

The Alkoxylation of Biodiesel and its Impact on Fuel Properties

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TABLE OF CONTENTS

TABLE OF CONTENTS	i
LIST OF TABLES	v
LIST OF FIGURES	vii
ABSTRACT.....	xi
DECLARATION	xiii
ACKNOWLEDGEMENTS	xiv
LIST OF PUBLICATIONS	xv
GENERAL INTRODUCTION.....	2
1.1 Context.....	2
1.2 Purpose	2
1.3 Process of Investigation and Thesis Structure	3
BIODIESEL LOW-TEMPERATURE PROPERTIES.....	6
2.1 The Problem	6
2.2 Factors Influencing Biodiesel Cloud Point	7
2.2.1 Fatty Acid Profile	7
2.2.2 Alcoholic Adduct.....	12
2.3 Low-Temperature Property Improvement	13
2.3.1 Additives	13
2.3.2 Feedstock Modification	15
2.3.3 Biodiesel Modification	16
2.4 Impact on Other Properties of Biodiesel	19
2.5 Proposed Solution	20
MATERIALS AND METHODS	25
3.1 Materials	25
3.2 Equipment	25
3.2.1 Chemical synthesis	25
3.2.2 Analytical Equipment	26
3.3 Biodiesel Synthesis	28
3.3.1 Methyl and Ethyl Biodiesel	28
3.3.2 Butyl Biodiesel.....	28

3.4	Epoxidation.....	30
3.5	Alkoxylation	31
3.6	Analytical Methods	33
	3.6.1 Biodiesel Purity	33
	3.6.2 Biodiesel Fatty Acid Profile.....	33
	3.6.3 Epoxy and Alkoxy Biodiesel.....	34
	3.6.4 Cloud Point	35
	3.6.5 Pour Point	35
	3.6.6 Viscosity	35
	3.6.7 Free Fatty Acid Content of Canola Oil	35
	INITIAL SYNTHESIS AND CHARACTERISATION	37
4.1	Biodiesel Synthesis	38
	4.1.1 Methyl Biodiesel	38
	4.1.2 Ethyl Biodiesel	43
	4.1.3 Butyl Biodiesel	44
4.2	Epoxidation of Methyl Biodiesel.....	48
	4.2.1 24 Hour Epoxidation of Methyl Biodiesel.....	48
	4.2.2 GC-FID Analysis	49
4.3	Alkoxylation of Epoxy Methyl Biodiesel.....	51
	4.3.1 Procedure	51
	4.3.2 GC-FID Analysis	52
4.4	Fourier Transform Infrared Analysis.....	53
	4.4.1 Synthesis of Epoxy and Alkoxy Ethyl Oleate	54
	4.4.2 FTIR Analysis.....	54
4.5	GC-MS Method Development	58
	4.5.1 GC-MS Analysis of Biodiesel	59
	4.5.2 GC-MS Analysis of Epoxy Biodiesel	61
	4.5.3 GC-MS Analysis of Alkoxy Biodiesel	63
4.6	Summary.....	65
	PRELIMINARY STUDIES	67
5.1	Epoxidation of Methyl Biodiesel.....	68
	5.1.1 Method	68
	5.1.2 Results and Discussion.....	70
5.2	Optimisation of the Epoxidation Step	71
	5.2.1 Results and Discussion.....	71
5.3	Alkoxylation of Epoxy Methyl Biodiesel.....	73
	5.3.1 Method	73
	5.3.2 Results and Discussion.....	74
5.4	Extension to Ethyl and Butyl Biodiesel.....	77
	5.4.1 Epoxidation.....	77

5.4.2	Alkoxylation.....	78
5.5	Cloud Point Assessment	79
5.5.1	Impact of Higher Alkoxy Content	80
5.6	Summary.....	81
BUTOXYLATION OF BUTYL BIODIESEL		83
6.1	Method	84
6.1.1	Synthesis of Epoxy Butyl Biodiesel.....	84
6.1.2	Optimisation of Alkoxylation Reaction Conditions	86
6.2	Results and Discussion.....	90
6.2.1	Effect of Temperature	90
6.2.2	Effect of Catalyst Concentration	91
6.2.3	Effect of Molar Ratio of Alcohol.....	92
6.2.4	Further Optimisation.....	93
6.3	Reaction Kinetics	95
6.4	Cloud Point Impact.....	99
6.4.1	Impact of Higher Conversion	100
6.4.2	Impact of Linearisation of Ester.....	102
6.5	Summary.....	104
OTHER ADDUCTS OF BUTYL BIODIESEL		106
7.1	Synthesis of Alkoxy Butyl Biodiesel	107
7.1.1	Method	107
7.1.2	Results and Discussion.....	110
7.2	Impact on Cloud Point	120
7.3	Impact on Pour Point	122
7.4	Impact on Viscosity.....	123
7.5	Summary.....	125
DISCUSSION AND CONCLUSIONS		127
8.1	Discussion	127
8.2	The Economics of Alkoxylated Biodiesel	132
8.3	Further Work.....	136
8.4	Conclusions.....	137
APPENDIX A		140
Chromatograms		140

APPENDIX B	150
Mass Spectra	150
NOMENCLATURE.....	158
BIBLIOGRAPHY	159

LIST OF TABLES

Table 2.1: Properties of Fatty acids and Esters. Source: (Knothe 2005).....	9
Table 2.2: Properties of Fats/oils and their esters. Source: (Knothe et al. 2004)	11
Table 2.3: Fatty Acid Compositions of Naturally Occurring Fats and Oils.	12
Table 4.1: Comparison of GC-MS conditions for Wilson <i>et al.</i> (1997) and this work.	58
Table 4.2: Fatty acid profile of biodiesel derived from canola oil.	59
Table 5.1: Optimisation of epoxy selectivity: reaction conditions.	71
Table 5.2: Selectivity for epoxy methyl biodiesel.	72
Table 5.3: Epoxy conversion, selectivity and glycol content for all alkyl esters.	77
Table 5.4: Alkoxy selectivity and by-product content for all alkyl esters.	78
Table 5.5: Cloud point for all alkyl esters.	79
Table 6.1: Effect of temperature on selectivity for butoxy butyl biodiesel and by-product content after 6h of reaction time.	91
Table 6.2: Effect of catalyst concentration on selectivity for butoxy butyl biodiesel and by-product content after 6h of reaction time.	92
Table 6.3: Effect of molar ratio of butanol on selectivity for butoxy butyl biodiesel and by-product content after 6h of reaction time.	93
Table 6.4: Effect of higher temperature and catalyst concentration on selectivity for butoxy butyl biodiesel and by-product content after 6h of reaction time.	94
Table 6.5: Specific reaction rate and corresponding coefficient of determination (R^2) value for the four experiments at different molar ratios of alcohol.	96
Table 6.6: Specific reaction rate and corresponding coefficient of determination (R^2) value for the four experiments at different molar ratios of alcohol, excluding the initial 10 minutes.	97
Table 6.7: Impurity profile and cloud point results for various butoxy butyl biodiesel batches.	100
Table 7.1: Alkoxylation of butyl biodiesel: retention time of major alkoxy peaks, transesterification fractions before and after purification of the product.	112
Table 7.2: Fragmentation pattern for alkoxy butyl biodiesel for ions a to d in Figure 7.4.	114
Table 7.3: Alkoxy selectivity and by-product content for all alkoxy esters.	115
Table 7.4: Transesterified alkoxy oleate content for all alkoxy esters.	120

Table 7.5: Flow properties of butyl biodiesel and modified biodiesel, including: cloud point, pour point and kinematic viscosity..	121
Table 8.1: Estimates of some critical biodiesel raw material costs.	134

LIST OF FIGURES

Figure 1.1: Flow chart of the process of investigation.....	4
Figure 3.1: Kettle reactor with stirrer/hotplate for synthesis.....	26
Figure 3.2: Test apparatus for cloud point determination.....	27
Figure 3.3: Reaction scheme for the epoxidation of biodiesel (methyl) including the main product and possible by-products: a – methyl oleate, b – 9,10-epoxy methyl stearate, c – 9,10-dihydroxy methyl stearate, d – 9(10)-keto methyl stearate.	31
Figure 3.4: Reaction scheme for the alkoxylation of epoxy biodiesel (methyl) including the main product and possible by-products: b – 9,10-epoxy methyl stearate, c – 9,10-dihydroxy methyl stearate, d – 9(10)-keto methyl stearate, e – 9(10)-hydroxy,10(9)-methoxy methyl stearate.	32
Figure 4.1: Chromatogram of standard solutions for contaminants associated with EN 14105.	39
Figure 4.2: GC-FID Chromatogram of methyl biodiesel with high monoglyceride.	40
Figure 4.3: Transesterification reaction mechanism.	41
Figure 4.4: GC-FID Chromatogram of methyl biodiesel with low monoglyceride.	42
Figure 4.5: Chromatogram of butyl biodiesel with high mono- and diglycerides.	45
Figure 4.6: Chromatogram of butyl biodiesel with low monoglyceride.	47
Figure 4.7: GC-FID chromatogram of methyl biodiesel analysed according to EN 14103.....	49
Figure 4.8: GC-FID chromatogram of methyl biodiesel epoxidised for 24h analysed according to EN 14103.	50
Figure 4.9: Conversion of methyl biodiesel to epoxy methyl biodiesel over time.....	50
Figure 4.10: GC-FID chromatogram of methoxy methyl biodiesel alkoxyated for 24h, analysed according to EN 14103.....	52
Figure 4.11: GC-FID chromatogram of methoxy methyl biodiesel alkoxyated for 24h, analysed according to EN 14105.....	53
Figure 4.12: Overlay of FTIR spectra of epoxy ethyl oleate, ethoxy ethyl oleate and glycol ethyl oleate. ...	55
Figure 4.13: Overlay of FTIR spectra of epoxy butyl biodiesel and butoxy butyl biodiesel.	56
Figure 4.14: Residue spectrum of the subtraction result of butoxy butyl biodiesel produced 22/7/08 and butoxy butyl biodiesel produced 7/7/08.....	57
Figure 4.15: Residue spectrum of the subtraction result of butoxy butyl biodiesel produced 22/7/08 and butoxy butyl biodiesel produced 7/7/08.....	57
Figure 4.16: Chromatogram of methyl biodiesel generated on GC-MS.	60
Figure 4.17: Chromatogram of methyl biodiesel generated on GC-MS showing the C18 peaks. The C18:1/3 peaks are those labelled 22.17 and 22.24 minutes.	60

Figure 4.18: Chromatogram of epoxy methyl biodiesel. Major peaks: methyl palmitate (16.31 min.), methyl oleate (22.07 min.), 9,10-epoxy oleate (28.90 min.), 9,10-dihydroxy methyl stearate (35.88 min.).	61
Figure 4.19: Mass spectra of methyl biodiesel derivatives: 9,10-epoxy methyl stearate.	62
Figure 4.20: Mass spectra of methyl biodiesel derivatives: 9,10-dihydroxy methyl stearate.	62
Figure 4.21: Chromatogram of methoxy methyl biodiesel. Major peaks: methyl palmitate (16.33 min.), methyl oleate/linolenate (22.08 - 22.16 min.), 9(10)-keto methyl stearate (29.09 min.), 9(10)-hydroxy,10(9)-methoxy stearate (33.30 min.), 9,10-dihydroxy methyl stearate (35.88 min.).	63
Figure 4.22: Mass spectrum of 9(10)-hydroxy,10(9)-methoxy methyl stearate.	64
Figure 4.23: Mass spectrum of 9(10)-keto methyl stearate.	64
Figure 5.1: Conversion of the unsaturated portion of methyl biodiesel to epoxy methyl biodiesel. Reaction conditions: molar ratio of 0.5 and 2 for formic acid and hydrogen peroxide to biodiesel, respectively; temperature of 60°C. Selectivity for epoxy methyl biodiesel (inset).	70
Figure 5.2: Graphical representation of the 5 trial batches for the optimisation of the epoxidation of methyl biodiesel.	72
Figure 5.3: Selectivity for methoxy biodiesel and fractions of by-product (glycol and ketone), including fractionated samples.	74
Figure 5.4: Chromatogram of methoxy methyl biodiesel. Major peaks: methyl palmitate (16.33 min.), methyl oleate/linolenate (22.08 - 22.16 min.), 9(10)-keto methyl stearate (29.09 min.), 9(10)-hydroxy,10(9)-methoxy stearate (33.30 min.), 9,10-dihydroxy methyl stearate (35.88 min.).	75
Figure 5.5: Methoxy methyl biodiesel at room temperature with precipitate.	76
Figure 5.6: Chromatogram of methoxy methyl biodiesel: (I) supernatant, (II) precipitate.	76
Figure 6.1: Chromatogram of butyl biodiesel.	84
Figure 6.2: Chromatogram of epoxy butyl biodiesel. Main peaks: butyl oleate/linolenate (31.38-31.56 min.), epoxy butyl stearate (38.45 min.).	86
Figure 6.3: Chromatogram of epoxy butyl biodiesel 20 min. in to the butoxylation. Main peaks: butyl oleate/linolenate (31.36 - 31.56 min.), epoxy butyl stearate (38.39 min.), butoxy butyl stearate (49.02 min.).	87
Figure 6.4: Chromatogram of butoxy butyl biodiesel at completion of butoxylation showing the absence of the epoxy butyl stearate peak but the presence of the keto butyl stearate/butyl eicosenoate (C20:1) at 38.73 min.	88
Figure 6.5: Mass spectrum of peak at 49.0 min. identified as 9-butoxy,10-hydroxy butyl stearate.	89
Figure 6.6: Mass spectrum of peak at 38.8 min. identified as 9(10)-keto butyl stearate.	89
Figure 6.7: Effect of temperature on conversion of epoxy butyl biodiesel.	90
Figure 6.8: Effect of catalyst concentration on conversion of epoxy butyl biodiesel.	91
Figure 6.9: Effect of molar ratio of butanol on conversion of epoxy butyl biodiesel.	93
Figure 6.10: Results of further optimisation work for the reaction conditions for the epoxidation of epoxy butyl biodiesel.	94

Figure 6.11: Kinetic plots for the various molar ratios of alcohol: 5:1 (a), 10:1 (b), 20:1 (c), 40:1 (d).....	95
Figure 6.12: Specific reaction rate versus molar ratio of alcohol.	97
Figure 6.13: Plot of $\ln k$ versus $1/T$ for the 3 temperatures of 40°C, 60 °C and 80°C.	98
Figure 6.14: Cloud point of butoxy butyl biodiesel from 2 wt% to 74 wt%.	101
Figure 7.1: Reaction scheme for the case of ethylhexoxy butyl biodiesel: a – butyl oleate; b – epoxy butyl oleate ; c – ethylhexoxy butyl oleate; d – ethylhexoxy ethylhexyl oleate.....	109
Figure 7.2: Chromatogram of epoxy butyl biodiesel. Major peaks: I - C16 butyl biodiesel; II - C18 butyl biodiesel (31.0-32.3 min.) – oleate/linolenate fraction is 31.5-31.6 min.; III - epoxy butyl biodiesel (37.5-38.4 min.).....	111
Figure 7.3: Chromatogram of octoxy butyl biodiesel. Major peaks: I - C18 octyl biodiesel (45.1-45.6 min.); II - octoxy butyl biodiesel (64.2-66.1 min.).....	112
Figure 7.4: Schematic of the molecular fragmentation pattern of the alkoxy butyl oleates.....	113
Figure 7.5: Octoxy butyl oleate purified without dichloromethane with particulates.....	117
Figure 7.6: Ethylhexoxy butyl biodiesel purified without dichloromethane (left) and with dichloromethane (right).....	117
Figure 7.7: Chromatogram of methoxy butyl biodiesel. Major peaks are: methyl oleate/linolenate (22.00 min.), butyl oleate/linolenate (31.45 min.), methoxy methyl oleate/linolenate (33.29 min.) and methoxy butyl oleate/linolenate (42.72 min.).....	118
Figure 7.8: Mass spectrum of ethoxy ethyl oleate.....	118
Figure 7.9: Mass spectrum of ethoxy butyl oleate.....	119
Figure 8.1: Conceptual process flow for ethylhexoxy butyl biodiesel production.....	133
Figure A.1: Chromatogram of methoxy butyl biodiesel. Major peaks are: methyl oleate/linolenate (22.00 min.), butyl oleate/linolenate (31.45 min.), methoxy methyl oleate/linolenate (33.29 min.) and methoxy butyl oleate/linolenate (42.72 min.).....	140
Figure A.2: Chromatogram of ethoxy butyl biodiesel. Major peaks are: ethyl oleate/linolenate (24.24 min.), butyl oleate/linolenate (31.51 min.), ethoxy ethyl oleate/linolenate (36.61 min.) and ethoxy butyl oleate/linolenate (43.63 min.).....	141
Figure A.3: Chromatogram of propoxy butyl biodiesel. Major peaks are: propyl oleate/linolenate (26.9 min.), butyl oleate/linolenate (31.51 min.) and propoxy butyl oleate/linolenate (46.30 min.).....	142
Figure A.4: Chromatogram of butoxy butyl biodiesel. Major peaks are: butyl oleate/linolenate (31.52 min.) and butoxy butyl oleate/linolenate (49.25 min.).....	143
Figure A.5: Chromatogram of <i>tert</i> -butoxy butyl biodiesel. Major peaks are: butyl oleate/linolenate (31.51 min.), keto butyl oleate (38.81 min.) and dihydroxy butyl oleate/linolenate (44 - 46 min.).....	144
Figure A.6: Chromatogram of pentoxy butyl biodiesel. Major peaks are: pentyl oleate/linolenate (34.84 min.), butyl oleate/linolenate (31.55 min.) and pentoxy butyl oleate/linolenate (52.28 min.).....	145

Figure A.7: Chromatogram of hexoxy butyl biodiesel. Major peaks are: hexyl oleate/linolenate (38.41 min.), butyl oleate/linolenate (31.51 min.) and hexoxy butyl oleate/linolenate (55.98 min.).....	146
Figure A.8: Chromatogram of octoxy butyl biodiesel. Major peaks are: octyl oleate/linolenate (45.34 min.), butyl oleate/linolenate (31.46 min.) and octoxy butyl oleate/linolenate (66.21 min.).	147
Figure A.9: Chromatogram of ethylhexoxy butyl biodiesel. Major peaks are: ethylhexyl oleate/linolenate (42.67 min.), butyl oleate/linolenate (31.56 min.) and ethylhexoxy butyl oleate/linolenate (59.91 min.).	148
Figure B.1: Mass spectrum of methoxy butyl oleate.	150
Figure B.2: Mass spectrum of ethoxy butyl oleate.	151
Figure B.3: Mass spectrum of ethoxy ethyl oleate.....	151
Figure B.4: Mass spectrum of propoxy butyl oleate.	152
Figure B.5: Mass spectrum of butoxy butyl oleate.	153
Figure B.6: Mass spectrum of pentoxy butyl oleate.	154
Figure B.7: Mass spectrum of hexoxy butyl oleate.	155
Figure B.8: Mass spectrum of octoxy butyl oleate.	156
Figure B.9: Mass spectrum of ethylhexoxy butyl oleate.....	157

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 alkoxyated 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 mm².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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