The Alkoxylation of Biodiesel and its Impact on Fuel Properties

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in

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ABSTRACT

A property of biodiesel that currently inhibits its use is its relatively poor low-temperature properties, most commonly expressed as cloud point. Improving the low-temperature properties of biodiesel to those for petroleum based diesel will remove one of the few physicochemical barriers to its more widespread application. Improvement of biodiesel low-temperature properties by alkoxylation is a potential method that is investigated in this thesis. While previous work has been performed with model compounds and synthetic laboratory conditions, this work investigates the likely success of a commercial process to produce alkoxylated biodiesel. Process parameters were constrained to atmospheric pressure, low temperatures and reasonable reaction times, while avoiding the use of organic solvents.

Epoxidation and alkoxylation of methyl biodiesel produced from canola oil was studied to determine the best conditions while simultaneously developing the analytical methods. A gas chromatography-mass spectrometry method was developed to determine conversion and selectivity for epoxy and alkoxy biodiesel. The best reaction conditions for the epoxidation step, based on conversion and selectivity, and the option of either in-situ generated peroxyformic acid or peroxyacetic acid as the oxygen carrier were determined. Optimal conditions were H_2O_2 / biodiesel molar ratio of 2:1, acetic acid / biodiesel molar ratio of 0.2:1, acid catalyst to acetic acid / peroxide of 2 wt% and a 6h reaction time at 60°C. The optimal reaction conditions for methyl biodiesel were then transferred to ethyl and butyl biodiesel. An acid catalysed alkoxylation with the same alcohol as the ester head-group was then performed and the cloud point impact was assessed. Alkoxylation of methyl and ethyl biodiesel resulted in reduced low-temperature tolerance while alkoxy butyl biodiesel displayed a slightly improved tolerance.

Since butoxylated butyl biodiesel was the most promising in terms of cloud point improvement, the next phase of work was concerned with maximising selectivity for butoxy biodiesel. A range of conditions including reaction time, temperature, catalyst concentration and molar ratio of alcohol were studied. Optimal conditions for the butoxylation of epoxy butyl biodiesel were: 80°C, 2 wt% sulfuric acid and a 40:1 molar ratio of butanol over a period of 1h. Conversion of epoxy butyl biodiesel was 100% and selectivity for butoxy biodiesel was 87.0%. The cloud point of butoxy butyl biodiesel (46% conversion of unsaturated fraction) was identical to that for butyl biodiesel. To determine the impact of higher conversion of unsaturated ester to butoxy ester, a batch of butyl biodiesel was subjected to 30h of epoxidation resulting in a conversion of 93%, corresponding to a butoxy content of 74 wt%. The cloud point of this material was 2°C, representing an increase of 5K over that for butyl biodiesel. Blends of the high conversion batch of butoxy biodiesel showed that cloud point was virtually unchanged at concentrations below 35 wt% and then increased 1K every 8 wt% to approximately 70 wt % butoxy biodiesel.

The last phase involved the investigation of the impact of longer and branched side-chains on the properties of butyl biodiesel. Longer straight-chain alcohols were added at the epoxidised double bonds, as were some branched isomers under the optimal conditions determined in phase two. Alcohols included: methanol, ethanol, *n*-propanol, *n*-butanol, *tert*-butanol, *n*-pentanol, *n*-hexanol, *n*-octanol and 2-ethylhexanol. Alkoxylation of butyl biodiesel with methanol, ethanol and propanol increased the cloud and pour point of butyl biodiesel. Alkoxylation with alcohols larger than butanol produced significant improvements in low-temperature properties as indicated by lower cloud and pour points. The lowest cloud point achieved was for ethylhexoxy butyl biodiesel at -6°C, a 6K reduction in cloud point over conventional methyl biodiesel. Alkoxylation also resulted in significant increases in kinematic viscosity, with the viscosity of ethylhexoxy butyl biodiesel being 9.76 $mm^2.s^{-1}$, more than double that for methyl biodiesel.

DECLARATION

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution to Paul Smith and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

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LIST OF PUBLICATIONS

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