Cloud formation and rainfall affected by pollutant oxidation of biodiesel emissions

May 29 2014

A study into how organic molecules in the atmosphere affect cloud formation has found that a main component of biodiesel, methyl oleate, reacts with ozone surprisingly fast. This process may counterbalance the growth of water droplets resulting from emissions, which would in turn inhibit cloud formation and therefore affect the water cycle in a highly complex way.

The research, published in the journal *Physical Chemistry Chemical Physics*, was performed by an international team of scientists working at the ILL (Institut Laue-Langevin) in Grenoble, France. Methyl oleate is an organic material that is being produced in larger amounts today due to the increasingly popular FAME (Fatty Acid Methyl Ester) biodiesels. The widespread use of these materials potentially raises their concentration in the atmosphere. They accumulate naturally on the surface of water, and therefore can lower the surface tension of water droplets. Such surfactants are important in cloud formation as the reduced surface tension allows droplets to grow larger, producing clouds and rainfall. Without any surfactants at all these droplets could only grow large enough to form clouds higher up in the atmosphere.

The team performed neutron reflectometry experiments on the powerful FIGARO instrument at the ILL where intense beams of neutrons were skimmed off single layers of methyl oleate molecules floating on water as they were exposed to gas phase ozone. Measurements of the intensity of reflected neutrons during the reaction allowed the scientists to determine how the concentration of the molecules on the surface changed over time and therefore how susceptible this organic material was to oxidative attack.

The research used neutrons to address two important questions - how quickly the oxidised methyl oleate was lost from the air-water interface and if the products of methyl oleate remained on the surface of the droplet, entered the water or evaporated into the air.

The study found that the methyl oleate degraded ten times quicker than oleic acid, a molecule found in the atmosphere generated from cooking meat. It also showed that the initial surfactant layer at the air-water interface was efficiently eradicated from the surface when exposed to ozone. The mechanism was attributed to the reaction of ozone with a carbon-carbon double bond in methyl oleate, breaking its backbone and thus shearing the molecule in half. This oxidation reaction causes the methyl oleate almost to lose completely its surfactant properties. In the atmosphere this would result in water droplets growing more slowly.

"Neutrons showed that that the surfactant disappears from the air-water interface surprisingly quickly" said Reading University's Dr Christian Pfrang, the lead author of the paper. "The surfactant isn't stable at the surface in the presence of ozone which means surface tension is increased and droplet growth could be slowed down, making it more difficult to form clouds. Furthermore the products aren't stable at all at the droplet surface and this would not have been predicted from the results of previous studies."

Richard Campbell, instrument leader, said "The ILL is the world leading neutron facility for kinetic studies due to its very stable and intense reactor source, and FIGARO is the optimum neutron reflectometer in the world where this research can be performed due to its very high intensity for surface excess studies. We were able to take scans every one to five seconds - necessary for the timescales we were working with

- whereas instruments at other facilities would generally require much longer. This capability allowed us to reveal the reaction mechanisms of an oxidation decay of an organic monolayer with greater time resolution and sensitivity than ever before."

The next step in the research is to examine the behaviour of different surfactants and their mixtures when exposed to ozone and other oxidants found in the atmosphere. "We're combining neutron reflectometry with computational modelling" said Federica Sebastiani, an ILL PhD student who worked on FIGARO. "We have models to examine more complex systems with multiple surfactants and we're going to look at these systems in greater detail than ever before."

More information: Paper: pubs.rsc.org/en/Content/Articl … p00775a#!divAbstract

Provided by Institut Laue-Langevin

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