

Process to Remove Heavy-End Contaminants from Commercial LP Gas Streams

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Keywords: LP, Gas, Propane, Decontamination, Heavy-Ends, Residue, Removal, Remediation, Activated Carbon

Abstract

Adept Science & Technologies, LLC (ASCENT) has tested activated carbon adsorption columns as a means to remove soluble heavy-end contaminants from commercial LP Gas. Process design parameters (i.e. expected flowrates and bed dimensions) were subject to constraints imposed by industry practices (to facilitate subsequent field implementation). Initial results show effective removal of contaminants representative of those commonly found in commercial LP Gas. Also examined was the effect of the process on odorant (i.e. ethyl mercaptan) content. These results are presented along with an assessment of the tested processes. Background information on analysis methods required for these tests is also provided.

Introduction

A growing LP Gas industry concern is the effect of heavy-end residues contamination of LP Gas streams on the proper functioning of fueling systems and on other LP Gas distribution system components. Premium quality LP Gas with low heavy-ends residue is costlier, and sources (mainly from natural gas processing as opposed to refineries) are limited.

This project is to quantify residues content in commercial LP Gas and to design and test an adsorption column/filtration process to remove such “heavy-end” contaminants. Activated carbon has been tested before as a means to clean LP Gas. One example is a patented process using a packed activated carbon column to effectively remove residual oil while retaining mercaptans.¹ Another, a Japanese government funded, multi-million dollar project by Cosmo Engineering Co. (CEC) resulted in a 2 ton/h (60 L/min) demonstration plant to remove residues from LP Gas.² Principals from both projects were consulted for this work.

To properly address the challenges to remove LP Gas heavy-end contaminants, it is necessary to know what the levels of these residues are likely to be, how they are to be measured, and to what average level they must be consistently reduced. International LP Gas maximum residue limitations (Table 1) provide one measurable basis to assess the level to which the decontamination unit should reduce the residues content for current and near-term applications (e.g LP Gas-powered forklifts).

When comparing residues limits, it is essential to note that the test method used will affect the measured quantity of residues. Methods calling for higher temperatures during evaporation of the LP Gas, for example, will drive off more of the lighter compounds (such as gasoline and lighter diesel fuel components), which is likely to result in underreporting of the total residue levels and of these lighter heavy-ends.

Table 1: Summary of LP Gas Residues Limits

Nation	LP Gas Specification	Residues Limit (ppm)	Test Method	Evaporation Temp. (°C/°F)
US	HD-5, ASTM D 1835, GPA 2140	500 (and oil stain from 0.3 mL of residue-solvent mixture)	ASTM D 2158 ³	38 / 100
California	HD-10, CCR §2292.6	“	“	“
Japan	Utility Grade	12 ⁴	JLPGA-S-05T	-
Australia	ALPGA Automotive Spec. 2000	20 (at 105°C)	JLPGA-S-05T/86	105 / 221
Europe	EN-589	100 (proposed reduction to 50 ppm limit)	EN ISO 13757	105 / 221

As present and near-term applications will require much cleaner LP Gas, it has been tentatively decided that the unit to be designed and tested is to consistently achieve a target average residues content below 25 ppm (more than an order of

magnitude lower than the current allowable American standards limit). Of note, however, are reported field problems caused by as little as 3 – 10 ppm of “oily residue”.

Residue Testing Methods

The selection of a suitable residue testing method was crucial for this project. To yield meaningful results, an applicable test method must have repeatable resolution on the order of 10 ppm; be relatively easy and safe to conduct; should require a minimal sample volume, and should be reasonably priced. The evaluations of five (5) standard in-use, and near-term proposed pertinent testing methods for use in this project are summarized here:

1. ASTM D 2158 is the current method prescribed by ASTM D 1835. It was found to underreport total residues, to have undesirably low resolution, and no means to determine residue composition.
2. Dixie Services Inc. (DSI) P397 provides resolution of 0.1 ppm. Its drawbacks are that it requires a large sample volume and the heating of residues (leading to loss of lighter residues).
3. EN ISO 13757 reports insufficient repeatability at high resolution, and requires heating of residues.
4. CEC method⁵ uses gas chromatography after extraction of residues with a solvent under pressure. The method, currently under review by the D02.H Subcommittee of ASTM, reports results to 0.1 ppm. However, this method currently does not have published repeatability and reproducibility data.
5. prEN 15470:2006 (E) [previously referred to as CEN/TC19 N 1221 – Annex E (a proposed replacement for EN ISO 13757)], is a gas chromatographic method with results reported to 1 ppm, with 95% repeatability and reproducibility at 20 ppm of 3.9 ppm and 12.9 ppm respectively. Heating of residues in this method underreports lighter contaminants. This method is also under preliminary consideration by ASTM Subcommittee D02.H.

Conclusions

Based on the evaluation of the test methods, prEN 15470:2006 (E) and the CEC method were considered the most suitable methods for subsequent experiments. Because of the immediate availability of the necessary equipment, and with the advice of the analysis laboratory, it was decided to use prEN 15470:2006 (E) [modified with a lower evaporation temperature of 25 °C (77 °F)].

First Small Scale Decontamination Test

Summary

Tests were conducted on one type of activated carbon to treat a liquid phase propane feedstock containing four (4) selected contaminants representative of those previously found in commercial LP Gas. “Propellant grade propane” (here meaning ~99.6% pure C₃H₈ with a heavy-ends specification of less than 1ppm and already processed by molecular sieve media to eliminate water and sulfur) was used as a base to which pure, known contaminants were added. A fifth contaminant, n-octane, was selected to be representative of some lighter contaminants (such as gasoline-range compounds) which have also been problematic in the propellant industry. Two (2) polyester filters of different mesh sizes were placed downstream of the activated carbon to obtain an initial assessment of the amount of effluent activated carbon fines that may be entrained by LP Gas flow through the test vessel.

Objectives

1. Determine the effect of a specific type of activated carbon on the removal of selected concentrations of “heavy” contaminants from propane.
2. Determine the amount of effluent activated carbon fines at a given process flowrate.
3. Measure process temperatures and pressures to better predict process conditions (particularly during the wetting procedure) in future experiments.

Experimental Set-up and Materials

Activated Carbon Vessel

A 26.5-in. (67.3 cm) column with an inner diameter of 2.87 in (7.29 cm) [internal cross-sectional area ~0.045 ft² (41.7 cm²)] with removable end caps, and rated for 250 psig (18.2 bar absolute) was designed and constructed. The length of the

vessel allowed for variation of bed lengths in experiments (ranging from a bed size occupying nearly the full length of the column to a shorter bed representative of proportions likely to be used in a full-scale column). The column was fitted with external pressure and temperature gauges and pressure relief valves. Filter housings were added downstream of the column. The design also includes interior mesh screens which support the column packing materials (inert support balls and adsorbent).

Activated Carbon

CEC previously developed a precious metal-impregnated activated carbon designed to remove heavy-ends from LP Gas and which could then be regenerated. This activated carbon mix, however, was determined to be prohibitively expensive.

Three (3) commercially available activated carbons types were obtained for possible use. Of these, a 12x40 (1680 x 400 μm) bituminous coal-based granular activated carbon was chosen for initial tests based on its cost effectiveness and reported past effectiveness to remove C12 – C21 range contaminants from LP Gas (where LP Gas storage vessels were contaminated with diesel). Additionally, the activated carbon manufacturer reported that the selected activated carbon may work well to remove heavy-ends contaminants while the removal of sulfur compounds (including ethyl mercaptan) would be negligible. Regeneration of this adsorbent is generally handled by the adsorbent manufacturer.

Support balls

1/8” (0.318 cm) and 1/4” (0.635 cm) ceramic balls were used to support the activated carbon and to evenly distribute propane flow inside the vessel.

Filters

100μm (149 mesh) x 0.100” (2.54 mm) thick and 5μm (2500 mesh) x 0.080” (2.03 mm) thick polyester felt filter sheets were cut to fit modified Impco VFF30 filter housings. The filters were used to assess the approximate size range and amount of effluent activated carbon fines which were entrained at specific flow conditions.

Contaminants

The following compounds (98-99+% pure) were added as contaminants for the feedstock (Table 2).

Table 2: Description of Added Contaminants for First Test

Contaminant	Description
n-Octane (C ₈ H ₁₈):	a representative compound of gasoline contamination
Pentadecane (C ₁₅ H ₃₂)	a representative compound of diesel contamination
Methyl linoleate	a plasticizer and known LP Gas contaminant
Diethyl adipate	a plasticizer and known LP Gas contaminant
Butyl benzyl phthalate	a plasticizer and known LP Gas contaminant

These contaminants are representative of the type and range of compounds that can be found in commercial LP Gas streams⁶. Gasoline and diesel contamination can occasionally occur when LP Gas is shipped through multi-product pipelines.

Procedure

Column Packing

The activated carbon vessel was loaded (from bottom up – the direction of process flow is up) with: (1) a 100μm (149 mesh) filter used as a support to prevent activated carbon fines from dropping into the upstream line (this filter should not be confused with the two filters used to trap and measure activated carbon fines downstream of the column). (2) a layer of 1/4” support balls, (3) a layer of 1/8” support balls, (4) the activated carbon, (5) a layer of 1/8” support balls, and (6) a layer of 1/4” support balls. (Table 3)

Table 3: Column Loading

Layer	Mass (lbs./kg)	Height (in/cm)
1/4-inch Support Balls	0.8 / 0.36	2.5 / 6.4
1/8-inch Support Balls	0.6 / 0.27	1.5 / 3.8
12x40 Activated Carbon	2.2 / 1.0	20 / 51
1/8-inch Support Balls	0.2 / 0.09	1.0 / 2.5
1/4-inch Support Balls	0.4 / 0.18	1.5 / 3.8

Preparation of Contaminated LP Gas Supply

The contaminants were pre-measured by weight into a clean beaker. The contaminants were added to the clean propane in proportions and levels similar to those in previously analyzed commercial LP Gas streams. The actual concentrations in the feedstock used for comparison with the results of the treated LP Gas were determined by the above mentioned gas chromatography (GC) based method.

A clean 25-gallon (95 L) propane tank was partially filled with propellant-grade propane. The contaminants were then poured into a clean propane delivery hose and the hose was reconnected to the tank. The contaminants were flushed from the hose into the tank as it was filled (to ~80% full) with propellant grade propane. The 25-gallon tank was then shaken and rolled to thoroughly mix the contaminants throughout the filled vessel.

Wetting

Pre-process “wetting” of the activated carbon is required to remove air from the activated carbon pores⁷. The wetting procedure consisted of two steps: (1) carbon dioxide (CO₂) pre-loading to minimize the amount of heat released during wetting with the process fluid, and (2) wetting with propellant-grade propane.

First, carbon dioxide was introduced into the activated carbon bed and pressurized to 14.7 psig (2 bar absolute). The temperature of the bed initially increased as expected from the exothermic loading of CO₂, and was allowed to cool and stabilize over ~1.5 h. The intent of CO₂ preloading is to reduce the heat of adsorption when propane is introduced. This was a procedure recommended by the manufacturer, but if found unnecessary in future tests may be eliminated to facilitate field implementation.

Next, propellant grade propane was introduced. The flow of propane was to be fast enough to allow the propane to act as a heat sink, (although the CO₂ also acts to reduce heat as it desorbs). There was an initial heat rise of ~60 °C (15.6 °F) as vapor flowed through the bed, followed by a rapid drop in temperature as liquid filled the system (Figure 1). The vessel valves were then closed and the activated carbon bed with liquid propellant grade propane was left undisturbed for ~1 h.

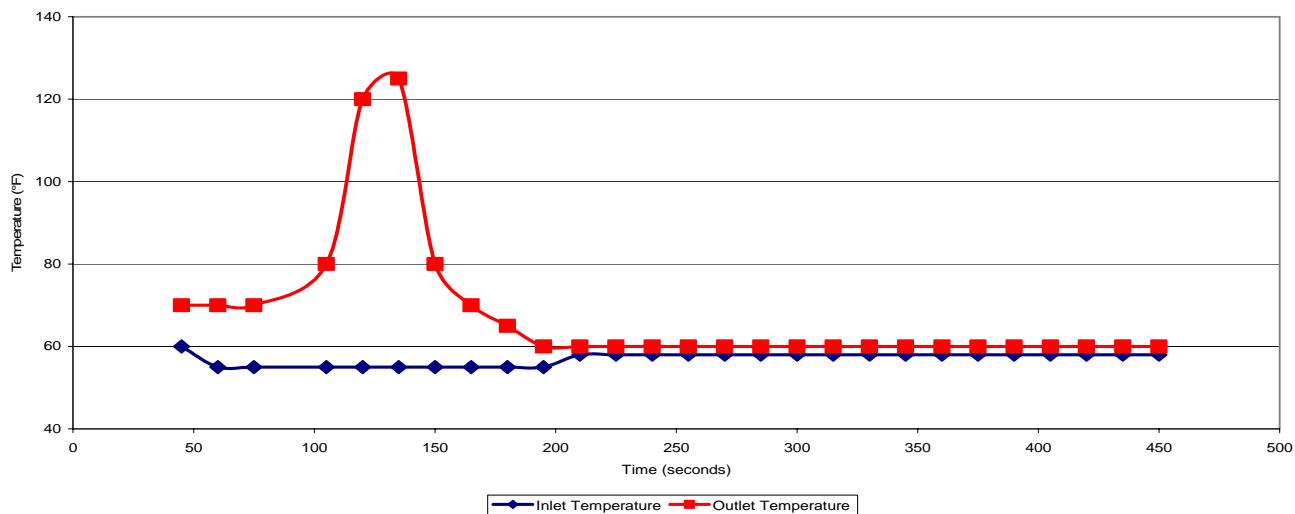


Figure 1: Column Temperature During Wetting Procedure

Decontamination and Sampling

After the wetting procedure, the contaminated supply tank was attached to the vessel containing the activated carbon bed, and flow of the contaminated LP Gas stream through the bed was initiated. Based on discussions with project advisors the process flow was directed upwards through the column against gravity. The flowrate was calculated by monitoring the drop in weight of the contaminated supply tank over time. Adjustments were made as needed to maintain the predetermined optimal flowrate. This desired flowrate was calculated based on the recommendations of project advisors and prior exchanges with CEC. The process was scaled down based on cross-sectional area to maintain the same superficial velocity of LP Gas flow in the pilot vessel.

The first sample was drawn after flowing through approximately one bed-volume of contaminated supply. Over the course of the first pilot test, nine (9) samples were drawn at regular time intervals (Figure 2). Two (2) additional samples - one of the contaminated supply and one of the propellant grade propane - were also taken. The temperature of the system was monitored, but not controlled. There were no significant temperature changes during the experiment. Ambient temperatures remained at approximately 70°F until night time when the temperature dropped to 62 °F (17 °C). Pressures were constant at 170 psig (12.7 bar absolute).

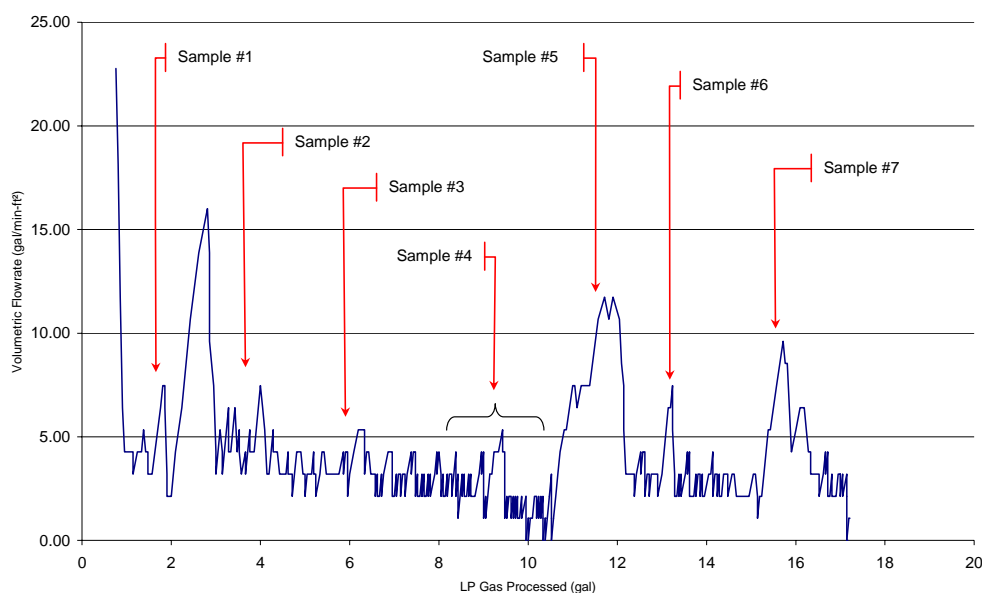


Figure 2: LP Gas Flowrates During First Test

Activated Carbon Fines

100 and 5µm filters were weighed (dry) prior to their installation downstream of the activated carbon. These filters were later removed after the contaminated propane testing was completed, and re-weighed dry.

Results and Discussion

Contaminant Removal

The analytical method [prEN 15470:2006 (E)] was modified (in addition to lowering the evaporation temperature) to use heptane as the internal standard because octane was one of the contaminants. Some samples were not analyzed. In-line (or on-site) analysis was also not possible. Sample #4 was selected for analysis because it had the lowest flowrate during sampling (closest to the predicted optimal flowrate and presumably with the greatest potential for contaminant removal). Sample #5 was selected for analysis because it had a higher flowrate during sampling and was taken shortly after Sample #4 was completed. Sample #6 was selected for analysis as an intermediate flowrate sample taken shortly after Sample #5.

The expected Contaminated Propane concentration (based on what was weighed and poured into the propane transfer hose) differs significantly from the concentration measured with the GC method (Table 4). Several possible factors could contribute to this discrepancy. One is that not all of the contaminant mixture was transferred from the weighed beaker to the

transfer hose. The mixture was viscous and a visible amount was unavoidably left coating the beaker wall. Given that the total contaminant volume added was 19.3 mL (0.65 oz), this loss of contaminant to the beaker may have been a significant source of error. Another possible source of contaminant loss was inside the transfer hose. Some of the contaminant may have either been absorbed by the hose or adhered to it. A third factor may have been whether the contaminants, once introduced to the tank, were mixed homogeneously throughout the propane as intended. Some contaminants may have been adsorbed by the propane tank wall. Although the GC test method itself may have been a source of some loss, it is not likely that the heavy contaminants would have evaporated off to a large extent. The test method was modified to keep the evaporation temperature relatively low (25 °C / 77 °F) to avoid such losses. Although there is an apparent correlation between the boiling points of the contaminants used and the amount of loss of each contaminant, the contribution of evaporation to residue loss is undetermined. Based on these results, a different method to introduce contaminants with minimal loss was used in the second small scale test.

Table 4: Theoretical and Actual Concentrations of Each Contaminant in First Test

Contaminants (order of increasing boiling pt.)	Concentration (mass ppm)		
	Expected (by weight)	GC	% Diff.
n-Octane	119	19	84%
Diethyl adipate	95	27	72%
Methyl linoleate	59	19	68%
Pentadecane	119	42	65%
Butyl benzyl phthalate	86	32	63%
Total	479	141	71%

Because the same GC method was used to measure both the Contaminated Propane supply and the processed samples, the above described concentration discrepancy was not considered a significant factor in the evaluation of the tested activated carbon's ability to remove heavy-ends. It should be noted that immediate on-site sample analysis was not possible for these tests, and therefore the results were not known until after all tests were completed.

The results from Samples #4, #5, and #6 clearly indicate removal of the contaminants selected for this initial protocol (Table 5). The results seem to show that either lower flowrate results in better n-octane removal or that between Samples #4 and #5 the activated carbon became loaded to the point that it was unable to further adsorb n-octane. Another possibility is that other larger contaminants began to displace n-octane in the adsorption sites. The additional analysis of Sample #6 does not provide any additional support to the idea that a lower flowrate would result in better n-octane removal. However, the analyst indicated that there was some evidence of a small leak in sample vessel #6. If this is the case, it is likely that the lighter molecules (i.e. propane) evaporated, leading to an erroneously high concentration of the contaminants (i.e. octane) left in the sample vessel. Whether n-octane could be further adsorbed by the activated carbon is uncertain at this point.

Table 5: Concentration of Contaminants in Samples from First Test

Sample	LP Gas Processed (gal.)	Average Sample Flowrate (gal/min-ft ²)	Concentration (mass ppm)					Total
			Octane	Pentadecane	Methyl linoleate	Diethyl adipate	Butyl benzyl phthalate	
Propellant-grade Supply	N/A	N/A	0	0	0	0	0	1
#4	8.4	1.9	11	0	0	0	0	12
#5	11.7	10.7	21	0	0	0	0	22
#6	13.0	7.5	20	0	0	0	0	24

Adsorption capacity of the activated carbon for the added contaminants was not determined. However, a predicted adsorption capacity based on manufacturer estimates and from project advisors' experience suggests that the volume of contaminated propane processed in this experiment was far less than what could be expected to be treated before the activated carbon pores are loaded. Breakthrough (the point at which the activated carbon no longer adequately removes selected contaminants) was determined in subsequent tests.

It can be concluded that full removal of the four other contaminants, over a processed volume of ~11.7 gallons (44.3 L), could be achieved using this bed dimension and a flowrate of 10.7 gal/min-ft² (436 L/min-m²). There was no measured distinction between the concentration of these contaminants in Samples #4, #5, and #6 (all are 0 ppm), so there is no indication of the effect of a change in flowrate for these contaminants.

Activated Carbon Fines

Both the 5 and 100 µm polyester filters had visible activated carbon fines, and a measurable increase in weight after drying (Table 6). The filters, however, were not visibly clogged with activated carbon fines and some of the additional mass can be attributed to metal piping shavings and thread compound which were also clearly visible on the filters. It was not possible to separately measure to what extent this metal and thread compound contributed to the mass increase. It was expected, and later determined that the amount of metal and thread compound found on the filters significantly decreased in future tests with the same vessel.

Table 6: Activated Carbon Particles Collected in First Test

Filter Size	Mass Collected (g / oz)
5 µm	0.10 / 0.0035
100 µm	0.17 / 0.0060

Proposed Next Steps

The initial tests successfully demonstrated contaminant removal, and supported further experiments.

Second Small Scale Propane Decontamination Test

Summary

Based on the results and recommendations gained from the first test, this second test was conducted to treat and determine the effect of activated carbon on odorized HD-5 LP Gas containing actual LP Gas residues and compounds representative of heavier residues (C20+). The activated carbon bed was also shortened to be in proportion to the design of the proposed full-sized column and to better characterize breakthrough of each contaminant. Also addressed were reduction of the apparent loss of contaminants added to the supply tank; better flow control at a low flowrate; and eliminating metal debris as a source of error from the filters.

Objectives

1. Determine the effect of a specific type of activated carbon on the removal of selected concentrations of “heavy” contaminants from propane processed at a pre-determined flowrate.
2. Measure effluent activated carbon fines at a given process flowrate.
3. Measure process temperatures and pressures to better predict process conditions in future experiments.
4. Achieve contaminant breakthrough.
5. Use a lower length to diameter bed ratio scalable to the full-sized DOT transportable full-sized vessel
6. Determine the effect of the process on mercaptan sulfur (i.e. odorant) concentration in the tested LP Gas.

Experimental Setup and Materials

Activated Carbon

The same type of activated carbon was used as in the first experiment.

Support balls

1/8”, 1/4”, and 1/2” ceramic balls were used to support the activated carbon and to evenly distribute flow inside the vessel.

Filters

New 100µm x 0.100” thick and 5µm x 0.080” thick polyester felt filter sheets were cut to fit modified Impco VFF30 filter housings. The filters were used to determine the approximate size and amount of effluent activated carbon fines which are entrained at specific flow conditions.

Contaminants

The following compounds were obtained and added to HD-5 LP Gas (Table 7):

Table 7: Description of Contaminants Added for Second Test

Contaminant	Description
n-Octane (C ₈ H ₁₈)	a representative compound of gasoline contamination
Diocyl adipate (C ₂₂ H ₄₂ O ₄)	a plasticizer and known LP Gas contaminant
American Welding & Tank Co. residues (a blend of many contaminants from LP Gas tanks)	7% recovered at n-C8 boiling point; 54% recovered at n-C11 boiling point; 95% recovered at n-C20 boiling point (Determined by ASTM D2887)
Mobil Rarus 427 compressor oil	ISO 100 (viscosity) with 100% recovered above n-C20 boiling point

The proportions added were weighted to ensure higher concentration of heavy (C20+) compounds. The actual concentrations in the feedstock used for comparison with the results of the treated LP Gas were determined by a gas chromatography based method.

The American Welding & Tank Co. residues were collected from used and recovered LP Gas tanks. These residues are thought to be representative of a range of contaminants found in commercial LP Gas streams, although not necessarily found in fuel system residues. ASTM D2887 analysis was used to provide the above characterization. Additionally, the total sulfur concentration (ASTM D 4294) was 6.56 mass %. ASTM D2887 was also used for the characterization of the compressor oil.

Procedure

Column Preparation

All valves to the column were vented, and the top cover and filter housings were removed. A flowmeter was installed downstream of the vessel. After removing support balls and activated carbon from the previous experiment, all exposed parts (e.g. filter housing interior, fittings with excess pipe compound) were first wiped clean with a cloth, and then the entire system was filled and flushed with pure propane. After flushing, the system was vented.

Prior to loading the activated carbon vessel, the apparatus was placed on a scale. The activated carbon vessel was then loaded (from bottom up – the direction of process flow is up) with: (1) a 100µm filter used as a support to prevent activated carbon fines from dropping into the upstream line, (2) a layer of 1/2" support balls, (3) a layer of 1/4" support balls, (4) a layer of 1/8" support balls, (5) the activated carbon, (6) a layer of 1/8" support balls, and (7) a layer of 1/4" support balls, and (8) a layer of 1/2" support balls (Table 8). The extra support balls were used as a means to shorten the activated carbon bed length within the same column used previously.

Table 8: Column Loading

Layer	Mass (lbs. / kg)	Height (in / cm)
1/2-inch Support Balls	0.8 / 0.36	3.5 / 8.9
1/4-inch Support Balls	1.4 / 0.64	4 / 10
1/8-inch Support Balls	1.0 / 0.45	2.5 / 6.4
12x40 Activated Carbon	0.6 / 0.27	7 / 18
1/8-inch Support Balls	1.0 / 0.45	3.1 / 7.9
1/4-inch Support Balls	1.0 / 0.45	3.5 / 8.9
1/2-inch Support Balls	0.8 / 0.36	2.9 / 7.4

Wetting

As before, a wetting procedure was conducted (CO₂ pre-loading followed by wetting of the activated carbon with propellant-grade propane). After flowing CO₂ through the column, the outlet valve was closed and the system was pressurized to 14.7 psig (2.0 bar absolute). There was no measurable temperature change. The system was then kept under pressure for ~1.5 hours. Propellant-grade propane was then introduced, but unlike the first test, there was no measurable increase in the temperature. This likely occurred because the bed in this test was smaller, which would result in less heat release, and because due to the smaller bed, the temperature probes were further from the activated carbon. Because there was no temperature differential, the outlet and inlet valves were closed once it was determined that liquid had entirely filled the column. The wetted system was left closed overnight.

Preparation of Contaminated LP Gas Supply

The contaminants were pre-measured by weight into a clean beaker. A clean 100-gallon (379 L) propane tank was then partially filled (~20%) with HD-5 LP Gas. A short metal standpipe with a fitting for the LP Gas delivery hose was attached to the tank inlet valve. The contaminants were then poured into the standpipe and flushed into the tank as it was filled (to ~85% full) with HD-5. The beaker used to pour the contaminants was re-weighed to account for contaminant loss.

The 100-gallon “contaminated supply” tank was then shaken and rolled to thoroughly mix the contaminants throughout the filled vessel. The tank was left undisturbed overnight. The next morning, the contaminated supply tank was rolled and shaken. A nitrogen supply line was then connected to the vapor valve of the supply tank, and a pressure head of ~185 psig (13.8 bar absolute) was applied to the contaminated supply.

Decontamination and Sampling

Following the wetting procedure, the contaminated supply tank was attached to the activated carbon vessel, and flow of the contaminated LP Gas stream through the bed was initiated. Adjustments were made as necessary to maintain a predetermined optimal flowrate. The flowmeter installed for this test did not function properly; so it did not improve flow monitoring and control vs. the first experiment. As before, flow was measured by monitoring the increase in weight of the receiving vessel over time. Flow adjustments were made manually by decreasing the vapor pressure in the receiving vessel and/or throttling the contaminated supply tank outlet valve. This receiving vessel was not used for sample collection.

Each aluminum sample vessel was first cleaned with pure propane, vented, and then filled with nitrogen to ~80 psig (6.5 bar absolute) as a means to control the pressure differential created when the LP Gas sample line is first connected for filling. The flowrate was controlled in the same way as above. The first sample was drawn after flowing through approximately one bed-volume of contaminated supply. Over the course of the pilot test, seven (7) samples were drawn at regular time intervals. An eighth sample was being collected as the contaminated LP Gas supply ran out. A sample of both the contaminated supply, and the HD-5 were also taken.

Activated Carbon Fines

100 and 5 μ m filters were weighed (dry) prior to their installation downstream of the activated carbon. These filters were later removed after the contaminated LP Gas testing was completed, and re-weighed (dry).

Results and Discussion

Contaminant Removal

A modified version prEN 15470:2006 (E) was again used for sample analysis, with heptane as the internal standard and a lower evaporation temperature (25 °C / 77 °F).

Table 9: Theoretical and Actual Concentrations of Each Contaminant in Second Test

Contaminants	Concentration (mass ppm)		
	Expected (by weight)	GC Determined	% Difference
n-Octane	53	15	72%
Diocetyl adipate	57	28	51%
American Welding & Tank Residues	211	98	54%
Mobil Rarus 427 Compressor Oil	346	196	43%
Total	667	337	50%

The expected contaminated LP Gas concentration (based on what was weighed and poured into the propane tank) again differed significantly from the concentration determined with gas chromatography (Table 9). This difference is a concern that should be addressed as test methods for this purpose are further developed. There was, however, a significant improvement in the efficiency of addition of the contaminants from the previous test. In this test, the amount of residual contaminants remaining on the beaker walls was accounted for by weight, but this resulted in only a slight reduction (0.6%) in the expected concentration. Although the shorter, steel transfer pipe likely led to better transfer of the contaminants to the tank, some of the contaminant may have adhered to the pipe surface or, once introduced to the tank, settled or been adsorbed onto the tank walls dispersing homogenously throughout the LP Gas. The possibility of the Contaminant Supply concentration changing over time should be addressed in future tests. One possible improvement in future work is to pre-dissolve the contaminants in a lighter solvent such as pentane or toluene prior to addition to the LP Gas.

The results indicate that for this flowrate and bed dimensions the activated carbon removes significant amounts of all added LP Gas contaminants. The amount of contaminant removed and the time to breakthrough varies for each contaminant (Figure 3 and Table 10). As LP Gas is processed, contaminants with a lesser affinity for activated carbon may be displaced by compounds that are more readily absorbed. The process was particularly effective in removing the compressor oil and dioctyl adipate (which contained the majority (~98%) of C20+ compounds used in this test). The concentration of these contaminants remained at below 10% of their initial concentrations (>90% removal) and below a combined 15 ppm until after 241 bed volumes (47 gal.) of LP Gas were processed.

Table 10: Concentrations of Heavy-Ends Contaminants (and Ethanethiol) for Second Test

Sample No.	LP Gas Processed		Sample Flowrates (gal/min-ft ²)		Concentration (mass ppm)					
	Bed Volumes	Gallons	Average	Max	Octane	Dioctyl Adipate	AW&T Residue	Compressor Oil	Total Residues	Ethanethiol
Supply	N/A	N/A	N/A	N/A	15	28	98	196	338	14.3
1	11	2	1.8	9.6	2	0	7	7	17	2
2	62	12	1.5	7.5	2	0	12	7	21	8.9
3	119	23	2.0	6.4	4	0	35	7	46	11.9
4	177	34	2.7	5.3	11	1	59	13	85	
5	241	47	2.0	4.3	5	2	47	11	65	
6	297	58	2.2	4.3	14	16	91	32	153	
7	332	65	1.9	5.3	11	25	86	35	157	

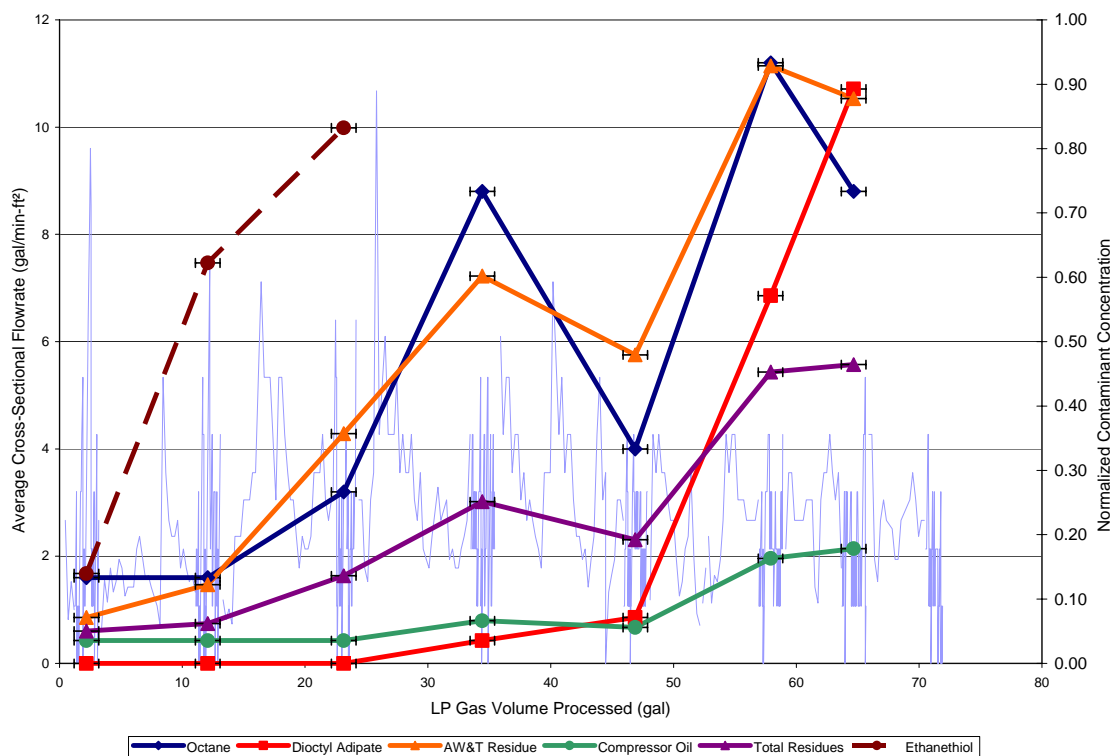


Figure 3: Flowrate Overlaid by Normalized Breakthrough Curves for Second Test

Because flow during sampling varied more than anticipated, for each sample are listed both the average flowrates during sampling and the maximum flowrate which occurred as the sample was being taken (Table 10). Both of these are relevant as a high average flowrate may not allow enough contact time with the activated carbon to achieve maximum contaminant removal or alternatively one or more of flowrate “spikes” during a 2-gal (7.6 L) sample may significantly impact the concentration taken for the whole sample. This is a likely reason that the concentrations of most contaminants in Sample #4, which had the highest average flowrate, were higher than those in Sample #5.

Table 11: Concentration of Sulfur Compounds for Second Test

Sample No.	LP Gas Processed		Concentration (mass ppm as S)							
	Bed Volumes	Gallons	Ethanethiol	1-Butanethiol	Diethyl Sulfide	Diethyl Disulfide	1-Heptanethiol	1-Octanethiol	Isopropyl Disulfide	Total
Supply	N/A	N/A	7.4	0.2	3.6	8.8	0.7	1.2	0.2	22.1
1	11	2	1.0	0.2	3.1	9.0				13.3
2	62	12	4.6	0.3	3.2	6.3	0.5	1.1		16.0
3	119	23	6.1	0.2	3.2	8.5	0.5	1.0		19.5

Analysis of sulfur compounds in the LP Gas suggests that they are less readily removed by the activated carbon than the heavy-ends residues (Table 11). Of particular note, ethyl mercaptan (ethanethiol) is initially reduced to 14% of its original level, then returns to 62% within 62 bed volumes, and 82% within 119 bed volumes (Figure 3 and Table 10). This suggests that heavy-ends removal can continue long after the ethyl mercaptan is no longer removed by the activated carbon.

Activated Carbon Fines

Both the 5 and 100µm polyester filters had visible activated carbon fines, and a measurable increase in weight. There was no measurable pressure drop at any point in the test that would indicate that the process was affected by these fines.

Table 12: Activated Carbon Particles Collected in Second Test

Filter Size	Mass Collected (g / oz)
100µm	0.03 / 0.001
5µm	0.05 / 0.002

Proposed Next Steps

The second tests demonstrate effective removal of heavy-end contaminants from LP Gas. Based on these results further pilot scale tests to determine effects of flowrate and the effects of lower heavy-ends concentration on the process; and full-scale tests of the column are recommended.

Full Scale Column & Process Design

A full sized column was designed as a next step in the testing process (Figure 4). The vessel design was subject to the following constraints to be DOT approved transportable, while providing adequate LP Gas flow (Table 13). DOT approval allows for the option to switch out and transport the entire column when the activated carbon no longer effectively removes contaminants (rather than in-situ regeneration or replacing the activated carbon in the column on-site).

Table 13: Full Sized Column Design Constraints

Footprint	48"x48" (1.2 m x 1.2 m)
Weight	<3,200 lbs. (1,450 kg) when full (able to be lifted with standard equipment)
Length	~72" (1.83 m) (able to fit inside a standard freight truck)
Pressure	rated to 250 psig (18.2 bar absolute) at 650°F (343 °C) (to allow for the option of future work with high temperature in-situ activated carbon regeneration)

The design also includes interior screens and a diffuser plate at the inlet designed to disperse the LP Gas evenly throughout the adsorption medium as well as to incorporate inert support balls for the adsorbent.

After CEC engineers calculated expected flow rates and made recommendations on the tank re-design dimensions (based on their prior work), the initial vessel design was further refined with a reduced outer diameter (24 in / 61 cm). This smaller diameter design reduces manufacturing cost and is likely to reduce undesirable channeling. The desired flow rate for the reduced diameter vessel was accordingly lowered. The length to diameter ratio in this large scale vessel was modeled in the second pilot experiment, and the flowrate in the pilot test was scaled to maintain the same cross-sectional flowrate as in the full-scale column. The pilot unit to full-scale ratio is 1:67.

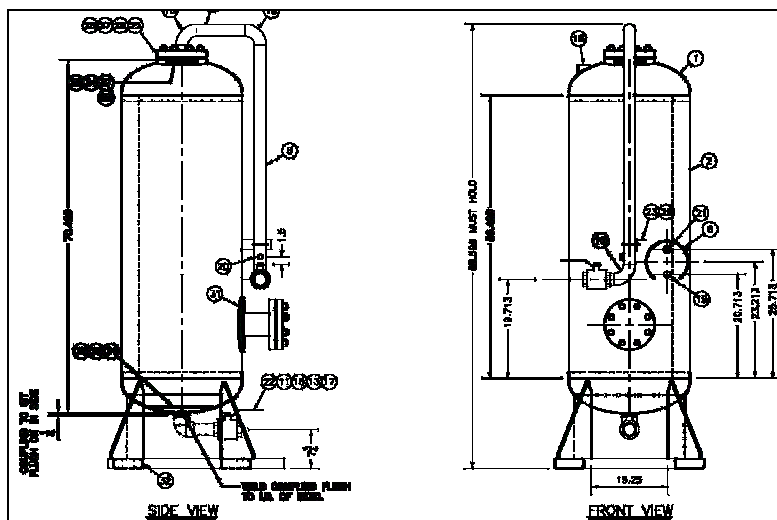


Figure 4: Full Sized Column Design

Economic Analysis

The results of the second pilot scale test and the above-described full-sized column were used for the below economic analysis. The scaled-up process flowrate was assumed to be 6 gal/min. Additionally, the following assumptions were made:

1. Replacement of activated carbon is required after the C20+ residues content exceeds 25 ppm. In the experiments used for this analysis, the last measured sample with C20+ content below 25 ppm was at 13 ppm (or <10% of the initial concentration) at which point 241 bed volumes had been processed. The total residues concentration at this measurement was 65 ppm (or <20% of the initial concentration). For this reason, 241 bed volumes was used as the capacity of the activated carbon before replacement.
2. The per-gallon revenue to be generated by the full scale plant is taken to be the additional cost paid for low-residue LP Gas in Southern California in fall of 2005 [\$0.10/gal (\$0.026/L) at \$2.10 to \$2.25/ gal (\$0.55 to \$0.59/L) retail pricing]. For a decontamination process to be economically viable, the total cost must be sufficiently below this \$0.10/gal premium to achieve payback over a reasonable period.

Table 14: Economic Analysis Summary

Annual Production (gal)	1,057,536
Fixed Capital	\$ 89,874
Working Capital	\$ 8,987
Total Capital Cost	\$ 98,862
Annual Manufacturing Cost	\$ 64,948
Annual Revenues	\$ 105,754
Project Life (years)	15
Tax Life (years)	15
Payout time (years)	2.74

The total cost per gallon of clean product is \$0.061. This analysis yields a payout time of 2.74 years. The project life was taken to be 15 years.

Lower concentrations of contaminants in the LP Gas will likely result in a greater volume of treated LP Gas prior to breakthrough, and thus a lower cost per volume of clean product.

Conclusions

These activated carbon tests have demonstrated that certain heavy-end contaminants can be largely removed from LP Gas. The latest tests show the process to be particularly effective in removing heavier contaminants (e.g. compressor oil).

Additionally, the results show that ethyl mercaptan concentration is reduced by the process, but begins to elute more quickly relative to other contaminants – suggesting that heavy-ends may continue to be removed while mercaptans are not. Initial economic analysis suggests that this process can be viable.

Future work

As mentioned above, proposed immediate next steps are pilot scale tests using a higher flowrate (desirable for larger commercial applications); pilot scale tests with a lower total heavy-ends and lower C20+ concentration; and full scale tests of the process.

Future work may include a comparison of analytical methods (i.e. CEN and CEC) or variations on these methods. ASCENT has also discussed with CEC the possible implementation of in-situ regeneration. This desirable aspect of the decontamination process is to be developed as a follow-up to this project.

Acknowledgements

ASCENT is grateful to PERC for support and funding of this project. For their ongoing assistance, we thank our advisors: John Ehlers, Bob Falkiner, George Maes, John O'Connor, Larry Osgood, Andy Pickard, Arnie Smith, Jean-Paul Trespaille, and Quan Zhuang. For their invaluable help we are also indebted to Ernie Reed (Aeropres Corporation); Mical Renz (Dixie Services, Inc.); Junichi Yodotani and T. Kioyosawa (Cosmo Engineering Co.); Al Roy and Jimmy Lam (Calgon Carbon); Jerry Gilliam and Walker Ogden (American Welding and Tank); Steve Moore (Expo Propane), Dan McCartney (Black & Veatch) and Bob Myers (PERC). Lastly we thank WLPGA for providing this opportunity.

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