Water and Solid Contaminant Control in LP Gas

by

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Battelle Applied Energy Systems

To

Propane Education

& Research Council

1140 Connecticut Ave. NW, Suite 1075

Washington, DC 20036

Battelle
The Business of Innovation

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FINAL REPORT

on

WATER AND SOLID CONTAMINANT CONTROL IN LP GAS

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VOLUME 1 – TECHNICAL REPORT AND APPENDICES

to

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The authors appreciate the efforts of Mr. Ross Warnell, Ferrellgas, in coordinating the sampling of propane at the test sites. Without Mr. Warnell's diligence, the samples could not have been collected.

EXECUTIVE SUMMARY

LP gas quality is becoming increasingly important as competition between fuels becomes more intense, and new end-uses with particular fuel requirements emerge. Traditional end uses such as residential, commercial, and industrial atmospheric burners have low sensitivity to most fuel quality parameters such as heating value, moisture content, particulates, heavy ends, and other contaminants. Even with these robust systems, issues of freeze-up due to excess moisture and high lockup pressure due to particulates in pressure regulators would periodically surface. Mitigation was usually tried-and-true methods such as methanol dosing for moisture and a good, solid rap on the regulator with a wrench to dislodge particles.

The objectives of this research project were to gather information about the sources and levels of water and solids contamination in LP gas, and to address possible and practical remediation methods.

Existing Requirements for Solids and Water

The existing requirements of LP gas fuel quality are contained in Gas Processors Association's Standard GPA 2140-97. In this study on water and solids/particulate contaminants, of particular relevance are the residue limits and test (ASTM D-2158) and the moisture/free water limits and tests (ASTM D-2713, Freeze Valve and the Cobalt Bromide Method).

For residual matter, ASTM D-2158 gives an upper limit of 0.05 ml remaining after evaporation (weathering) of 100 ml of liquid LP gas at 38 C. More than 0.05 ml remaining after the weathering indicates unacceptable levels of high vapor pressure substances (oils) and particulates. The freeze valve method (ASTM D-2713) indirectly measures the freezing point of the propane liquid. If excess moisture is present, it will freeze as the liquid cools during the pressure reduction (adiabatic expansion). The sample passes the test if the time to freeze the valve to close-off is 60 seconds or longer. However, the test is purely empirical. The preface of GPA 2410 states the presence of methanol, even in small quantities, can make the results of the freeze valve test not applicable. While the presence of methanol affects the significance of the freeze valve times, the fact that the sample does not freeze indicates that there will not likely be freeze-up problems with this sample. Methanol is often added, albeit sometimes unnecessarily and virtually never scientifically, to address moisture issues. While the cobalt bromide (CoBr) method requires a more complex apparatus and is sensitive to apparatus moisture contamination, it also is a pass/fail type of test. The result is that if a sample is found to be "on spec", it is likely acceptable in most end uses, because the dryness of "on spec" propane is so stringent. However, the converse of this thought is that "off spec" propane moisture level measurement can only accurately be stated as being higher than "on spec", using these methods.

Sampling

The intent of the sampling program was not to collect a statistically valid set of samples for all recognized variables. This would have involved a prohibitively large number of samples. Instead, it was decided to obtain samples from different sources in different geographical locations as an illustrative data set.

The geographical regions for obtaining LP gas samples are listed in Table ES-1. The "Comment" column is included as it gives the background of the sample. These comments were derived from the industry consultants who guided Battelle in selection sampling sites.

Table ES-1. Sampling locations.

Supply Area	Location	Comment
Chicago I	Carol Stream, IL	Refinery
Chicago II	Chesterton, IN	Refinery
Denver I	Conifer, CO	Refinery (historically high propylene content)
Denver II	Colorado Springs, CO	Refinery / local production (stringent air quality standards in effect)
Detroit	Jackson, MI	Refinery
Home Depot – 1	Columbus, OH	Retail location
Home Depot – 2	Columbus, OH	Retail location
Houston I (sample not returned)	Houston, TX	Refinery / local production (air quality standards in effect)
Houston II	Corpus Christi, TX	Refinery / local production (air quality standards in effect)
Kansas City	Wichita, KS/MO	Refinery
L.A. Basin (North)	Lancaster, CA	Refinery
L.A. Basin (South)	San Diego, CA	Refinery
Midwest	Columbus, OH	Pipeline
New England	Chepachet, RI	Imported product
New Jersey I	Woodbridge, NY	Major East Coast Supplier
Northern California I	Elk Grove, CA	Historically high propylene content
Northern California II	Gurneville, CA	Historically high propylene content
Seattle	Auburn, WA	Refinery (air quality attainment region)
St. Louis	Godfrey, IL	Local production
Tampa	Tampa, FL	Imported product
Upper Midwest	Wausau, WI	Refinery

The samples were collected in standard, new, aluminum forklift cylinders. Each cylinder was evacuated before being shipped to Battelle, so that it would not contain water vapor. We also obtained two 20 lb cylinders (a few weeks apart) from a Home Depot in Columbus, Ohio, and we filled and refilled a new, evacuated aluminum cylinder at a bulk plant center in Columbus, Ohio.

Testing for Water

As previously mentioned, the commonly-used methods for moisture testing in LP gas, the freeze valve test (D-2713) and the cobalt bromide test (both listed in GPA-2140), are pass/fail and not quantitative. For these reasons, we selected a commercial, off-the-shelf dew point sensor to quantitatively measure the water content.

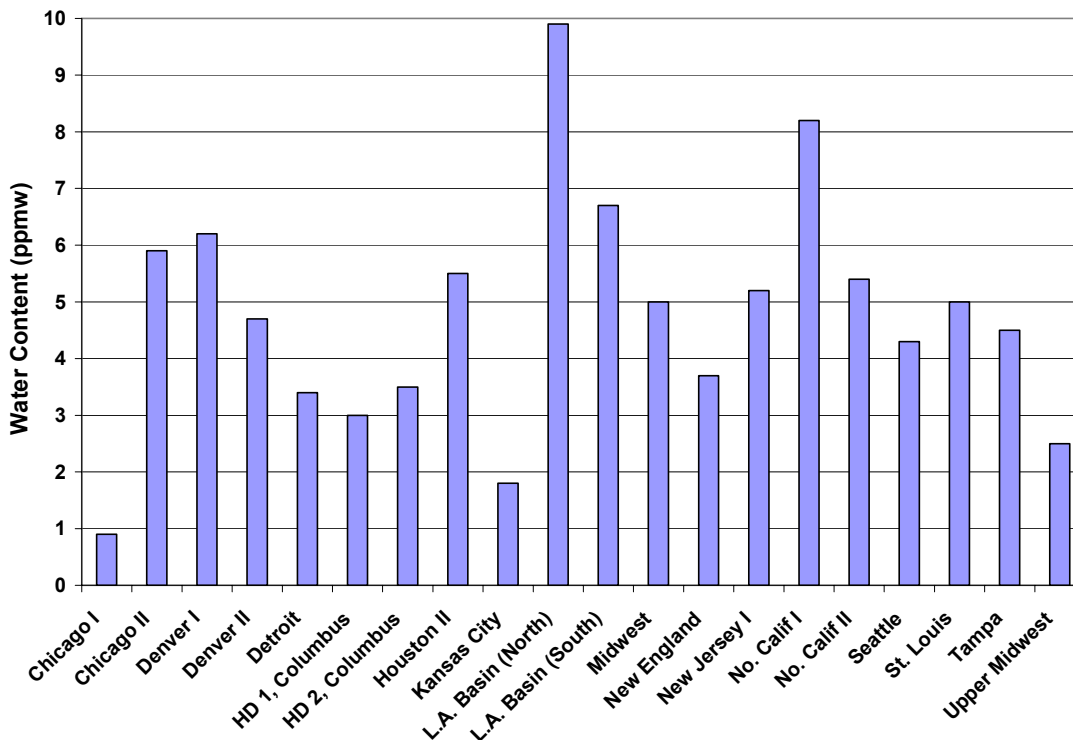Figure ES-1 shows the moisture data as a bar chart. As can be seen, there were no samples above 35 ppm water.

Figure ES-1.   Moisture levels of collected samples[*].

The freeze valve time data referenced by D-2713 can be graphically represented by the circle markers and solid lines as shown in Figure ES-2. It shows that as the concentration of water increases (moving to greater values on the x-axis), the freeze time decreases. The star represents Falkiner's (Fuels and Lubricants Handbook, Totten 2003) statement that 60 seconds on the freeze test corresponds to a water concentration of about 35 ppm by weight. Thus, there is a "transition band" between about 35 ppmw and 45 ppmw where the dryness may depend on the temperature, the amount of methanol, and the application. To emphasize this, the graph has been shaded – darker on the left to indicate acceptably dry propane, and lighter on the right to represent unacceptably "wet" propane.

The average moisture content of each fork lift cylinder that was tested is plotted as a histogram and included in Figure ES-2. For example, the figure shows that there were 9 samples with moisture content between 2.5 ppmw and 5 ppmw. Clearly, the moisture levels of the tested samples are well into the "acceptable" dry range.

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[*] When using liquid propane and liquid water, 1 ppm weight is approximately 0.5 ppm, volume. When using propane vapor and water vapor, 1 ppm weight is approximately 2.4 ppm, volume.
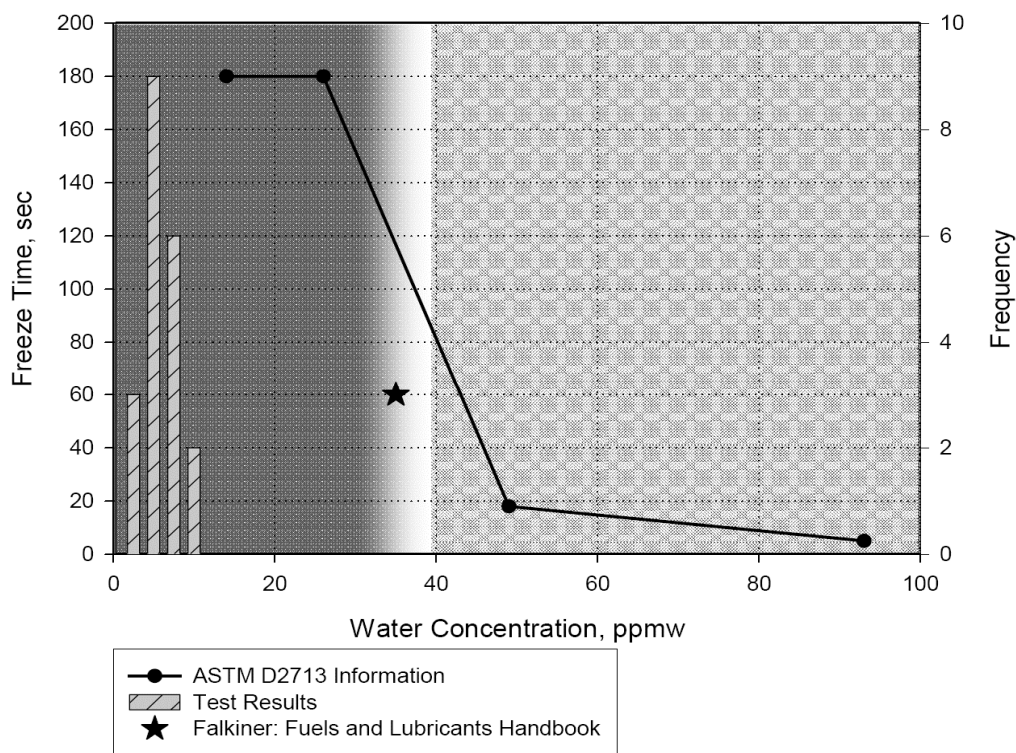
Figure ES-2. Moisture map with histogram data.

Testing for Solids

The particles remaining in the fork lift cylinder after evaporation of the propane were analyzed in a Horiba LA-900 Laser Particle Size Analyzer. The sizer presents the data as the number of particles in each particle size bin (divided by size).

The results of the particle size analysis are plotted in Figure ES-3. The measured particle size is shown on the x-axis. The percentage frequency of occurrence is shown on the y-axis. Most of the particles fall between 1 micron and 10 microns. For purposes of reference, it is noted that this is typically the size of a bacterium. The larger particles are about the size of a human hair, while the smallest particles are approximately the size of some viruses, and invisible to the eye.

The data show a fairly wide range of particle sizes, from a minimum of 0.2 microns and maximum of 900 microns. The vast majority of samples have distribution peaks from 1 to 10 microns, one sample has somewhat of a peak at approximately 0.5 microns (2523, Midwest-Columbus, OH, pages B28 to B-32), and four samples have peaks in the range of 10 to 80 microns. Two data samples have additional peaks of between 700 and 900 microns: 2536 (Northern California II-Gurneville, pages B-39 and B-40), and 2464 (St. Louis-Godfrey, IL, pages B-43 and B-44), with the Gurneville sample providing more particles in this range. However, the number of particles in this range is still small compared to the lower size particles.
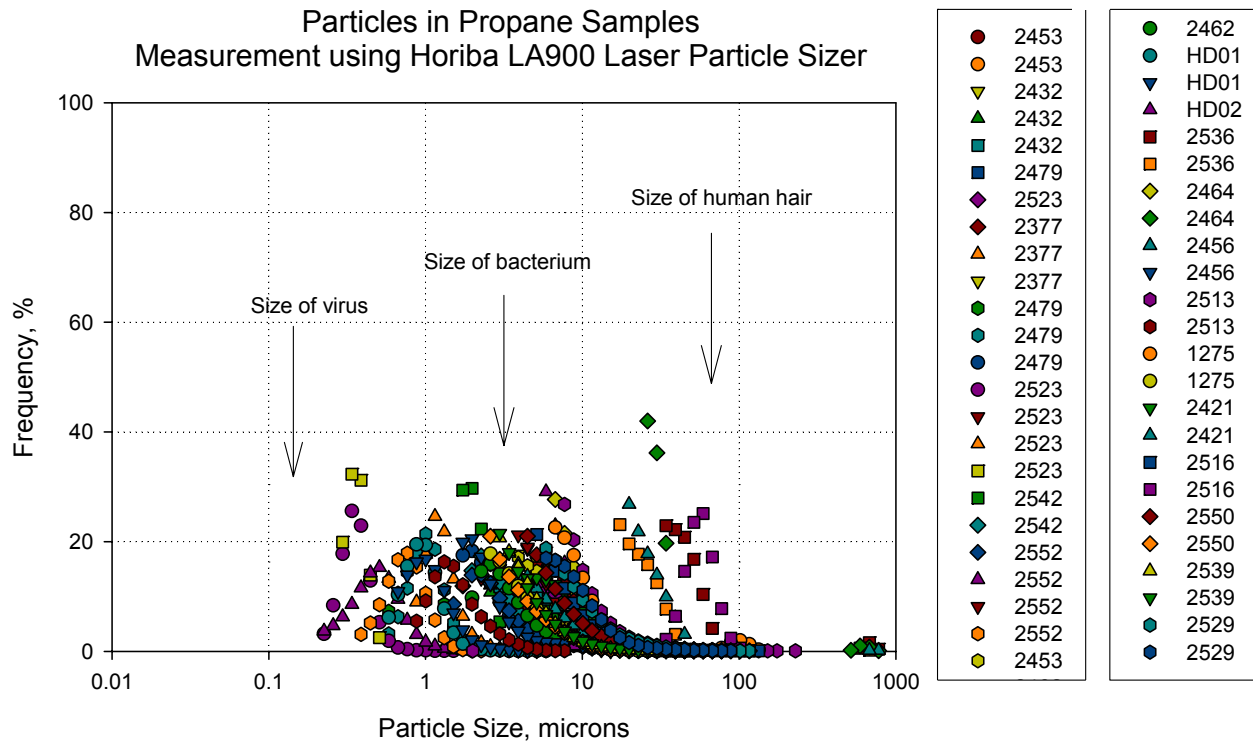
Figure ES-3. Particle size histogram of samples, sample replicates, and sample dilutions.

Energy dispersive spectroscopy (EDS) identified the outer surface of the particles to be composed of carbonates. This result was confirmed by infrared spectroscopy analysis. The backscattered electron imaging (BEI) image suggested that the particles consisted of a metallic component (such as iron) and lighter elements such as carbon, oxygen and sulfur. The particles are likely from interactions of the hydrocarbon fluid (including sulfur compounds as contaminants and an odorant), the steel distribution piping and transportation and storage vessels. An external laboratory conducted further analyses on the samples and confirmed the presence of iron, carbon, oxygen, aluminum, and silicon. The source of the aluminum could be the fork lift cylinders used as sample collection vessels.

A small amount fibrous material was also found in the sample selected for further analysis. One type of fiber was identified to contain silicon and oxygen (components of glass and some sands). A second type of fiber had a cellular appearance, as opposed to the granular, crystalline structure of the other fiber type. The source of these fibers is unknown. Possible sources include hose reinforcement fibers or loose filter fibers. These fibers comprised a small fraction of the solids collected, with the majority being the metallic-based fibers discussed earlier.

Testing for Hydrocarbon Composition

Each forklift cylinder was analyzed for hydrocarbon composition using a gas chromatograph using flame ionization, as outlined in ASTM D-2163, "Analysis of LP Gases and Propylene Concentrates by Gas Chromatography," contained in GPA 2140 (GPA 1997). We identified the amount of each of the following hydrocarbon present in terms of volume percent: methane, ethane, propane, isobutene, n-butane, and propylene.

Figure ES-4 shows all the sample compositions on one graph. Note that the y-axis is logarithmic. To avoid representational problems when a species is absent, when a species had zero concentration, we assigned it a value of 0.0012 percent (a value of 0.001 percent would not be visible about the horizontal axis).
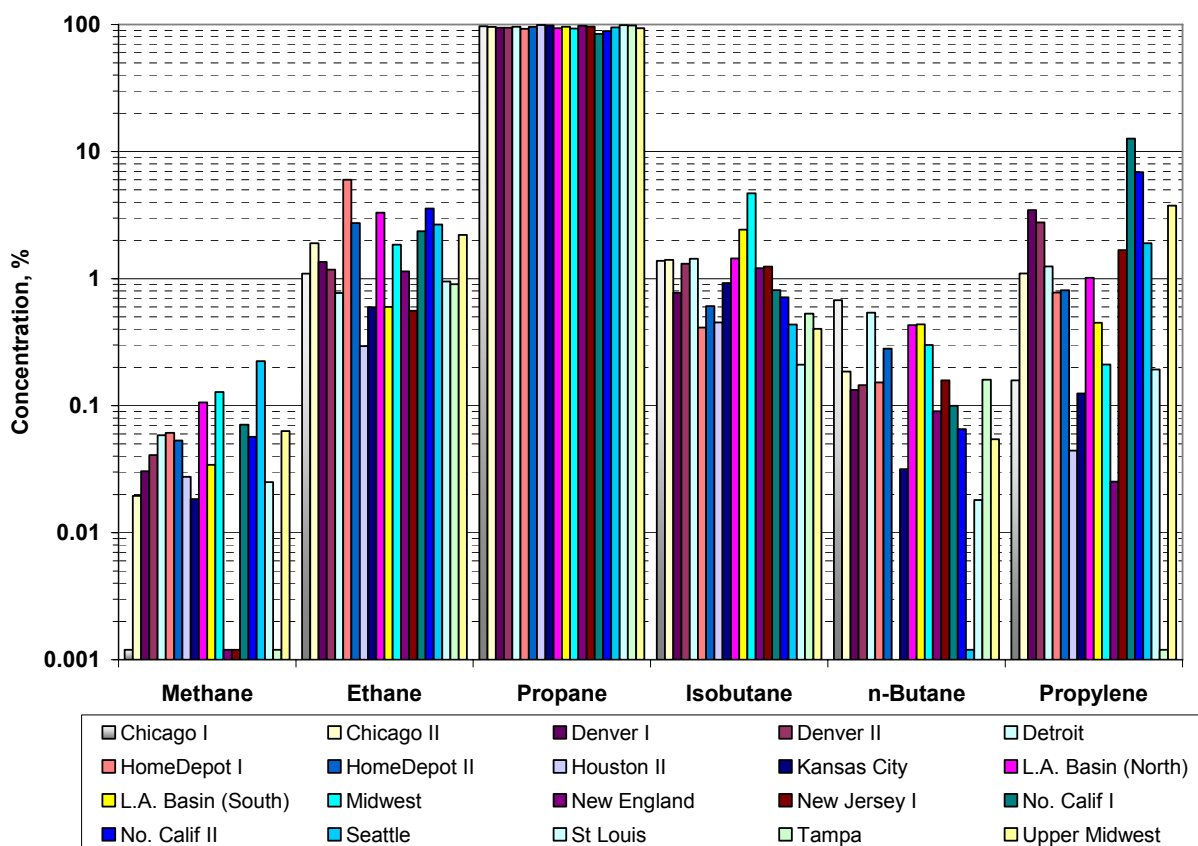

Figure ES-4.   Hydrocarbon analysis.

The Northern California sources were suspected to have high levels of propylene. Indeed, both samples were above five percent (6.9 percent for Gurneville and 12.6 percent for Elk Grove). Neither of these samples would meet the HD-5 specification (GPA 2140). The level of propylene found in the Gurneville sample would meet the California Air Resource Board's requirement for propane used as engine fuel[*], but the Elk grove sample exceeds the propylene limit allowed in that specification.

Sources and Remediation: Water

Several sources of water exist along the propane production and distribution system. Two sources of moisture in propane production include naturally occurring in natural-gas derived LPG and caustic washing in refinery-derived LPG. Water can also enter the LPG system during underground storage. Underground storage is common at many terminals, either in mined caverns or in salt domes. Ground water is likely present, even if in small quantities, in both situations. Normally, the entire propane distribution system, from pipelines and transport tanks to end user storage tanks, is closed and under positive pressure. However, these systems may periodically be opened to the atmosphere for inspections and servicing. As tanks are opened to the atmosphere, moisture-laden air, particularly in the coastal regions, can enter the tank. However, a more common source of tank moisture is from intentional means such as hydrotesting and steam cleaning between loads. As most marketers do not have the filtration and dehydration equipment that is typically installed at production and terminal facilities, water contamination is addressed by additives rather than removal. While these additives, such as methanol, do not make off-spec propane on-spec, they can prevent regulator freeze-ups, one of the main concerns of marketers.

The standard technique of water remediation in the propane industry, downstream of the production plants, is by the addition of anhydrous methanol. Because methanol's affinity for water is much stronger than its affinity for propane, the water and methanol bind together, effectively removing at least some of the water from the propane. A "rule-of-thumb" exists for neutralizing moisture in ASME containers that calls for the introduction of at least one pint of genuine absolute anhydrous methanol (99.85 percent pure) for each 100 gallon of water capacity of the container.

Methanol is traditionally over-used – if one pint is good, more must be even better. This over-dosing is sometimes compounded by the fact the over-dosing may be replicated at multiple points along the distribution chain, even when the propane is sufficiently dry. One marketer explained that when filling a bobtail truck from a bulk tank, his procedure called for first filling the connecting hose with methanol. This procedure was performed with no measurements being made as to the dryness of the propane – more is better. However, a drop in temperature can result in most of the methanol phase separating to the bottom of the tank. Although the methanol does vaporize with the propane and water, it does have a lower boiling point than water. Therefore, methanol will continue to concentrate in tanks that cannot be completely emptied. The effect on equipment (for example burners, vaporizers, injectors, and elastomeric materials such as hoses) is a topic for additional research. Some studies have found that stress corrosion cracking (SCC) was observed as a result of the interaction of the methanol, water and steel. Again, this is an area for additional research.

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[*] CARB's engine fuel specification, available from www.arb.ca.gov/regs/title13/2292.6.pdf, is also commonly referred to as "HD-10".

Several issues exist in using methanol to address moisture-in-propane problems.

- To properly dose methanol in propane, there should be an accurate measurement of the moisture level in propane
- Easily-made moisture level measurements (freeze-valve) are affected by methanol, and are go-no-go tests – if the sample shows "wet", there is not a good correlation between the freeze valve times and moisture content in the "wet" region
- Even if accurate measurements are made, there is no simple method to determine the desired amount of methanol.

The only way to avoid over-use of methanol is to have simple, easy-to-use, cost-effective, rugged, robust, and accurate measurement methods, most likely on-line instrumentation. Unfortunately, the adjectives used in the previous sentence are <u>all</u> important. Accurate on-line instruments are currently available, at a cost of thousands of dollars, and they are not necessarily easy-to-use.

The alternative to treating the moisture problem is to remove the moisture from the propane stream, as is done at the production sites and terminals. Methods that could be employed to remove moisture at a bulk plant scale involve moisture-removing filters or desiccants such as molecular sieves. Unfortunately, some of these sieves do not operate selectively. Efficient removal of moisture may also mean efficient removal of mercaptans. While such a system could be relatively cost effective to install, a sieve system would also require an odorization system downstream. While constant monitoring of the sieve system is required to maintain optimum moisture control, monitoring of the odorization system would be absolutely imperative, as un-odorized propane is inherently unsafe in all but a select few end-use applications. Some bulk plants are nearly small terminals themselves – in these instances, these marketers may have a sensitive market that would justify the costs of the purchase, operation, maintenance, and monitoring of such a system. These systems would then be designed and installed by the same entities that service production plants and terminals. Clearly, the design and operation of these systems introduce degrees of complexity not often found in small terminals and bulk plants.

Sources and Remediation: Solids

Many of the solids identified in this study are iron-based. The particles are the result of mill scale, generated during the production of steel, or from corrosion of various metallic components in the distribution chain. Some of the storage and transportation vessels and interstate pipelines are over fifty years old. Since most of these systems transport a variety of hydrocarbons of varying dryness and corrosivity, there is reason to believe that these systems could continuously emitting corrosion products into the fluid streams.[†]

Episodic equipment failures, including plugged filters, in-operational pumps, valves, and control systems can inadvertently place sub-standard, "off-spec" propane in the distribution chain. While large, system-wide upsets are extremely rare, much smaller events are more common and can affect individual bulk plant operators as severely. The low-profile incidents may actually go unnoticed until an end-use customer is affected, through inoperable or low-performing equipment such as engines.

[†] SwRI's report on PERC Docket 10951(SwRI 2006) identified that "solids" found in forklift carburetion equipment were compounds of heavy ends, i.e., compounds having 20 or more carbon atoms. These solids were detected at sub-micron levels. These identified solids remained in engine fuel vaporizers. The present study identified the solids that were contained in the fuel after ambient temperature evaporation ("weathering").

Many vendors offer a complete range of filter media with varying pore size and efficiency ratings, materials, type of construction, and overall size and flowrate capability. For near-complete filtration of the particles identified in this study, a filter of no more than 0.5 micron, with an efficiency of at least 99 percent would be required. However, as replacement media and maintenance costs are greatly affected by this choice, we recommend that the individual marketer select a system that considers customer end use, maintenance acceptability, and particulate characteristics of the propane stream.

The types of filter construction somewhat follows the pore size and filter efficiency. Pleated filters are available in a wide range of pore sizes (0.2 to over 100 microns), efficiencies (90 percent to 99.98 percent), and filter materials (polypropylene, cellulose, glass fibers). Of these, polypropylene (higher efficiencies, smaller pore sizes, 15 to 25 percent more cost than cellulose) and cellulose elements are acceptable for use in propane streams[*]. Because of cost, cellulose is a good choice for prefilters. Wound filters are formed by winding filter media material, as yarns, onto an inner cage that remains part of the filter element. Wound filters are typically less efficient and have larger pores than pleated elements. They also typically have longer loading times, and because of lower cost (10 to 30 percent less than pleated filters), they are good choice for prefilters. Material recommendations are the same as pleated elements.

Whatever filter system is choice, it must be properly monitored. Pressure drop across the filter system is indicative of filter loading and should be monitored daily. Periodic checks should also be made on the propane leaving the filter system. Either frequent batch sampling or to-be-developed on-line analysis methods/instruments must be used to determine replacement. Also, while operators may use normal operations and nominal fuel quality to predict filter life, anecdotal evidence indicates that it is the unplanned, unexpected, infrequent, and non-periodic upsets in fuel quality that will determine any filter loading rate.

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[*] A cautionary note: chemical compatibilities tables list the compatibility of liquid propane and polypropylene as satisfactory to excellent, depending on the source. However, several references cautioned the use of propane vapor with polypropylene, listing it as UNSATISFACTORY. Care should be taken in using polypropylene filter media to ensure that is exposed to liquid propane.

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INTRODUCTION

LP gas quality is becoming increasingly important as competition between fuels becomes more intense, and new technologies with particular fuel requirements emerge. Traditional end uses such as residential, commercial, and industrial atmospheric burners have low sensitivity to most fuel quality parameters such as heating value, moisture content, particulates, heavy ends, and other contaminants. Even with these robust systems, issues of freeze-up due to excess moisture and high lockup due to particulates in pressure regulators would periodically surface. Mitigation was usually tried-and-true methods such as methanol dosing for moisture and a good, solid rap on the regulator with a wrench to dislodge particles.

Engines fueled by LP gas (also referred to interchangeably in this report as "propane")[*] represent a highly-visible exception to the contaminant-tolerant end-uses. Vaporizers and carburetion and injection systems can be very susceptible to plugging with particles and sludge from heavy ends and the interaction of other contaminants. Continued and expanded uses of LP gas in engines and new uses in distributed generation systems using microturbines and fuel cells will require higher constraints on fuel quality, and the traditionally tolerant end uses may pose additional constraints. Lower emissions and higher efficiency requirements are expected to be less tolerant of contaminants. For example, the vapor composition changes as LP gas vaporizes in a storage tank, because of the differing vapor pressures of ethane, propane, propylene, butane, water, methanol, and sulfur (odorant) compounds. The interaction of these compounds is also not thoroughly understood. The effect of this varying composition on the combustion efficiency and emissions of low NOx burners and condensing heat exchangers is unknown and is a need for further study.

Propane "dryness", or the absence of water, is arguably the most critical of specifications for the typical end-use customers. Unfortunately, moisture is also the most likely contaminant. Its sources are many, and sometimes the sources are intentional. Periodic hydrotesting of LP gas containers is undertaken to ensure that the container meets its pressure requirements. An example is the five-year requalification testing of cargo, or "bobtail" tanks. Anecdotal evidence in the industry suggests that purging water completely after a hydrotest (especially from bobtail tanks) sometimes poses a problem in that the water is difficult to remove completely, and methods for gauging when this has occurred have varying reliability.

In addition to freeze-up, the presence of water may impair the ability of the odorant to meet standards, because water can cause oxidation (rusting) on the inside of the container. The odorant (usually a mixture whose main component is ethyl mercaptan) may be adsorbed on oxidized surfaces and lead to "odorant fade" wherein the odor is reduced to an undetectable level.

As noted, water may react with transportation and storage container walls. Typically, the result is the formation of iron oxides (rust). In the presence of odorant and possible sulfur compound contaminants, some sulfides of iron may also be generated (black powder). Mechanical stresses could cause these compounds to flake off the surface and be carried along in suspension with the LP gas. If some of the solid contaminants settle out or become adsorbed to surfaces, especially in stagnation regions, buildup and blockage can occur. Also, for some applications, solid contaminants may be unacceptable to the customer.

In order to assess remediation methods for water and solids contamination in LP gas, it is important to have accurate information about water and solids contamination in the system today. This project is one

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[*] LP gas is nearly universally propane in the US and Canada.

of several that the Propane Education and Research Council (PERC) has undertaken to assess LP gas fuel quality. For this study, PERC has commissioned Battelle to obtain data that a) indicates the nature of solids species found in LP gas, b) gives an indication of the levels of water and solids contamination, and c) assesses practical remediation methods. The limited data that are planned imply that the assessments are intended to be illustrative rather than statistically comprehensive. The report documenting this work is included in two volumes: Volume 1 – Technical Report and Appendices (this volume), and Volume 2 – Particle Analysis Data.

Objectives

The objectives of this research project are to gather information about the sources and levels of water and solids contamination in LP gas, and to address possible and practical remediation methods.

Existing Requirements

The existing requirements of LP gas fuel quality are contained in Gas Processors Association's Standard GPA 2140-97. The GPA specifications are generally recognized to be used in selling and buying of LPG mixtures. ASTM has approved test methods by which compliance with these specs may be achieved. GPA includes these methods and two additional GPA methods in the 2140 standard:

- ASTM D-1265-92: Sampling Liquefied Petroleum Gases
- ASTM D-1267-95: Vapor Pressure of Liquefied Petroleum Gases
- ASTM D-1657-89: Density or Relative Density of Light Hydrocarbons by Pressure Hydrometer
- ASTM D-1837-94: Volatility of Liquefied Petroleum Gases
- ASTM D-1838-91: Copper Strip Corrosion by Liquefied Petroleum Gases
- ASTM D-2158-92: Residues in Liquefied Petroleum Gases
- ASTM D-2163-91: Analysis of Liquefied Petroleum (LP) Gases and Propylene Concentrates by Gas Chromatography
- ASTM D-2713-91: Dryness of Propane (Valve Freeze Method)
- ASTM D-2784-92: Sulfur in Liquefied Petroleum Gases
- GPA 2174-93: Obtaining Liquid Hydrocarbon Samples Using a Floating Piston Cylinder
- Propane Dryness Test (Cobalt Bromide Method)

In addition to these specific test methods, GPA 2140 also includes preface materials that discuss other issues such as odorization and methanol. The preface also includes a fairly comprehensive table on LP gas specifications, such as chemical composition, vapor pressure, residue, corrosivity, sulfur, and moisture/free water. The chapter on LP gas in ASTM's Fuels and Lubricants Handbook (Totten 2003) gives a thorough description and historical perspective on these test methods.

In this study on water and solids/particulate contaminants, of particular relevance are the residue limits and test (ASTM D-2158) and the moisture/free water limits and tests (ASTM D-2713, Freeze Valve and the Cobalt Bromide Method).

The residual matter limit is 0.05 ml remaining after evaporation (weathering) of 100 ml of liquid LP gas at 38 C. More than 0.05 ml remaining after the weathering indicates unacceptable levels of low vapor pressure substances (oils) and particulates. If 1/10 of the remaining 0.05 ml were solids, the particulate level would be 50 ppm (vol). The D-2158 test method also includes an oil stain observation, where

solvent (pentane or cyclopentane) is added to the remaining residue, bringing the volume to 10 ml. A smaller volume of 0.3 ml is injected onto a filter paper, and if there is no visible oil ring on the filter paper after 2 minutes, the sample is acceptable. While this part of the test is referred to as an "oil stain", suspended particulates would also cause a failure.

Meaningful moisture tests are much more difficult to interpret. This is in partly due to the dryness specification that requires the water content to be well *below* the equilibrium saturation level. In fact, propane in 30 to 100 percent saturation range is considered "wet". Water saturated propane fails the dryness criteria by a wide margin (Totten 2003). This requirement then implies that there is no free water. Totten also indicates that propane dryness is perhaps the most critical of all specifications for downstream marketers and users, as it impacts operations reliability when reliability is needed most, i.e., in cold environments.

The freeze valve method (D-2713) indirectly measures the freezing point of the propane liquid. A sample of propane is captured in a container and throttled through a small-orificed valve. If excess moisture is present, it will freeze as the liquid cools during the pressure reduction (adiabatic expansion). The sample passes the test if the time to freeze the valve to close-off is 60 seconds or longer. Falkiner states "it is generally accepted that a 60-second freeze time is about equivalent to a -26 C dew point and less than approximately 35 ppm (weight) water in the LP gas liquid phase" (Totten 2003). Williams and Lom (1982, page 134) mention that if the time to freeze off is greater than three minutes, the propane is noted as acceptably dry, having a dissolved water content of below 20 ppm. These authors then comment that "this test is of course purely empirical. Some LPG suppliers, however, claim it to be of use for production control purposes." In fact, *Good Practices for the Care and Custody of Propane in the Supply Chain* (EEA /PERC 2005, page 24) suggests that

> "Terminal operator should do freeze valve dryness testing on propane prior to methanol injection whenever a change in sales tank line-up is made, based on facility management's requirements."

Also, an August 2000 propane specification sheet found on Dixie Pipeline's website (Dixie Pipeline, 2000) shows that there are two moisture content specifications: 1) a "PASS" per ASTM D-2713 (freeze valve), and 2) a maximum of a +25 F liquid phase dew point, as measured by a hygrometer. From data in Williams and Lom (1982, page 58), the estimated water content at a liquid phase dew point of + 25 F was approximately 20 ppm, weight. It is not known if both specifications are used simultaneously. The authors of this current report are not suggesting that this practice is not prudent or should not be required. Rather we are suggesting that in light of Williams and Lom's comments, there is still debate on the effectiveness of readily available and easily performed moisture tests.

The preface of GPA 2410 states the presence of methanol, even in small quantities, can make the results of the freeze valve test not applicable. Falkiner's approximation mentioned above of a water content of 35 ppmw and -26 C would not apply, as the methanol lowers the freeze point — the actual moisture content of the sample would not be known but would likely be higher. While the presence of methanol affects the significance of the freeze valve times, the fact that the sample does not freeze indicates that there will not likely be freeze-up problems with this sample. Indeed, the result would not be a "pass" with methanol on the propane, but marketers perform the test to identify potential freeze-up problems with regulators or other devices with orifices. If methanol prevents freeze-ups in the freeze valve and then regulators, then the propane passes the marketers' tests. Methanol is often added, albeit sometimes unnecessarily and virtually never scientifically, to address moisture issues. Methanol decreases the solubility of water in fuels, and can cause phase separation when added to water-saturated fuel. The resulting phase-separated water and methanol mixture is non-freezing, so it will not cause blockages in valves and regulators attributed to ice. Methanol in proper concentrations in the separated phases will prevent freezing down to the normal boiling point of propane (-43 C) (Totten 2003). There are potential

negative effects from the use (or more likely the over-use) of methanol. These issues are discussed later in this report.

The cobalt bromide (CoBr) method requires a more complex apparatus and is sensitive to apparatus moisture contamination. There are no references in the section of GPA 2140 where the CoBr method is described, but Totten (2003) references a 1932 article in a propane trade publication (Hachmuth 1932). That source mentions that the relationship between the CoBr color change and the propane humidity levels are also a function of sample temperature, and the method calls for the sample to be cooled to 32 F. Therefore, the bulk vapor humidity is somewhat different than the captured sample, and there is no single value ppm of water that corresponds to a CoBr pass/fail test or a dew point (Totten 2003). The end result of this discussion is that if a sample is found to be "on spec", it is likely acceptable in most end uses, because the dryness of "on spec" propane is so stringent. However, the converse of this thought is that the measurement of the moisture level in "off spec" propane can only accurately be stated as being higher than "on spec", using these methods. Williams and Lom (1982, page 132) also found the CoBr method to be imprecise and qualitative only.

Electronic instrumentations for moisture include hygrometers and dew point sensors. These methods have not readily been shown reliable for propane marketer use. A dew point sensor was used in the testing phase of this project, and while the results are accurate, its requirements of frequent cleaning and recalibration would prevent its use as a field test instrument.

Previous Studies

No studies relating directly to issues of water and solid contamination were found in refereed journals during the literature search. Some anecdotal studies are mentioned here; several "handbook"-type references that are available are also mentioned here.

A privately funded study on LP gas fuel composition was conducted in the spring of 2001. As the study was privately funded, the specific details of the study are not available for reference, and only the highlights are presented here. The study examined the composition of commercially available fuel at different geographical locations in the United States and Canada for use in motor vehicles. Samples were obtained from 44 locations and each sample was tested for moisture content using a Drager tube. Methanol, silicon, and particulate matter (collected in filters), and metals were also quantified. Water content was reported at 5 to 45 ppm, with nine of the 44 samples at or above the 35 ppm nominal cutoff. Ten samples had measurable particulate amounts; however the results were not presented as being from an ASTM 2158 residue test. As mentioned above, a result of this test is the amount of residue remaining after the evaporation of a 100 ml sample of LP gas. Therefore, it is unknown whether these levels are significant. There was no correlation between moisture and particulate levels. This was not unexpected. If excessive moisture was the cause of high particulate counts, it was a long-term exposure, and a high or low moisture level measurement in this study was only a one-time measurement. This specific measurement could be a low level in a historically high-moisture region, or vice-versa.

The ADEPT Group completed a fuel quality study where propane was used in microturbines (ADEPT/PERC 2003). In this study, the researchers analyzed 16 fuel samples for quality and heavy ends. The specifics of these analyses were not included in the project final report (they were included in intermediate progress reports). Heavy ends (C16+) and some particulates were issues in the study, although the particulates were not quantified. The report also discussed filtration methods to address some of the concerns. The authors recommended coarse filter screens ("rock catchers") upstream of the engine fuel system filler ports and the onboard storage tank liquid withdrawal port. The authors discussed using activated charcoal filtration for the removal of heavy ends, with a cautionary note that these filters also

remove the odorants – care must therefore be taken in the use of these filters as unodorized propane is present downstream. The authors recommend replacement of the media once per month; however without performance data, this is speculative. The authors of the present study are aware of a PERC-funded project for the bulk cleanup of propane streams, especially heavy-end removal, using activated charcoal, also performed by ADEPT (PERC Docket 11649). Activated charcoal is also commonly used in vapor streams.

One issue that was raised during the present study is the lack of publicly available literature. We used the most up-to-date engineering and science databases, and no studies were found, including the above two referenced studies. While the first was known to be a private study, as previously mentioned, the second was a public study. The ADEPT Group also performed a group project (ADEPT 2000) that evaluated the effects of propane fuel blends on the emissions and durability of selected engines. This report and the other ADEPT report were found on ADEPT's web site, but were not referenced in the standard literature databases.

While the 44-sample study and the 16-sample study are more than cursory investigations, they are not statistically deep because of the regional and temporal nature of the LP gas supplies in the US. Such a statistical study would require hundreds of samples, with periodic samples at the same locations. These studies indicate that fuel quality is nominally acceptable, even excellent, from the aspects of particles, water, and heavy ends. As noted, they do not address the episodic upsets that can significantly affect the various fuel quality parameters.

PARAMETERS OF THE CURRENT STUDY

Sampling

Several rationales for collecting test samples were considered. Options included collecting samples at different stages in the distribution system, collecting samples from geographically distinct regions, and collecting samples from different sources. To collect a statistically valid set of samples for all recognized variables would have involved a prohibitively large number of samples. Instead, it was decided to obtain samples from different sources in different geographical locations as an illustrative data set.

The geographical regions for obtaining LP gas samples are listed in Table 1. The "Comment" column is included as it gives the background of the sample and the production area, if available. These comments were derived from the industry consultants who guided Battelle in selection sampling sites.

Table 1.   Sampling locations.

Supply Area	Location	Comment
Chicago I	Carol Stream, IL	Refinery
Chicago II	Chesterton, IN	Refinery
Denver I	Conifer, CO	Refinery (historically high propylene content)
Denver II	Colorado Springs, CO	Refinery / local production (stringent air quality standards in effect)
Detroit	Jackson, MI	Refinery
Home Depot - 1	Columbus, OH	Retail location
Home Depot - 2	Columbus, OH	Retail location
Houston I (sample not returned)	Houston, TX	Refinery / local production (air quality standards in effect)
Houston II	Corpus Christi, TX	Refinery / local production (air quality standards in effect)
Kansas City	Wichita, KS/MO	Refinery
L.A. Basin (North)	Lancaster, CA	Refinery
L.A. Basin (South)	San Diego, CA	Refinery
Midwest	Columbus, OH	Pipeline
New England	Chepachet, RI	Imported product
New Jersey I	Woodbridge, NY	Major East Coast Supplier
Northern California I	Elk Grove, CA	Historically high propylene content
Northern California II	Gurneville, CA	Historically high propylene content
Seattle	Auburn, WA	Refinery (air quality attainment region)
St. Louis	Godfrey, IL	Local production
Tampa	Tampa, FL	Imported product
Upper Midwest	Wausau, WI	Refinery

The samples were collected in standard aluminum forklift cylinders. Aluminum was a recommended vessel material in Williams and Lom (1982, page 121). New forklift aluminum cylinders were purchased from Worthington Industries. Each cylinder was evacuated before being shipped to Battelle, so that it would not contain water vapor. At Battelle, the serial numbers of the cylinders were recorded and each

cylinder was packaged with a hose and fittings to expedite filling the cylinders at the sampling locations. The cylinders were shipped to the sampling locations by a freight carrier. Individuals at each sampling location had been notified to expect the forklift cylinders. We also obtained two 20 lb cylinders (a few weeks apart) from a Home Depot in Columbus, Ohio, and we filled and refilled a new, evacuated aluminum cylinder at a Ferrellgas center in Columbus, Ohio.

Testing for Water

As previously mentioned, the most commonly used methods for moisture in LP gas are the freeze valve test (D-2713) and the cobalt bromide test (both listed in GPA-2140). The short freeze valve test times are indicative of moisture problems, and most testing laboratories do not offer the CoBr test because of low demand and short shelf life of the chemicals. In either test the result is *pass/fail*, and the amount of water is not determined quantitatively.

For these reasons, we evaluated alternative laboratory methods to measure the water content quantitatively. A variation of Karl Fischer titration[*] was examined, but it is primarily used with liquids, and use with a gas would lead to expensive plumbing and safety issues. Another concept that was considered was absorption of the water into a desiccant and measurement of the water absorbed by weighing. The system that was used is shown schematically in Figure 1.

To test the concept a small LP gas cylinder was used as the source. The gas stream was passed through a reactor containing desiccant and then flared. The desiccant container was weighed before and after the test. On the first test it was observed that the entrance region in the desiccant container had turned a deep brown indicating that the fine porous structure of the desiccant was trapping other contaminants. The brown, oily contaminant was analyzed chemically and was shown to be higher hydrocarbons. Clearly, this unexpected trapping of higher hydrocarbons negated the approach because it would be impossible to separate the weight contribution of the water from that of the higher hydrocarbons. A glass cylinder containing glass wool was interposed between the valve and the desiccant to trap the higher hydrocarbons. However, the hydraulic radius of the close-packed desiccant still continued to trap higher hydrocarbons, and this concept was abandoned for the following reasons:

- Difficult to stop the deposition of substances other than water on the desiccant
- If removed in an earlier filter, difficult to ensure that water is not also removed
- The amount of water vapor to be trapped is expected to be of the order of 1 gm, making it very difficult experimentally to ensure accuracy
- If the results were unacceptable, that would only be known after the cylinder had been emptied of LP gas and another sample would have to be retrieved from the field sampling location.

Instead, we sought a commercial sensor with the following properties:

- Detection range of about 1 ppm weight to 100 ppm weight[†] of water
- Unaffected by hydrocarbons and methanol
- Acceptable cost and delivery schedule.

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[*] A method, or the process, of using a standard solution to determine the strength of another solution.
[†] When using liquid propane and liquid water , 1 ppm, weight is approximately 0.5 ppm, volume.
  When using propane vapor and water vapor 1 ppm, weight is approximately 2.4 ppm, volume.
  When using propane and methanol, 1 ppm, weight is approximately 0.6 ppm, volume.
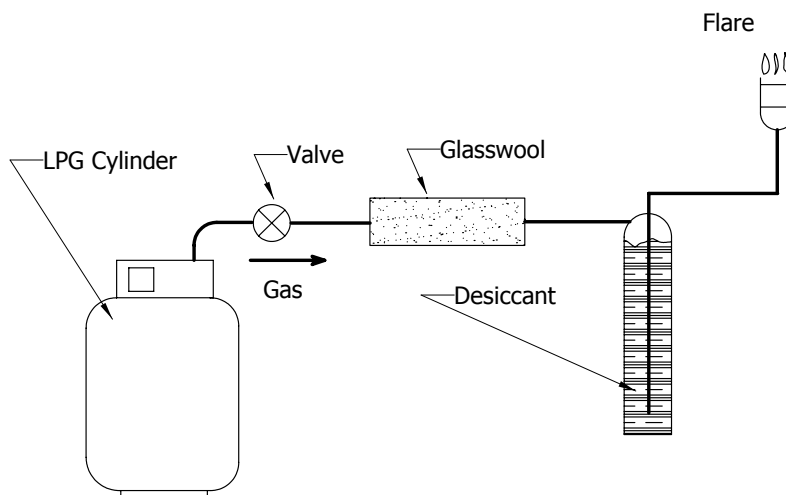
Figure 1. Method considered initially for measurement of moisture in propane — NOT SUCCESSFUL.

We purchased a commercial dew point sensor that was calibrated by the manufacturer for dew points between -110 C and -20 C. This sensor is described in Appendix A. Using the vendor-supplied calibration curve, the output voltage from the sensor, and the system pressure, the concentration of water can be calculated. The test configuration is shown in Figure 2. To have an approximate idea of how much of the LP gas remains in the forklift cylinder, the cylinder is placed on a weighing scale. The liquid LP gas goes from the cylinder to a vaporizer by means of a valve that can be used to control the flow rate. The gaseous LP gas then flows through another valve that can be used to control the pressure in the vaporizer, and then through a unit that houses the water sensor. Finally, the LP gas is flared. The vaporizer was designed and fabricated such that it has a small removable container, a "residue collector", at its lowest point. It is assumed that if any solids or oily residues remain, they will collect in the residue collector, and can be removed after the test for examination. After each test, the forklift cylinder was opened, visually examined, and then flushed with reagent-grade acetone. The acetone and collected debris are housed in a glass container until tested.

First, the system was tested with dry nitrogen, then with commercial grade propane. During these tests, arrangements were made to inject a drop of water into the path of the gases before the sensor with the intention of ensuring that the sensor registered the sudden, large amount of water (i.e., the sensor was functional), and noting how rapidly it reacted, and how rapidly it returned to equilibrium. It appeared to respond in the order of a few seconds, and equilibrated back in a matter of a few minutes as shown in Figure 3 which is a graph of water concentration as a function of time. At this stage the sensor and system were deemed to be working properly, and testing of the collected forklift cylinder samples was begun.

The test data consist of measurement of system pressure, dew point, and flow rate (in later tests) every thirty seconds. The average water content is calculated for each cylinder.
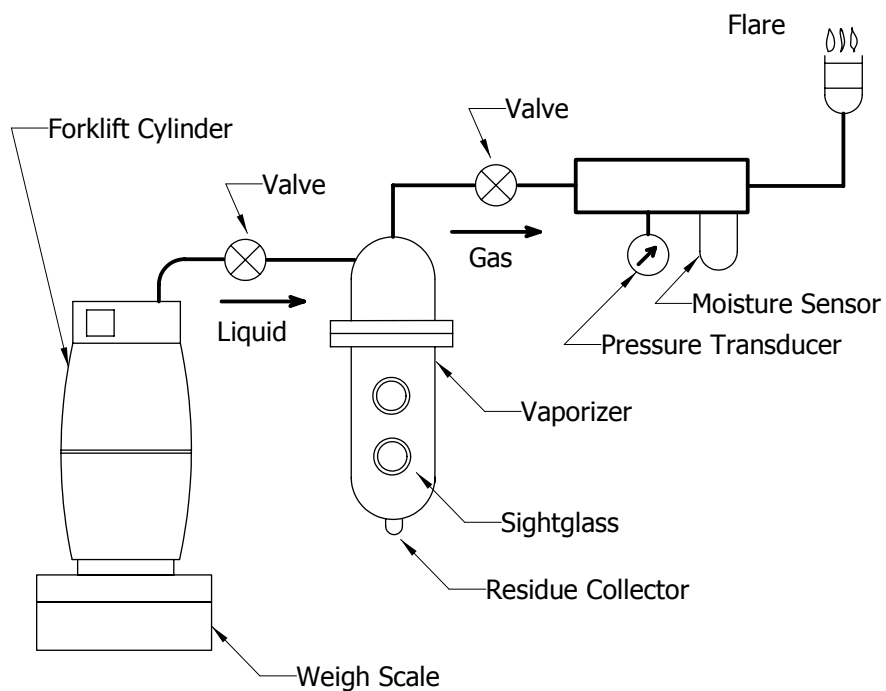
Figure 2. **Schematic of method successfully used for measurement of moisture in propane.**
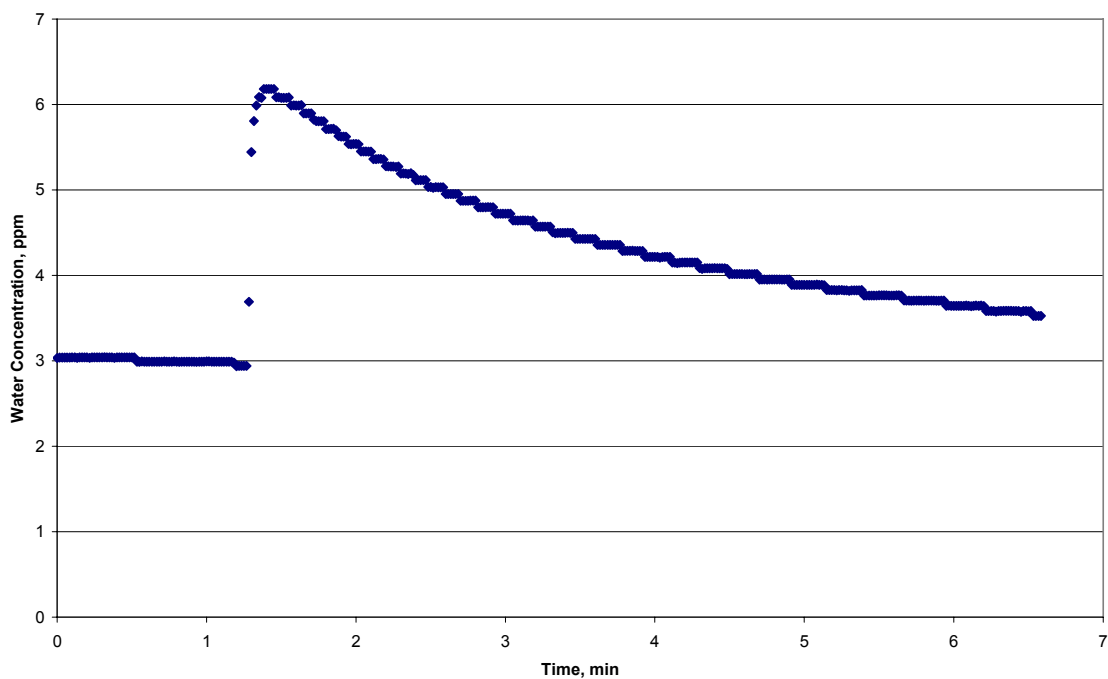

Figure 3. **Moisture sensor response test.**

Testing for Solids

Some laboratories offer a volumetric residue of solids measurement as part of a residue analysis. This does not give particle size distribution or composition.

Before any field samples were received, we attempted to develop a methodology for analyzing the sample particulates. To examine the particle size distribution, we assessed solid residue that was discovered in the oily liquid that remained after completion of some hose tests in an associated PERC project (Battelle/PERC 2005). The particles were analyzed in a Horiba LA-900 Laser Particle Size Analyzer. The procedure is described as follows. The particles were suspended in an inert liquid and stirred. A laser beam was then directed into the swirling liquid and a receptor measured the size and number of solid particles instantaneously captured in the laser beam. At the end of the test the analyzer calculated the number of particles in each bin (divided by size). The caution is that the machine works best with spherical particles and may be less accurate for flat particles (whose "size" as caught in a laser beam will depend on the orientation of the particle with respect to the laser beam). Before testing the collected samples, the instrument was calibrated using a standard sample.

The test report for this preliminary sample is shown in Figure 4. The upper portion of the figure shows three frequency diagrams. Each of the diagrams is a particle size distribution for the solvent used to extract the particulates. The top diagram, labeled "Hexane bottoms", shows a small number of particles in the broad range of 2 to 200 microns (as indicated by the low height of the plot) and a large number of particles in the 500 to 700 microns. Similarly, the second plot, labeled "Hexane fines", show a distribution of particles peaking at approximately 0.1 microns, and the third plot, labeled "Isopar G", shows a bimodal distribution, with peaks centered at 0.8 microns and 50 microns. The tables under the plots contain the mean, median, standard deviation, and the specific area (total surface area of the particles detected divided by the sample volume). These parameters give an indication of the size of the particles. The second and third columns are the cumulative distribution data. For example, in the table labeled "Hexane bottom", the cumulative distribution indicates that 10 percent of the particles were larger than 654 microns, and 70.7 percent of the samples are greater than 70 micron. Actually, the plots are the most illustrative way to present the data.

Electron microbeam instruments are useful for determining the chemical compositions of microvolumes of specimens. For example, X-rays have characteristic energies/wavelengths that can be detected using a solid state energy dispersive spectrometer (EDS) detector. EDS analysis was applied to the solid particles referred to above. The overall result was that most of the outer surface of the particles consisted of carbonates. This result was confirmed by IR (infrared spectroscopy). Carbonates form on metals in the presence of water and carbon. The base metal of the sample was unknown.

Secondary electron imaging (SEI) pictures of the particles at magnifications of 260X and 1000X are shown in Figures 5 and 6. Figure 7 is a 1000X backscattered electron imaging (BEI) picture of the same region as in Figure 6. The BEI gives contrast according to the atomic number of elements present. Higher atomic number elements (for example, iron and other metals) are brighter in the BEI image and lower atomic number elements (for example, carbon, oxygen, and sulfur) are darker.

The LP gas from Columbus, Ohio was the first sample to be tested. Figure 8 is a photograph looking down into the vaporizer. The residue collector can be seen at the center of the picture. Figure 9 is a photograph of the residue collector after removal from the vaporizer. The oily residue is evident. A closer look reveals a black mass of solid (fibrous) residue at the top edge of the oily residue. Figure 10 is a photograph of the descanted oily liquid from the residue cup.
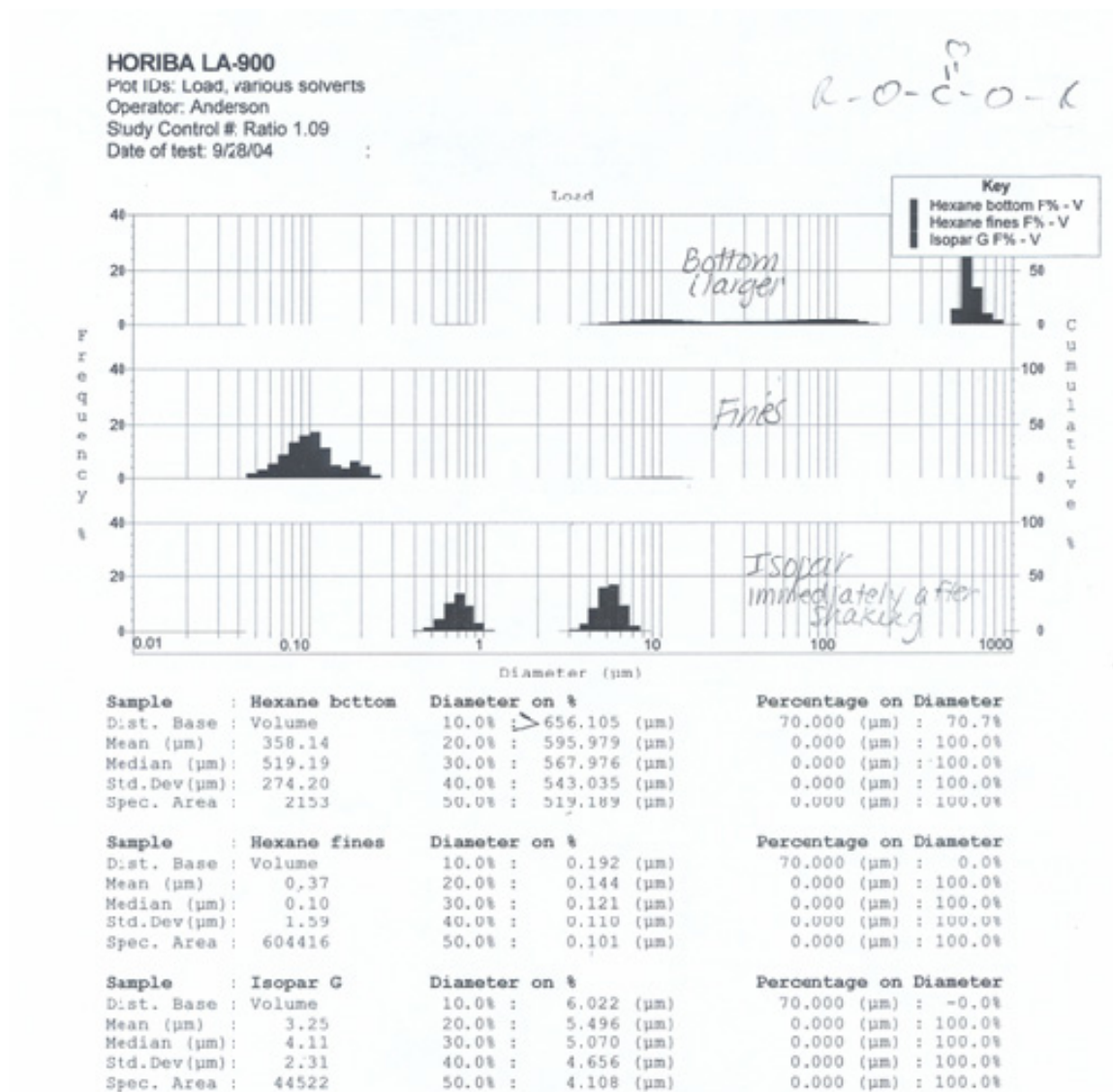
Figure 4. Particle analysis of propane sample on hose remediation project.
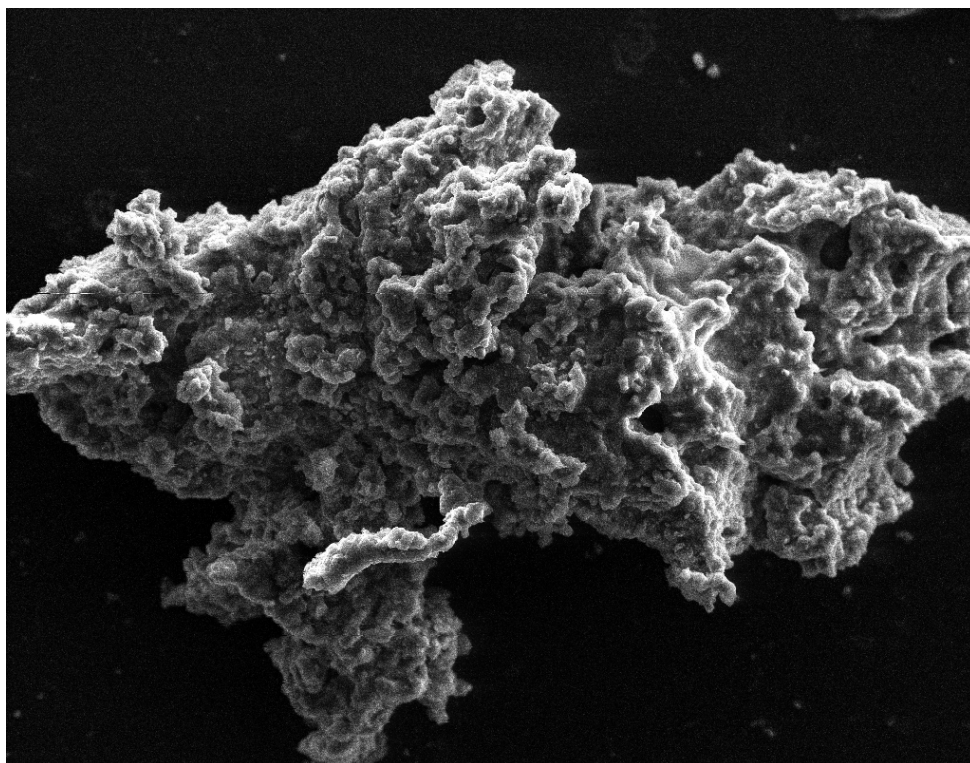
Figure 5. **SEI photo of particles at magnification of 260X.**
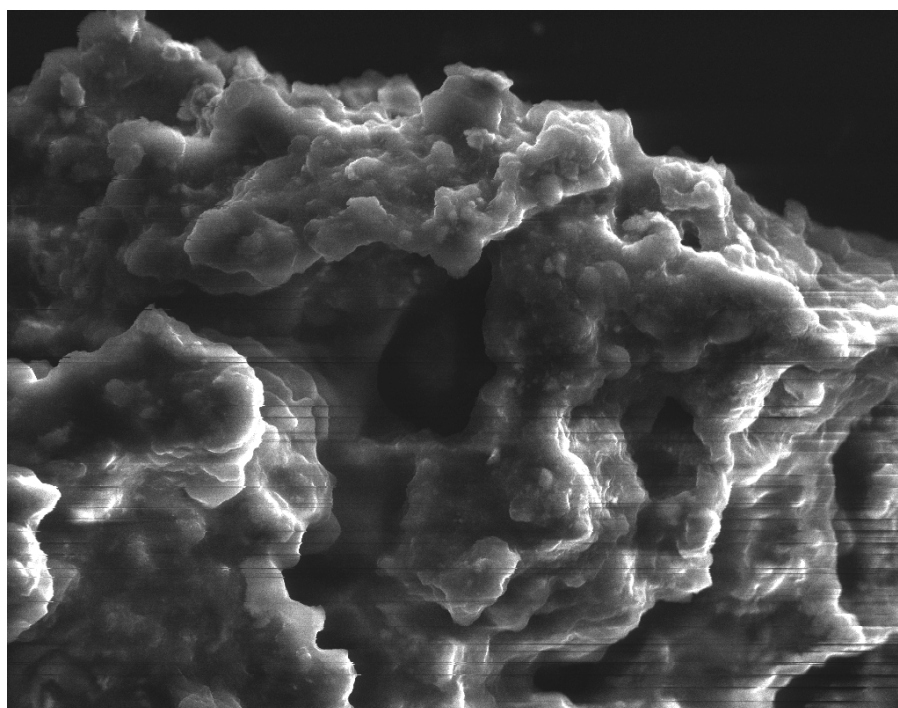
Figure 6. **SEI photo of particles at magnification of 1000X.**
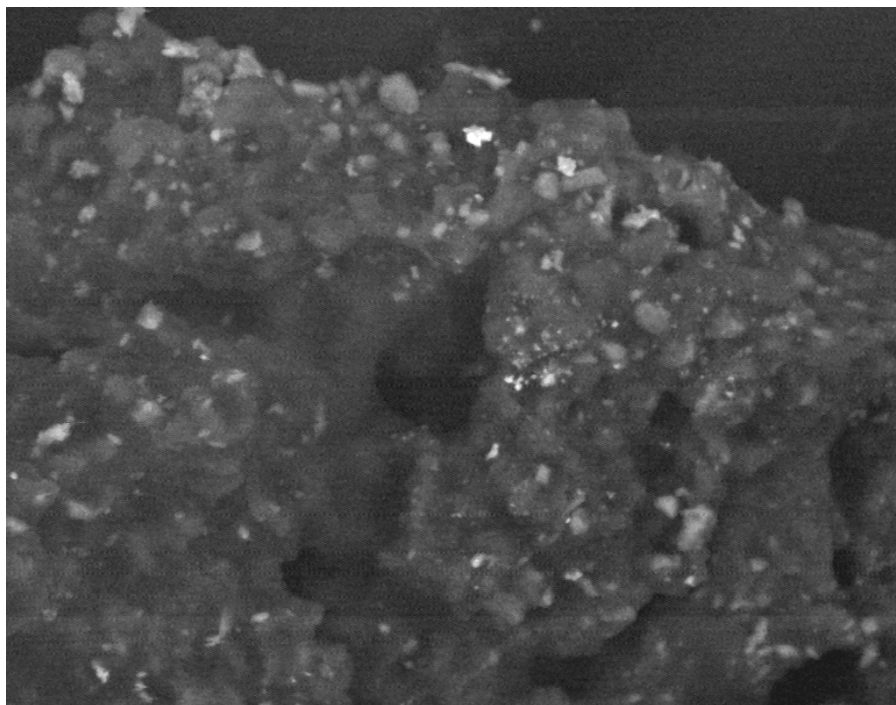
Figure 7. BEI photo of particles at magnification of 1000X.

Figure 8. Inside view of vaporizer chamber.

Figure 9. Residue collector.
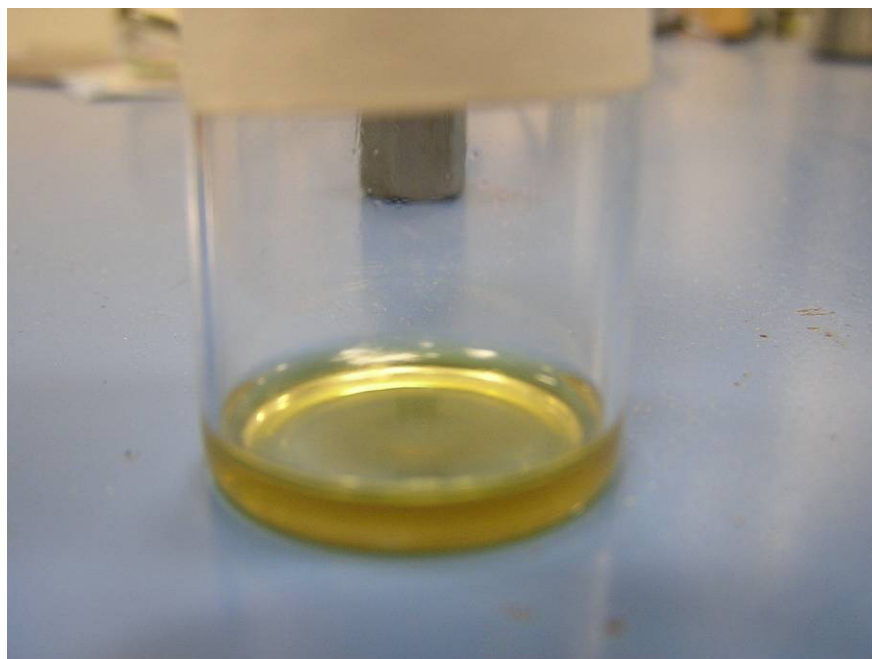
Figure 10.   Decanted liquid from residue collector.

The solid residue in Figure 9 was analyzed using scanning electron microscopy. Figure 11 shows a 1000x magnification picture that indicates the fibrous nature of the mass. The two rectangles indicate locations where the elemental analysis was performed. A small portion of the sample was rinsed in acetone to remove oils, then carbon-coated for examination. Metallic debris that appeared to be present in the original sample was not analyzed. This metallic debris was by far the largest volume of particles. There appeared to be at least two types of fibers present in the sample. One was a very fine mesh glass composed of silicon and oxygen (components in glass, and also silicon dioxide, SiO_2, is a common compound in some sand). The diameter of the fibers varied but was mostly around 1 to 2 microns. The other appeared to be a natural fiber (10 to 50 microns wide in places) because of what seemed to be cell wall structure (Figure 12) – very irregular as opposed to granular, crystalline and aligned. The source of the fibers is unknown, but upon speculation, two possible sources of the fibrous material are hose reinforcement fibers or broken-down filter media.

Figure 11.   Scanning Electron Microscope photograph at 1000X.

Figure 12.   Scanning Electron Microscope photograph at 100X.

The residue collector was removed after each test and examined. In all cases, it was found to contain a liquid residue and some solids. The amount of the residue, and its appearance, varied with the test.

The solid residue in each sample was subjected to a particle size analysis in a Horiba LA900 Laser Particle Size Analyzer. The data sheets of these analyses are shown in Volume 2 of this report. An example of the data sheets is shown in Figure 1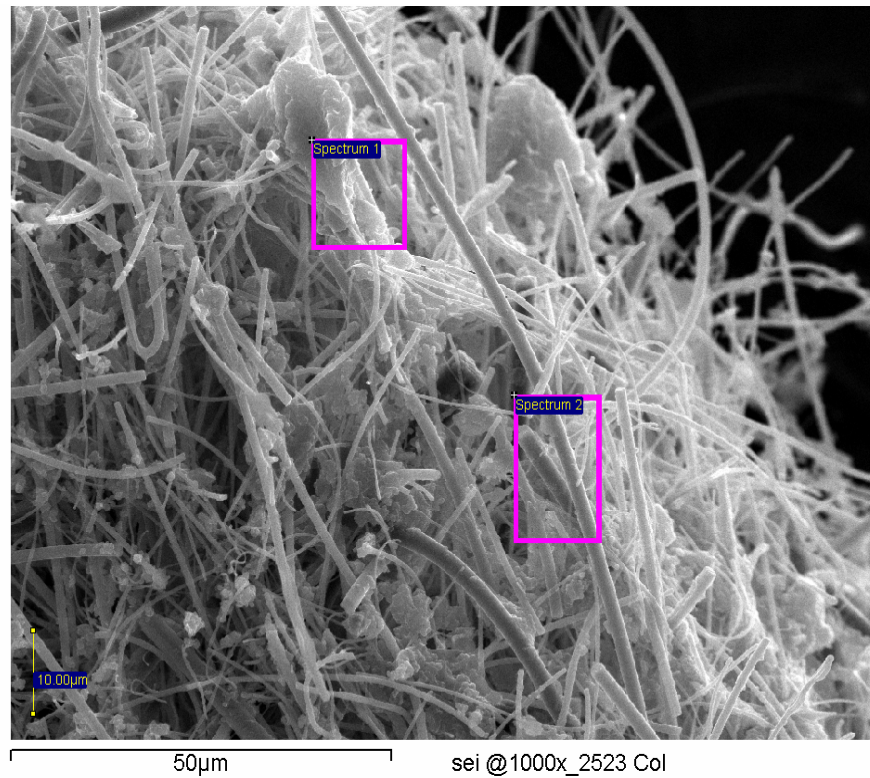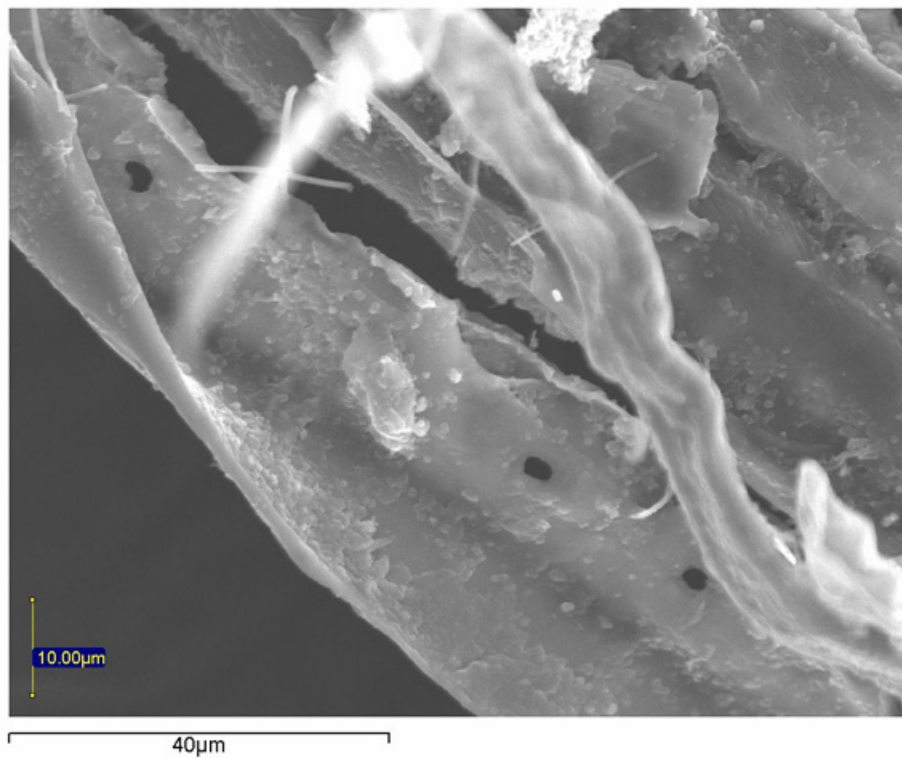3. This sheet is of a different format than that shown in Figure 4, as the instrument was upgraded between the preliminary data set in Figure 4 and that shown in Figure 13 and Volume 2. The upper part of the figure is a frequency plot of the particles counted. In this example, the peak (most frequently counted) occurs at approximately 7 microns, and no particles were observed larger than approximately 50 microns. The tabular data under the plot are instrument parameters used in the analysis and the frequency data. The entry "10.0 % = 10.755μm" means that 10 percent of the particles counted were larger than 10.755 microns.

To assess the physical composition of the particles, samples were sent to Galbraith Laboratories for analysis. Typically, the amount of solid material was not adequate to conduct all tests. Consequently, tests were undertaken in a prioritized sequence until the sample was exhausted. The testing indicated the presence of iron, carbon, oxygen, aluminum, and silicon. The expectation is that the aluminum might be a residue from the tank fabrication, and the silicon and oxygen could be present as small pieces of sand or glass.

Testing for Hydrocarbon Composition

In order to identify and correlate fuel quality issues as much as possible, we analyzed the composition of each forklift cylinder that we received. Samples were analyzed with a gas chromatograph using flame ionization, as outlined in ASTM D-2163, "Analysis of LP Gases and Propylene Concentrates by Gas Chromatography," contained in GPA 2140 (GPA 1997). We identified the amount of each of the following hydrocarbon present in terms of volume percent: methane, ethane, propane, isobutane, n-butane, and propylene. These results are discussed below.
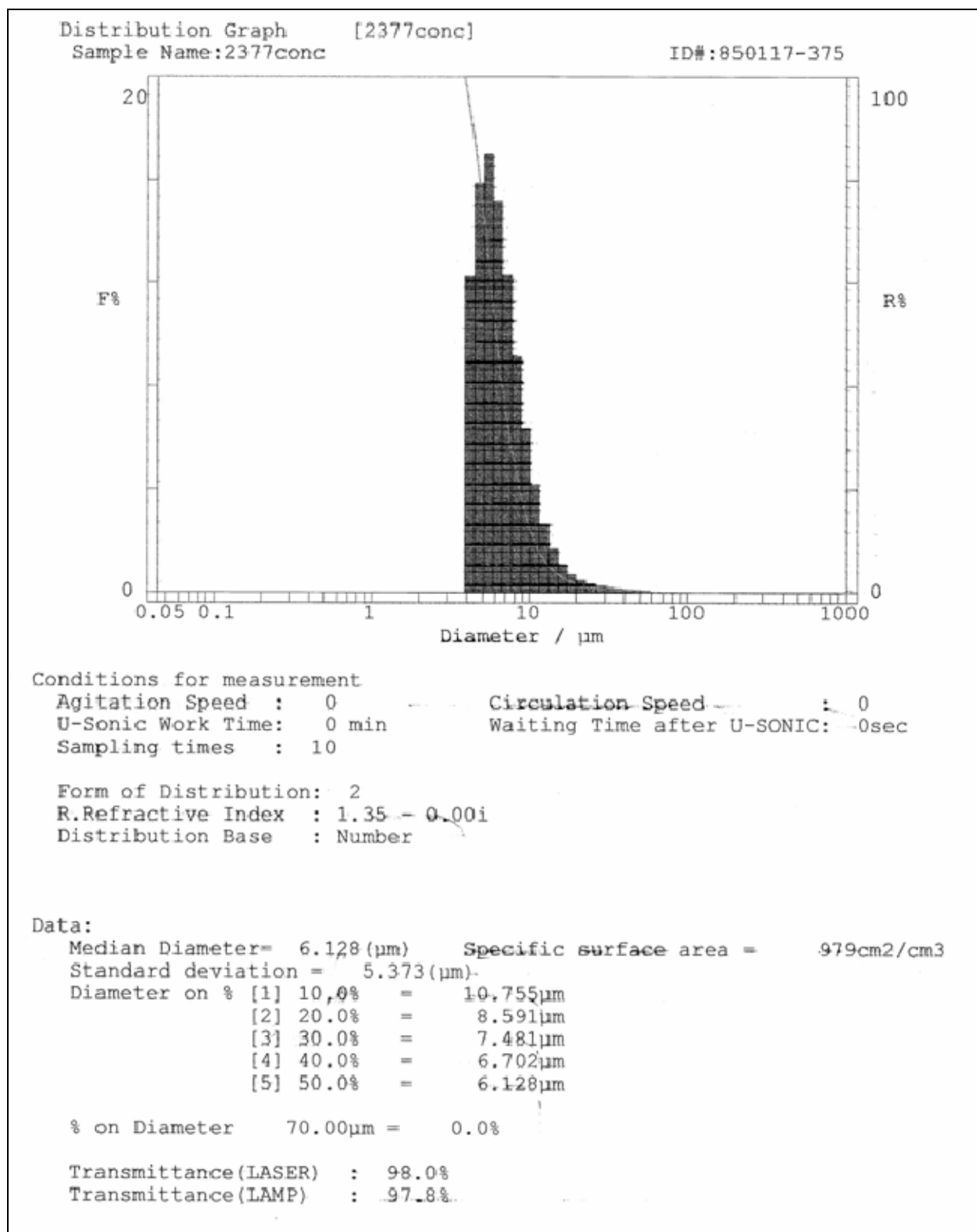
Figure 13.   Example of a data sheet resulting from particle size analysis.

RESULTS

Water Testing / Hydrocarbon Composition

Table 2 shows the data sets for all collected samples for hydrocarbon composition (in percent volume) and moisture content (in parts per million by weight). The hydrocarbon analyses and the compliance to the three specifications are discussed later.

Figure 14 shows the moisture data as a bar chart. As can be seen, there were no samples above previously determined limit of 35 ppm water.
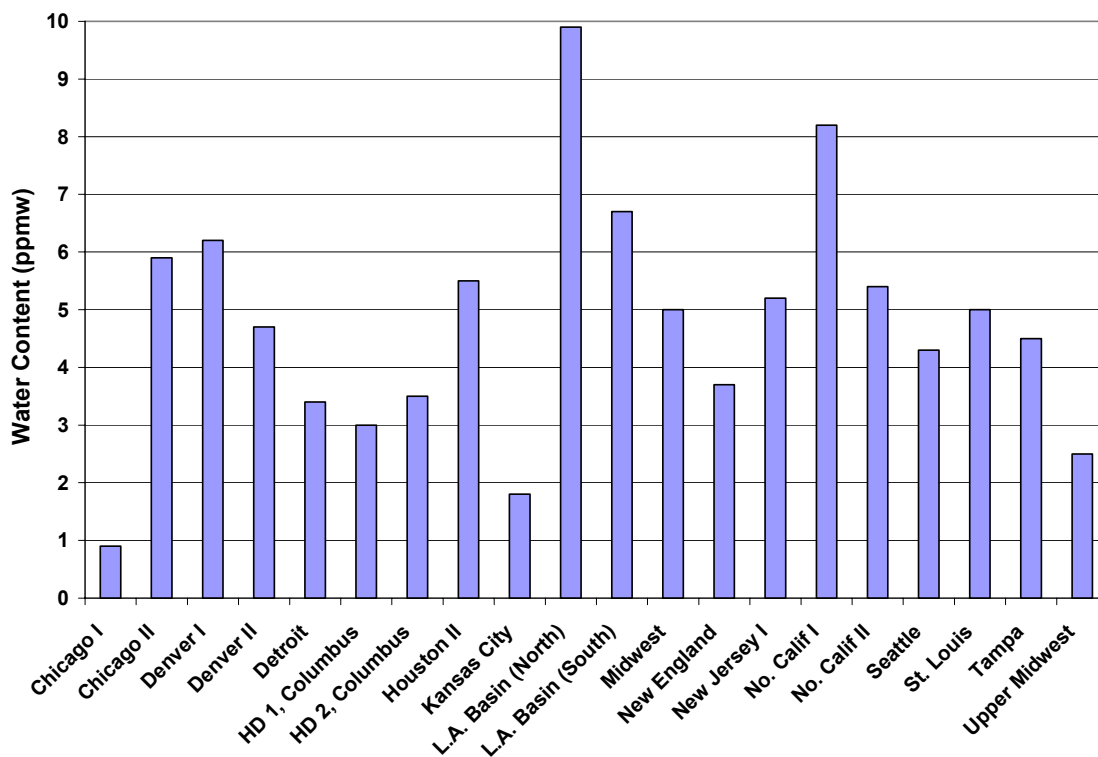
Figure 14.   Moisture levels of collected samples.

A note in ASTM's freeze valve method (D-2713) refers to data from a series of tests conducted in 1967 where freeze times were related to moisture levels. The original data were not accessed because of the lack of adequate referencing in the standard. However, in the context of Falkiner's article in the Fuels and Lubricants Handbook (Totten 2003), it appears that the moisture levels in D-2713 are stated in ppm by weight rather than ppm by volume. The data referenced by D-2713 can be graphically represented by the circle markers and solid lines as shown in Figure 15. It shows that as the concentration of water increases (moving to greater values on the x-axis), the freeze time decreases. The star represents Falkiner's statement that 60 seconds on the freeze test corresponds to a water concentration of about 35 ppm by weight. Thus, there is a "transition band" between about 35 ppmw and 45 ppmw where the dryness may depend on the temperature and the composition. To emphasize this, the graph has been shaded – darker on the left to indicate acceptably dry propane, and lighter on the right to represent unacceptably "wet" propane.

Table 2. Hydrocarbon composition of samples collected for water/solids contamination study.

Supply Area	Location	Methane %	Ethane %	Propane %	iso-Butane %	n-Butane %	Propylene %	Moisture ppm,w	Particle Sample #	Specifications Met[1]		
										Commercial Propane	HD-5	CARB Engine Fuel[2]
Chicago I	Carol Stream, IL	0.00	1.09	96.69	1.38	0.68	0.16	0.9	2377	✓	✓	✓
Chicago II	Chesterton, IN	0.02	1.90	95.39	1.41	0.19	1.10	5.9	2432	✓	✓	✓
Denver I	Conifer, CO	0.03	1.35	94.26	0.78	0.13	3.45	6.2	2479	✓	✓	✓
Denver II	Colorado Springs, CO	0.04	1.18	94.56	1.31	0.15	2.77	4.7	2456	✓	✓	✓
Detroit	Jackson, MI	0.06	0.77	95.95	1.43	0.54	1.25	3.4	2453	✓	✓	✓
Home Depot I	Columbus, OH	0.06	6.01	92.59	0.41	0.15	0.78	3.0	HDP01	✓	✓	✓
Home Depot II	Columbus, OH	0.05	2.73	95.51	0.61	0.28	0.81	3.5	HDP02	✓	✓	✓
Houston II	Corpus Christi, TX	0.03	0.29	99.18	0.45	~0.00	0.04	5.5	2462	✓	✓	✓
Kansas City	Wichita, KS	0.02	0.59	98.31	0.92	0.03	0.12	1.8	2552	✓	✓	✓
L.A. Basin (North)	Lancaster, CA	0.11	3.31	93.71	1.44	0.43	1.01	9.9	2513	Butane too high (> 2.5 %)	Butane too high (> 2.5 %)	✓
L.A. Basin (South)	San Diego, CA	0.03	0.60	96.05	2.43	0.44	0.45	6.7	2542	✓	✓	✓
Midwest	Columbus, OH	0.13	1.85	92.67	4.68	0.30	0.21	5.0	2523	Butane too high (> 2.5 %)	Butane too high (> 2.5 %)	✓
New England	Chepachet, RI	~0.00	1.14	97.54	1.20	0.09	0.03	3.7	2550	✓	✓	✓
New Jersey I	Woodbridge, NY	0.00	0.56	96.36	1.24	0.16	1.68	5.2	2516	✓	✓	✓
Northern California I	Elk Grove, CA	0.07	2.36	84.03	0.81	0.10	12.63	8.2	2421	✓	Propane too low (< 90 %), propylene too high (> 5 %)	Propane too low (< 85 %), propylene too high (> 10 %)
Northern California II	Gurneville, CA	0.06	3.56	88.73	0.71	0.07	6.87	5.4	2536	✓	Propane too low (< 90 %), propylene too high (> 5 %)	✓
Seattle	Auburn, WA	0.22	2.67	94.77	0.44	0.00	1.89	4.3	2539	✓	✓	✓
St Louis	Godfrey, IL	0.03	0.95	98.61	0.21	0.02	0.19	5.0	2464	✓	✓	✓
Tampa	Tampa, FL	0.00	0.90	98.41	0.53	0.16	~0.00	4.5	1275	✓	✓	✓
Upper Midwest	Wausau, WI	0.06	2.21	93.52	0.40	0.05	3.75	2.5	2529	✓	✓	✓

[1] Met the hydrocarbon composition and moisture level requirements. Other requirements of sulfur, corrosivity, and vapor pressure were not addressed in this study.

[2] CARB's engine fuel specification, available from www.arb.ca.gov/regs/title13/2292.6.pdf, is also commonly referred to as "HD-10".
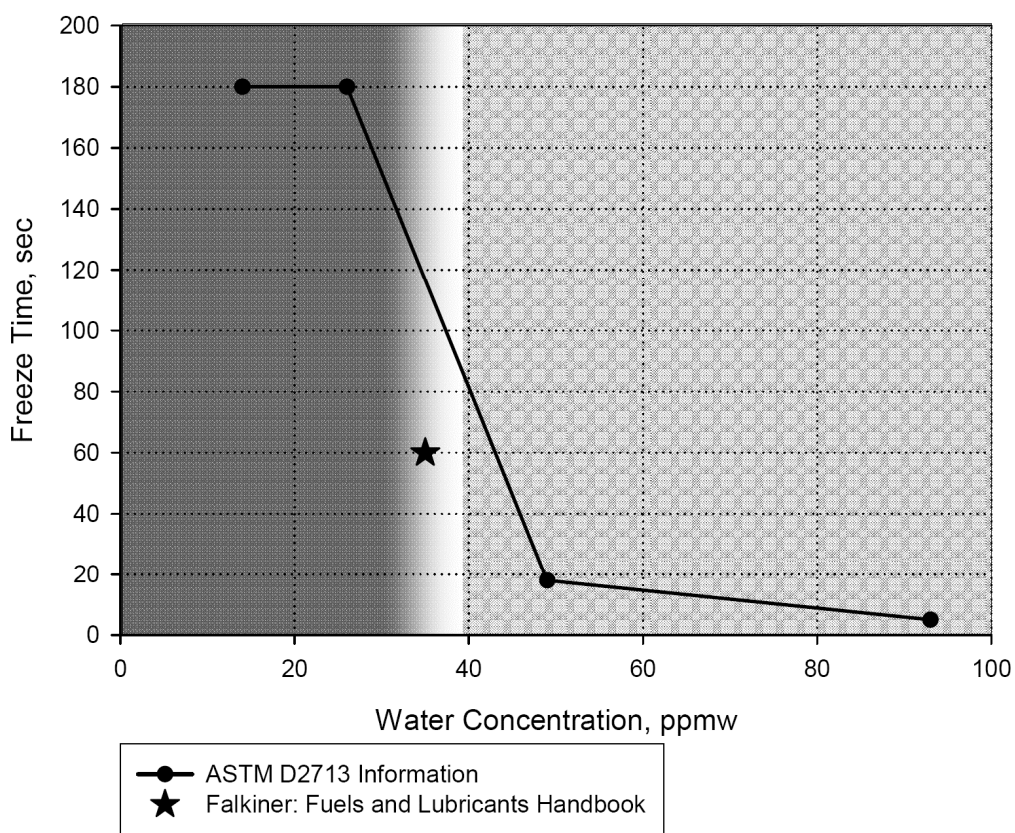
Figure 15. Freeze valve time versus water concentration and acceptable areas of moisture.

The average moisture content of each fork lift cylinder that was tested is plotted as a histogram in Figure 16. The histogram was created by putting the measured average water concentration into bins. The first bin contained all samples with water content of between 0 ppmw and 2.5 ppmw; the second bin contained all samples with water content of between 2.5 ppmw and 5 ppmw, and so on. For example, Figure 16 shows that there were 9 samples with moisture content between 2.5 ppmw and 5 ppmw. Clearly, the moisture levels of the tested samples are well into the "acceptable" dry range.

To show this in the context of the generally acceptable limits on water content, we superposed the histogram (Figure 16) on Figure 15, to create Figure 17. The y-axis for the histogram is now the secondary y-axis on the right hand side of the graph. Again, it is easy to see that all samples, including the retail samples, are dry according to accepted standards.

Figure 16. **Moisture Histogram: number of samples for given moisture level bin.**

Figure 17. **Moisture map with histogram data.**

Solids Testing

The data sheets in Volume 2 were plotted as a histogram based particle size, as shown in Figure 18. While there were twenty propane samples, there are 48 data sets in Volume 2 and plotted in Figure 18. The data point labels are the laboratory sample number – this is shown the last column in Table 2. The additional data sheets and plotted points are sample replicates and sample dilutions and concentrations, performed in order to capture as much data as 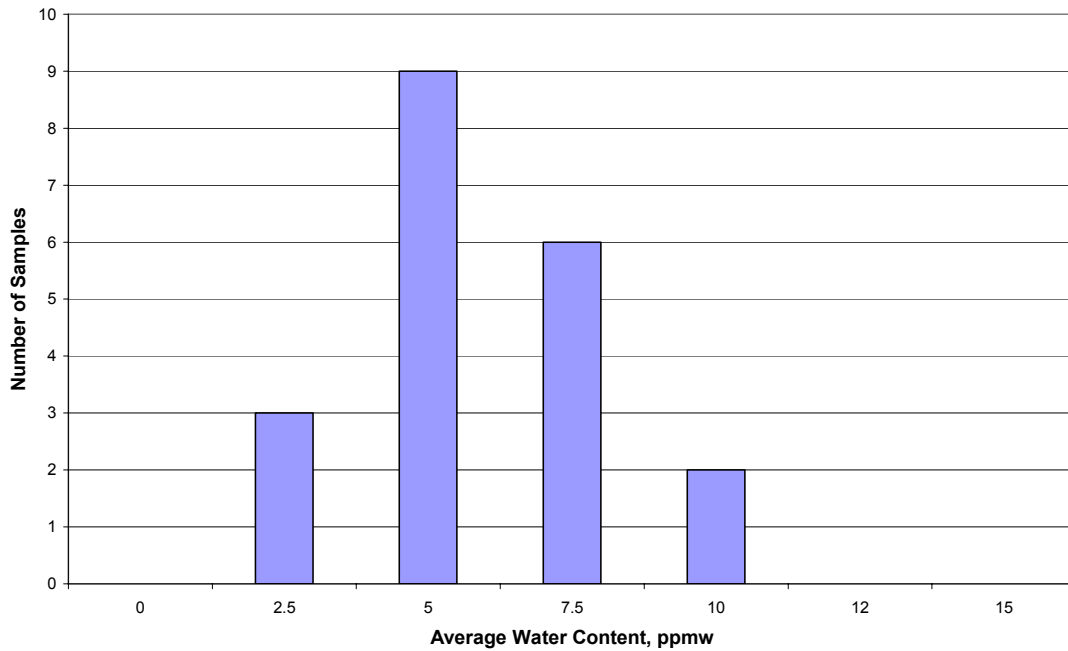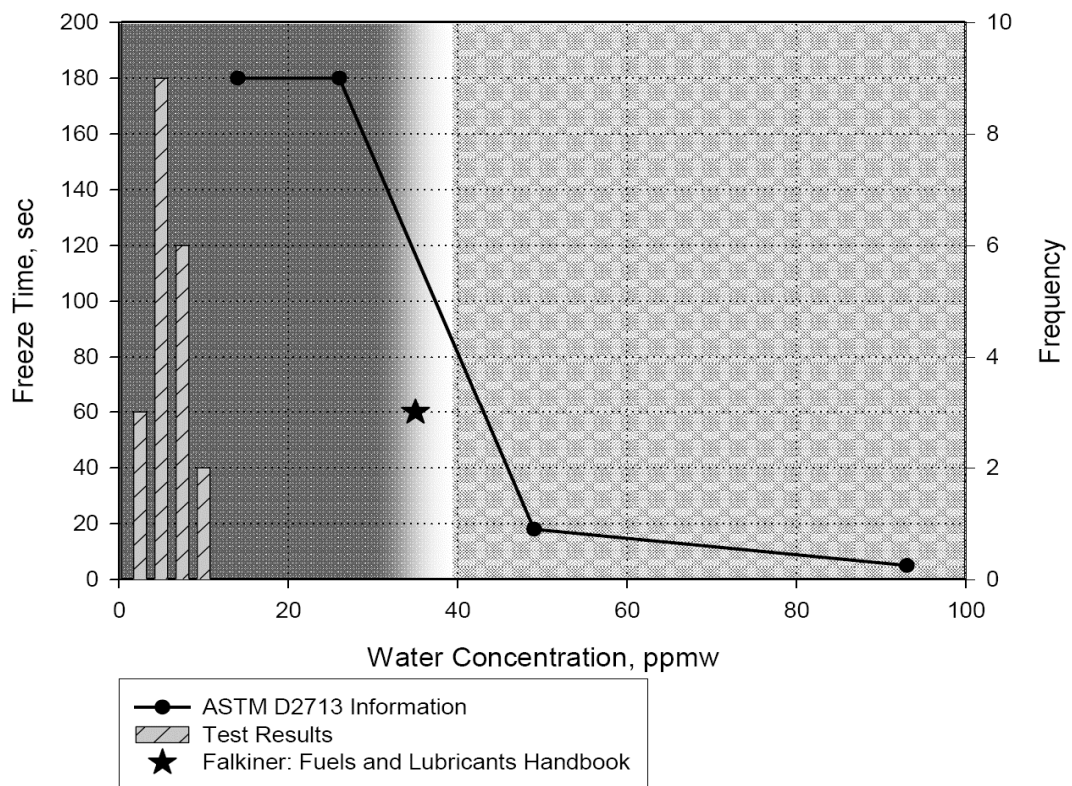possible. For example, data sample number 2377 (Chicago I, Carol Stream) has three data sheets in Volume 2 – the first data sheet was for the concentrated sample (*2377conc*), the second sheet is for the same sample but diluted (*2377dila*), and the third data sheet is a replicate of the diluted sample (*2377dilb*). All three data sheets are plotted in Figure 18. The measured particle size is shown on the x-axis. The percentage frequency of occurrence is shown on the y-axis. Most of the particles fall between 1 micron and 10 microns. For purposes of reference, it is noted that this is typically the size of a bacterium. The larger particles are about the size of a human hair, while the smallest particles are approximately the size of some viruses, and invisible to the eye.

The data show a fairly wide range of particle sizes, from a minimum of 0.2 microns and maximum of 900 microns. The vast majority of samples have distribution peaks from 1 to 10 microns, one sample has somewhat of a peak at approximately 0.5 microns (2523, Midwest-Columbus, OH, pages B28 to B-32), and four samples have peaks in the range of 10 to 80 microns. Two data samples have additional peaks of between 700 and 900 microns: 2536 (Northern California II-Gurneville, pages B-39 and B-40), and 2464 (St. Louis-Godfrey, IL, pages B-43 and B-44), with the Gurneville sample providing more particles in this range. However, the number of particles in this range is still small compared to the lower size particles.
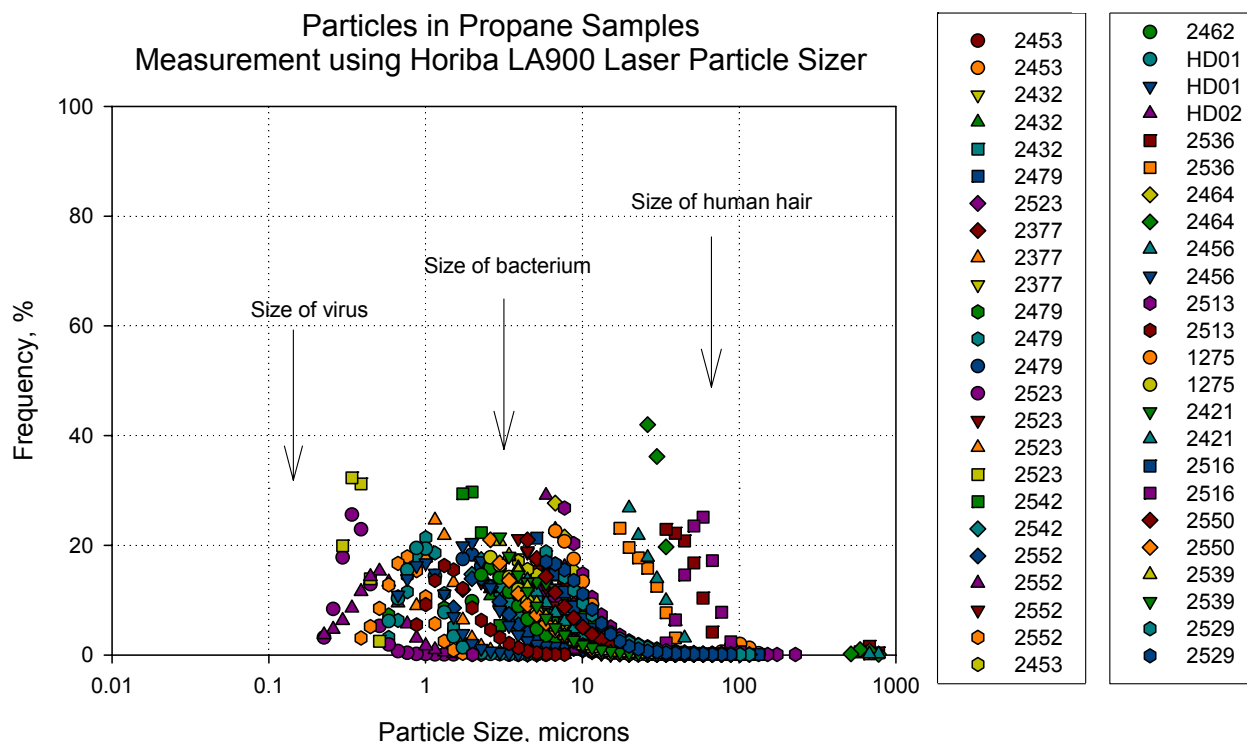

Figure 18.   Particle size histogram of samples, sample replicates, and sample dilutions.

Sources and Remediation of Moisture and Solids

Sources of Moisture

Williams and Lom (1982, pages 57-58) describe two sources of moisture in propane at the production step: naturally occurring in natural-gas derived LPG, and in caustic washing in refinery-derived LPG. If the LPG is to be stored at refrigerated conditions, moisture levels must be reduced to prevent free water formation. This is accomplished by coalescing filters (free water removal only) and exposure to adsorbents. Some refineries produce propane with low moisture levels (< 10 ppm) by drying (or dehydrating) with calcium chloride (a liquid desiccant) or exposure to molecular sieves or other adsorbents. As noted by Williams and Lom, not all refineries chemically dry the LPG, relying solely on filtration and liquid scavengers (methanol) added downstream. However, calculations in Williams and Lom show that a hot propane stream, for example at 110 F, can contain 320 ppm of soluble water. If that stream is cooled to 32 F, the saturation point is only 6 ppm. For a 10,000 gallon volume, this cooling would result in a formation of over three gallons of free water. A more reasonable example, where the propane stream was acceptable "dry" at 35 ppm, the cooling process to 32 F would result in slightly more that a quart of free water. The moisture capturing methods mentioned above are often included at terminals, so this free water would likely be removed prior to further storage, transport, and distribution. As mentioned earlier, however, removal of no more than the free water still results in off-spec propane.

Production rates rarely exactly equal consumption rates. For this reason, and to provide the necessary surpluses for peak usage times (such as winter), storage is necessary at several points along the distribution chain. Underground storage is common at many terminals, either in mined caverns or in salt domes (Guthrie 1960, pages 3-13 and 3-14; Williams and Lom 1982, pages 188 to 190). Ground water is likely present, even if in small quantities, in both situations. However, the more significant water source with underground storage in caverns is the water or water/salt (brine) used to create the cavern and to push the propane from the cavern. In addition, a water table above the cavern is sometimes used to contain the propane, slowly dripping water through rock fissures into the cavern. Again, as terminals employ the use of adsorbents to remove the water after underground storage, it should be expected that propane leaving these terminals meets the required specification (typically the freeze valve test, ASTM D-2713).

Tanks do not inherently have the sources of moisture that underground storage systems do. Liquid pumps, gravity, and vapor pressure assist in moving the LPG from one point to another in tank systems (stationary for storage and portable for distribution). Normally, the entire propane distribution system, from pipelines and transport tanks to end user storage tanks, is closed and under positive pressure. However, these systems may periodically be opened to the atmosphere for inspections and servicing. As tanks are opened to the atmosphere, moisture-laden air, particularly in the coastal regions, can enter the tank. Daily and seasonal temperature swings can increase the dew point sufficiently high that condensation can occur on the interior tank walls. Upon refilling these tanks with LPG (or any other product), the water will be mixed with the lading and depending on the amount of water present, an "on-spec" product becomes an "off-spec" product. However, a more common source of tank moisture is from intentional means. Many truck transports (with capacities of approximately 9000 gallons) and cargo tanks ("bobtails" with capacities approximately 3500 gallons) may be dedicated to propane, some are not, and few railcars are dedicated exclusively to propane service. Between different loads, railcars are sometimes steam cleaned to lessen the amount of lading carry-over. In addition, regulations require that many tanks be pressure tested at specific intervals, typically every five years. For safety reasons, the pressures tests are nearly universally hydrotests, where the vessel is filled with water and pressurized to the required test

pressure. Efforts are made to remove as much water as possible, however residual amounts remain. Many tanks have internal valves and recessed piping due to safety regulations, and these recessed fittings result in trapped volumes of water. This free water tends to be persistent because of the low solubility of water in propane. Therefore, a small amount of water in a transportation tank can adversely affect many subsequent loads, making some of these subsequent loads "off-spec". As most marketers do not have the filtration and dehydration equipment that is typically installed at production and terminal facilities, water contamination is addressed by additives rather than removal. While these additives, such as methanol, do not make off-spec propane on-spec, they can prevent regulator freeze-ups, one of the main concerns of marketers.

This study found that moisture levels were in the "dry" portion of the acceptance criterion. The previously mentioned privately-funded study found one sample at 45 ppm, 7 samples between 30 and 40 ppm, with the remainder below 30 ppm, including 16 samples at 10 ppm and under (out of 44 samples). Based on the data of the current study and most of the data from the privately-funded study, there was not a rampant moisture problem *during these studies*. However, high levels of moisture have been anecdotally observed. On a companion project (Docket 11354), a sample was collected from a bulk storage tank that was less than 10 percent propane, *with the remainder being water*. There were several hundred gallons of this product at an engine fueling station. The issues then are how to monitor for these system upsets and how to remove the moisture as it occurs. In the section entitled "Remediation of Moisture", we will address moisture removal from propane, not the gross contamination that was mentioned above.

Sources of Solids

Many of the solids identified in this study, such as those shown in Figure 5, are iron-based. While later samples were not analyzed with backscatter electron imaging, their physical appearance and ferromagnetic properties indicated they also were predominantly iron-based. Falkiner in Totten (2003) identifies iron oxide and iron sulfide particles as common contaminants in LPG. The particles are the result of mill scale, generated during the production of steel, or from corrosion of various metallic components in the distribution chain. Some of the storage and transportation vessels and interstate pipelines are over fifty years old. Since most of these systems transport a variety of hydrocarbons of varying dryness and corrosivity, there is reason to believe that these systems could continuously emit corrosion products into the fluid streams. Baldwin (1998) identifies "black powder" as a common contaminant of hydrocarbon pipelines. Baldwin describes black powder as various forms of iron sulfide, and labels it as the "… least understood and most prominent contamination problem in pipelines …" This powder is the result of the corrosion of steel by sulfur compounds, such as H_2S, mercaptans and elemental sulfur. Black powder does not need moisture to occur, and it can also be accelerated by microbial assimilation of chemical constituents of the pipe. Baldwin also mentions that iron sulfides can be formed from iron oxides. Baldwin also describes that these particles can agglomerate into longer "strings".

Other metallic compounds were not identified in this study. While corrosion of other metals, such as copper, is possible, the vast majority of metal inventory in the fluid streams is steel.

As previously mentioned, the materials identified in Figures 11 and 12 were fibrous and silicon and oxygen-based and natural fiber-based. While the sources of these fibers are of interest, they represented a very small fraction of the particles found.[*]

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[*] SwRI's report on PERC Docket 10951(SwRI 2006) identified that "solids" found in forklift carburetion equipment were compounds of heavy ends, i.e., compounds having 20 or more carbon atoms. These solids were detected at sub-micron levels. These identified solids remained in engine fuel vaporizers. The present study identified the solids that were contained in the fuel after ambient temperature evaporation ("weathering").

While the above overview addresses the normal operational sources of contaminants in propane, we have not addressed the periodic upsets that affect all petrochemical operations. In these episodic events, there are often human factors considerations. Time constraints and demand for product will often compel staff to make questionable decisions. For example, a terminal dehydrator could be operating below specifications. If demand is such that performing the necessary repairs would cause transport backups at the terminal and prevent timely deliveries to end-use customers, the repairs could be delayed until the chaos subsides. In another example, an operator may forego the generally-accepted requirement of performing a freeze valve test. Both of these simple examples could allow excessively moist propane to move further down the distribution line, especially if they happen during the same upset. Episodic equipment failures, including plugged filters, in-operational pumps, valves, and control systems can inadvertently place sub-standard, "off-spec" propane in the distribution chain. Such an incident occurred in April 2005 involving the Dixie Pipeline, a 1300-mile hydrocarbon pipeline between Mt. Belvieu, TX, and Raleigh, NC. Contamination affected the propane delivered through it (an average of 100,000 barrels a day) and affected the pipeline for nearly two months (LP Gas 2005). While such large, wide-reaching upsets are extremely rare, much smaller events are more common and can affect individual bulk plant operators as severely.

The low-profile incidents may actually go unnoticed until an end-use customer is affected, through inoperable or low-performing equipment such as engines.

Remediation of Moisture

As mentioned in the previous section, production facilities and terminals often have specialized equipment for the removal of water from LPG. The intent of this section is to identify and evaluate remediation methods that can be applied at bulk plant operation.

The standard technique of water remediation in the propane industry, downstream of the production plants, is by the addition of anhydrous methanol. Because methanol's affinity for water is much higher than its affinity for propane, the water and methanol may form a separate liquid phase, effectively removing at least some of the water from the propane product. A "rule-of-thumb" exists, whose origin is unknown. This concentration is documented in RegO®/ECII *LP-Gas Serviceman's Manual*: (RegO®, 2002, page 8)[*]:

> "A rule of thumb for neutralizing moisture in an ASME container calls for the introduction of at least one pint of genuine absolute anhydrous methanol* (99.85 percent pure) for each 100 gallon of water capacity of the container.
>
> * IMPORTANT-Avoid substitutes - they will not work. The secret of the effectiveness of methanol over all other alcohols is its high affinity for water plus a boiling point lower than all other alcohols, and most important: a boiling point lower than water."

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[*] The source of this "rule-of-thumb" comes from the 1940s and 1950s experiences of an equipment salesman, Sam McTier of Lake Forest, Illinois, who experienced complaints about regulator freeze-ups. As the freeze-ups occurred in cold weather, he assumed that the problems were due to excessive water in the propane. Through trial and error, he determined the necessary amount of methanol needed to prevent these freeze-ups. The "genuine absolute methanol" requirement was included as there were less scrupulous service personnel selling methanol diluted with water. The salesman represented RegO, and the RegO Serviceman's Manual was one of the few technical references available in the young propane industry. The methanol discussion was included where it has resided basically unaltered for more than 50 years.

It should be noted that the recommendation is based on container size, <u>not</u> propane volume. The intent of this recommendation is to neutralize the moisture that has formed on the vessel walls, not necessarily the moisture contained in the propane. The Canadian propane storage code (CSA B149.2, CSA 2000) recommends the same dosage of methanol. This rule of thumb is referenced in several places, often without reference back to RegO's manual. The Ontario (Canada) Propane Association website (**www.propane.ca**) uses the same language as the RegO manual, and that site references the RegO manual. Other sites, such as Growmark Energy's propane website (Growmark 2006), a Flame Engineering equipment manual (Flame Engineering 2006), and several Internet bulletin boards use RegO's wording with no reference to the source. Williams and Lom (1982) give a recommended concentration of at least 0.05 percent methanol (equivalent to 0.4 pints per 100 gallons, or 500 ppm volume) in propane that has not been dried to less than 20 ppm water in propane. The RegO-referenced concentration equates to 0.125 percent, or 1250 ppm volume of methanol in propane.

The interactions of methanol, water, and propane are described in great detail by Falkiner (Totten, 2003 pages 43ff). Falkiner calls methanol "unique in the LPG world", because it is the only alcohol with a molecular weight lower than propane, and it can enter into the propane vapor, like water. These properties allow the methanol to travel with the water in the propane vapor, which makes it effective in preventing freeze-ups in liquid and vapor phases. Because of its relative small molecular size, methanol is very effective in dissolving water and hydrocarbon hydrates.

While Falkiner describes the benefits of methanol and its interaction with water and propane, he also notes in several instances that the use of methanol is "an area of recommended research and standardization". The reason for this suggestion is that methanol is traditionally over-used – if 1 pint is good, more must be even better. This over-dosing is sometimes compounded by the fact the over-dosing may be replicated at multiple points along the distribution chain, even when the propane is sufficiently dry. One marketer explained that when filling a bobtail truck from a bulk tank, his procedure called for first filling the connecting hose with methanol. This procedure was performed with no measurements being made as to the dryness of the propane – more is better.

Falkiner cautions that when methanol is overused, a drop in temperature can result in most of the methanol phase separating to the bottom of the tank. An example is given: if warm propane contains one percent methanol were cooled to -4 F, more than half of the methanol would phase separate and settle to the bottom of the tank as a non-freezing water/methanol mixture. If this happened in a railcar or bulk tank, the settled volume could be 100 to 300 gallons. This mixture could be passed downstream, with the potential for small delivery quantities to contain gross quantities of methanol/water.

Although the methanol does vaporize with the propane and water, it does have a lower boiling point than water. Therefore, methanol will continue to concentrate in tanks that cannot be completely emptied. The effect on equipment (for example burners, vaporizers, injectors, and elastomeric materials such as hoses) is a topic for additional research. The monthly magazine Butane-Propane News (BPN) recently ran an article that described a propane-fueled fuel cell project (BPN 2006). The project coordinator noted a potential incompatibility between the propane tank dehydration additives (methanol) and the fuel cell reformer/scrubber. While it was not explicitly mentioned in the article, it is assumed that for such a high profile research project a new tank was installed. If and when such advanced equipment like fuel cells becomes more commonplace, there should be a concern about not only the over-use of methanol, but also the inventory of methanol already in place in marketers' bulk and customers' storage tanks. In addition, Risson, et al. (2003) considered the effect of methanol pooled in the bottom of carbon steel propane storage tanks. In a number of instances, stress corrosion cracking (SCC) was observed as a result of the interaction of the methanol. The hypothesis was that the methanol degraded in the presence of water and formed formic acid. The remainder of the paper discussed the development of a test method for screening

tank steels, and there was no specific data of the composition of the methanol/water/propane mixture in the pool.

Since the failure of bulk and customer tanks by SCC is not epidemic, there is no reason for a panicked response; however this paper should not be dismissed as anecdotal. Again, this is an area for additional research.

Several technical papers were found which addressed the interactions of methanol, water, and hydrocarbons. Blanco (2001), Esteban (2000), D.B. Robinson Research (2000), and Zhang (2001) all address equilibrium equations of state for various tertiary mixtures of propane/water/methanol. The data in these studies could be used to replace the "rule-of-thumb" and to determine if methanol can achieve a particular dew point depression.

This leads to the crux of the problem in using methanol to address moisture-in-propane problems.
- To properly dose methanol in propane, there should be an accurate measurement of the moisture level in propane
- Easily-made moisture level measurements (freeze-valve) are affected by methanol, and are go-no-go tests – if the sample shows "wet", there is not a good correlation between the freeze valve times and moisture content in the "wet" region
- Even if accurate measurements are made, there is no simple method to determine the desired amount of methanol

Therefore, to avoid problems downstream with moisture, the marketer will likely add methanol, using the one pint per 100 gallons, plus more for good measure – and ignore the potential, albeit future, problems. The only way to avoid this is to have simple, easy-to-use, cost-effective, rugged, robust, and accurate measurement methods, most likely on-line instrumentation. Unfortunately, the adjectives used in the previous sentence are all important. Accurate on-line instruments are currently available, at a cost of thousands of dollars, and they are not necessarily easy-to-use.

The alternative to treating the moisture problem is to remove the moisture from the propane stream, as is done at the production sites and terminals. Unfortunately, these methods are often themselves small chemical plants and may be difficult to put into practice at a bulk plant. These systems, which utilize refrigeration, liquid or solid desiccants, or other moisture getters, are expensive, and their costs do not scale down directly. While specific design costs are not known, experience with scaling other simple chemical systems would indicate that a bulk plant system that must pass 10,000 gallons a day at 100 gallons per minute will not be one fiftieth of the cost of a gas plant system that will handle thousands of barrels a day, running around the clock, continuously. Some bulk plants are nearly small terminals themselves – in these instances, these marketers may have a sensitive market that would justify the costs of the purchase, operation, maintenance, and monitoring of such a system. These systems would then be designed and installed by the same entities that service production plants and terminals. Clearly, the design and operation of these systems introduce degrees of complexity not often found in small terminals and bulk plants.

Methods that could be employed to remove moisture at a bulk plant scale involve moisture-removing filters or desiccants such as molecular sieves. Molecular sieves work on the principal that the solid matrix, usually a synthetic clay or zeolite, has very uniform pore spacing. Smaller molecules like water are adsorbed onto the sieve material, while larger molecules such as propane pass by the pores. Sieves, such as the 13X or the 4A materials made by ADCOA (2006) and other manufacturers, are excellent at absorbing water and even some longer-chained hydrocarbons (such as heavy ends). These adsorbents are used at production plants and can remove moisture to less than one part per million. Adsorbents at production plants are regenerated with hot propane gas – usually produced by small vaporizers/heaters. The adsorbents can also be used in a once-through manner, which eliminates the need for producing hot

propane vapors. While this material is not extremely expensive, replenishment of the adsorbent materials must be factored into the operating costs. Also, constant monitoring is required to ensure that sieve material is not loaded. Indicating sieve materials are available, but this would require a sight glass in the sieve vessel. Unfortunately, these sieves are also excellent at removing sulfur compounds such as H_2S and mercaptans – the former being a nice but not typically needed feature at a bulk plant and the removal of the latter presents a very serious problem at a bulk plant. Sieves can remove mercaptans down to single ppm levels, and required odorization levels are on the order of 20 ppm (NFPA 58-2004, section A.4.2.1). Unfortunately, some of these sieves do not operate selectively. Efficient removal of moisture may also mean efficient removal of mercaptans. While such a system could be relatively cost effective to install, a sieve system would also require an odorization system downstream. While constant monitoring of the sieve system is required to maintain optimum moisture control, monitoring of the odorization system would be absolutely imperative, as un-odorized propane is inherently unsafe in all but a select few end-use applications.

In searching for filters that address the removal of solid, a few filter materials are advertised as having moisture removal capabilities. Appendix B is a brief list of vendors identified using industrial catalog (Thomas Register) sources, Internet searches, and phone and email follow-up. This list is not intended to be exhaustive but only a guide as to the products and services that are available. These vendors have identified filter systems that are applicable with propane, cover the flow rates that are typical of bulk plants (approximately 100 gpm), and cover the range of particulates identified in this study. In the table, Allied Group, Filtration Technologies, Nowata Filtration, and Parker Hannifin have identified their filter systems as having moisture removal capabilities. A distinction was made between coalescent filters and moisture removal filters. Coalescing filters remove water droplets that are suspended in the vapor stream (aerosols). This aerosolized water indicates severely off-spec propane, as these droplets are not in solution with the propane. Coalescing filters work by using the dynamic forces of the droplets, similar to centrifugal cyclone separators, to group smaller droplets into larger and larger droplets. The gravitational forces on the larger droplets overcome the suspension/buoyancy forces, and the droplets fall from the stream and are removed <u>as a liquid</u> from the system. In this study, <u>moisture removal</u> means some adsorption/absorption mechanism is used to remove moisture to subsaturation levels. Unfortunately, no data were available on the effectiveness and loading capacity for water on these filters, but the vendors expressed support in working with clients to select appropriate systems.

Remediation of Solids

The removal of solids is somewhat more straightforward than moisture removal. Off-the-shelf filtration systems can be selected to remove the particulates in question. Standard filtration methods remove contaminants by passing the fluid (liquid or vapor) through a media with fairly narrowly defined pore sizes. Filters are rated for pore size (typically microns, or one millionth of a meter) and capture efficiency. Smaller pore sizes will trap smaller contaminants. Pore sizes can range from as low as 0.01 micron to over 100 microns. Coarser filter elements such as screens are rated by mesh size – the smaller the mesh size, the larger the screen openings. For example, a 1 micron pore size is equivalent to a mesh of 12,000. A pore size of 149 microns is equivalent to a mesh of 100.

Filter efficiencies are given in terms of percent of particles captured or sometimes a "Beta ratio". Beta is defined as the ratio of the number of particles of a given size and larger upstream of a filter to the number of particles of the same size and larger downstream. The above filter efficiency of 99.98 percent means that of the 100 percent of the particles upstream, 99.98 percent are captured, leaving only 0.02 percent downstream. Beta would be 100/0.02 or 5000. A 90 percent efficiency filter has a Beta ratio 10.
One must careful in comparing filter elements. Two filters could each be rated at the same pore size (micron), but with distinctly different efficiencies. For example, one manufacture lists two 1-micron

filters, one at 90 percent efficient (Beta = 10) and a second at 99.98 percent (Beta = 5000*). As rated, the higher efficiency filter captures 99.98 percent of particles one micron or larger in size. In contrast, the less efficient filter captures 90 percent of particles one micron or larger. Even with particles as large as 5 microns, this filter's efficiency is 99.9 percent (Beta of 1000). The higher efficiency filter is rated for particles as low as 0.2 microns, but its efficiency at this particle size is only 90 percent. If complete capture of a specific particle size is desired, a high efficiency filter is needed. One must remember that the main function of a filter is to plug – a filter that resists plugging also resists capturing particles. High efficiency, low micron rated filters will generate more pressure drop (clean) than lower efficiency, larger micron filters. A compounding issue with this is that the higher efficiency, lower micron filters will require replacement more frequently.

For removal of black powder and other relatively fine corrosion products, Falkiner (Toller 2003) recommends a two to ten micron filter, with an efficiency of 99.98 percent. Falkiner says this type of filter has been found to be effective to remove these materials with good filter life. However, Baldwin (1998) suggests that in order to trap iron sulfide particles, filters must be designed to remove submicron particles. Figure 18 (page 22) shows the distribution of particles collected during the current project. To remove the majority of these particles with a greater than 99 percent capture efficiency, Baldwin's recommendation is more accurate.

While each vendor typically specializes in the particular type of filter media they supply and recommend, many vendors offer a complete range of filter media with varying pore size and efficiency ratings, materials, type of construction, and overall size and flowrate capability. The next few paragraphs give an overview of these variations and their applicability to a typical bulk plant operation.

As mentioned previously, for near-complete filtration of the particles identified in this study, a filter of no more than 0.5 micron, with an efficiency of at least 99 percent would be required. However, as replacement media and maintenance costs are greatly affected by this choice, we recommend that the individual marketer select a system that considers the following:
- Customer end use – if a marketer is serving a primarily residential, commercial, and industrial market that uses the propane in typical fired-burners, such as heaters/furnaces, water heaters, cooking appliances, heating ovens, and grain dryers, there is little to be gained by filtering particles smaller than 10 microns. However, a marketer that has a substantial engine fuel customer base could justify filtering down to the submicron level.
- Maintenance acceptability – backflushing of filters can greatly extend the life of filter media. Typical backflushing recommendations are to perform this step when the filter pressure drop increases by 3 to 4 psi above pre-backflushing levels. However, backflushing requires additional piping and controls, and the backflushed product must be captured and disposed. To increase the service life of the media without backflushing, more elements must be installed to distribute the particle loading over several elements. This also requires more filter vessels. An alternative approach, one that is used at production facilities, is to stage different grades of filters. A larger pore size, less efficient could be used as a prefilter for a small pore size, higher efficiency final filter. In hydraulic systems, this has been shown to extend the final filter life from months to years. Of course, the required maintenance must be performed on the prefilter, as a breakdown there could load the final filter very quickly.
- Particulate characteristics of the propane stream – this includes both the incoming terminal-to-bulk plant stream and the stream leaving the bulk tanks. The former is a function of the cleanliness of the produced stream and the transportation from the terminal to the bulk plant. The

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* Some manufacturers referred to a Beta of 5000 as "absolute", implying that all particles are captured, although other manufacturers use the term for filters with Beta ratios of 75 (98.67%), 100 (99%), 1000 (99.9%), and 10,000 (99.99%)

samples collected in this project were that type of samples, taken directly from the transport truck delivering propane to a bulk plant. The latter is a function of the condition of the bulk tank and associated piping through to the dispensing hose from the bobtail.

Once a marketer has analyzed the above issues, then decisions can be made about the entire filtration system, based on costs and payback periods. The payback issue will be extremely complex. As noted in Baldwin's (1998) analysis of black powder costs in the natural gas industry:

> "Very few companies seem to have quantified how much black powder problems are costing them. From this viewpoint, any expenditure that might alleviate or solve the problem is considered additional maintenance or capital expense, and not weighed against the probable reduced cost of maintenance and operation gained by ameliorating the problem."

The issue for the marketer them becomes "what is the contamination costing me?" Again, this requires a critical look at the operational data of the bulk plant and its customers – the history of problems caused by particulate contamination. Unfortunately, as in the natural gas industry, much of the data is only anecdotal. When problems were discovered, there were often no analyses of the particulates if they were found. This is particularly true when the incidents are the results of episodic upsets in the production or distribution systems.

The types of filter construction somewhat follows the pore size and filter efficiency.
- Membrane filters are used in extremely critical applications such electronics and pharmaceutical production. They are typically very high efficiency (99.9 percent and higher), small pore sizes, and as a result, are extremely expensive. These should not be considered for use by the typical marketer.
- Pleated filters are available in a wide range of pore sizes (0.2 to over 100 microns), efficiencies (90 percent to 99.98 percent), and flow capacities (a few gpm to several hundred gpm per filter housing). The pleated materials can be polypropylene, cellulose, glass fibers, and combinations of these. In general, cellulose elements have a larger pore size and lower efficiency than either glass fibers or polypropylene, but they may be acceptable for the larger sizes of particulates. They would also be good choices as prefilters. Glass fibers are typically used with higher temperature and more corrosive fluids. The costs of polypropylene elements are 15 to 25 percent more than comparable cellulose filters, although they can accumulate more loading. These are general statements and the vendors should be consulted for specific element costs.
- Wound filters are formed by winding the filter media material, as yarns, onto an inner cage that remains as part of the filter element. Many materials can be used as media – polypropylene, glass fibers, cellulose, nylon, polyester, cotton and rayon. Polypropylene media provide higher efficiencies and lower pore sizes than the other fibers except for glass. Because of the formation of the yarns, wound elements are typically less efficient and have larger pores than pleated elements. However, because of this, wound elements also typically have longer loading times (in part, because they trap less material). However, because of their lower cost (10 to 30 percent less than pleated filters), they are a good choice for prefilters. The costs discussed here are general trends. Questions about the most economical element - such as, if a pleated cellulose filter is still a premium cost over a wound poly or cellulose filter, which is a better prefilter? - must be held with the vendor.

A cautionary note: chemical compatibilities tables list the compatibility of liquid propane and polypropylene as satisfactory to excellent, depending on the source. However, several references cautioned the use of propane vapor with polypropylene, listing it as UNSATISFACTORY. Care should be taken in using polypropylene filter media to ensure that it is exposed to liquid propane.

Loading times, or filter lifetimes, are greatly impacted by the particle count of the propane stream. Some vendors advertise load rates in their literature, but when questioned about the assumptions that these data assumed, the reply was the same as the vendors that do not advertise loading rates: each filtration system must be selected and designed to meet the particular needs of the installation. In short, no vendor would give suggestions on filter life without a detailed (and for-fee) design analysis.

Appendix B is a brief list of vendors identified using industrial catalog (Thomas Register) sources, Internet searches, and phone and email follow-up. This list is not intended to be exhaustive but only a guide as to the products and services that are available. These vendors have identified filter systems that are applicable with propane, cover the flow rates that are typical of bulk plants (approximately 100 gpm), and cover the range of particulates identified in this study.

Whatever filter system is chosen, it must be properly monitored. Pressure drop across the filter system is indicative of filter loading and should be monitored daily. Periodic checks should be made on the propane leaving the filter system. Either frequent batch sampling or to-be-developed on-line analysis methods/ instruments must be used to determine replacement. The Southwest Research Institute (Southwest Research Institute/PERC 2005) has reviewed possible technologies. Although operators may use normal operations and nominal fuel quality to predict filter life, anecdotal evidence indicates that unplanned, unexpected, infrequent, and non-periodic upsets in fuel quality is what determines any filter loading rate.

Hydrocarbon Composition

Figure 19 shows all the sample compositions on one graph. Note that the y-axis is logarithmic, and to avoid representational problems when a species is absent, when a species had zero concentration, we assigned it a value of 0.0012%. Figure 20 is the same data, with the propane values removed and the graph's top scale reduced to 10 percent, to expand the effect of the minor constituents.

As noted in Table 1, the Northern California sources were suspected to have high levels of propylene. Indeed, both samples were above five percent (6.9 percent for Gurneville and 12.6 percent for Elk Grove. Both of these samples would not meet the HD-5 specification (GPA 2140). The level of propylene found in the Gurneville sample would meet the California Air Resources Board's requirement for propane used as engine fuel[*], but the Elk Grove sample exceeds the propylene allowed in that specification.

This hydrocarbon analysis is discussed in detail in another PERC Report (LP Gas Surveys, Docket 11354).

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[*] CARB's engine fuel specification, available from www.arb.ca.gov/regs/title13/2292.6.pdf, is also commonly referred to as "HD-10".
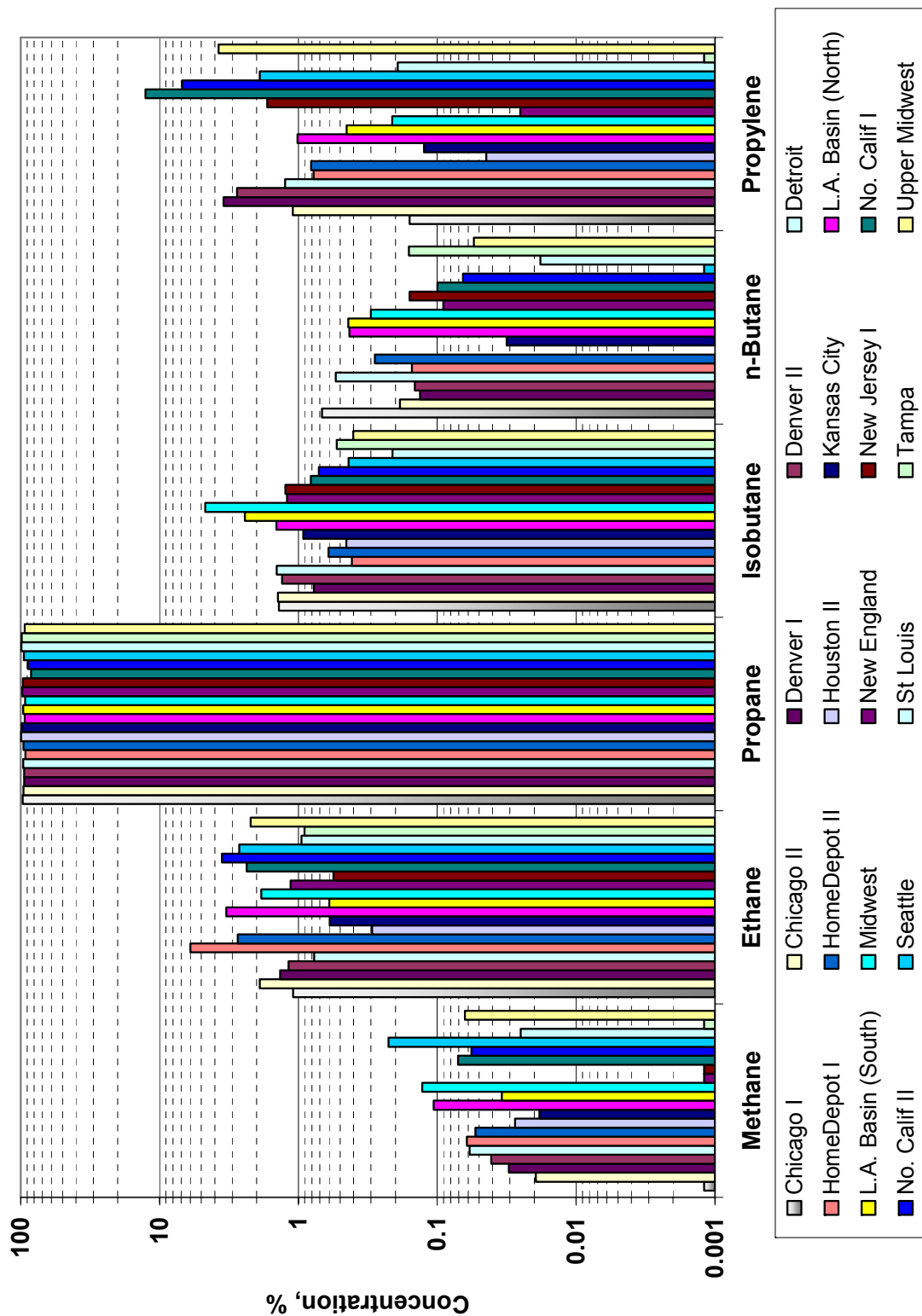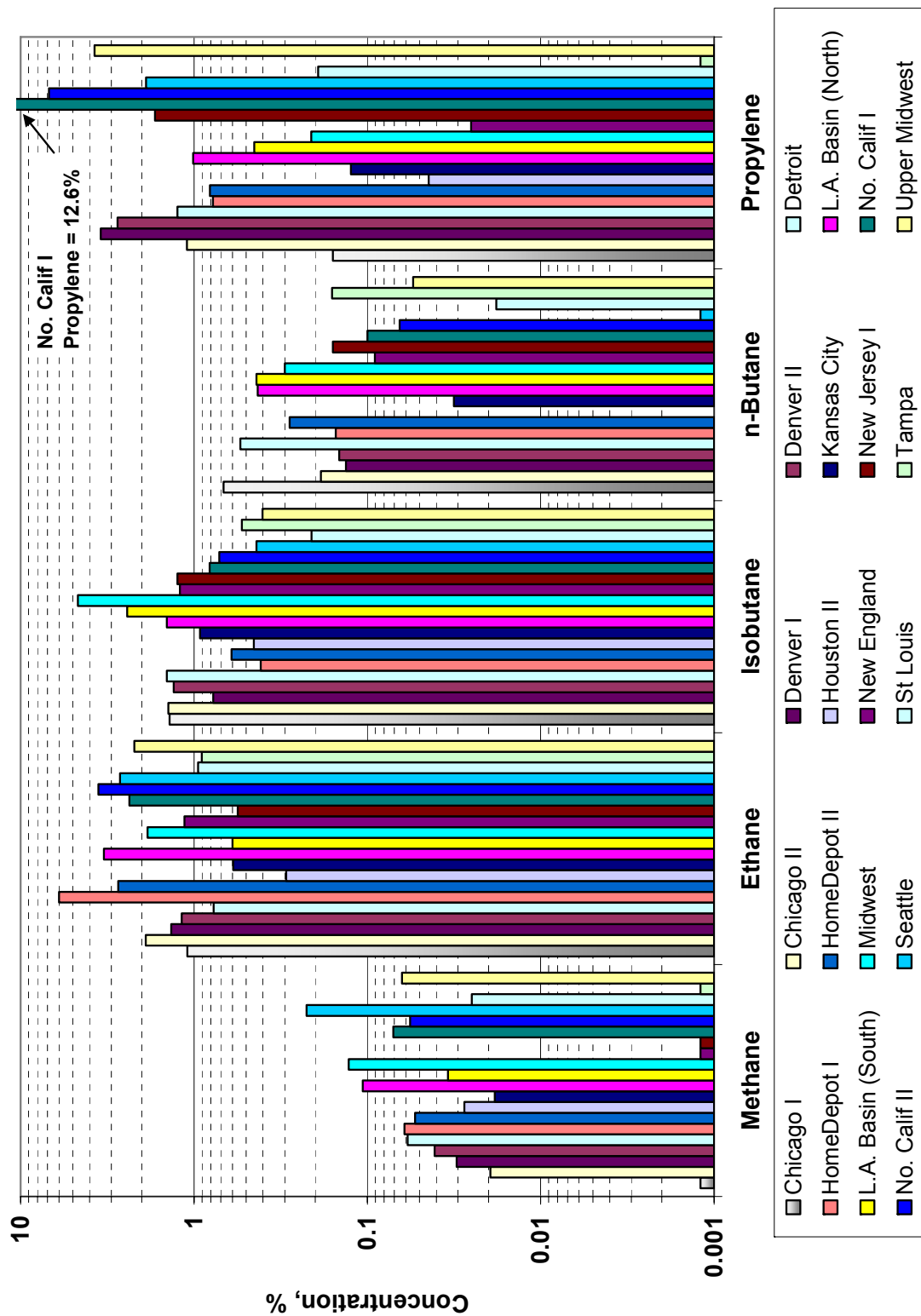
Figure 19. Hydrocarbon analysis.

Figure 20.   Hydrocarbon analysis. — minor constituents only (no propane shown).

CONCLUSIONS

Propane samples were taken from a reputable marketer at several geographical locations, and a few samples were obtained from retail locations. The sampling was representative of national locations with different sources of LP Gas. The number of samples was not large enough to draw statistically valid conclusions, but was large enough to be illustrative of the LP Gas distribution system.

Samples were analyzed for: hydrocarbon composition, solid particle contamination, and moisture content. The hydrocarbon composition was obtained by gas chromatography. Solids were analyzed for particle size distribution by laser particle sizing analysis, and one solids sample was analyzed by energy dispersive spectroscopy (EDS), infrared (IR) spectroscopy, secondary electron imaging (SEI), and backscattered electron imaging (BEI).

Energy dispersive spectroscopy (EDS) identified the outer surface of the particles to be composed of carbonates. This result was confirmed by infrared spectroscopy analysis. The BEI image suggested that the particles consisted of a metallic component (such as iron) and lighter elements such as carbon, oxygen and sulfur. The particles are likely from interactions of the hydrocarbon fluid (including sulfur compounds as contaminants and an odorant), the steel distribution piping and storage vessels. An external laboratory conducted further analyses on the samples and confirmed the presence of iron, carbon, oxygen, aluminum, and silicon. The source of the aluminum could be the fork lift cylinders used as sample collection vessels.

A small amount fibrous material was also found in the sample selected for further analysis. One type of fiber was identified to contain silicon and oxygen (components of glass and some sands). A second type of fiber had a cellular appearance, as opposed to the granular, crystalline structure of the other fiber type. The source of these fibers is unknown. Possible sources include hose reinforcement fibers or loose filter fibers. These fibers comprised a small fraction of the solids collected, with the majority being the metallic-based fibers discussed earlier.

All solids collected were analyzed with a laser particle sizer. The sizer gave a distribution of the particles in the sample. Particles were identified between approximately 0.2 microns to 900 microns. The overall peak of the combined distributions of the twenty samples was broadly spaced between 1 and 10 microns, with an additional peak between 10 and 80 microns.

Types of filter media were identified that could remove these particles. General guidelines on filter selection were given for the particles found in this study. A filter system for a specific bulk plant, however, should be designed with the particle distribution of that bulk plant and an analysis of the plant's maintenance capabilities, and its customers' end-use needs.

Samples were also analyzed for moisture content, using an electronic dew point sensor. Acceptable freeze valve times of 60 seconds indicate moisture levels of approximately 35 ppm. Moisture content of the samples ranged from 1 to 10 ppm moisture, indicating very dry propane. Methods were discussed of controlling excess moisture, which has historically involved the use of methanol. Some filters have moisture capturing/absorbing capabilities, but water occurs throughout the transportation system from such sources as the brine used to push propane from underground storage caverns, cooling of warm, moist propane, condensing moisture from air, tank cleaning, and tank hydrotesting. The most effective control of moisture appears to be the continued use of methanol, but the propane streams should be monitored for actual moisture levels to determine proper dosing of methanol. Additional research is needed to generate easy-to-use correlations of the required methanol necessary to offset specific moisture levels in propane streams. While the industry-standard freeze valve test shows that streams are too moist, it does not

indicate the level of moisture. Additional work is needed to generate easy-to-use moisture measurement methods that are robust to the potential presence of methanol, as it can affect the results of the freeze valve test.

Eighteen of the 20 of the samples met the hydrocarbon composition specifications of commercial propane as listed in GPA 2140-97. Nineteen samples met the requirements of the California Air Resources Board for propane engine fuel (HD-10), with the Elk Grove sample having too low of a propane level and too high of a propylene level. In addition, 16 of the 20 samples met the hydrocarbon composition requirements of HD-5, that is, a propane content of at least 90 percent, a propylene content of no more than five percent, and a butane content of no more than 2.5 percent.

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Appendix A

Dew Point Sensor

DT 20

Model : DT20		
Maker : Alpha Moisture Systems (England)		
24V loop powered display	o 4/20mA, 24V DC, loop powered o 2wire configuration o 12-28 v DC o 3½ digit LED display o Built-in Autocal facility o Accuracy:: +/- 2ºC, over -110ºC to 0ºC dewpoint	
analogue	o 24V, 4.20mA loop powered o 2 or 3 wire configuration o 12-28v DC o Linear output in °C dewpoint o Built-in Autocal facility o Temperature compensated	

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SYSTEMS

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CERTIFICATE OF TEST & CALIBRATION

Customer	:	Delta Instrument LLC	Date	:	12/11/04
Customer Ref.	:	DI04-3106 Rev.2			
			Cert. Ref.	:	04X0329
Instrument No.	:				
Sensor No.	:	DT01-100468	Examiner	:	HF

Applied Dew Point ^{0}C	Instrument Reading ^{0}C	Deviation ^{0}C
-93.3	-93.1	0.2
-79.4	-79.1	0.3
-70.3	-70.0	0.3
-60.1	-59.7	0.4
-51.1	-50.9	0.2
-43.7	-43.4	0.3
-33.1	-32.8	0.3
-22.2	-22.0	0.2

Comments & Observations:
Tested within specification : +/- 2 ^{0}C Dew Point

The instrument and/or Sensor under test was calibrated by comparison to a reference optical Dew Point Hygrometer, which is certified and calibrated directly by *The National Physical Laboratory, England. Certificate Nos. 08C041/94020 & 08C041/93013A.*
The instrument and/or Sensor under test was calibrated by comparison to a optical Dew Point Hygrometer, which is certified against a Standard Hygrometer, calibrated directly by *NIST, USA – Test Report No. 2002.29828*

We hereby certify that the equipment detailed above has been tested and calibrated by the undersigned, and its performance was found to meet our specification unless noted otherwise in the Comments and Observation section above.

For and on behalf of
Alpha Moisture Systems

H. Hetche

For Quality Assurance Manager

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CERTIFICATE No.FM38600
BS EN ISO 9001:2000

INVESTORS IN PEOPLE UK

VAT No. 607207563   Alpha Moisture Systems Ltd. (Registered in England) Registration No. 3902302

Appendix B

Selected Filter Information

Propane Filter Commercial Availability

Company	Description	Particle Size (μ)	Reference / Contact
Allied Group Inc. Mendham, NJ	The Allied Group has filters for propane applications that can filter particles to 0.3 micron, handle pressures over 3500 psi, and handle both high and low flows. Their current applications can remove water and oil at an efficiency of 99.99%, or higher depending on the conditions at the time of filtering. For the range of applications for this study (<250 psi; ambient temperature; ~100 gal/min.), they would use one of three materials; microglass with phenolic resin filters as the pre-filter, fiberglass filter elements with a microglass inner layer or sintered stainless steel (which may not be as effective as the other two). Multiple filters would be needed to handle the flow, probably 4 to 6. Dimensions of a multiple-filter housing would be approximately 36" long x 4-5 " outside diameter.	0.3	http://www.alliedfilters.com/ info@alliedfilters.com 800-728-8311
Alternate Energy Systems, Inc. Peachtree City, GA	Strainers used for large particles, no fine filters; coalescent filters for moisture removal and "heavy ends", both for liquid and vapor phases. No data on web site about effectiveness or capacity of coalescent filters.	> 25	http://www.altenergy.com/ http://www.altenergy.com/accesori.htm#Strainers%20and%20Filters 800-410-9161
Como Filtration Systems Janesville, WI	Elements are capable 5gpm, several would be ganged to achieve 100gpm; can remove some free water	1 to 5	http://www.comoindustrial.com/index.html info@como.biz 800-451-0028
Filtration Technologies L.L.C St. Louis, MO	Filtration Technologies manufacturers fuel gas filtration products which can be applied to propane in the gaseous state to remove particulate as well s water and oil based aerosols. The Triton fuel gas filter is a combination of filtration and coalescing technologies. It combines particulate filtration and mist elimination in one unit. The final coalescing layers remove water and oil aerosols down to the 0.3 micron range.	0.3	http://filtrationtechnologies.com/filtraweb1_files/page0005.htm 314-432-2896
Hilliard Corporation Elmira, NY	Hilco® elements – polypropylene, natural fibers,	1 to 5	http://www.hilliardcorp.com/hilco.php3 607-733-7121
HY-PRO Filtration Fishers, IN	Filters generally for non-aquous applications. Products similar to Parker. Operating pressure to 400 psig, flowrates to 300 gpm In-tank return and return-line assemblies 600 gpm max flow rate 1000 psi max operating pressure Coreless element technology		http://www.filterelement.com/ 317-849-3535 sburd@hyprofiltration.com
Krystil Klear Filtration® Winamac, IN	Industrial filters and the housings—cartridge filters, liquid filter bags, strainer baskets, in-line strainer housing.	1 to 5	http://www.krystilklear.com 800-869-0325

Propane Filter Commercial Availability

Company	Description	Particle Size (µ)	Reference / Contact
	Several element types (polypropylene, natural fibers, stainless steel mesh)		
North American Filter Company Newark, NY	Polypropylene filter cartridges, in parallel for 100 gpm service	1 to 5	http://www.nafcoinc.com/ (800) 265-8943
Nowata Filtration Nowata, OK	Polypropylene, natural fibers, carbon, water absorption, elements and housings to several 100 gpm	0.5	http://www.nowata.com/ 800-259-2204
Pall Corporation East Hills, NY	Wide range of polypropylene and carbon filters, would need to gang together to reach 100 gpm	0.2 to 5	http://www.pall.com/products.asp 800-645-6532
ParkerHannifin **Process Filtration Division** Indianapolis, IN	Extremely wide range of filter types and capacities, full catalog available on web site	0.03 to 100	http://www.parker.com/ead/cm2.asp?cmd=1779 Catalog from http://www.parker.com/processfiltration/cat/english/ParkerpdfCatalog04.pdf 888-238-5356
Pollard Industries, LLC Baton Rouge, LA	Several lines of filter equipment – entire engineered, packaged systems, individual housings, individual filter elements; broad range of element types, including sintered metal, natural/ polymer fiber, coalenscent, > 100 gpm	< 1	http://www.pollardindustries.com/products/default.htm 225-926-6311
Precision Filtration Products Pennsburg, PA	Industrial filters, All types, All brands. Filter housings, Filter vessels, Filtration and Purification Systems. Filter Cartridges, Filter Bags, Filter More of a supplier than an OEM	1 to 5	http://www.precisionfiltration.com/ 866-242-5888
Velcon Filters Inc. Colorado Springs, CO	Polypropylene, screen elements, carbon filters	1 to 5	http://www.velcon.com/aviation/aviSelect.html 800-531-0180

NOTES AND ADDITIONAL REFERENCES:

- Propane gas is **not** compatible with Polypropylene; **Liquid Propane is compatible**. (Ref. http://www.sorbio.com/chemicals.cfm)
- Apple Rubber o-ring seal compatibility matrix: http://www.applerubber.com/sdg/guide2/material_guide/illust.cfm (registration required)