High-Pressure Crystallisation Studies of Biodiesel and Methyl Stearate

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Research into air pollution has shown that the combustion of fossil fuels contributes to 98% of global carbon dioxide emissions. There is an urgent requirement to reduce CO2 emissions by reducing consumption of fossil fuels. Hence there is growing interest in the use of biodiesel obtained from sustainable, biomass-based sources. In 2003, the EU set a target for the use of biodiesel of 5.75% of total fuel consumption by 2010. The current target for 2020 is 10 %.(Yusuf *et al.*, 2011)

The widespread use of biodiesel as a renewable fuel offers many potential advantages, but at the same time presents challenges for modern internal combustion engines, particularly for those that involve high-pressure injection of fuel into the combustion chamber. At the typical elevated pressures used in such engines, biodiesel can crystallise and block fuel filters and injection nozzles, thereby causing engine failure. In this study, optical studies and Raman spectroscopy of a typical biodiesel sample contained in a diamond-anvil cell show that biodiesel initially crystallises at ca. 0.2 GPa and then undergoes a series of structural changes on futher increase of pressure. On account of the complex composition of biodiesel, this study focused on one of its main components – methyl stearate. Using a combination of Raman spectroscopy, X-ray powder diffraction and neutron powder diffraction, it was shown that methyl stearate exhibits rich polymorphic behaviour when subjected to elevated pressures up to 6.3 GPa. Under non-hydrostatic conditions, pressures as low as 0.1 GPa converted Form V(Liu *et al.*, 2018) to crystallites of Form III that typically adopt plate-like morphologies. This observation has implications for the pressure-induced crystallisation of biodiesel containing high proportions of methyl stearate because of the potentially serious consequences for blocking of injection nozzles in engines. Four phase transitions over the pressure range of 0.1 GPa to 6.3 GPa were also observed. Form III was recovered on decompression to ambient pressure. High-pressure neutron powder diffraction studies of a perdeuterated sample showed that Form V persisted up to 3.11 GPa.(Liu *et al.*, 2019) This contrast in behaviour between the X-ray and neutron studies may be a consequence of deuteration, or of compression under non-hydrostatic versus hydrostatic conditions.

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