Air-Conditioning, Heating and Refrigeration Technology Institute

Final Report

AHRTI Report No. 09005-01

ASHRAE SPC 177P FRACTIONATION APPARATUS EVALUATION

Final Report

Date Published – January 2013

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Funding for this project was provided by (listed alphabetically):
- Air-Conditioning, Heating and Refrigeration Institute (AHRI)
- Copper Development Association (CDA)
- Heating, Refrigeration and Air Conditioning Institute of Canada (HRAI)
- New York State Energy Research and Development Authority (NYSERDA)

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1 EXECUTIVE SUMMARY

Usability of fractionation apparatus designed by members of ASHRAE SPC 177P, MOT for Measuring Fractionated Compositions of Refrigerant Blends was tested using standard laboratory conditions. The apparatus was built with “off the shelf” parts and was subjected to three fractionation tests conducted on a blend of R125/600 (50.0/50.0 by mass %) at temperatures of (-36.6^{o}C) “cold run” and 54.4^{o}C “hot run”. Detailed drawing of the final apparatus used is included in Figure 11.

The overall conclusion is that the apparatus is useful in fractionation testing with a few modifications as proposed. Users also need to observe certain identified precautions for high boiling components that tend to condense (like butane).

Following is a list of primary findings and observations resulting from this testing program:

1. The liquid sampling loop from the initial design did not work. The sample in the loop was partly flushed during the test. The design was modified to have one valve on the liquid line flushing directly into an evacuated sampling fixture that is equipped with a vacuum gauge and a sampling septum. Use of the vacuum gauge assists in avoiding the potential problem of exceeding the saturation pressure of sample components.

2. The mechanical mixing helps the test to run with a steady flow, but is not critical to obtaining a good composition reading.

3. For the high boiling point refrigerants, it is critical to avoid condensation of the sample before testing in the GC. Mitigating actions are: quick processing, pre-heating the sample, or processing the sample under a slight vacuum (or otherwise keeping the working pressure lower than the saturated pressure of the component being tested at ambient temperature).

4. The above changes, to the apparatus and to the procedure, reduced the spread of the measured liquid compositions from the predicted values from initial range of 0.2 to 5.5 wt% (span of 5.3 wt%) away from predicted values to being in the range of -0.8 to 1.6 wt % (span of 2.4 wt%) away in the final test.

2 INTRODUCTION

Environmental concerns on climate change and the high global warming potential of hydrofluorocarbon (HFC) refrigerants in common use today have driven the search for refrigerants with much lower ozone depletion potential (ODP) and global warming potential (GWP). This has resulted in the development of several refrigerant blends with flammable components. Safety being of paramount importance, many manufacturers have utilized multiple component refrigerants blends which provide the best compromise of refrigerant properties and safety. Key to this optimization is the fractionation of these blends if misused or in the event of a leak.

ASHRAE has recognized this safety issue with fractionation and requires a fractionation analysis of any multiple component refrigerant blends as described in ASHRAE Standard 34, “Designation and Safety Classification of Refrigerants”. Unfortunately, manufacturers of new blends have experienced difficulties in performing these fractionation experiments and disagreement between laboratories has occurred. To meet this need, ASHRAE formed a committee (SPC 177P) to better define and clarify the method of test (MOT) for fractionation experiments; the cognizant technical committee for this effort is TC 3.1—Refrigerants and Secondary Coolants.

SPC 177P has representatives from leading laboratories in the field of new refrigerant development. Currently these labs include Arkema, DuPont, Honeywell, Intertek, National Institute of Standards and Technology (NIST), Safety Consulting Engineers (SCE), and Underwriters Laboratories (UL). These labs have participated in (a) a series of round robin fractionation testing, (b) round robin GC analysis of blends over a wide composition range, and (c) testing to evaluate their ability to generate accurate calibration standards.

After sharing apparatus designs and procedures used by the various participating labs, this MOT is provided. Since this MOT is also intended for refrigerant blend manufactures that may not have capabilities and resources as extensive as those available to the currently participating labs it was felt that a simple, relatively inexpensive, yet reliable apparatus and method should be defined in the MOT. Such an apparatus has been designed. To ensure that this was an effective and practical solution, actual testing using this MOT was needed.

SCE was awarded a contract to build and test the fractionation apparatus as designed by the SPC 177P. This report covers the findings obtained by SCE in the process of building the proposed apparatus and using it per the proposed MOT.

3 SCOPE

The scope of the work includes building the apparatus according to the design specified in the initial draft of proposed Standard 177. Then, using this apparatus, two fractionation tests were performed on R125/600 blend (50.0/50.0 by mass %) per ASHRAE Std 34-2010 specification:

Fractionation Test 1 (cold run) – loading 90% of max. DOT fill at (-36.6^{o}C)
Fractionation Test 2 (hot run) – loading 90% of max. DOT fill at 54.4^{o}C

The committee agreed on selecting this particular blend for testing as most likely to exhibit stratification during the fractionation process (due to large difference in boiling points, density and molecular weights). If the method of test performs well for the blend that has components this far-off in physical properties, it will perform well for the blend of components with their respective properties closer. Therefore, no more blends were considered for any future testing.

(The test was to be run according to the initial draft of proposed ASHRAE Standard SPC 177P, MOT for Measuring Fractionated Compositions of Refrigerant Blends. The cold test was planned to be run in methanol bath; the hot test was planned to be run in water or water/glycol bath. The GC calibration mixtures were to be prepared in vapor phase.)

The accuracy of results was evaluated by comparing the test results to theoretical prediction from NIST software Refleak simulating refrigerant leaks. The evaluation included exchanging current information with MOT members. At the conclusion of the evaluation, the first test (cold run) was planned to be repeated with all the modifications resulting from the evaluation of two initial tests.

4 FIRST FRACTIONATION TEST (-36.6^{o}C)

Using 90% of max. DOT fill, 1L tank of R125/600 (50.0/50.0 mass %) blend at a temperature of (-36.6^{o}C).

4.1 Initial Design

Preliminary design was based on the requirements in the initial draft of proposed ASHRAE Standard 177P. The testing setup can be built using 'off the shelf' parts without additional machining. The Swagelok ® brand name was selected for the component parts as the price and delivery time were acceptable.

The initial setup for the fractionation apparatus included a stainless steel 1L double-ended sample cylinder, needle valves with minimal dead space, a variety of fittings, and several feet of stainless steel tubing. The liquid line included a dip tube (the smallest, readily available ID tubing was used to minimize the loss on clearing the tube – 0.055"), two valves, and a sample loop between them. A separate 75 mL SS sample cylinder with inlet and outlet valves was used to flash the liquid from the sampling loop to a pre-vacuumed volume.
A drawing of the initial setup is shown in Figure 2, and in pictures in Figure 1.

Figure 1: Initial version of fractionation apparatus

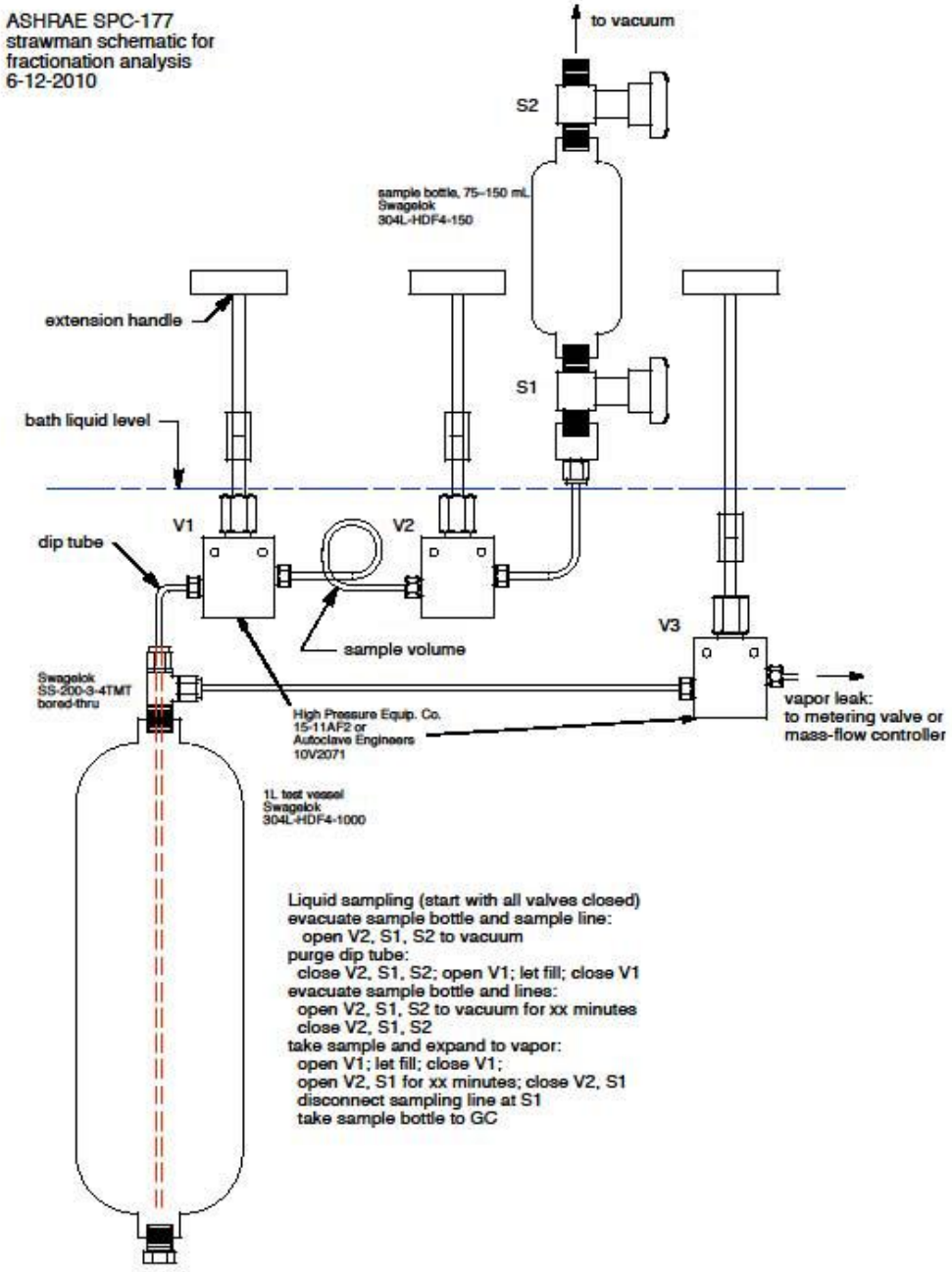

Figure 2: Initial version of fractionation apparatus

The price list of Swagelok parts purchased is included in Appendix B of this report. The delivery time varied from a few days to two weeks.

4.2 GC Calibration

An HP 5890 Series II gas chromatograph was used for tracking composition changes. The chromatograph was equipped with a Chromosorb 102 (60/80) packed column, constructed from a 27 ft long 1/8" SS tube, and a TC (thermo-conductivity) detector. The oven temperature was set to a cycle of 130°C for 8 min, ramping at 10°C/min, and then held at 180°C for 12 min. The detector was kept at 200°C. The time of each GC run was ~18 min to resolve the components. The sample size analyzed was 0.5 mL. Standard 2 mL GC syringes equipped with a shutoff valve were used to transfer the gas samples.

A typical GC chromatogram for this binary blend is shown in Figure 3.

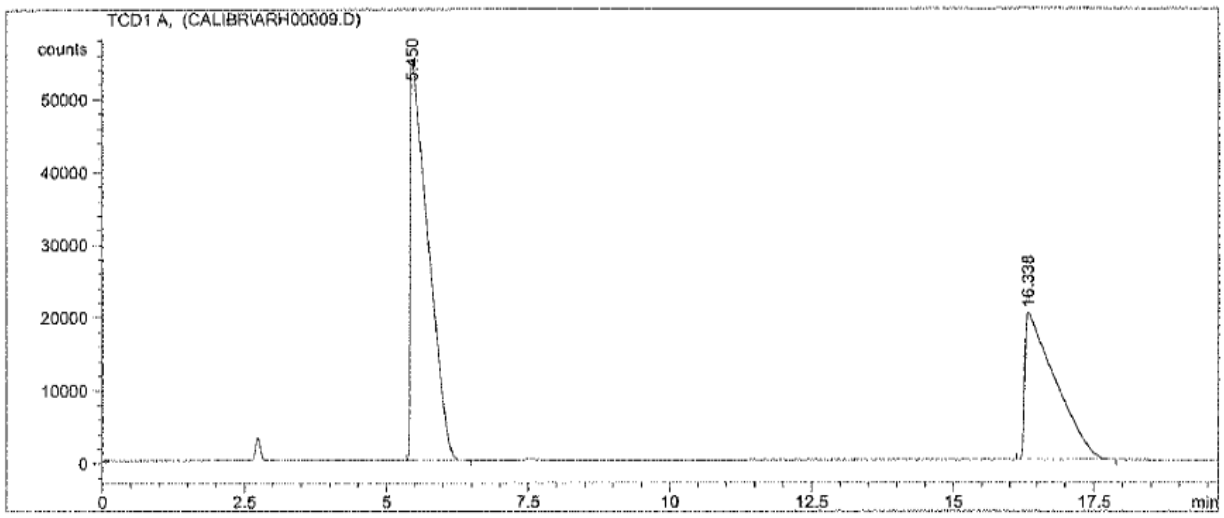

Figure 3: typical chromatogram for the binary blend R125/600

As this is binary system, a five-point calibration curve was constructed to link mass% of the one component with the area% resulting from GC. The other component's mass% was determined by subtraction from 100%. The data points for the calibration curve are listed in the Table 1 below.

Table 1
Standard Mixtures (in wt % or mol% vs. area%)

R125 Wt%	R125 Mol %	GC R125 Area %
0	0	0
26.25	14.7	15.03
49.2	31.9	32.968
77	61.9	60.22
100	100	100

The standard mixtures were prepared in vapor phase by weight in four-gal jugs. The calibration curve is shown in Figure 4.

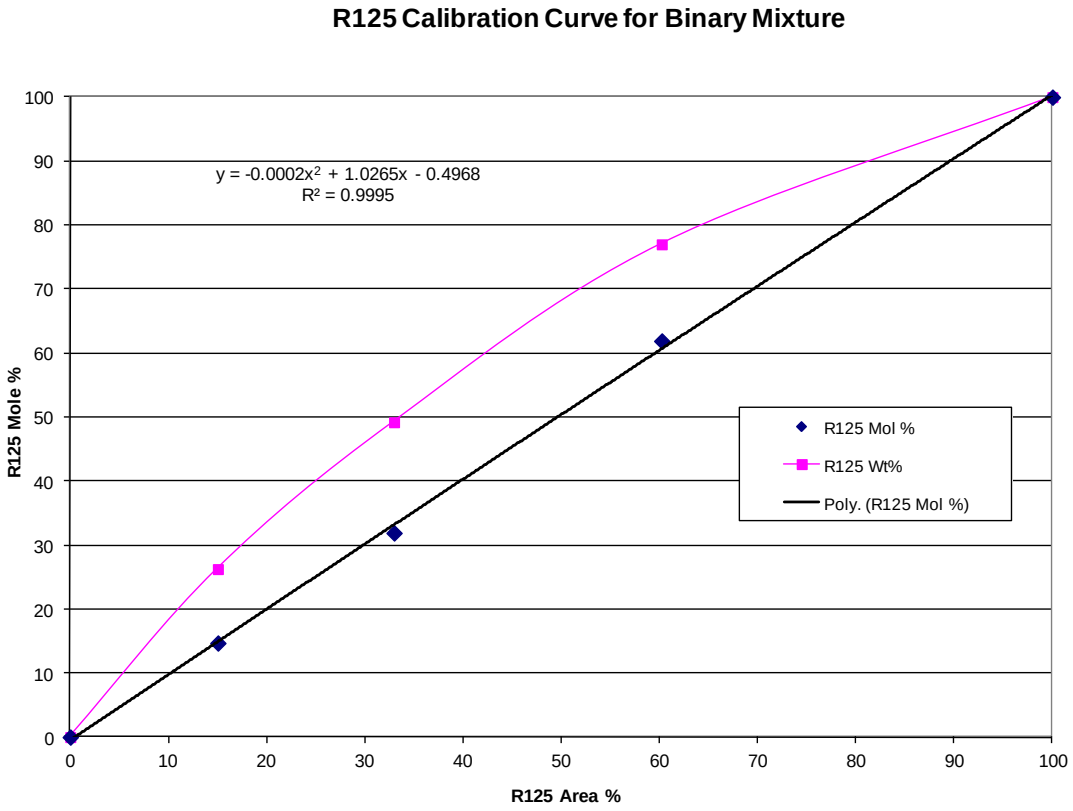

Figure 4: Calibration curve for R125/600 blend

4.3 Initial Fractionation Test Procedure

The test was performed at 90% of max. DOT fill (70.7% by volume liquid fill at -36.6°C), using a 1 Liter SS cylinder maintained at the test temperature of (-36.6°C). The blend is then vapor leaked from the cylinder at the rate of 2% (or less) by weight of initial charge per hour to a point of 2% mass loss (of the initial charge). A sample for GC is taken and then the vapor leaking is continued in the same manner to 10% , 20%, 30%, and so on of mass loss until the leak stops (by equalizing pressure with ambient pressure, or by evaporating all the liquid phase).

Throughout the vapor leak process, the 1L cylinder with the sample blend is kept in the constant temperature methanol bath (-36.6°C). The cylinder is shaken manually every hour to mix the liquids inside. HDPE hollow core balls are used to insulate the top surface of the bath. The refrigerant blend is leaked from the vapor phase, through the vapor line.

The vapor line in these tests consisted of a Swagelok needle valve, flexible PTFE tubing, gas mass flow meter (Omega FMA 1700/1800 Series), Tygon tubing and data recorded by a National Instruments (NI) data acquisition system. Vapor samples were acquired using a GC syringe equipped with a needle by piercing the Tygon tubing section of the vapor line, just past the flow meter.

The leak rate was set by the needle valve in the vapor line and was monitored by the mass flow meter.

The composition changes of liquid and vapor phase of the charged refrigerant blend were determined by gas chromatography. At each test point (0%, 2%, 10%, 20%, etc. mass loss) vapor and liquid samples of the refrigerant blend from the test cylinder were acquired and analyzed by a GC. At the same test points a weight of the sample left in cylinder was also recorded. This allowed for precise mass loss monitoring.

The blend composition changes (vapor and liquid) resulting from the test were compared to composition changes predicted for this blend by Refleak 3.1, a NIST software tool designed for simulation of refrigerant leaks.

Initially, the method for acquiring liquid samples used a detachable sampling fixture. This fixture consisted of a 75 mL cylinder, and two Swagelok valves (SS-ORS2) mounted to a sampling loop connected to the main sample cylinder. At the test point, the fixture was attached to the sampling loop on the liquid line ended with a dip tube in the 1 L tank. The fixture and the part of the line from the first needle valve on the 1 L tank were evacuated prior to acquiring the sample into the sampling loop. The liquid from the sampling loop was then flushed into the sampling fixture. First flush was discarded (to clear the dip tube) and second flush was analyzed by GC.

4.4 Fractionation Test Results (-36.6^{o}C)

After preparing the mixture in the 1L cylinder (see loading weights in Table 2), the cylinder was cooled to the test temperature of (-36.6 ^{o}C) overnight before drawing the first sample.

Table 2

Loading weights for cold run (-36.6°C)

1000 cc sample cylinder 90% of max. DOT fill (70.7% for -36.6C)					
Composition	Desired Wt. %	Weight to be charged (g)	Seq. of Charging	Weight resulting (g)	Wt. % Resulting
R125	50	270.7	2	270.9	50.0
R600	50	270.7	1	270.4	50.0
Total Weight		541.3		541.3	

Right at the beginning of the test it was noticed that the GC results didn't match the predicted fractionation results. After investigating this matter it was found that the sample loop didn't fill up with pure liquid, instead it was filled with a quantity of liquid phase in equilibrium with vapor phase material. After flushing the sample from the loop to the evacuated fixture the resulting composition was therefore different from flushing liquid.

After consulting with MOT committee members the decision was made to alter the setup by removing the loop and one valve, so the liquid line had only one valve and liquid was flushed directly into the evacuated sampling fixture.

The liquid sampling fixture was also changed to include a pressure gauge for monitoring the pressure of the acquired samples. While flushing the sample into the fixture the target pressure in the fixture was set to a 100-200 mmHg above atmospheric pressure (so it was around 950 mmHg). Changes to the fractionation apparatus are shown in Figure 5.

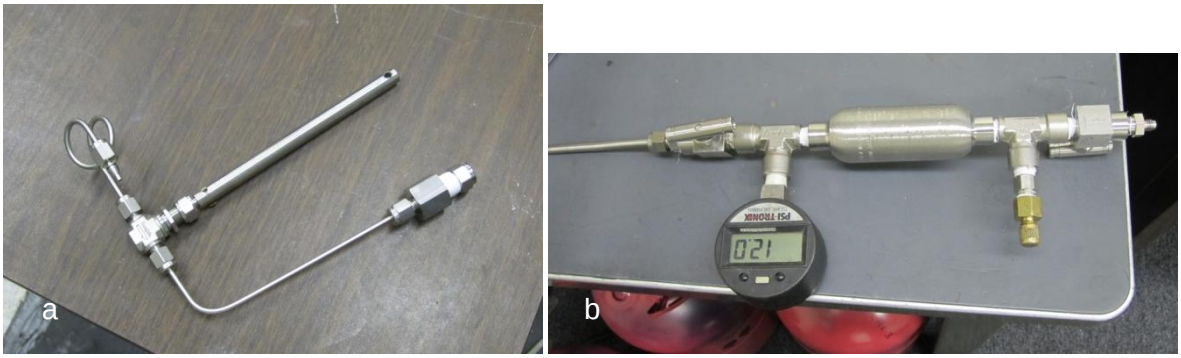

Figure 5: Sample loop removed from setup (a); liquid sample fixture with a gauge (b)

The leakage stopped at 44.15% mass loss as the pressure in the tank equalized with ambient.

The composition data is shown in Figure 6 on the graph, as well as tabulated in Tables 3, and 4.

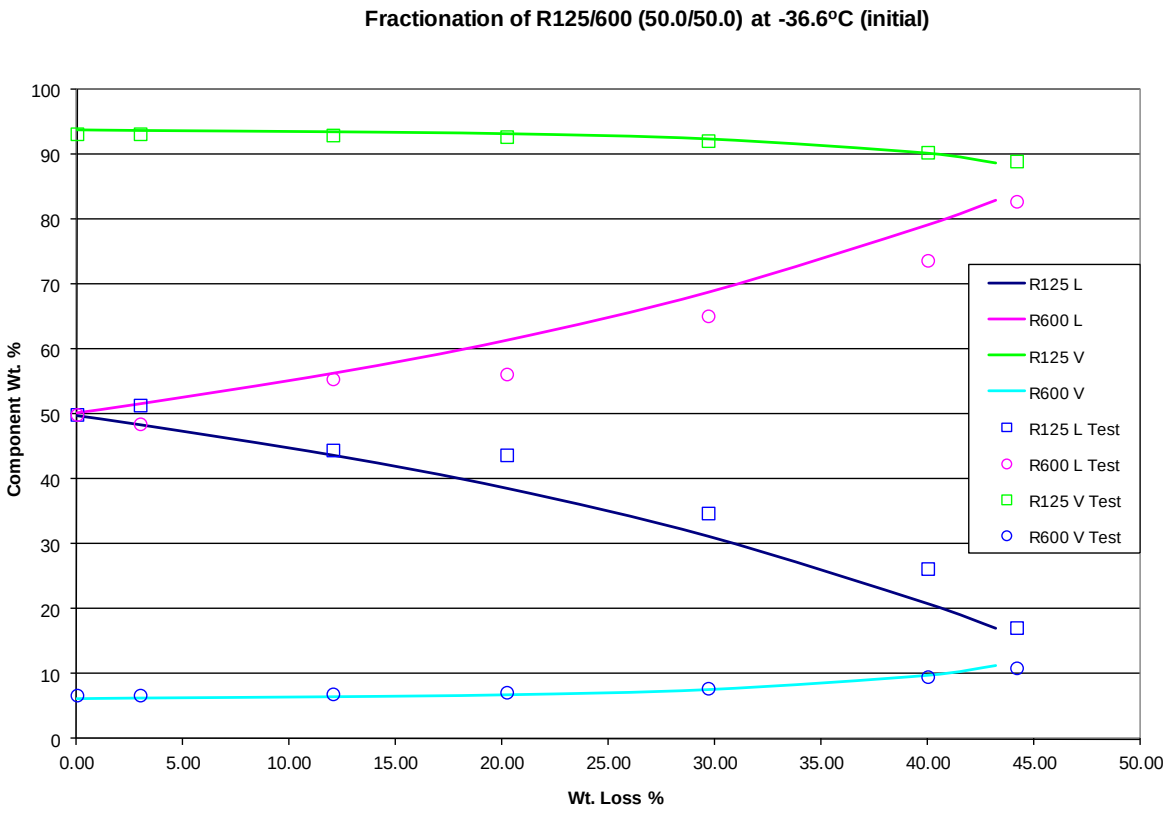

Figure 6: Fractionation (cold run) results

The markers on the graph are test results, the continuous lines are Refleak predicted values. (*The changes to the initial setup for this run include removing a sampling loop and modifying liquid sampling fixture.)*

Table 3
Test data points for Cold Run (-36.6°C)
for 90% max. DOT fill (70.7%)

% Mass Loss	R125 Liquid wt %	R600 Liquid wt%	R125 Vapor wt%	R600 Vapor wt%
0.00	50.01	49.99	93.25	6.75
2.97	51.44	48.56	93.25	6.75
12.03	44.52	55.48	93.06	6.94
20.19	43.77	56.23	92.81	7.19
29.66	34.81	65.19	92.19	7.81
39.98	26.25	73.75	90.40	9.60
44.15	17.16	82.84	89.05	10.95

Table 4

Refleak 3.1 simulated data at (-35.0°C)* for 90% max. DOT fill (70.7%)

% Mass Loss	R125 Liquid Wt %	R600 Liquid wt%	R125 Vapor wt%	R600 Vapor wt%
0.00	49.8	50.2	93.9	6.1
2.97	48.4	51.6	93.8	6.2
12.03	43.7	56.3	93.6	6.4
20.19	38.6	61.4	93.3	6.7
29.66	31.2	68.8	92.5	7.5
39.98	20.8	79.2	90.3	9.7
43.17	17	83	88.8	11.2

*-Refleak didn't converge at (-36.6°C)

Refprop calculated data at (-36.6°C) for 90% fill

% Mass Loss	R125 Liquid Wt %	R600 Liquid wt%	R125 Vapor wt%	R600 Vapor wt%
2	49.2	50.8	93.9	6.1
10	45.2	54.8	93.8	6.2
20	39.2	60.8	93.4	6.6
30	31.5	68.5	92.6	7.4
40	21	79	90.5	9.5
50	8	92	80.7	19.3
60	0	100	0.3	99.7
70	0	100	0	100
80	0	100	0	100

4.5 Observations from a "Cold Run"

Several observations can be made on the basis of this test:

1. The initial design had to be changed, as the sampling loop was not effective (partial flush). Direct flushing of the liquid phase into a pre-vacuumed sampling fixture with pressure monitoring was more effective and produced better results relative to NIST Refleak predictions.
2. It was observed at times that when drawing a liquid sample from the bottom of double-ended cylinder the best results were on the third flush, not the second. The neck line shape of bottom may hold some liquid that is not well mixed with the bulk liquid in the cylinder, causing shift in reading concentration. Mixing the cylinder vigorously by shaking it up and down before drawing a liquid sample seemed to help to get a bulk liquid sample, with a composition close to the predicted one.
3. It is noticeable on the graph that the vapor observed composition[1] follows very closely the Refleak predicted composition (difference varied from -0.3 to 0.7 wt%), while the liquid phase composition from the test is shifted further away from the predicted values (difference varied from 0.2 to 5.5 wt%).
   For liquid phase the average difference between Refleak prediction and test value was 2.6 wt% with a standard deviation of 2.3 (over the mass loss range tested).
   For vapor phase the average difference was 0.3 wt% with a standard deviation of 0.35.

[1] Measurement uncertainty for the GC setup used is ±0.7 wt% for the blend of R125/600. See note on GC in Appendix A.

5 SECOND FRACTIONATION TEST (54.4°C)

90% of max. DOT fill, 1L tank of R125/600 (50.0/50.0 mass %), blend at the hot test temperature of 54.4°C.

5.1 Design

No changes to design were introduced in this test. The setup was exactly the same as at the end of the first cold run (-36.6°C), meaning that the sample loop was removed and the liquid sampling fixture was modified to include a vacuum gauge.

5.2 GC Calibration

The same calibration curve (from the first cold run) was used for this test (at 54.4°C).

5.3 Fractionation Test Procedure

No significant changes to procedure were introduced. The bath for this run was filled with water. Before taking a liquid sample, the main sample cylinder was inverted a few times to get the liquid out of the lower neck.

5.4 Fractionation Test Results

The loading weights for this run are shown in Table 5. The run was stopped at 95% mass loss. Both graph and tabulated data are shown below, in Figure 7 and Tables 6 and 7.

Table 5

Loading weights for hot run (54.4°C)

1000 cc sample cylinder 90% of max. DOT fill (88.7% for 54.4°C)					
Composition	Desired Wt. %	Weight to be charged (g)	Seq. of Charging ↑	Weight resulting (g)	Wt. % Resulting
R125	50	339.6	2	341.3	50.1
R600	50	339.6	1	340	49.9
Total Weight		679.2		681.3	

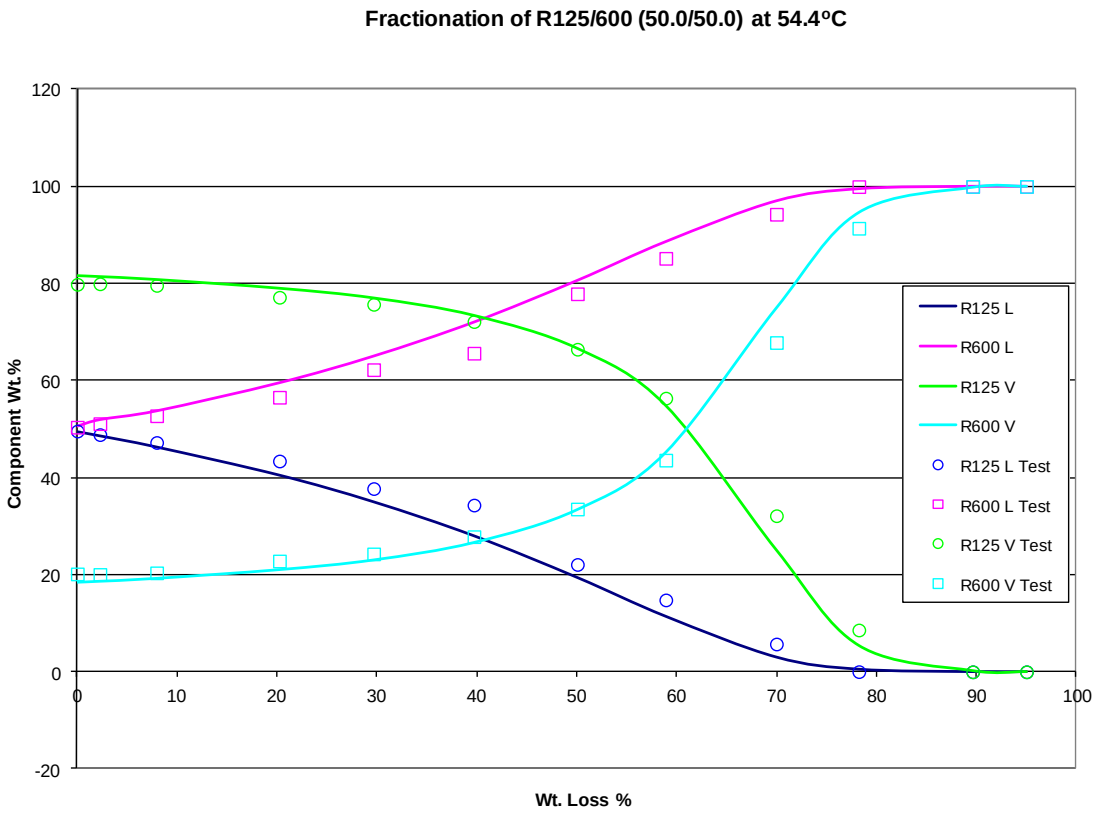

Figure 7: Fractionation of R125/600 blend at 54.4°C. *The setup for this run is the same as for the first cold run; includes removing a sampling loop and modifying liquid sampling fixture to include vacuum gauge.*

Table 6
Test data for hot run (54.4°C) (in wt%)

% Mass Loss	R125 L	R600 L	R125 V	R600 V
0	49.60	50.40	79.83	20.17
2.26	48.87	51.13	79.94	20.06
7.94	47.25	52.75	79.61	20.39
20.23	43.43	56.57	77.17	22.83
29.66	37.75	62.25	75.71	24.29
39.7	34.35	65.65	72.16	27.84
50.05	22.12	77.88	66.46	33.54
58.9	14.81	85.19	56.39	43.61
69.97	5.73	94.27	32.16	67.84
78.22	0.03	99.97	8.61	91.39
89.62	0.00	100.00	0.00	100.00
95	0.00	100.00	0.00	100.00

Table 7

Refleak 3.1 simulated data at 54.4°C for 90% max. DOT fill (88.7%) (in wt%)

% Mass Loss	R125 L	R600 L	R125 V	R600 V
0	49.45	50.55	81.7	18.3
2.26	48.6	51.9	81.5	18.5
7.94	46.3	53.7	80.9	19.1
20.23	40.5	59.5	79.1	20.9
29.66	35	65	77.1	22.9
39.7	28	72	73.5	26.5
50.05	19.4	80.6	66.7	33.3
58.9	11.4	88.6	54.9	45.1
69.97	3	97	25.1	74.9
78.22	0.5	99.5	5.4	94.6
89.62	0	100	0.2	99.8
95	0	100	0	100

Refprop calculated data at 54.4°C for 90% fill (in wt%)

% Mass Loss	R125 L	R600 L	R125 V	R600 V
2	48.7	51.3	81.5	18.5
10	45.5	54.5	80.6	19.4
20	40.7	59.3	79.2	20.8
30	34.9	65.1	77	23
40	27.9	72.1	73.5	26.5
50	19.6	80.4	66.9	33.1
60	10.6	89.4	53.2	46.8
70	3.2	96.8	25.8	74.2
80	0.3	99.7	3.7	96.3
90	0	100	0.2	99.8
95	0	100	0	100

5.5 Observations from a “Hot Run”

1. The test at higher temperature ran much smoother; the flow was steady and did not have to be pushed with mixing at lower pressure points as was needed for the cold run.

2. Again, the vapor composition coming off the test followed predicted values much closer then the liquid composition values.

   For the liquid phase, the average difference between Refleak prediction and test value was 1.86 wt% with a standard deviation of 2.01 (value of the difference varied from -0.5 to 6.5 wt% over the tested mass loss range).

   For the vapor phase, the average difference was 0.16 wt% with a standard deviation of 2.65 (value of the difference varied from -1.9 to 7.1 wt% over the tested mass loss range).

6 THIRD FRACTIONATION TEST (-36.6°C MODIFIED)

90% of max. DOT fill, 1L tank of R125/600 (50.0/50.0 mass %), blend at the cold test temperature of (-36.6°C).

6.1 Design

A mechanical mixing of the liquid in the tank was added in this run. The mixing was accomplished by putting the tank with liquid into a slightly rocking motion around the pivot point above the surface of the bath. The concept of the current setup is illustrated in Figure 8. Additionally the tubing from the valve on the liquid line to the sampling fixture was changed from 0.055" ID to 0.088" ID to make it easier to flush. The dip tube inside the tank stayed at 0.055" to minimize loses on the first flush.

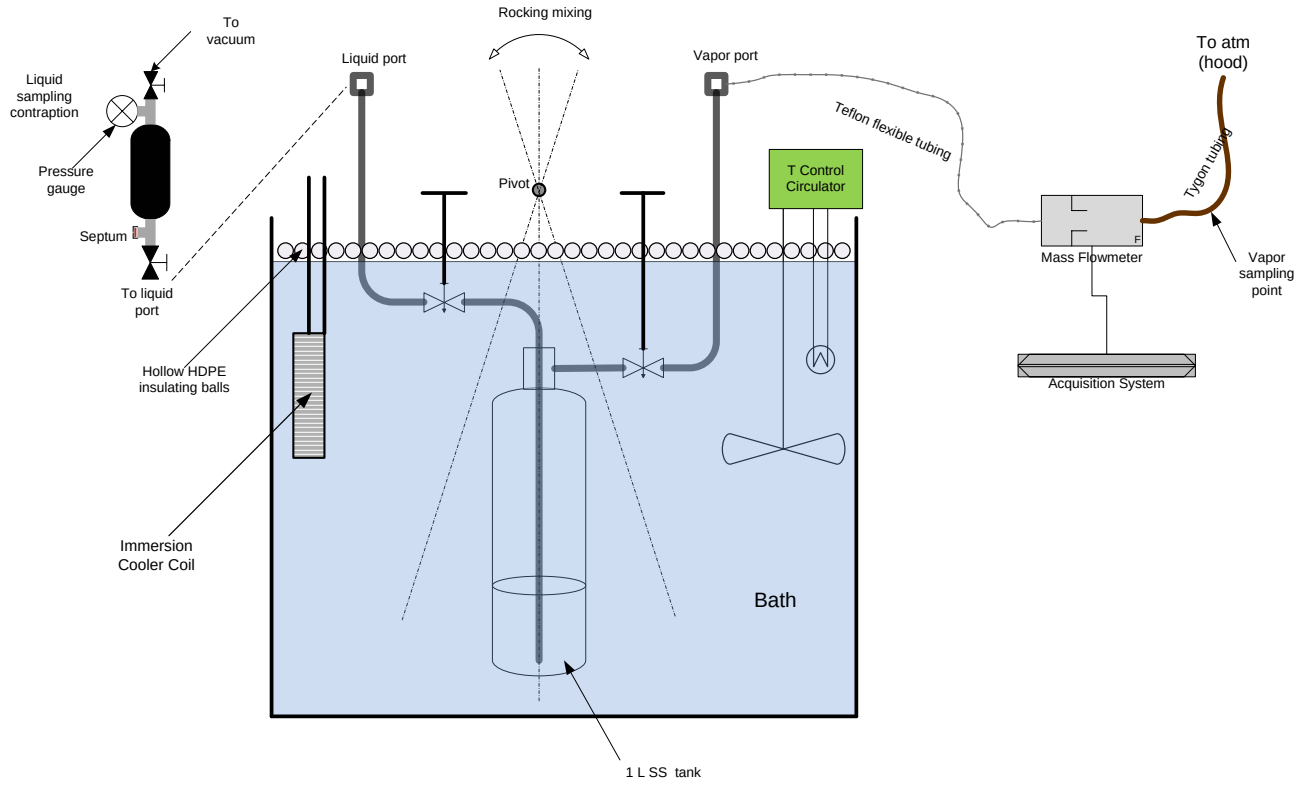

Figure 8: Fractionation setup with mixing

6.2 GC Calibration

A calibration curve was verified by running a calibration mixture (after remixing tanks) again and finding GC response.

Table 8 shows current calibration data points and Figure 9 shows the changes to the curve.

Table 8

Calibration data point updated.

Composition		Nov/Dec 2011	3/6/2012
R125 Wt%	R125 Mol %	GC R125 Area %	GC R125 Area %
0	0	0	0
26.25	14.7	15.028	14.24
49.2	31.9	32.968	32.6
77	61.9	60.222	60.79
100	100	100	100

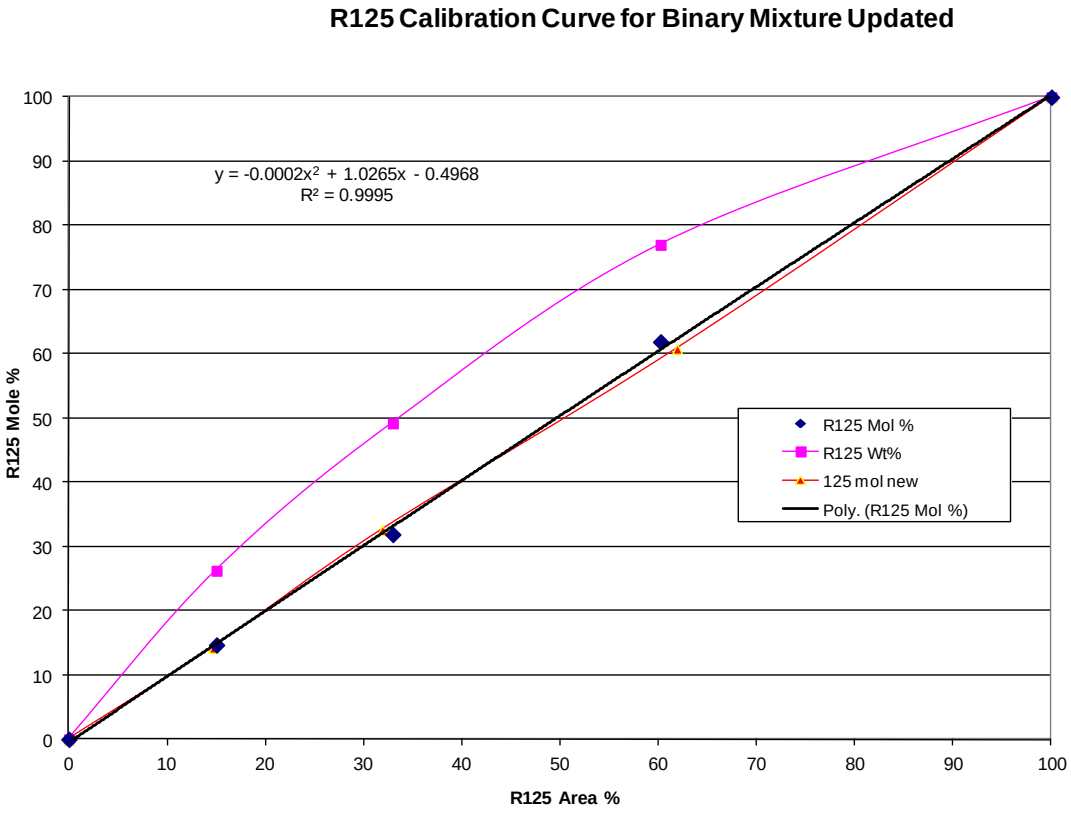

Figure 9: Updated calibration curve

The calibration curve stayed valid during the three month long time of testing.

6.3 Fractionation Test Procedure

The procedure stayed the same. There was, however a difference in the processing of GC samples. The samples were processed as quickly as possible from the moment of sample acquisition to minimize sample condensation while waiting for processing.

6.4 Fractionation Test Results (-36.6°C Modified)

The loading weights are shown in Table 9. The test stopped at 43.5% of mass loss. The results are displayed on the graph in Figure 10, and tabulated data is shown in Table 10 and 11.

Table 9

Loading weights for second cold run (-36.6°C modified)

1000 cc sample cylinder 90% of max. DOT fill (70.7% for -36.6C)					
Composition	Desired Wt. %	Weight to be charged (g)	Seq. of Charging	Weight resulting (g)	Wt. % Resulting
R125	50	270.7	2	272.8	50.2
R600	50	270.7	1	270.7	49.8
Total Weight		541.3		543.5	

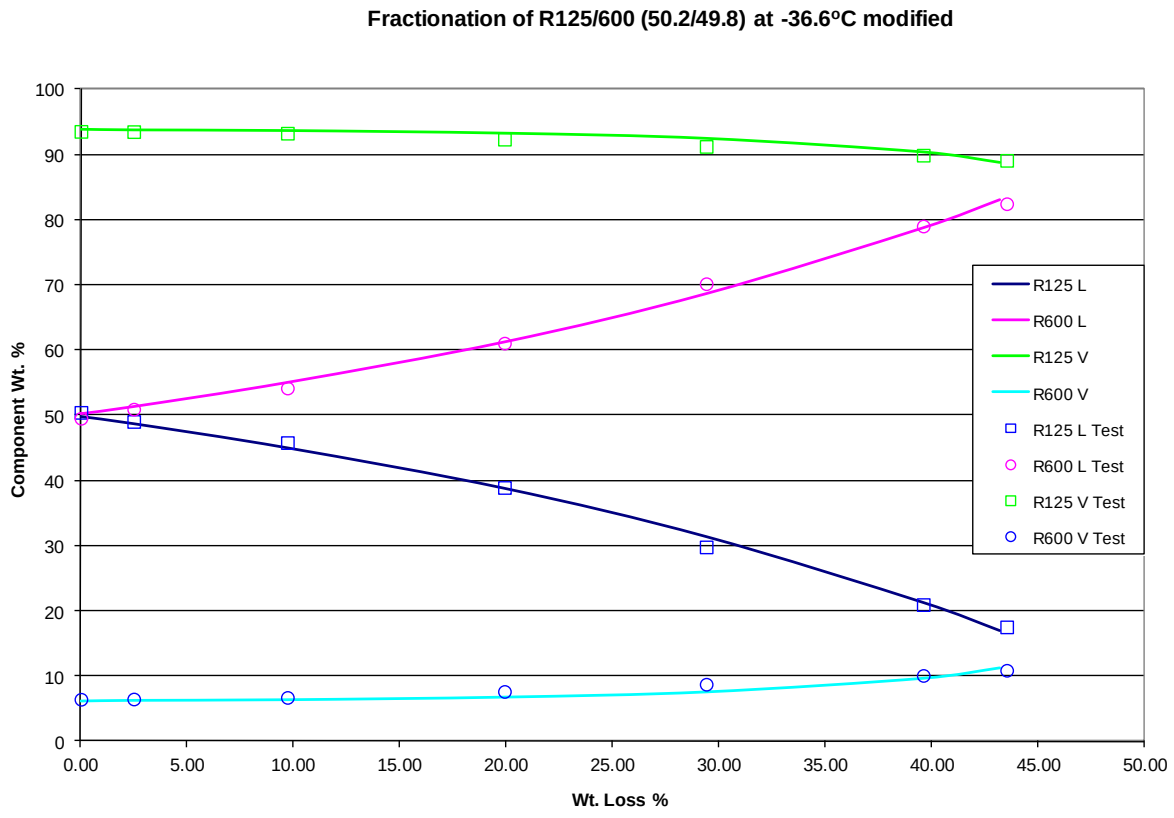

Figure 10: Fractionation of R125/600 blend cold run 2. *The setup for this run includes changes from the first run; removing a sampling loop and modifying liquid sampling fixture to include vacuum gauge, as well as addition of continuous mixing during the leak.*

Table 10
Test data for second cold run (-36.6°C mod)

% Mass Loss	R125 Liquid wt %	R600 Liquid wt%	R125 Vapor wt%	R600 Vapor wt%
0.00	50.46	49.54	93.56	6.44
2.48	49.06	50.94	93.52	6.48
9.70	45.82	54.18	93.28	6.72
19.90	38.93	61.07	92.36	7.64
29.38	29.81	70.19	91.25	8.75
39.58	20.97	79.03	89.91	10.09
43.50	17.54	82.46	89.11	10.89

Table 11

Refleak 3.1 simulated data at (-35.0°C)* for 90% max. DOT fill (70.7%) (in wt%)

% Mass Loss	R125 Liquid Wt %	R600 Liquid wt%	R125 Vapor wt%	R600 Vapor wt%
0.00	49.8	50.2	93.9	6.1
2.48	48.7	51.3	93.8	6.2
9.70	45	55	93.7	6.3
19.90	38.8	61.2	93.3	6.7
29.38	31.4	68.6	92.5	7.5
39.58	21.3	78.7	90.4	9.6
43.17	17	83	88.8	11.2

*- Refleak didn't converge at -36.6°C

Refprop calculated data at (-36.6°C) for 90% fill (in wt%)

% Mass Loss	R125 Liquid Wt %	R600 Liquid wt%	R125 Vapor wt%	R600 Vapor wt%
2	49.2	50.8	93.9	6.1
10	45.2	54.8	93.8	6.2
20	39.2	60.8	93.4	6.6
30	31.5	68.5	92.6	7.4
40	21	79	90.5	9.5
50	8	92	80.7	19.3
60	0	100	0.3	99.7
70	0	100	0	100
80	0	100	0	100

6.5 Observations from a "Cold Run Modified"

1. There is significant improvement in the composition of the liquid samples following the predicted values. The difference between predicted and test values varied for the liquid phase from -0.8 to 1.6 wt% and for the vapor value from -0.3 to 1.3 wt% (over the tested mass loss range).
   The average difference for the liquid phase (over tested mass loss range) was 0.1 wt% with a standard deviation of 0.8, the average difference for the vapor phase was 0.5 wt% with a standard deviation of 0.5.
2. Mixing seems to improve the flow of vapor at low pressure points (towards the end of the run)
3. How quickly the sample is analyzed by GC from the moment of acquisition seemed critical to get a good reading on the liquid composition (*see: discussion below*).

Table 12

Composition vs. Time to GC processing.

R125 wt%	Butane wt%	Comment
29.81	70.19	quick injection, OK
32.29	67.71	20 min later
34.18	65.82	1 hr later
33.26	66.74	2 hrs later, heated to 70°C

Discussion:

As summarized in the Table 12 above, a liquid sample at 29.38% mass loss point was acquired into the sampling fixture and quickly processed on the GC, producing a good reading. The additional samples were taken from the sampling fixture 20 min later, and then 1 hr later. Finally, the fixture with its remaining sample was heated and maintained at 70°C for 1/2 hr and retested again.

The saturation pressure for butane (less volatile component) at (-36.6°C) is 151.1 mmHg. At 21°C it is 1604.8 mmHg. The target pressure in the liquid sampling fixture was kept below ~1000 mmHg; thus it was lower than the saturation pressure at ambient temperature for butane.

Sampling the liquid phase at (-36.6°C) is a dynamic process; a liquid at this temperature flushes (evaporates) rapidly into the sampling cylinder. Decompressing liquid into a lower pressure volume will also contribute to local cooling. As a result, a sample vaporized into a sampling fixture may initially be at a much lower temperature than the original sample, thus exhibiting much lower saturation pressure and therefore condensing in the process. The longer we keep the sample at these conditions, the more butane will condense, thus changing the vapor composition.

Heating the sample in the sampling fixture revaporizes the liquefied butane (increases the saturation pressure), thus increasing the butane concentration in vapor phase. In our case, the fixture was kept in the oven only for 1/2 hour, which may not have been enough to bring all of the butane back into the vapor phase (especially butane absorbed into microstructure of steel walls). It may require baking for a longer time, possibly hours.

Typically, the observed rule of sampling at 80% of the saturation pressure of the less volatile component may need to be reexamined for this case, as the temperature of the sample being acquired changes dynamically and for an interval of time it may not be high enough to prevent a condensation.

4. Detailed drawing of the final design of fractionation vessel and liquid sampling apparatus is shown in Figure 11.

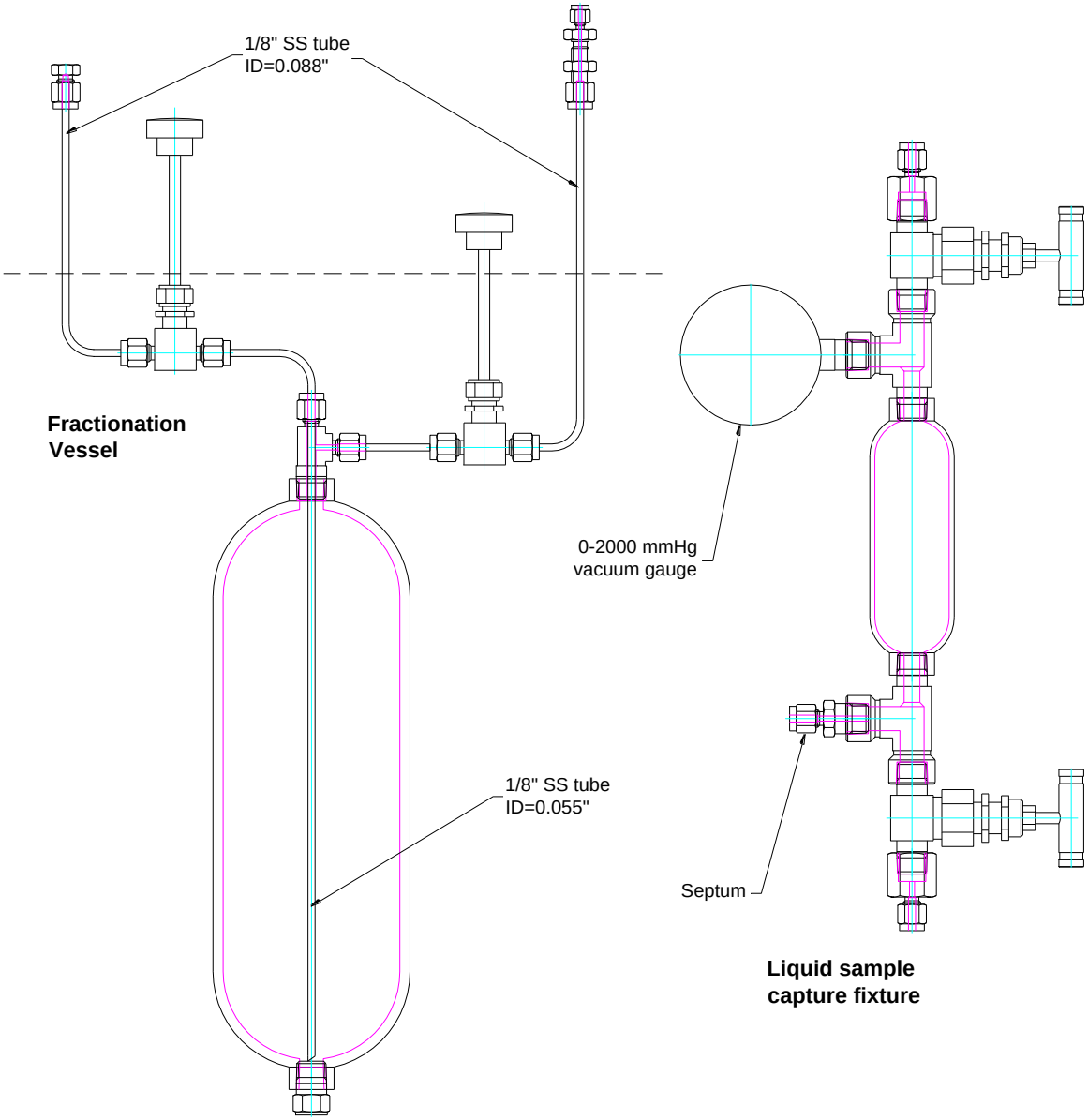

Figure 11: Detailed drawing of the final design of fractionation vessel and liquid sampling apparatus.

7 APPENDIX A INSTRUMENTATION

The instrumentation used in the setup of this test:

1 HP 5890 Series II Gas Chromatograph with TCD detector – the typical literature-based uncertainty range for concentration values resulting from GC analysis is ±2.5%. Evaluating accuracy of GC measurements is a complex process, as it includes accounting for many factors and it maybe a study in itself. Some information on the spread of results of GC analysis was included in the previous round-robin study led by SPC 177P. In this study, the measurement uncertainty for the GC setup used in SCE laboratory was determined to be within ±0.7 wt % (for the blend of R125/600 (70.0/30.0, and/or 30.0/70.0 by mass%)).

2 Immersion Cooler “Cole-Parmer” Polystat Model A12800-32 – Set point range (-40 to -100^{o}C). Temperature readout accuracy ±0.1^{o}C.

3 “Cole-Parmer” Polystat Temperature Controller Model 12112-11. Temperature readout accuracy ±0.1^{o}C.

4 Scale A&D GX-6000. Range – 6100 grams, accuracy ±0.1 grams.

5 Gas Mass Flowmeter “Omega” FMA 1700/1800. Range 0-500mL. Accuracy ±1.5 of full scale.

6 Pressure-Lok® Precision analytical syringe – 2 mL.

7 National Instruments NI9215 Acquisition Module. Voltage range 0-10V.

8 APPENDIX B PRICE SHEET

Swagelok

REMIT TO:

CAMBRIDGE VALVE & FITTING INC.
PO Box 595
BILLERICA, MA 01821
PH: 781-272-8270 FX: 978-667-5261
info@cambridgevalve.com

QUOTE
98501170

Cust Order No

Bid Number

Sold To: TIAX01
TIAX LLC
EMAIL INVOICE
MA

Ship To: TIAX01
TIAX LLC
15 ACORN PARK
CAMBRIDGE MA 02140

Quote Date	FOB Description	Expiration Date	Terms	Quote Number
01/29/10	Shipping Point	02/28/10	NET 30 DAYS	98501170

Item	Description	Quantity	Unit Price		Amount
1	304L-HDF4-1000 304 SS Double-end Cylinder, 1/4 in. FNPT, 1000 cm3	1	297.80		297.80
2	304L-HDF8-1000 304 SS Double-end Cylinder, 1/2 in. FNPT, 1000 cm3	1	297.80		297.80
3	SS-400-3-4TMT Stainless Male Run Tee, 1/4 in. OD - 1/4 in. Male	1	26.90		26.90
4	SS-43GS4 SS 1-Piece 40G Series Ball Valve, 1.4 Cv, 1/4 in.	1	86.00		86.00
5	SS-4F-T7-2 Stainless Inline Filter, 1/4 in. Tube Fit.-1/4 in.	1	60.20		60.20
6	SS-4F-T7-7 Stainless Inline Filter, 1/4 in. Tube Fit.-1/4 in.	1	60.20		60.20

REMIT TO:

CAMBRIDGE VALVE & FITTING INC.
PO Box 595
BILLERICA, MA 01821
PH: 781-272-8270 FX: 978-667-5261
info@cambridgevalve.com

QUOTE
98501170

Cust Order No

Bid Number

Sold To: TIAX01
TIAX LLC
EMAIL INVOICE
MA

Ship To: TIAX01
TIAX LLC
15 ACORN PARK
CAMBRIDGE MA 02140

Quote Date	FOB Description	Expiration Date	Terms	Quote Number
01/29/10	Shipping Point	02/28/10	NET 30 DAYS	98501170

Item	Description	Quantity	Unit Price		Amount
7	SS-SS4 Stainless Very Fine Metering Valve, 1/4 in. Tube F	1	124.00		124.00
8	SS-401-PC Stainless Port Connector, 1/4 in. OD	3	5.50		16.50
9	SS-200-R-4BT Stainless Bored-Through Reducer, 1/8 in. OD - 1/4	1	10.20		10.20
10	SS-41S2-A Stainless 1-Piece Ball Valve, 1/8 in. Tube Fitting	1	88.30		88.30
11	SS-41S2 Stainless 1-Piece Ball Valve, 1/8 in. Tube Fitting	2	91.19		182.38
12	SS-200-3 Stainless Union Tee, 1/8 in. OD	1	23.60		23.60

REMIT TO:

CAMBRIDGE VALVE & FITTING INC.
PO Box 595
BILLERICA, MA 01821
PH: 781-272-8270 FX: 978-667-5261
info@cambridgevalve.com

QUOTE
98501170

Cust Order No

Bid Number

Sold To: **TIAX01**
TIAX LLC
EMAIL INVOICE
MA

Ship To: **TIAX01**
TIAX LLC
15 ACORN PARK
CAMBRIDGE MA 02140

Quote Date	*FOB Description*	*Expiration Date*	*Terms*	*Quote Number*
01/29/10	**Shipping Point**	**02/28/10**	**NET 30 DAYS**	**98501170**

Item	*Description*	*Quantity*	*Unit Price*		*Amount*
13	SS-201-PC Stainless Port Connector, 1/8 in. OD	4	7.40		29.60
14	SS-4-P Stainless Pipe Plug, 1/4 in. M NPT	1	4.70		4.70
15	SS-8-P Stainless Pipe Plug, 1/2 in. M NPT	1	9.00		9.00

Quote Total
1,317.18

RETURN POLICY: Standard price list items with a good prior volume sales history may be returned for credit, less a 20% restocking charge. Orders for special non-price list items are non-returnable. All returns are subject to inspection and approval and must be completed within 90 days of the shipping date.

Customer Contact & Phone Number	*Sales Agents*
JOSE BAIROS **617-498-7030**	**010**

CHICAGO FLUID SYSTEM TECHNOLOGIES
BADGER FLUID SYSTEM TECHNOLOGIES

PH: 630-545-0003 FX: 630-545-0004

INVOICE
1553195

PLEASE REMIT TO:
SLOT # 303248 - P.O. BOX 66973 - CHICAGO, IL 60666-0973 - PHONE (630) 545-0003

Cust Order No CC:ANDRWE KUSMIERZ

Requisition Number

Our Order No 100307031

Sold To: SAFETY
SAFETY CONSULTING ENGINEERING
2131 HAMMOND DRIVE
SCHAUMBURG IL 60173

Ship To: SAFETY
SAFETY CONSULTING ENGINEERING
2131 HAMMOND DRIVE
SCHAUMBURG IL 60173

FOB FOB Ship Point

Date Shipped	Shipping Instructions	Territory	Order Date	Sales Tax Code	Invoice Date	Invoice Number
01/27/12	UPS	02	01/25/12	001	01/27/12	1553195

Item	Description	QUANTITY Ordered	Balance Due	Shipped	Unit Price	Disc	Amount
1	SS-200-3-4TMT MALE RUN TEE,SS,1/8in OD 1/4in MALE NPT x 1/8in TU 5 BUSINESS DAYS EMAIL INVOIE: AKUSMIERZ@CHILWORTHGLOBAL.COM AUTH: 142693	2		2	41.40		82.80

Contact us or visit the Swagelok Web site at www.swagelok.com for Swagelok product warranty information. NO OTHER WARRANTIES APPLY AND IN NO EVENT SHALL SELLER OR MANUFACTURER BE LIABLE FOR ANY CONSEQUENTIAL OR INCIDENTAL DAMAGES. U.N. Convention on Contracts for the Sale of International Goods is specifically excluded.

Terms	Sub Total	Sales Tax Rate	Sales Tax	Shipping & Handling	TOTAL
AMERICAN EXPRESS	82.80	8.2500%	6.83	8.93	98.56

Standard price list items with a high volume sales history may be returned for credit, less a restocking charge. Orders for special items are non-cancellable and non-refundable. All claims and shortages must be reported within 24 hours of receipt of shipment. Hold all materials, including the packing slip, for our inspection.

Customer Contact & Phone Number
ANDREW KUSMIERZ
847-925-8100

Customer Copy

Tax Exemption Number
008 100.00

CHICAGO FLUID SYSTEM TECHNOLOGIES

BADGER FLUID SYSTEM TECHNOLOGIES
360 WINDY POINT DRIVE
GLENDALE HEIGHTS IL 60139
PH: 630-545-0003 FX: 630-545-0004

ORDER
100307031

Cust Order No CC:ANDRWE KUSMIERZ

Bid Number

Sold To: SAFETY
SAFETY CONSULTING ENGINEERING
2131 HAMMOND DRIVE
SCHAUMBURG IL 60173

Ship To: SAFETY
SAFETY CONSULTING ENGINEERING
2131 HAMMOND DRIVE
SCHAUMBURG IL 60173

Order Date	FOB Description	Terms	Order Number
01/25/12	FOB Ship Point	AMERICAN EXPRESS	100307031

Item	Description	Quantity	Unit Price	Disc	Amount
1	SS-200-3-4TMT MALE RUN TEE,SS,1/8in OD x 1/4in MALE NPT x 1/8in TUBE OD	2	41.40	0	82.80

5 BUSINESS DAYS

Rel	Quantity	Shipped	Target Date
1	2		02/03/12

EMAIL INVOIE:
AKUSMIERZ@CHILWORTHGLOBAL.COM
AUTH: 142693

Order Total
82.80

Standard Price List items with a high volume sales history may be returned for credit, less a restocking charge. Orders for Special items are non-cancellable and non-refundable. All claims and shortages must be reported within 24 hours of receipt of shipment. Hold all materials, including the packing slip, for our inspection.

Customer Contact & Phone Number	Sales Agents
ANDREW KUSMIERZ 847-925-8100	008