



final report

Project code: P.PSH.0191

Prepared by: Dr S.Clarke, Dr M.Fisher, R.Pillar, K.Nguyen,
K.Constantopoulos, C.Congiusta, D.Vincent,
S.Mathew, Prof J.Matisons, Dr M.Ginic-Markovic
Flinders University

Date submitted: January 2008

PUBLISHED BY
Meat & Livestock Australia Limited
Locked Bag 991
NORTH SYDNEY NSW 2059

Modification of tallow for better performance as biodiesel

Meat & Livestock Australia acknowledges the matching funds provided by the Australian Government to support the research and development detailed in this publication.

This publication is published by Meat & Livestock Australia Limited ABN 39 081 678 364 (MLA). Care is taken to ensure the accuracy of the information contained in this publication. However MLA cannot accept responsibility for the accuracy or completeness of the information or opinions contained in the publication. You should make your own enquiries before making decisions concerning your interests. Reproduction in whole or in part of this publication is prohibited without prior written consent of MLA.

Contents

	Page
1	Roles and Responsibilities Summary 4
1.1	Technical Status Summary for Milestones 4 & 65
1.2	Key Observations from Milestone 4 & 6 8
2	Section 1 Polymer based additives 10
2.1	Introduction..... 10
2.2	Experimental 10
2.2.1	Nuclear Magnetic Spectroscopy: 10
2.2.2	FTIR 11
2.2.3	DSC 11
2.2.4	Preparation of mixtures for DSC and CFPP Analysis 13
2.2.5	Preparation of Biodiesel / Additive Mixtures for DSC..... 14
2.2.6	Preparation of Biodiesel / Additive Mixtures for CFPP 15
2.3	Materials 15
2.4	Synthesis..... 15
2.4.1	Further modification of mono-ester C4 and C18 polymers: 16
2.4.2	Imide type copolymers:..... 17
2.4.3	Poly(styrene-co-allyl alcohol) grafted stearate:..... 18
2.4.4	Synthesised copolymers..... 19
2.4.5	Poly(lauryl acrylate-co-maleic anhydride) copolymer: 20
2.5	DISCUSSION 21
2.5.1	Modification of commercial copolymers 21
2.5.2	Imide type copolymers:..... 23
2.5.3	Synthesised Copolymers 24
2.5.4	Comb Polymers (P1-P8 inclusive) 25
2.5.5	Clariant Polymer-Based Additives 27
2.5.6	Winter POW-R Plus 27
2.6	Cloud Point and Cold Filter Plugging Point Characterisation 28
2.6.1	Synthesised Polymers 28
2.6.2	Commercial Additives 29
2.6.3	Synthesised P4 in Toluene 31

2.6.4	Surfactants	32
2.7	DSC Results of polymer/ toluene/ surfactant blends in BDT01DV	34
2.8	CFPP Results of polymer/ toluene/ surfactant blends in VCBD	37
2.9	SUMMARY	39
3	Section 2: Low molecular weight additives.....	41
3.1	Introduction.....	41
3.2	Experimental	41
3.2.1	Characterization	41
3.3	Materials:.....	41
3.4	Synthesis.....	41
3.5	DISCUSSION	43
3.5.1	Synthesis	43
3.6	Cloud Point and Cold Filter Plugging Point Characterisation	52
3.7	Branched Ester Additives (Bulky Head Group):	54
3.8	SUMMARY	55
3.9	References	56
4	Section 3: Urea fractionated tallow based biodiesel	57
4.1	Introduction.....	57
4.2	Experimental	58
4.3	Materials	58
4.4	Urea Fractionation of Biodiesel.....	59
4.5	Characterisation	60
4.5.1	Determination of the Effect of Cooling Rate on Urea Fractionation Efficiency using DSC	60
4.5.2	Gas Chromatography –Mass Spectrometry (GC-MS)	60
4.6	Discussion	61
4.7	Cloud Point and Cold filter Plugging Point Characterisation	67
4.7.1	Urea Fractionated Biodiesel	67
4.8	Summary	69
4.9	References	70

1 Roles and Responsibilities Summary

Milestones 4 and 6, initiated on the 11th August 2006 and to be concluded by the 3rd November 2006, have been completed with the following complement of personnel:

Name	Role	Initiation of Employment	Completion of Employment
Dr Stephen Clarke	Program Leader	Inception	
Dr Mark Fisher	Program Manager	27 th March 2006	22 nd February 2007
Ms Rachel Pillar	Researcher	13 th February 2006	27 th October 2006
Ms Kim Nguyen	Researcher	16 th March 2006	3 rd November 2006
Ms Kristina Constantopoulos	Researcher	3 rd July 2006	20 th October 2006
Mr Carlo Congiusta	Researcher	10 th July 2006	3 rd November 2006
Mr David Vincent	Researcher	4 th September 2006	3 rd November 2006
Mr Simon Mathew	Researcher	14 th August 2006	3 rd November 2006

The team for this Milestone period has been reinforced with skills in pure synthetic organic chemistry, with the addition of Mr Simon Mathew. Mr David Vincent, a talented synthetic chemist, has also been added to the team.

This team has the requisite skills to rapidly address the directions prescribed in the “Modification to Milestones 4 and 6” document.

Key responsibilities of Researchers have been apportioned in the following manner for Milestones 4 and 6:

Name	Key Responsibilities¹
Dr Stephen Clarke	Advisory
Dr Mark Fisher	Project Monitoring & Reporting; Research Direction
Ms Rachel Pillar	Analytical
Ms Kim Nguyen	Polymer Chemistry; Synthetic Additives
Ms Kristina Constantopoulos	Polymer Chemistry; Synthetic Additives
Mr Carlo Congiusta	CFPP investigations; Ozonolysis for Additives
Mr David Vincent	Fractionation; Synthetic Additives
Mr Simon Mathew	Synthetic Additives

Note 1: First mentioned activity the major activity.

Modification of tallow for better performance as biodiesel

1.1 Technical Status Summary for Milestones 4 & 6

The experimental aims of the program at completion of Milestones 4 & 6 are defined in the two Tables below:

Milestone 6 Polymer Chemistry for CFPP Modification		
	Completed?	Comments
Styrene Maleic Anhydride Copolymer Sourcing	✓	Commercially available material from Aldrich. Insoluble in biodiesel.
Ring Opening of Styrene Maleic Anhydride Commercial Copolymer with various Alcohols	✓	Opening of all anhydrides difficult to achieve. Generally the opening with lower alcohols generated polymers insoluble in biodiesel, but using hexadecyl and octadecyl alcohol gave soluble alcohols.
Analysis of the Influence of Alcohol opened Styrene Maleic Anhydride Copolymers upon Crystallisation	✓	Poor solubility of these alcohol opened anhydride polymers in biodiesel noted. CFPP not conducted due to these problems. Hexadecyl and octadecyl alcohols, soluble in biodiesel, did not improve the DSC onset.
Ring Opening of Maleic Anhydride Copolymers with Long Chain Primary Amines (<i>extended initiative of the Program</i>)	✓	Imidation of the anhydride with dodecyl amine successfully achieved. Improved solubility noted and the DSC onset temperature lowered slightly.
Analysis of the Influence of Imidated Styrene Maleic anhydride Polymers on Crystallisation (<i>extended initiative of the Program</i>)	✓	Imidation with dodecyl amine gave biodiesel soluble polymer, with onset temperatures lowered slightly by DSC.
Sourcing of maleic anhydride isobutylene copolymers (<i>extended initiative of the Program</i>)	✓	Commercially available low molecular weight materials from Aldrich. Starting polymers are insoluble in biodiesel.
Ring Opening of Maleic Anhydride on co-isobutylene Copolymer with various Alcohols and primary amines (<i>extended initiative of the Program</i>)	✓	Polymers using opening of the anhydride with hexanol, octanol and 2 octyl dodecyl alcohol still insoluble in biodiesel. Opening with dodecylamine generated soluble products which lowered Tonset slightly.

Modification of tallow for better performance as biodiesel

Milestone 6 Polymer Chemistry for CFPP Modification		
	Completed?	Comments
Monomer Sourcing Acrylate Maleic Anhydride Copolymers	✓	Monomers successfully received for polymerisation.
Acrylate Maleic Anhydride Copolymers	✓	Successful synthesis of coded polymers P1.....P8 in this category.
Analytical Testing of Acrylate Maleic Anhydride Copolymers	✓	P4 is a critical polymer in CFPP modification. CFPP is strongly coupled to onset in crystallisation (DSC).
Formulation of Acrylate Maleic Anhydride Copolymers	✓	Two surfactant combinations – one commercial and the other synthesised (see Milestone 4 comments) enhance the effect on CFPP measurement.
Opening of Anhydride Unit on Acrylate Maleic Anhydride Copolymers	✓	Similar procedures adopted to styrene maleic anhydride – both esters and imides generated using long chain alcohols and primary amines.
Analytical Testing of Ring Opened Acrylate Maleic Anhydride Copolymers	✓	DSC analysis for onset and curve change during crystallisation suggested that a continuation to CFPP work was not warranted.

Milestone 4 – Low Molecular Weight Additives/CFPP Measurement/Depletion		
Goal	Completed?	Comments
Alternative Assessment Methods: CFPP using in-house developed instrument	✓	Rig generated at Flinders has suspect reproducibility; purchase of manual rig (\$5000) exceeds the anticipated total cost of all samples to be measured: OUTSOURCE to Intertek.
Dumbbell shaped molecules via ozonolysis	✓	One end branched terminal vinyl compound synthesised & ozonolysed to the methyl ester; di-isopropyl azelate also synthesised; DSC at 3.5%w/w suggests no significant benefit by adding to biodiesel.
Ozonolysis of Jojoba oil wax esters	✓	DSC suggests no benefit by adding to biodiesel at 3.5%w/w.
Wax Esters (similar to oleyl stearate)	✓	Oleyl palmitate and oleyl myristate produced; 3.5%w/w in biodiesel their influence on the onset temperature was not large enough to warrant further examination.
Branched alcohol esters	✓	The compounds 2 ethyl 1 hexyl stearate, 3 methyl 1 butyl stearate and Geubert

Modification of tallow for better performance as biodiesel

		alcohol esters were synthesised; at 3.5%w/w increases in onset temperatures were noted.
--	--	---

Milestone 4 – Low Molecular Weight Additives/CFPP Measurement/Depletion		
Goal	Completed?	Comments
Flat molecules with Alkyl tails via ether linkages	✓	The menthol- bromododecane reaction completed; improvements at 3.5%w/w suggest ether linkages twice as good as ester linkages, but improvement still small.
Cyclisation (cyclopropyl) reactions at the oleate vinyl group	✓	Technically too difficult for industrial purposes; terminated
“Olestra- like” sucrose surfactants	✓	IMPORTANT POLYMER COADDITIVES: sucrose 5 myristate, sucrose 5 oleate synthesised; sucrose 5 stearate made sucrose 3.1 laurate made sucrose 5 laurate made
Sourcing of commercial additive packages	✓	4 more commercial additives evaluated (Clariant; Octel Starreon); one still outstanding (Winter Pow-R); small benefits noted at specified addition levels in both onset and CFPP
Insertion Complexing Agents	✓	Calix[8]arene functionalised with dodecyl and octedecyl ether but poor performance in changing onset of crystallisation.
Modification by removal: onset temperatures and enthalpy of crystallisation vs weight fraction of unsaturates (methyl oleate)	✓	Predictive curve showing how the onset temperature and crystallisation enthalpy will change for a set (stearate/ palmitate weight fraction) in methyl oleate
Urea fractionation of Biodiesel: Effect upon Onset/CFPP	✓	Procedures developed to remove 7% and 25%w/w of biodiesel. ~1.6°C change in DSC onset for 7%w/w removal (8.4°C to 6.8°C); and 5.7°C change with 25%w/w removal (8.4°C to 2.7°C)

1.2 Key Observations from Milestone 4 & 6

1. Milestone 4 in revised format has completed our evaluation on low molecular weight additives for addition. It appears that in terms of the onset of crystallisation using these low molecular weight additives there is only a modest improvement in this parameter, of the order of 1°C.
2. The problem of partitioning these low molecular weight compounds between saturated and unsaturated phases has a major role impact upon the efficiency of these low molecular weight species.
3. The specific benefit gained from this aspect of the program is that it has enabled us to produce a number of new surfactant materials, of fundamental importance to the CFPP modification. Most notably sucrose derivatives, both alone and in combination, appear to be important.
4. We have continued to evaluate commercially available additives for biodiesel. Two products from Clariant were examined – Dodiflow 1000 and Dodiflow 2000. Dodiflow 1000 showed the most significant change in the onset temperature, but only modest improvements in the CFPP of about 2°C. HiTEC 672 was more effective in CFPP testing, lowering CFPP by ~ 3°C. Two products from Octel Starreon – Bioflow 875 and 8500HEC40 - performed less favourably than Clariant Dodiflow 1000 with respect to DSC onset.
5. An attempt at the manufacture of a CFPP rig was made by Flinders, but the rig provided irreproducible results. On a cost benefit basis we concluded that using a third party commercial CFPP rig was the best way to go. Intertek Caleb Brett was used for the majority of measurements.
6. With regard to the fractionation of biodiesel prescribed in Milestone 4, we have generated DSC data showing how the onset and enthalpy of crystallisation varies across the range of unsaturated/ saturated weight fractions. We have used it as a predictive tool to assess the effectiveness of the urea fractionation process in lowering the onset temperature/CP.
7. We have practically employed urea fractionation in Milestone 4, as an alternative to “winterisation”, to assess how much we can lower the onset temperature by removal of saturated components, to achieve a usable product. Fractionation has been achieved at both 7% and 25% w/w removal.
8. At 7% w/w removal of principally methyl stearate and methyl palmitate using urea fractionation, the onset temperature is only lowered from 8.4°C to 6.8°C, a modest 1.6°C change.
9. At 25% w/w removal of principally methyl stearate and methyl palmitate using urea fractionation, the reduction in onset temperature is much more significant (from 8.4°C to 2.7°C, a change of 5.7°C).

Modification of tallow for better performance as biodiesel

10. Throughout Milestones 4 and 6 we have noted a strong linear correlation between the DSC determined onset temperature (T_{onset}) and CFPP measurements. Notably $T_{\text{onset @5C/min}} \sim \text{CFPP}$ for the body of work completed here.
11. A number of commercial polymers have been purchased, modified or synthesised in our laboratories, for use as CFPP modifiers. Of all the materials examined one synthesised polymer has shown particular activity. Designated P4, this polymer is a combination of lauryl acrylate, stearyl methacrylate and maleic anhydride.
12. The activity of P4 polymer has been (usually; but see note 13 below) enhanced by the addition of surfactants, and particularly surfactant combinations. Of particular importance are commercially available Span65/Span85 and a combination of “Olestra-like” surfactants synthesised in our own laboratories, Sucrose Myristate and Sucrose Oleate.
13. Using this polymer in “as is” biodiesel will provide a maximum benefit of about 4°C in CFPP (principally driven by $T_{\text{onset}}/\text{CP}$ changes; see note 10). Curiously, addition of a surfactant package (sucrose based) makes this result slightly worse.
14. P4 in the presence of surfactant begins to have a major influence in 25% w/w depleted biodiesel, generated by urea fractionation. Specifically, the use of P4 with the sucrose myristate/oleate surfactant package in 25% w/w depleted biodiesel is capable of lowering the CFPP by 7°C (to -3°C).
15. When a fractionation procedure is used, in addition to an additives package consisting of an optimised polymer and surfactant, we have lowered the CFPP from ca 9.5°C to -3°C – a change of 12.5°C. This comes at the cost of a 25% w/w loss of starting product.

2 Section 1 Polymer based additives

2.1 Introduction

In all biodiesel fuels the uncontrolled crystallisation of saturated ester molecules at low temperatures is ubiquitous. To date, however, there is no known solution to solve this problem and only very limited research has been specifically directed towards the crystallisation behaviour in biodiesel fuels, least of all, tallow-based biodiesel fuel, which has a very high level of saturated esters. It has therefore been necessary in this Biodiesel Research Project to look to the diesel fuel industry for literature where considerable research has been carried out to address paraffin crystallisation. In diesel fuels the same problem occurs but not on the same scale as for biodiesel fuels.

Additive mixtures have been devised that offer some control of the paraffin crystallisation in diesel fuels to improve their behaviour at low temperatures. In particular, cloud point additives have been found that lower the crystallisation temperature but their action is limited to only a few °C. As paraffin crystallisation cannot be avoided, cold filter plugging point (CFPP), pour point depressant (PPD) and wax antissettling (WASA) additives work as growth inhibitors by effecting crystal size. CFPPs and PPDs are mostly polymer-based additives. Based on the known ingredients of commercially available additives, recent patent literature and journal articles, it can be inferred that effective polymers for CFPP and PPD additives are ethylene-co-vinyl acetate copolymers, styrene-maleate copolymers and poly(meth)acrylate polymers^{1 2 3 4}. It was therefore considered reasonable that these polymers should form the basis of polymer-based additives for tallow-based biodiesel. In addition, WASAs are always used in conjunction with CFPP additives. WASAs adsorb onto the surface of the growing crystals thereby lowering the interfacial free energy and the adhesion energy of the crystals¹. Commonly used WASAs are the Span surfactants (e.g. Span 85, 65, 80, 60, 40 and 20) and imide based molecules².

The aim of the present study was to prepare polymer-based additives suitable for effecting the CP and/or CFPP of tallow-based biodiesel. Blends of biodiesel/polymer mixtures with commercially available surfactants and synthesised surfactants have also been undertaken.

2.2 Experimental

Characterisation

2.2.1 Nuclear Magnetic Spectroscopy:

¹H NMR were recorded on a Varian VXR-300 spectrometer (at 300 MHz) or a Varian Gemini-200 spectrometer (at 200 MHz) at ambient temperature. The splitting patterns were designated as follows: s (singlet); d (doublet); dd (double doublet); t (triplet); q (quartet); m (multiplet) and br (broad). ¹³C NMR were recorded on a Varian VXR-300 (at 300 MHz). Chemical shifts are denoted in δ (ppm) referenced to the residual solvent peaks (CDCl₃: ¹H NMR δ = 7.26 ppm, ¹³C NMR δ = 77.0 ppm).

1 Marie, E.; Chevalier, Y.; Brunel, S.; Eydoux, F. Germaud, L.; Flores, P. J. Colloid Interface Sc. 2004, 269, 117-125

2 Yu-hui, G.; Ben-xian, S. Energy & Fuels 2006, 20, 1579-1583

3 Krull et al.; Clariant GmbH, Frankfurt (DE); US Patent No. 7,041,738 B2, May 9, 2006

4 Tæubert, H. et al.; Leuna Polymer GmbH; CA 2 542 846, 15 October 2004

2.2.2 FTIR

Infrared spectra were recorded using a Nicolet Nexus 8700 FT-IR Spectrophotometer (Thermo Electron Corporation). Powder samples were analysed using the 'Smart Collector™' Diffuse Reflectance Infrared Fourier Transform (DRIFT) Accessory. A rice grain of sample was ground in a mortar and pestle and then mixed with dry, ground KBr powder. This sample was loaded into the DRIFT sample holder and a spectrum was acquired using the following parameters:

Detector = MCT/A
Beamsplitter = KBr
Source = IR
Scan range = 4000 – 500cm⁻¹
Background = Dry, ground KBr powder
Number of scans = 256
Resolution = 4cm⁻¹
Gain = 4.0
Mirror velocity = 1.8988
Aperture = 74

All other sample spectra were acquired using the 'Smart Orbit™' ATR Accessory fitted with a Type IIA diamond crystal. A small amount of sample was placed onto the crystal and a spectrum was collected using the following parameters:

Detector = DTGS TEC
Beamsplitter = KBr
Source = IR
Scan range = 4000 – 500cm⁻¹
Background = Air
Number of scans = 64
Resolution = 4cm⁻¹
Gain = 4.0
Mirror velocity = 0.6329
Aperture = 100

Spectra were analysed using OMNIC version 7.1 software (Thermo Electron Corporation).

2.2.3 DSC

DSC testing was performed using a DSC 2920 Modulated DSC (TA Instruments). Results were analysed using Universal Analysis 2000 version 3.3B software (TA Instruments). The onset temperatures, peak temperatures and enthalpies of crystallisation of saturated and unsaturated fractions were determined by performing linear peak integrations on events in the DSC cooling curve. The onset temperature of crystallisation was taken to be the cloud point of the sample, as discussed in the Milestone 2 and Milestone 3 & 5 technical reports.

Biodiesel control samples were analysed in quadruplicate using the following procedure (Biodiesel 80°C Test Procedure):

Modification of tallow for better performance as biodiesel

Temperature calibration and cell constant = high purity indium
Baseline = -90°C to 90°C
Sample size = 5.0±0.5mg
Pan type = Aluminium Hermetic (TA Instruments)
Heating rate = 5°C/min
Gas flow rate and composition = 50ml/min high purity nitrogen (BOC Gases)
Scan parameters = 1) equilibrate at 80°C, 2) isothermal for 1 min, 3) ramp 80°C to -80°C, 4) isothermal for 1 min, 5) ramp -80°C to 80°C.

This procedure varies slightly from that employed in previous Milestones to enable the saturated enthalpy of crystallisation to be accurately determined; heating to 80°C (as opposed to 50°C) prevents structural pre-ordering within the biodiesel and therefore extinguishes the high-temperature exotherm that commonly overlaps with the saturated crystallisation exotherm.

Biodiesel / additive mixtures were also analysed using the Biodiesel 80°C Test Procedure, however analyses were typically performed only once.

DSC Result Evaluation:

In order to compare the effectiveness of different additives in altering the crystallisation behaviour of biodiesel, the parameters listed below were established.

1. $\Delta T_{saturates}$

This parameter is used to evaluate whether a *blend* of additives has an effect on the saturated onset temperature of crystallisation (cloud point) of a biodiesel sample. It is calculated according to equation 1:

$$T_{onset\ saturates}(biodiesel) - T_{onset\ saturates}(biodiesel + additive) \quad \text{Equation 1}$$

$\Delta T_{saturates}$ gives the *absolute* effectiveness of an additive blend in lowering cloud point; it does not enable comparisons to be made between additives on a per weight basis.

2. $\Delta T_{saturates}$ (w/w)

This parameter is used to evaluate whether a *single* additive (as opposed to an additive blend) has an effect on the saturated onset temperature of crystallisation (cloud point) of a biodiesel sample. It is calculated according to equation 2:

$$\frac{T_{onset\ saturates}(biodiesel) - T_{onset\ saturates}(biodiesel + additive)}{[additive]} \quad \text{Equation 2}$$

where [additive] is equal to the % w/w additive concentration in biodiesel:

$$\frac{mass_{additive}}{mass_{biodiesel+additive}} \times 100$$

Calculating the effect of an additive on the cloud point of a biodiesel sample according to equation 2 gives the effectiveness of that additive in lowering cloud point on a *per weight basis*. A *large positive* value of $\Delta T_{\text{saturates}}$ (w/w) indicates a beneficial effect on cloud point.

3. ΔH normalised

This parameter indicates whether an additive reduces the level of crystallinity associated with the saturated components of biodiesel. It is determined according to equation 3:

$$\frac{\Delta H_{\text{saturates}}_{\text{biodiesel+additive}}}{\Delta H_{\text{saturates}}_{\text{biodiesel}}} \quad \text{Equation 3}$$

The *smaller the value* obtained from equation 3, the more effective the additive in disrupting the crystallisation (cloud point) process (a value of 1 indicates that the biodiesel crystallinity is unchanged).

2.2.4 Preparation of mixtures for DSC and CFPP Analysis

The cold flow properties of biodiesel and conventional petrodiesel are extremely important. Unlike gasoline, petrodiesel and biodiesel can both start to freeze or gel as the temperature gets colder. If the fuel begins to gel, it can clog filters or can eventually become too thick to pump from the fuel tank to the engine. The Cold Filter Plugging Point (CFPP) is the temperature at which fuel crystals have agglomerated in sufficient amounts to cause a test filter to plug. The CFPP is less conservative than the cloud point (CP), and is considered by some to be a better indication of low temperature operability.

CFPP was tested at two different locations, ASG Analytik Pty Ltd and Intertek Caleb Brett Adelaide. CFPP at ASG Analytik was analysed on a Herzog HCP842, which complies with ASTM 6371-05 Standard Test Method for Cold Filter Plugging Point for Diesel and Heating Fuels. Intertek use an ISL brand CFPP analyser which is NATA certified. At both laboratories members of the group were the sole operators on testing days to minimise the risk of samples being taken without permission. Before commencing a run each sample must be filtered and then is poured into a 90ml test jar up to the indicated 45ml mark. The Herzog HCP842 was an automated apparatus that simply required the user to place the sample into the cold bath housing and press run. The ISL apparatus was much more labour intensive, filtering the sample, placing sample in bath, inserting filter, connecting sensors, attaching vacuum line and inserting thermometer. After which you were able to set the initial sampling temperature to at least 5°C above the CP (~10°C). CFPP results recorded are integers of °C and each sample was tested at least twice; depending on the amount of samples tested on the day there was time to run each sample three times. In the following report, some CFPP data is given as a single value while others are a range over 2 degree, this is because over multiple runs the value of the CFPP may deviate. According to NATA a variation of 1°C for each sample is acceptable.

2.2.5 Preparation of Biodiesel / Additive Mixtures for DSC

The majority of additives were tested at 3.5% w/w concentration in biodiesel to ensure that any effects of the additive on the biodiesel crystallisation characteristics were detectable. This was also set in the Milestone definitions as the max add level.

To prepare a biodiesel / additive mixture, biodiesel methyl esters (~ 965 mg) were added to the additive (~ 35 mg) in a small sample vial. This mixture was then warmed in hot water and shaken to homogenise the contents.

Where information on the recommended treatment concentration of commercial additives was available, biodiesel / additive mixtures were made according to those recommendations.

2.2.6 Preparation of Biodiesel / Additive Mixtures for CFPP

The majority of additives were tested at 0.5% w/w or 3.5% w/w concentration in either Victoria Chemicals biodiesel (coded as VCBP in our laboratories; tallow based product sourced by Mike Jureidini, SAFF), or urea fractionated biodiesel experimentally derived from the current work program (coded as BDT25DV in our laboratories and resultant from VCBP).

To prepare a biodiesel / additive mixture, either VCBP or BDT25DV (~ 43.425 g) were combined with the additive (~ 1.575 g) in a Kartell 50ml storage bottle. This mixture was then warmed on a hot plate equipped with a magnetic stirrer. The sample was heated to 60°C and stirred for 15 minutes, then removed from the heat and shaken vigorously to homogenise the contents.

2.3 Materials

Commercially available reagents and starting materials were used without further purification unless otherwise stated. Methanol, lauryl acrylate, stearyl acrylate, lauryl methacrylate, stearyl methacrylate, maleic anhydride, dibutyl maleate, toluene, benzoyl peroxide were supplied by Aldrich.

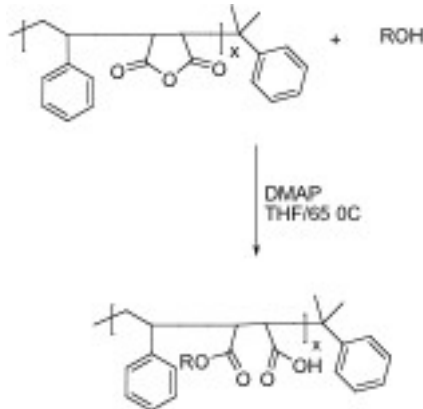
Commercial polymers were also purchased from Aldrich, prior to modification.

2.4 Synthesis

Modification of Commercial Copolymers

Monoester type copolymers:

Copolymer (2g), alcohol (3ml/excess) and DMAP (0.05g) were added to a reaction flask containing THF (60ml) (Scheme 1). The reaction mixture was stirred until a transparent and homogeneous solution was obtained. The flask, equipped with a condenser, was immersed in an oil bath at ~ 65 °C for up to 2 days. Isolation of the polymer was achieved by precipitation into vigorously stirring hexane (300 mL). The polymer was collected by decanting off the solvent. White solid polymer was collected by vacuum. The polymer was then washed with hexane (twice) and dried. Alcohols used were methanol (trial), butane-1-ol, hexane-1-ol, octane-1-ol, 2-octyl-1-dodecanol, 1-hexadecanol and 1-octadecanol. In the case of hexadecanol and octadecanol, the polymer was precipitated in hot hexane to remove the excess alcohol.



Scheme 1: Chemical reaction of styrene-maleic anhydride and alcohols.

Specific polymers made are listed in **Figure 1 & 2**.

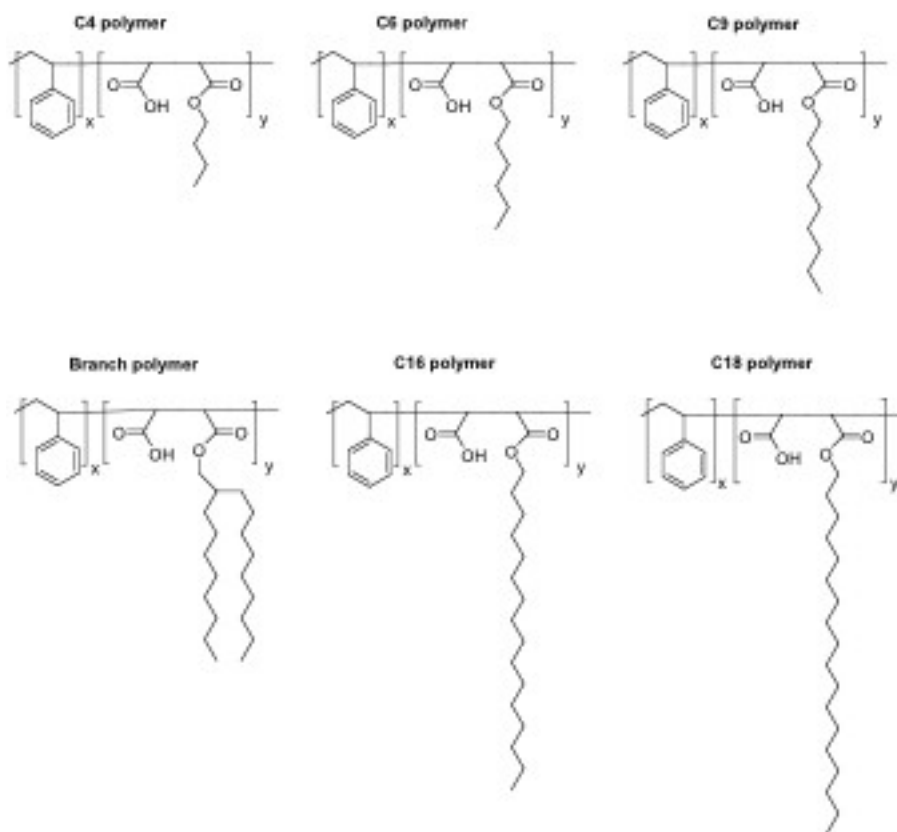


Figure 1: Chemical structure of modified, mono-esters styrene-maleic anhydride

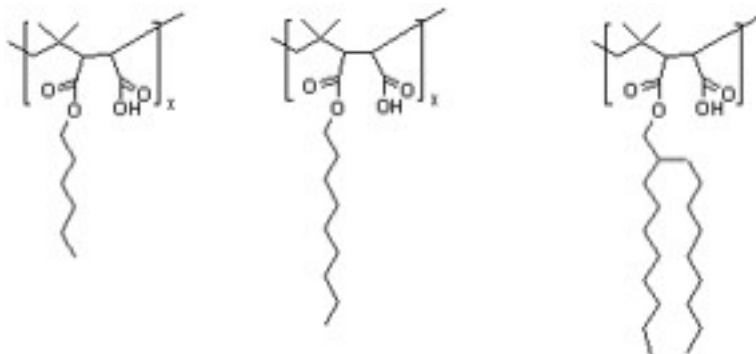


Figure 2: Chemical structure of modified, mono-esters isobutylene-maleic anhydride

2.4.1 Further modification of mono-ester C4 and C18 polymers:

It was found that modified, mono-ester polymers with short alkyl chain (C4, C6 and C9) were insoluble in biodiesel. A further esterification on the mono-ester obtained was carried out using boron trifluoride (BF_3) as Lewis base.

C4 polymer (0.5g) was introduced into a two necked-flask equipped with a condenser. The flask was flushed thoroughly with nitrogen. Dry THF (10ml), boron trifluoride 14 % in methanol (0.2ml)

Modification of tallow for better performance as biodiesel

and butanol (0.2ml) were added to the reaction flask. The reaction mix was refluxed for 3hrs and then stirred at 55 °C for two days.

Ether (20ml) was added to the reaction mix and the mixture was washed with water (3x10ml) and dried over magnesium sulphate. After removal of solvent a clear sticky material was obtained. To remove unreacted butanol, hexane was added and polymer was precipitated out as a white material, which was then collected and analysed by FTIR.

2.4.2 Imide type copolymers:

Copolymer with a maleic anhydride component (2g/0.00125mol) and hexadecylamine (1g/0.004 mol, excess) were dissolved in DMF (20ml). The reaction mix was stirred at 65 °C for 5h, and then stirred at 140 °C for 15h. After the reaction was cooled to room temperature, 36 % HCl solution (10ml) and THF (20ml) were added to reaction mixture. The resultant mix was allowed to stir at 60 °C overnight.

Ether (70ml) was then added. The mixture was poured into a separating funnel and washed with water to remove DMF (10 x 50ml). During the water washing process, NaCl salt was used to help break up any emulsion formed. The organic layer was separated and dried with magnesium sulphate. After removal of solvent a brown-yellow material was obtained which was then washed with hot hexane (100ml) to remove unreacted amine. The product was collected and analysed by FTIR. Polymers prepared are detailed in Figure 3.

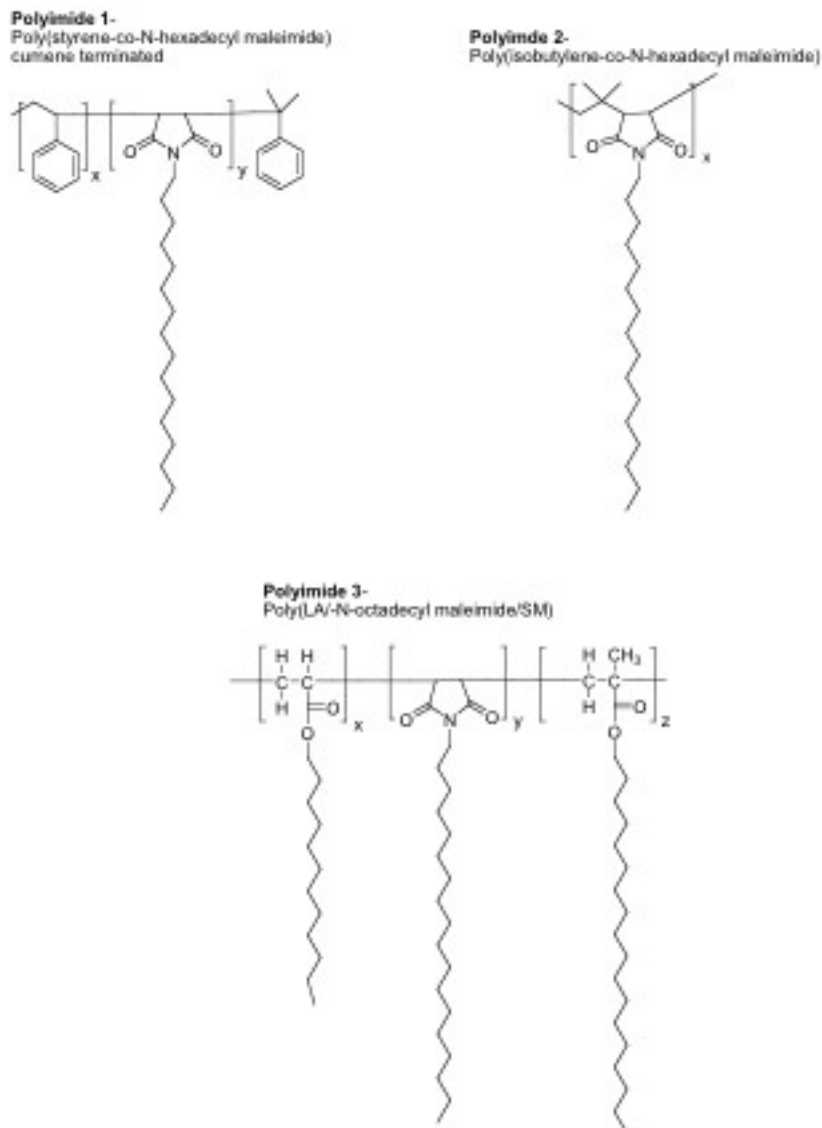
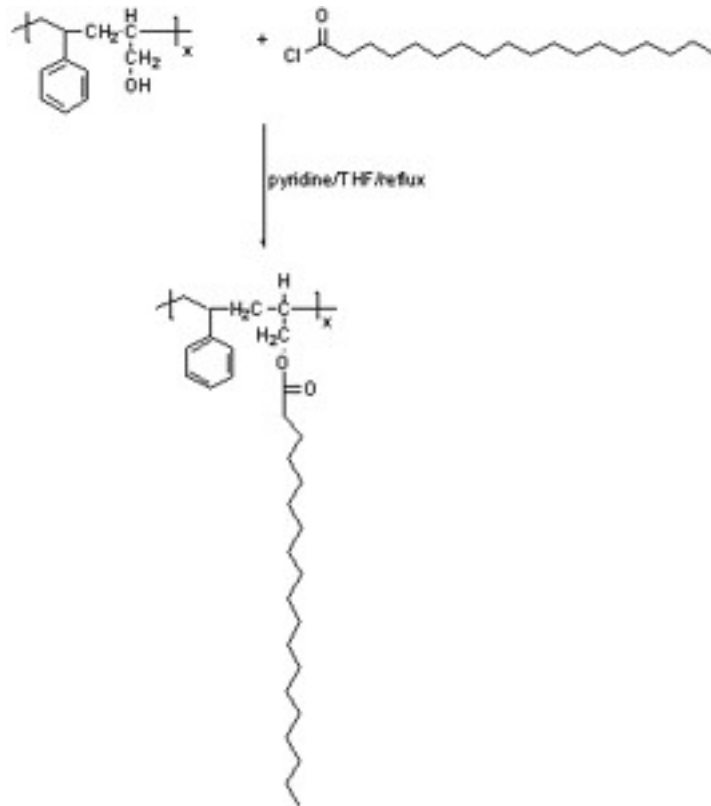


Figure 3: Structure of polyimide type copolymers

2.4.3 Poly(styrene-co-allyl alcohol) grafted stearate:

Poly(styrene-co-allyl alcohol) (4g/0.0021mol), THF (30ml), pyridine (10 drops) were introduced into a 100ml reaction flask. Then a solution of stearoyl chloride (7ml/0.021mol) in THF (10ml) was added drop-wise into the reaction flask. During the stearoyl chloride addition, white precipitate was observed. The reaction was refluxed for 4 hours. Next day, more pyridine (10 drops) was added to the reaction flask and the reaction was continued reflux for 5 hours. Then white salt was filtered off. Isolation of the polymer was achieved by precipitation into vigorously stirring methanol (200 mL). The polymer was collected by decanting off. White solid material was obtained which was collected by vacuum filtration. The solid product was washed with methanol twice and air-dried and characterized by FTIR. Scheme 2 details the reaction process.



Scheme 2: Esterification of poly(styrene-co-allyl alcohol)

2.4.4 Synthesised copolymers

Poly(styrene-co-lauryl acrylate) copolymer

The polymerisation of styrene–lauryl acrylate (Figure 4) was carried out in toluene at 75-80 °C with benzoyl peroxide as initiator. Lauryl acrylate (4.8g/0.02 mol/5.5ml) was charged to a 100ml two necked flask containing toluene (10ml). The reaction flask was placed into silicon oil bath for 10 mins. Then benzoyl peroxide (0.1g) was added to the reaction mix. Styrene (2.08g/0.02 mol) in toluene (10ml) was added drop-wise into the reaction mix. The reaction was left to stir for 24h. Then the reaction mix was precipitated in methanol (300ml), washed with methanol (2 x 50ml) and dried. The polymer was analysed by ¹H NMR and FTIR.

Poly(styrene-co-lauryl acrylate)

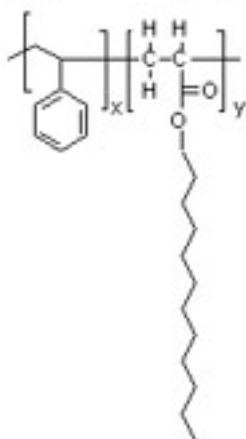


Figure 4: Structure of poly(styrene-co-lauryl acrylate)

2.4.5 Poly(lauryl acrylate-co-maleic anhydride) copolymer:

Lauryl acrylate (10.8ml/0.04mol), maleic anhydride (1.96g/0.02mol) and toluene (50ml) were introduced into a 100ml two necked-flask. The reaction solution was stabilized at 75-80 °C for 5 min. Then benzoyl peroxide (0.22g) was added. The reaction mix was left to stir. Then three hours later another charge of benzoyl peroxide (0.22g) was added. The reaction was stirred at 75-80 °C overnight. Isolation of the polymer was achieved by precipitation into vigorously stirring methanol (300 mL). The polymer was collected by decanting off the solvent. The polymer was then redissolved in small amount of toluene and precipitated again in methanol (300ml). The solvent was decanted off and the resulting polymer was washed with methanol (2 x 20ml). The polymer was dried in the oven overnight. Poly(lauryl acrylate-co-maleic anhydride) (Figure 5) obtained was analysed by ¹H NMR and FTIR.

Poly(lauryl acrylate-co-maleic anhydride)

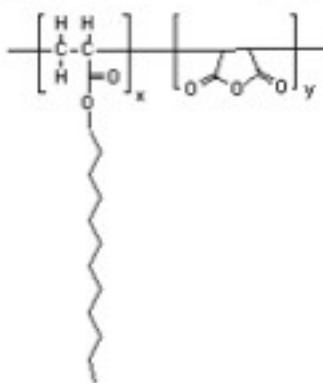


Figure 5: Structure of Poly(lauryl acrylate-co-maleic anhydride)

(Representative procedure for poly(alkyl acrylate-alkyl methacrylate-maleic anhydride terpolymers)

P4 – LA/SM/MAn: A 250 mL, 2-necked round bottom flask equipped with a stirrer and purged with nitrogen was charged with lauryl acrylate (0.04 mol) and stearyl methacrylate (0.008 mol) dissolved in 50 mL of toluene. Maleic anhydride (1.96 g; 0.02 mol) was then added to the vigorously stirring solution and toluene (15 mL) was used to wash down the inside of the reaction flask. The temperature was increased to 65-75 °C prior to adding benzoyl peroxide (0.24 g), using, if necessary, a minimum amount of toluene to wash down the inside of the reaction flask. After 3 hours, an additional amount of benzoyl peroxide (0.24 g) was added and the temperature increased to 80-85 °C. After another 3 hours, the heat was turned off and the reaction mixture left to stir overnight. Isolation of the polymer was achieved by precipitation into vigorously stirring methanol (400 mL). The polymer was collected by decanting off approx. 300 mL of solution and then winding the polymer onto a plastic spatula. The polymer was placed into a teflon petri dish, covered loosely with aluminium foil and placed in the oven overnight to drive off any residual solvent. ¹H and ¹³C NMR indicated that no residual monomer remained in the polymer.

2.5 DISCUSSION

It has been clearly shown that styrene-maleic anhydride, ethylene vinyl acetate and ethylene isobutylene copolymers all have utility as bio/diesel modifiers. In the short time available in this program it has, however, been impossible to cover all options. One type of copolymer that we have concentrated upon comprises styrene, maleic anhydride or maleate elements. Styrene-maleic anhydride polymers and maleic anhydride copolymers in general, have a broad capacity for variation, permitting scope for chemical modification. The anhydride is chemically reactive with a variety of functional groups, particularly alcohols or primary amines, forming ester/ acid or imide type copolymers, respectively. Furthermore, styrene maleate copolymer is also found in commercially available HiTEC 672, which gave an improved CP depression for tallow based biodiesel (Milestone 3 & 5 report). So the anhydride is particularly potent. In terms of commercial availability two copolymers, styrene-maleic anhydride and isobutylene-maleic anhydride were investigated.

2.5.1 Modification of commercial copolymers

Mono-ester type copolymers:

Esterification of styrene-maleic anhydride copolymers with aliphatic alcohols have been reported⁵. The synthetic procedure was carried out as described in Bol. Soc. Chil. Quim. Vol. 46(2), 2001. Styrene-maleic anhydride polymer with molecular weight of 1,900 and isobutylene-maleic anhydride with molecular weight of 6000 from Aldrich were successfully modified by grafting alcohols (for examples methanol, butane-1-ol, hexane-1-ol, octane-1-ol, hexadecane-1-ol, octadecane-1-ol and 2-octyl-dodecane-1-ol) in the presence of 4-dimethylaminopyridine (DMAP) as catalyst in THF. Incomplete opening of all anhydride units was observed. Carboxylic acid groups obtained from anhydride opening are problematic. Modified polymers were analysed by FTIR. Representative FTIR spectra below (Figure 6) are representative spectra of styrene-maleic anhydride before (top) and after (below) esterification. Absorptions at 1855 and 1773 cm⁻¹ correspond to the maleic anhydride group and the carbonyl of an ester group is at 1724 cm⁻¹.

5 Lambla M., Killis, A., Magnin, H, Eur. Polym. J., 15, 489, 1979.

6 Aoyagi, J., Shinohara, I., J. Appl. Polym. Sci., 16, 449, 1972.

Modification of tallow for better performance as biodiesel

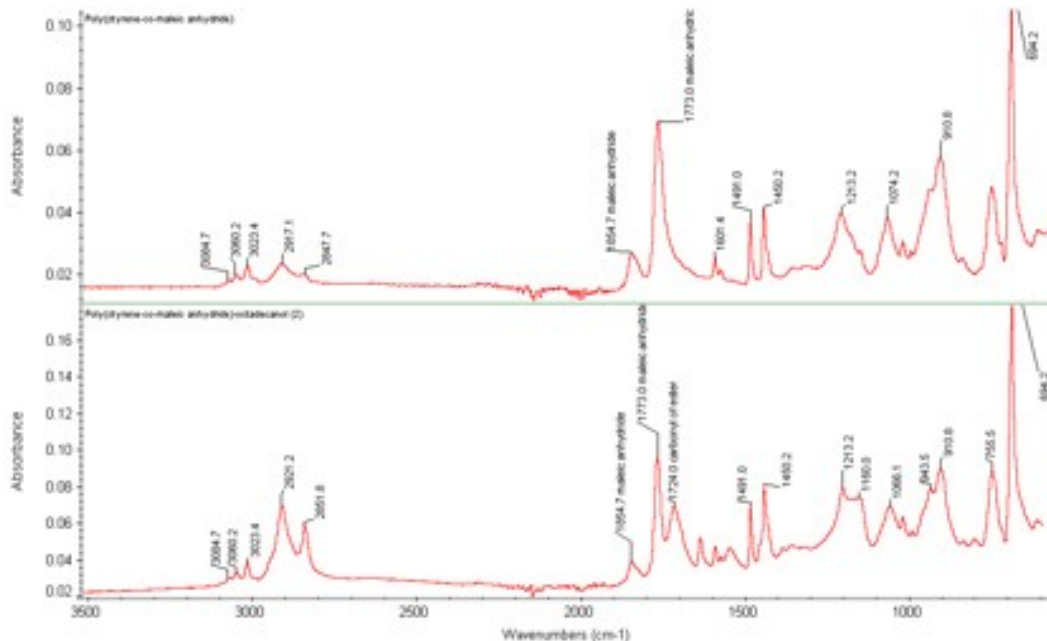


Figure 6: FTIR of styrene-maleic anhydride before and after reacting with alcohol.

The conversion of the reaction was calculated according to Lindt⁷. Distinctive absorptions were chosen to monitor - an absorption band at 694 cm⁻¹, characteristic of styrene which does not change with the reaction, and the peaks at 1855 and 1773 cm⁻¹, corresponding to maleic anhydride residue. The conversion p was defined as

$$p = (1 - A_t/A_0) \times 100,$$

where:

A_0 = initial ratio between absorption at 1724 and 694 cm⁻¹

A_t = ratio between absorption at 1724 and 694 cm⁻¹ at reaction time t

The percentage of ester conversion is summarised in Table 1.

Polymer	Reaction time (hrs)	Percentage Conversion (%)
Methanol (trial)	143	100
Butane-1-ol	118	51
Hexane-1-ol	115	49
Octane-1-ol	58	77
Hexadecanol	48	55
Octadecanol	48	52
2-octyl-1-dodecanol (branched alcohol)	96	40

Table 1: The Percentage Ester Conversion of Styrene-Maleic Anhydride.

⁷ Baruah, S. D., Laskar, N. C., J. Appl. Polym., Sci., 60, 649-656, 1996.

Poor solubility of these modified polymers in biodiesel was noted (except for C16 and C18 polymers). Further esterification was carried in the hope of improving the solubility of these modified polymers in biodiesel, by introducing more alkyl chains into the polymer. The reaction pathway selected involved the use of boron trifluoride, as a Lewis acid, and alcohols. Unfortunately, boron trifluoride reacted with residual maleic anhydride, in addition to the carboxylic acid forming other products. FTIR (Figure 7; top) shows absorption bands for the modified C4 polymer with residue maleic anhydride peaks at 1856 and 1773 cm^{-1} and a carbonyl peak at 1724 cm^{-1} . However, after the polymer was treated with boron trifluoride, these peaks disappeared (Figure 7; bottom). Boron trifluoride has apparently reacted with maleic anhydride, producing unexpected components. No perceived benefit was envisaged from this reaction, so C4, C6 and C9 alcohol reactions with the maleic anhydride unit were terminated.

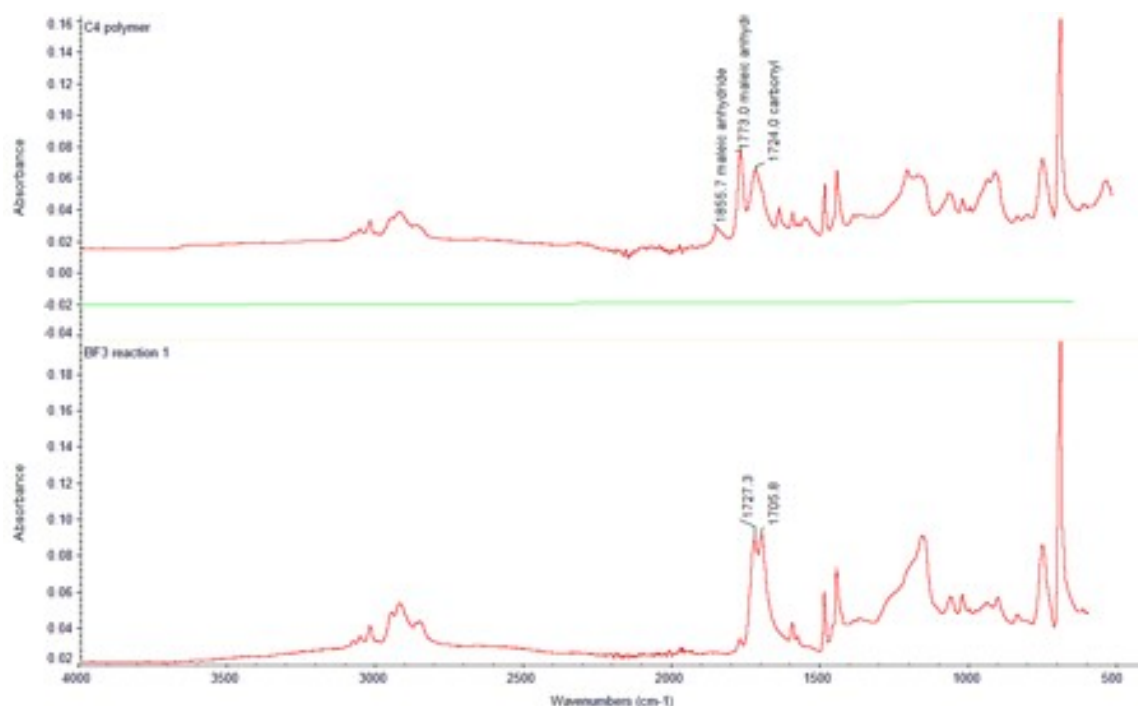


Figure 7: FTIR of mono-ester C4 polymer before and after BF_3 treatment

2.5.2 Imide type copolymers:

Styrene-maleic anhydride or isobutylene-maleic anhydride reacts with primary amines producing imide type copolymer. This type of polymer is actually found in Dodiflow V4313 from Clariant (known as N-stearyl maleimide octadecyl copolymer). It is used as a polymeric additive in diesel fuel.

In our work hexadecyl and octadecyl amine were used and three copolymers were obtained and tested by DSC. FTIR (Figure 8; top) shows the starting polymer, isobutylene-maleic anhydride, with two distinctive maleic anhydride absorptions at 1849 and 1770 cm^{-1} . When the polymer reacted with hexadecylamine the intensity of maleic anhydride bands were decreased and two new absorptions at 1734 and 1692, typical of an imide type structure were observed (Figure 8; bottom).

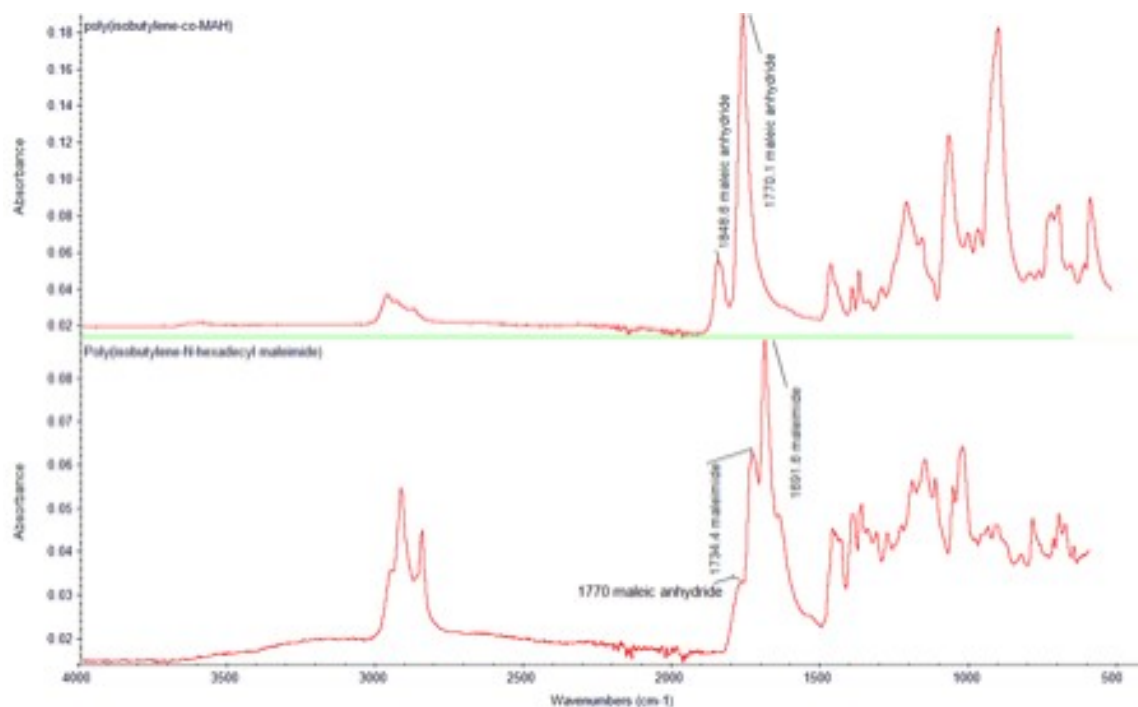


Figure 8: FTIR of isobutylene-maleic anhydride before and after reacting with hexadecylamine

Poly(styrene-co-allyl alcohol) grafted stearate:

Saturated C18 units were grafted onto the allyl alcohol of this polymer as ester linkage by reacting the polymer with stearoyl chloride in the presence of pyridine. FTIR shows a new carbonyl peak at 1734 cm^{-1} which indicated that ester groups were formed. However, a persistent OH peak at 3400 cm^{-1} indicated incomplete grafting.

2.5.3 Synthesised Copolymers

Poly(styrene-co-lauryl acrylate)

Poly(styrene-co-lauryl acrylate) and poly(lauryl acrylate-co-maleic anhydride) copolymers were prepared using benzoyl peroxide as initiator. The polymers obtained were analysed by ^1H NMR and FTIR. Proton NMR spectra confirmed that there are no $-\text{CH}=\text{C}-$ signals in the region between 5.8 – 6.2 ppm. This indicated that no monomers remained in the polymer. FTIR (Figure 9) revealed a characteristic carbonyl peak of maleic anhydride at 1851 and 1781 cm^{-1} and a carbonyl peak at 1728 cm^{-1} related to the ester repeat unit. For poly(styrene-co-lauryl acrylate), besides the ester carbonyl peak there are also peaks corresponding to aromatic C-H stretching at 3026, 3062, 3080 and 698 cm^{-1} of the styrene.

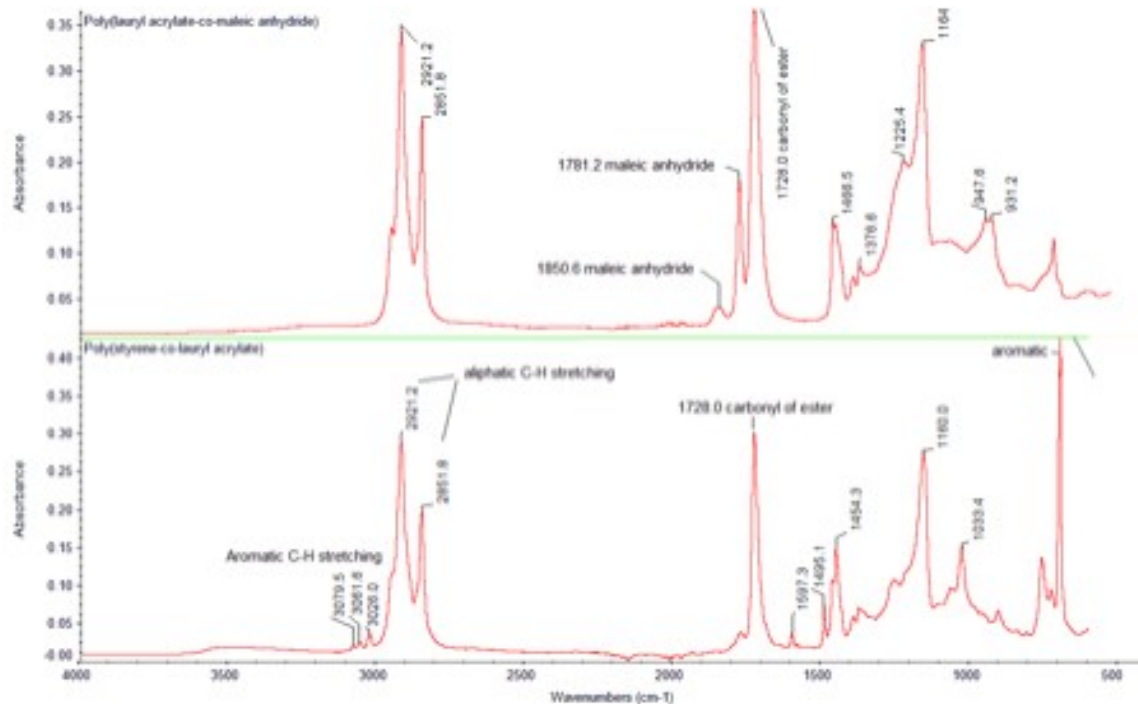


Figure 9: FTIR of lauryl acrylate-maleic anhydride (top) and styrene-lauryl acrylate (below)

2.5.4 Comb Polymers (P1-P8 inclusive)

Poly(meth)acrylate-maleic anhydride terpolymers were synthesised based on the general procedures outlined by Shmakova-Lindeman⁸. Eight different polymers (**Figure 10, Table 2**) were prepared by polymerizing varying mole ratios of acrylic acid, methacrylic acid and maleic anhydride olefinic monomers under free radical forming conditions. The polymerization was conducted by heating a mixture of the monomers and free radical initiator dissolved in toluene at a temperature range between 65-85 °C under inert atmosphere. After approximately 6 hours the heat was turned off and the reaction mixture allowed to return to room temperature and left to stir overnight. The polymer was isolated by precipitation into vigorously stirring methanol, collected and placed in an oven overnight to remove any residual solvent. All polymers contained no residual starting materials based on NMR and ATR-FTIR characterization.

⁸ Shmakova-Lindeman, O. E. US Patent 20050215437, 29 September 2005.

Modification of tallow for better performance as biodiesel

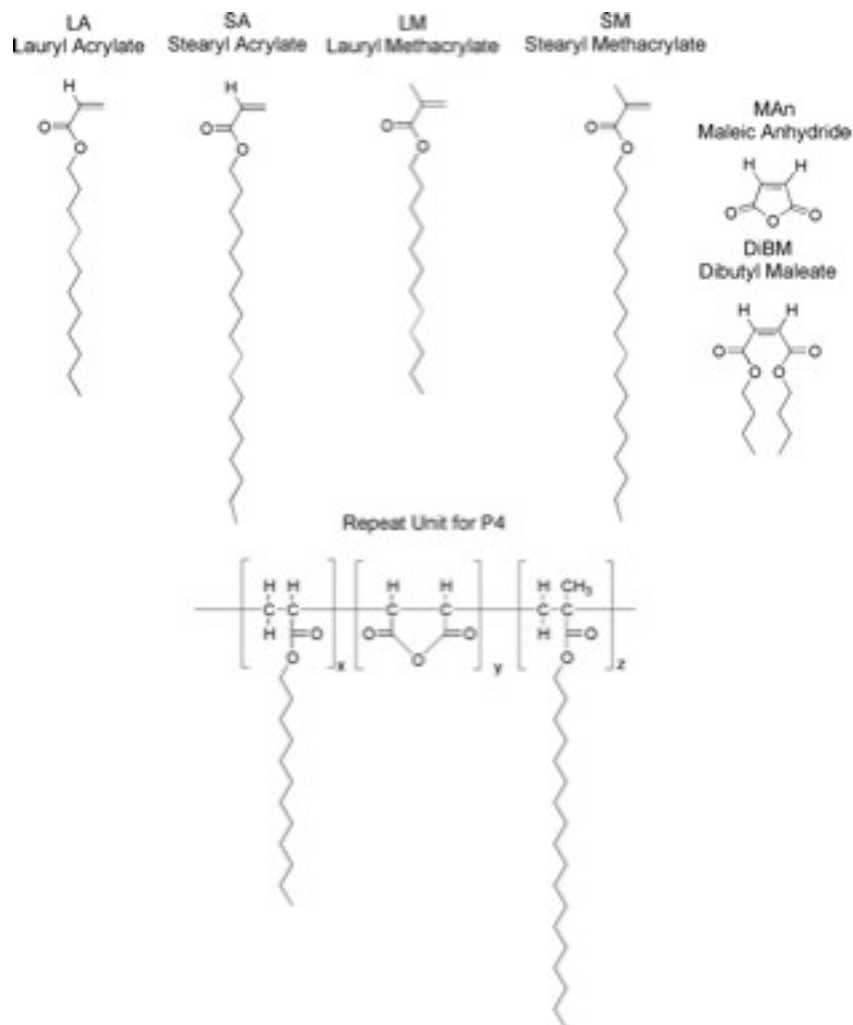


Figure 10: Structures of acrylic acid, methacrylic acid and maleic anhydride olefinic monomers used in comb polymers (P1-P8) including an example of a terpolymer repeat unit.

Polymer	Monomers	Mole Ratios	$T_{onset}^{(a)}$ (°C)
P1	SA/LM/DiBM	2 : 0.5 : 1	9.91
P2	LA/SM/DiBM	2 : 0.5 : 1	8.54
P3	SA/LM/MAn	2 : 0.5 : 1	9.27
P4	LA/SM/MAn	2 : 0.5 : 1	7.59
P5	SA/SM/MAn	2 : 0.5 : 1	10.00
P6	LA/MAn	2 : 1	8.16
P7 ^(b)	LA/SM/MAn	2 : 0.5 : 1	7.66
P8	LA/LM/MAn	2 : 0.5 : 1	9.47

Table 2: Polymer names and mole ratios of monomers used in the synthesis of P1-P8 inclusive and their relative T_{onset} values. (a) 1.75% polymer/1.75% toluene in tallow-based biodiesel

Modification of tallow for better performance as biodiesel

BDT01DV (CP 10.21 °C); (b) double the amount of benzoyl peroxide used compared to P4 (refer Experimental Section).

Based on the T_{onset} data, the following observations were made regarding the combination of monomers in the terpolymers and their subsequent effectiveness at lowering the cloud point of tallow-based biodiesel:

- C18 acrylate (SA) was less effective than C12 acrylate (LM);
- Variation in chain length between the acrylate and methacrylate monomers produced more favourable results than when the chain lengths were the same length (e.g. P4 versus P8 and P3 versus P5);
- Maleic anhydride monomer was more effective than dibutyl maleate monomer;
- Of all the monomer combinations tried, P4 was found to be the most effective polymer-based additive at lowering the cloud point and CFPP of tallow-based biodiesel.

2.5.5 Clariant Polymer-Based Additives

Clariant's Dodiflow 1000 and Dodiflow 2000 were supplied directly to us by Clariant. Confidentiality dictated that no analysis on the samples could be undertaken. Dodiflow 2000 was determined not to be a good additive for tallow-based biodiesel, however, Dodiflow 1000 was found to be the best commercially available additive (refer CP/CFPP characterization below).

2.5.6 Winter POW-R Plus

In the Milestones 3 & 5 Report it was reported that Winter POW-R contained 40-45% heavy aromatic naphtha (mixture of o-, m-, p- xylene), 40-43% polymer (ethylene vinyl acetate), 5-6% of a reasonably high boiling point, polar solvent (diethylene glycol monomethyl ether) and an amine substituted resin (4-5%). It has now come to our attention that there are 3 different commercially available additives on the market which go by the name of 'Winter POW-R Plus/Winter Power'. Therefore, it is necessary to clarify that the "Winter Power" additive that has been tested throughout the Biodiesel Project, which was previously thought to be polymer-based, was actually Winter Power 4033 and not Winter POW-R as previously thought. Winter Power 4033 is not a polymer-based additive.

It should be noted that Nalco Inc. and Penray produce additives with details shown in Table 3 below:

<p>Trade Name: Winter Power 4033 Ingredients: petroleum distillates; alkylnitrates; butoxyethanol Primrose Oil Co. Inc, Dallas, Texas, USA. www.primrose.com</p>	<p>Trade Name: Winter POW-R Plus Ingredients: Heavy aromatic naphtha (40-70%), ethoxylated octyl phenol (1-5%), naphthalene Nalco Inc Not tested in this program</p>	<p>Trade Name: Winter Pow-R Plus Ingredients: 40-45% heavy aromatic naphtha (o,m,p xylene) 40-43% polymer (ethylene vinyl acetate), 5-6% high boiling point polar solvent (diethylene glycol monomethyl ether, amine substituted resin (4-5%) Manufacturer: Penray, Distributors: Detroit Diesel Corp Australian Distributors Specialty Automotive Products</p>
---	---	---

Table 3 Penray's product is the only ethylene-vinyl-acetate polymer-based additive available commercially on the market that we have been able to identify. Unfortunately, we were unable to obtain a sample of this product in time for testing.

2.6 Cloud Point and Cold Filter Plugging Point Characterisation

2.6.1 Synthesised Polymers

Table 4

Additive / Biodiesel Mixture	Additive Concentration (% w/w)	Cloud Point (°C)	$\Delta T_{\text{saturates}}$ (°C)	$\Delta T_{\text{saturates}}$ (% w/w)
BDT01DV		10.21		
Toluene/BDT01DV	3.5	8.58	1.63	0.466
P1:Tol(50/50w/w)/BDT01DV	3.5	9.91	0.3	0.086
P2:Tol(50/50w/w)/BDT01DV	3.5	8.54	1.67	0.477
P3:Tol(14/86w/w)/BDT01DV	3.5	9.27	0.94	0.269
P4:Tol(50/50w/w)/BDT01DV	0.5	9.66	0.55	1.10
P4:Tol(50/50w/w)/BDT01DV	3.5	7.59	2.62	0.749
P4:Tol(7/93w/w)/BDT01DV	3.5	7.54	2.67	0.763
P4/BDT01DV	3.5	7.87	2.34	0.669
P5:Tol(10/90w/w)/BDT01DV	3.5	10.00	0.21	0.060
P6:Tol(50/50w/w)/BDT01DV	3.5	8.16	2.05	0.586
P7:Tol(50/50w/w)/BDT01DV	3.5	7.66	2.55	0.729
P8:Tol(50/50w/w)/BDT01DV	3.5	9.47	0.74	0.211

Note: P4 (LA/SM/Man) and P7 (LA/SM/MAN Double the initiator concentration) returned comparable DSC exotherms, allowing us to use P7 once our supply of P4 was insufficient to complete CFPP testing due to the amount of polymer needed to run each test.

Table 5

Additive / Biodiesel Mixture	Additive Concentration (% w/w)	Cloud Point (°C)	$\Delta T_{\text{saturates}}$ (°C)	$\Delta T_{\text{saturates}}$ (% w/w)
PiBcoHDMI:Tol (50/50w/w)/BDT01DV	3.5	8.53	1.68	0.480
PScoAXS:Tol (10/90w/w)/BDT01DV	3.5	8.59	1.62	0.463
PScoHDMI:Tol (50/50w/w)/BDT01DV	3.5	8.71	1.50	0.429

Modification of tallow for better performance as biodiesel

PScoLA:Tol (15/85w/w)/BDT01DV	3.5	8.99	1.22	0.349
PScoMAHewODOL:Tol (50/50w/w)/BDT01DV	3.5	9.13	1.08	0.309
PScoMAHewHDOL:Tol (50/50w/w)/BDT01DV	3.5	9.78	0.43	0.123
PolyFuran:Tol (50/50w/w)/BDT01DV	3.5	9.96	0.25	0.071

PiBcoHDMI = Poly(isobutyl-co-hexadecylmaleimide)

PScoAXS = Poly(styrene-co-allyl alcohol)

PScoHDMI = Poly(styrene-co-hexadecylmaleimide)

PScoMAHewODOL = Poly(styrene-co-maleicanhydride esterified with octadecanol)

PScoMAHewHDOL = Poly(styrene-co-maleicanhydride esterified with hexadecanol)

2.6.2 Commercial Additives

DSC and CFPP analysis were used to assess the effect of six different commercially available additives on the crystallisation behaviour of tallow-based biodiesel. Two of these additives, HiTEC 672 and Winter Power 4033, had previously been tested by DSC under Milestones 3&5, however they have been re-evaluated within the current Milestones at 3.5 % w/w concentration. Table 6 below summarises the cloud point (saturated onset temperature of crystallisation), cold filter plugging point (CFPP), $\Delta T_{\text{saturates}}$, $\Delta T_{\text{saturates}}$ (w/w) and normalised ΔH values obtained.

Table 6

Additive / Biodiesel Mixture	Additive Concentration (% w/w)	Cloud Point (°C)	CFPP (°C)	$\Delta T_{\text{saturates}}$ (°C)	$\Delta T_{\text{saturates}}$ (% w/w)	$\Delta H_{\text{normalised}}$
Winter Power 4033 / BDT01DV	3.5	8.63	6	1.18	0.33	0.87
HiTEC 672 / BDT01DV	3.5	8.49	5	1.32	0.38	0.87
8500HEC40 / BDT9.4	2.0	8.89	-	1.18	0.58	0.92
BioFlow 875 / BDT9.4	2.0	9.36	-	0.71	0.34	0.91
Dodiflow 2000 / BDT01DV	2.0	8.87	-	0.94	0.42	0.95
Dodiflow 1000 / VCBD	1.0	-	8 – 9*	-	-	-
Dodiflow 1000 / VCBD	2.0	7.18	7 – 8*	1.21	0.59	0.91
Dodiflow 1000 / VCBD	3.5	-	7 – 8*	-	-	-
Dodiflow 1000 / BDT01DV	2.0	8.45	-	1.36	0.70	0.94
Dodiflow 1000 / BDT01DV	3.5	8.95#	-	1.26	0.37	0.88

Modification of tallow for better performance as biodiesel

Reference Biodiesel Cloud Points: BDT9.4 = 10.07°C; BDT01DV = 9.81°C (# = 10.21°C); VCBD = 8.39°C.

Reference Biodiesel CFPP: +8.0°C; * = +10°C.

Of all the commercial additives tested Dodiflow 1000 was most effective, lowering the onset temperature of crystallisation (cloud point) of BDT01DV by 1.36°C. This change was achieved using only 2 % w/w concentration of additive such that the efficiency of Dodiflow 1000 on a per weight basis was significantly greater than that of the other commercial additives tested ($\Delta T_{\text{saturates}}$ (w/w) = 0.70). Despite this, when Dodiflow 1000 was used at higher concentration in biodiesel (3.5 % w/w in BDT01DV), its effectiveness in lowering cloud point was not improved. This suggests that Dodiflow 1000 does not act as merely a 'solvent' for the saturated components of biodiesel and that the dosage of this additive must be optimised to achieve the best possible effect on cloud point.

Whilst Dodiflow 1000 did lower the enthalpy of biodiesel crystallisation slightly ($\Delta H_{\text{normalised}} = 0.94$), it did not produce any significant changes to the shape of the saturated crystallisation exotherm (see figure 11). This lack of impact upon the process of biodiesel crystallisation is reflected in how the CFPP value obtained for 2 % w/w Dodiflow 1000 in Victoria Chemicals Biodiesel is effectively the same as the cloud point measured by DSC. Contrary to the observations made above with respect to cloud point, adding Dodiflow 1000 at higher concentration in biodiesel did reduce the CFPP. However, the effects observed were not significant. The best commercial additive for lowering the CFPP was HiTEC 672, which at 3.5% w/w in BDT01DV lowered the CFPP to + 5.0°C. This value is much lower than the cloud point measured by DSC. In addition, figure ... shows that the shape of the crystallisation exotherm is much broader than for neat biodiesel and indeed the normalised enthalpy of crystallisation for 3.5 % w/w HiTEC 672 in biodiesel is low ($\Delta H_{\text{normalised}} = 0.87$). These factors indicate that HiTEC 672 alters the size and/or shape of the crystals formed during the cooling process.

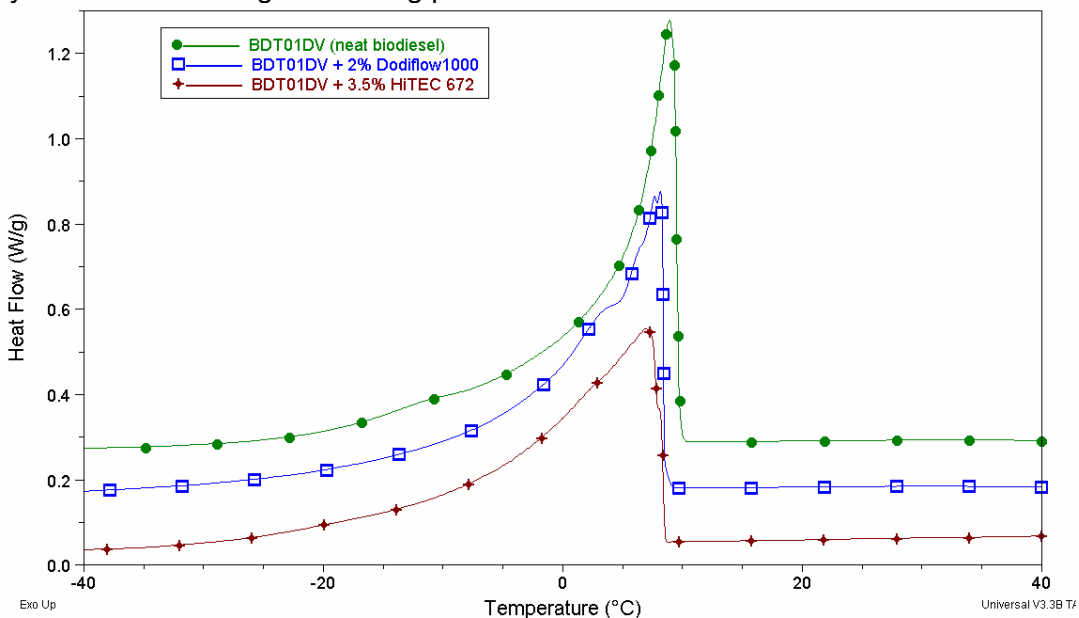


Figure 11: Overlay of DSC results obtained for BDT01DV (neat biodiesel), 2% w/w Dodiflow 1000 in BDT01DV and 3.5% w/w HiTEC in BDT01DV. Note how the shape of the crystallisation exotherm for the 3.5% w/w HiTEC mixture is much broader than for neat biodiesel.

2.6.3 Synthesised P4 in Toluene

We have adjudged the P4 polymer to be a most suitable polymer additive. As a vehicle for rapid dissolution, Toluene was selected as a solvent for that polymer. Table 7 presents details of P4 and toluene in biodiesel.

Table 7

Additives in Laboratory Control BDT01DV			Same Additive Package in Victoria Biodiesel		
P4 or P7 concentration in BDT01DV (% w/w)	Toluene concentration in BDT01DV (% w/w)	CP (°C)	CFPP (°C)	$\Delta T_{\text{saturates}}$ (°C)	$\Delta T_{\text{saturates}}$ (%) w/w)
0	0	10.21	10		
0	3.5	8.58	-	1.63	0.466
0.25	0.25	9.66	8	0.55	1.100
0.25	3.25	7.54	-	2.67	0.763
1.75	1.75	7.59	6	2.62	0.749
3.5	0	7.87	-	2.34	0.669

It is clear that toluene alone has a suppressing role on the DSC determined cloud point, lowering the onset from 10.2°C to 8.58°C at the maximum additive incorporation of 3.5%w/w. Also apparent are synergies between toluene and P4 or P7 additive. Specifically, polymer added on its own cannot match the tandem application polymer and solvent, albeit only a fine differentiation. Despite a relatively small presence of toluene on the weight fraction scale, it must be remembered that on the mole fraction scale the presence of toluene is accentuated because of the differentiation in molecular weight between toluene (92 Dalton) and fatty acid methyl esters (about 290 Dalton). Therefore, the solvency effect of toluene can be easily misrepresented on the weight fraction scale.

With regard to the onset temperature of crystallisation (CP), of all the polymers tested, polymers P4 (LA/SM/Man) and P7 (LA/SM/Man; double the initiator concentration) returned the greatest drop in onset/CP. They lowered the cloud point of BDT01DV by 2.67 °C (Table 7). This was an important factor in its selection as the polymer of choice.

Investigation of the P4: toluene ratio indicated that 0.25%P4 with 3.25% toluene reduced the cloud point in an almost identical manner to 1.75% P4 and 1.75%. However, reducing the concentration to 0.25% P4 and 0.25% toluene the change in ΔT is not very significant (Table 7; 0.55 °C). From all permutations tested it is clear that further research is needed to find the optimum blend of polymer: toluene to maximise the change in cloud point with the minimum amount of additive needed.

Analysis of CFPP data for polymer/ toluene incorporation (Table 7) suggests that the concentration of our preferred polymer (P4/P7) in toluene is still struggling to achieve large benefits in CFPP reduction. 0.25%P4/0.25% toluene and 1.75%P4/1.75% toluene have CFPP outputs of 8°C and 6°C, respectively. There appears to be poor sensitivity to concentration reflected by these measurements. Given that the average CFPP for starting biodiesel is about 10°C, the changes of 2°C and 4°C, respectively at low and higher concentrations, are reflective of the degree of difficulty with tallow based methyl esters. The levels of polymer addition are arguably high and seem to improve at the higher concentrations. This is contrary to conventional wisdom, suggesting that at higher concentrations of polymer additives the benefits appear to diminish.

2.6.4 Surfactants

Surfactants are commonly used at low concentrations in commercial biodiesel additive packages to modify the size and/or shape of the crystals formed [reference]. In order to select the best surfactant for inclusion in polymer / biodiesel formulations a total of twelve 'purchased / commercial' surfactants and five 'synthesised' surfactants were assessed by DSC and CFPP at 1% w/w concentration in biodiesel. Many of these surfactants did not dissolve well in biodiesel (without warming or the use of a solvent) as a result of their high polarity. In fact, the surfactants tested could be classified into two groups; those that dissolved and those that didn't. Interestingly, there were significant differences between the effects of soluble and insoluble surfactants on the crystallisation behaviour of biodiesel. This is illustrated in Figure 12, which shows an overlay of the DSC results obtained for BDT01DV (neat biodiesel), 1% Span 65 in BDT01DV (insoluble) and 1% Span 85 in BDT01DV (soluble).

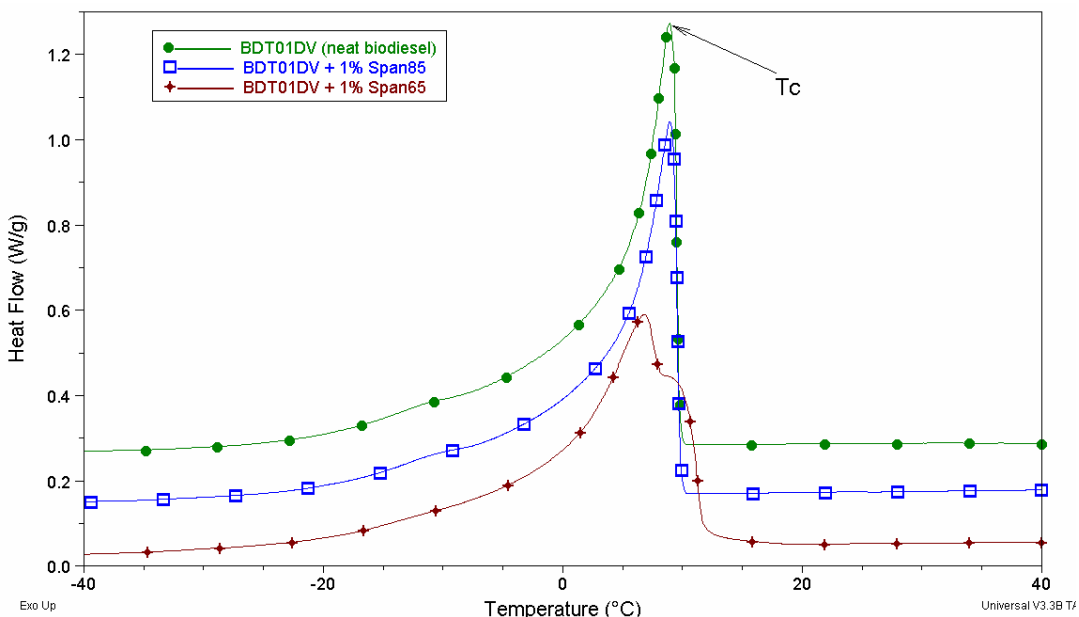


Figure 12 Overlay of DSC results obtained for BDT01DV (neat biodiesel), 1% w/w Span 85 in BDT01DV and 1% w/w Span 65 in BDT01DV. Note how the shape of the crystallisation exotherm for the insoluble 1% w/w Span 65 mixture is much broader than for neat biodiesel and how the onset of crystallisation is shifted to higher temperature. The crystallisation temperature (Tc) for the neat biodiesel sample is annotated.

Modification of tallow for better performance as biodiesel

The surfactants that did not dissolve well in biodiesel at room temperature generally had a considerable effect on the process of biodiesel crystallisation. Not only did they shift the onset of crystallisation (cloud point) to higher temperature, they also appeared to change the type of crystals being formed. The DSC results for the 1% w/w Span 65 mixture show that the saturated crystallisation exotherm is much broader than that of neat biodiesel and involves the formation of two distinct types of crystals (polymorphs). In contrast, the 1% Span 85 mixture appears to have no impact on the process of crystallisation. Analogous observations can be made with respect to the other soluble / insoluble surfactants and it appears that sparingly soluble surfactants could have a beneficial impact upon CFPP if included in polymer / surfactant / biodiesel blends.

Table 8 below summarises the solubility, cloud point (saturated onset temperature of crystallisation), T_c (crystallisation temperature, refer to Figure 12), $\Delta T_{\text{saturates}}$ and normalised ΔH values obtained for the surfactant / biodiesel mixtures assessed (based on results obtained under Milestones 3 & 5, all mixtures were prepared at 1% w/w concentration of surfactant in biodiesel).

Table 8

Surfactant / Biodiesel Mixture	Surfactant Chemistry	Solubility	Cloud Point (°C)	T_c (°C)	$\Delta T_{\text{saturates}}$ (°C)	$\Delta H_{\text{normalised}}$
Tween 80 / BDT9.2	PEG sorbitan monooleate	N	8.98	6.25	0.52	0.99
Tween 85 / BDT9.4	PEG sorbitan trioleate	Y	10.25	9.54	-0.18	0.96
Span 20 / BDT01DV	sorbitan monolaurate	N	10.38	7.73	-0.57	0.99
Span 60 / BDT01DV	sorbitan monostearate	N	11.76	6.99	-1.95	0.90
Span 65 / BDT01DV	sorbitan tristearate	N	11.74	6.77	-1.93	0.91
Span 80 / BDT01DV	sorbitan monooleate	Y	9.70	8.49	0.11	1.01
Span 85 / BDT01DV	sorbitan trioleate	Y	9.77	8.92	0.04	0.91
*Poly (THF) / BDT01DV	linear poly (tetrahydrofuran)	Y	10.21	9.02	-0.40	0.90
^Poly (THF) / BDT01DV	linear poly (tetrahydrofuran)	Y	9.75	8.36	0.06	0.90
POESH / BDT01DV	polyoxyethylene sorbitol hexaoleate	Y	9.74	8.83	0.07	0.90
Triton X45 / BDT01DV	PEG 4-tert-octylphenyl ether	Y	9.75	9.05	0.06	0.90
Triton X100 / BDT01DV	PEG tert-octylphenyl ether	Y	9.83	9.03	-0.02	0.91
Surfactant / Biodiesel Mixture	Surfactant Chemistry	Solubility	Cloud Point (°C)	T_c (°C)	$\Delta T_{\text{saturates}}$ (°C)	$\Delta H_{\text{normalised}}$
*PGPR / BDT01DV	polyglycerol polyricinoleate	Y	10.28	7.90	-0.21	0.98

Modification of tallow for better performance as biodiesel

PGPR / BDT01DV	polyglycerol polyricinoleate	Y	9.85	7.87	0.22	0.94
Lactem PQ 25K / BDT01DV	monoglyceride lactic acid esters	Y	11.05	6.57	-0.98	0.98
sucrose5laurate / BDT01DV	synthetic surfactant - refer to section 2	N	9.12	8.54	0.69	0.98
sucrose5myristate / BDT01DV	synthetic surfactant - refer to section 2	N	8.79	8.29	1.02	0.92
sucrose5oleate / BDT01DV	synthetic surfactant - refer to section 2	Y	9.89	8.94	-0.08	0.92
sucrose5stearate / BDT01DV#	synthetic surfactant - refer to section 2	Y	11.0	8.20	-0.79	0.87

Reference Biodiesel Cloud Points: BDT9.4 = 10.07°C; BDT01DV = 9.81°C (# = 10.21°C); BDT9.2 = 8.65°C.

* = trialled at 0.1 % w/w surfactant concentration in biodiesel

^ = trialled at 0.5 % w/w surfactant concentration in biodiesel

The crystallisation temperature (T_c) results shown in Table 8 support the general observations made above with respect to insoluble surfactants; whilst the majority of such surfactants increased the onset temperature of crystallisation, they also broadened the shape of the exotherm creating a large hysteresis between T_{onset} and T_c . If low T_c is taken to be indicative of the performance of a surfactant with respect to CFPP, Tween 80, Lactem PQ 25K, Span 60 and Span 65 would be the optimal surfactants to use in a polymer / biodiesel surfactant blend. Of these surfactants only Lactem PQ 25K is soluble in biodiesel, however commercial use of this surfactant would be largely impractical a result of its short shelf life. Therefore, Tween 80, Span 60 and Span 65 were recommended for use in further investigations (either neat or as a blend with another surfactant).

Tween 80, PGPR (at 1 % w/w), sucrose5laurate and sucrose5myristate were the only surfactants to lower the cloud point of biodiesel outside of experimental error limits. Of these surfactants only PGPR was soluble in biodiesel, however as for Lactem PQ 25K it has a short shelf life. The cloud point results alone suggest that it would be prudent to use Tween 80 and the sucrose esters in polymer/ biodiesel / surfactant formulation studies. However sucrose5myristate was selected for further investigation as it displays the additional benefit of lowering the saturated enthalpy of crystallisation to a greater degree than the other cloud point-lowering surfactants.

2.7 DSC Results of polymer/ toluene/ surfactant blends in BDT01DV

Table 9 below presents a full description of the incorporation of surfactants, as well as favoured polymer P4, into unmodified biodiesel.

When adding in surfactants, we tried to add them at 5% of the overall additive mixture, usually blended with toluene at 50/50% w/w, with the remaining 95% comprising the polymer and toluene in equal amounts. Some variations with the concentration of the surfactant set at 10% of overall additive mixture were also trialled.

Modification of tallow for better performance as biodiesel

Table 9

Additive / Biodiesel Mixture	Additive Concentration (% w/w)	Cloud Point (°C)	$\Delta T_{\text{saturates}}$ (°C)	$\Delta T_{\text{saturates}}$ (% w/w)
BDT01DV		10.21		
Toluene/BDT01DV	3.5	8.58	1.63	0.466
P4T/BDT01DV	0.5	9.66	0.55	1.10
P4T/BDT01DV	3.5	7.59	2.62	0.749
95%P4T&5%SMT/DT01DV	3.5	7.67	2.54	0.726
95%P4T&5%SM(NoTol)/BDT01DV	3.5	7.65	2.56	0.731
95%P4T&5%SMSOT/BDT01DV	3.5	8.29	1.92	0.549
95%P4T&5%Span85:Tol[50:50w/w]/BDT01DV#	3.5	6.84	3.37	0.963
95%P4T&5%Span85:Tol[50:50w/w]/BDT01DV#	3.5	7.97	2.24	0.640
95%P4T&5%SST/BDT01DV#	3.5	7.82	2.39	0.683
95%P4T&5%SST/BDT01DV#	3.5	7.95	2.26	0.646
95%P4T&5%GeminiSurfactant:Tol[50:50w/w]/BDT01DV	3.5	8.13	2.08	0.594

= Sample made 2 times with each having different concentrations of polymer/toluene/surfactant (shown in Table 10)

P4T = P4: Toluene (50/50% w/w)

SMT = Sucrose Myristate: Toluene (50/50% w/w)

SMSOT = Sucrose Myristate: Sucrose Oleate: Toluene (25/25/50% w/w)

SST = Span 65: Span 85: Toluene (25/25/50% w/w)

A typical co-additive procedure was to create separate 50/50 mixtures of Polymer/Solvent and Surfactant/Solvent. These two entities were then usually blended in the ratio of 95/5 (Polymer in Toluene/Surfactant in Toluene) to give a total weight fraction of 3.5% additive in Biodiesel.

P4T = P4: Toluene (50/50% w/w), S85T = Span85: Toluene (50:50% w/w)

Modification of tallow for better performance as biodiesel

Table 10: Comparative Flinders Biodiesel Vs Victoria Biodiesel.

Additive / Biodiesel Mixture	Additive Conc. (% w/w)	ppm of Polymer	ppm of Toluene	ppm of Surfactant	Cloud Point (°C)	CFPP (°C)
Sample #1 95%P4T&5%SST/ BDT01DV	3.5	16,543.92	17,450.62	906.70	7.82	
Sample # 2 95%P4T&5%SST/ BDT01DV	3.5	16,149.91	16,937.80	787.89	7.95	
CFPP Sample of above polymer/ surfactant combination/VCBD	3.5	17371.80	18344.10	972.30	6.70	5 - 6

Reference Biodiesel cloud points: BDT01DV = 10.21°C; VCBD = 8.44 °C

In the course of our investigations we have used Flinders University Biodiesel (BDT01DV) as a screening tool for CFPP analysis. Larger quantities needed for CFPP analysis dictated a translation of screened candidates to Victoria Biodiesel (VCBD). Table 10 shows comparative DSC data.

After observing that the Span 85 & toluene surfactant blend at two different concentrations gave a significant variation in CP, we decided to blend the Span 65, Span 85 and toluene at similar concentrations and found that there was very little difference in the CP.

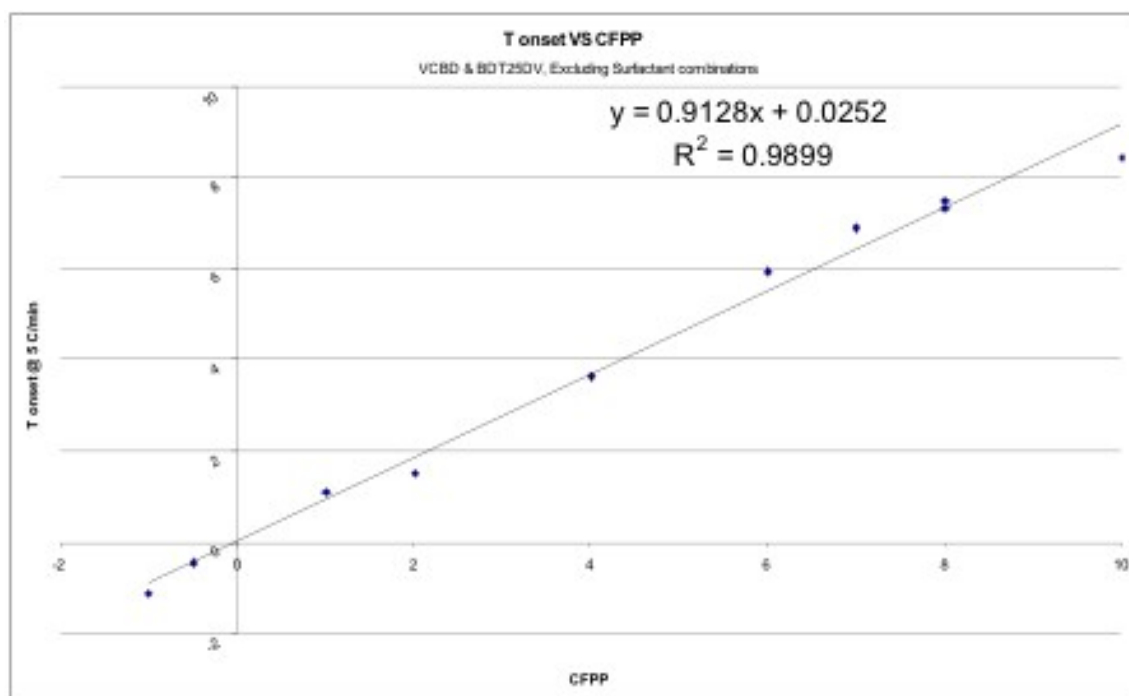


Figure 13

Modification of tallow for better performance as biodiesel

From the Figure 13, we can see that a plot of T_{onset} Vs CFPP appears linear. At this stage, and particularly in the absence of surfactant co additives, we should be able to accurately predict the CFPP of samples solely on the basis of the DSC determined onset temperature (closely related to CP).

It is important to understand that the CFPP measurement has a slower cooling rate than the 5°C/min cooling rate used in DSC experiments. We have demonstrated, in the previous Milestone 3 & 5 meeting, that slower cooling rates dictate higher onset temperatures in both DSC and rheology. We believe that the DSC onset temperatures, corrected to the approximate cooling rate of the CFPP measurement, will be ca 2-3°C higher than those generated at 5°C/min. That is to say, the correlation line will be translated, in a parallel fashion, about 2-3°C higher on the y-axis in the above Figure 13.

2.8 CFPP Results of polymer/ toluene/ surfactant blends in V CBD

Table 11:

Additive / Biodiesel Mixture	Additive Concentration (% w/w)	Cloud Point (°C)	CFPP (°C)	$\Delta T_{\text{saturates}}$ (°C)	$\Delta T_{\text{saturates}}$ (% w/w)
VCBD	-	8.44	10		
P4T/VCBD	0.5	7.50	8	0.94	1.88
95%P4T&5%SMT/VCBD	0.5	7.26	8	1.18	2.36
95%P4T&5%SST/VCBD	0.5	7.44	8	1.00	2.00
95%P4T&5%SMSOT/VCBD	0.5	7.33	7	1.11	2.22
P4T/VCBD	3.5	5.95	6	2.49	0.711
90%P4T&10%SMT/VCBD	3.5	6.00	7	2.44	0.697
95%P4T&5%SMT/VCBD	3.5	5.76	6 - 7	2.68	0.766
95%P4T&5%SMSOT/VCBD	3.5	5.84	7 - 8	2.60	0.743
95%P4T&5%SST/VCBD	3.5	6.70	5 - 6	1.74	0.497

P4T = P4: Toluene (50/50% w/w), SMT = Sucrose Myristate: Toluene (50/50% w/w), SMSOT = Sucrose Myristate: Sucrose Oleate: Toluene (25/25/50% w/w), SST = Span 65: Span 85: Toluene (25/25/50% w/w)

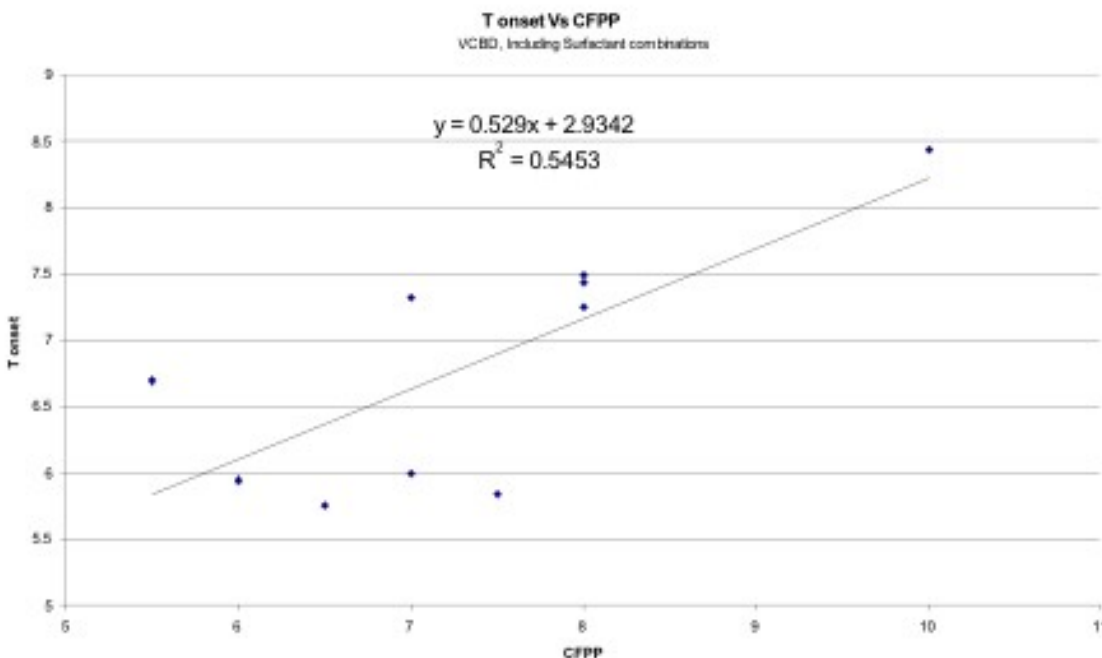
When the CFPP was run with normal V CBD and V CBD with P4: toluene (No surfactants), at the CFPP temperature (the temperature at which the measurement fails to suck up 20ml of biodiesel in 60 seconds) the sample usually stays in the pipette because the filter is blocked and frozen over. When the surfactants are added, once the CFPP temperature is reached and the test stops,

Modification of tallow for better performance as biodiesel

all of the sample collected in the 20ml pipette flows back into the containment vessel, indicating that the size of the crystals are smaller and are only becoming just large enough to disallow passage through the filter, but, not large enough to block the filter when the pressure is reduced and gravity takes over. We have collected some video evidence of this happenstance which can be found with the documentation submitted at the conclusion of this milestone.

The best result came from the combination of P4: toluene with the Span 65 & Span 85 combination of surfactants at 3.5% total additive mixture. Adding the surfactants in at lower concentrations seems to be the trend in current systems. We then tried the surfactant, sucrose myristate at two different combinations 5% and 10% of 3.5% additive overall. At the higher concentration (10%) it returned both a higher CP and CFPP, however, even lower concentrations of surfactant are yet to be explored. At the lower concentration (5%) different surfactants were trialed, sucrose myristate, sucrose myristate and sucrose oleate and finally Span 65 and Span 85. This is where the relationship between CP and CFPP begins to decouple, the CP for sucrose myristate @ 5% is 5.76°C while the corresponding CFPP is 6°C - 7°C, and similarly sucrose myristate @ 10% has a CP of 6.00°C and CFPP of 7°C. The correlation here is consistent, the higher the CP, the higher the CFPP, which has been the trend for all of the samples without surfactants, however, the Span 65 and Span 85 combination does not seem to follow this trend. The spans combination has a lower CFPP than CP which goes against the trend observed for all previous results, this would be due to the formation of the smaller crystals being able to pass through the filter in the CFPP test but which would not show up on a DSC exotherm. The lowest CFPP obtained without surfactants was 6.00°C and with the Spans combination we can drop the CFPP by another 1.00°C, in one of the three trials of the sample.

At 0.5% additive levels, the sucrose myristate and sucrose oleate combination gives the lowest CFPP of 7.00°C, however, when the additive level is increased the lower CFPP with respect to the other surfactant combinations is reversed and it has the highest CFPP. Even though the CP/CFPP relationship may not hold when surfactants are added, it is interesting to note that the span combination with the highest CP has the lowest CFPP and



Figure

14: Graph depicting trend of T_{onset} Vs CFPP with the inclusion of surfactants as additives.

When surfactants are added, the linearity is interrupted and the trend between CP and CFPP is obliterated. This is due to the fact that the CFPP tests, samples with surfactants had smaller crystals forming, allowing the majority passage through the filter, achieving a lower CFPP value. This lower CFPP value is not decipherable on the DSC, thus making it near impossible to predict the CFPP value from a DSC exotherm.

CFPP Testing –

The CFPP test is a commonly used tool to identify the temperature where biodiesel forms crystals large enough to prevent fuel making it to the engine. Having attempted to build our own apparatus, we noticed that even if we had made ours operational then there would still be many variables we could not control, which could potentially alter the CFPP values obtained. A sample with a known CFPP of 8 °C allowed us to take an identical sample to each of the 2 laboratories where we tested CFPP. At ASG Analytik, which had a relatively new machine, the CFPP obtained was also 8 °C, however, this instrument was not NATA approved. At Intertek Caleb Brett, where the apparatus is NATA certified, the CFPP of our known sample was 10 °C. The major causes for concern in the interlaboratory variation relate to vacuum control and cooling bath profiles. Interlaboratory variation needs to be considered in any discussion on CFPP data arising from this program.

2.9 SUMMARY

Modification of tallow for better performance as biodiesel

The use of polymers in isolation generates a strong correlation between CFPP and CP. This indicates that these 2 parameters are strongly coupled. We have isolated a terpolymers, P4, having a strong influence upon CP, and by definition CFPP. When surfactants are added CFPP begins to decouple from CP, and added benefits arise. We have identified 2 surfactant packages Span 65/ Span 85 and sucrose myristate/ sucrose oleate as promising candidates for use in Tallow FAME. The benefit achieved with CFPP is 4 - 5 °C. Care should be taken that favoured packages are examined in vegetable oil based biodiesel beyond the scope of this program.

3 Section 2: Low molecular weight additives

3.1 Introduction

The use of low molecular weight additives in conjunction with polymeric additives has a high precedence within the bulk of the literature associated with crystallisation inhibition of bio- and petroleum-based diesels. The types of molecules which are used for this purpose are molecules which can affect the 3-D network formed by the saturated portion of the biodiesel at low temperatures, much like the polymeric additives mentioned previously. Such low molecular weight additives include molecules like surfactants, wax esters, alkyl amines, ethers and branched esters. In the report for Milestone 3 & 5 some of these compounds were investigated, but only to probe the possible efficacy of such materials as additives within the biodiesel. Thus this milestone afforded the opportunity to investigate the synthesis of new additives with favourable properties as an extension of the previous milestone.

3.2 Experimental

Refer to Section 1 for all other characterization techniques

3.2.1 Characterization

GC-MS Conditions: Chromatograms and mass spectra were generated on a Varian CP-3800 gas chromatogram containing a Varian DB-5, 30M x 0.25 mm x 0.25 μ m 5% phenyl 95% dimethylpolysiloxane column attached to a Varian Saturn 2200GC/MS/MS. Samples were injected using a Varian CP-8400 autosampler. GC-MS Carrier gas was He at a flow rate of 1.25 ml/min Injector split was 1:20 and temperature was 220° C. Oven temperature was held at 150°C for 3.5 mins and ramped to 275°C at a rate of 5°C/min. Ionisation was by electron impact and ion detection limits 40-400 m/z (when required the detection limit was extended to 650).

Ozonolysis Conditions: Ozone is generated by electrical discharge of pure oxygen by an ozone generator (Fischer M500) and introduced directly into the reaction mixture by a quickfit equipped glass rod terminated with a frit. Oxygen was pumped at 100 L/hr and the ozone generator was set to 100 mA for 180 minutes for each run.

3.3 Materials:

Commercially available reagents and starting materials were used without further purification unless otherwise stated.

3.4 Synthesis

(Representative procedure an ozonolysis reaction)

Ozonolysis of Jojoba Oil: Jojoba oil (1 g), Triethylamine (1 g) and methanol (20 ml) were combined in dichloromethane (20 ml) within a 100 mL 2-necked round bottom flask equipped with a glass rod terminated with a glass frit. The solution was cooled to 0°C and ozone was introduced at a rate of 31 mg/min. Excess ozone/oxygen was allowed to escape via the unused flask outlet. After 3 hours, the ozone generator was turned off and the solution was purged with oxygen for 30 minutes to remove residual ozone. The solution was transferred to a separating funnel with additional dichloromethane (20 mL) and washed with 3M HCL (2 x 20 mL) to remove triethylamine. After washing with water, the organics were dried (MgSO₄), filtered and evaporated to give the ozonolysis products as a clear liquid. The products were analysed by GC-MS.

(Representative procedure for ester synthesis from an acid chloride and alcohol)

Methyl Tridecanoate: A 250 mL, 2-necked round bottom flask equipped with a stirring bar and purged with nitrogen was charged with isopropanol (1.80 g; 3.0×10^{-2} mol; 2.3 mL) and dissolved in 50 mL of diethyl ether. Triethylamine (3.34 g; 3.3×10^{-2} mol; 4.6 mL) was added in 1 mL portions via a disposable syringe and a rubber septum. The septum was replaced with a pressure equalizing funnel. To the stirring solution, nonanoyl chloride (5.30 g; 3.0×10^{-2} mol; 5.4 mL) in 25 mL diethyl ether was then added dropwise over 20 minutes via the pressure equalizing funnel. Upon addition of the nonanoyl chloride to the reaction mixture a white precipitate resulted (TEA.HCl salt). No internal increase in temperature was observed. The reaction mixture was refluxed for 3-4 hours after which time the heat was turned off and the reaction mixture left stirring overnight. The reaction mixture was washed with ice cold demineralised water (x 3). After addition of HCl (1.0 M), the aqueous layer was separated and the organic layer washed with 5% NaHCO₃ solution (x 2), dried over MgSO₄, filtered and concentrated *in vacuo* to afford a yellow liquid (yield 57%). ¹H NMR (300 MHz, CDCl₃) δ_H 0.80 (t, 2H), 1.14 (d, 6H), 1.20 (b, 10H), 1.53 (m, 2H), 2.17 (t, 2H), 4.92 (m, 1H); ¹³C NMR (300 MHz, CDCl₃) δ_C 13.8, 21.6, 22.5, 24.1, 24.9, 28.7, 28.9, 29.1, 31.7, 34.5, 35.1, 67.0, 173.1.

(Representative procedure for sucrose ester synthesis)

Sucrose Myristate (5 equivalents): Sucrose (1.71 g, 0.005 mol) and dry DMF (5 mL) were heated in a 3 neck 250mL RBF (equipped with a condenser, thermometer and pressure equalising dropping funnel) with a heat gun until solution was achieved. Dry Pyridine (0.03 mol, 2.86 g, 2.43 mL) was added and the solution cooled to 60°C. A solution of myristoyl chloride (0.025 mol, 6.17g, 6.8 mL) in CH₃CN (5 mL) and acetone (10mL) was added dropwise to the vigorously stirred solution over a 30 min period. After the addition of the acid chloride the solution was stirred at 60°C for 1 hour, cooled to room temperature and acetone (75 mL) added. Sodium bicarbonate (2.5 g) water (0.125mL) were added to the flask to decompose the pyridine hydrochloride by-product. After the evolution of CO₂ ceased, Na₂SO₄ to remove water and mixture filtered through celite on a sintered funnel. At this point if the solution is brown, charcoal can be added to decolourise. The solvent removed by high vacuum distillation (water bath 45°C) and dried on high vacuum to afford the desired mixture as a pale yellow solid (7.71 g, 98%). Analysis of the mixture by chromatographic means was impossible so bulk analysis by 1H NMR afforded the ration of sucrose to fatty acid. This was achieved through the silylation of the sucrose ester with BSTFA in CHCl₃ solution, evaporation and removal of excess BSTFA by drying on high vacuum (0.1 mmHg) NMR ratio of TMS ethers to terminal methyl signal of fatty acid residue was calculated via integration and gave a total of 5 fatty acid esters present in the mixture.

(Representative procedure for tallowate syntheses with branched alcohols)

Nerol Tallowate: Tallow (25 g) was added to a 250 mL round bottom flask and heated to 55°C. Nerol (26.85 g, 0.17 mol) was added to NaOH (0.325 g, 8.1 mmol) and the mixture sonicated for 1 hour. The resulting solution was added to the heated tallow using nerol (5 mL) to transfer the remaining NaOH into the flask. The mixture was stirred vigorously for 12 hours at 55°C under a nitrogen atmosphere. The reaction mixture was poured into a pre-heated separation funnel, hexane was added and methanol (25 mL) was added. The separating funnel was shaken then hot water (100 mL) added then the aqueous content removed. The washing procedure was repeated 6 times then the organics were subjected to rotary evaporation for 1 hour to drive off any volatiles to yield (15 g) of a yellow liquid. 1H NMR analysis of the final mixture indicated the transesterification worked successfully.

(Representative procedure for ether syntheses)

3-methylbutyl-11-undecenyl ether: A solution of 3-methylbutanol (1.5 g, 1.854 mL, 0.017 mol) in dry THF (17 mL) was cooled to 0°C under an inert atmosphere. NaH (0.018 mol, 0.432g) was added portionwise and the solution stirred for 10 minutes at 0°C. The solution was brought to reflux and 11-bromoundecene (0.017 mol, 3.97 g, 3.73 mL) in THF (10 mL) was added dropwise to the solution and then the mixture was refluxed with stirring overnight. The reaction mixture was quenched with water (20 mL) and the organics washed with water (20 mL) and dried over CaCl₂ and left to stand for 10 minutes. The solvent was filtered and evaporated. The residue was subjected to vacuum distillation collecting the final fraction (210-220°C @ 10 mmHg) to give the desired product (2.62 g, 64%) as a colourless oil. ¹H NMR (300 MHz, CDCl₃) δ_H 0.9 (d, 6H), 1.28 (m, 12H), 1.46 (q, 2H), 1.55 (t, 2H) 1.69 (septet, 1H), 2.03 (q, 2H), 3.4 (dt, 2H), 4.95 (m, 2H), 5.79 (m, 1H); ¹³C NMR (300 MHz, CDCl₃) δ_C 22.64, 25.11, 26.19, 28.90, 28.92, 29.07, 29.11, 29.42, 29.47, 29.53, 29.78, 33.80, 38.60, 69.26, 70.99, 114.08, 139.22.

3.5 DISCUSSION

3.5.1 Synthesis

Synthesised additives can be classed into categories according to their chemical structure or their mode of action within the biodiesel. These include:

- ozonolysis products
- wax esters
- fatty acid esters of branched alcohols
- substituted methyl oleate (at the point of unsaturation on the oleate chain)
- aromatic and aliphatic ethers
- surfactants (sucrose esters and gemini surfactants)

Unlike the previous milestone where a systematic approach was taken to primarily investigate substituents effects either side of the ester functional group, this milestone was a survey of the possible families of compounds that could be developed into additives for tallow-based biodiesel. Selections from each of the groups are discussed below.

Ozonolysis Products: As part of the agreed milestones, some work investigating the use of ozonolysed derivatives as additives into biodiesel was to be carried out. Some of this work is an extension of the work carried out in the previous milestone, which involved the ozonolysis of methyl oleates.

To extend the usefulness of the ozonolysis reaction it was employed to break the components of jojoba oil into various products. Jojoba oil has a much more diverse composition than biodiesel in that it possesses unsaturated wax esters. Such wax esters in Jojoba oil possess from 36 to 44 carbon atoms and up to 2 points of unsaturation.¹ Jojoba wax esters exhibit superior stability for an unsaturated wax ester. The major wax esters in Jojoba oil are summarised in the table below.

Four Major Jojoba Esters	%
Docos- <i>cis</i> -13-enyl Eicos- <i>cis</i> -11-enoate	37
Eicos- <i>cis</i> -11-enyl Octadec- <i>cis</i> -9-enoate	30
Eicos- <i>cis</i> -11-enyl Docos- <i>cis</i> -13-enoate	10
Tetracos- <i>cis</i> -15-enyl Eicos- <i>cis</i> -11-enoate	7
Other components including 21 other wax esters	16

Table 1: The four major Jojoba esters.²

The use of wax esters and their effect as additives in biodiesel are discussed in a following section; therefore it may serve as an avenue towards ozonolysis products with unique properties. As shown in previous milestone reports, the ozonolysis reaction occurs at the points of unsaturation within molecules. It is for this reason that the ozonolysis of methyl oleates was studied previously and the corresponding mechanism of the reaction accompanies the previous work.

GC-MS analysis of the ozonolysis products was performed by GC-MS. Due to the nature of products being wax esters themselves and for the most part involatile, characterisation of the complicated reaction mixture could not be performed by GC-MS.

As mentioned previously, the ozonolysis of 3-methylbutyl-11-undecenyl ether was also performed to further investigate the use of ozonolysis in the synthesis of useful additives for inclusion into biodiesel. The reaction achieved as well as the theoretical products expected are outlined below in Figure 1.

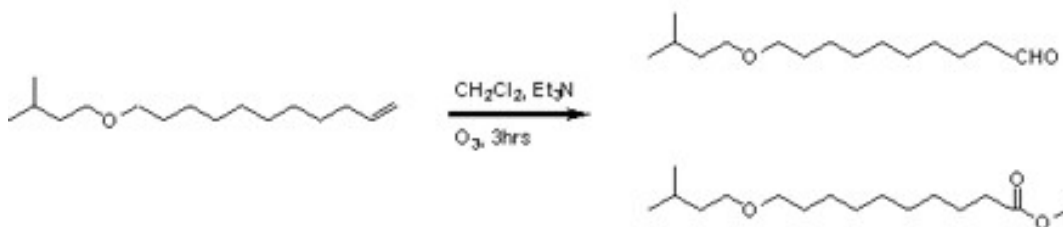


Figure 1: Ozonolysis of 3-methylbutyl-11-undecenyl ether.

As shown by the reaction above, the 2 possible products are the aldehyde and the methyl ester. These were identified by GC-MS through the presence of fragments in the mass spectrum of the eluant. The GC-MS below of the reaction mixture indicated that the reaction had progressed somewhat, but the nature of the substrate had caused multiple products, all of which could not be identified.

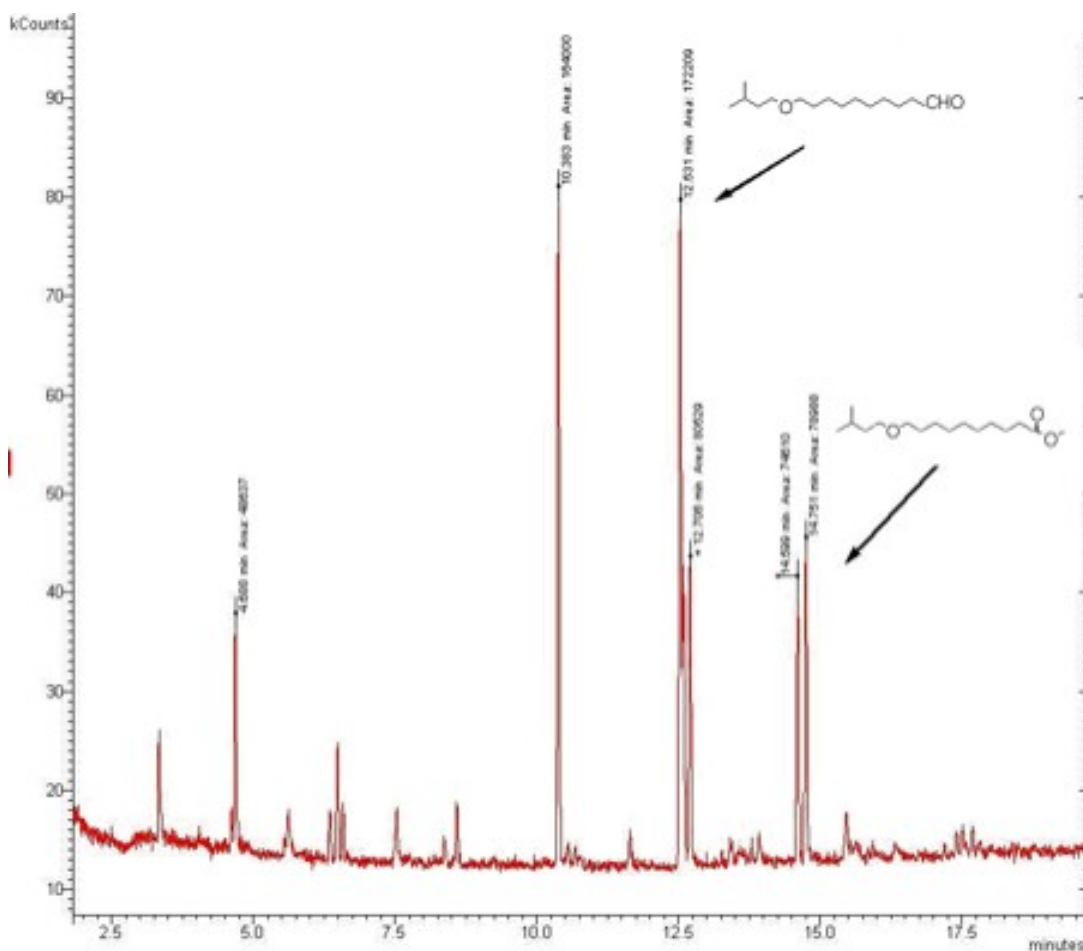


Figure 2. GC-MS of product mixture from the ozonolysis of 3-methylbutyl-11-undecenyl ether.

Due to the difficulty in characterisation of the reaction mixture and the poor efficiency exhibited by the ozonolysed derivatives (with respect to lowering the crystallisation onset), this section of the agreed milestones was concluded to focus on more promising areas of synthesis, which are highlighted in the following sections.

Wax esters: The study of A-B type wax esters was briefly investigated as an additive in Milestone 3 as discussed in the previous report. The result of this investigation was the interesting effect of oleyl laurate on the biodiesel. It was found that the presence of wax esters within the biodiesel matrix served as a type of surfactant, creating a new exotherm at a much lower temperature, as shown below (from -32°C to -23°C).

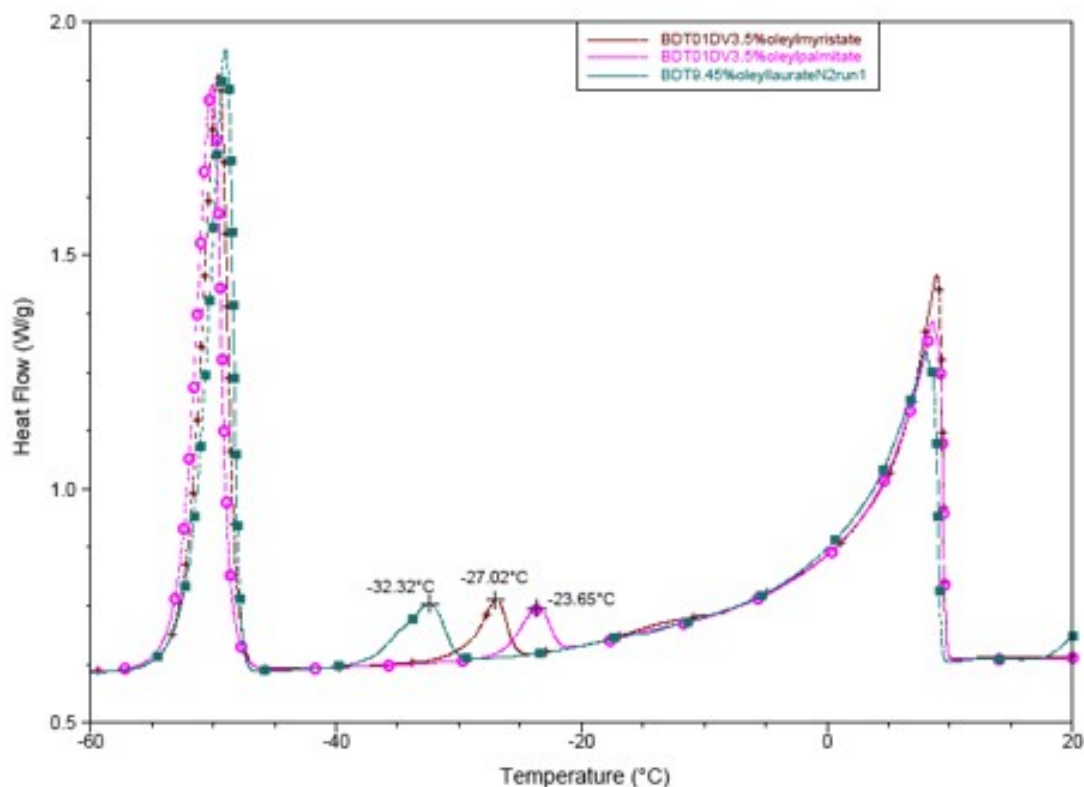


Figure 3. DSC of Wax esters in Tallow-based Biodiesel.

In addition to these two wax esters, oleyl myristate, palmitate (represented in the DSC above) and behenate were synthesised according to an established method shown below in Figure 4 (refer to experimental section above).

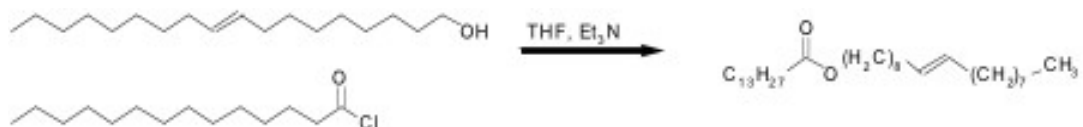


Figure 4. Synthesis of oleyl myristate wax ester.

Once again the trend of alkyl chain length and the efficacy of such additives were displayed with the long alkyl chains (C_{18}) being worse than C_{12} - C_{16} additives. This is an important observation with regard to designing additives for application in biodiesel with high levels of saturates.

Fatty Acid Esters of Branched Alcohols: Along the course of the program, the use of branched alcohols have been used and proven to have effects on the final biodiesel product which are incredibly favourable. The best example of this is the use of isopropanol instead of methanol in the transesterification process. The resulting esters had excellent properties with regard to the CP and CFPP observed. This result is due to the unfavourable steric interaction of the branched isopropyl unit and its effect in disrupting the crystal packing arrangement of saturates in the biodiesel. To further extend this work a trial transesterification was performed with the highly unsaturated alcohol nerol. Nerol is a naturally occurring monoterpene found in many essential oils and has wide use in the perfume industry.

As shown below in Figure 5, the resulting neryl esters have higher degrees of unsaturation, essentially likening them to biodiesel produced from vegetable feed stocks. In addition to the synthesis of neryl tallowate, this alcohol was utilised in the synthesis of neryl octanoate, nonanoate and decanoate.

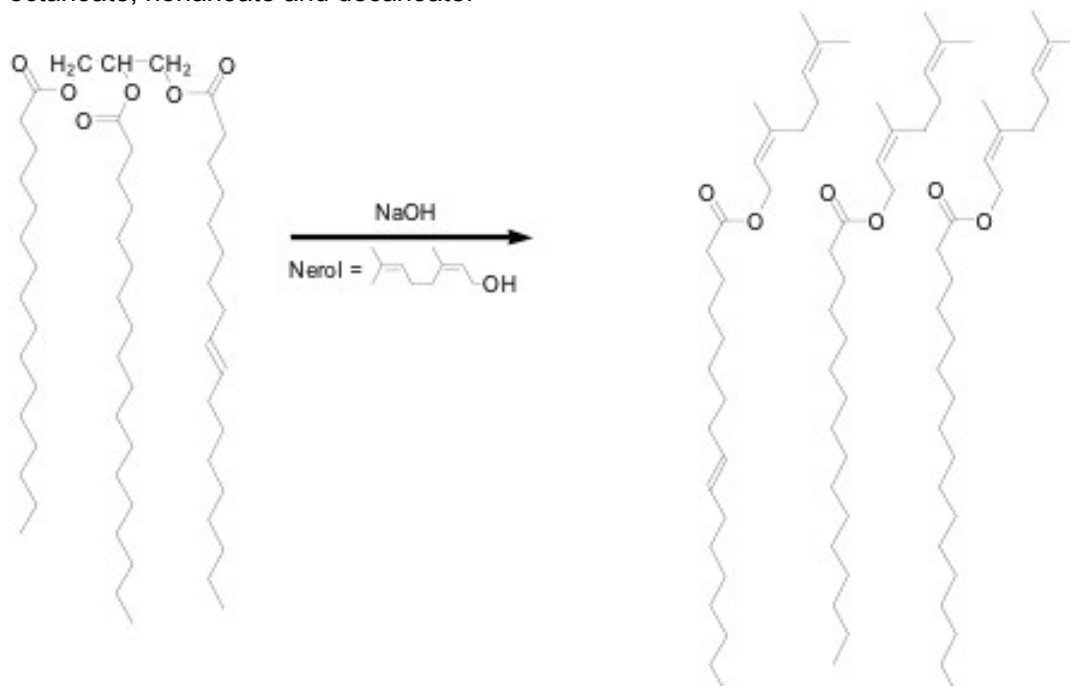


Figure 5. Synthesis of Neryl tallowate

Much like the FAME's of polyunsaturated vegetable oils, the neryl tallowate displays excellent properties with regard to the crystallisation onset observed. The use of these as additives however at the 20% level afforded poor results in terms of the onset of crystallisation.

In addition to branched esters, carbocycle functionalised esters was synthesised, utilising 2-cyclopropylmethanol as the alcohol as shown below in Figure 6. The impetus behind this was to add a sterically demanding ester functionality to the fatty acid chain, which in turn may disrupt the crystal packing of the saturates at low temperatures.

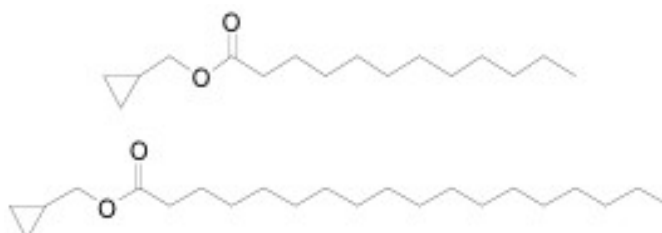


Figure 6. Cyclopropylmethanol ester synthesised as additives

Productions of the esters were performed according to established procedures for ester synthesis within the group. Such naphtha esters proved to be an interesting avenue to additives in the last milestone and to close the off this investigation the syntheses of the two additives pictured above was achieved. These compounds, especially the stearate had an unusual effect

on the saturate exotherm by DSC but as it did not affect the crystallisation onset this direction was abandoned for more promising additives.

Other branched alcohols for study in such systems include synthesis of 2-hexadecyl-1-eicosanol, shown below in Figure 7. The synthesis of this particular alcohol was achieved by the Guerbet reaction of 2 equivalents of octadecanol³, which is industrially prepared from the hydrogenation of stearic acid. Such saturated, branched alcohols have applications as non-ionic surfactants. Due to their saturated structure they possess excellent stability against oxidation and it is for this reason that they are used extensively in lubricating oils. Furthermore the utility of products derived from fatty acids in such reactions complements the work on urea fractionation of Biodiesel which is discussed in greater detail in following sections.

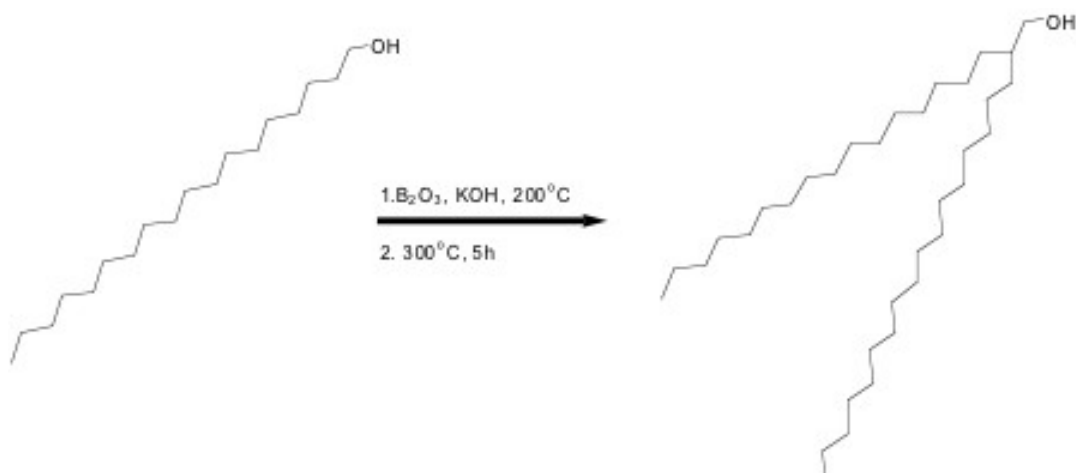


Figure 7. Synthesis of 2-hexadecyl-1-eicosanol using the Guerbet reaction.³

In addition to these syntheses, production of branched diesters of azelaic acid were undertaken. This survey of the usefulness of azelaic acid in diester synthesis was an important addition to this section of the Milestone as well as complementing the ozonolysis portion of the milestones as azelate derivatives are the major product of the ozonolysis reaction of oleates, as shown in the previous milestone. The alcohols used being isopropanol and the Guerbet alcohol mentioned above. The synthesis of diisopropyl azelate is outlined below in Figure 8.

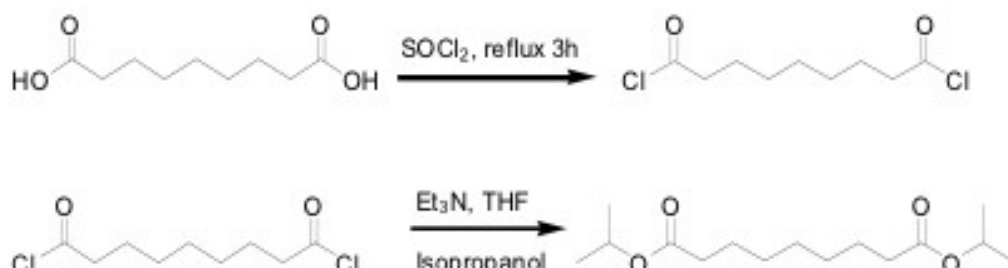


Figure 8. Synthesis of Diisopropyl azelate

The effect such diesters had on the crystallisation onset of the biodiesel were negligible at best. Further investigation into the use of diester additives suggested that the alkyl chain component of the diester needs to be around 20 carbons long for the production of favourable interactions to affect bulk properties appreciably.⁴

Substituted methyl oleate: in order to enhance the solvent properties of methyl oleate, it was proposed to exploit the point of unsaturation within this molecule in the hope that this would increase such properties. The literature presents very few options with regard to manipulating an alkene with similar substitution as methyl oleate. One of these reactions invoked a reverse-electron demand Diels-Alder reaction using tetrachlorocyclopentadiene, but the resulting tetrachloro compound would produce the unfavourable HCl gas upon combustion. Thus the reaction of diethyl malonate to produce a cyclopropyl group using the double bond of methyl oleates was decided. The reaction was facilitated by iodine and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) as shown below in Figure 9.

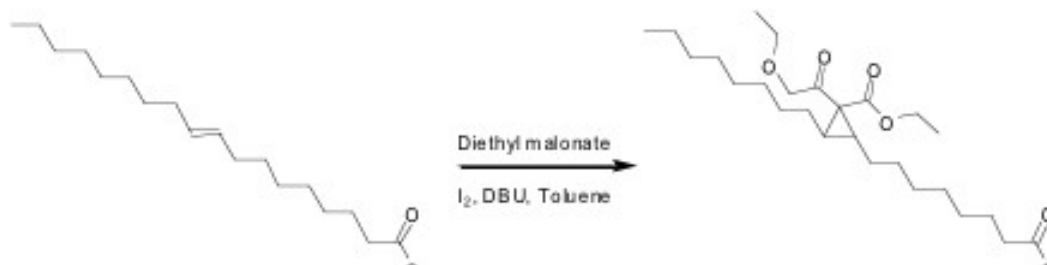


Figure 9. The cyclopropanation reaction of diethyl malonate and methyl oleate.

GC-MS analysis of the reaction mixture after washings revealed that the methyl oleates had not reacted at all with the malonate anion produced from proton abstraction by DBU. For this lack of reactivity and the lack of applicable avenues for such transformations, this section of work was prioritised under other sections of work which afforded more promising results, as seen in following sections.

Aromatic and Aliphatic Ethers: In Milestone 3, the synthesis of menthol laurate (shown below in Figure 10) had a small effect on the cloud point of the biodiesel whereas the parent menthol had an appreciable effect. Thus it was surmised that the extra polarity of the ester functional group may have played a part in the compounds inability to affect the packing of saturates within the biodiesel matrix.



Figure 10. Menthol Laurate (previously synthesised) and menthyl dodecyl ether

Thus the synthesis of menthyl dodecyl ether was carried out as shown above as a means to investigate the effect of reducing the polarity of the linker-group. Albeit the changes in the onset were small, the ether analogue dropped the onset of crystallisation by 1°C as opposed to the ester which could only provide a 0.5°C improvement. This is an important observation, as although this particular system does not provide a large decrease in onset a means of doubling the ability of the molecule to affect the onset has been found. This plays an important role in the optimisation of the wax esters discussed previously and the sucrose esters which are discussed in the following section.

In addition to this, other sterically demanding ethers were synthesised as precursors for ozonolysis. Figure 11 below outlines the synthesis of a terminal alkene further functionalised as the 3-methyl butyl ether.

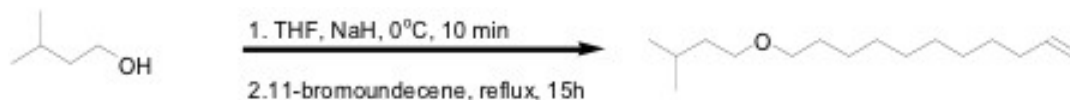


Figure 11. Synthesis of 3-methyl butyl-11-undecenyl ether

Although this compound was to be subjected to ozonolysis, characterisation of its behaviour in biodiesel was recorded by DSC. Although this particular compound afforded no decrease in onset, the enthalpy of the saturate exotherm was lowered, which is an outcome rarely seen with low molecular weight additives and has implications on the molecules ability to disrupt the crystallinity of saturated methyl esters within the biodiesel matrix.

Peralkylated calixarenes are primarily inclusion compounds and another class of aromatic ethers which were explored. Previously, the calix[8]arene macrocycle, a cyclic polyphenol, was procured and could not be tested due to its insolubility in biodiesel. Shown below in Figure 12 is the peralkylation of calix[8]arene to the soluble perdoodecyl calix[8]arene. Unfortunately the poor result from the inclusion of this compound at additive levels was attributed to the size of the calixarene cavity and the reversible nature of guest inclusion inside such cavities.

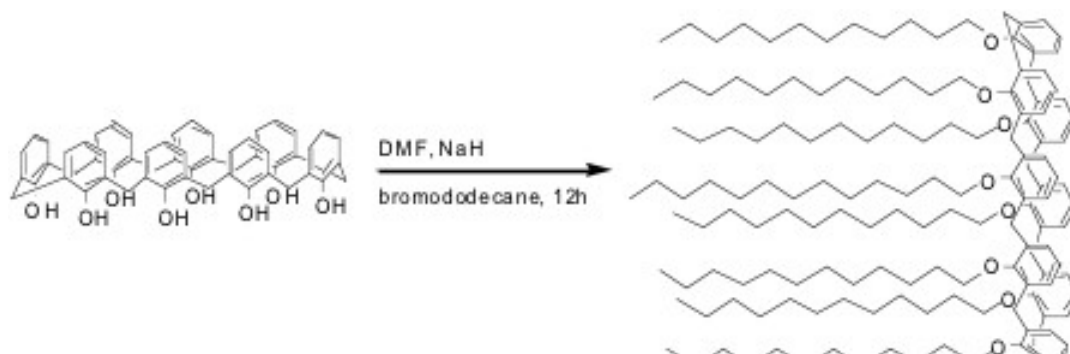


Figure 12. Synthesis of peralkylated calix[8]arene.⁵

Surfactants: A new area being explored in this milestone is the efficacy of certain types of non-ionic surfactant. The use of sucrose esters was highlighted in Milestone 3 and as a result of this further investigation into the use of sucrose esters as surfactants in biodiesel was carried out. Alternative surfactants that were also investigated are Gemini type surfactants⁶ including fatty acid derivatives of hydroquinone and rosolic acid, pictured below in Figure 13.

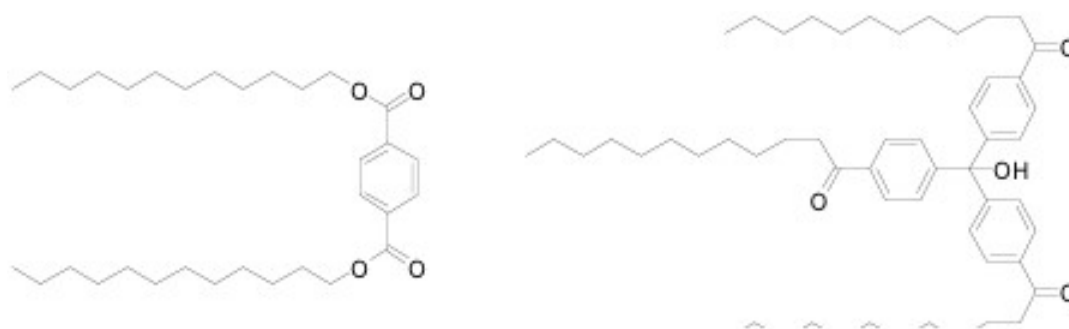


Figure 13. Gemini surfactants utilising hydroquinone and rosolic acid.

A bulk of additives work was carried out in the area of surfactants, primarily because of the prevalence of such compounds used in conjunction with polymeric additives to favourably alter biodiesel properties. Also, until now no work has been done concerning the use of fatty acid sucrose esters as surfactants for this particular purpose.

The primary uses of sucrose esters industrially include fat substitutes⁷, non-ionic detergents⁸ and pesticides⁹. In the preceding milestone, the sucrose polyester synthesised was an octalaurate. Through the use of molecular modelling, it was shown that the presence no free hydroxyl groups decreased the surfactant properties of the sucrose octaester it tends to cause aggregation in a much similar fashion to that of methyl stearate within biodiesel. Thus it was proposed to use specific equivalents of the acid chloride reactant in the synthesis of the sucrose ester, as shown below in Figure 14.

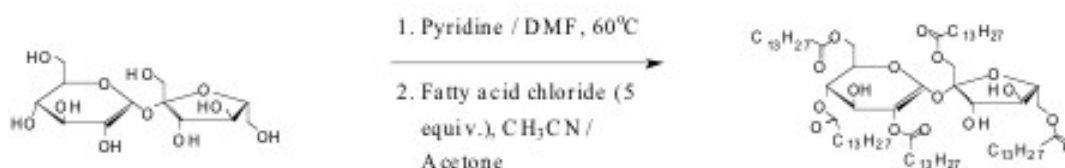


Figure 14. Synthesis of sucrose ester surfactants (Sucrose Myristate – 5 equivalents).

Through the control of the stoichiometry of the reactants, the final distribution of products could be controlled. In addition to this, an optimisation study was undertaken to initially render the surfactant soluble in biodiesel, then to alter the chain length (as introduced by the acid chloride) to maximise alteration of the saturate crystallisation exotherm via DSC.

The corresponding sucrose oleates was synthesised using the same method with oleoyl chloride in the place of myristoyl chloride. As discussed in the next section, the combination of these two compounds essentially mirrors the efficacy of the SPAN 65/85 combination developed for use in DSC analyses and CFPP measurements. The added bonus is that the sucrose ester combination is more efficient and easier to incorporate into the biodiesel than the commercially available SPAN surfactant combination.

3.6 Cloud Point and Cold Filter Plugging Point Characterisation

Table 2 below summarises the cloud point (saturated onset temperature of crystallisation), cold filter plugging point (CFPP), $\Delta T_{\text{saturates}}$ and normalised ΔH values obtained for all low molecular weight synthetic additives tested (except the sucrose esters, for which the CP and CFPP results are reported in section 1 above).

Table 2

Additive / Biodiesel Mixture	Additive Concentration (% w/w)	Cloud Point (°C)	CFPP (°C)	$\Delta T_{\text{saturates}}$ (°C)	$\Delta H_{\text{normalised}}$
oleyl laurate / BDT9.4	3.5	9.86	-	0.21	0.95
oleyl myristate / BDT01DV	3.5	9.58	-	0.23	0.95
oleyl palmitate / BDT01DV#	3.5	9.63	-	0.58	0.95
oleyl stearate / BDT9.4	3.5	10.10	+ 8.0	0.04	1.02
oleyl behenate / BDT01DV	3.5	10.20	-	-0.01	0.93
menthyl dodecane ether / BDT9.4	3.5	9.06	-	1.01	0.94
menthyl laurate / BDT9.4 [^]	5.0	9.04	-	0.47	-
SM29 Twig / BDT01DV#	3.5	9.64	-	0.57	0.87
2-hexadecyl-1-eicosanol azelate #	3.5	11.3	-	-1.09	0.88
methyl tridecanoate / BDT01DV	3.5	9.27	-	0.54	0.90
neryl tallowate	neat	-6.19	+ 3.0*	16.26	0.62
3-methyl-1-butyl stearate	neat	20.8	-	-	-
2-ethyl-1hexyl stearate	neat	9.58	-	-	-
methyl stearate	neat	31.0	-	-	-

Reference Biodiesel Cloud Points: BDT9.4 = 10.07°C ([^] = 9.51); BDT01DV = 9.81°C (# = 10.21°C).

Reference Biodiesel CFPP: + 8°C.

* = sample tested at 25 % w/w in VCBD.

Wax Esters

In Milestones 3 & 5, oleyl stearate was found to lower the crystallisation onset temperature of ~ 75 % of the saturated components of biodiesel to ~ 2.4°C. However, this result was achieved by the addition of 20 % w/w oleyl stearate, a concentration which is above the level permitted by the European Standards. Thus, the effectiveness of oleyl stearate and several other wax esters was assessed at 3.5 % w/w concentration. Figure 15 shows an overlay of the DSC results obtained for 20 % w/w and 3.5 % w/w oleyl stearate in BDT9.4.

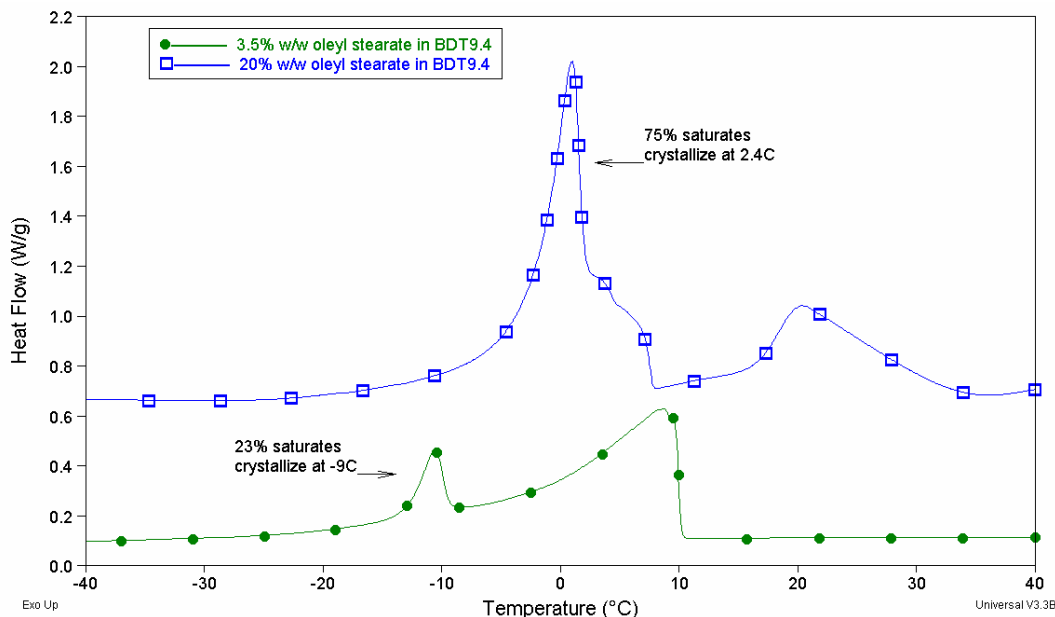


Figure 15: Overlay of DSC results obtained for 3.5% w/w and 20% w/w oleyl stearate in BDT9.4 samples.

At 3.5% w/w only 23% of saturated components crystallize at a lower onset temperature. Although this temperature is much lower than that obtained by using a higher additive concentration (-9°C as opposed to 2.4°C), the cloud point of the remaining 77 % of saturates is shifted to a higher temperature. In addition, the level of crystallinity associated with the 3.5% w/w additive mixture was higher than that of the neat biodiesel so that any benefits associated with the 23 % saturated component reduction were likely to be obscured. This was confirmed by CFPP; the addition of 3.5% w/w oleyl stearate did not lower the CFPP of the biodiesel.

A range of other wax esters were then assessed at 3.5 % w/w in biodiesel to determine whether shortening or lengthening the alkyl chain of the saturated part of the wax ester molecule would prevent an increase in onset temperature whilst still reducing the crystallisation onset temperature of part of the saturated biodiesel component. The results obtained showed that the proportion of saturated components shifted to lower crystallisation onset temperature was reduced by altering the saturated alkyl chain length of the wax ester such that oleyl laurate (C12), oleyl myristate (C14), oleyl palmitate (C16) and oleyl behenate (C20) lowered only 9 %, 7 %, 8 % and 25 % of saturates to lower crystallisation onset temperature respectively. In addition, there were no significant benefits to either the enthalpy of crystallisation or the cloud point of the remaining saturated components. Thus, for wax esters to be used effectively as cloud point / CFPP modification additives in biodiesel they would need to be used at a higher concentration than that permitted under the European Biodiesel Standards.

Ethers vs. Esters

Part of the driving force behind the crystallisation of biodiesel stems from associations between the ester headgroups. Thus, an ether synthesised from menthol and bromododecane was used to study the effect of removing the ester functionality from a bulky headgroup / long alkyl chain additive on biodiesel crystallisation. A comparison between the DSC results from menthyl dodecane and menthyl laurate (table 2) shown that replacing the ester group with an ether more than doubles the effectiveness of the additive in lowering the onset temperature of crystallisation. Although the drop in cloud point achieved through the use of the ether additive was only 1°C, this is far more significant than results achieved through the use of ester-based additives at 3.5 %

w/w concentration. Consequently, future investigations into the development of tallow-based biodiesel additives should focus on the use of ether, as opposed to ester, linkages in the additive structure.

Branched 'Tail' Additives

Two potential additives with 'twig-like' modifications on their alkyl chains (SM29 Twig and 2-hexadecyl-1-eicosanol azelate) were assessed at 3.5 % w/w in biodiesel as potential cloud point additives. The major difference between the two additives is in the position of the 'twig'; in SM29 Twig, the 'twig' is close to the end of the alkyl chain, whereas in 2-hexadecyl-1-eicosanol azelate it is located near to the ester headgroup. The SM29 Twig additive lowered both the enthalpy and the onset temperature of crystallisation slightly ($\Delta H_{\text{normalised}} = 0.87$, $T_{\text{saturates}} = 0.57$). Despite this, the synthetic difficulties associated with creating this additive render it commercial unviable. The 2-hexadecyl-1-eicosanol azelate increased the cloud point of biodiesel, however it was as successful as the SM29 Twig at lowering the enthalpy of crystallisation. Once again, the commercial use of this additive is unlikely.

Odd Carbon Chain Ester:

Within the diesel industry, hydrocarbons containing an odd number of carbon atoms in their alkyl chains have been shown to have a lower crystallisation temperature [reference]. Within Milestones 3&5 the effectiveness of C9 methyl and isopropyl esters in lowering the cloud point of tallow-based biodiesel was assessed, however the short carbon chain length of these additives meant that they were partitioned into the unsaturated phase. Therefore, methyl tridecanoate (a C13 methyl ester) has been assessed as a cloud point additive at 3.5 % w/w in biodiesel. The DSC results presented in Table 2 show that a small reduction in T_{onset} and ΔH was obtained through the use of methyl tridecanoate ($\Delta T_{\text{saturates}} = 0.54$, $\Delta H_{\text{normalised}} = 0.90$). The magnitude of this effect is not significant enough to warrant further investigation at the specified additive concentration level.

3.7 Branched Ester Additives (Bulky Head Group):

The results obtained under Milestones 3&5 have shown that the use of alkyl esters containing bulky headgroups (such as isopropyl, naphthyl) as additives at low concentrations in biodiesel is ineffective at lowering cloud point. Despite this, if alternative alcohols were ever to become a viable option for transesterification with tallow to produce biodiesel then there are three options in particular that could be used to great effect: nerol (a natural product derived from geraniums), 2-ethyl-1-hexanol and 3-methyl-1-butanol.

The cloud point obtained through testing neat neryl tallowate was -6.19°C , a value that is approximately 16°C lower than the cloud point for the corresponding methyl tallowate. In addition, the enthalpy of crystallisation is significantly lower ($\Delta H_{\text{normalised}} = 0.62$) as a result of disruptions to the packing of the ester head groups. At only 25 % w/w concentration in biodiesel methyl esters, neryl tallowate produced a 5°C drop in CFPP. The potential use of such a novel alcohol in the transesterification process or to produce an 'additive' for use at higher than 3.5 % w/w concentrations is attractive, however potential problems such as cost and oxidative stability would have to be addressed.

Figure 15 shows a comparison between the DSC curves obtained for neat methyl stearate, 2-ethyl-1-hexyl stearate (2E1HS) and 3-methyl-1-butenyl stearate (3M1BS).

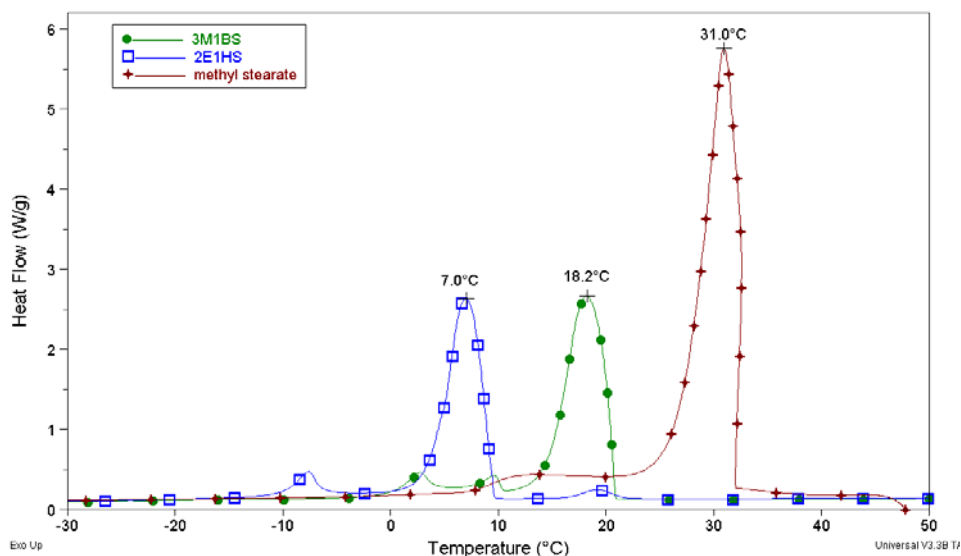


Figure 15 Overlay of the DSC results obtained for neat methyl stearate, 2-ethyl-1-hexyl stearate and 3-methyl-1-butenyl stearate. The temperatures of crystallisation are noted on the curves.

If the cloud point / cold filter plugging points problems encountered through the use of tallow-based biodiesel are considered to stem from the high concentration of saturated long-chain esters in such biodiesel (particularly methyl stearate), then figure... shows the potential for eliminating this problem through the use of alternative alcohols for transesterification. Both 2-ethyl-1-hexyl stearate and 3-methyl-1-butenyl stearate have significantly lower crystallisation temperatures (T_c) than methyl stearate, suggesting that the use of these alcohols (particularly 2-ethyl-1-hexyl stearate) in either a total or partial transesterification of tallow could have a significant beneficial impact upon cloud point and/or cold filter plugging point. This is something that could potentially be developed for the Australian or US biodiesel markets.

3.8 SUMMARY

A range of novel additives were selected for synthesis and studied through a combination of DSC and CFPP measurements to meet the requirements of Milestone 4. These have been discussed from a synthetic point of view and will be expanded on in the following section concerning the analysis of additives. It is clear that the utilisation of sucrose ester mixtures of specific total stoichiometry provide powerful tools to serve as surfactants for the biodiesel problem of an oil-in-oil emulsion. From searching the literature and internet as well as other resources, there are limited agents available that have this property, thus their use in this particular system is more than noteworthy. It is essential to optimise the synthesis of the sucrose ester and develop a structure-function relationship with the stoichiometry of acid chloride used, type of linkage used (ester vs. ether), the use of other sugar derivatives (e.g. Cyclodextrins) and the relative amounts of the co-surfactants, biodiesel and polymer additives in the final product. With regard to other additives there is a lot to revisit with regard to redesigning promising candidates which were overlooked (i.e. Wax esters, diesters), given the extensive knowledge obtained throughout the course of the program. Such co-additives, especially wax esters, have shown much promise in diversifying the morphology of the saturates exotherm via DSC. The development of new co-additives as well as the optimisation of current co-additives discovered during the program serves as an avenue to further increase the efficiency of such low molecular weight additives for tallow-based biodiesel.

3.9 References

- (1) Torres, M., Lloret, C., Sosa, M., Maestri, D. *European Journal of Lipid Science and Technology* 2006, 108 513-520.
- (2) Liebert, M. A. *J. Am. Coll. Tox.* 1992, 11.
- (3) Sulzbacher, M. *J. Appl. Chem.* 1955, 5, 637-41.
- (4) Shahgaldian, P., Coleman, A.W., Kuduva, S.S., Zaworotko, M.J. *Chem. Commun.* 2005, 1968 - 1970.
- (5) Tracy, D. J., Li, R., Dahanayake, M.S., Yang, J. ; Inc., R., Ed. 1997.
- (6) Akoh, C. C. *Crit. Rev. Food. Sci. Nutr.* 1995, 35, 405-30.
- (7) Hill, K., Rhode, O. *Lipid - Fett* 1999, 101, 25-33.
- (8) Chortyk, O. T. *J. Agric. Food Chem.* 1996, 44, 1551-57.

4 Section 3: Urea fractionated tallow based biodiesel

4.1 Introduction

Urea fractionation is the process of separating the components of organic mixtures such as fatty acids, esters, alcohols and other derivatives by the formation of isolable saturate-rich crystalline urea complexes. The process is not new and began when Bengen, in a patent application filed in 1940, reported that fatty acid compounds containing six or more carbon atoms formed well defined crystalline complexes or inclusion compounds with urea in water, ethanol and methanol, whereas cyclic and branched chain compounds did not.¹ Urea inclusion complexes are so named because they are a combination of two compounds; hydrogen-bonded urea molecules in the shape of helical spirals that form narrow channels, and long chain hydrocarbons that sit within these channels (Figure 1). The urea channel is between 5.0 and 6.0 Å in diameter and the inclusion of straight chain saturated hydrocarbons is favoured because these have cross sectional widths of around 4.1 Å. The formation of urea inclusion complexes containing hydrocarbons with bulky side groups or double bonds is unfavourable, mainly because of their greater cross sectional width.² The ease of formation of urea complexes also increases with increasing carbon chain length, so the process lends itself well to the fractionation of longer (>C₁₆) carbon chain molecules.³

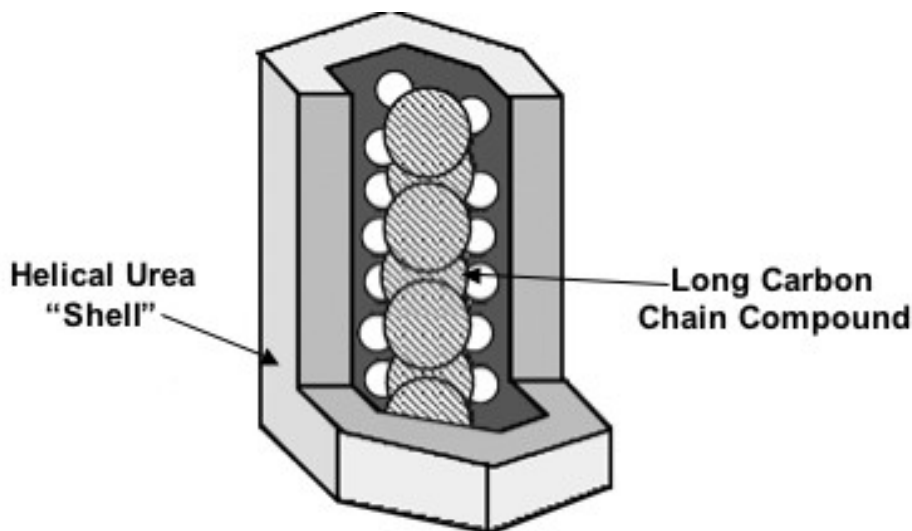


Figure 1 Diagram showing how hexagonal crystals of urea form around the long hydrocarbon chain of compounds

The preparation of urea complexes is relatively simple but is dependant upon the solubility of the material being fractionated. Briefly, the process involves the dissolution of the compound of interest, with heating, in a solvent to which urea has been added. The mixture is then cooled to room temperature over several hours to allow the formation of long, needle-like crystals. The crystals are filtered off and both the crystals and the filtrate are treated with hot acidified water to separate the organic components. During the process, the solvent and the urea are recycled and can be re-used in further fractionations. Urea fractionation has, in the past, been used to isolate oleic, linoleic and linolenic acids from safflower oil,^{4, 5} to separate unoxidised fatty acids from oxidised fatty acids⁶ and to fractionate fatty acids from fish⁷, blackcurrant⁸, borage⁹, linseed⁵ and rapeseed oils¹⁰. Urea fractionation for the separation and use of saturated methyl esters and unsaturated methyl esters from soy-based biodiesel (or soy methyl esters SME) is currently the subject of a US patent that describes how the cloud point (CP) of SME with a

saturated methyl ester content of ~13% was reduced from 0°C to -26°C after treatment with urea.¹¹ The SME results indicated that the removal of saturated methyl esters from tallow-based biodiesel using urea fractionation would be worth investigating. To this end, small-scale urea fractionation experiments using tallow-based biodiesel were performed. The experiments showed that the CP of tallow-based biodiesel could be reduced to around 4°C without the addition of additives and to around -3°C with additives (see ‘cloud point (CP) and cold filter plugging point (CFPP) characterization’, section 3).

4.2 Experimental

Refer to section 1 for characterization procedures.

Theoretical Urea Fractionation Experiment:

In order to predict the likely outcomes of removing long-chain saturated methyl esters from biodiesel via urea treatment, a series of methyl oleate / methyl palmitate / methyl stearate mixtures were created and analysed by DSC using the Biodiesel 80°C Test Procedure detailed in section 1. The mixtures were prepared so that the ratio between methyl palmitate and methyl stearate was held at approximately 1:1, mimicking the natural composition of beef tallow-derived biodiesel (which contains roughly 23 % methyl palmitate and 22 % methyl stearate).

Table 1: Summarises the compositions of the mixtures that were prepared.

Mixture	Mass _{MO} (mg)	Mass _{MP} (mg)	Mass _{MS} (mg)	Weight Fraction MO
100% MO	100	0	0	1.00
80% MO 20% MP+MS	81.1	11.4	10.1	0.79
65% MO 35% MP+MS	83	21.8	22.6	0.65
60% MO 40% MP+MS	59.9	20	20	0.60
50% MO 50% MP+MS	50.3	26.4	25.1	0.49
40% MO 60% MP+MS	40.9	31	30.6	0.40
20% MO 80% MP+MS	20.3	40.8	40.4	0.20
100% MP+MS	0	25.7	24.9	0.00

MP = methyl palmitate

MS = methyl stearate

MO = methyl oleate

4.3 Materials

All materials were used as delivered. Tallow based biodiesel was supplied by either Victorian Chemical Co. Pty. Ltd., 83 Maffra St., Coolaroo, Vic., Australia 3048 or prepared at Flinders University by the transesterification of CT9 beef tallow, with the latter given the code BDT06DV. Chloroform, urea, methanol and ethanol were supplied by Sigma-Aldrich Australia, methyl undecanoate, methyl oleate, methyl palmitate and methyl stearate were supplied by NuChek Prep.

4.4 Urea Fractionation of Biodiesel

Urea fractionation experiments were performed using either Victoria chemicals tallow-based biodiesel or with BDT06DV. The following describes a typical urea fractionation experiment using ethanol as the solvent. To tallow-based biodiesel (25g) was added urea (7.5g) and ethanol (150 ml) in a sealed Schott bottle containing a stirrer bar. The container was placed into a beaker containing water that was initially at room temperature. The water bath containing the biodiesel-urea mixture was placed onto a hot-plate fitted with a magnetic stirrer and the water was slowly heated with continuous stirring of the biodiesel-urea mixture until a homogeneous mixture formed (Figure 2). The water bath was removed from the heat and allowed to cool to room temperature overnight to allow the formation of long, needle-like crystals (Figure 3). The crystals were removed from the filtrate in vacuo and both the crystals and filtrate were retained. 3/4 of the solvent was removed from the filtrate in vacuo. To the filtrate and the precipitate was added, separately, hot acidified water (70°C/pH 3) to release the urea from the methyl esters. The resultant organic methyl ester products were washed repeatedly with hot acidified water (3 x 200 ml), (70°C/pH 3) and then hot water (3 x 200 ml). Excess water was removed from the organic products in vacuo (72mbar/60°C) to yield two fractions of urea-treated biodiesel, one derived from the filtrate (herein described as the urea filtrate fraction) and one from the precipitate (herein termed the urea precipitate fraction).



Figure 2 Photograph of the set-up of a typical urea fractionation experiment showing the homogenised biodiesel/urea/solvent mixture

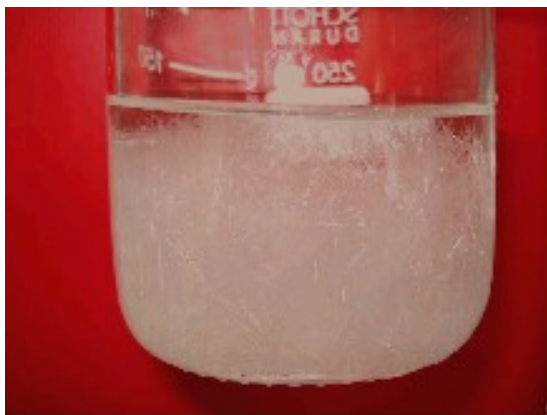


Figure 3 Photograph of long, needle-like urea inclusion complex crystals

4.5 Characterisation

DSC and Cold Filter Plugging Point (CFPP) Analysis of Urea-Treated Biodiesel

Refer to section 1 for DSC and CFPP characterization methods and procedures

4.5.1 Determination of the Effect of Cooling Rate on Urea Fractionation Efficiency using DSC

Tallow-based biodiesel (25 g), ethanol (150 ml) and urea (5 g) were stirred with heating to 70°C. 2 x 3 mg samples of the mixture were loaded into the DSC as described in section 1. DSC operating conditions were identical to those described in section 1 with the following exceptions; sample 1 was equilibrated at 72°C and the temperature was ramped down to -10°C at 0.5°C/min and sample 2 was equilibrated at 72°C and the temperature was ramped down to 0°C at 2.0°C/min.

4.5.2 Gas Chromatography –Mass Spectrometry (GC-MS)

Refer to section 2 for GC-MS conditions

GC-MS analyses focussed only on the three major methyl ester components of tallow-based biodiesel, namely methyl oleate, methyl stearate and methyl palmitate as these make up around 85% of the mixture. For this reason percentage compositions of mixtures quoted in this report total around 85% and not 100%.

Preparation of Stock Solution and 1 Point Standards; A stock solution containing methyl undecanoate as an internal standard was prepared as follows; 200mg of methyl undecanoate was added to a 200 ml volumetric flask and topped up with CHCl₃ to produce a 0.1% methyl undecanoate solution. 1 point standards for GC-MS analysis of methyl-ester standards were prepared as follows; 10 mg each of methyl oleate, methyl palmitate and methyl stearate were separately added to 3 x 10 ml volumetric flasks and each was topped up with the stock solution to produce 3 solutions containing 0.1% methyl oleate and methyl undecanoate, methyl palmitate and methyl undecanoate and methyl stearate and methyl undecanoate respectively. 1 ml of each 1 point standard was placed into a 1 ml analysis vial and injected into the GC-MS .

Determination of 'K' from 1 Point Standards; 'K' is a common constant that describes the relationship between the concentrations and peak areas of both the internal standard and the analytes.¹² The molar concentration of methyl undecanoate and methyl oleate, palmitate and stearate were calculated and a K value for each was determined using the following equation;

$$K = (Cis/Ca) \times (Aa/Ais)$$

where;

Cis = the concentration of the internal standard (methyl undecanoate),

Ca = the concentration of the analyte (methyl oleate, palmitate or stearate),

Aa = the area under the GC peak of the analyte and

Ais = the area under the GC peak of the internal standard.

Average K was then determined as follows;

$$\text{Average K} = \{K(\text{methyl oleate}) + K(\text{methyl palmitate} + K(\text{methyl stearate}))\}/3.$$

Preparation of Urea Fractionated and Control Biodiesel Samples ; Samples of the urea fractionated and control biodiesel were prepared as follows; 10 mg of biodiesel was added to a 10 ml volumetric flask that was topped up with the 0.1% methyl undecanoate stock solution to

produce a 0.1% solution of the biodiesel with 0.1% methyl undecanoate as the internal standard. 1 ml of each solution was placed into a 1 ml analysis vial and injected into the GC-MS .

Determination of the Concentration of Methyl Esters In Urea Fractionated and Control Biodiesel Samples; The molar concentration of methyl oleate, palmitate and stearate in the urea fractionated and control biodiesel samples were determined using the following equation;

$$\mathbf{Ca(unknown) = (Cis/Average K) \times (Aa/Ais)}$$

where;

Ca(unknown) = the concentration of either methyl oleate, palmitate or stearate in moles/L,

Cis = The concentration of the internal standard (methyl undecanoate),

Average K = the average constant previously determined,

Aa = the area under the GC peak of the analyte and

Ais = the area under the GC peak of the internal standard.

Determination of the % of each Methyl Ester in Urea Fractionated and Control Biodiesel Samples; The number of moles of methyl oleate, palmitate and stearate in the urea fractionated and control biodiesel samples were first calculated from the previously determined concentrations using the following equation;

$$\mathbf{moles(methyl\ ester) = C \times V}$$

where;

moles(methyl ester) = the number of moles of each methyl ester in each 0.1% sample.

C = the concentration of methyl oleate, palmitate or stearate in moles/L as previously determined

V = the volume of the 10 ml volumetric flask in litres (0.01 Litres).

The number of grams of methyl oleate, palmitate and stearate in the urea fractionated and control biodiesel samples were then calculated using the following equation;

$$\mathbf{grams(methyl\ ester) = n/MW}$$

where;

grams(methyl ester) = the number of grams of methyl ester in the 0.1% sample

n = the number of moles of either methyl oleate, palmitate or stearate previously determined

MW = the molar mass of either methyl oleate, palmitate or stearate.

The % of methyl oleate, palmitate and stearate in the urea fractionated and control biodiesel samples were then calculated using the following equation;

$$\mathbf{\%(methyl\ ester\ in\ sample) = \{grams(methyl\ ester\ in\ 0.1\% \ sample)/total\ mass\ (in\ grams)\ of\ biodiesel\ in\ original\ 10\ ml\ volumetric\ flask\} \times 100}$$

4.6 Discussion

Theoretical Urea Fractionation Experiment:

Eight different blends of methyl oleate / methyl palmitate / methyl stearate were analysed by DSC to determine the effect of varying the ratio between methyl oleate and methyl palmitate / methyl stearate on cloud point and crystallisation enthalpy. In all eight mixtures, the methyl palmitate to methyl stearate ratio was the same as that present in beef tallow methyl esters so that only the relative proportions of saturates and unsaturates were varied, mimicking the urea fractionation process. The results obtained are shown in figures 4 and 5 below.

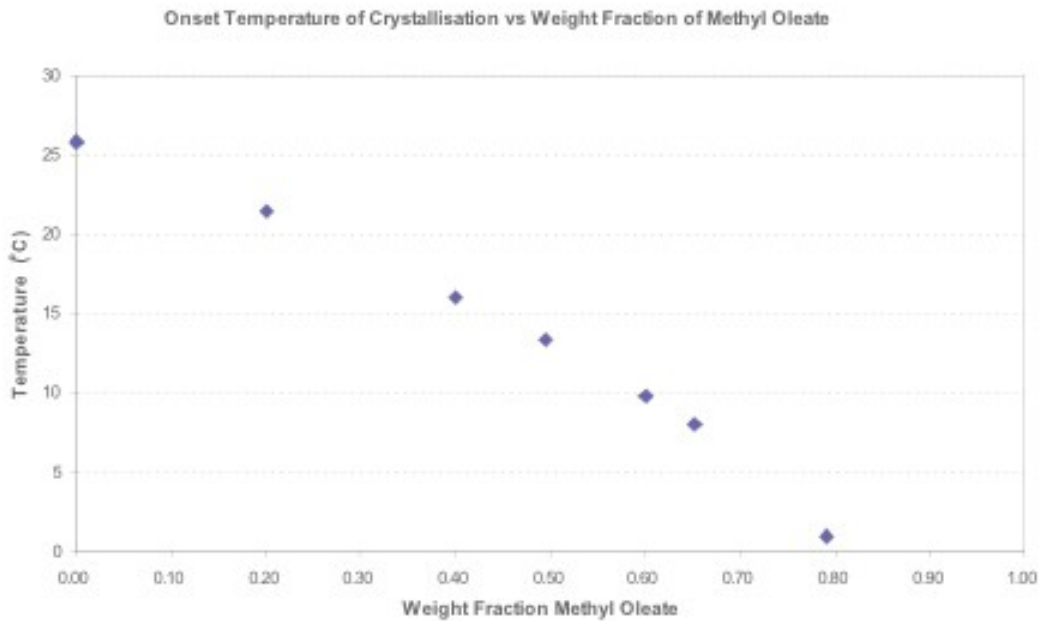


Figure 4:

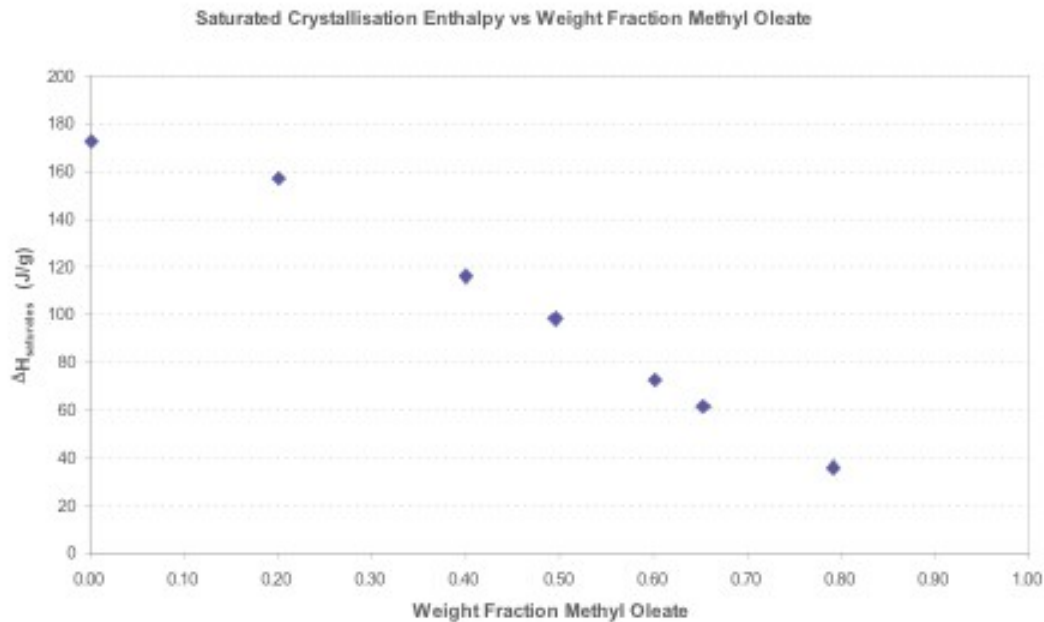


Figure 5:

Figure 4 shows a plot of the onset temperature of crystallisation (cloud point) as a function of the weight fraction of methyl oleate in a methyl oleate / methyl palmitate / methyl stearate mixture. As the amount of methyl oleate is increased, the cloud point decreases in an exponential fashion. Thus, removing the saturated methyl ester components from tallow-based biodiesel should lower cloud point. In addition, removing a greater amount of saturates should result in a proportionately greater effect in lowering cloud point. Given that the cloud point of tallow-based biodiesel

Modification of tallow for better performance as biodiesel

produced from CT9 (beef tallow) is 9-10°C, Figure 5 predicts that removing 5 % methyl palmitate / methyl stearate by urea fractionation should lower the cloud point by ~ 2°C.

Similar observations can be made with respect to the enthalpy of crystallisation. Figure ... shows that increasing the weight fraction of methyl oleate in a methyl oleate / methyl palmitate / methyl stearate mixture decreases the enthalpy of crystallisation in a sigmoidal fashion. Thus, not only will removing the saturated components from tallow-based biodiesel lower cloud point; it will also reduce the level of crystallinity associated with the saturated crystallisation exotherm by ~ 20 J/g. This could potentially increase the effectiveness of cloud point and/or cold filter plugging point modification additives.

On the basis of the theoretical experiments performed, using urea to selectively remove long-chain saturated methyl esters from tallow-based biodiesel is likely to reduce cloud point and aid in further cloud point / cold filter plugging point reduction via the incorporation of additives.

Practical Urea Fractionation Experiments

Urea Fractionation of Biodiesel at 2°C/min-Experiments #1a and #1b

NOTE: BDT06DV was fractionated and urea fractions were designated BDT10DV and BDT11DV (urea precipitates) and BDT09DV and BDT12DV (urea filtrates). Biodiesel/urea/ethanol ratio was 25g/10g/150ml

#1a: An experiment was performed using a heated mixture containing 25g of BDT06DV biodiesel, 10g of urea and 150ml of ethanol in a 500 ml beaker that was cooled on the laboratory benchtop. Although the urea appeared to dissolve during the heating process, a fine, white precipitate started to immediately form on the inside surface of the beaker during heating and it was apparent that this was occurring because the surface of the beaker was cooler than the interior. Urea crystals formed more rapidly after the beaker was removed from the heat and the yield of the urea precipitate fraction BDT10DV was low at 1g, (4%), with the urea filtrate fraction BDT09DV yielding 21g, (84%) for a total yield of 88%.

#1b: The experiment was repeated using 5g of urea and the cooling rate was measured and found to be around 2°C/min. The smaller amount of urea did not solve the problem of crystal formation at the beaker surface and the yield was identical to experiment #1a. GC-MS analysis of the control, the urea filtrate fraction BDT11DV and the urea precipitate fraction BDT12DV from #1b showed that the unsaturated content of the filtrate was depleted, as was the saturate content, whilst the precipitate contained predominantly saturates, but also a relatively large amount of unsaturates (Table 2).

METHYL ESTER	Control BDT06DV (%)	Filtrate BDT11DV (%)	Precipitate BDT12DV (%)
Methyl Stearate	23	19	40
Methyl Palmitate	22	17	24
Methyl Oleate	28	21	17

Table 2 composition of urea fractions obtained using a cooling rate of 2°C/min

Determination of the Effect of Cooling Rate on Urea Fractionation Efficiency using DSC

Given the results of the initial urea fractionations it was considered prudent to investigate how the cooling rate would effect the urea fractionation procedure. Two experiments were performed using a pre-heated mixture of biodiesel/urea and ethanol. The first used the same cooling rate

as the initial urea fractionation of biodiesel, 2.0°C/min, and the second used a slower rate, 0.5°C/min.

Sample 1 (cooling rate of 2.0°C/min)

A cooling rate of 2.0°C/min produced a range of crystalline urea complexes containing methyl esters of lower molecular mass that formed at lower temperatures (Figure 6). The saturated methyl esters, methyl palmitate and methyl stearate produce exotherms corresponding to the onset of crystallisation at 23°C and 32°C respectively. Saturate-rich urea complexes would be expected to show exotherms in DSC thermographs somewhere between these two temperatures. An exotherm at 20.3°C showed that urea complexes containing high concentrations of long chain unsaturated as well as saturated methyl esters were present as the CP of the saturates was depressed by the presence of unsaturates. It was concluded that a cooling rate of 2.0°C/min produces a mixture of long chain unsaturated and saturated urea complexes, together with a number of shorter chain urea complexes.

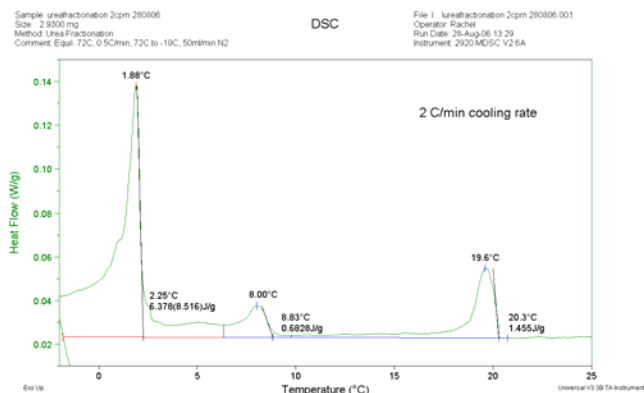


Figure 6 DSC thermograph of biodiesel/urea/ethanol mixture cooled at 2.0°C/min showing how a mixture of products forms from 0°C to 20°C.

Sample 2 (cooling rate of 0.5°C/min)

The cooling rate of 0.5°C/min (Figure 7) recorded a single exotherm at around 24.7°C in the DSC thermograph. The fact that the onset temperature was slightly lowered in comparison to that of pure methyl stearate at 32°C, indicated that a small quantities of unsaturated methyl ester-urea complexes existed. It was concluded that the exotherm corresponded to the formation of predominantly saturated methyl ester urea complexes that contained small amounts of long chain unsaturated methyl esters. This suggested that a slower cooling rates produce urea complexes that contain higher levels of saturated and lower levels of unsaturated methyl esters.

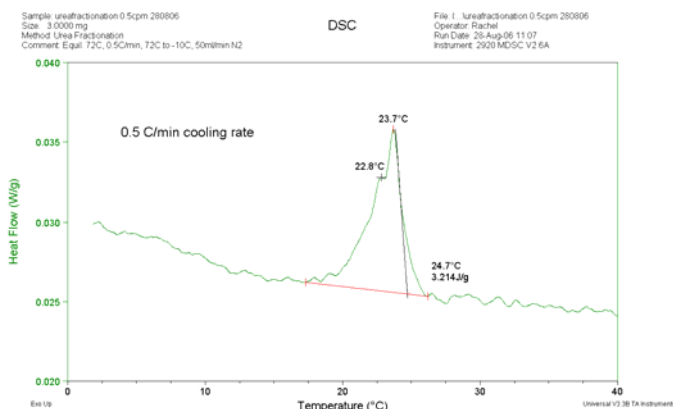


Figure 7 DSC thermograph of biodiesel/urea/ethanol mixture cooled at 0.5°C/min showing an exotherm at 24.7°C corresponding to a mixture of methyl palmitate and stearate with a small amount of methyl oleate

Urea Fractionation of Biodiesel at 0.2°C/min-Experiment #2

NOTE: BDT06DV was fractionated and urea fractions were designated BDT15DV (urea precipitate fraction) and BDT16DV (urea filtrate fraction). Biodiesel/urea/ethanol ratio was 25g/7.5g/150ml

Prompted by the results of the DSC cooling rate experiment, a urea fractionation was performed using 25g of biodiesel, 150ml ethanol and 7.5g of urea and a cooling rate of 0.2°C/min. In the procedure, the biodiesel/urea/ethanol mixture was stirred and heated in a sealed Schott bottle that was immersed in a beaker of water to form a water jacket. This was done to assist the dissolution of the urea and to reduce heat loss and therefore slow the rate of cooling. The urea in the sample was seen to completely dissolve upon heating and no precipitate was observed on the inside surface of the Schott bottle during or immediately after the heating process. GC-MS analysis of the control (BDT06DV), the urea filtrate fraction (BDT16DV) and the urea precipitate fraction (BDT15DV) showed that the unsaturated content of the urea filtrate fraction at 45% was enhanced in comparison to the 21% unsaturated content in the filtrate derived at a rate of 2°C/min (Tables 2 and 3). The 29% saturate content of the urea filtrate fraction BDT16DV, was also slightly reduced in comparison to the 36% content in the BDT12DV filtrate derived at a rate of 2°C/min (Tables 2 and 3). The urea precipitate fraction BDT15DV comprised 72% saturates and just 1% unsaturates in comparison to the 64% saturate and 17% unsaturated content of BDT11DV precipitate derived at a rate of 2°C/min (Tables 2 and 3). Yields of urea precipitate and urea filtrate in this experiment were similar to those of experiment #1, and DSC analysis of the filtrate BDT16DV showed that the CP was reduced by 1°C in comparison to the control (see ‘cloud point (CP) and cold filter plugging point (CFPP) characterization’, section 3)

METHYL ESTER	Control BDT06DV (%)	Filtrate BDT16DV (%)	Precipitate BDT15DV (%)
Methyl Stearate	22	10	46
Methyl Palmitate	23	19	26
Methyl Oleate	28	45	1

Table 3 composition of urea fractions obtained using a cooling rate of 0.2C/min

The result of this, and of the DSC cooling rate experiment, showed that slower cooling rates favour the removal of high concentrations of saturated methyl esters.

Large Scale Urea Fractionations of Biodiesel-Experiment #3

NOTE: Victoria biodiesel was fractionated and urea fractions were designated BDT21DV (urea precipitate fraction) and BDT22DV (urea filtrate fraction). Biodiesel/urea/ethanol ratio was 25g/7.5g/150ml

Total yields from small-scale (~25 g) fractionations were found to be relatively low (< 90%) and a large-scale urea fractionation procedure was performed to investigate whether yields could be improved. Experiment #3 used the same ratio of biodiesel/urea/ethanol as experiment #2, but the amount of each compound was multiplied by 4. In summary, 100 g of tallow-based biodiesel, 30 g urea and 600 ml ethanol were initially heated, with stirring, in a 1 Litre Schott bottle within a 2.5 Litre beaker filled with water and the mixture was cooled on the benchtop at 0.2°C /min. Urea fractions were obtained and the total yield, comprising 7.2 g (7.2%) urea precipitate (BDT21DV) and 86.5 g (86.5%) urea filtrate (BDT22DV), was 93.7%. GC-MS analysis of the control showed that Victoria biodiesel contained 41% methyl oleate, a concentration that was 13% higher than that found in BDT06DV biodiesel derived from CT9 beef tallow (Table 4). As a consequence, the large-scale urea precipitate fraction, BDT21DV, contained ~5% more methyl oleate than was found in the previous urea precipitate fraction BDT15DV (Tables 2 and 3). Experiment #3 showed that large-scale fractionations remove similar concentrations of saturates as smaller scale procedures but that better overall yields can be obtained. DSC analysis of BDT22DV was also performed and it was shown that the CP was reduced by around 2°C in comparison to the control (see 'cloud point (CP) and cold filter plugging point (CFPP) characterization', section 3)

METHYL ESTER	Control Vic BD (%)	Filtrate BDT22DV (%)	Precipitate BDT21DV (%)
Methyl Stearate	20	17	53
Methyl Palmitate	22	19	31
Methyl Oleate	41	52	6

Table 4: Composition of urea fractions obtained using a scaled-up fractionation procedure

Urea Fractionation using Larger Amount of Urea

NOTE: Victoria Biodiesel was fractionated and urea fractions were designated BDT24DV (urea precipitate fraction) and BDT25DV (urea filtrate fraction). Biodiesel/urea/ethanol ratio was 25g/17.5g/68.75ml

A final large scale fractionation was performed using a greater amount of urea to determine what effect a high concentration of urea would have on the final composition of the urea fractions. The initial mixture comprised 1000 g of biodiesel, 700 g of urea, 2500 ml methanol and 250 ml ethanol within a 5 Litre beaker completely wrapped in aluminium foil (bottom, sides and top) to reduce heat loss. The beaker containing the fractionation mixture was heated to 70°C with stirring, and the beaker was placed into a 10 Litre bucket of hot (80°C) water on the benchtop to ensure a slow cooling rate. Urea fractions were obtained and total yield comprising 250 g (25%) urea precipitate (BDT24DV) and 700 g (70%) urea filtrate (BDT25DV) was 95%. The composition of the urea filtrate fraction BDT25DV, was almost identical to the filtrate from experiment #3, but with 2% less saturates overall. Interestingly, the urea precipitate fraction contained 27% less saturated methyl esters and 10% more unsaturated methyl esters than the precipitate in experiment #3. The large scale of the experiment necessitated the use of a beaker and the cooling rate, although hard to control, was roughly 0.5°C/min. It was hard to homogenise

the initial mixture, possibly because methanol is a poorer solvent than ethanol and, as in experiment 1, a fine, white precipitate started to immediately form on the inside surface of the beaker during heating and after heating, there was evidence that some urea had not dissolved. After cooling, it was also evident that biodiesel and methanol had formed separate phases overnight. Solubility problems notwithstanding, DSC and CFPP analysis of the filtrate BDT25DV from the experiment showed that CP and CFPP were reduced by around 6°C in comparison to the control. The CFPP of BDT25DV was also reduced by around 12°C to -3°C with the addition of additives (see ‘cloud point (CP) and cold filter plugging point (CFPP) characterization’, section 3). Given the low solubility of the biodiesel and urea in the methanol solvent, it would be worth investigating the effect of a poorer solvent on the final composition of the urea filtrate using smaller concentrations of urea. Unfortunately, time did not permit the investigation of this aspect of the process in this instance.

METHYL ESTER	Control Vic BD (%)	Filtrate BDT25DV (%)	Precipitate BDT24DV (%)
Methyl Stearate	20	15	31
Methyl Palmitate	22	17	26
Methyl Oleate	41	52	16

Table 5 composition of urea fractions obtained from experiment #4

4.7 Cloud Point and Cold filter Plugging Point Characterisation

4.7.1 Urea Fractionated Biodiesel

Table 6 shows the cloud point and cold filter plugging point (CFPP) results obtained from analysing a range of filtrates (residual methyl esters) and precipitates (predominantly long-chain saturated methyl esters) obtained by urea **fractionation** of tallow-based biodiesel. The corresponding beef tallow methyl ester results, as well as those for commercially available tallow-based biodiesel (and corresponding urea filtrate fractions) and soy-based biodiesel are included for comparative purposes.

Table 6

Sample	Description	T _{onset} (°C)	ΔH (J/g)	CFPP
BDT06DV	beef tallow methyl esters	9.95	83.0	-
BDT09DV	filtrate from urea fractionation of BDT06DV	8.87	81.0	-
BDT10DV	precipitate from urea fractionation of BDT06DV	19.9	136.1	-
BDT16DV	filtrate from urea fractionation of BDT06DV	8.97	84.0	-
BDT17DV	second-round filtrate from urea fractionation of BDT06DV	8.40	79.4	-
VCBD	Victoria Chemicals Biodiesel	8.39	78.2	10
BDT22DV	filtrate from urea fractionation of VCBD	6.73	65.95	8
BDT25DV	filtrate from urea fractionation of	2.73	50.10	4
BDT23DV	soy methyl esters	-3.98	27.7	-

As discussed above, two fractions are produced by the treatment of biodiesel with urea; a ‘precipitate’ fraction containing long-chain saturated methyl esters (predominantly methyl stearate and methyl palmitate) and a ‘filtrate’ fraction containing the residual methyl esters. The

Modification of tallow for better performance as biodiesel

DSC results obtained for samples BDT09DV (filtrate) and BDT10DV (precipitate) highlight the differences between these two fractions in terms of cloud point (T_{onset}) and enthalpy of crystallisation. The BDT09DV sample contains less methyl stearate and methyl palmitate than the initial biodiesel (BDT06DV), resulting in a drop in T_{onset} and the enthalpy of crystallisation (ΔH) of $\sim 1^{\circ}\text{C}$ and 2 J/g respectively. In contrast, the precipitate fraction displays a T_{onset} of $\sim 20^{\circ}\text{C}$ and a ΔH of 136 J/g . These values are significantly higher than those obtained for the original biodiesel and, by comparison with data obtained for methyl oleate / methyl palmitate / methyl stearate mixtures above, affirm that the precipitate fraction comprises of long-chain saturated methyl esters (such as methyl stearate and methyl palmitate).

Treating the filtrate fraction with urea (second-round urea filtrate) does not significantly lower cloud point / enthalpy of crystallisation and therefore does not successfully remove residual saturated methyl esters; the T_{onset} measured for BDT17DV was only 0.4°C lower than that for its parent urea filtrate fraction (BDT16DV). However, the T_{onset} and ΔH results obtained for samples BDT22DV and BDT25DV show that treating biodiesel with a higher concentration of urea and increasing the scale of the reaction results in the removal of more saturated components. The BDT25DV fraction (created from Victoria Chemicals Biodiesel) was particularly successful as T_{onset} was lowered by $\sim 5.7^{\circ}\text{C}$ and the enthalpy of crystallisation was a mere 50.1 J/g , almost 30 J/g lower than the original biodiesel. As a result of this, BDT25DV was used to investigate the potential for combining urea fractionation with an additive package to lower cloud point and / or cold filter plugging point.

Interestingly, the improvements in cloud point and cold filter plugging point that can be achieved by treating tallow-based biodiesel with urea are insignificant when compared to soy-based biodiesel, which has a T_{onset} of $\sim -4^{\circ}\text{C}$ and a ΔH of only 27.7 J/g . This serves to highlight the difficulties faced in developing a commercial tallow-based product.

Results for Urea Fractionated Biodiesel with synthesised polymers with Surfactants
Table 7

Additive / Biodiesel Mixture	Additive Concentration (% w/w)	Cloud Point ($^{\circ}\text{C}$)	CFPP ($^{\circ}\text{C}$)	$\Delta T_{\text{saturates}}$ ($^{\circ}\text{C}$)	$\Delta T_{\text{saturates}}$ (% w/w)
BDT25DV		3.65	4		
P4T/BDT25DV	0.5	1.52	2	2.13	4.260
95%P4T&5%SMT/BDT25DV	0.5	1.32	3 – 4	2.33	4.660
95%P4T&5%SST/BDT25DV	0.5	1.58	3	2.07	4.140
P4T/BDT25DV	3.5	-0.43	-1 – 0	4.08	1.166
95%P4T&5%SMT/BDT25DV	3.5	-0.48	-2 – -1	4.13	1.180
95%P4T&5%SMSOT/BDT25DV	3.5	-0.10	-3	3.75	1.071
95%P4T&5%SST/BDT25DV	3.5	-0.57	-	4.22	1.206
P4(No Tol)/BDT25DV	3.5	-1.11	-1	4.76	1.360
95%P4(No Tol)&5%SMT/BDT25DV	3.5	-0.99	-2 – -1	4.64	1.326
P6:Tol(50/50w/w)/BDT25DV	3.5	2.53	-	1.12	0.320
Dodiflow1000/BDT25DV	2	1.12	1	2.53	0.723

P4T = P4: Toluene (50/50% w/w)

SMT = Sucrose Myristate: Toluene (50/50% w/w)

SMSOT = Sucrose Myristate: Sucrose Oleate: Toluene (25/25/50% w/w)

SST = Span 65: Span 85: Toluene (25/25/50% w/w)

The original VCBD exhibited a CFPP of 10 °C, and then with fractionation this was reduced to 4 °C, a drop of 6 °C. This then facilitated addition of additive packages in an attempt to further lower the CFPP. Two additive level packages were trialled, 0.5% and 3.5%. Given that there are no CFPP standards in Australia, it would be possible to market the Urea Fractionalised biodiesel 'as is', but we would need to lower the CFPP in anticipation of winter. Given that the current guidelines suggest that a CFPP of 6 °C is adequate for summer months, we can comfortably pass this test, but during the winter months a CFPP of 0 °C would require an additive package.

At 0.5% additive level, the best result achieved was with the polymer and toluene on their own, without the addition of surfactants. Once the three different surfactant packages were added we saw an increase in the CFPP, which was unexpected, and contrary to how the surfactant package should behave in these systems. From DSC work, it would appear that the surfactant combinations exhibit a lower CP than the polymer: toluene combination, but the CFPP results contradict this. At 3.5% additive level, the best DSC result achieved was with P4 not mixed with anything. This is an unrealistic concentration and should not be considered a viable option.

The SMSOT combination had little effect on the CFPP at 0.5% additive but when added at 3.5% it dropped the CFPP from +4 °C to -3 °C, a change of 7 °C which was the best additive package trialled. While the CP for P4 in the absence of toluene was the best, the CFPP result was far less impressive. In fact it performed poorly in the test - the only sample to return a worse CFPP value was P4:Toluene at 3.5%. However, once surfactant combinations were trialled, CFPP values improved dramatically. Even at 3.5% additive mixtures, the surfactant is only added in at 875ppm, at this concentration we were able to achieve a drop in CFPP of 2 °C from the best non surfactant combination (P4:No toluene) to 3.5%(95%P4T&5%SMSOT in BDT25DV).

4.8 Summary

The use of urea fractionation as a method to selectively reduce saturate content in tallow-based biodiesel was investigated and found to be highly effective. Slower cooling rates were found to favour the inclusion of saturates in urea complexes and larger scale fractionations were found to increase overall yields of product. Yields of saturate-reduced biodiesel (urea filtrates) of between 85% and 70% were able to be obtained and up to 16% of the saturates comprising methyl stearate and methyl palmitate were easily removed. Finally, it was suggested that a future study into solvent effects on the final composition of urea fractionated biodiesel would be instructive.

4.9 References

- 1 Bengen F., German Patent Application O. Z. 12438, Mar. 18, **(1940)**
- 2 Smith A., *J. Chem. Phys.*, 18, 150, **(1950)**
- 3 Swern D., *Ind. Eng. Chem.*, 47, (2), **(1955)**
- 4 Swern D. et al., *J. Am. Oil Chem. Soc.*, 29, 614, **(1952)**,
- 5 Swern D. et al., *J. Am. Oil Chem. Soc.*, 30, 5, **(1953)**
- 6 Schlenk H. et al. *J. Am. Chem. Soc.*, 72, 5001, **(1950)**
- 7 Ratnayake W. et al., *Fat. Sci. Technol.*, 90, 381, **(1988)**
- 8 Traitler H. et al., *J. Am. Oil Chem. Soc.*, 65, 755, **(1988)**
- 9 Shimada Y. et al., *J. Am. Oil Chem. Soc.*, 75, 1539, **(1988)**
- 10 Hayes D., et al, *J. Am. Oil Chem. Soc.*, 75, 1403, **(1998)**
- 11 S. Bist and B. Tao, U. S. Patent Application 2005023956, Oct 20, **(2005)**
- 12 Harvey D., *Modern Analytical Chemistry*, **(2000)**, McGraw-Hill, Singapore.