was 1200 rpm for all mixtures. The equivalence ratio of DME was kept constant at  $\Phi_{\text{DME}} = 0.222$ , whereas the equivalence ratio of the MTBE was increased in

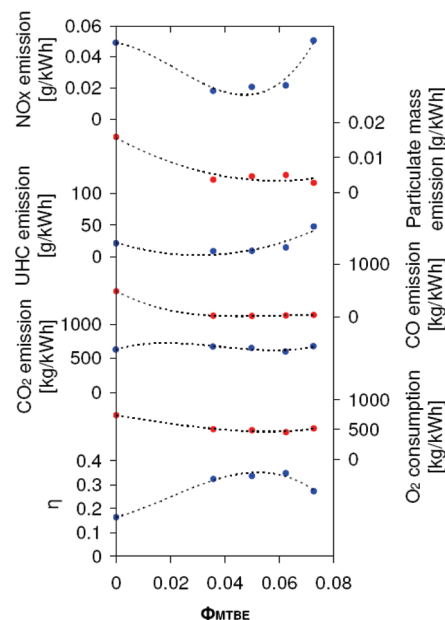
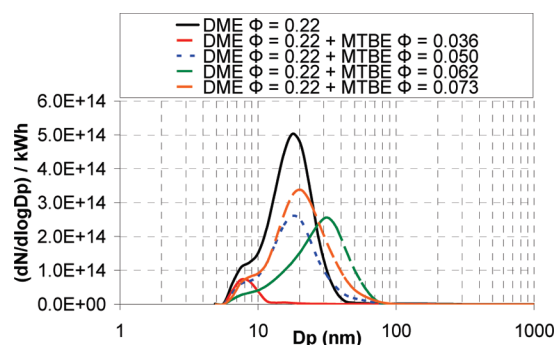


**Table 5. IMEP for Different Equivalence Ratios of MTBE**

IMEP (kPa)	88	316	363	401	391
$\Phi_{\text{DME}}$	0.222	0.222	0.222	0.222	0.222
$\Phi_{\text{MTBE}}$	0.000	0.036	0.050	0.062	0.073
$\Phi_{\text{Total}}$	0.222	0.307	0.342	0.372	0.397

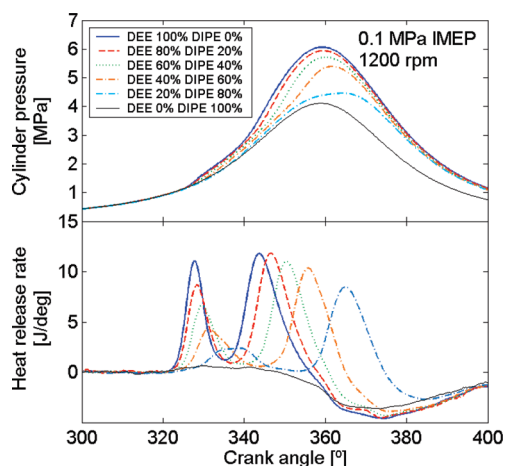
five progressive steps from  $\Phi_{\text{MTBE}} = 0.000$  to 0.073. The total equivalence ratio of DME and MTBE in combination thus increased from  $\Phi_{\text{Total}} = 0.222$  to 0.40 as the addition of MTBE was increased. Details of the fuel–air stoichiometries are given in Table 5. The engine load was not constant for all experiments. At its optimum condition ( $\Phi_{\text{MTBE}} = 0.0624$ ), the engine load was approximately 400 kPa and is thus comparable to the engine operating condition used in Section 3.1. Figure 16 shows the combustion chamber pressure and heat release rate histories of the combustion. Despite an incremental rise in the overall equivalence ratio from  $\Phi_{\text{Total}} = 0.222$  to 0.40 by the addition of MTBE, the time of ignition was progressively retarded as the amount of MTBE was increased. It can be observed in Figure 16 that the low-temperature heat release was progressively suppressed by the addition of MTBE, while retardation of the high-temperature heat release phase occurred. The peak heat release rate of the high-temperature combustion phase was initially increased as the equivalence ratio of the MTBE is increased from  $\Phi_{\text{MTBE}} = 0.000$  to 0.036 and then to  $\Phi_{\text{MTBE}} = 0.050$ , but subsequently reduced again upon a further increase of the MTBE equivalence ratio to  $\Phi_{\text{MTBE}} = 0.062$  and then to  $\Phi_{\text{MTBE}} = 0.073$ . Figure 20 shows that the highest thermal efficiency was achieved for an MTBE equivalence ratio of  $\Phi_{\text{MTBE}} = 0.062$ . It can be seen from the emission of gaseous pollutants in Figure 20 that the highest two values of equivalence ratio of MTBE, which retard the combustion beyond TDC, caused a slight increase in the concentration of UHC in the exhaust gas, indicating a deterioration of the combustion efficiency. It is thought that MTBE is responsible for elimination of radicals forming from the thermal decomposition of DME molecules, thereby delaying and finally entirely suppressing the combustion process. The MTBE was thus used to control the time of ignition of the charge. This suggests that a binary mixture of two ether molecules with different ignition characteristics in conjunction are effective at controlling the time of ignition of volatile ethers under HCCI operating conditions in an internal combustion engine. Similar results have been shown with mixtures of DME and other fuels of higher resistance to autoignition.<sup>39,40</sup> A comparison of the efficiency and pollutant emission data of these experiments with those of diffusion combustion (Figure 6, and Figure 7), shows that HCCI combustion was able to achieve similarly high engine efficiencies as diffusion combustion. The emission of  $\text{NO}_x$  for HCCI combustion was 2 orders of magnitude lower than diffusion combustion, whereas the emission of particulates from HCCI combustion of the volatile ethers was still lower than for diffusion combustion with diesel fuel. The particulate size spectral density in Figure 21 shows that the experiments produced a single mode of particles between 5 and 80 nm in diameter. UHC and CO emissions were considerably higher for HCCI combustion than for diffusion combustion.

**3.2.3. HCCI of a Direct-Injected Binary Mixture of DEE and DIPE.** The experiments presented in Section 3.2.2 showed that a binary mixture of two ether molecules with different ignition characteristics can be used to control the time of ignition of HCCI combustion by separate injection at two different locations. DME was a fuel that was gaseous under atmospheric conditions. A further series of experiments was carried out with liquid ethers to achieve this type of combustion and to show

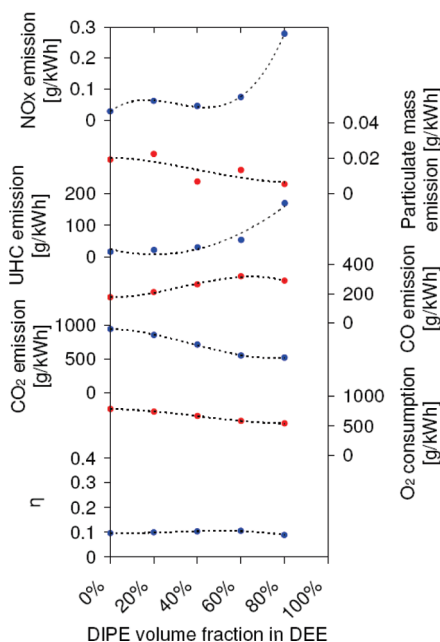
**Figure 20.** Gaseous exhaust emissions for HCCI combustion of DME with varying amounts of MTBE.**Figure 21.** Particulate size density for HCCI combustion of DME with varying amounts of MTBE.

that both fuels may be premixed as a single fuel prior to injection directly into the combustion chamber. DEE and DIPE were mixed on a volumetric basis in six incremental steps consisting of one, two, three, four, and five fifths DIPE in DEE. The engine speed was 1200 rpm and the engine load was kept constant at 100 kPa. The fuel quantity injected per cycle was adjusted in each case, so that this constant engine load was achieved under all conditions. The cylinder pressure and heat release histories of the experiments are shown in Figure 22. The combustion chamber pressure and heat release rates show that as the proportion of DIPE in DEE increases, the ignition is progressively retarded. An increase in the proportion of DIPE suppressed the proportion of heat released during the low temperature combustion phase. The value of the heat released during the later high-temperature combustion phase remained approximately constant. The mixture of 1/5 DEE and 4/5 DIPE by liquid volume gave the best combustion phasing for this engine with geometric compression ratio of 15:1. As observed for the mixtures of DME and MTBE, the combustion efficiency deteriorated slightly for mixtures containing high concentrations of the branched ether molecule. This was reflected in the increasing emission of UHC, especially for the 4/5 mixture of DIPE in DEE. The highest thermal efficiency was achieved for a mixture of 3/5 DIPE and 2/5 DEE due to the better combustion efficiency and lower emission of

(39) Yeom, K.; Bae, C. *Energy Fuels* 2007, 21, 1942–1949.(40) Yeom, K.; Bae, C. *Energy Fuels* 2007, 23, 1956–1964.

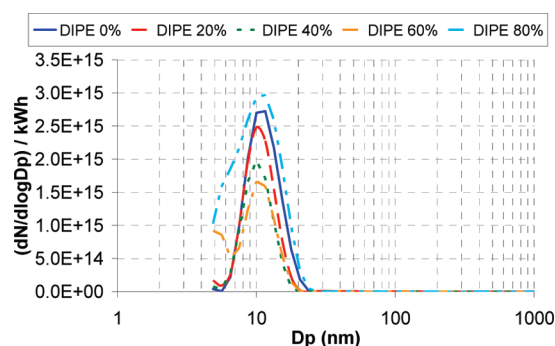


**Figure 22.** Cylinder pressure and heat release rate for HCCI combustion of DEE with varying concentration of DIPE in the intake air.



**Figure 23.** Exhaust gas concentration for HCCI combustion of DEE and DIPE in varying proportions.

UHC. The thermal efficiencies measured in this series of experiments were significantly lower than for the diffusion combustion experiments presented in Section 3.1 or the homogeneous charge experiments presented in Section 3.2.2. The reason for this low efficiency is thought to be the low engine load, which has been reported to reduce efficiency considerably.<sup>19</sup> The emission of particulate mass was relatively similar for the mixtures of DEE and DIPE as can be seen in Figure 23. The particulate size spectral density in Figure 24 showed that only very fine particles on the order of 5 and 30 nm diameter were generated. The experiments demonstrated that it is possible to control the ignition timing of HCCI combustion by varying the composition of an ether fuel consisting of a binary mixture of a straight-chained and a branched ether. This concept was implemented even when using liquid premixed ethers under direct fuel injection into the combustion chamber, resulting in low  $\text{NO}_x$  and particulate emissions, with the potential for high thermal efficiencies.



**Figure 24.** Size spectral density of particulates for HCCI combustion of direct injected mixtures of DEE and DIPE.

**Table 6.** Equivalence Ratio for DEE and DIPE Mixtures

DEE (vol. %)	DIPE (vol. %)	DEE (mass %)	DIPE (mass %)	DEE ( $\Phi$ )	DIPE ( $\Phi$ )	Combined ( $\Phi$ )
100	0	100.00	0.00	0.316	0.000	0.3165
80	20	79.14	20.86	0.249	0.071	0.3214
60	40	58.72	41.28	0.183	0.140	0.3236
40	60	38.73	61.27	0.125	0.216	0.3423
20	80	19.16	80.84	0.075	0.345	0.4213

#### 4. Conclusions

Combustion and emissions of volatile ethers of low molecular weight were investigated through diffusion and homogeneous-charge combustion experiments in a diesel engine. The heat release characteristics, as well as the emission of gaseous pollutant and nanoparticles were measured for DME in diffusion combustion. Results were compared with those produced by the combustion of conventional diesel fuel oil at comparable engine conditions. The HCCI combustion of various volatile ethers of low molecular mass was studied. It was observed that molecular structure of the ethers strongly influenced the ignition and combustion process, and that by blending various ethers of different molecular structure with each other, the combustion timing within an HCCI engine could be reliably controlled.

**4.1. Diffusion Combustion.** (1) The combustion of the simplest ether DME provided comparable engine efficiency as diesel fuel in diffusion combustion. (2) Sootless combustion could be achieved when operating a diesel engine under diffusion combustion of DME. (3) At constant IMEP an increase in the fuel injection pressure from 25 to 40 MPa lead to a significant increase in the peak heat release rate for DME and diesel fuel accompanied by a significant increase in  $\text{NO}_x$  concentration. (4) An increase in the fuel injection pressure from 25 to 40 MPa lead to a significant reduction in total particulate mass formed from the combustion of fossil diesel fuel but to no considerable changes in particulate mass concentration from the combustion of DME. (5) It was observed that an alkyl ester lubricity additive added to DME in concentrations ranging from 50 to 5000 ppm contributed to the emission of small nucleation mode particles (around 5–40 nm in diameter). The experiments suggested that these particles may consist of droplets of this additive condensing in the exhaust gas. The experiments also suggested that droplets from the engine lubricant oil may contribute to the formation of nucleation mode particles.

**4.2. Homogeneous Charge Combustion.** (1) The homogeneous charge combustion of ethers was able to produce almost  $\text{NO}_x$ -free exhaust gas, while achieving lower particulate

emissions than for operation of the engine on diesel fuel in diffusion combustion mode. (2) EGR could be used to control the ignition timing of a homogeneous charge of ethers and air. The main drawback was some deterioration of combustion efficiency for high rates of EGR. (3) The molecular structure of ethers had an important influence on their ignition and combustion characteristics. An increase in the alkyl chain length of the ether molecules lead to an increase in its ignition quality, while branching of the chain length lead to a severe reduction of its ignition quality. (4) A fuel using different proportions of ethers of different

molecular structures and thus of different ignition qualities was successfully used to control the ignition timing of homogeneous charge combustion in a diesel engine. The two fuel components could be gaseous or liquid and could be injected into the engine separately or as a joint mixture. (5) Using different proportions of two volatile ethers of different ignition qualities in HCCI combustion was observed to lead thermal efficiencies of the engine comparable to that of diffusion combustion, while leading to lower  $\text{NO}_x$  and particulate emissions, at the expense of higher CO and UHC emissions.