

Investigation of Diesel Formulations and Model Mixtures under High-Pressure Environment

Chi Long Chan^{1*}, Sally Lee¹, Kenneth Lewtas², Nicholas J. Brooks¹

¹Department of Chemistry, Imperial College London, Molecular Sciences Research Hub, White City Campus, London SW7 2AZ, UK

²Lewtas Science & Technologies, 246 Banbury Rd, Oxford OX2 7DY

Keywords: fuel, X-ray scattering, microscopy

*e-mail: clc409@ic.ac.uk

Modern diesel engines operate at increasingly high injection pressure with ever reducing injection nozzle sizes as both have been shown to improve engine combustion efficiency and reduce emission [1,2]. The injection pressure can be upward of 3000 bars in some cases and this will likely increase further while having to accommodate smaller nozzle size to further increase efficiency and drive down emissions.

Understanding pressure induced crystallization of diesel is vitally important as any crystal formation can be potentially damaging, causing blockages, negatively affecting engine efficiency, lead to poorer performance as well as higher emission. However, there is a damaging lack of clarity on how diesels behave in high pressure environments at a molecular level, primarily due to a lack of investigative platform. The situation is further complicated with the increasing percentage of biodiesels (FAME) that are incorporated into modern fuel formulations. It has been reported that FAME incorporation results in faster accumulation of water content due to its hygroscopic nature [3]. This can result in high percentage of water content, including bacterial growth [4] which can potentially change the chemical profiles of diesels and hence their crystallization profile.

In addition, the numerous diesel additives available for consumers and industries, which are added to improve the function and storage of diesel fuel, can further complicate the physical properties. Therefore, a way to systematically study the crystallization of different diesel formulations under high pressure conditions is critical in intelligently designing new formulations. This methodology can also extend to other industry that involve waxy substance under high pressure, for example, the crystallization process is a crucial step in certain food product such as chocolate production [5].

The pressure-induced crystallization of model and commercial diesel formulations was investigated using the combination of high-pressure microscopy and high-pressure X-ray diffraction.

We have constructed a system where diesel samples can be sealed and observed under bright field and phase contrast microscopy under pressure of up to 4000 bars at controlled temperatures. This allowed us to visually examine the first crystallisation points, the crystal growth as well as the morphology of the resulting crystals. An illustrative result is shown in Figure 1 where crystal morphology and growth can be closely observed under high pressure. The effect of pressure application rate

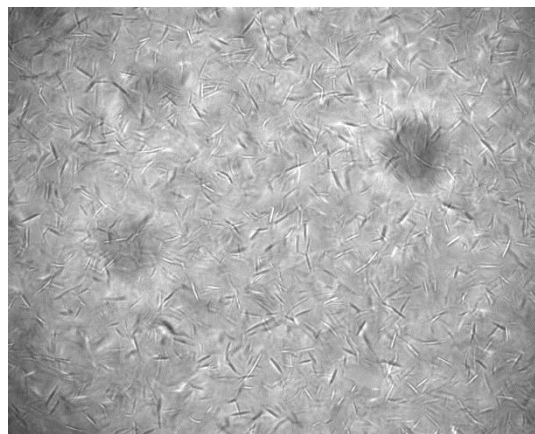


Figure 1. Bright field microscope image of diesel at 2000 bar, 25 °C, 20X magnification.

(ramp vs pressure jump) on crystals growth rate as well as morphology can also be studied.

In addition, we have employed high pressure small and wide angle X-ray diffraction (SAXS / WAXS) at controlled temperature and up to 3500 bar. This has allowed us to examine the pressured-induced crystallization at a molecular length scale. SAXS and WAXS provide insights into both the long- and short-range molecular packing. Therefore, we can track not only the formation of crystals but also how the crystal structure and hydrocarbon chain interactions change in response to changes in pressure and temperature.

Combined with other characterization strategies, including DSC / GCMS / LC / NMR, we can analyse and study the different fractions of diesels and more accurately determine how the different components are involved in the pressure induced diesel crystallization process.

Acknowledgments: This project is funded by EPSRC.

- [1] X. Wang, Z. Huang, W. Zhang, O. A. Kuti, K. Nishida, *Appl. Energy* **2011**, 88, 1620–1628.
- [2] C. Bae, K. Kim, J. Hwang, Y. Park, J. Lee, *Fuel* **2017**, 197, 528–540.
- [3] S. S. de Jesus, G. F. Ferreira, M. R. Wolf Maciel, R. Maciel Filho, *Fuel* **2019**, 235, 1123–1130.
- [4] G. Sørensen, D. V. Pedersen, A. K. Nørgaard, K. B. Sørensen, S. D. Nygaard, *Bioresour. Technol.* **2011**, 102, 5259–5264.
- [5] H. Schenk, R. Peschar, *Radiat. Phys. Chem.* **2004**, 71, 829–835.