



Understanding the impact of cavitation on hydrocarbons in the middle distillate range



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HIGHLIGHTS

- Ultrasound used to study the impact of cavitation on hydrocarbon fuels.
- Resultant pyrolytic degradation produces small particles of amorphous and graphitic-like carbon.
- Kinetically or thermally driven agglomeration produces micron sized particles.

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ABSTRACT

Hydrocarbons in the middle distillate range (C_8 – C_{26}) have been treated with ultrasound at 20 kHz – a frequency sufficient to drive acoustic cavitation. The high temperatures experienced as a result of the implosion of fuel vapour bubbles are sufficient to produce pyrolytic degradation and dehydrogenation, as well as a growth mechanism that results in the formation of small particles that have similarities with the primary soot particles produced during diesel combustion. These nanosized particles agglomerate as a result of kinetically driven collisions during cavitation to form a dispersion of micron sized particles in the treated hydrocarbon. The particles are carbonaceous in character, being a mixture of amorphous and graphitic-like carbon. The mass of material produced increases with the C/H atomic ratio of the hydrocarbon undergoing cavitation and is decreased through the addition (1–3% v/v) of low boiling paraffinic hydrocarbons, possibly as a result of lowering the temperature developed inside imploding cavities. Dispersions of microparticles contain equilibrated levels of nanoparticles. If sufficiently high numbers of these smaller primary particles are present they agglomerate due to thermally driven collisions during post-cavitation storage. When this happened a sharp rise in the number of 1–2 μm particles was seen after only a few days. Some evidence is presented for the behaviour of ultrasonically treated hydrocarbons being related to the degradation of diesel fuel exposed to hydrodynamic cavitation in the fuel systems of modern common rail direct injection diesel engines.

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1. Introduction

Ultrasound has become a common laboratory tool used to generate acoustically driven cavitation and chemical reactions in liquids (sonochemistry) [1,2]. The compression and rarefaction of the sound waves when passed through a liquid produces bubbles; the formation, growth and collapse of which is known as cavitation. These bubbles, which are comprised of vapour and dissolved gases, shrink and expand under the influence of the acoustic field. Individual bubbles experience interference from their surroundings and consequently expansion to an unstable size can result,

followed by an implosive collapse. This produces localised hot spots ($\sim 5000\text{ K}$) which are characterised by very rapid heating and cooling rates ($>10^9\text{ K s}^{-1}$) [3–7].

The acoustic sonication of a range of hydrocarbons that fall within the middle distillate range (C_8 – C_{26}) has now been studied as a means of simulating some of the chemistry that may occur in diesel fuel whilst in the high pressure fuel systems of modern common rail direct injection compression ignition engines. The cavitation of fuel in these systems is hydrodynamic in origin, as opposed to acoustic, and can result from the pressure drop across an orifice or when fast moving flows turn sharp corners. Some of the first reports of non-aqueous sonochemistry were published over fifty years ago and suggest that the sonication of aromatic and heterocyclic compounds produces ring cleavage and acetylene

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production [8–10]. Subsequently Suslick and co-workers found that alkanes undergo sonochemical reactions which are similar to high temperature (>1200 °C) pyrolysis [11]. For example, the products of *n*-decane sonolysis are hydrogen, methane, acetylene and a series of alkenes including ethylene, propylene, butene, pentene, etc. This is consistent with the operation of a radical chain Rice mechanism [12]. Riesz and Misik in related work trapped and identified the radicals produced during the sonolysis of a number of different organic liquids, including *n*-alkanes. Their results were also consistent with a pyrolysis mechanism [13,14].

Cataldo found that the prolonged sonication of benzene, toluene, styrene and tetralin produced insoluble dark matter [15]. Infrared spectroscopy of the material from benzene sonolysis suggested that the product contained a cross-linked structure similar to radiation-damaged polystyrene. Decalin and tetralin sonication caused aromatisation reactions, although decalin was also cracked to *o*-xylene and ethylene. Somewhat similar findings have also been reported by Katoh and co-workers, who produced C₆₀ fullerene from benzene sonolysis [16]. In subsequent work, the same group produced carbon nanotubes by applying ultrasound to liquid chlorobenzene containing suspended ZnCl₂ particles [17]. A large number of sono-polymerisation reactions have also been reported [18–22].

Four different types of reaction have therefore been observed in the ultrasonic destruction of non-aqueous liquids: Radical pyrolysis, thermal cracking, radical polymerisation and dehydrogenation. This results in the possibility of both larger and smaller molecules being formed in hydrocarbons that have undergone cavitation.

In 1995 Price and co-workers explored the possibility of using ultrasound for accelerated aging of diesel fuels in an attempt to predict long-term storage stability [23,24]. Common rail high pressure diesel injection systems were not widely available in the market at this time. Experiments with dodecane showed evidence for thermal cracking after 20 h of sonication, with detection of C₇–C₁₀ species by gas chromatography mass spectrometry. After automotive grade diesel was sonicated for >6 h, sediment was produced with an average molecular weight of 40,000 amu. The material was deep brown in colour, almost completely soluble in tetrahydrofuran (THF) and had a UV–Vis absorption spectrum characteristic of aromatic species. Infrared analysis suggested the presence of ester carbonyl groups, unsaturated hydrocarbons and possibly indole-like groups.

More recently an experimental investigation into the impact of hydrodynamic cavitation on diesel has been reported by Lockett and Jeshani [25]. Samples of commercial diesel were subjected to 40 h of cavitation across an injector at a pressure of 550 bar. The fuel was cooled to 70 °C after cavitation before being re-cycled through the injector. The optical absorptivity of each diesel at 405 nm was observed to increase as a result of chemistry undergone by aromatic hydrocarbons present in the fuels. The increase in absorptivity was found to be greater for fuel exposed to both cavitation and temperature than for fuel maintained at 70 °C for 40 h in a water bath. Additionally it was found that a greater increase in absorptivity during cavitation was observed for fuel that had been stored for a year before testing.

This paper reports the results of ultrasound experiments on a number of pure hydrocarbons (1-methylnaphthalene, decalin, tetralin, hexadecane) and hydrocarbon mixtures (diesel and 1-methylnaphthalene combined with a range of different aromatic, naphthenic and paraffinic hydrocarbons to make two component mixtures). The formation of insoluble products generated by cavitation has been studied along with the critical physical and compositional properties of the liquids that control the chemistry taking place. This is related to the behaviour of diesel fuel in the high pressure fuel systems of common rail direct injection compression ignition engines.

2. Experimental

2.1. Ultrasound treatment of hydrocarbons

Sonication experiments were carried out with a VCX 500 ultrasonic processor (ex. Sonics Materials Inc.) and a 13 mm extender horn which delivers ultrasound to a 50 mL sample of hydrocarbon contained within a jacketed glass beaker. Cold water (5 °C) was passed through the jacket to keep the liquid hydrocarbon below its flash point – for safety reasons a cut-off temperature was set at 55 °C. A PTFE lid was used to prevent splashing whilst dry air was blown over the surface of the fuel to ensure that there was no condensation inside the reaction vessel (Fig. 1). The whole apparatus was housed inside a box fitted with a safety cut-out mechanism and insulated to reduce acoustic noise.

Ultrasound is produced at a frequency of 20 kHz and when the amplitude of the processor is set to 65% the transfer of energy to the hydrocarbon occurs at 6 kJ mL⁻¹ h⁻¹. The probe is made of titanium alloy (Ti 6Al-4V) and consists of 90% titanium, 6% aluminium and 4% vanadium. This material is susceptible to cavitation erosion and becomes tarnished during use. The probe was polished on silicon carbide paper between each experiment to maintain a smooth and shiny tip surface.

In a typical experiment 50 mL of hydrocarbon was sonicated for a set period of time, during which a darkening occurred due to the build-up of a dispersion of carbonaceous particles. Gravimetric analysis of these particles was carried out by adding 50 mL of *n*-heptane to the sonicated hydrocarbon and shaking. The sample was then split between two centrifuge tubes and spun at 4000 r min⁻¹ for 20 min. The deposit sediment was collected, dried and weighed on a 0.7 μm Whatman glass microfiber filter (Grade GF/F).

2.2. Hydrocarbon materials

Hydrocarbons were sourced from the Sigma–Aldrich Corporation in their highest available purity. The diesel fuel used was an EN590 ‘zero’ sulphur diesel (sulphur <10 ppm, density 0.844 g cm⁻³, viscosity 2.8 mm² s⁻¹ at 40 °C, water content 45 mg/kg, mono-aromatics 27.1% m/m, di-aromatics 3.5% m/m, tri-aromatics 0.4% m/m, carbon 86.4% m/m, hydrogen 13.1% m/m, oxygen <0.04% m/m) which contained no performance additives or fatty acid methyl ester

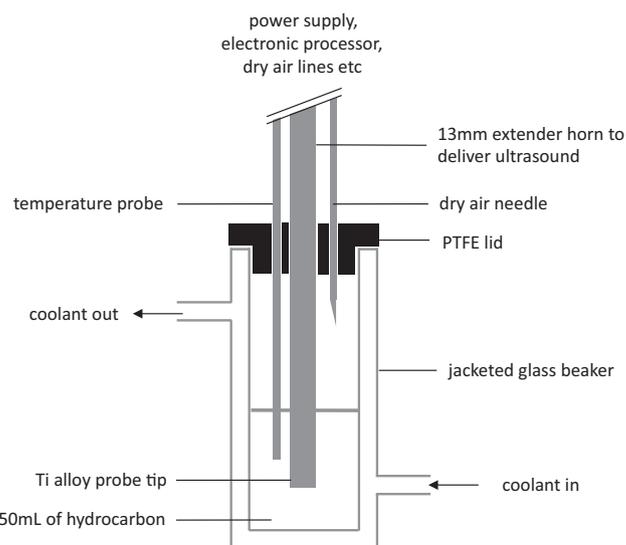


Fig. 1. Schematic of the experimental apparatus used for the sonication of hydrocarbon liquids.

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