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Methanol Fuel Quality Specification Study For Proton Exchange Membrane Fuel Cells

Final Report

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Executive Summary

Fuel cell power from methanol presents an extraordinary opportunity for environmental improvement. It also presents significant challenges from an infrastructure perspective. One such challenge will be the provision of “PEM fuel cell grade” methanol when and where it is required. A preliminary requirement of this challenge is to determine the boundaries of “fuel cell grade”.

Most fuel cell engine testing to date has been performed using very pure grades of methanol to minimize the potential for reformer catalyst contamination. Concerns have been raised regarding the requirement for fuel additives such as flame luminosity indicators, odorants, and lubricants. Such compounds could be detrimental to reformer catalyst operation. To become economically viable, the fuel cell engine must be able to use a widely available, easily distributed and affordable grade of methanol. This will only become possible if the mechanisms of degradation are understood, the sources of contamination are determined, and viable alternatives or clean-up techniques are found.

The overall goal of this project was to examine the distribution side of the methanol infrastructure. This project comprises of five main tasks: 1) a comprehensive evaluation of what the most likely contamination mechanisms are 2) chemical analysis of a variety of methanol grades to identify probable grade restrictions for fuel cell use 3) an analysis of the supply infrastructure to determine the most probable sources of contamination 4) an evaluation of automotive guidelines to determine the requirement for additives in an automotive methanol fuel 5) a physical evaluation of additive and contaminant impact on reformer conversion.

Significant research has been carried out to determine which compounds are most damaging to methanol conversion over copper zinc oxide catalysts. A literature review was performed in order to A) determine which contaminants and additives could be present in various grades of methanol, and to B) summarize the impact these contaminants and additives may have on methanol reforming processes.

Significant literature was found to support objective A of the literature review, however, little was found that describes the potential effects of contaminants and additives on methanol reforming.

The literature search was supplemented by a thorough chemical analysis of methanol samples from a number of supply sites, spanning all grades likely to be applied to automotive service. XCELLSiS consulted with Methanex to determine which chemical tests would provide the most useful information in analyzing the available grades of methanol and methanol infrastructure samples. XCELLSiS selected West Coast Analytical Service, Inc. of Santa Fe Springs, California to conduct these tests.

The supply chain was analyzed in order to determine if the contaminants found in the chemical analyses are avoidable through more strict controls or if they are indicative of a more pervasive problem. It was found that many of the contaminants detected in the distribution infrastructure samples can be categorized by their source. Contaminants from the production process include acetic acid, acetone, 2-butanone, and water. Petrochemical contaminants from cross-contamination (contact with residue of another chemical) include various hydrocarbons. Leaks in water vessels, which transport methanol, introduce water and chloride. In addition, the

plumbing used to transport the methanol provides another potential mode for methanol contamination. Heavy metals can be introduced to the methanol from plumbing systems that are constructed of materials incompatible with methanol. For example, galvanized plumbing can be considered a potential source of nickel and zinc contamination. Furthermore, pipe joint compounds, which typically contain lead, provide another potential source of contamination. Most of the contaminants detected in the chemical analyses and discussed above are generally avoidable through more strict controls.

The current requirements for methanol fueled vehicles were reviewed. The California Code of Regulations (see Appendix C) currently requires methanol to have both a bitterant and an odorant. Of current concern are the effects that these additives will have on the methanol reformer's copper zinc oxide catalyst. The additives should ideally have the following properties:

- will not damage the reformer catalyst
- will match the thermal and physical properties of methanol
- will add to the energy content
- will impart a disagreeable taste or smell
- will not be capable of being easily eliminated
- will not add to emissions levels
- will be readily available
- will not add appreciably to the cost of the fuel

Relative to the bitterant requirement, at ambient conditions, the M-100 fuel methanol must have a distinct and noxious taste for purposes of preventing purposeful or inadvertent human consumption. Currently, Bitrex (denatonium benzoate) is the most economical of foul-tasting additives, due to its relatively low bitterness threshold and corresponding low cost in use.

The odorant requirement maintains that upon vaporization at ambient conditions, the M-100 fuel methanol must have a distinctive odor potent enough for its presence to be detected down to a concentration in air of not over one-fifth of the lower limit of flammability.

Although methanol burns with a colorless flame creating a potentially hazardous scenario, the code of regulations does not currently require M-100 fuel methanol to contain an additive which would provide a luminous flame if the methanol were to ignite, but the regulation does require an on-board flame arrester. In selecting an additive for flame luminosity, aromatics would be the best candidates to increase the luminosity of methanol flames as they are capable of forming azeotropic mixtures with methanol and of increasing the C:H ratio with the minimum amount of additive. However, all of these compounds are potentially poisonous to the catalyst because of their complex hydrocarbon content.

Six samples were taken from points in the distribution supply chain and were evaluated in the small-scale reformer evaluation hardware. Those six samples represent all the likely grades of methanol that one would encounter when selecting an optimal fuel for PEM fuel cell vehicle use. **Manufacturing Facility, Sample #2**, the least contaminated fuel tested, served as a baseline for comparison with the other samples. Evaluation of fuel conversion levels in the test reformer using this fuel showed a rapid initial drop in conversion, followed by relative stabilization at a very slow degradation rate. The remaining samples showed similar behavior, though the

amplitude of the initial drop and the slope of the subsequent “plateau” region increased in proportion to the level of contamination in the fuel. Of particular impact were alcohols, chloride, and complex hydrocarbons.

In addition, three additives and ethanol were evaluated in isolation. Bitrex, a bitterant, was evaluated at 15 ppm; Sodium chloride, a potential flame luminosity additive, was evaluated at 50 ppm; Ethanethiol, an odorant, was evaluated at 2.5 ppm, and ethanol was evaluated at 100 ppm. **Manufacturing Facility, Sample #2** was again used as a baseline to check the magnitude and reversibility of the catalyst degradation caused by these contaminants. Ethanol and sodium chloride both caused the catalyst to degrade very rapidly. When the reforming process was switched back to the **Manufacturing Facility, Sample #2**, the catalyst showed complete reversibility. Bitrex and ethanethiol caused less pronounced degradation in catalyst activity, but the degradation did not appear to be reversible. Only limited additive testing was performed due to time restrictions of the program, and further tests should be performed in order to confirm preliminary indications.

The following list provides several recommendations for further steps that would aid in the development of a PEM fuel cell methanol fuel specification:

- Currently, there is very little information on potential additives and their compatibility with copper zinc oxide catalyst. Additional studies on potential methanol fuel additives should be made.
- A list of methanol compatible materials of construction should be well defined. During the construction of new facilities or upgrades to older facilities these materials should be used to help maintain methanol quality.
- Dedicated methanol systems or appropriate quality control measures (including vessel cleaning as needed) are essential to maintain methanol’s high purity throughout the methanol distribution infrastructure.
- Education and Awareness: People involved in the handling and distribution of methanol for fuel cell use should be adequately trained to understand the various mechanisms of methanol contamination, methods and practices to prevent contamination, and the chemical compatibilities of the methanol reformer used in fuel cell vehicles.
- Specific analysis and quantification of the effects of various individual contaminants on copper zinc oxide catalyst should be performed. This would allow identification of specific contaminants that have a particularly degrading effect. The current effort gave a preliminary indication of specific sensitivity to non-methanol alcohols, but this effect and similar effects by other specific contaminants needs to be confirmed by further testing.
- Additional catalyst degradation testing is required to evaluate non-accelerated degradation to establish predicted catalyst lifetimes in vehicular usage. This data would allow cross calibration of the accelerated lifetime testing performed under the current study.
- Additional testing is required to quantify the overall system effect of fuel contamination, i.e. the downstream effect on fuel cell performance.

- Further examination is required to determine if contaminant/additives could be removed from a methanol fuel prior to the fuel entering the fuel cell system. For example, one could potentially envisage a device, like a fuel filter, that could remove contaminants, such as chloride, from the fuel before the fuel enters the fuel processor.

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1 Introduction

Fuel cell power from methanol presents an extraordinary opportunity for environmental improvement. It also presents significant challenges from an infrastructure perspective. One such challenge will be the provision of “PEM fuel cell grade” methanol when and where it is required. A preliminary requirement of this challenge is to determine the boundaries of “fuel cell grade”.

Most fuel cell engine testing to date has been performed using very pure grades of methanol to minimize the potential for reformer catalyst contamination. Concerns have been raised regarding the requirement for fuel additives such as flame luminosity indicators, odorants, and lubricants. Such compounds could be detrimental to reformer catalyst operation. To become economically viable, the fuel cell engine must be able to use a widely available, easily distributed and affordable grade of methanol. This will only become possible if the mechanisms of degradation are understood, the sources of contamination are determined, and viable alternatives or clean-up techniques are found.

The overall goal of this project is to examine the distribution side of the methanol infrastructure. The potential for contamination in the shipment of methanol will be evaluated. An analysis of the impact of important additives and supply chain materials will follow. The possibility of avoiding materials problems in the supply chain will also be analyzed.

2 Background

Adaptation of fuel cells to vehicle use poses some significant challenges. In addition to being cost-competitive with current and projected conventional technology, the fuel cell power subsystem must be able to provide acceptable dynamic response to power demand fluctuations, high enough power density to fit within the weight and space limitations of vehicle design, and quick start-up. It must also satisfy other considerations, such as ruggedness, driveability, safety, and long operating lifetimes. [1]

One issue that has a great bearing on the adaptability of fuel cells to transportation applications is the conversion of the primary fuel, such as methanol, to hydrogen or a hydrogen-rich gas mixture suitable for use in a fuel cell. [1] Hydrogen can be produced from methanol and other alternative fuels by steam reforming or partial oxidation. The desired features for such a reformer include rapid start-up, dynamic performance responsive to fluctuating loads, efficient and complete fuel conversion, small size and weight, simplicity of construction and operation, long life, and low cost. To be suitable for transportation applications, therefore, the fuel cell power system must respond rapidly to wide fluctuations in power demand, as well as operate in the nominal idle, cruise, and sustained high-power conditions. The fuel reformer must, in turn, operate with highly variable fuel flow rates yet maintain high conversion yields and efficiencies at all points in the typical driving profiles.

When considering different fuels for use in fuel cell powered vehicles, methanol has clear advantages in terms of fuel storage and distribution because it can be used with minimal disruption to the present liquid fuel (gasoline, diesel) distribution network. In addition, methanol has a relative thermodynamic advantage compared to other hydrocarbon fuels, which contain carbon-to-carbon bonds. Methanol can be reformed to hydrogen at much lower temperatures (250° – 300° C) compared to other hydrocarbon fuels, which require much higher reforming temperatures (800° – 900° C). However, this low temperature reforming advantage can be compromised if methanol is contaminated with hydrocarbons like constituents of gasoline or diesel fuel. If the methanol fuel is contaminated with these compounds it will impact the fuel cell power subsystem by reducing reforming efficiencies.

A brief introduction to the fuel cell power subsystem will lead into a description of methanol reforming processes and catalyst activity.

2.1 Introduction to the Fuel Cell Power Subsystem

PEM fuel cells operate using hydrogen and oxygen as the reactant gases. Oxygen is readily available from air, but hydrogen must be derived from other sources. The fuel cell power subsystem described here uses steam reforming of methanol to supply the hydrogen to the fuel cell. A simplified diagram of the subsystem is found in Figure 1.

2.1.1 Reformer

Methanol and water are supplied to the reformer system (described further in Section 2.2) which generates hydrogen, carbon monoxide, carbon dioxide, as well as unreacted methanol and water. The reformer system, with copper zinc oxide as the reaction catalyst, is the focus of this report.

2.1.2 Clean-up via Selective Oxidation

Since carbon monoxide is a fuel poison, it must be removed. The most common process for doing so is called selective oxidation. Selective oxidation is very similar to partial oxidation, except that the quantities of air employed are smaller, so that the temperatures generated by the oxidation are lower. At low temperature ranges, carbon monoxide will oxidize selectively over hydrogen.

2.1.3 Fuel Cell

The central component of a fuel cell is a polymer electrolyte membrane. This membrane has the special property that it allows protons to travel through it. It will not allow electrons to travel through it, nor is it permeable to gases. Catalytic reactions on one side of the membrane cause hydrogen gas to split into two protons, which travel through the membrane, and two electrons which travel externally through a load. On the other side of the membrane, oxygen reacts with the protons and the electrons to make water and energy. Because electrons have flowed through a load, this energy can be captured directly as electricity.

2.1.4 Combustor

As long as fuel cell systems emit hydrogen in their exhaust, and hydrogen is considered an emission, there will be a need for burners in fuel cell engines. The heat produced from this combustion can be used in a number of ways, including as an energy supply for fuel processing stages or as a means of increasing reactant pressures via turbo-compression. In almost all methanol based fuel cell applications, a process called catalytic combustion is used in place of standard flame combustion. Using platinum based combustion catalysts, extremely lean fuel streams can be completely oxidized, greatly reducing combustion temperatures as compared to conventional flame burners. Complete combustion can be achieved while maintaining temperatures of less than 500 °C. Combustion at these temperatures is a very clean operation, with no production of harmful CO, NOX, or SOX.

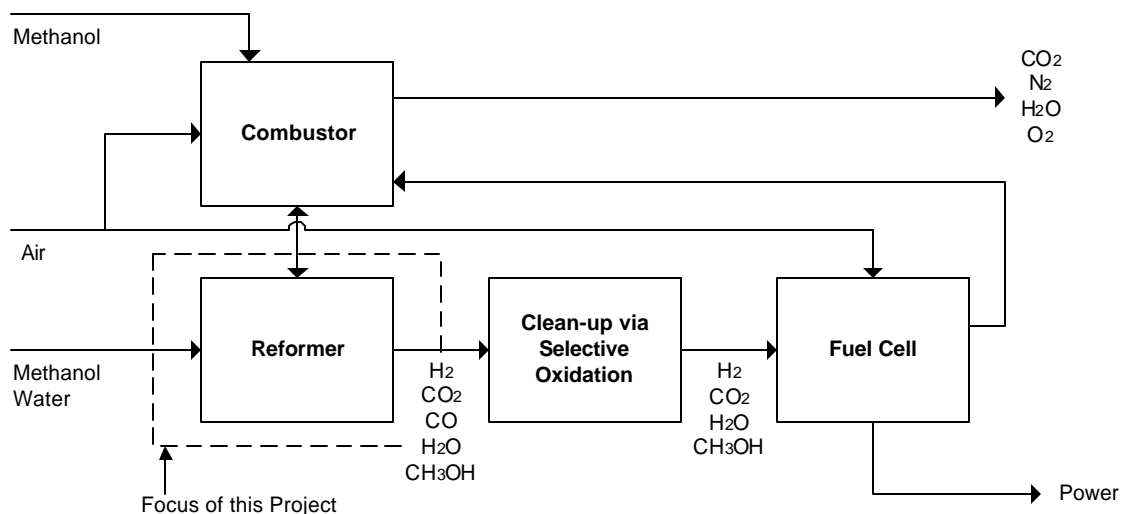


Figure 1. Simplified Flow Diagram of the Fuel Cell Power Subsystem.

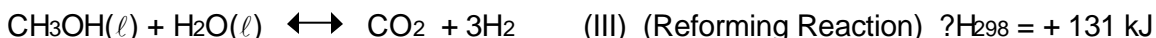
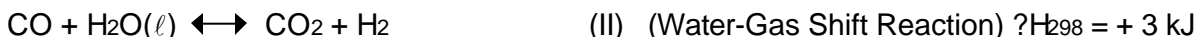
2.2 Methanol Steam Reforming

With the addition of heat at elevated temperatures (450° C to 850° C) hydrocarbons in the presence of steam will decompose over nickel based catalysts to produce a mixture of methane, hydrogen, carbon oxides, and steam. A portion of the reformer product stream is burned to provide heat for the endothermic reforming process. The efficiency of a steam reformer depends on the extent to which this heat energy is recovered.

Steam reforming of methanol is a special case. The lack of carbon-carbon bonds and the presence of the hydroxyl group allow decomposition at very low temperatures (250°C to 300°C) over copper zinc oxide catalysts. Low temperature reforming of methanol yields a product gas containing hydrogen, carbon oxides, water, and low concentrations of methanol. Due to the low operating temperatures, thermal losses can be minimized, and fuel processor thermal efficiencies can be very high. [1]

The major drawback of steam reforming is that the catalysts employed are inactive below their target temperature range. Thus some form of heat generation must first elevate the catalyst beds temperatures (to 250°C in the case of methanol) before reforming can begin. This can lead to fairly slow startup times.

There are three reactions in methanol steam reforming: decomposition of methanol to hydrogen and carbon monoxide, followed by the reaction of carbon monoxide with steam to produce carbon dioxide and more hydrogen, and the reforming reaction between methanol and steam to produce carbon dioxide and hydrogen. These three reactions can be written for the given reactants and products [2]:



Theoretically, the reformed gas generated by the methanol steam reforming reaction should be composed of 75% H₂ and 25% CO₂. In practice, however, the gas also contains some residual methanol, water, and a small amount of carbon monoxide (CO). [3]

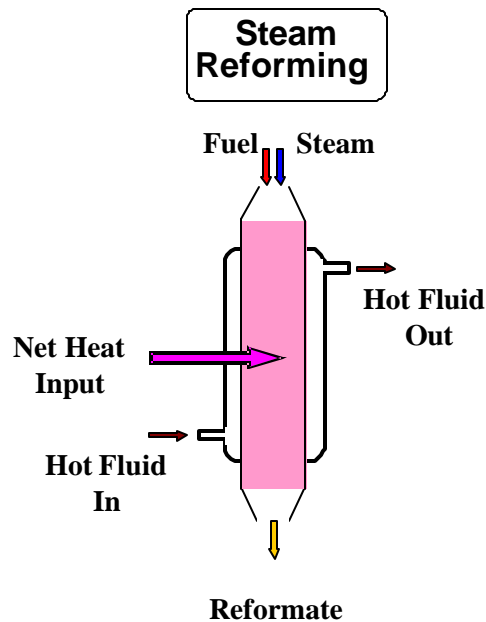


Figure 2. Steam Reforming

2.3 Copper Zinc Oxide Catalyst

In the reduced state, the steam reforming catalyst studied under this contract consists of copper and zinc oxide supported on alumina. The active constituent of the catalyst is the copper component. The activity of the catalyst, in the absence of a diffusion limitation, is directly proportional to the copper area and initial activity increases with increasing copper content.

Catalyst structure critically affects activity and lifetime, and thus, catalysts of apparently similar chemical composition perform differently. With a well-formulated catalyst, not maltreated, poisoning is the major cause of loss of activity. [4]

In an example cited in *Influences of Catalyst Formulation and Poisoning on the Activity and Die-Off of Low Temperature Shift Catalysts*, similar catalysts operating under commercial conditions in various full-scale plants and in a laboratory-scale reactor with poison-free gases show a variation in activity with time. Since all the results were obtained over approximately the same temperature range, different rates of poisoning rather than thermal sintering would appear to be the most important factor contributing to the various rates of loss of activity. This was subsequently confirmed, since, after 2 months on line, no poisons could be detected by chemical analysis in the catalyst discharged from the laboratory-scale units. The different rates of loss of activity on the full-scale can be attributed to the different poison levels and types of poison prevailing in different plants.

As part of the work detailed in *Influences of Catalyst Formulation and Poisoning on the Activity and Die-Off of Low Temperature Shift Catalysts*, it was found that sulfur and chlorine are the most important poisons for low temperature shift catalysts. The distribution of poisons in catalyst discharged for examination from a commercial plant after 12 months of operation is shown in the table below. Serious deactivation is observed only with catalyst that has been allowed to absorb chlorine.

Effect of Poisoning on a Catalyst in Commercial Operation

Position of Catalyst in Bed	Weight %		Activity Relative to that at Bottom of Bed, %
	SO ₃	Cl	
Top	1.4	0.08	15
	0.7	0.04	15
	0.4	0.01	72
	0.2	0.01	75
Bottom	0.2	0.01	100

The author, John S. Campbell, assumed that poisoning occurs by a blocking off of active sites rather than by a more sophisticated mechanism. X-ray diffraction experiments indicate that the great majority of the sulfur absorbed in the catalyst is taken up in the form of zinc sulfide and is therefore unable to attack the copper. Thus, a major reason for the addition of zinc oxide to the catalyst is to protect the copper from poisoning. In the case of chlorine contamination, the structure of the catalyst is destroyed. In addition, experiments were carried out to determine the sensitivity of low temperature shift catalyst to aromatic hydrocarbons. Benzene at concentrations up to 500 ppm had no effect; toluene depressed the activity of the catalyst very slightly, but the effect was reversible and the activity recovered after the toluene supply was cut off. Very high concentrations of toluene (500 ppm) resulted in wax formation in the pores of the catalyst and permanent catalyst deactivation. [4]

It should be noted that the previously mentioned degradation studies dealt with shift catalyst operation in large scale, steady state industrial shift reactors. This data, while qualitatively relevant to the use of copper zinc oxide catalyst is not directly relevant to the specific catalyst or specific application (small scale, dynamic methanol reformers) studied in the current evaluation.

3 Project Objectives and Scope of Work

The objective of the project was to determine the best case combination of methanol grade, additive requirement and composition, and supply chain procedures to yield an affordable, widely available supply of methanol.

This project comprises five main tasks: 1) a comprehensive evaluation of what the most likely contamination mechanisms are 2) chemical analysis of a variety of methanol grades to identify probable grade restrictions for fuel cell use 3) an analysis of the supply infrastructure to determine the most probable sources of contamination 4) an evaluation of automotive guidelines to determine the requirement for additives in an automotive methanol fuel 5) a physical evaluation of additive and contaminant impact on reformer conversion. Below is a summary description of each task:

1) Literature Review

Significant research has been carried out to determine which compounds are most damaging to methanol conversion over copper zinc oxide catalysts. A thorough literature search enabled a summarizing of these compounds and their probable impact.

2) Chemical Analysis of Available Grades

The literature search was supplemented by a thorough chemical analysis of methanol samples from a number of supply sites, spanning all grades likely to be applied to automotive service. The chemical analysis provided a means to analyze the supply chain distribution.

3) Supply Chain Analysis

The supply chain was analyzed to understand the mechanisms of contamination.

4) Additive Requirement Analysis

The current requirements for additives in methanol fuel applications were reviewed, as was a variety of compounds within each additive family. From this research, additives were selected to be evaluated in the small-scale reformer hardware.

5) Methanol-Steam Reforming Catalyst Degradation Analysis

An array of fuels, additives and contaminants were tested using XCELLSiS' small-scale reformer evaluation hardware. Changes in conversion were determined, logged, and characterized. Against a baseline methanol sample direct from a manufacturing facility, the impact of variation in grade, additive and contaminants were evaluated. The evaluation provides a basis for future work in determining the best combination of fuel grade, additive and supply chain procedures to ensure availability of a practical "PEM fuel cell grade" methanol infrastructure.

4 Literature Review

A literature review was performed in order to A) determine which contaminants and additives could be present in various grades of methanol, and to B) summarize the impact these contaminants and additives may have on methanol reforming processes.

A search for relevant literature was conducted at the University of California San Diego Library and at relevant websites including the American Methanol Institute, Argonne National Laboratory, and the Center for Environmental and Energy Research at Princeton University. Previous work completed at XCELLSiS GmbH and material provided by Methanex Corporation was also included, as well as literature provided by Bob Wimmer at Georgetown University's Advanced Vehicle program. In addition, BASF, an international catalyst manufacturer, provided information on catalyst poisons relevant to their products.

Significant literature was found to support objective A of the literature review, however, little was found that describes the potential effects of contaminants and additives on methanol reforming.

The following section summarizes the findings for each paper. References for the papers are found at the end of the report.

4.1 Literature on Contaminants

4.1.1 Fuel Contaminant Removal and Methanol Burners for Reformer and Thermal Management System Start-up

Argonne National Laboratories prepared a report in December 1996 detailing their work in support of International Fuel Cells Corporation's (IFC) program on the development of a 100-kW phosphoric acid fuel cell for a full size transit bus. Discussed in the report was methanol fuel contaminant removal.

The report states that commodity methanol can be contaminated with up to 1% diesel fuel or gasoline through current liquid-fuel distribution systems. The diesel fuel and gasoline contain sulfur compounds that will contaminate the methanol fuel. Methanol by itself contains very little sulfur. International Fuel Cell Corporation set the allowable sulfur limit in the methanol fuel to less than 1 ppm.

Argonne National Laboratory identified the sulfur compounds found in diesel fuel to be C1-C4 alkyl-substituted benzothiophenes, 0-C3 alkyl-substituted dibenzothiophenes, and their isomers. The sulfur compounds found in unleaded gasoline were identified to be benzothiophene, methylbenzothiophene, their isomers, and possibly C1-C3 alkyl substituted thiophenes.

4.1.2 70 Years of Catalysts for Methanol Synthesis – Historical and Recent Developments

BASF presented a paper to the 1993 World Methanol Conference. The paper reviewed the history of methanol synthesis and discussed recent developments in commercial catalysts, which produce methanol efficiently from hydrogen and carbon oxides.

Because methanol production from hydrogen is reversible, the catalyst properties discussed in this paper are also relevant to the production of hydrogen from methanol over copper zinc oxide catalysts.

The paper states that the efficiency of the methanol synthesis catalyst is greatly impaired by impurities in the process gas. The feed gas can contain impurities that are deposited on the catalyst pellets and then they, themselves, act as catalysts for side-reactions. By-products can also arise in consequence of impurities in the catalyst itself.

4.1.3 BASF-Catalyst K3-110 – Technical Leaflet

The technical leaflet on BASF Catalyst K 3-110 provides relevant information on copper zinc oxide catalysts. It states that sulfur and chlorine compounds are the most frequently occurring catalyst poisons in commercial operation. Sulfur and chlorine compounds are introduced through the process feed. The compounds bind to the active sites on the catalyst and prevent the conversion of methanol to hydrogen.

4.1.4 XCELLSiS Report

An internal XCELLSiS report cites possible contaminations and their sources. Contaminations from production include, but are not limited to, higher alcohols, principally ethanol, propanols and butanols; hydrocarbons, principally n-paraffins and waxes covering a wide range of chain lengths; esters, mainly methyl formate and methyl acetate; ethers, mainly dimethyl ether; and ketones such as acetone and methyl ethyl ketone. Contaminations from the supply infrastructure include gasoline and diesel fuels. Note that all these impurities can be removed with distillation techniques.

4.1.5 Quality Control Information Memorandum

The Quality Control Information memorandum issued by Methanex discusses quality control tests used to monitor contamination. Possible contaminants include:

Heavy alcohols – the process used to produce methanol will produce high heavy alcohols.

Carboxylic acids can be formed as a by-product

Ammonia – the reformer catalyst used in methanol production can produce ammonia

Ketone and aldehyde impurities from contact with carbon dioxide during production

Non-volatile matter from a range of compounds in contact with the methanol, such as fibers from gaskets, packings, iron from rust, salts, etc.

Water – possible sources include shipping vessels, railcars and trucks if left open, or storage tanks, which may have leaks to atmosphere

Ethanol – produced during methanol production from improper operation of the distillations columns

4.1.6 Methanol Fuel for Fuel Cell Vehicles

In a fax regarding methanol fuel for fuel cell vehicles, David Friedman of the California Energy Commission lists possible contaminants that could be found in M-100 used for fuel applications.

The list was based on the M100 specifications that were developed by the Air Resources Board in 1994. Friedman noted that the specifications do not necessarily represent the exact levels of compounds that might be found in M-100, but rather the maximum allowable established for M-100 in internal combustion engines based on what might be picked up by the fuel during transportation and distribution. The contaminants include:

Methanol:	96% by volume (min.)
Other Alcohols and Ethers:	2% by mass (max.)
Hydrocarbons: (gasoline or diesel derived fuel)	2% by mass (max.)
Acidity as acetic acid:	0.1% by mass (max.)
Chlorine as chloride:	0.0002% by mass (max.)
Lead:	2mg/L (max.)
Phosphorus:	0.2 mg/L (max.)
Sulfur:	0.002% by mass (max.)
Gum (heptane washed):	5 mg/L (max.)
Total Particulate:	5 mg/L (max.)

Additional components to ensure flame luminosity, an odorant, and a bitterant.

4.1.7 A Study of M-85 Fuel Quality Issues

Acurex Environmental Corporation prepared this report for the California Energy Commission in July 1995. In the report, the conductivity of M85 at various retail stations was studied, in addition to other fuel characteristics. The study showed that methanol was leaching significant quantities of foreign material into the fuel.

The study found that the conductivity for the first liter of fuel pumped from the station was much higher than the rest of the fuel pumped. This provided a strong indication that the conductivity changes were resulting from something in the dispenser as opposed to the fuel in the storage tank or the delivery truck. Also, since it occurred in the first 1,000 ml, most likely the conductivity change resulted from something leaching out of the dispenser hose into the methanol between fuelling.

In addition to the conductivity analysis, the first liter out of the dispenser and the first liter after a four-gallon purge were analyzed for metals. The study found that the highest concentrations of metals in the fuel were zinc and calcium. Calcium was present in high concentrations both in the before and after purge samples indicating that it is in the bulk fuel, most likely the result of sand and other contaminants. Zinc, however, is significantly higher in the first liter than the after purge liter. This is a strong indication that it is leaching out of the dispenser hose into the methanol when fuel sits in the dispenser hose between uses. Zinc oxide is contained in the dispenser hose filler material.

4.1.8 Influences of Catalyst Formulation and Poisoning on the Activity and Die-Off of Low Temperature Shift Catalysts

In an example cited in *Influences of Catalyst Formulation and Poisoning on the Activity and Die-Off of Low Temperature Shift Catalysts*, similar catalysts operating under commercial conditions in various full-scale plants and in a laboratory-scale reactor with poison-free gases show a variation in activity with time. Since all the results were obtained over approximately the same temperature range, different rates of poisoning rather than thermal sintering would appear to be the most important factor contributing to the various rates of loss of activity. This was

subsequently confirmed, since, after 2 months on line, no poisons could be detected by chemical analysis in the catalyst discharged from the laboratory-scale units. The different rates of loss of activity on the full-scale can be attributed to the different poison levels and types of poison prevailing in different plants.

As part of the work detailed in *Influences of Catalyst Formulation and Poisoning on the Activity and Die-Off of Low Temperature Shift Catalysts*, it was found that sulfur and chlorine are the most important poisons for low temperature shift catalysts. The distribution of poisons in catalyst discharged for examination from a commercial plant after 12 months of operation is shown in the table below. Serious deactivation is observed only with catalyst that has been allowed to absorb chlorine.

Effect of Poisoning on a Catalyst in Commercial Operation

Position of Catalyst in Bed	Weight %		Activity Relative to that at Bottom of Bed, %
	SO ₃	Cl	
Top	1.4	0.08	15
	0.7	0.04	15
	0.4	0.01	72
	0.2	0.01	75
Bottom	0.2	0.01	100

The author, John S. Campbell, assumed that poisoning occurs by a blocking off of active sites rather than by a more sophisticated mechanism. X-ray diffraction experiments indicate that the great majority of the sulfur absorbed in the catalyst is taken up in the form of zinc sulfide and is therefore unable to attack the copper. Thus, a major reason for the addition of zinc oxide to the catalyst is to protect the copper from poisoning. In the case of chlorine contamination, the structure of the catalyst is destroyed. In addition, experiments were carried out to determine the sensitivity of low temperature shift catalyst to aromatic hydrocarbons. Benzene at concentrations up to 500 ppm had no effect; toluene depressed the activity of the catalyst very slightly, but the effect was reversible and the activity recovered after the toluene supply was cut off. Very high concentrations of toluene (500 ppm) resulted in wax formation in the pores of the catalyst and permanent catalyst deactivation.

4.2 Literature Review on Additives

4.2.1 Methanol Fuel Additive Demonstration

Southwest Research Institute (SwRI) was tasked with developing methanol fuel additive packages that minimized air quality concerns, while addressing other safety and operational concerns for methanol fuel. Their report discusses the results of a literature search for methanol fuel additives, a laboratory test program emphasizing flame luminosity, fuel lubricity, and flammability, a comparison between laboratory data and real world situations, and hydrocarbon speciation of exhaust emissions from a vehicle operating on potential additives.

Through a literature search on methanol fuel additives and laboratory tests, potential methanol additives packages were identified. Toluene and a proprietary alcohol-soluble material were identified for luminosity improvement. Fatty acids and organic amine salts were effective in improving lubricity. Butane and butene lowered the flammability limit. Bitrex was identified as the most promising taste deterrent, and an alcohol-soluble dye was identified as the best colorant option.

4.2.2 Flame Luminosity of Methanol

Charles M. Kinoshita of the Hawaii Natural Energy Institute and Michael Lee of the Department of Mechanical Engineering, University of Hawaii co-authored a paper on flame luminosity of methanol and additive fuel mixtures. In their paper, Kinoshita and Lee state that the luminosity of methanol/additive mixtures is found to be a function of the mixture's carbon/hydrogen ratio. Flame luminosity increases with increasing mixture C/H ratio to a maximum. Additives that form positive azeotropes with methanol and that have high C/H ratio are found to be the best candidates for enhancing the luminosity of methanol flames. Additives that were used in their study were hexane, heptane, octane, gasoline, cyclohexane, cyclohexene, toluene, and benzene. Kinoshita and Lee noted that only a limited number of methanol/additive mixtures were examined in their study.

4.2.3 Survey of Safety Related Additives for Methanol Fuel

A report issued by Southwest Research Institute (SwRI) for the Environmental Protection Agency examines the feasibility of using particular additives in M-100 motor vehicle fuel. The additives were evaluated for their effectiveness, cost, ease of production, associated health problems, and estimated effects on vehicle performance. SwRI's results indicate that:

For flame luminosity enhancement, the most practical and effective additives appear to be highly complex mixtures of hydrocarbons.

For taste deterrence, two additives appear viable: gasoline or other complex mixtures of hydrocarbons and Bitrex.

Dyes appear to be the best way to discourage the use of methanol as a degreasing or cleaning agent. Commercial methanol products have typically been blue in color, and a continuation of this practice would be logical for fuel methanol.

The use of an emetic to induce vomiting if methanol is consumed appears impractical as the necessary concentration of an emetic in methanol required to induce vomiting was found to be about eight volume percent, which is too high.

Mercaptans have been shown to be effective odorants for methanol at concentrations as low as 200 mg per gallon methanol.

4.2.4 Methanol Fuel Safety: A Comparative Study of M-100, M-85, Gasoline, and Diesel Fuel as Motor Vehicle Fuels

This report issued by the EPA discusses safety-related aspects for methanol fuel use in motor vehicles. The effects of ingestion are evaluated and a variety of preventative measures including the use of methanol fuel additives are discussed. The report also provides a list of odorants, taste deterrents, and colorants.

The following paragraph was excerpted directly from the report.

A number of different additives have been proposed for M-100 to give it taste, odor, and color. In Sweden one ppm of a violet-blue colorant is added to give M-100 an identifiable appearance, and 1 ppm of t-butyl mercaptan is added to give it an identifiable odor. A blue dye is also added to methanol in windshield washer fluid to give it an identifiable color. The most common additives to methanol for fuel use in the United States have been the addition of various hydrocarbons as in M-85. Much smaller amounts than 15% gasoline can accomplish this task, however, with some estimates stating that as little as 1 to 2% hydrocarbon can deter against its ingestion. Concentrations of these levels may be reached simply by fuel methanol picking up hydrocarbon contaminants in storage and distribution. Other potential odorants, taste deterrents, and colors or dyes identified by EPA staff are shown in Tables 12, 13, and 14, respectively.

4.3 Summary of Findings

All literature indicates that complex hydrocarbons, Bitrex, mercaptans, and blue dyes are the most likely methanol fuel additives for flame luminosity, taste deterrence, odorant, and colorant candidates, respectively. As determined with hydrocarbon contaminants, complex hydrocarbons that provide flame luminosity will have undesirable effects in the methanol reformer. In addition, additives that have high melting and boiling properties may stick in the vaporizer, just before the reformer, causing various problems. It is possible, though, that they could be removed before entering the reformer system. No other information detailing the effects these additives have on methanol to hydrogen conversion has been found.

5 Chemical Analysis

The objective of Task 2 was to evaluate methanol samples from a number of supply sites, spanning all grades likely to be applied to automotive service through chemical analysis. The chemical analyses serve as a baseline for the evaluation of the supply infrastructure (Task 3).

XCELLSiS consulted with Methanex to determine which chemical tests would provide the most useful information in analyzing the available grades of methanol and methanol infrastructure samples. The selected tests were also based on the literature review of methanol contaminants and additives.

XCELLSiS selected West Coast Analytical Service, Inc. of Santa Fe Springs, California to conduct the tests. All samples tested at West Coast Analytical Service, Inc. were analyzed for: Water by Karl Fisher Titration, Total Solids by EPA 160.3, Conductivity by EPA 120.1, Chloride by Ion Chromatography (IC), Metals Screen by Inductively Coupled Plasma – Mass Spectrometry (ICPMS), Volatile Organics by Gas Chromatography – Mass Spectrometry (GCMS), Fuel Hydrocarbons by Modified EPA 8015.

In addition, XCELLSiS Nabern had eleven of the samples analyzed at BASF for high boiling hydrocarbons. High boiling hydrocarbons are not normally detected by Gas Chromatography because they stick to the column of the GC, and thus, they do not reach the detector.

5.1 Description of Tests

A brief description of each test is provided here:

5.1.1 Water by Karl Fisher Titration

During the methanol production process, methanol is distilled in a series of distillation columns to create a product that is greater than 99.9% by weight pure methanol. The remainder is essentially water (less than 500 ppm) with residual impurities such as ethanol, acetone, and acetic acid, which are found in the product methanol in low ppm levels. The IMPCA specification (considered as the industry standard for commercial methanol specifications) sets the maximum concentration of water at 0.1%. Since the methanol has a water content of less than 500 ppm when it leaves the plant gate, it is anticipated that the product may pick up residual water during the distribution of the product to the end customer. Examples of residual water sources may include, but are not limited to, the following: residual water from tank steam cleaning processes, exposure to atmospheric water through tank breathing, and sea water ingress.

The methanol was tested for water using Karl Fischer titration. This titration relies on the reaction of water with sulfur dioxide and iodine in the presence of base. It is a well-known, well-understood reaction, and it is easily automated. However, it is not without potential problems. Many samples are hygroscopic, absorbing atmospheric moisture during handling. Also, the sample must be dissolved in a suitable solvent prior to titration, but the solvent itself must be as anhydrous as possible. Methanol or pyridine is frequently used. Some compound types, especially aldehydes and ketones, will interfere with the Karl Fischer titration, necessitating the use of different reagents.

5.1.2 Total Solids by EPA 160.3

Detection of solids indicates the presence of impurities in methanol. The method used to detect the total solids, EPA 160.3, uses total residue by gravimetric determination.

5.1.3 Conductivity by EPA 120.1

The conductivity of a liquid measures the ability of the liquid to transfer an electrical charge. For solutions of compounds (e.g. methanol), the conductivity will be dependent on the polarity of the solvent and the presence of any ionic species. Specifically, methanol is a polar solvent and metals will form ionic species in solution. Thus, conductivity can be a measure of the presence of dissolved metals. Conductivity was performed using EPA Method 120.1.

5.1.4 Chloride by Ion Chromatography (IC)

During the transport of methanol by ocean-going vessel there is the potential for seawater ingress. For example, if the ship was traveling through rough seas, then seawater could potentially enter in through the cover of a cargo hold if there was not a perfect seal on the cover. In addition, seawater vapor could enter the cargo hold of a marine vessel through natural breathing. Therefore, due to the natural content of salt in the ocean, there is a potential for salts (like NaCl) to contaminate the methanol. However, historically, chloride concentrations have been less than 0.1 ppm, measured at the bulk storage terminal, which demonstrates the low potential for this type of contamination.

Chloride is detected via ion chromatography, where chromatography is the science of separating mixtures of compounds, elements, or ions. The separation of these mixtures into components occurs as the result of the components having different partition ratios between the mobile phase (gas or liquid) and the stationary phase (column), and therefore different rates of travel through the column. The use of ion exchange resins as the stationary phase in columns is the basis of Ion Chromatography (IC) for separating ionic components. The analysis of common anions, such as chloride, can be used to measure traces of contamination.

5.1.5 Metals Screen by Inductively Coupled Plasma – Mass Spectrometry (ICPMS)

Inductively coupled plasma-mass spectrometry (ICPMS) can be used to screen samples for metals contamination. In a typical test, a sample is put into solution usually by digesting or diluting in acid. The sample solution is spiked with known concentrations of three elements (usually Sc, In, and Tb). Standards of common elements, blanks, and the sample solution are then introduced to the ICPMS. The element concentrations in the samples are then determined one of two ways: (1) for the elements that are in the standards, the elements are determined quantitatively (within 15% for most) or (2) for the elements not in the standards, the elements are estimated (within 50%) by comparison with internal standard responses. Unlike many other spectroscopic techniques ICPMS has a fairly uniform response, so fairly accurate estimates can be made.

5.1.6 Volatile Organics by Gas Chromatography – Mass Spectrometry (GCMS)

Mass spectrometry (MS) is an analytical chemistry technique used for molecular structure determination and detection. In general, molecular species are made to form ions, which are then analyzed for their mass/charge ratio.

The presence of volatile organics indicates contamination from a variety of sources. Gas chromatography-mass spectrometry (GCMS) is used to detect these volatile organic compounds. Components separated by the GC enter the source of a mass spectrometer where they are ionized.

5.1.7 Fuel Hydrocarbons by Modified EPA 8015

The presence of fuel hydrocarbons in methanol is indicative of contamination within the distribution chain caused by using non-dedicated equipment. Modified EPA Method 8015 detects fuel hydrocarbons by using Gas Chromatography – Flame Ionization Detection.

5.2 Sampling Methods

There were several sampling methods used to collect methanol at points throughout the distribution chain. It is important to understand what the differences in the sampling methods are, and the effect these differences may have on the results from the chemical analyses of the samples.

Several independent surveyors selected by Methanex took the majority of samples. The sampling procedure follows the American Petroleum Institute's Manual of Petroleum Measurement Standards, Chapter 8 – Sampling. In Section 1 - Standard Practice for Manual Sampling of Petroleum and Petroleum Products – definition 3.26 describes a running sample as a sample obtained by lowering a beaker or bottle to the level of the bottom of the outlet connection or swing line and returning it to the top of the oil at a uniform rate such that the beaker or bottle is between 70 percent and 85 percent full when withdrawn from the oil. The following methanol samples were taken using this method:

- Manufacturing Facility, *Sample #1*
- Ocean Tanker, Gulf Coast Vessel
- Bulk Storage, Terminal A, *Sample #1*
- Bulk Storage, Terminal B, *Sample #1*
- Bulk Storage, Terminal C, *Sample #1*
- Bulk Storage, Terminal C, *Sample #2*
- Tanker Truck, Dedicated Truck A
- Tanker Truck, Dedicated Truck B, *Sample #1*;
- Tanker Truck, Non-Dedicated Truck
- End-User, Non-Dedicated Storage Tank A
- End-User, Non-Dedicated Storage Tank B

The rest of the samples were taken at the XCELLSiS facility or they were shipped as product in one-gallon containers from the distributor directly to the analytical lab. Those which were sampled at XCELLSiS used the following procedure: first, a new, 500 ml HDPE bottle was filled one-third full using a dedicated pump with the methanol to be analyzed. The bottle was covered and rinsed, and the methanol was discarded. The bottle was then completely refilled with the methanol to be analyzed.

5.3 Supply Distribution Sample Points

The various samples represent the entire distribution chain, from the manufacturer at the beginning of the chain to the end-user. The complete results of the analyses on the above samples are found in Appendix A, and a discussion of these results is found in the following section.

6 Supply Chain Analysis

Task 3 of the contract analyzed the current methanol distribution infrastructure in order to determine if the contaminants found in the chemical analyses are avoidable through more strict controls or if they are indicative of a more pervasive problem.

The results of the chemical analyses were shared with Methanex, and Methanex provided their insight on various causes of the contamination found in the samples. Their interpretations have been incorporated into this section.

6.1 Supply Chain Background

Methanol can be produced by several processes from a variety of different feedstock. Approximately 93 percent of all methanol is produced from natural gas in a two-stage commercial process. The remainder is essentially produced from coal and oil residues. In addition, the production of methanol from renewable resources has been demonstrated. The principal use of methanol has been as a commodity chemical and little is currently used as motor fuel.

Methanex is the leader in methanol manufacture and marketing. Its methanol is distributed to various chemical industries for the production of acetic acid, formaldehyde, MTBE, windshield washer fluid, and various other solvents. Because Methanex' manufacture and distribution of methanol is typical of the methanol industry, its distribution infrastructure serves as the focus of the supply chain analysis.

Depending on its actual distribution route, methanol can be transported in very large quantities, typically 45,000 metric tons, via ocean tanker, or in smaller cargoes (55 tons per railcar) by rail or road. There is typically a bulk storage terminal at major ports from which methanol can be delivered to customers.

A diagram depicting the current distribution infrastructure is presented here.

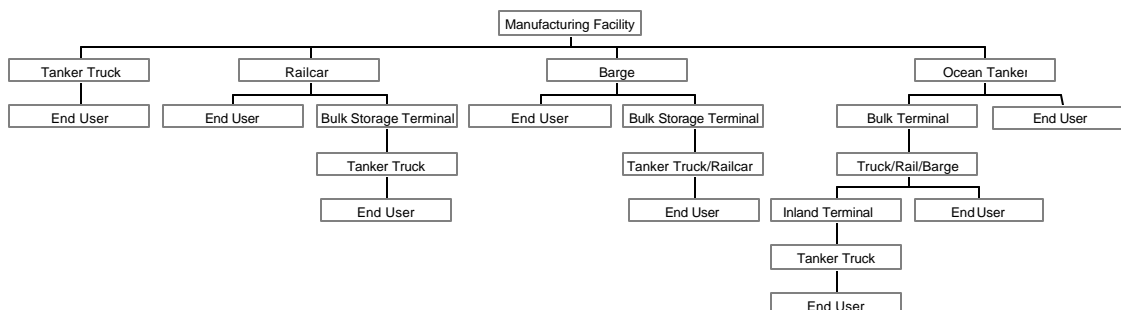


Figure 3. Methanol Distribution Infrastructure

6.2 Quality Control Procedures

Methanex employs quality control procedures to ensure that their methanol meets their customer specification and is not contaminated. A typical testing pattern would entail the following for product requiring transportation by an ocean going vessel:

1. Vessel is tested for cleanliness

When a vessel first arrives it is tested for cleanliness. Cleanliness is determined with the completion of a wall wash test. This test requires that an independent surveyor first visually check the tank for cleanliness. If the tank is deemed cleaned by visual examination then the surveyor will physically enter the tank, spray methanol on the wall of the tank and collect a sample after it has run down the wall. The wall wash sample is then tested for impurities.

2. Product Test

Upon approval of the wall wash test, the product in the storage tank at the methanol production site is tested prior to the loading of the first foots.

3. First Foot Samples

If the product in the storage tank meets the specification, the first foots are then loaded onto the vessel. The name, "first foots", is a term used throughout industry to signify that there is approximately one foot of product in the storage compartment.

When the first foots have been loaded, the loading process is stopped and the first foots are sampled. The first foots are tested prior to the vessel being fully loaded.

4. Final Samples

Once loaded, each compartment is sampled and tested.

5. Discharge Samples

Upon arrival at the discharge terminal, each vessel compartment is sampled and tested. After discharge into storage tanks, the product is tested again.

To ensure product quality when the product is sent by rail or truck, Methanex verifies that each railcar and truck is clean and acceptable for loading. After the product is loaded into the cars or truck, it is sampled, and the samples are retained for follow-up testing, if required.

6.3 Mechanisms for Methanol Contamination – Supply Chain Analysis

Each point in the infrastructure is discussed here in terms of the most likely mechanisms by which the methanol would become contaminated.

6.3.1 Manufacturing Facility

The manufacturing facility is the beginning of the supply chain. At the manufacturing facility, by-products in the production process have the potential to cause contamination in the methanol product. Methanol at the manufacturing facility is stored in carbon steel tanks. It also has many of the solubilizing and corroding characteristics of water. Corrosion of carbon steel at significant rates could potentially lead to carbon steel byproducts contaminating the methanol.

Two samples of methanol from one of Methanex' manufacturing facilities were analyzed. Presented here is an evaluation of the results of the analyses:

Sample #1 – This methanol sample was taken directly from an onsite storage tank, by a Methanex employee. The sample was approximately one liter in volume. Water and chloride concentrations were low at 60 ppm and 0.03 ppm, respectively. The analysis also found trace amounts (ppm levels) of ketones, namely acetone and 2-butanone, which are inherent to the methanol production process.

Sample #2 - The second sample, approximately 500 ml in volume, was taken from a stainless steel drum of methanol at XCELLSiS' facility. The dedicated drum was filled at the same manufacturing facility as Sample #1. The methanol remaining in the drum after Sample #2 was taken, was evaluated in the reformer hardware. Of the samples analyzed, Sample #2 contained a moderate amount of water at 400 ppm. Note that this amount is expected from the manufacturing facility, and is within the IMPCA specification. Chloride was low at 0.05 ppm. 2-butanone and acetone were present at 4.5 ppm and 1 ppm, respectively. High boiling hydrocarbons were present at 2.1 ppm. Methylene chloride was present at 0.7 ppm, and metals were present in trace amounts.

Both samples are the 'cleanest' of all the tested samples. Very few contaminants were found. Those that were, namely 2-butanone and acetone, are byproducts of the methanol reaction step and can be carried over in the distillation process.

6.3.2 Ocean Tanker

Although it is possible to transport methanol in non-dedicated ocean tankers, railcars, and barges, most vessels are dedicated solely to the transport of methanol. As such, seawater ingress is the most likely source of contamination during an ocean tanker shipment. Leaks in the cargo hold and tank ballasting are the most probable sources for this type of contamination. Tank ballasting is rarely practiced, however, as it is usually only performed during emergency situations such as rough seas.

In addition, if a non-dedicated tanker is used and the cargo hold is not properly cleaned or inspected prior to loading the methanol, residue from the product last contained within the cargo hold will likely contaminate the methanol.

A sample was taken from an ocean tanker on the Gulf Coast. An analysis of that sample follows here:

Gulf Coast Vessel – This sample was drawn from the ocean tanker before it was offloaded into a bulk terminal storage facility. The analyses found that the sample contained a significant amount of chloride, 27 ppm. The chloride contamination may have resulted from an ingress into the cargo hold of the ocean tanker vessel or from contamination during sampling. Chlorides are a known poison for reformer catalysts. In addition, this sample was tested for chlorides at BASF, where 8.7 ppm were found. High boiling hydrocarbons were detected, by BASF, at 48.5 ppm, and 1,2-dichloroethane (EDC) was found in a trace amount. It is likely that EDC was introduced to the sample through cross contamination. EDC (a commodity chemical and a precursor to PVC) is distributed in tanker ships throughout the world. This type of contamination is an example of cross contamination when methanol is not transported in a dedicated methanol marine vessel.

6.3.3 Rail Car

Like ocean tankers, most railcars used to transport methanol are dedicated to methanol service; therefore, the potential for contamination is considered to be low. Railcars are typically constructed from mild steel. Mild steel is a low carbon steel, and methanol has many of the solubilizing and corroding characteristics of water. Corrosion of carbon steel at significant rates could potentially lead to carbon steel byproducts contaminating the methanol. A rail car sample was taken at a non-dedicated distributor site; however, the sample was taken after it had been pumped through a non-dedicated pumping system and into a storage tank. Therefore, it is not representative of methanol quality found in a rail car. The sample is discussed later, in the context of a non-dedicated distributor tank.

6.3.4 Bulk Storage

Bulk storage in terminals provides dedicated, intermediate storage for methanol in transport to an end-user. In general, a bulk storage terminal will generally contain methanol from one manufacturer, but from different manufacturing facilities. The manufacturer must conform to the International Methanol Producers and Consumers Association (IMPCA) standards (found in Appendix C).

Three different terminals were used in the evaluation of methanol quality for this contract. A description of each one, as well as the different samples that were taken at each terminal follows here:

Terminal A – This terminal is a coastal storage facility located in California. Methanol is typically shipped from a manufacturing facility by marine vessel to this terminal. Three different samples were taken from the methanol stored here:

Sample #1 – This sample was taken directly from one of the tanks at the terminal by SGS. The sampling container used was a clear glass bottle and sampling followed the American Petroleum Institute sampling standard. This sample had high product quality. Chloride and water concentrations were lower than the majority of other samples. High boiling hydrocarbons were detected at 8.2 ppm. Trace amounts of lead (0.4 ppb), chloroform (0.2 ppm), and MTBE (0.7 ppm) were found in the sample. Lead may have been introduced to the methanol from the application and exposure to a pipe joint compound, exposure to a lead-based paint, or exposure to lead gaskets.

Sample #2 – A dedicated, stainless steel drum was filled with methanol from Terminal A, and it was shipped to XCELLSiS. At XCELLSiS, a 500 ml sample was taken using a dedicated pumping system. Water was detected at 0.040%, and chloride was present at 0.11 ppm. 2-butanone was present at 3.5 ppm, and acetone was present at 1 ppm. 2-propanol was rather high at 8 ppm. Metals were detected in trace amounts. In addition to the analyses, this sample was evaluated using the reformer hardware.

Sample #3 – A different, dedicated, stainless steel drum was also filled with methanol from Terminal A. It, too, was shipped to XCELLSiS where a sample was drawn from the drum. This sample showed different results than either Sample #1 or Sample #2. Here, water was present at 0.03%, and chloride was found to be 0.06 ppm. Diesel fuel hydrocarbons were present at a significant level, 10 ppm. Trace amounts of 2-butanone (3.6 ppm), acetone (0.6 ppm), methylene chloride (0.8 ppm), MTBE (1.1 ppm), toluene (0.2 ppm), and undecane (0.8 ppm) were found in the sample.

Terminal B – This bulk storage terminal represents the same distribution path as that for Terminal A. One sample was taken directly from this facility. Trace amounts of 2-butanone (3.3 ppm), acetone (0.8 ppm), and undecane (0.3 ppm) were found in this sample. High boiling hydrocarbons were detected at 8.9 ppm.

Terminal C – This terminal is an inland storage facility. Two 1-liter samples were taken from the same tank at this facility (*Sample #1* and *Sample #2*). These samples represent methanol that has gone through several handling processes before it was received at the terminal. Typically, the product received by this terminal originates from one of Methanex' overseas manufacturing facilities. This product is delivered from the plant site to a coastal bulk storage terminal where it is stored in one of the terminal's storage tanks. The product is then delivered to the inland terminal via barge.

Contaminant levels, which were the same for both samples, were slightly higher than those from bulk terminals located on the coast (except for the chloride detected in the marine vessel sample). Organic compounds, such as benzene (0.1 ppm, 0.2 ppm), MTBE (0.2 ppm, 0.1 ppm), butyl acrylate (1 ppm, 0.7 ppm), o-xylene (0.2 ppm, 0.2 ppm), styrene (0.1 ppm, 0.1 ppm), and undecane (0.6 ppm, 0.8 ppm) were found in these two samples (*Sample #1* and *Sample #2*, respectively). They were not found in the samples from the coastal storage terminals. In addition, high boiling hydrocarbons were detected in *Sample #1* at 8.5 ppm.

Methanex theorizes that the product was delivered in a barge, which last contained a petroleum product like gasoline due to the concentrations of benzene, MTBE, and o-xylene that were detected. In addition, these compounds are sometimes found in plasticizers, paints, and resins, which the methanol may have been in contact with in some part of the distribution system. Plasticizers are typically found in chemical transfer hoses, paints are found on process vessels and piping, and resins are found in tank linings.

6.3.5 Tanker Truck

Methanol can be transported in either a dedicated or non-dedicated truck. Dedicated tanker trucks only transport methanol making it highly unusual for a customer to receive contaminated product from such a truck. On the other hand, the non-dedicated tanker truck may handle just a certain class of chemicals, like alcohols, or it may handle a wide array of chemicals. Typically, the non-dedicated tanker truck cargo tanks are steam cleaned between products. If the tanker truck was inadequately cleaned prior to loading the potential exists that residue from the last chemical transported in the truck will contaminate the methanol.

Contaminants found in trucks transporting methanol may have been introduced by the same mechanisms as those discussed in the bulk storage terminal section. Samples from two dedicated trucks and a non-dedicated truck were analyzed.

Dedicated Truck A – This sample represents methanol from a dedicated methanol tanker truck. The tanker truck was loaded at Bulk Storage Terminal A. The methanol loaded onto the truck was originally shipped from one of Methanex' manufacturing facilities to the bulk terminal by marine vessel. The methanol was offloaded into one of the storage tanks, and then it was later loaded into this dedicated truck. This sample was taken directly from Truck A by SGS using American Petroleum Institute standards.

Chloride levels were measured at 0.40 ppm, and trace amounts of lead (4 ppb) and EDC (0.1 ppm) were also found in the sample. High boiling hydrocarbons were detected at 10.7 ppm. The concentration of zinc (1.98 ppm) was relatively high compared to the other samples. Since zinc was not detected in the Bulk Storage Terminal A samples, and the dedicated truck pulled its methanol from this terminal, the presence of zinc in the truck sample suggests that the storage vessel on the truck may be made of a galvanized, zinc coated, or alloyed metal. Another possibility is that the zinc contamination resulted from plasticizers in hose leaching into the methanol. All other metals screened for were either non-detectable or present in very low concentrations.

Dedicated Tanker Truck B - Here, methanol was loaded into a dedicated tanker truck from Bulk Storage Terminal A. This methanol followed the same distribution path as that of the other dedicated truck sample. Two samples were from this truck were analyzed:

Sample #1 This sample, 500 ml in volume, was taken directly from Truck B by SGS personnel. In this truck sample, water and chloride were low at 0.039% and 0.4 ppm. 2-butanone and 2-propanol were significant at 5 ppm and 12 ppm, respectively. In addition to the sample, a dedicated, 55-gallon, stainless steel drum of methanol was taken from the truck and shipped to XCELLSiS for reformer evaluation.

Sample #2 This 500 ml sample was taken from the above drum of methanol at the time that it arrived at the XCELLSiS facility. Unless the sample was contaminated between the time the drum was filled and the time the 500 ml sample was taken from it, the contaminants should be present in the same amounts. However, though the same contaminants were found that were in Sample #1, they were in higher concentrations. Water and chloride were found to be 0.077% and 0.09 ppm, respectively. 2-butanone and 2-propanol were 5.4 ppm and 28.0 ppm, respectively.

Non-Dedicated Truck Methanol was taken from a non-dedicated tanker truck owned by a methanol distributor. Like the dedicated tanker trucks, this product was first shipped from a manufacturing facility to a bulk storage terminal by marine vessel. The product was offloaded into one of the storage tanks and later loaded into the non-dedicated truck. This sample was taken by SGS.

Several contaminants were found in this sample. First, total solids detected in this sample were at a level of 2 ppm. The amount of chloride was high at 1.67 ppm. Gasoline fuel hydrocarbons, the largest contaminant present, were measured to be 320 ppm. C9-C10 Alkylbenzenes were also high at 47 ppm. High boiling hydrocarbons were detected at 12 ppm. Zinc was present at 1.96 ppm. Compared to the dedicated truck samples, a large number of volatile organics were detected by GCMS. They are:

- 1,2,4-trimethylbenzene - 17 ppm
- 1,2-dichloroethane - 0.2 ppm
- 1,3,5-trimethylbenzene - 5.3 ppm
- 2-butanone - 5.4 ppm
- 4-isopropyltoluene - 0.1 ppm
- acetone - 0.9 ppm
- chloroform - 1.6 ppm
- m/p-xylene - 0.3 ppm

- isopropylbenzene - 0.5 ppm
- MTBE - 4.9 ppm
- n-butylbenzene - 0.3 ppm
- n-propylbenzene - 2.6 ppm
- other alkylbenzenes - 21 ppm
- o-xylene - 0.7 ppm
- sec-butylbenzene - 0.2 ppm
- toluene - 0.8 ppm

It is likely that these contaminants were introduced to the sample through cross contamination or by the mechanisms discussed above.

6.3.6 End-User

An end-user may choose to use equipment dedicated solely to methanol, combinations of dedicated and non-dedicated equipment, or equipment that is shared among the various chemicals he distributes. The end-users examined in this analysis were of the latter two groups. Each used non-dedicated equipment at some point in their distribution. In general, the product from distributors such as these is typically used in 'low-quality' type applications (i.e., windshield washer fluid, fondue fuel, solvents) where the purity of the product is not critical to the application.

Non-dedicated Storage Tank A – This sample represents methanol taken from a non-dedicated distributor. This product was first shipped from a Methanex manufacturing facility to a bulk storage terminal by marine vessel, where the product was offloaded into a storage tank and later loaded into the distributor's tanker truck (non-dedicated) from where it was pumped into Storage Tank A at the distributor's storage site.

A number of contaminants were present in this methanol sample. Chloride levels were measured at 1.67 ppm, and the methanol was also contaminated with constituents of gasoline-like alkanes and alkyl-substituted benzenes. The fuel hydrocarbons test detected gasoline constituents at 320 ppm. High boiling hydrocarbons were detected at 22.9 ppm. Trace amounts of EDC (0.2 ppm), chloroform (1.6 ppm), m/p-xylene (0.1 ppm) and MTBE (4.6 ppm) were also found in the sample. The concentration of zinc was measured at 1.6 ppm, and all other metals screened for in the analysis were either non-detectable or present in low concentrations. It is likely that these contaminants were introduced to the sample through cross contamination. In addition, it is suspected that the zinc was introduced through the use of galvanized or zinc coated materials of construction or from plasticizers in hose that leach into the methanol.

Non-dedicated Storage Tank B – The distributor from whom this sample was taken handles a wide array of chemicals from xylenes and toluene to isopropanol, ethanol and methanol to acids such as hydrochloric acid and sulfuric acid. Most of these chemicals are received by the distributor in railcars and offloaded into a dedicated chemical tank. The products are then typically packaged in barrels or chemical totes and distributed to the customer.

The methanol for this sample was shipped by dedicated railcars from a Methanex manufacturing facility to the distributor. The methanol was offloaded from the railcar and loaded into a dedicated methanol storage tank. The offloading system, comprised of piping, pump, and transfer hose is only dedicated to a certain class of chemicals. For example, alcohols

(methanol, ethanol, isopropanol, etc.) are grouped together in one type of chemical class; ketones would be grouped in another class. Because of this type of offloading system the potential exists for methanol to be exposed to alcohol residues remaining in the transfer lines and pump housing.

For this particular sample both ethanol and isopropanol were found in the sample. Ethanol was found in the sample at a concentration of 180 ppm, while isopropanol was found in the sample at a concentration of 42 ppm. High boiling hydrocarbons were detected at 11.2 ppm.

Once the methanol has been loaded into a storage tank it is ready to be packaged. The packaging system at this particular distributor employs dedicated plumbing for all products from the storage tanks to just before the suction side of the barreling pump. A chemical hose is used to connect the suction side of the pump to the dedicated chemical pipe.

Between products the pump is reversed and product flows back to the appropriate tank. The chemical hose is then connected to a new product line and the system is flushed with that product. To flush the system of residue from the previous product, approximately one gallon of new product is run through the system and then the rinsing product is discarded into a waste tank. The potential for contamination does exist at this point as 1-gallon of product flushed through the system may not be sufficient to clear any residue from the previous product from the transfer lines or pump housing.

The analysis of this sample revealed trace amounts of chemicals not normally found in methanol. Methylene chloride, ethyl benzene, o/m/p-xylene, toluene and other alkyl-substituted benzenes were found in ppm levels in the methanol sample. It has been confirmed that some of these chemicals (xylene and toluene) are packaged at this site and it is suspected that others (like methylene chloride, ethyl benzene, etc.) are constituents of other products also distributed here.

The chloride level in this sample was measured at 0.522 ppm, which is slightly higher than the IMPCA specification for chloride of 0.5 ppm. It is suspected that chloride was introduced to the methanol sample through hydrochloric acid (HCl) contamination as HCl is packaged and distributed through the same common packaging system.

Electronic Grade – Electronic grade methanol was purchased through Gallade Chemical. Gallade purchases its electronic grade methanol from J.T. Baker. The electronic grade is guaranteed to meet all specifications that J.T. Baker sets. These specifications primarily limit the acceptable amount of metals in the methanol and do not set limits on the amount of hydrocarbons or other contaminants that may be present. J.T. Baker confirmed that their methanol is shipped to them in dedicated tank wagons, and it is stored in a dedicated tank in Phillipsburg, New Jersey. However, the pumping system that transfers the methanol from the transport container into the storage container is used for other chemicals in addition to methanol. These chemicals include 1-methyl-2-pyrrolidinone (NMP), isopropanol, acetone, and hexane.

Three electronic grade methanol samples were analyzed by West Coast Analytical Services.

Sample #1 was shipped in a pre-packaged, one-gallon plastic container from Gallade Chemical directly to West Coast Analytical Services. Results from chemical analyses indicate that acetone (2.5 ppm), isopropanol (31 ppm), methylene chloride (1 ppm), and 2-butanone (9.5

ppm) were present in significant quantities. High boiling hydrocarbons were detected at 10.4 ppm.

Sample #2 In addition, a subsequent analysis was conducted on another sample of electronic grade methanol from J.T. Baker. XCELLSiS has used the J.T. Baker electronic grade methanol for previous testing. As a result, a large, dedicated carbon-steel supply tank and delivery system were used to supply electronic grade methanol to the evaluation hardware where the methanol was evaluated. Sample #2 was taken just before the methanol supply entered the evaluation hardware. The analysis from this sample of J.T. Baker electronic grade methanol detected 15 ppm toluene, in addition to 5 ppm acetone, 5 ppm 1-methyl-2-pyrrolidinone (NMP), and 1 ppm methylene chloride. These results were duplicated in a second test (Electronic Grade, Sample #3).

Sample #3 Another sample was taken of the electronic grade methanol at the reformer hardware inlet in order to confirm the results of the analyses of Sample #2.

Commercial Grade – The commercial grade purchased from Gallade is also distributed through a non-dedicated supply system. From the dedicated bulk storage terminal A, the methanol is transported by truck to a holding tank in Santa Fe Springs, California. The truck is not dedicated to methanol; it is used to ship other alcohols. The tank at Santa Fe Springs is dedicated to methanol, but the pumping system is used for other alcohols. Two samples of this commercial grade were analyzed.

Sample #1 was shipped from Gallade directly to West Coast Analytical Services in a one-gallon low-grade steel container. The contaminants that are present in this sample, toluene (1.6 ppm), methylene chloride (0.7 ppm), xylene (0.2 ppm), acetone (47 ppm) are all chemicals that Gallade distributes. High boiling hydrocarbons were detected at 13 ppm.

Sample #2 - An epoxy phenolic-lined, 5-gallon container of this methanol was shipped to XCELLSiS' facility for reformer evaluation. A sample of this methanol was drawn at the XCELLSiS facility and then shipped to West Coast Analytical Services. Contaminants present in this sample are: solids - 32 ppm, water - 0.030%, chloride - 0.06 ppm, gasoline fuel hydrocarbons - 10000 ppm, 2-butanone - 20 ppm, acetone - 100 ppm, ethylbenzene - 90 ppm, hexane - 200 ppm, m/p-xylene - 330 ppm, styrene - 20 ppm, and toluene - 2900 ppm.

Dedicated 5Gallon Container – Here, methanol was shipped in a 5-gallon container from a manufacturing facility directly to the end-user's site. The container was a carbon steel drum coated with a petroleum-based phenolic epoxy resin, which is applied during the manufacture of the drum. Note that similar chemicals may also be applied to stainless steel drums during their manufacture, but these drums may be placed through a pacification process (typically a nitric acid bath followed by a water rinsing) if requested by the customer. Pacified stainless steel drums are typically used when product purity is essential. Regular steel drums are unable to go through the same pacification process, as the nitric acid will instantly corrode the steel.

The methanol sat in the 5-gallon container for several months before it was used. The methanol had an unusual yellow tint upon analysis. Contaminants present in this sample are: solids - 40.1 ppm, water - 0.13%, chloride - 0.12 ppm, 2-butanone - 3.2 ppm, acetone - 1 ppm, decane - 0.6 ppm, toluene - 2 ppm, undecane - 1 ppm. All metals were found in trace quantities. Methanex noted that their investigations point to the fact that it is difficult to ensure on

spec product (per their specification) when methanol is delivered in drums. A potential exists even for new drums to have contaminants remaining from the drum manufacturing process. Cutting oils and chemicals from the steel manufacturing process may be present when the drum is being manufactured.

6.4 Conformance of Samples to Target Specifications

A variety of specifications exist for methanol, which include, but are not limited to, the following: ASTM (American Society for Testing and Materials), IMPCA (International Methanol Producers and Consumers Association), sales specifications, and specifications for M-100 fuel methanol. These specifications can be found in Appendix C. The California Vehicle Emission Standards for M-100 fuel methanol are more lenient than any of the other specifications mentioned above. It provides that methanol shall be at least 96 vol. %, other alcohols 2 mass %, and hydrocarbons 2 mass %. The ASTM and IMPCA specifications are stricter, with the IMPCA specification slightly more so than the ASTM specification. These both require the methanol to be 99.85% minimum. Finally, certain sales specifications, such as the one used by Methanex, are even stricter than either the ASTM or IMPCA specifications.

All samples that originate from Methanex are intended to meet their sales specifications at the time they are sold to a distributor or end-user. The commercial and electronic grade samples follow the specifications set by the individual distributor. These specifications are also provided in Appendix C. The electronic grade specification, provided by J.T. Baker, primarily limits the amount of metals in the methanol. Gallade Chemical provides a Certificate of Analysis where the methanol is analyzed by a third party. In this case, it is SGS. Both Gallade and J.T. Baker's specifications are very similar to the IMPCA spec.

6.5 Conductivity

The conductivity of a liquid measures the ability of a liquid to transfer an electrical charge. For solutions of compounds (methanol), the conductivity will be dependent on the polarity of the solvent and the presence of any ionic species. Specifically, methanol is a polar solvent and metals will form ionic species in solution. Thus, conductivity can be a measure of the presence of dissolved metals.

The conductivity was measured by EPA test method 120.1 for each sample that was tested in the small-scale reformer evaluation hardware. In addition, a metals screen by inductively coupled plasma – mass spectrometry was conducted on all of the samples. All of these results are found in Appendix A with the rest of the chemical analyses.

As reported in the Task 2 section, the metals screen by ICPMS revealed only trace amounts of metals in each sample. The level of zinc was the highest, present in the 1.6 to 2.0 ppm range for Dedicated Tanker Truck A, Sample #1 – 1.98 ppm; Non-dedicated Storage Tank A – 1.6 ppm; and Non-dedicated Tanker Truck – 1.96 ppm. All other metals present were less than 1 ppm. Second to the zinc was sodium, which was present in almost every sample, except for Commercial Grade, Sample #1. The highest level of sodium appeared in the Non-dedicated Tank B, Sample #1 at 0.76 ppm.

Results from conductivity by EPA 120.1 (detection limit 0.1 μ mhos/cm) were:

Dedicated Tanker Truck B, Sample #2	3.0 μ mhos/cm
Commercial Grade, Sample #2	4.1 μ mhos/cm
Non-Dedicated Storage Tank A, Sample #1... ..	12.1 μ mhos/cm
Dedicated Bulk Storage Terminal A, Sample #3 ...	3.87 μ mhos/cm
Manufacturing Facility, Sample #2	2.16 μ mhos/cm

The Study of M-85 Fuel Quality Issues report for the California Energy Commission found that conductivity changes in M-85 fuel samples were resulting from something in the fuel dispenser as opposed to the fuel in the storage tank or the delivery truck. Also, since it occurred in the first 1,000 ml, most likely the conductivity change resulted from something leaching out of the dispenser hose into the methanol between fuelling. In addition, the study found that the highest concentrations of metals in the fuel were zinc and calcium. Calcium was present in high concentrations both in the before and after purge samples indicating that it is in the bulk fuel, most likely the result of sand and other contaminants. Zinc, however, is significantly higher in the first liter than the after purge liter. This is a strong indication that it is leaching out of the dispenser hose into the methanol when fuel sits in the dispenser hose between uses. Zinc oxide is contained in the dispenser hose filler material. Thus, it is probable that some hose leaching may have occurred in the methanol samples.

6.6 Supply Chain Conclusions and Recommendations

Many of the contaminants detected in the distribution infrastructure samples can be categorized by their source. Contaminants from the production process include acetic acid, acetone, 2-butanone, and water. Petrochemical contaminants from cross-contamination (contact with residue of another chemical) include various hydrocarbons. Leaks in water vessels, which transport methanol, introduce water and chloride. In addition, the plumbing used to transport the methanol provides another potential mode for methanol contamination. Heavy metals can be introduced to the methanol from plumbing systems that are constructed of materials incompatible with methanol. For example, galvanized plumbing can be considered a potential source of nickel and zinc contamination. Furthermore, pipe joint compounds, which typically contain lead, provide another potential source of contamination.

Most of the contaminants detected in the chemical analyses and discussed above are generally avoidable through more strict controls. The list presented here provides a few general recommendations that will help to reduce contamination:

- **Materials of Construction:** A list of methanol compatible materials of construction should be well defined. During the construction of new facilities or upgrades to older facilities these materials should be used to help maintain methanol quality.
- **Dedicated Systems:** Dedicated methanol systems or appropriate quality control measures (including vessel cleaning as needed) are essential to ensure methanol's high purity is maintained throughout the methanol distribution infrastructure.
- **Education and Awareness:** People involved in the handling and distribution of methanol for fuel cell use should be adequately trained to understand the various mechanisms of methanol contamination, methods and practices to prevent contamination, and the chemical compatibilities of the methanol reformer used in fuel cell vehicles.

7 Additive Requirement Analysis

Task 4 of the contract deals with current requirements for methanol fuelled vehicles and provides an analysis and probable array of additives for use in methanol reforming for PEM fuel cell modules.

7.1 Background on Additive Regulations and Requirements

Methanol fuel can go a long way in reducing the risks associated with today's fuels. Only a fraction of the number of fires that occur with gasoline's use today would likely occur if methanol were used instead, due to the low volatility and high flammability limits of methanol. [13] The frequency and severity of personal injury and property damage from such fires would also tend to be lower due to the low heat release rate when methanol burns. In addition, available information suggests that a large share of the cancer incidences estimated to occur as a result of emissions from today's motor fuels would also not occur with methanol fuels. [13]

Despite these safety advantages, there are also safety concerns and uncertainties unique to methanol, which need to be addressed if methanol is used as a fuel. One such concern is the lack of a luminous flame when methanol burns in certain situations. The added hazard, which an invisible flame represents, and the effectiveness of additives to enhance the luminosity of methanol fires need to be studied further in order to properly quantify the hazards of methanol fires.

The second area where concern may arise is accidental ingestion of methanol. Methanol is tasteless, odorless, and colorless, and toxic if small amounts are ingested. These properties have led to projections of large increases in injuries and fatalities resulting from accidental ingestion if methanol replaces gasoline, unless certain precautions are taken. Precautions likely to be part of any methanol fuel program include adding compounds to methanol to provide a taste, odor, and/or luminous flame; and requiring the use of flame arresters on vehicle fuel tanks, which prevent fuel tank exposure to external ignition sources, such as cigarettes.

7.2 Current Regulations and Requirements

The California Code of Regulations currently requires methanol to have both a bitterant and an odorant. The methanol specification can be found in the California Code of Regulations in Title 13, Section 2292.1, *Fuels Specifications for M-100 Fuel Methanol* (Appendix C of this report).

Relative to the bitterant requirement, at ambient conditions, the M-100 fuel methanol must have a distinct and noxious taste for purposes of preventing purposeful or inadvertent human consumption. In addition, the odorant requirement maintains that upon vaporization at ambient conditions, the M-100 fuel methanol must have a distinctive odor potent enough for its presence to be detected down to a concentration in air of not over one-fifth of the lower limit of flammability.

Although methanol burns with a colorless flame creating a potentially hazardous scenario, the code of regulations does not currently require M-100 fuel methanol to contain an additive which

would provide a luminous flame if the methanol were to ignite, but the regulation does require an on-board flame arrester.

7.3 Array of Required Additives

A probable array of additives suitable for use in a methanol fueled PEM fuel cell vehicle was reviewed. Of current concern are the effects that these additives will have on the methanol reformer's copper zinc oxide catalyst. A discussion on potentially suitable additives is organized below according to the type of fuel safety enhancement. These additives would ideally have the following properties:

- will not damage the reformer catalyst
- will match the thermal and physical properties of methanol
- will add to the energy content
- will impart a disagreeable taste or smell
- will not be capable of being easily eliminated
- will not add to emissions levels
- will be readily available
- will not add appreciably to the cost of the fuel

7.3.1 Additives for Taste

Methanol does not have a strong or distinctive taste to identify its presence. The addition of a bitter or foul tasting substance may deter accidental poisoning. The usual fatal dose by direct ingestion of methanol is between 50 and 100 ml, although 25 to 50 ml has often been fatal if not treated promptly. [13]

Although little information exists on the addition of materials to methanol to make it undrinkable, denaturants have been added to commercial ethanol to render it unfit for human consumption. By definition, a denaturant is a substance that makes an alcohol unfit for drinking without impairing usefulness for other purposes. A table of all the potential bitterants (and odorants) is found in Appendix B.

Many if not all of the denaturants are unsuitable for use in methanol reformers for various reasons. The production of brucine, quassin, and quinine is dependent on environmental factors, and current supplies often do not meet the demand. Brucine and strychnine are highly toxic, and their use is not recommended for this reason. [12] In addition, additives, such as Super Vilex (denatonium saccharide), are not suitable because they contain compounds that poison the copper zinc oxide catalyst. In this case, Super Vilex contains sulfur.

Currently, Bitrex (denatonium benzoate) is the most economical of foul-tasting additives, due to its relatively low bitterness threshold and corresponding low cost in use. Bitrex is currently used in paints, detergents, and many other household materials, and is expected to be in sufficient quantities to be used in a fuel application. [12]

7.3.2 Additives for Odor

Methanol does not have a strong or distinctive odor to identify its presence, and when pure, has such low odor intensity that one could be exposed to hazardous levels without realizing it. The addition of odorants would help identify the presence of methanol.

The current OSHA PEL for methanol is 200 ppm (260 mg/m³) TWA. The Immediately Dangerous to Life or Health value for methanol is set at 25,000 ppm, and the lower explosive limit is approximately 67,000 ppm. The values for the odor threshold have been reported to range from 100 to 2000 ppm. Varying levels of impurities in methanol may account for this discrepancy, since compounds of low odor are greatly influenced by the presence of odorous impurities. Odorant requirements include the need of the additive to co-evaporate with methanol and to be detectable at a much lower concentration than methanol vapor alone.

The most effective odorants tested in a study by Keller, Nakaguchi, and Ware were determined to be n-butyl mercaptan and ethyl acrylate. However, n-butyl mercaptan contains sulfur. Other malodorous substances include toluene, xylenes, gasoline, acrolein, crotonaldehyde, and t-butyl mercaptan. The difficulty with these is that they poison the reformer catalyst. [12]

7.3.3 Additives for Flame Luminosity

When the fuel specifications were originally adopted for M-100 fuel methanol in 1992, a requirement was included that it produce a luminous flame throughout the entire burn duration. The reason for this luminosity requirement was that M-100 burns without a readily visible flame under maximum daylight conditions. The deadline for compliance with this requirement was delayed to January 1, 1995, because an acceptable luminosity additive had not been identified at the time of adoption of the fuel specifications. As the January 1995 deadline approached, however, it became clear that a suitable additive could not be identified which satisfied the criteria set by the State of California Air Resources Board; namely, a reasonable cost additive that would enhance luminosity without increasing emissions. Because of the rapidly approaching January 1995 deadline, the Board was approached in December 1994 with an interim proposal to allow M-100 vehicles to be equipped with a fire suppression system instead of requiring only the addition of a luminosity-enhancing agent to the fuel. This proposal allowed several hundred M-100 vehicles currently in operation in California to continue in service until an acceptable alternative could be identified since these vehicles were already equipped with fire suppression systems.

When the luminosity requirement was first proposed, there was concern that unsuspecting accident victims and firefighters would not be able to detect the invisible flame of an M-100 fire and could potentially be seriously injured. The ensuing negative publicity could potentially end the use of M-100 fuel as a motor vehicle fuel in California. In light of the study conducted by the U.S. EPA [13], however, it is apparent that the risk for fire is low and the potential for the above-mentioned scenario very small. In addition, there is other evidence, which further mitigates the risks associated with the use of M-100. First, the majority of the M-100 vehicles currently in operation are transit buses, which are already equipped with fire suppression equipment. Second, the remaining M-100 vehicles are medium-duty fleet vehicles, which are fueled at a central location by trained personnel. In those instances, the risk would be very low that an untrained person would come in contact with an M-100 fuel spill or fire. Therefore, a luminous additive is not required at this time. However, a large market of methanol fueled passenger vehicles would require stricter safety regulations, most likely including the addition of a luminous additive.

In considering a viable additive for flame luminosity in methanol fueled vehicles, the article by Kinoshita entitled *Flame Luminosity of Methanol/Additive Fuel Mixtures* [11] reports two key points. First, luminosity of a mixture is a function of the mixture's carbon to hydrogen ratio (C:H). The luminosity increases to a maximum as the C:H increases and then slightly

decreases. Most hydrocarbon fuels form hot carbon particles (soot) during combustion, which emit gray-body radiation in the visible spectrum. Because the O-H and C-H bonds are stronger in methanol, the C-C radicals (soot) typically formed during combustion give way to the stronger O-H and C-H radicals, which radiate primarily in the ultraviolet and infrared regions.

Second, additives that form positive azeotropes with methanol and have a high C:H are best at enhancing luminosity throughout the duration of the flame. A mixture of methanol and additive that form a non-azeotropic solution has the disadvantage of having a flame that either is initially luminous and then becomes less luminous during combustion or vice versa depending on the volatility of the additive compared to that of methanol. An azeotropic mixture promotes a flame that is luminous over the entire combustion period.

In selecting an additive with a high C:H ratio, aromatics have the highest among hydrocarbons; therefore, aromatics would be the best candidates to increase the luminosity of methanol flames as they are capable of forming azeotropic mixtures with methanol and of increasing the C:H ratio with the minimum amount of additive. The following aromatics in decreasing tendency to form soot are: acetylenes, olefins, paraffins, and alcohols. However, all of these compounds are potentially poisonous to the catalyst because of their complex hydrocarbon content.

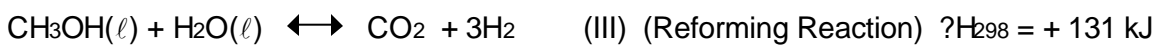
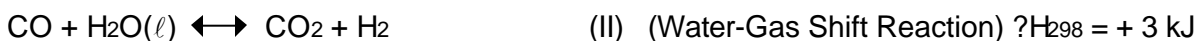
8 Reformer Degradation Analysis

PEM fuel cells operate using hydrogen and oxygen as the reactant gases. Steam reforming of methanol over a copper zinc oxide catalyst yields a product gas containing hydrogen, carbon oxides, and water. Contaminants and additives in the methanol fuel affect the copper zinc oxide catalyst differently. Certain contaminants and additives work to poison the catalyst by blocking its active sites. This results in decreased methanol conversion.

8.1 Summary of Analysis

XCELLSiS' small-scale reformer evaluation hardware was used to determine, log, and characterize changes in methanol conversion. A photograph of the hardware can be found in Appendix D.

The primary reactions involved in methanol reforming are as follows:



Ideally, the perfect catalyst would promote reaction 1 to the exclusion of reactions 2 and 3, generate the greatest possible conversion of methanol to hydrogen. In reality, however, all three reactions occur, and they proceed to varying degrees of completion. [1] As a result, the product gas that is generated by a methanol steam reformer, called reformat, will comprise a mixture of hydrogen, carbon dioxide, carbon monoxide, water and methanol. In an ideal reformer, conversion of methanol would be 100%, but in reality this never happens, and some quantity of methanol will pass through the reformer unconverted. The better, or more “active” the reformer catalyst, the less methanol slips through for a given ratio of methanol flow to catalyst mass. As catalysts age, the level of methanol “slippage” increases due to thermal sintering (reduction of catalyst surface area) and poisoning (blockage of catalyst sites by contaminants). Thus the amount of methanol measured in the reformat stream is a good indicator of catalyst health.

The degree of methanol conversion is important in fuel cell systems for a number of reasons. As methanol conversion drops, the amount of hydrogen generated by a reformer decreases proportionally. In a fuel cell application this would adversely affect overall system efficiency. Methanol entering the fuel cell can also transfer across the polymer electrolyte membrane to the cathode. There it will oxidize further reducing fuel cell performance due to the mixed potential created and possible hot spots. For a given fuel cell design, there will be a maximum inlet concentration of methanol beyond which severe performance loss and potential fuel cell damage will ensue.

Thus methanol conversion is a good metric for gauging the negative impact of fuel contaminants due to reformer catalyst poisoning. It does not, however, give any indication of potential down-stream poisoning of fuel cell catalysts due to these contaminants. This issue is beyond the scope of the current effort.

A total of six samples taken throughout the distribution supply chain were evaluated in the small-scale reformer evaluation hardware. Those six samples represent all the likely grades of methanol that one would encounter when selecting an optimal fuel for PEM fuel cell vehicle use. For each sample, an accelerated lifetime test was performed by flowing a fixed amount of a mixture of steam and vaporized methanol (steam to carbon ratio 1.5:1) over a cylindrical bed containing approximately 80 g of a proprietary copper-zinc oxide catalyst (Catalyst X), at a controlled temperature of 280 °C and a pressure of 40 psig. This simulates conditions that could be expected in a vehicular fuel cell application, except that the throughput of methanol per gram of catalyst was significantly higher than what is used in standard operation. This increased throughput is the “acceleration” factor and was employed for the following reasons:

In the timeframe of the program, there was insufficient time to perform representative lifetime tests, as the degradation observed for some of the samples is extremely slow and would have required hundreds or even thousands of hours of testing to see statistically relevant degradation.

Vehicular applications comprise a wide range of driving conditions. Different drivers and different driving scenarios would generate a great variety of flow profiles for the reformer. Thus defining a “typical” flow rate or even a “typical” flow profile is an arbitrary choice, and would not cover all conditions. Thus it is experimentally valid to pick a single flow rate and compare all fuel samples on the basis of that flow rate. This gives a qualitative reference to compare the gross behavior of catalyst.

The limitation of accelerated testing is that without proper calibration, based on extensive data collection, it is impossible to correlate the accelerated case to a non-accelerated case. As there is very little data on reformer catalyst degradation in real-world vehicular use, this is definitely the case in the current effort. It is impossible to translate the degradation effects observed in the accelerated tests performed to a prediction of catalyst lifetime in vehicle usage. Currently there is even insufficient data to clearly state a defined limit for “acceptable” methanol content in reformat for fuel cell operation. Development of this data and the described limits is necessary, but beyond the scope of the current effort. Thus the data generated by the current study can only show qualitatively the relative level of degradation generated by various fuels. The absolute level of methanol slippage in each test case is therefore less important than the relative variation in slippage between cases.

Comparison of the data has been facilitated by the use of normalization. The methanol sample taken from the Manufacturing Facility was expected to generate the least catalyst degradation as it had the lowest level of contamination. An arbitrary test duration of 100 hours was chosen for this sample, as this proved sufficient time for methanol conversion to stabilize at a plateau level. The methanol content detected in the reformat stream of this sample at the 100 hour point was then normalized to 1 as a reference value for all subsequent tests.

8.2 Description of Analytical Apparatus

A heated flame ionization detector (HFID) gas analyzer was used to measure the methanol content in reformat as an indication of methanol conversion. The detector is a burner in which a regulated flow of sample gas passes through a flame sustained by a regulated flow of hydrocarbon free air and fuel gas. Within the flame, the hydrocarbon components of the

sample undergo an ionization process that produces electrons and positive ions. A 250 volt polarized electrode ring collects these ions, causing a very low current to flow. This low current is amplified. The current flow is directly proportional to the hydrocarbon content of the sample. Though an alcohol, methanol still registers in the HFID as a hydrocarbon, and the methanol content can be determined through proper calibration.

8.3 Results and Discussion

8.3.1 Methanol Contamination Evaluation

The samples tested in the reformer degradation analysis are:

- **Manufacturing Facility, *Sample #2***
- **Bulk Storage, Terminal A, *Sample #2* and *Sample #3***
- **Tanker Truck, Dedicated Truck B, *Sample #2*,**
- **End-User, Electronic Grade, *Sample #2*,**
- **End-User, Non-Dedicated Storage Tank A, and**
- **End-User, Commercial Grade, *Sample #2*.**

The five most concentrated contaminants for each of these samples are shown in Figures 1 through 6.

Manufacturing Facility, *Sample #2* was determined to be the “cleanest” of all the samples that were analyzed. Presuming that it would perform better than the other samples, it was tested first. This sample was reformed for a total of 100 hours (the time was determined arbitrarily as the time, which allowed methanol conversion to stabilize to a plateau level). Methanol concentration in the reformat generated by this sample increases significantly for approximately the first 40 hours, and then levels out to a slower slope, eventually flattening. The methanol concentration measured in this reformat after the 100 hour test serves as the baseline level for normalization of the data from all of the other samples (i.e. the ppm level of methanol measured at this point normalizes to a unit-less value of 1, and all other unit-less values are a ratio to this level). The reformat methanol content for all of the samples, as detected by the HFID is presented in normalized form in Figure 7. Tests were arbitrarily cut off when the normalized content reached a value of 2. A discussion of the results for the remaining samples follows Figure 7.

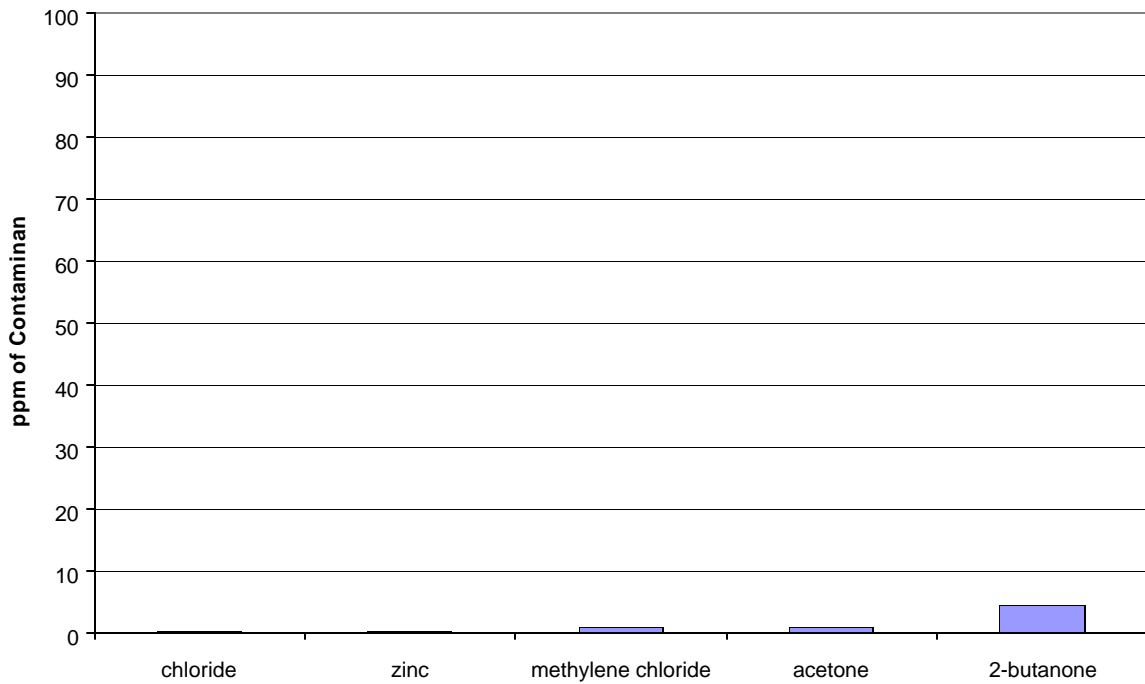


Figure 4: Top Five Contaminants found in Manufacturing Facility, Sample #2 - chloride - 0.05 ppm, zinc - 0.07 ppm, methylene chloride - 0.7 ppm, acetone - 1 ppm, and 2-butanone - 4.5 ppm.

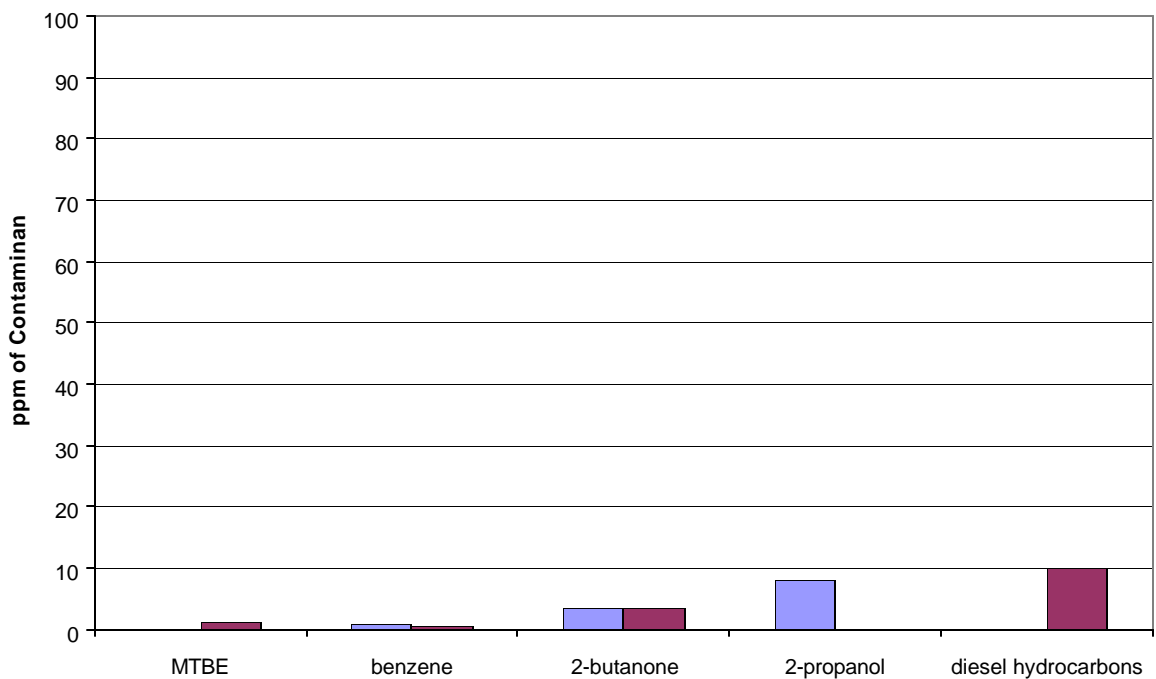


Figure 5: Top Five Contaminants found in Bulk Storage, Terminal A, Samples #2 and #3 - benzene – 1 ppm, 2-butanone – 3.5 ppm, and 2-propanol – 8 ppm; **Sample #3** - MTBE – 1.1 ppm, benzene – 0.6 ppm, 2-butanone – 3.6 ppm, and diesel hydrocarbons – 10 ppm.

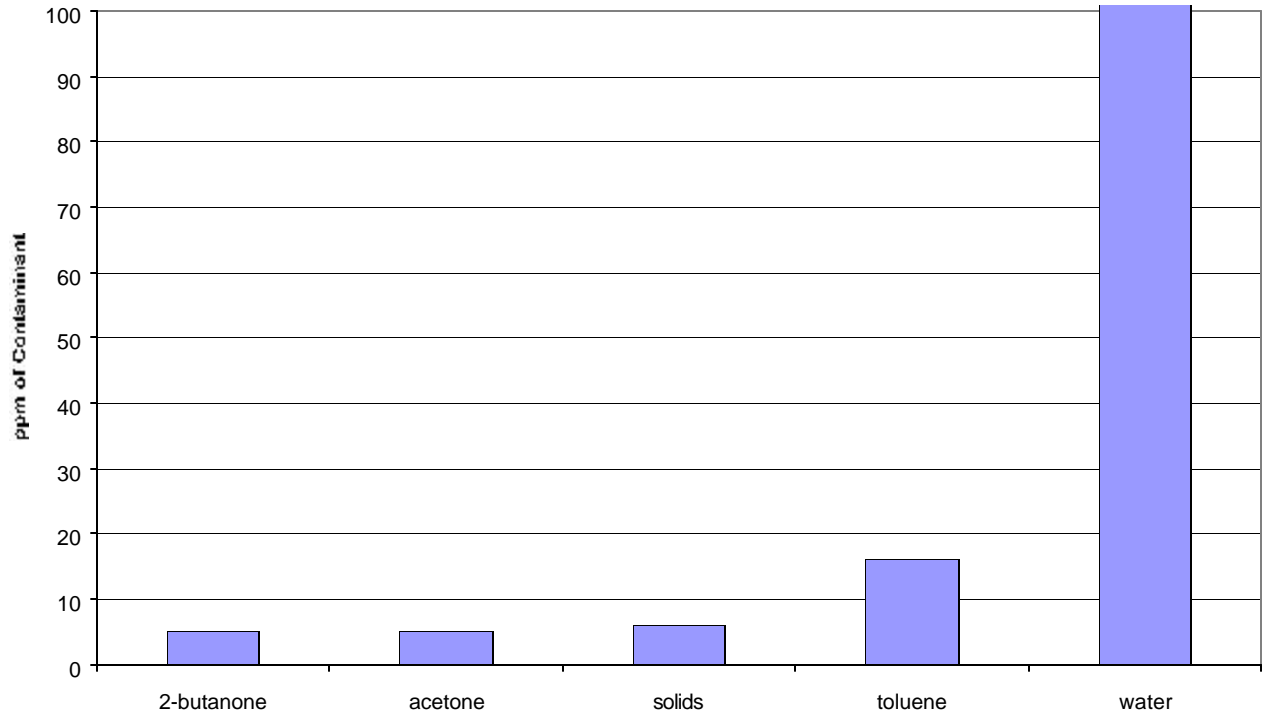


Figure 6: Top Five Contaminants found in End-User, Electronic Grade, Sample #2 - acetone – 5.2 ppm, solids – 6 ppm, 2-butanone – 5 ppm, toluene – 16 ppm, and water – 4000 ppm.

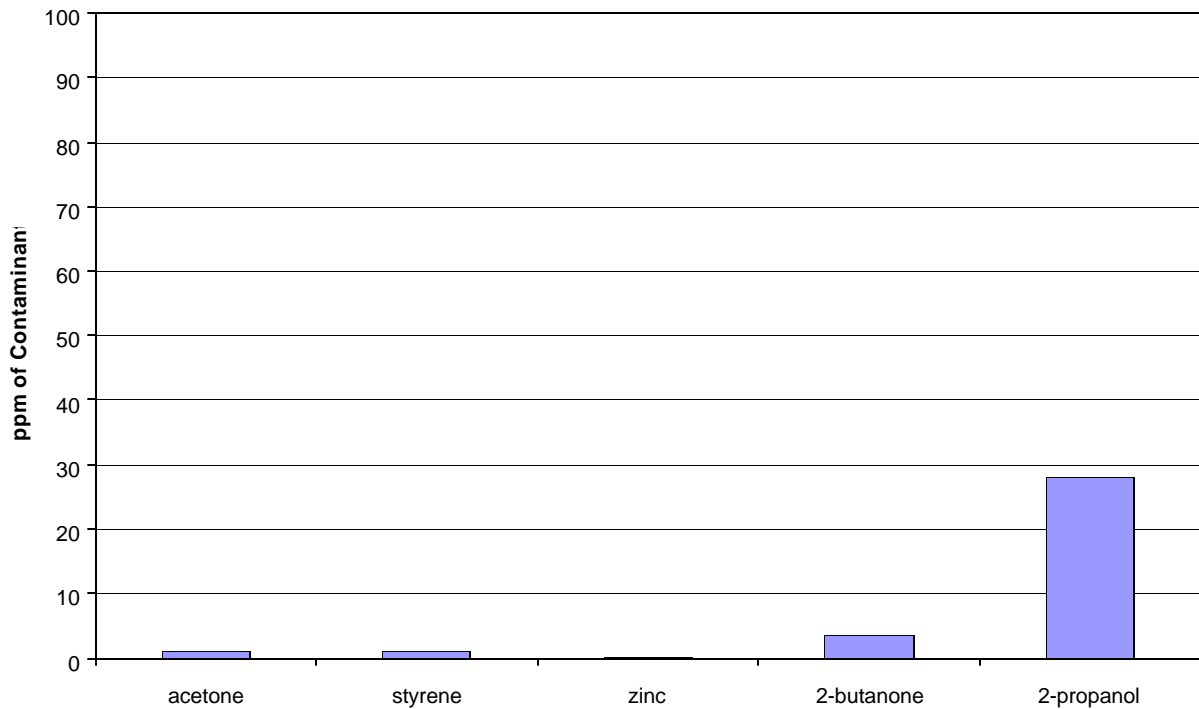


Figure 7: Top Five Contaminants found in Tanker Truck, Dedicated Truck B, Sample #2 - acetone – 1 ppm, styrene – 1.2 ppm, zinc – 0.31 ppm, 2-butanone – 3.7 ppm, 2-propanol – 28 ppm.

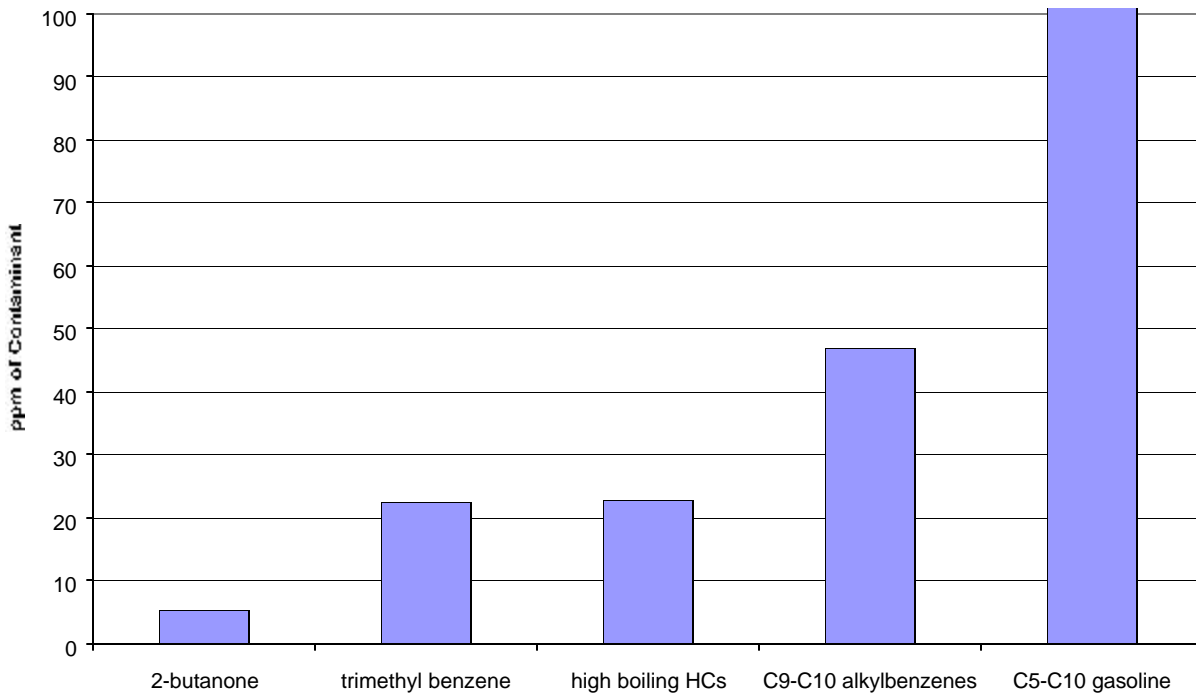
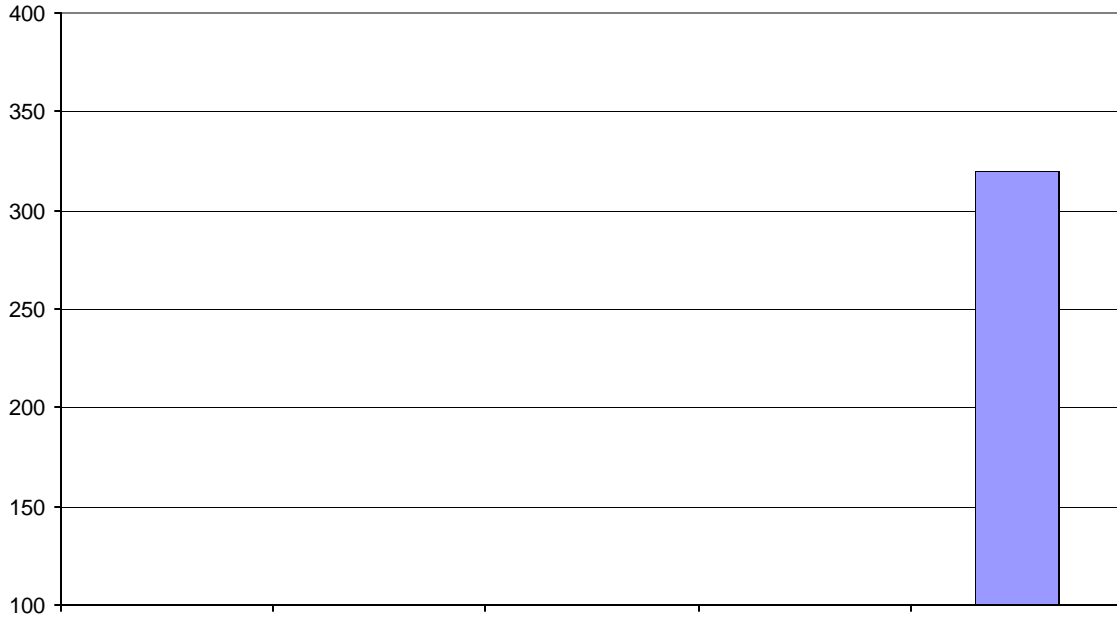


Figure 8: Top Five Contaminants found in End-User, Non-Dedicated Storage Tank A - 2-butanone – 5.4 ppm, trimethyl benzene – 22.4 ppm, high boiling hydrocarbons – 22.9 ppm, C9-C10 alkylbenzenes – 47 ppm, C5-C10 gasoline – 320 ppm. For comparison to the other figures, the scale of ppm of Contaminant is cut-off 100 ppm.

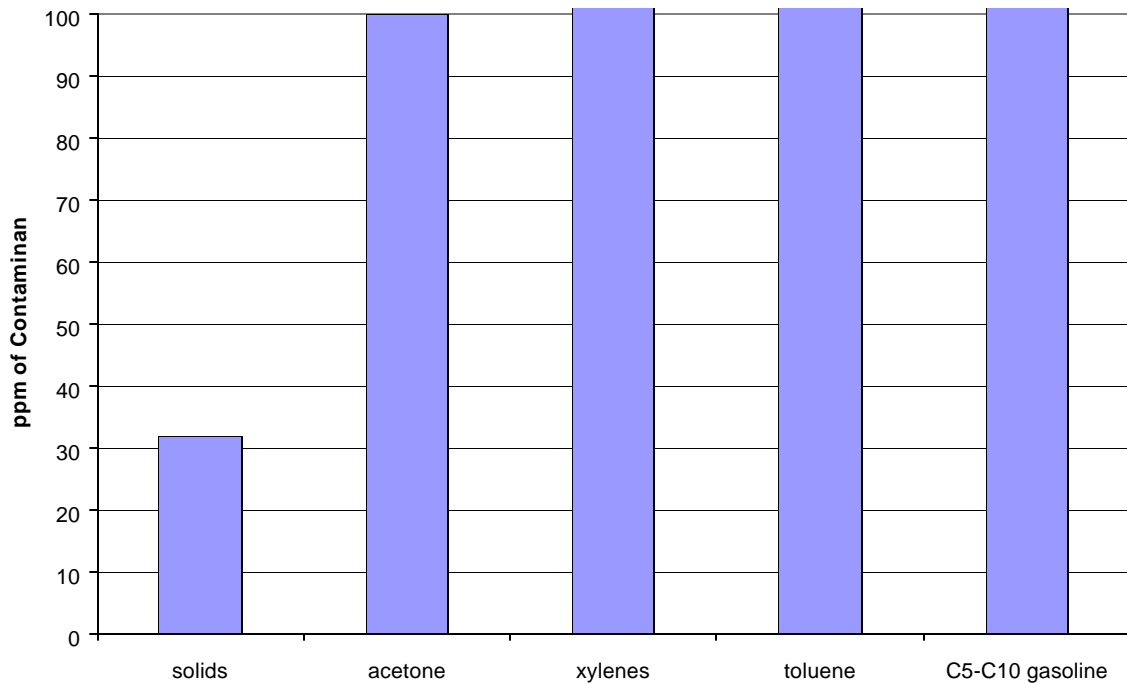
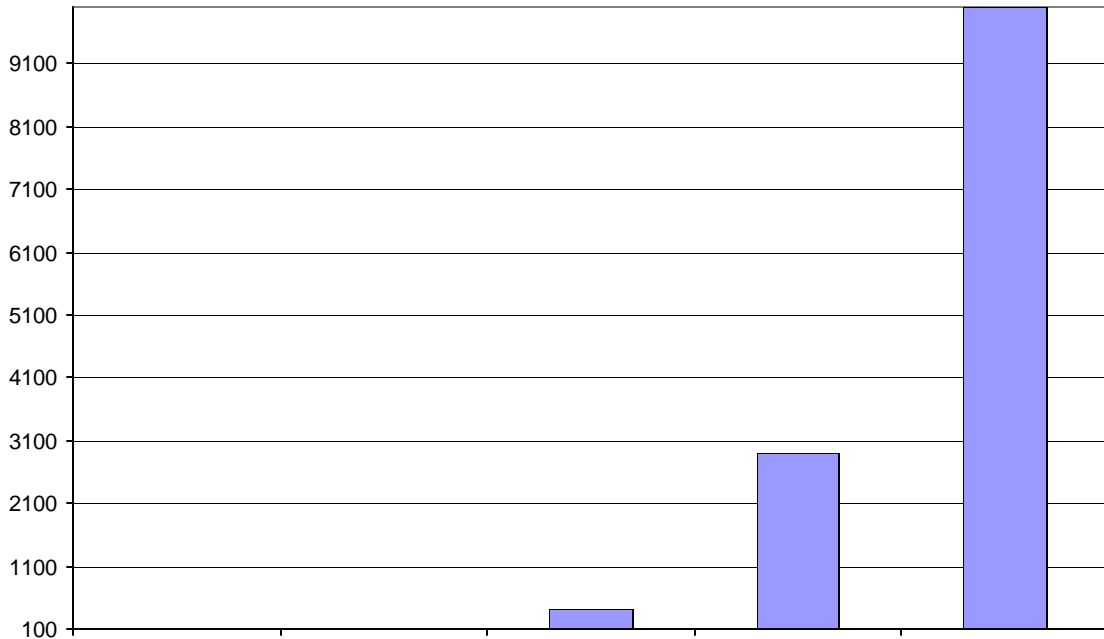
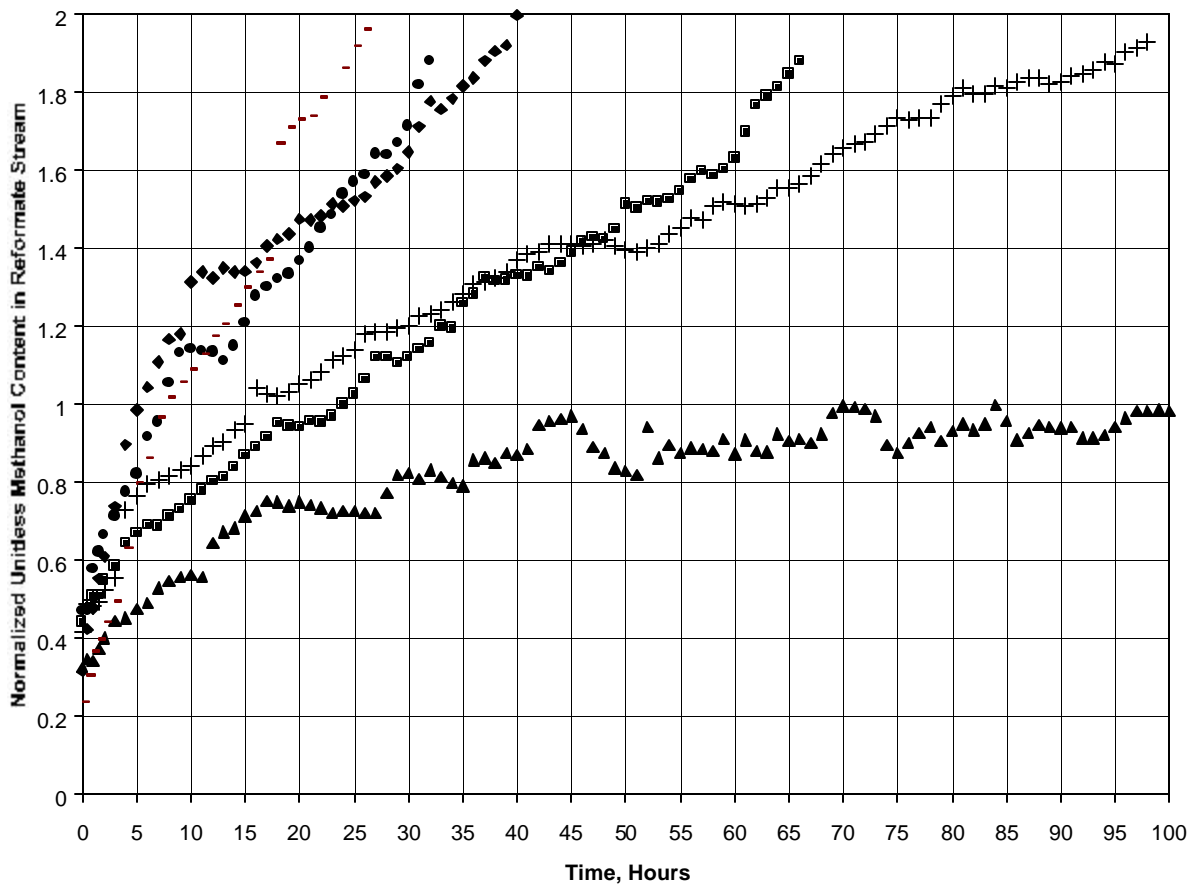


Figure 9: Top Five Contaminants found in End-User, Commercial Grade, Sample #2 - Solids – 32 ppm, acetone – 100 ppm, xylenes – 430 ppm, toluene – 2900 ppm, C5-C10 gasoline – 10,000 ppm. For comparison to the other figures, the scale of ppm of Contaminant is cut-off at 100 ppm.



Key:

- = Manufacturing Facility, Sample #2
- + = Bulk Storage, Terminal A, Samples #2 & #3
- = End-User, Non-dedicated Storage Tank A
- ◆ = End-User, Electronic Grade, Sample #2
- = End-User, Commercial Grade, Sample #2
- ▲ = Tanker Truck, Dedicated Truck B, Sample #2

Figure 10: Normalized unit-less methanol content in hydrogen reformate stream as a function of time for six different methanol samples - The curves are normalized, using the Manufacturing Facility, Sample #2 result after 100 hours as a baseline.

Bulk Storage, Terminal A, Sample #2 and Sample #3 – Both *Sample #2* and *Sample #3* were used for degradation evaluation. As shown in Figure 7, there is a seamless transition. The chemical analyses for the two samples are almost identical with the exceptions being 10 ppm diesel fuel hydrocarbons found in Sample #3 and 8 ppm 2-propanol found in Sample #2.

End-User, Non-Dedicated Storage Tank A – The decline in performance of this sample is slightly worse than that of the dedicated bulk terminal samples; however, the dedicated terminal sample shows more signs of leveling off the amount of methanol in the product stream, whereas, the non-dedicated tank continues a sharp slope upward. The non-dedicated tank

contains more contaminants than does the dedicated terminal. These include 320 ppm gasoline and 47 ppm alkyl benzenes.

End-User, Electronic Grade, Sample #2 – Though apparently less contaminated, the performance of this sample is worse than that of Non-Dedicated Storage Tank A. This is surprising given the high levels of gasoline and alkyl benzene in the Storage Tank sample. The only obvious contamination in the Electronic Grade sample is the 16 ppm toluene present or possibly the solids. It is possible these have a highly degrading effect. Unfortunately, there was insufficient time to confirm this with additional testing.

End-User, Commercial Grade, Sample #2 - The chemical analyses conducted by West Coast Analytical Services showed a high degree of contamination in the sample: 32 ppm solids, 10,000 ppm gasoline fuel hydrocarbons, 20 ppm 2-butanone, 100 ppm acetone, 90 ppm ethyl benzene, 200 ppm hexane, 430 ppm xylene, 20 ppm styrene, and 2,900 ppm toluene. The results of the test show that it degrades the catalyst more rapidly than the other samples.

Tanker Truck, Dedicated Truck B, Sample #2 - The primary contaminant found in this sample is 2-propanol in an amount of 28 ppm. Initially, it was believed that this sample would fare rather well since it only contains a small amount of contaminant in comparison to other samples such as the commercial grade sample. Contradictory to this belief, the sample proved to degrade more rapidly than any other sample that was tested. One cause for this may be due to the presence of 2-propanol. No other sample contains such a high level of this alcohol. The effect of 100 ppm ethanol on the reformer catalyst was also evaluated and is presented below in the additives section. It had a large degrading effect over a short time period, in keeping with the apparently similar impact of 2-propanol. There was insufficient testing time to repeat the test and confirm this hypothesis.

In general, the increasing presence of hydrocarbons and other contaminants found as methanol moves further and further from the manufacturing facility had a clear and significant impact on the methanol conversion capacity of the catalyst over time. If the methanol content present in reformat generated from the Manufacturing Facility sample after 100 hours of the accelerated test was considered to be a lifetime cutoff point, then this cutoff point would be reached in only 7 hours using Commercial Grade methanol. Obviously, the presence of supply chain generated contaminants will have a huge impact on the operating lifetime of reformer beds, and the resulting cost of catalyst. Therefore, it is essential that the contaminants either be avoided or removed.

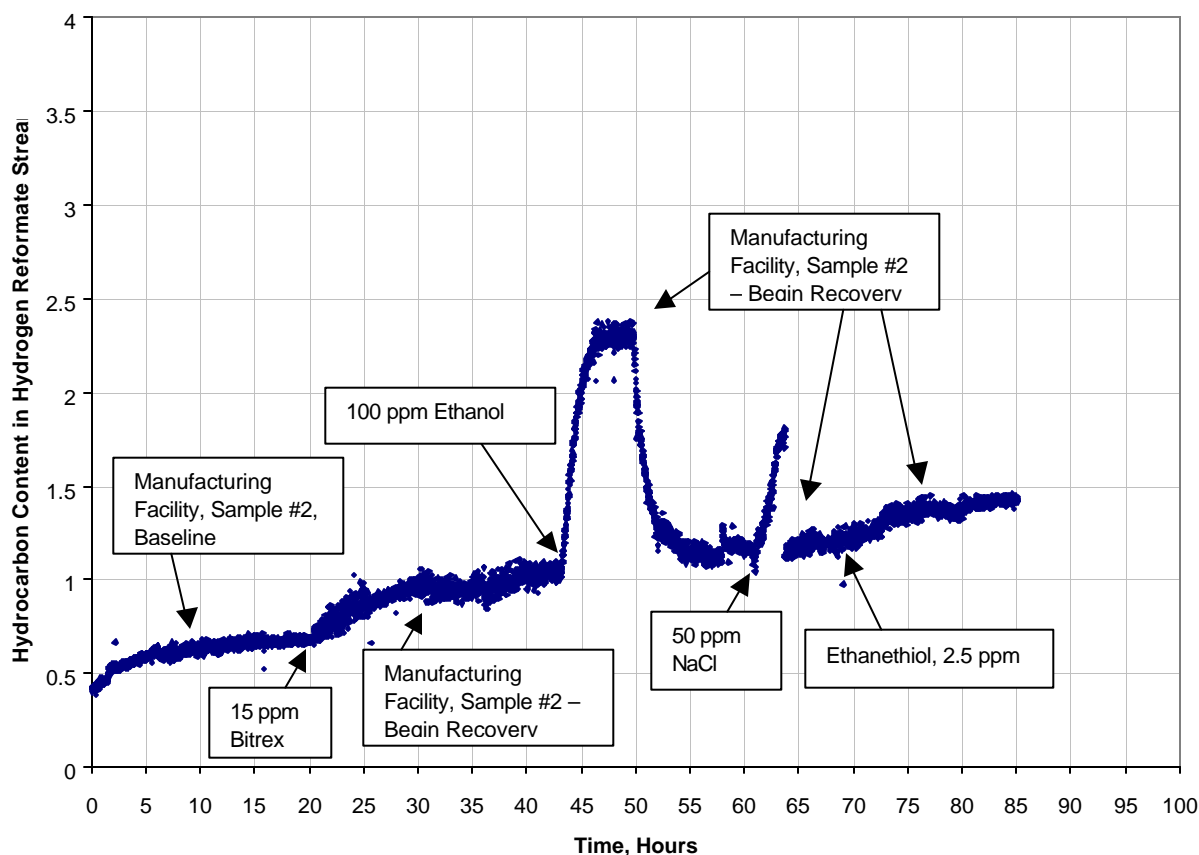


Figure 11: Evaluation of Bitrex, ethanol, sodium chloride, and ethanethiol - The curve is normalized using the Manufacturing Facility, Sample #2.

8.3.2 Additives Evaluation

Three different additives and an alcohol were investigated in order to understand the effect they would have on the copper zinc oxide catalyst. For the first 20 hours of reforming, Manufacturing Facility, Sample #2 was used, so that the initial degradation would not interfere with the performance of the Bitrex solution.

After 20 hours, Bitrex, a bitterant, was dissolved into the Manufacturing Facility, Sample #2 at 15 ppm. A noticeable degradation in the catalyst is apparent in Figure 11. At 30 hours, clean Manufacturing Facility, Sample #2 was reformed, in order to examine the effects of reversibility. The degradation of the catalyst does not appear to be reversible for the Bitrex solution.

At approximately 43 hours, 100 ppm ethanol in manufacturing grade methanol was introduced into the reformer. The results show a very steep degradation effect. After several hours, the manufacturing sample was reintroduced, and the results indicate that the apparent degradation effect is completely reversible.

Sodium chloride is a potential flame luminosity additive. At approximately 61 hours, 50 ppm sodium chloride was introduced into the reformer. Again, the results indicate a sharp degradation in the catalyst's activity. This is conclusive with the fact that chloride is a known poison to the copper zinc oxide catalyst. After several hours, the manufacturing grade sample was again reintroduced. Initial results indicate that the effect sodium chloride has on the sample is reversible. However, further tests should be conducted, in order to conclude this decisively.

Ethanethiol is a potential odorant additive. At approximately 68 hours, 2.5 ppm ethanethiol was introduced into the reformer. The ethanethiol caused degradation in the catalyst's activity at a rate higher than that of the manufacturing grade methanol alone. After approximately 10 hours of operation, the manufacturing grade sample was reintroduced into the reformer. No apparent reversal of the catalyst's activity was noted.

9 Project Results

This section summarizes the results that were achieved for each task.

9.1 Literature Review

Literature was found which provided information on methanol contaminants and additives, which are potentially damaging to methanol conversion over copper zinc oxide catalysts. However, little was found which describes their effects on methanol conversion.

9.2 Chemical Analysis

Chemical analyses of methanol supply distribution points were completed. These points represent the manufacturer at the beginning of the supply chain to the end-user. The chemical analyses served as a baseline for the evaluation of the supply infrastructure (Task 3). XCELLSiS consulted with Methanex to determine which chemical tests would provide the most useful information in analyzing the available grades of methanol and methanol infrastructure samples. The selected tests were also based on the literature review of methanol contaminants and additives. All samples tested were tested at West Coast Analytical Service, Inc., where they were analyzed for: Water by Karl Fisher Titration, Total Solids by EPA 160.3, Conductivity by EPA 120.1, Chloride by Ion Chromatography (IC), Metals Screen by Inductively Coupled Plasma – Mass Spectrometry (ICPMS), Volatile Organics by Gas Chromatography – Mass Spectrometry (GCMS), Fuel Hydrocarbons by Modified EPA 8015.

9.3 Supply Chain Analysis

The supply chain was analyzed to better understand the source of methanol contamination, and how this might be avoided. Many of the contaminants detected in the distribution infrastructure samples can be categorized by their source. Contaminants from the production process include acetic acid, acetone, 2-butanone, and water. Petrochemical contaminants from cross-contamination (contact with residue of another chemical) include various hydrocarbons. Leaks in water vessels, which transport methanol, introduce water and chloride. In addition, the plumbing used to transport the methanol provides another potential mode for methanol contamination. Heavy metals can be introduced to the methanol from plumbing systems that are constructed of materials incompatible with methanol. For example, galvanized plumbing can be considered a potential source of nickel and zinc contamination. Furthermore, pipe joint compounds, which typically contain lead, provide another potential source of contamination.

9.4 Additive Requirement Analysis

The current requirements for methanol fuelled vehicles were reviewed. The California Code of Regulations currently requires methanol to have both a bitterant and an odorant. Of current concern are the effects that these additives will have on the methanol reformer's copper zinc oxide catalyst.

Relative to the bitterant requirement, at ambient conditions, M-100 fuel methanol must have a distinct and noxious taste for purposes of preventing purposeful or inadvertent human consumption. Currently, Bitrex (denatonium benzoate) is the most economical of foul-tasting

additives, due to its relatively low bitterness threshold and corresponding low cost in use. Bitrex was evaluated in the small-scale reformer hardware at 15 ppm.

The odorant requirement maintains that upon vaporization at ambient conditions, the M-100 fuel methanol must have a distinctive odor potent enough for its presence to be detected down to a concentration in air of not over one-fifth of the lower limit of flammability.

Although methanol burns with a colorless flame creating a potentially hazardous scenario, the code of regulations does not currently require M-100 fuel methanol to contain an additive which would provide a luminous flame if the methanol were to ignite, but the regulation does require an on-board flame arrester. In selecting an additive for flame luminosity, aromatics would be the best candidates to increase the luminosity of methanol flames as they are capable of forming azeotropic mixtures with methanol and of increasing the C:H ratio with the minimum amount of additive. However, all of these compounds are potentially poisonous to the catalyst due to their high content of complex hydrocarbons.

9.5 Methanol-Steam Reforming Catalyst Degradation Analysis

Six samples were taken from points in the distribution supply chain and were evaluated in the small-scale reformer evaluation hardware. Those six samples represent all the likely grades of methanol that one would encounter when selecting an optimal fuel for PEM fuel cell vehicle use. **Manufacturing Facility, Sample #2** served as a baseline for comparison with the other samples. It displayed an initial rapid degradation, followed by a stabilization of the catalyst. Based on this sample's performance, methanol from a manufacturing facility is suitable for methanol reformer use, and the quality of the methanol should be maintained throughout the supply chain. All of the other samples showed significantly increased levels of degradation, with a general relationship to the level of contamination present in the fuel. However, preliminary indications show that specific contaminants have a greater effect on the catalyst than others do, and the absolute level of contamination is not the most important variable. The worst performance was measured for the dedicated tanker truck sample, which was not the most contaminated fuel. It did contain elevated levels of 2propanol, however, which may have caused an accelerated effect. The level of degradation observed with the manufacturing facility sample after 100 hours was observed after only 7 hours with the tanker truck sample. Obviously this increased degradation is cause for concern and needs further evaluation. It is fair to conclude that the increasing presence of hydrocarbons and other contaminants found as methanol moves further and further from the manufacturing facility has a clear and significant impact on the hydrogen production capacity of the reforming catalyst used (as measured by methanol conversion). However, additional testing is required to define the specific impact of specific contaminants.

In addition, three additives and an alcohol were evaluated. Bitrex, a bitterant, was evaluated at 15 ppm; Sodium chloride, a potential flame luminosity additive, was evaluated at 50 ppm; Ethanethiol, an odorant, was tested at 2.5 ppm, and ethanol was evaluated at 100 ppm. **Manufacturing Facility, Sample #2** was used to check the reversibility of the catalyst degradation caused by the additives and the alcohol. The alcohol (ethanol) caused a 230% increase in reformat methanol content in 10 hours of testing. When the reforming process was switched back to the **Manufacturing Facility, Sample #2**, the catalyst showed complete reversibility. Sodium chloride contamination caused a 55% increase in reformat content within 5 hours, which was again reversed by switching back to the clean fuel. Bitrex caused a 40%

increase in reformat methanol content over 10 hours, but the degradation was not reversible. The odorant ethanethiol caused a 15% increase in reformat methanol content, and again this degradation was not reversible.

10 Problems Encountered

A discussion follows on problems that were encountered during the contract and how they were resolved.

FID Analyzer

Unforeseen failures of the Flame Ionization Detector to properly function created minor delays in evaluating methanol samples in the reformer hardware. The internal flow controller for both the FID and its spare failed. The flow controller controls the flow of sample gas into the oven chamber of the analyzer. The controller for both analyzers failed open such that as the flow of the product gas varied so did the percent hydrocarbon output from the analyzers. Both analyzers were shipped overnight to the manufacturer to be repaired and were returned one week later. While at the manufacturer, the analyzers were recalibrated in order to read a higher percentage hydrocarbon. However, once in operation at XCELLSiS, it was observed that the manufacturer did not calibrate one of the analyzers correctly. In addition, this analyzer failed to zero. The analyzer was immediately returned to the manufacturer, and operation continued without the spare FID analyzer. Later in the week, the functioning analyzer failed to span, and it too was sent back to the manufacturer to be repaired. This contributed to the delay in the completion of the electronic grade testing.

Variability of the Electronic Grade Methanol

The Electronic Grade methanol was the first grade to be evaluated using the reformer hardware. This grade had been successfully used in the past for other PEM fuel cell vehicles. The first 100-hour test went smoothly; however, when the test was repeated, the conversion data was poor. The reduction temperature and procedure were closely monitored, and all variables monitored were within design specifications. The procedure was again repeated, and the catalyst duplicated the poor conversion.

A sample of the electronic grade methanol was taken at the inlet to the test stand, and this sample was sent to West Coast Analytical for analysis. Laboratory results indicated that the electronic grade methanol was contaminated with 15 ppm toluene, 5.6 ppm acetone, and 5 ppm 1-methyl-2-pyrrolidinone (NMP). Since the first evaluation went smoothly, and the performance of the subsequent tests was affected by the presence of the contaminants, the poor conversion in the reformer can be attributed to the particular batch of electronic grade methanol used. Thus, the variability in the quality of this methanol grade limits its usefulness as a PEM fuel cell vehicle fuel.

11 Recommendations

The following list provides several recommendations that would aid in the development of a PEM fuel cell methanol fuel specification:

- Currently, there is very little information on potential additives and their compatibility with copper zinc oxide catalyst. Additional studies on potential methanol fuel additives should be made.
- A list of methanol compatible materials of construction should be well defined. During the construction of new facilities or upgrades to older facilities these materials should be used to help maintain methanol quality.
- Dedicated or appropriately cleaned methanol systems are essential to ensure methanol's high purity is maintained throughout the methanol distribution infrastructure.
- Education and Awareness: People involved in the handling and distribution of methanol for fuel cell use should be adequately trained to understand the various mechanisms of methanol contamination, methods and practices to prevent contamination, and the chemical compatibilities of the methanol reformer used in fuel cell vehicles.
- A more in-depth analysis and quantification of the effects different contaminants have on copper zinc oxide catalyst is required. This would include more testing in order to evaluate the long-term effects that certain specific contaminants and additives may have on the catalyst. In addition, multiple samples from the same point in the distribution chain should be evaluated as to their variability and/or consistency with each other.
- The methanol samples taken throughout the distribution supply chain were evaluated in the small-scale reformer evaluation hardware via an accelerated lifetime test. This was accomplished by flowing a fixed amount of a mixture of steam and vaporized methanol over a cylindrical bed at a relatively high throughput. The accelerated testing is an effective means to quickly determine the catalyst's response to varying grades of methanol fuel; however, in order to make this determination, the dynamic performance of the reformer in response to fluctuating loads is neglected. Real world situations call for the dynamic performance of the fuel cell engine; therefore, future study should include catalyst degradation as a result of varying methanol fuel grades over an array of fuel flow rates to enable a complete understanding of the performance and degradation of the reforming catalyst under vehicle compatible conditions. This would allow calibration of the accelerated test data to enable predictive capability without requiring extended test periods.
- Recovery potential of the copper zinc oxide catalyst was addressed briefly in the fuel additive study. Future tests should include an examination of the recovery of the catalyst's activity for different contaminants.
- Alternative methods for in-situ fuel cleanup need to be evaluated, to determine if the contamination can be addressed by methods less drastic than an overhaul of the supply infrastructure.

- The downstream impact of reformate contamination on fuel cell performance needs to be analyzed and quantified.
- Contaminant tolerant catalysts need to be developed.

Appendix A – Chemical Analyses

Appendix B – Additive Tables

Appendix C – Methanol Fuel Specifications

Appendix D – Reformer Evaluation Hardware Photograph

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