EFFECT OF BIODIESEL IMPURITIES ON FILTERABILITY AND PHASE SEPARATION FROM BIODIESEL AND BIODIESEL BLENDS

- National Biodiesel Conference 2008

Outline

- Summary of Observations in Minnesota in December of 2005 with B2.5 Blends and B100
- Performance of Soy Biodiesel from Various Sources as B100 and B2.5 Blends in Various Filtration Tests
- Summary of Experience in Winter 2006-2007 with “Improved Biodiesel”
- On Going Observations and Issues

Summary of Our Minnesota Experience in December 2005 with B2.5 Blends

- Early December 2005 refinery dispenser filter for B2.5 plugged in several hours when temperature dropped near 0 F.
- During same period many Minnesota customers reported plugged vehicle filters
- Problems associated with extreme cold (< 0 F), and concentrated in vehicles stored outside overnight and where fuel was stored in above ground tanks

Observations During the December 2005 Period

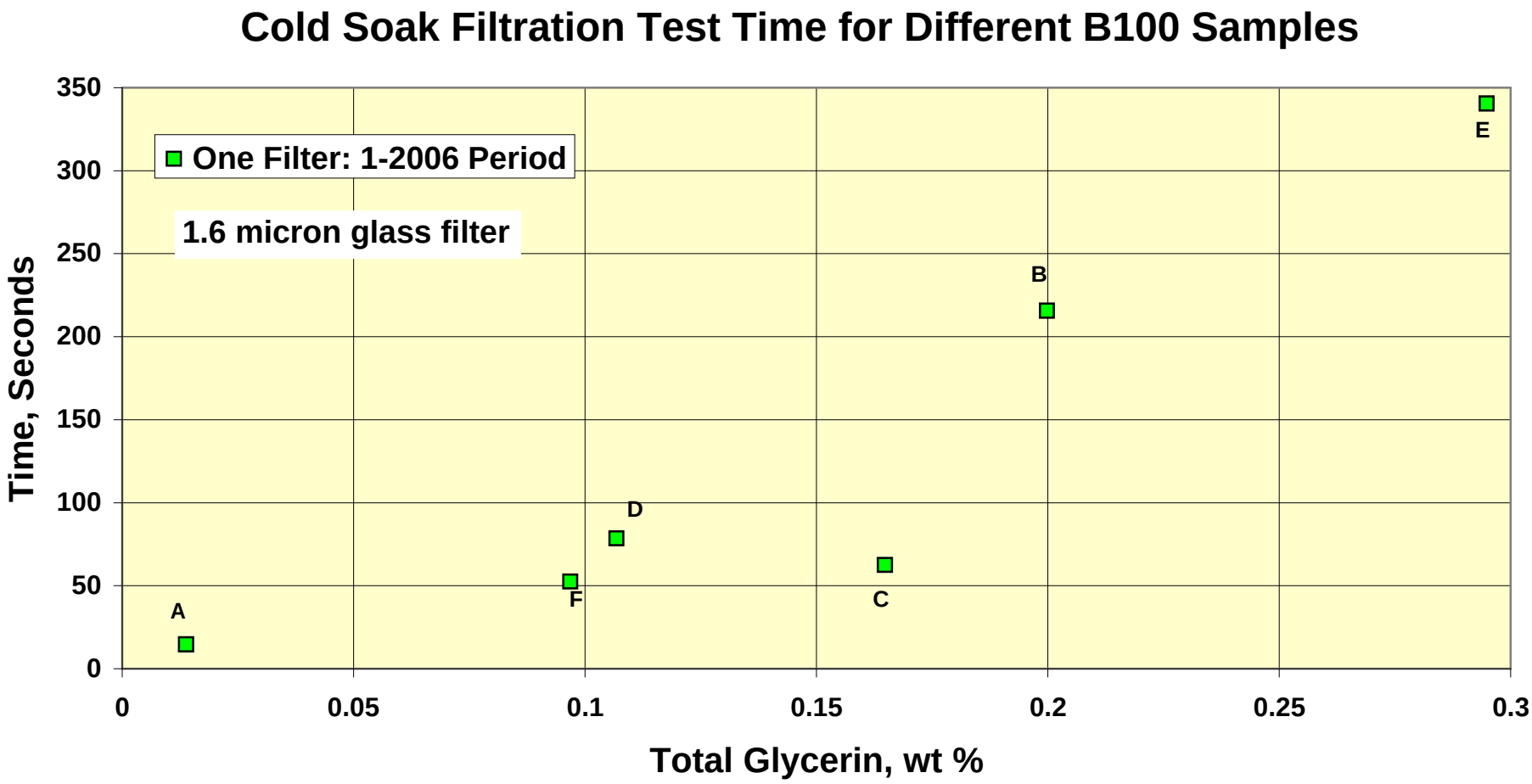
- Our Biodiesel met ASTM D 6751 including total glycerin level of 0.20 wt %
- Retain samples of B100 showed “whitish” precipitate after storing several days at 48 F.
- Some of the B100 precipitate remained even when heating samples to 70 F.
- State of Minnesota and others reported they found B100 in the state that did not comply with ASTM D 6751, especially with total glycerin levels being greater than 0.240 wt %.

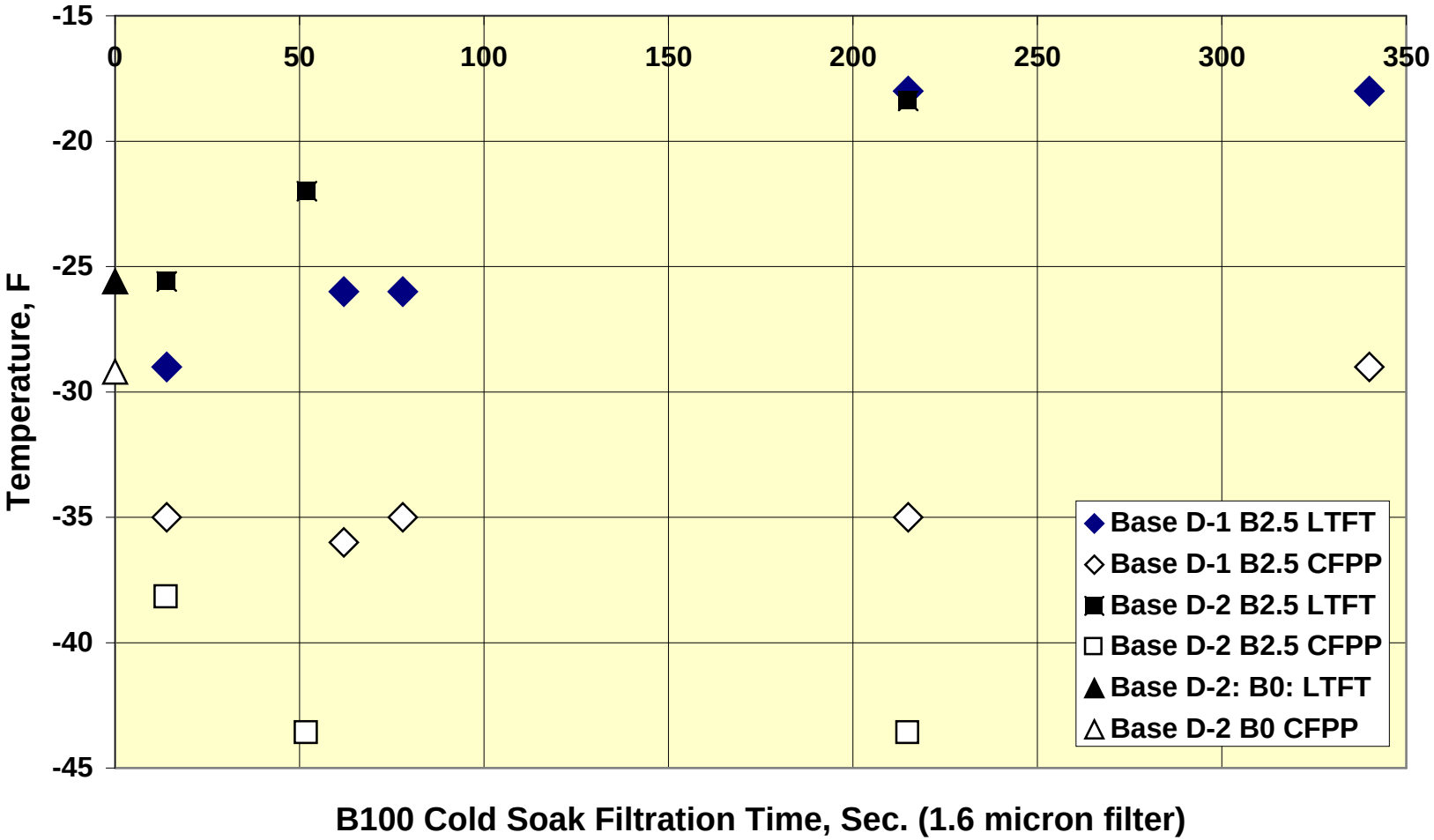
Filtration Studies

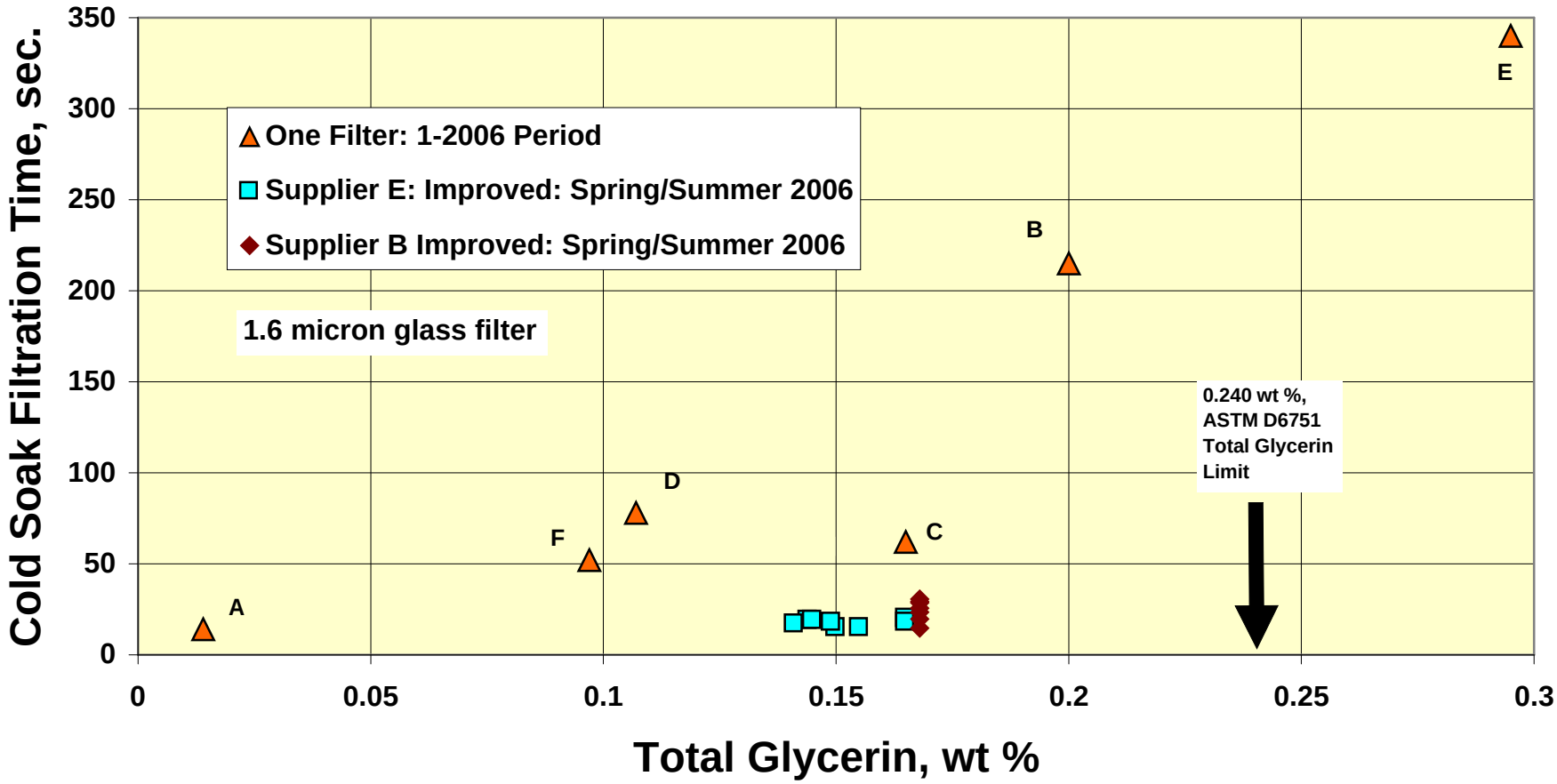
- Sourced Soy B100 from Six Suppliers
- Investigated B100 Filtration and Low Temperature Filtration of Biodiesel Blends
  - "Cold Soak Filtration Test" (B100)
  - Course Filter/Fast Cool (CFPP)(B2.5)
  - Finer Filter/Slow Cool (LTFT)(B2.5)

Cold Soak Filtration Test

- Proposed by Mn. Dept. of Commerce
- Similar to Distillate Particulate Test (ASTM D 6217)
- Cold soak consists of chilling a 300 ml sample for 16 hours at 40ºF, then warm it to room temperature and filter with a 1.6 micron glass fiber filter with stainless steel filter support
- Test measures time to filter sample


Cold Soak Filtration Test Time for Different B100 Samples
One Filter: 1-2006 Period
1.6 micron glass filter
Time, Seconds
Total Glycerin, wt %
350
300
250
200
150
100
50
0
0
0.05
0.1
0.15
0.2
0.25
0.3
A
F
D
C
B
E


-15
-20
-25
-30
-35
-40
-45
0
50
100
150
200
250
300
350
Temperature, F
B100 Cold Soak Filtration Time, Sec. (1.6 micron filter)
Base D-1 B2.5 LTFT
Base D-1 B2.5 CFPP
Base D-2 B2.5 LTFT
Base D-2 B2.5 CFPP
Base D-2: B0: LTFT
Base D-2 B0 CFPP


Cold Soak Filtration Time, sec.
350
300
250
200
150
100
50
0
0
0.05
0.1
0.15
0.2
0.25
0.3
Total Glycerin, wt %
One Filter: 1-2006 Period
Supplier E: Improved: Spring/Summer 2006
Supplier B Improved: Spring/Summer 2006
1.6 micron glass filter
0.240 wt %, ASTM D6751 Total Glycerin Limit
A
B
C
D
E
F

Summary of Our Minnesota Experience in Winter 2006-2007

- Before winter 2006-2007 we had transitioned our biodiesel tank to “Improved” B100 with cold soak filtration times near that for “distilled” soy methyl esters.
- Dramatic reduction in filter plugging problems of our customers for B2.5

Evidence for Solubility Effects in B100 and Biodiesel Blends

- Composition of B100 Precipitates above the Cloud Point
- Composition of Extracts from Plugged Dispenser Filters

B100 with 32 F Cloud Point Held for Several Days at 48 F

Analysis of Glycerides in Filter Cake from Filtration of Soy B100 After Holding for Several Days at 40 F

Compound	Weight % of Filter Cake
Monopalmitin	9.1
Monoolein	0.5
Monostearin	6.0
Diglycerides	Not Detected
Triglycerides	Not Detected

Composition by ASTM D 6584

Analysis of Glycerides in Filter Cake from Filtration of Soy B100 After Holding for Several Days at 40 F

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Monopalmitin	9.1
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Monostearin	6.0
Diglycerides	Not Detected
Triglycerides	Not Detected

Monopalmitin in B100 Sample 0.070 wt %

Winter 2006-2007 Issues

- Refinery dispenser filters plugged on 12-1 and 12-5 after first winter excursion below 10 F.
- Refinery dispenser filters plugged on 1-16-07 after second winter excursion below 10 F.

Plugged Dispenser Filter Work Up Procedure:

- Remove pleated filter paper and observe
- Extract solubles from filter paper with acetone
- (filter any acetone insolubles collected in acetone)
- Evaporate acetone
- Filter precipitate from acetone free extract held at 40 F
- Analyze filter cake using ASTM D 6584 with standards used to identify monopalmitin and monostearin

Acetone Free Extract of Plugged Dispenser Filters At 40 F

Composition of Filter Cake from Filtration (40 F (4.4C)) of Acetone Free Extract from Dispenser Filters.

Filter Removal Date	12/1/2006	12/5/2006
Acetone Free Extract, g	77	69
Filter Cake, g	7.98	5.91

Filter Cake Composition

Monopalmitin, Wt % of Filter Cake	26.4	41.9
Monoolein, Wt % of Filter Cake	1.0	0.0
Monostearin, Wt % of Filter Cake	12.8	25

Component Concentration Based on what was Extracted from the Dispenser Filter

Filter Removal Date	12/1/2006	12/5/2006
Acetone Free Extract, g	77	69
Filter Cake, g	7.98	5.91

Concentration of Components in the Acetone Free Extract

Monopalmitin, Wt % of Acetone Free Extract	2.74	3.59
Monoolein, Wt % of Acetone Free Extract	0.10	0.00
Monostearin, Wt % of Acetone Free Extract	1.33	2.14

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Monostearin, Wt % of Acetone Free Extract	1.33	2.14

Monopalmitin in B2.5 0.0015 wt %

Conclusions

- Two types of Biodiesel impurities are observed to effect filter performance.
- One type is recognized by B100 filtration times at room temperature with cold soak filtration test. This type is indicated to be problematic for vehicle filters
- The substantial reduction in cold soak filtration times for our biodiesel between winters 2005-2006 and 2006-2007 is believed to explain the reduction in field problems of our customers of B2.5.

Conclusions

- The second type is believed to be the monoglycerides of saturated fatty acids.
- High concentrations of the monoglycerides of saturated C16 and C18 fatty acids, monopalmitin and monostearin were found on “plugged” diesel fuel dispenser filters that experienced prematurely short service lives when filtering low Cloud Point B2.5 blends near 0°F (-18°C).

Conclusions

- The phase separation experienced by monopalmitin and monostearin is not reliably predicted by the Cloud Point test. It is suggested that sufficient “time” is required for nucleation and crystallization to produce this phase separation.
- CFPP test results do not appear sensitive to biodiesel impurity effects that are detected in LTFT testing. CFPP should not be used for biodiesel blends unless validated by actual cold engine operability testing.

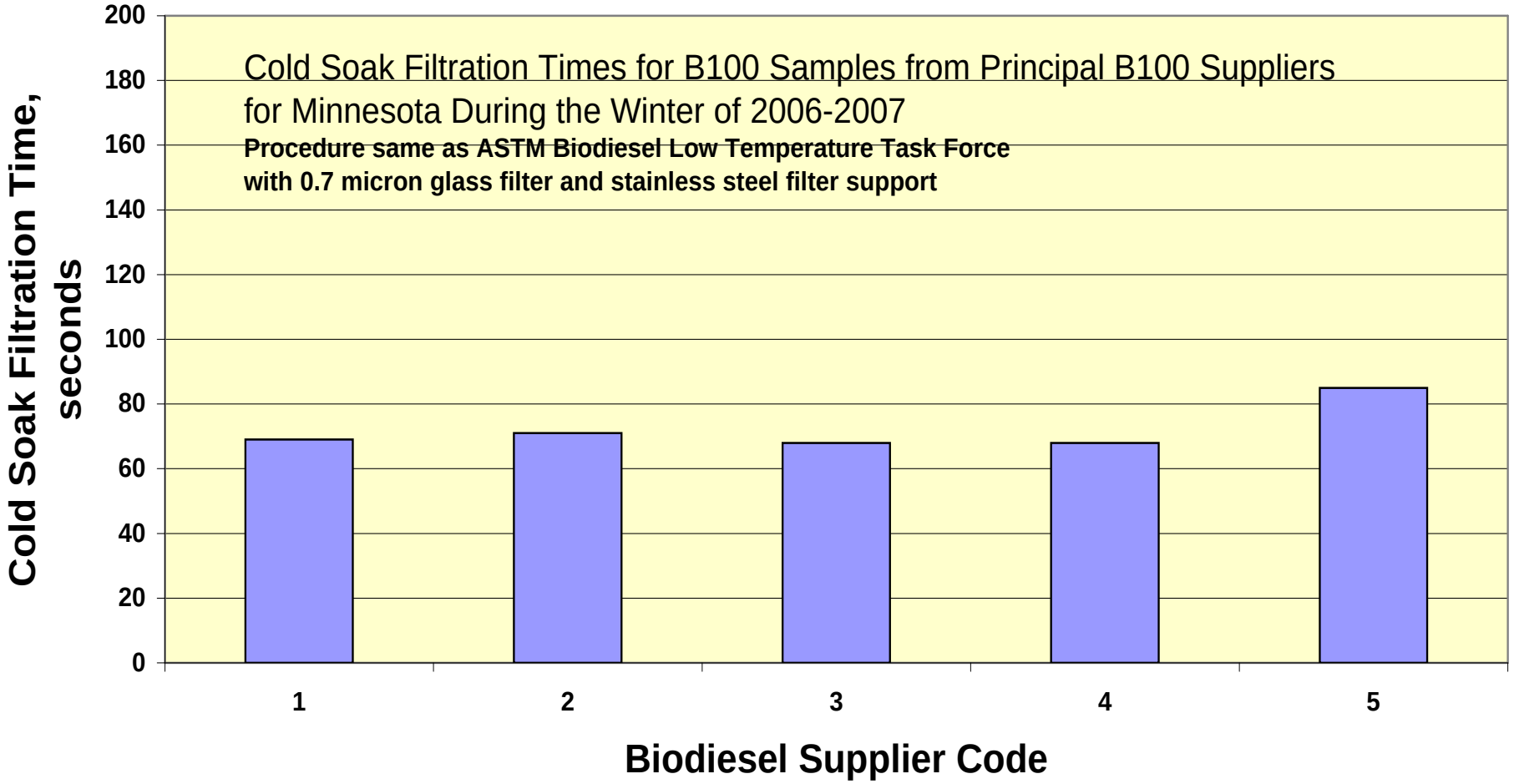
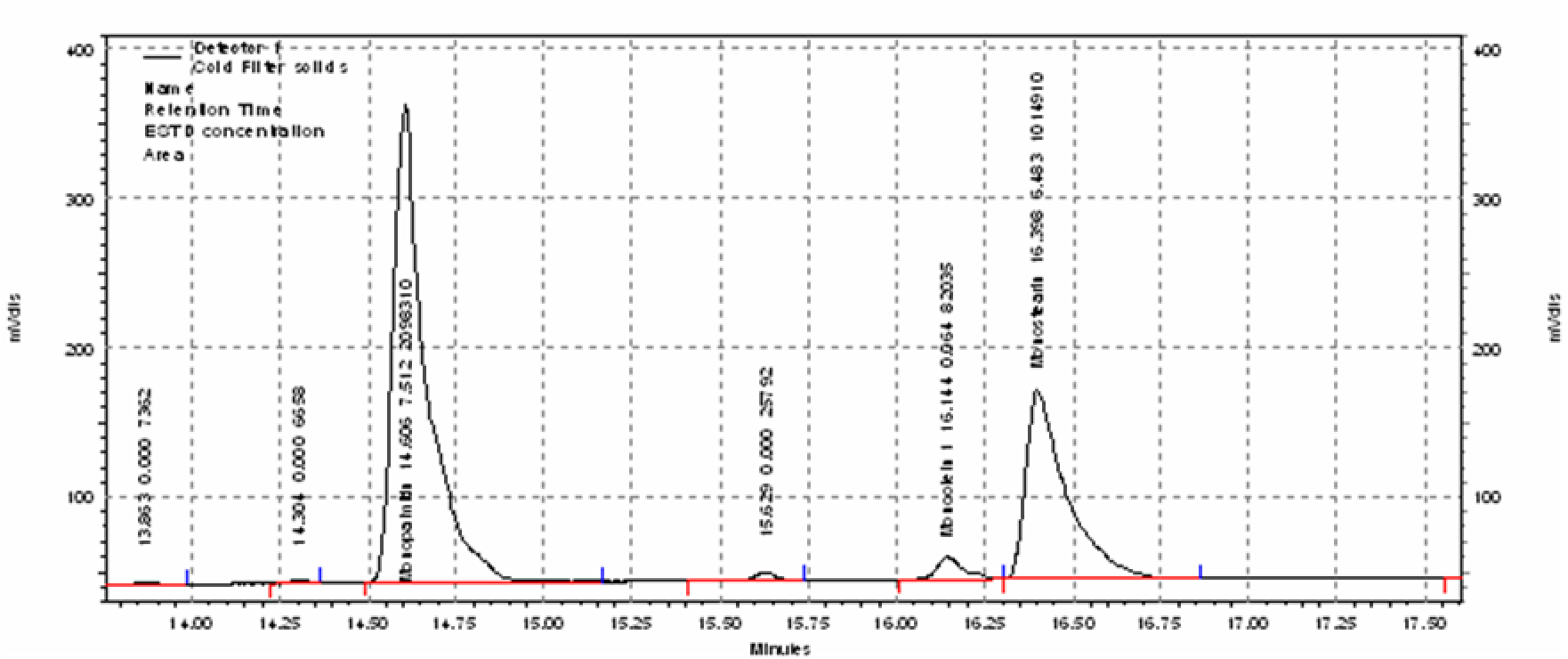

Cold Soak Filtration Times for B100 Samples from Principal B100 Suppliers for Minnesota During the Winter of 2006-2007
Procedure same as ASTM Biodiesel Low Temperature Task Force with 0.7 micron glass filter and stainless steel filter support
Cold Soak Filtration Time, seconds
200
180
160
140
120
100
80
60
40
20
0
1
2
3
4
5
Biodiesel Supplier Code

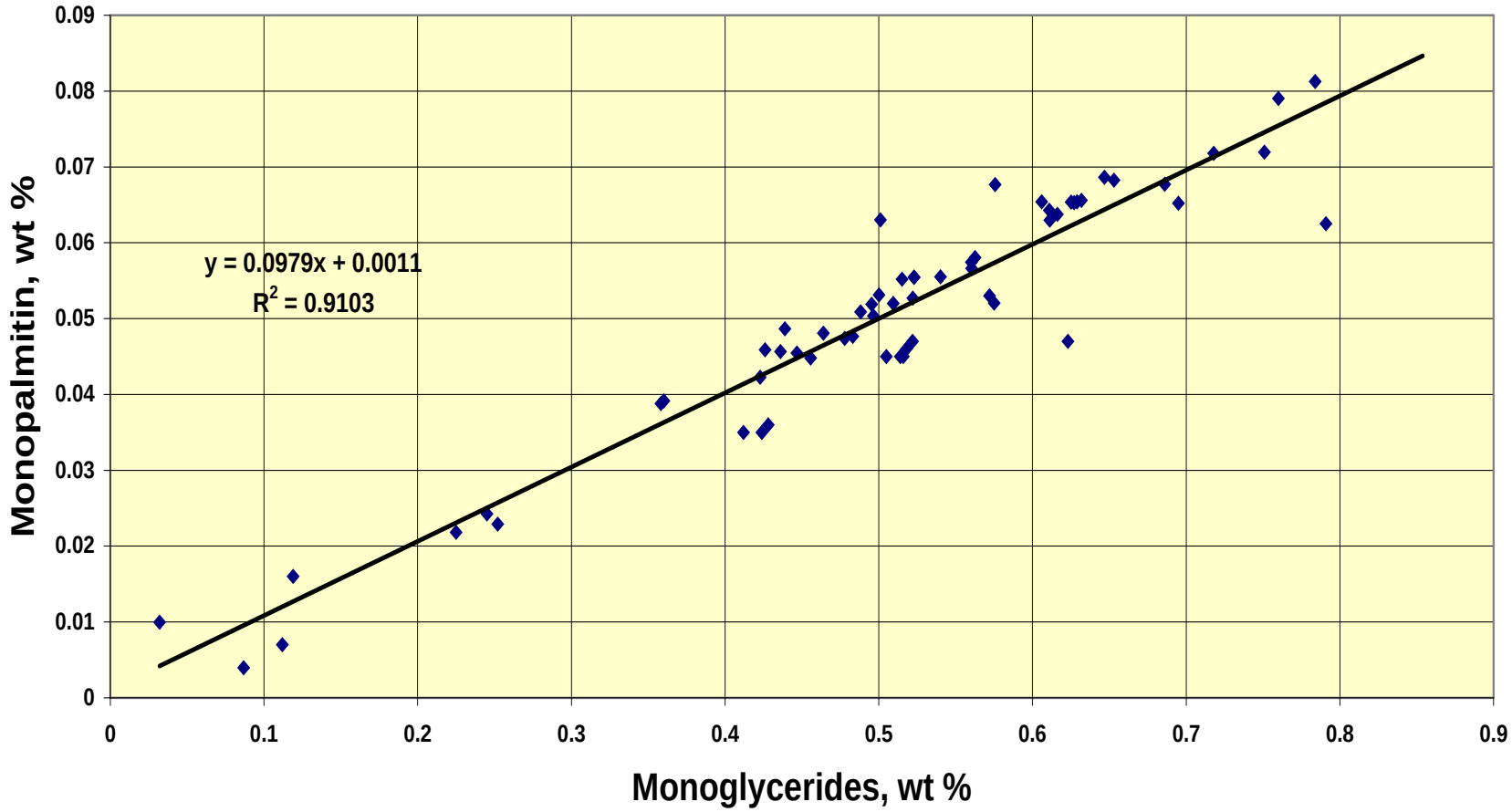
TABLE 3. Fatty acid composition of experimental fat products

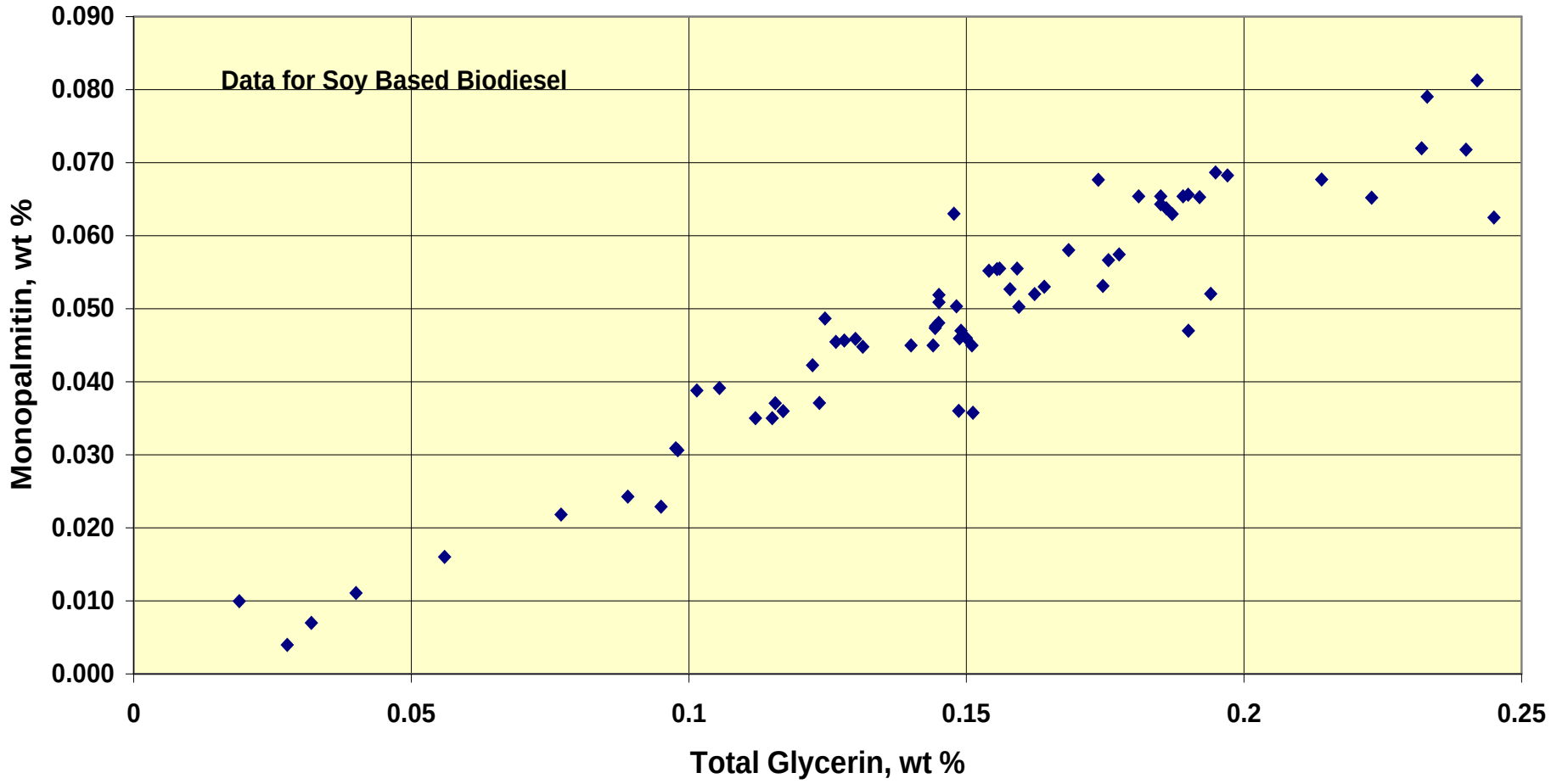
TEST FAT[A]	FATTY ACIDS (g/100 g Fat Product)									
	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	SFA	UFA
PFFA	0.5	1.5	44.8	0.3	4.4	32.1	7.9	0.2	51.2	40.5
SBFFA	–	0.1	12.1	0.1	3.2	12.1	54.8	9.0	15.4	76.0
CPO	–	1.2	40.0	0.3	3.7	36.9	9.9	0.2	44.9	47.3
Tallow 1	0.1	2.5	23.9	2.7	25.3	32.4	3.1	0.4	51.8	38.6
Tallow 2	0.1	2.5	23.5	2.7	24.3	33.7	3.2	0.4	50.4	40.0
RG1	0.3	0.9	25.0	1.6	6.0	37.1	11.8	0.4	32.6	51.2
RG2	0.1	0.9	26.7	4.7	4.4	39.0	12.3	0.4	32.3	56.8
RG3	0.2	0.2	11.6	0.5	5.0	37.7	21.9	1.0	17.2	61.09
Palm kernel meal[B]	44.3	14.7	7.9	–	2.3	14.7	2.9	–	75.1	17.6

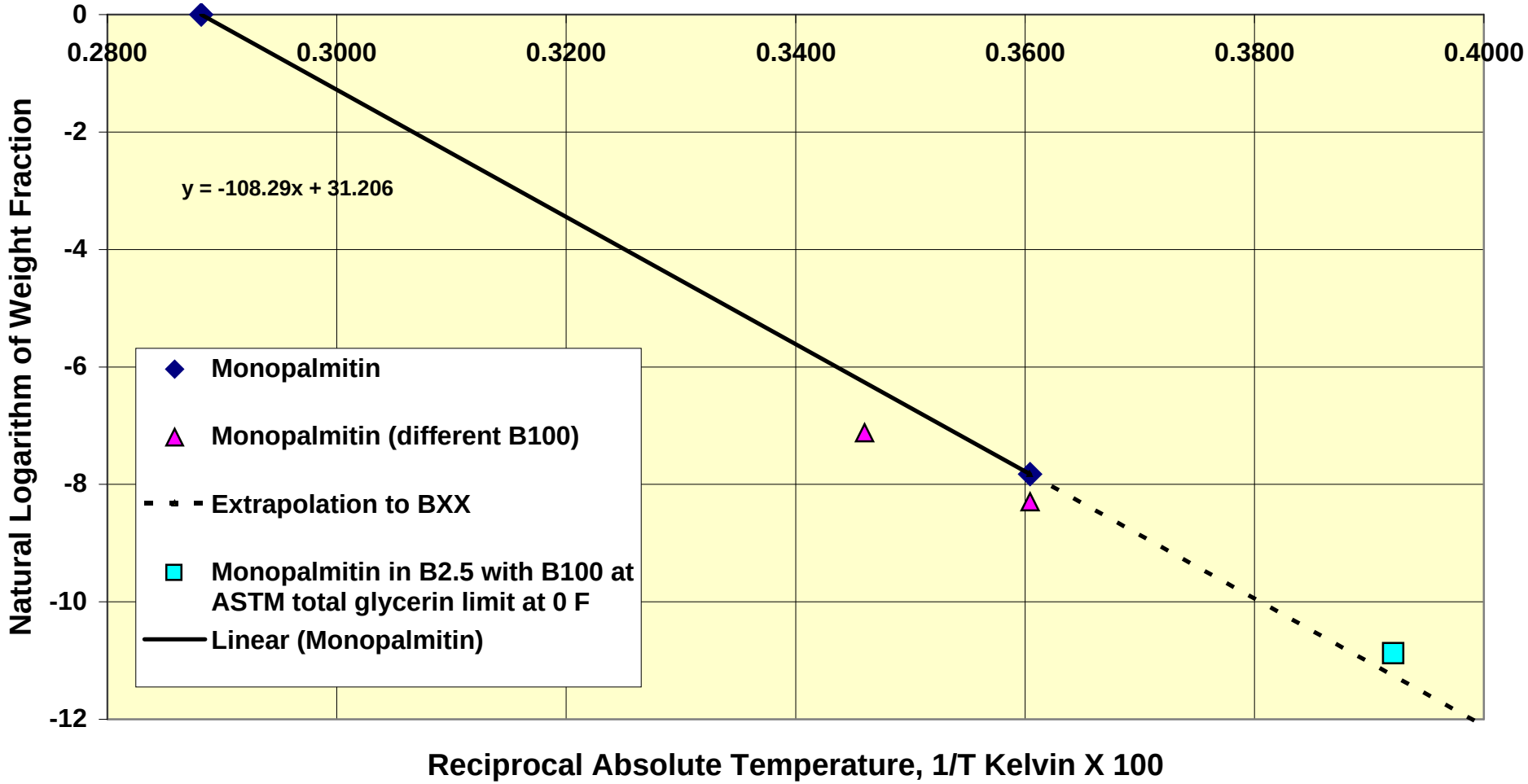
[A]PFFA = Palm free fatty acids; SBFFA = Soybean free fatty acids + acidulated soapstock; CPO = Crude palm oil; Tallow 1 and Tallow 2 = Beef tallow samples provided by two different renderers; RG1 and RG2 = Restaurant greases from oleine palm oil; and RG3 = Restaurant grease from soybean oil.

[B]Values for full-fat palm kernel meal are for the fat portion (47.1%) of this product.


Detector f
Cold Filter solids
Name
Retention Time
EOTD concentration
Area
13.863 0.000 7362
14.304 0.000 6658
Fibrosterin 14.605 7.512 2058310
15.629 0.000 257.92
Fibrosterin 1 16.144 0.064 83035
Fibrosterin 16.366 6.483 1014910
400
300
200
100
mV/dIs
14.00
14.25
14.50
14.75
15.00
15.25
15.50
15.75
16.00
16.25
16.50
16.75
17.00
17.25
17.50
Minutes


0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Monopalmitin, wt %
y = 0.0979x + 0.0011
R2 = 0.9103
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Monoglycerides, wt %


Data for Soy Based Biodiesel
Monopalmitin, wt %
0.090
0.080
0.070
0.060
0.050
0.040
0.030
0.020
0.010
0.000
0
0.05
0.1
0.15
0.2
0.25
Total Glycerin, wt %


0
-2
-4
-6
-8
-10
-12
0.2800
0.3000
0.3200
0.3400
0.3600
0.3800
0.4000
y = -108.29x + 31.206
Natural Logarithm of Weight Fraction
Reciprocal Absolute Temperature, 1/T Kelvin X 100
Monopalmitin
Monopalmitin (different B100)
Extrapolation to BXX
Monopalmitin in B2.5 with B100 at ASTM total glycerin limit at 0 F
Linear (Monopalmitin)

Material Balance for Filtration of Acetone Extract from Dispenser Filters

Filter Removal Date	12/1/2006	12/5/2006
Acetone Free Extract, g	77	69
Acetone Insoluble Particulate, g	0.42	0.12
Filter cake of acetone free extract, g	7.98	5.91
Acetone Insoluble Particulate, Wt %	0.55	0.17
Filter cake of acetone free extract, Wt %	10.36	8.57
Fluid phase, Wt %	89.09	91.26

Additional Data on a 2007 Dispenser Filter

Filter Removal Date	1/16/2007
Acetone Free Extract, g	76
Filter Cake, g	3.8

Filter Cake Composition

Monopalmitin, Wt % of Filter Cake	36.3
Monoolein, Wt % of Filter Cake	0.3
Monostearin, Wt % of Filter Cake	20.0

Concentration of Components in the Acetone Free Extract

Monopalmitin, Wt % of Acetone Free Extract	1.82
Monoolein, Wt % of Acetone Free Extract	0.03
Monostearin, Wt % of Acetone Free Extract	1.00

Filter Cake from Filtration of Acetone Extract (After Acetone Evaporation).