Contract No:

This document was prepared in conjunction with work accomplished under Contract No. 89303321CEM000080 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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Next Generation Solvent Vapor Pressure Testing

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July 2022
SRNL-STI-2022-00243, Revision 0

SRNL.DOE.GOV

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Prepared for
U.S. Department of Energy

SRNL-STI-2022-00243
Revision 0

Keywords: *CSSX, NGS, SWPF*

Retention: *Permanent*

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Savannah River National Laboratory is operated by Battelle Savannah River Alliance for the U.S. Department of Energy under Contract No. 89303321CEM000080.

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EXECUTIVE SUMMARY

Previous work by Savannah River National Laboratory (SRNL) indicated that the actual Next Generation Solvent vapor pressure would be higher than the Original Caustic Side Solvent Extraction (CSSX) solvent vapor pressure, but below a bounding vapor pressure using Raoult's Law. Since solvent vapor pressure has a significant impact on Composite Lower Flammability Limits (CLFL) and attendant accident analyses, obtaining an additional margin from the bounding NGS vapor pressure would be valuable. In order to quantify how much margin might be gained from the NGS bounding solvent, SRNL researchers were requested to perform vapor pressure testing with the Next Generation Solvent (NGS) by Savannah River Mission Completion (SRMC). The vapor pressure curve for the NGS formulation set to be deployed at the Salt Waste Processing Facility (SWPF) has been determined by SRNL up to 55°C (131°F) using headspace Gas Chromatography (GC). It was expected that NGS would have a higher vapor pressure than the Original CSSX solvent; however, experimental results indicate a lower vapor pressure. At this time, it is uncertain if this difference is due to the 7x increase in concentration of the large calixarene in the solvent (0.007M BOBCalix in Original CSSX solvent vs. 0.05M MaxCalix in NGS) or to minor batch-to-batch variations in Isopar-L constituents. The NGS and the Original CSSX solvent vapor pressure data were fitted to the Antoine Equation. The Antoine equation gives a more accurate representation of the expected vapor pressure of the solvents outside of the temperature range tested. The Antoine equation fitting for NGS is given below:

$$P = 10^{6.364 - \frac{1788.4}{(T+219.3)}}$$

Where,

p is the vapor pressure (partial pressure) of NGS in mmHg and
T is the temperature in °C.

It is recommended that SRMC either continue using the more conservative Isopar-L vapor pressure calculations at SWPF with the equation developed for the Original CSSX solvent, or the equation presented above for the NGS solvent. Additionally, it is recommended to study the variability in Isopar-L vapor pressure between lots.

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LIST OF ABBREVIATIONS

CSSX	Caustic-Side Solvent Extraction
GC-FID	Gas Chromatography – Flame Ionization Detector
MCU	Modular CSSX Unit
NGS	Next Generation Solvent
SRMC	Savannah River Mission Completion
SRNL	Savannah River National Laboratory
SWPF	Salt Waste Processing Facility
TTR	Technical Task Request

1.0 Introduction

The Next Generation Solvent (NGS) is set to replace the Original Caustic Side Solvent Extraction (CSSX) solvent at the Salt Waste Processing Facility (SWPF). NGS was used in the Modular CSSX unit (MCU, which SWPF has replaced) in a blend with the Original CSSX solvent, and as a standalone mixture. The modifier concentration in the NGS formulation used at MCU was 0.5 M. Table 1-1 gives the solvent compositions for both the current NGS formulation and the Original CSSX solvent.

Table 1-1. Solvent Composition Comparison

Component	**Function**	**Original Solvent Concentration**	**NGS Concentration**
MaxCalix 1,3-*alt*-25,27-bis(3,7-dimethyloctyl-1-oxy) calix[4]arenebenzo-crown-6	Extractant	-	0.05 M
BOBCalixC6 Calix[4]arene-bis(*t*-octylbenzo-crown 6)	Extractant	0.007 M	-
Cs-7SB 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol	Modifier	0.75 M	0.65 M[†]
TiDG *N,N',N''*-Tris(3,7-dimethyloctyl)guanidine	Suppressor	-	0.003 M
TOA Tri-n-octylamine	Suppressor	0.003 M	-
Isopar-L C_{12}-isoparaffinic hydrocarbon	Diluent	~ 69 wt%	~ 71 wt%

[†] The NGS formulation set to be used at SWPF has a higher modifier concentration (increased to match Original CSSX solvent density) than the previous formulation used at MCU.

Technical gaps have been identified in the implementation of NGS at SWPF.[1,2] Savannah River National Laboratory (SRNL) has recently performed a number of literature reviews to address these gaps with respect to flammability concerns at SWPF.[3-5] Current SWPF flammable gas generation calculations use an Isopar-L vapor pressure curve based on experimental testing with the Original CSSX solvent.[6] No such testing to date has been performed with NGS. Previous work by SRNL indicated that the actual NGS vapor pressure would be higher than the Original CSSX solvent vapor pressure, but below a bounding NGS solvent vapor pressure using Raoult's Law (Figure 1-1).[5] Since solvent vapor pressure has a significant impact on Composite Lower Flammability Limits (CLFL) and attendant accident analyses, obtaining an additional margin from the bounding NGS vapor pressure would be valuable. It is suggested that the decrease in Cs-7SB concentration for NGS compared to the Original CSSX solvent would lead to a slightly higher vapor pressure at all temperatures in SWPF vessels. In order to quantify how much margin might be gained from the NGS bounding solvent, SRNL researchers were requested to determine the Isopar-L vapor pressure for NGS by Savannah River Mission Completion (SRMC), via a Technical Task Request (TTR).[7]

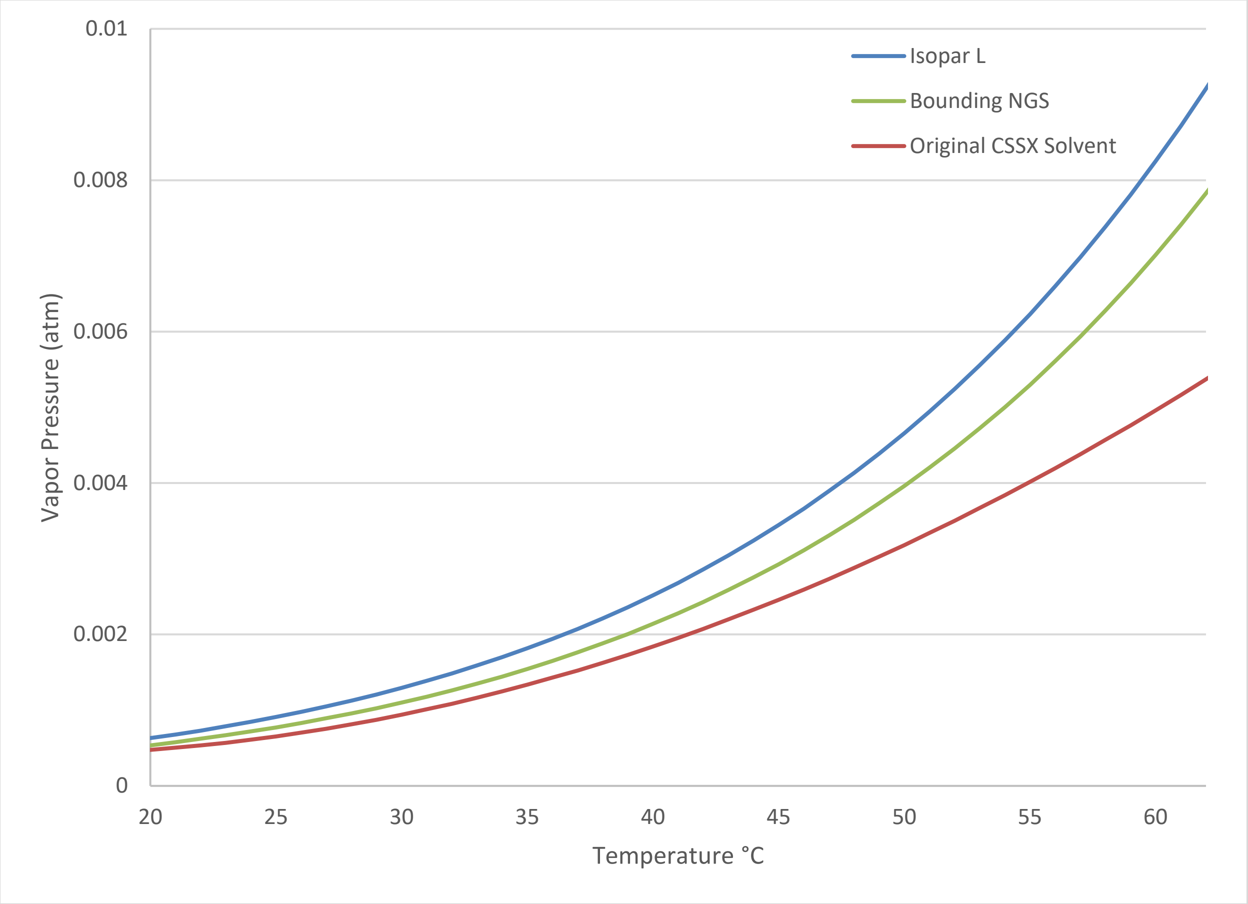

Figure 1-1. Comparison of the Vapor Pressure as a Function of Temperature of Pure Isopar-L, Bounding NGS Vapor Pressure Curve, and the Original CSSX Solvent

The vapor concentration of Isopar-L above the Original CSSX solvent was determined using Gas Chromatography with Flame Ionization Detector (GC-FID) at 62°F (16.7°C), 82°F (27.8°C), and 110°F (43.3°C) in 2007 at the Materials and Chemistry Laboratory, Inc (MCL, Inc.).[6] Additionally, MCL, Inc. had previously performed flash point analyses on samples of irradiated and non-irradiated CSSX solvent.[8] This testing found no statistically-significant observable difference between the flash points or irradiated and non-irradiated solvent. SWPF currently uses (in flammability safety calculations[9]) the data from these tests to give the following equation for determining vapor pressure

$$p = 2.193\ x\ 10^{-6} * T^2 - 6.335\ x\ 10^{-5} * T + 8.673\ x\ 10^{-4} \tag{1}$$

Where,

p is the vapor pressure (partial pressure) of the Original CSSX solvent in atm and
T is the temperature in °C.

Presented here is testing performed by SRNL using GC-FID to determine the vapor concentration of Isopar-L above NGS at 16.7, 30, 43, and 55°C.

2.0 Experimental Procedure

2.1 NGS Solvent Preparation

MaxCalix, TiDG, and Cs-7SB were procured from Marshallton Laboratories and used as received. Isopar-L was taken from barrels delivered to SRNL from SWPF and used as received. The NGS solvent formulation, as shown in Table 1-1, was prepared by weighing the appropriate amounts of organic solvent into a glass volumetric flask and dissolving with Isopar-L.

2.2 GC-FID NGS Headspace Experiments

The GC was calibrated with pure Isopar-L as shown in Figure 2-1 and Table 2-1. For the calibration, high accuracy was maintained in the peak area range between points 1 and 5. Calibration point 6, however, was quantified as a negative value for the calculated micrograms injected. Therefore, all NGS data presented herein was maintained at a peak area above calibration point 6. Example chromatograms for Isopar-L and NGS are given in the appendix.

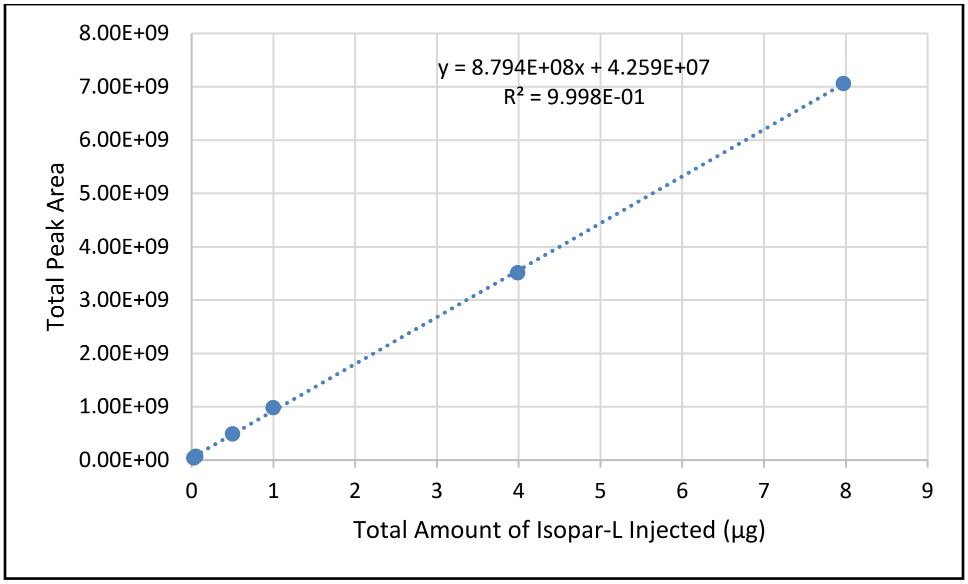

Figure 2-1. Plot of the GC-FID calibration with Isopar-L

Table 2-1. Calibration of Isopar-L by GC-FID

Calibration Point	Total Isopar Injected (µg)	Total Peak Area	Total Isopar Injected Calculated (µg)
1	7.97	7.06E+09	7.80E+00
2	3.99	3.51E+09	3.86E+00
3	0.996	9.81E+08	1.05E+00
4	0.498	4.89E+08	4.99E-01
5	0.049	6.86E+07	3.18E-02
6	0.025	3.69E+07	-3.44E-03

The instrument setup is shown in Figure 2-2. The GC samples were prepared by placing 5 mL of the NGS solvent into a 20 mL crimp-top headspace vial (which actually holds a total volume of 21 mL). Vials were initially equilibrated at room temperature (22°C) for 24 hours in the room temperature tray labeled below. After the initial equilibration, vials were brought to their desired testing temperatures (16.7°C, 30°C, 43°C, and 55°C) using either the Peltier cooling tray or heating module labeled below and allowed to equilibrate for at least 4 hours. After equilibration, a 300 µL aliquot of the headspace gas was sampled and injected into the GC. Eight replicates were performed at each testing temperature with blanks performed between every four samples. No blanks were observed with a quantifiable peak area during testing.

Figure 2-2. Instrument Setup

2.3 Calculation of Vapor Pressure from Concentration of Isopar-L in Headspace

Vapor pressures were determined as previously described.[9] The partial pressure of Isopar-L in the vapor can be defined as

$$p_i = x_i p \tag{2}$$

Where,

p_i is the partial pressure of Isopar-L in the vapor,
x_i is the mole fraction of the Isopar-L in the vapor, and
p is the total pressure of the vapor.

It is assumed that only Isopar-L in NGS contributes to the vapor pressure of NGS such that the vapor pressure of NGS is equal to the partial pressure of Isopar-L in the headspace over the solvent. For ideal gas mixtures, the mole fraction is equal to the volume fraction. The vapor pressure was calculated by dividing the measured Isopar-L concentrations by the molecular weight of Isopar-L (163 g/mol;[9] it should be noted that current safety data sheet (SDS) for Isopar-L has a calculated molecular weight of 162 g/mol) and using the following form of the ideal gas law.

$$P = \frac{nRT}{V} \tag{3}$$

2.4 Quality Assurance

The functional classification specified in the TTR is Safety Significant. Thus, this document was reviewed by Design Verification by Document Review. Calculations to convert raw GC data to vapor pressure data are reviewed by Design Verification. The requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

The results from the vapor pressure data are given below in Table 3-1. The values given for the eight replicates are calculated using the total peak area for Isopar-L, the calibration data given above, and the injection volume. The values represented in red font were confirmed to be outliers using Grubbs' Test. However, in calculating the vapor pressure curves found below, only the most egregious outliers, which are also bolded and italicized in Table 3-1, were excluded from the individual data. These egregious outliers are excluded from the "Mean (-outliers)" category in Table 3-1. The Isopar-L concentrations were converted to the Isopar-L vapor pressure in atmospheres as described above in Section 2.3. A plot of the vapor pressure vs. temperatures is given in Figure 3-1.

Table 3-1. NGS Isopar-L Vapor Pressure Data

Test ID	**Test Temperature**			
	16.7°C	**30°C**	**43°C**	**55°C**
	Isopar-L Concentration (µg/mL) in Headspace, at 16 mL of Headspace			
NGS-A	0.43	1.22	2.73	4.70
NGS-B	0.91	1.22	3.55	6.27
NGS-C	***49.64***	1.21	2.89	4.43
NGS-D	0.59	1.43	2.74	4.69
NGS-E	0.58	1.35	2.54	5.03
NGS-F	0.54	1.72	2.36	4.65
NGS-G	0.60	1.44	2.37	5.06
NGS-H	0.45	***4.43***	2.39	4.67
Mean	6.72	1.75	**2.70**	**4.94**
Std. Dev.	17.35	1.10	0.40	0.58
%RSD	258.16%	62.48%	14.76%	11.69%
Mean (-outliers)	**0.59**	**1.37**	N/A	N/A
Std. Dev. (-outliers)	0.16	0.18		
%RSD (-outliers)	27.18%	13.45%		

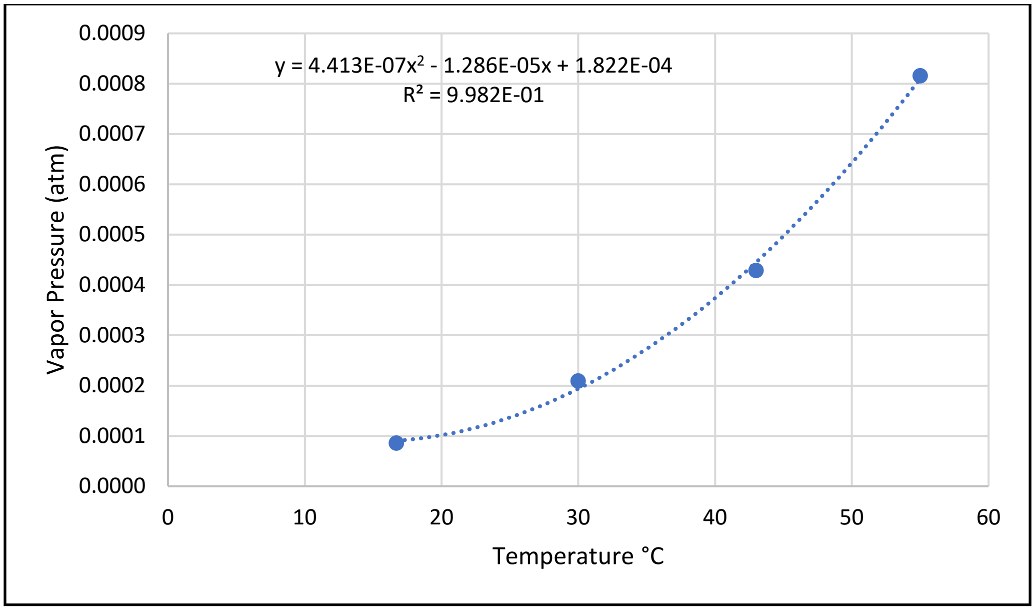

Figure 3-1. Plot of the NGS Vapor Pressure vs. Temperature

The above curve can be fitted in the same manner as the Original CSSX solvent to give the following equation for determining vapor pressure:

$$p = 4.413\ x\ 10^{-7} * T^2 - 1.286\ x\ 10^{-5} * T + 1.822\ x\ 10^{-4} \tag{4}$$

Like the Original CSSX vapor pressure equation,[9] this equation should not be used for extrapolation outside of the temperature range tested, 16.7– 55°C (62-131°F). The use of these equations above their temperature range would underpredict the actual vapor pressure.

A comparison of the NGS vapor pressure data to the Original CSSX solvent vapor pressure data by MCLinc is given in Figure 3-2. It was expected that NGS would have a higher vapor pressure than the Original CSSX solvent, but the NGS vapor pressure curve is actually lower than the Original CSSX solvent curve. This may be due to the 7x increase in concentration of the large calixarene in the solvent (0.007M BOBCalix in Original CSSX solvent vs. 0.05M MaxCalix in NGS) since larger molecules can cause further deviation from Raoult's Law.[10] However, it should be noted that Isopar-L is a distillation fraction of aliphatic branch-chained hydrocarbon compounds ($C_{10}H_{22}$ to $C_{15}H_{32}$) and there is a potential for variability between sample lots in the compounds that compose Isopar-L, as well as in the ratios of these compounds within Isopar-L. So for example, an Isopar-L lot that contains a large concentration of the lower molecular weight hydrocarbons that make up the distillation fraction would be expected to have a larger vapor pressure than another lot that contains a larger concentration of the higher molecular weight hydrocarbons. Testing with multiple Isopar-L lots would be necessary to determine how significant of an impact lot variability has on the vapor pressure of the solvent. At 25°C the vapor pressure of n-decane is 9x that of n-dodecane, so the difference between lots could be quite significant. Thus, a true comparison of the two solvents would require the use of the same Isopar-L lot for both solvents.

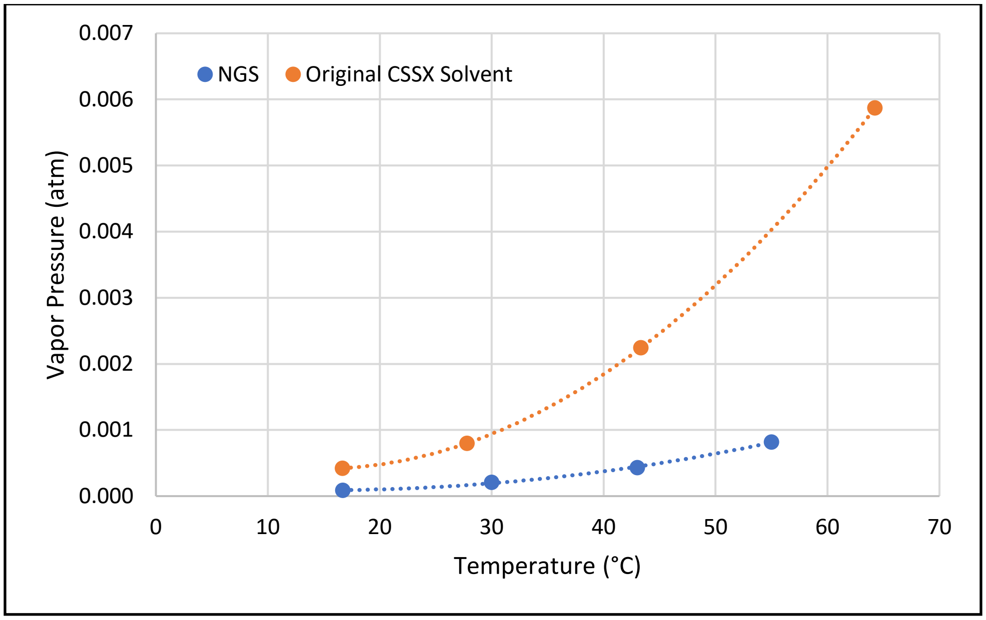

Figure 3-2. Comparison of Original CSSX Solvent and NGS Vapor Pressure Curve

Additional headspace GC data was obtained at 82°C for NGS and is presented in Table 3-2. This data was obtained during initial setup of the instrument. The headspace vials were equilibrated for 2hr (compared to 4hr for all other runs) at the test temperature and is perhaps why there is a large variance in the Isopar-L concentrations in Table 3-2.

Table 3-2. NGS Isopar-L Vapor Pressure Data at 82°C

82°C	
ug/mL Isopar-L in Headspace, at 16mL of headspace	
NGS-A	25.59
NGS-B	***64.67***
NGS-C	21.56
NGS-D	29.33
NGS-E	30.11
NGS-F	12.74
NGS-G	15.89
NGS-H	18.11
Mean	27.25
Std. Dev.	16.35
%RSD	59.99%
Mean (-outliers)	21.90
Std. Dev. (-outliers)	6.72
%RSD (-outliers)	30.67%

If we include the data obtained at 82°C for NGS, a more accurate picture of the vapor pressure outside the range tested can be obtained by fitting the data to the Antoine Equation:

$$Log(p) = A - \frac{B}{(T+C)} \quad (5)$$

Where,

p is vapor pressure in mmHg,
T is the temperature in °C, and
A, B, C are the Antoine constants.

Antoine constants for pure Isopar-L were previously developed to approximate vapor pressure data from Exxon.[11] Their values are given in Table 3-3.

Table 3-3. Antoine Constants for Pure Isopar-L

A	7.482
B	1867
C	219.3

By setting *C* equal to the pure Isopar-L value of 219.3, the Antoine constants *A* and *B* can be determined for NGS and the Original CSSX solvent. Rearranging the Antoine equation gives the following equations that can be used to determine the vapor pressure of the solvents at a temperature.

NGS:

$$P = 10^{6.364 - \frac{1788.4}{(T+219.3)}} \tag{6}$$

Original CSSX solvent:

$$P = 10^{6.42 - \frac{1633.1}{(T+219.3)}} \tag{7}$$

Table 3-4 gives a comparison of the measured values to the calculated values using either the Antoine equation or the polynomial fittings given above. A plot comparison using the Antoine equation for NGS and the Original CSSX solvent is given in Figure 3-3.

Table 3-4. Comparison of Measured vs. Calculated Vapor Pressure

Temperature (°C)	**NGS Vapor Pressure (atm)**				
	Measured	Antoine Equation		Polynomial Fitting	
		Calculated	% Deviation	Calculated	% Deviation
16.7	8.56E-05	8.04E-05	-6.07%	9.05E-05	5.75%
30	2.09E-04	2.04E-04	-2.47%	1.94E-04	-7.43%
43	4.29E-04	4.62E-04	7.79%	4.45E-04	3.77%
55	8.16E-04	9.19E-04	12.65%	8.10E-04	-0.73%
82	3.92E-03	3.53E-03	-9.91%	2.09E-03	-46.51%
Temperature (°C)	**Original CSSX Solvent Vapor Pressure (atm)**				
	Measured	Antoine Equation		Polynomial Fitting	
		Calculated	% Deviation	Calculated	% Deviation
16.67	4.23E-04	4.15E-04	-1.8 %	4.21E-04	-0.53 %
27.78	7.99E-04	8.50E-04	6.41 %	8.00E-04	0.09 %
43.33	2.24E-03	2.09E-03	-6.7 %	2.24E-03	-0.2 %
64.24	5.87E-03	6.02E-03	2.53 %	5.85E-03	-0.38 %

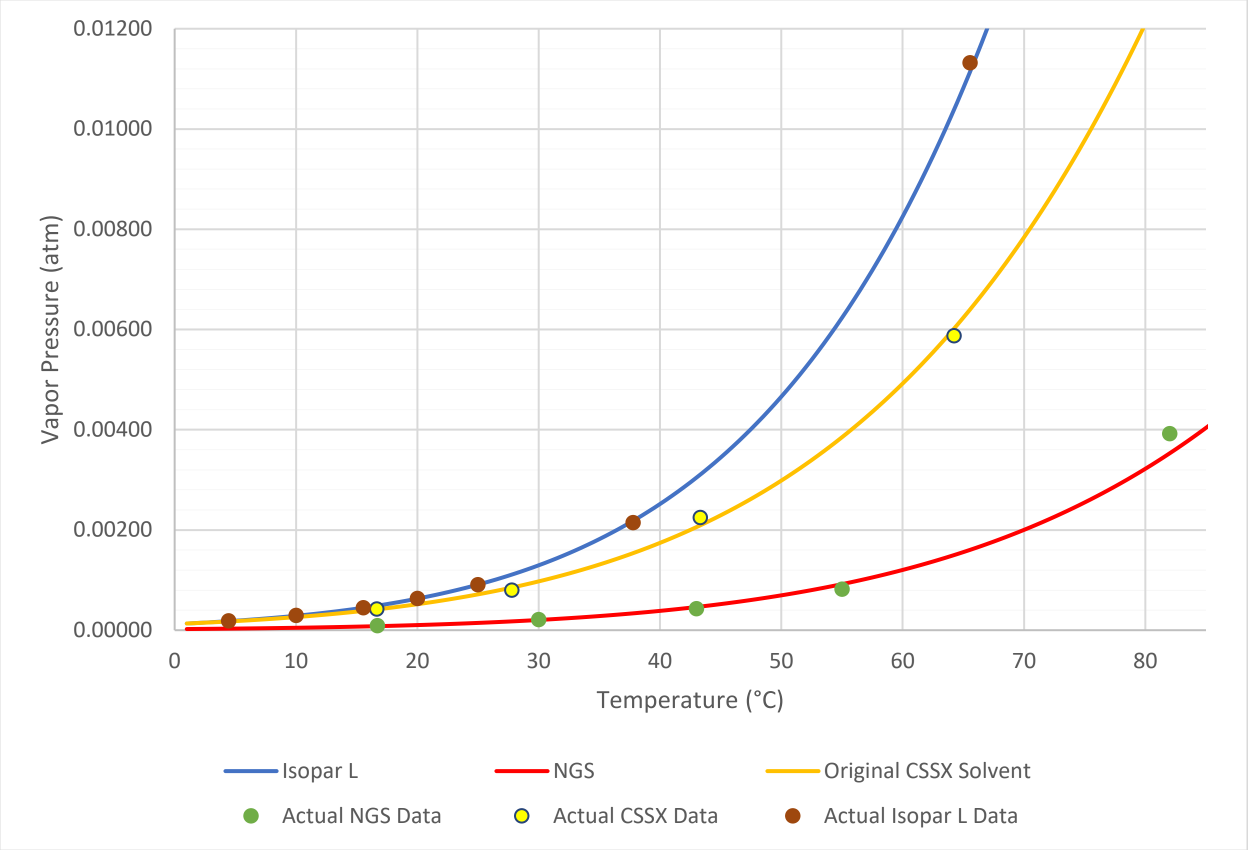

Figure 3-3. Vapor Pressure Comparison of Solvents and Pure Isopar-L

4.0 Conclusions

The vapor pressure curve for the NGS solvent formulation planned to be deployed at SWPF has been determined by SRNL up to 55°C (131°F) using headspace GC. NGS appears to have a lower vapor pressure in comparison to the Original CSSX solvent, which is suspected to be due to the 7x increase in concentration of the large calixarene in the solvent (0.007M BOBCalix in Original CSSX solvent vs. 0.05M MaxCalix in NGS). However minor batch-to-batch variations in Isopar-L constituents could also play a factor in the lower NGS vapor pressure values reported here.

The NGS and the Original CSSX solvent vapor pressure data were fitted to the Antoine Equation. The Antoine equation gives a more accurate representation of the expected vapor pressure of the solvents outside the temperature range tested. The Antoine equation fitting for NGS is given below:

$$P = 10^{6.364 - \frac{1788.4}{(T+219.3)}}$$

Where,

p is the vapor pressure (partial pressure) of NGS in mmHg and
T is the temperature in °C.

It is recommended that SRMC either continue using the more conservative Isopar-L vapor pressure calculations at SWPF with the equation developed for the Original CSSX solvent or the equation presented above for the NGS solvent. Additionally, it is recommended to study the variability in Isopar-L vapor pressure between lots.

5.0 References

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Appendix A. Example GC Chromatograms

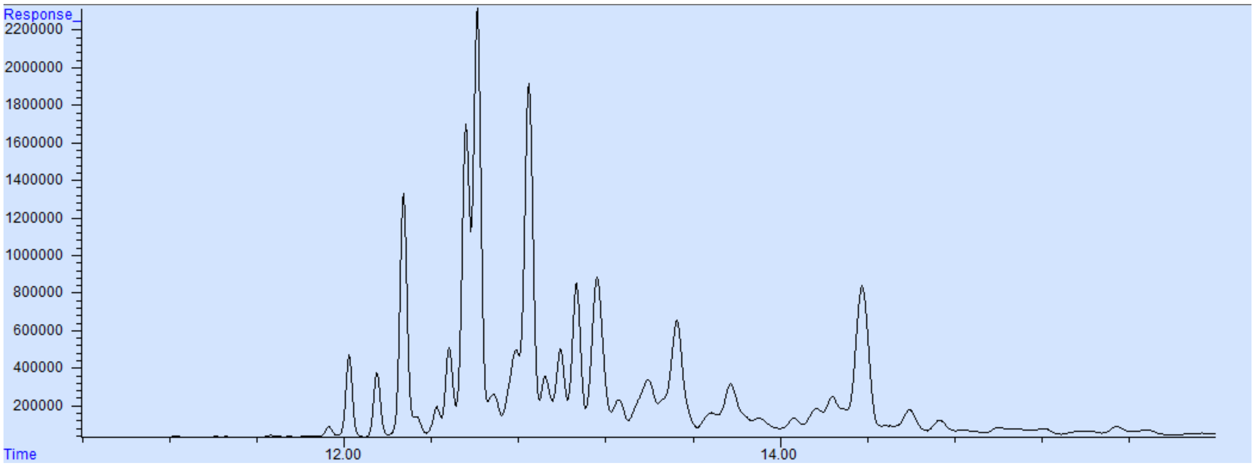

Figure A-1. GC Chromatogram of NGS Showing Peaks from Isopar-L

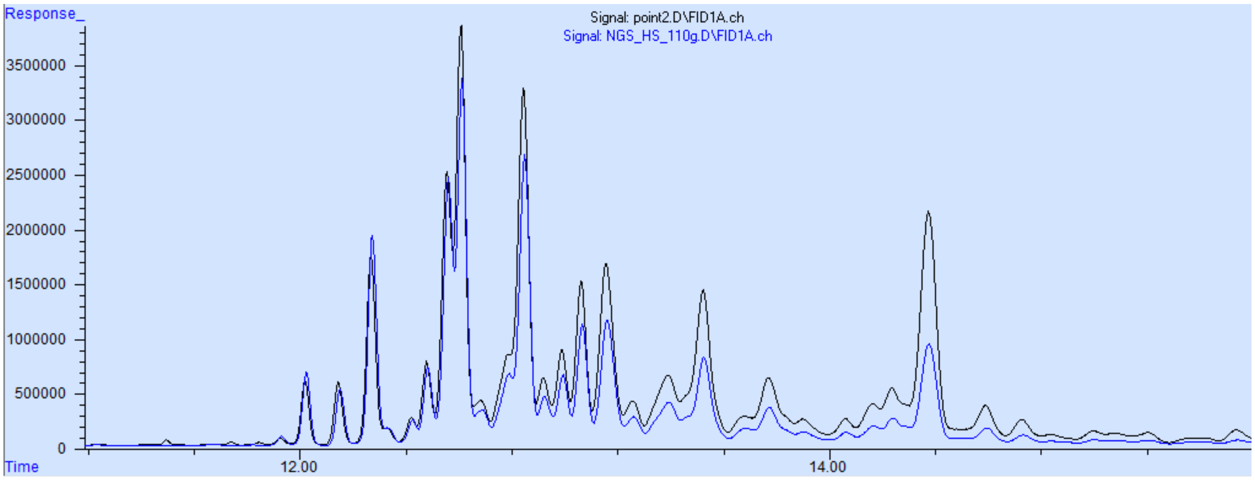

Figure A-2. GC Chromatogram of Pure Isopar-L and NGS

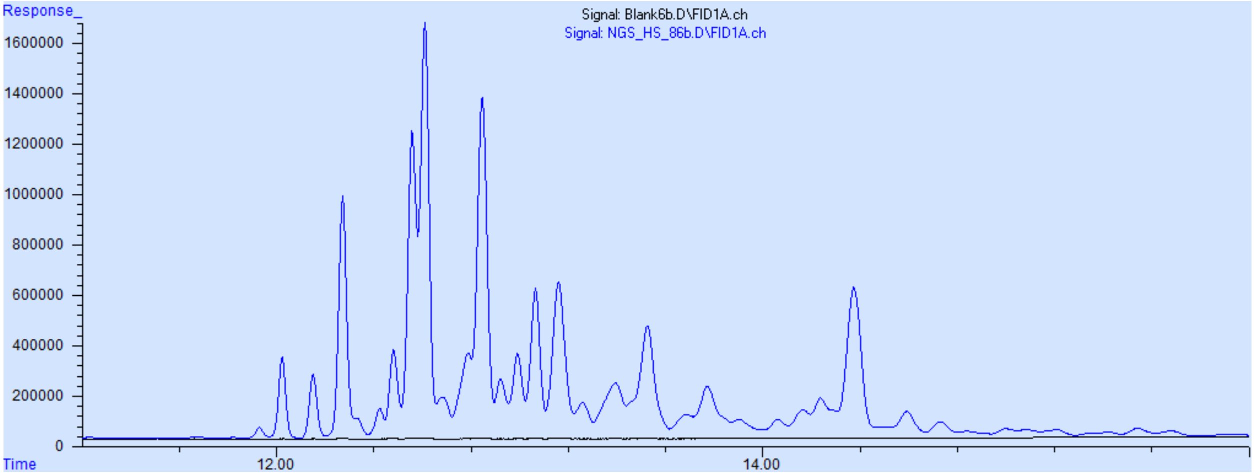

Figure A-3. GC Chromatogram Showing Comparison of NGS and a Blank

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