

Final Report

Air Products and Chemicals, Inc.

“An Investigation Into The Acceptability Of Stabilized Methanol
As A Fuel For Phosphoric-Acid Fuel Cell Power Systems”

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Dr. Vernon P. Roan, Principal Investigator

Mr. J. Patrick Sterchi, Research Assistant

University of Florida Fuel Cell Research and Training Laboratory
Department of Mechanical Engineering

Gainesville, Florida

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Introduction

While pure gaseous hydrogen is the ideal fuel for fuel cell power systems, it is also relatively expensive, difficult to transport, and difficult to store onboard transportation systems. Consequently, there has been, and is, considerable interest in utilizing liquid hydrocarbon fuels for transportation fuel cell applications. For a liquid fuel to be a feasible alternative to hydrogen, it must be possible and practical to utilize a fuel processing system to transform the liquid fuel into a hydrogen-rich gas. More specifically, the hydrogen-rich gas must be compatible with long-term operation of the fuel cell system within which it would be utilized, with little or no degradation in performance.

Clearly, the implication is that a suitable fuel-fuel processor combination must maintain the ability to provide almost complete conversion of the liquid fuel feedstock into an acceptable hydrogen-rich gas over a long period of time and many cycles of operation. “Acceptable” hydrogen-rich gas in this case means a maximum concentration of hydrogen and virtually zero concentration of contaminants which would degrade the fuel cell stack life and/or performance. To meet this acceptability requirement, the fuel processor must also not undergo any significant decrease in its ability to convert the liquid hydrocarbon in a continuing and consistent manner. A prime mechanism for the fuel processor to experience a significant decrease in conversion ability would be through a deactivation of the catalyst in a catalyst-driven processor such as the steam reformer.

Catalyst deactivation can occur for many reasons including excess temperature, rapid temperature transients, or the introduction of oxygen. However, with the introduction of a new

liquid fuel, it is obvious that deactivation can occur as a result of one or more contaminants contained in the liquid fuel.

The production of stabilized methanol through a process developed by Air Products, Inc. with the support of the Department of Energy represents the potential introduction of a new liquid fuel produced from the immense supply of domestic coal. However, in its “as produced” form, the stabilized coal-based methanol does not have the purity of commercial grade methanol. It contains small amounts of a number of compounds including a type of “mineral oil” used in the production process.

Air Products and DOE subsequently supported research to determine the feasibility of the “as produced” stabilized methanol in various types of engines as well as for fuel cell applications. The University of Florida had facilities and equipment in the Fuel Cell Research and Training Laboratory to perform this type of research, as well as two operational methanol-fueled fuel cell engines. As a result, an agreement was reached for the University of Florida to undertake the evaluation of the stabilized methanol as a suitable fuel for steam-reformed methanol/phosphoric acid fuel cell systems.

Since it was obviously important not to damage the operational fuel cell engines, the proposed procedure was to fabricate small steam reformers using catalyst pellets of the type (copper oxide-zinc oxide) typically used for methanol steam reformation. The apparatus was designed so as to allow determination of areas of deactivation if they occurred as a result of the stabilized methanol fuel. A parallel reformer operating simultaneously with commercial grade methanol was used as a control.

Initial results showed very rapid degradation of the catalyst exposed to the stabilized methanol. Results pointed to a probable coating of the catalyst with non-reacted “mineral oil” as

the likely cause. Subsequent tests and modifications to the rig were performed as well as the utilization of a higher temperature catalyst to avoid rapid catalyst degradation. Higher temperatures did, as expected, result in less effect due to the mineral oil but it also resulted in a more unfavorable balance among hydrogen, methane, carbon dioxide, and carbon monoxide in the reformat.

The results to date indicate that for the relatively low-temperature steam reforming of methanol, the “mineral oil” would most likely have to be removed prior to being a suitable fuel. On the other hand, the limited higher temperature results indicate that possibly for auto-thermal reforming and probably for partial oxidation reforming, the stabilized methanol would be acceptable as a fuel. Obviously, further experimentation is needed to verify these applications.

Experimental Approach

Background

One of the primary concerns of using stabilized methanol in a fuel cell system was the presence of possible “contaminant” species in the methanol. Chemical analysis by multiple independent testing facilities indicated the presence of small quantities of species other than methanol present in the stabilized methanol. Partial results of these analyses are shown in Table 1. Copies of the complete analyses are located in Appendix A.

Table 1: Chemical Analysis of Stabilized Methanol (only 4 dominant specie are shown)

Species	Atlantic Analytical Laboratory (% w/w)	Intertek Testing Services (% w/w)	Air Products Inc. LaPorte, TX Data* (% w/w)
Methanol	98.7	-	97.23
Ethanol	0.18	0.1433	0.678
Water	0.46	0.4286	0.529
“Mineral” Oil**	0.49	0.2208	0.189

* A different sample was used for LaPorte, TX data

** Actual chemical composition unknown but similar to common mineral oil

Of particular interest with respect to the different species present in the stabilized methanol was the mineral oil. The effect that mineral oil might have on fuel cell components was uncertain, although there was the possibility that it could have a detrimental effect on fuel cell system hardware. For this reason, instead of using the stabilized methanol initially in the brassboard fuel cell engine at the University of Florida (and risk permanent damage to the system), a sub-scale experimental steam reformer rig was designed and built to determine the “reformability” of the stabilized methanol.

1st Generation Rig

The rig initially built to conduct research using stabilized methanol (1st generation rig) consisted of two identical reformer flow paths. This design was used so that during experimentation, commercial grade methanol would flow through one side of the rig as a control while stabilized methanol design would flow through the other. This allowed for a direct, real-time comparison of the behavior of the two types of methanol within each respective fuel processor. The temperature range (250°C-300°C) and pressure (1atm) used during experimentation are typical of methanol steam-reforming, and flow rates used during experimentation were scaled to mimic the existing 25kW laboratory brassboard fuel cell engine steam reformer. The catalyst used was a low-temperature water-gas shift catalyst (CuO/ZnO on alumina) that is typical for the methanol steam-reforming process, and similar to that used in the brassboard fuel cell engine reformer. Each flow path included a pumping sub-system, a vaporizer sub-system, and a reactor sub-system. Figure 1 shows a general schematic showing how these components were integrated to form either one of the two reformer flow paths.

Vaporizer Design

Calibrated peristaltic pumps were used to pump the water and methanol from their respective reservoirs to the vaporizer sub-system. During experimentation, a steam to carbon ratio of approximately 1.5:1 was used to simulate operating conditions in the brassboard system. Each vaporizer consisted of a stainless steel tube wrapped with an electrically resistive heating element (heat tape) as shown in Figure 2. High temperature insulation covered the entire assembly to reduce heat loss to the environment. Each side of the entire experimental rig had one vaporizer assembly, which consisted of separate water and methanol vaporizers. The vaporizer

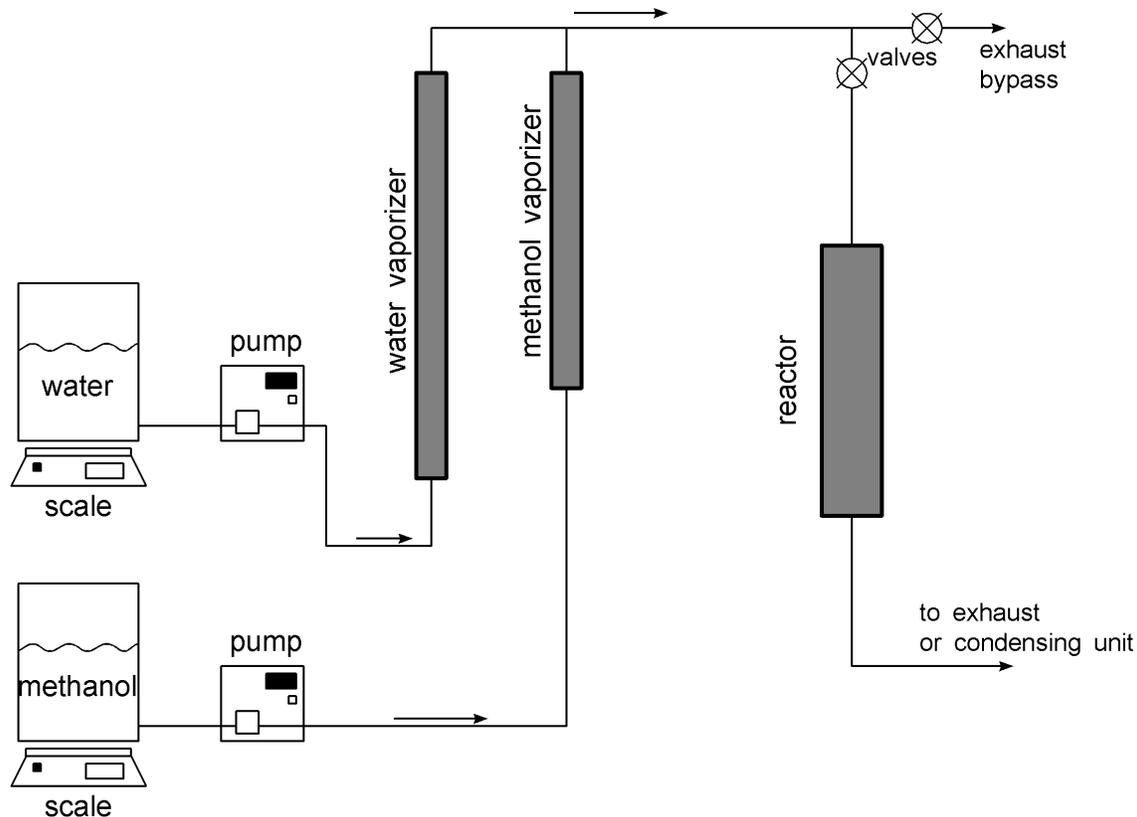


Figure 1: 1st Generation Experimental Methanol Steam-Reformer Rig Schematic
(one of two parallel flow paths)

assembly was outfitted with thermocouples as shown in Figure 2, and was capable of producing superheated vapor at 300°C for the flow rates used over the course of experimentation.

Reactor Design

Superheated vapor from the vaporizers was piped to the reactor sub-system (Figure 3) through ¼” stainless steel tubing. The reactor sub-system included ten electrically resistive heating elements (heat bands) that added energy to the reactor bed in order to offset the endothermic steam-reforming reaction and maintain near isothermal operation. Thermocouples were used to monitor the temperature at the core of the reactor at the locations shown in Figure

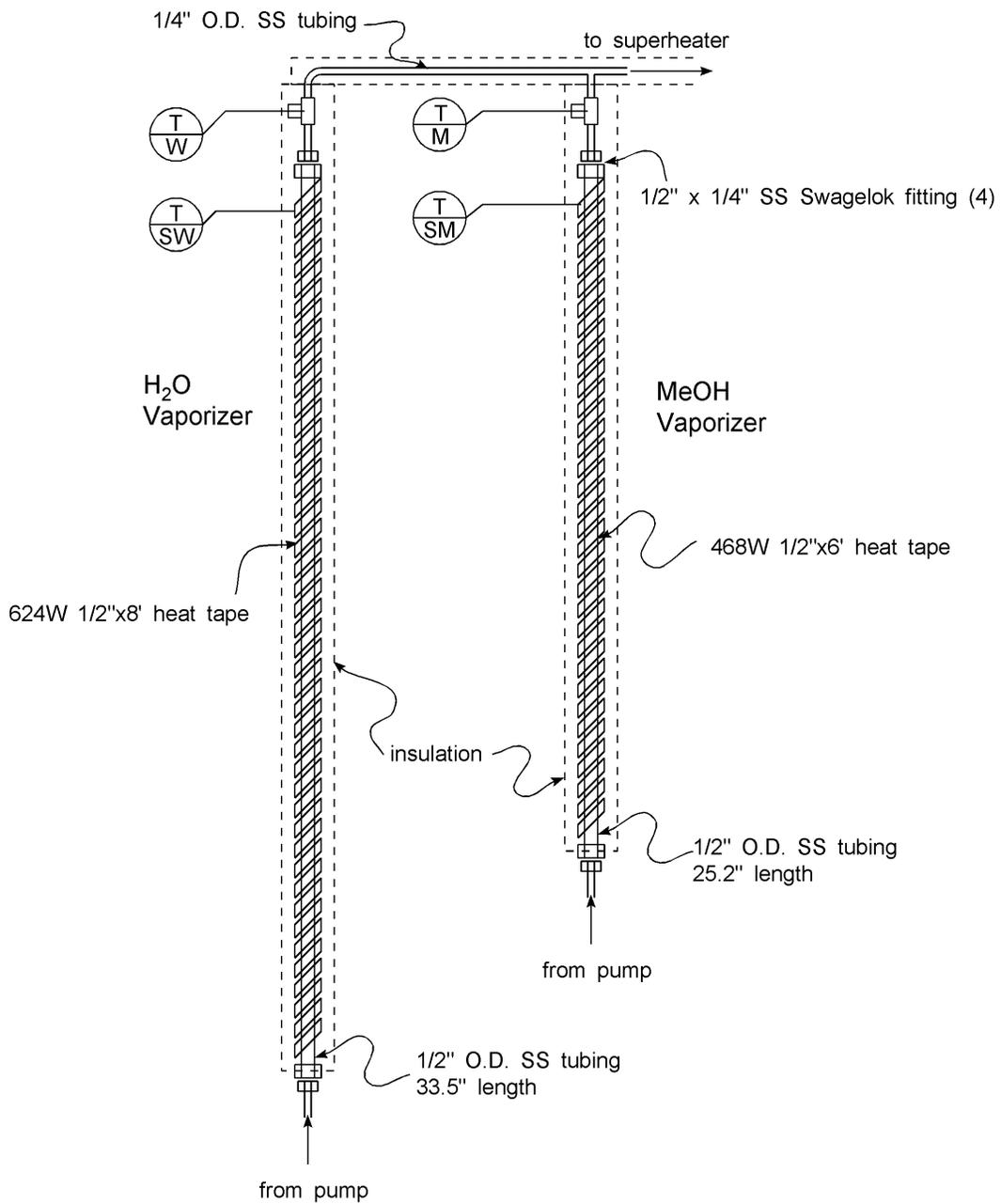


Figure 2: Vaporizer Assembly Schematic

3, and these temperature measurements were used to thermostatically control the heat bands individually. Removable end fittings were used at each end of the reactor to allow for removal and replacement of catalyst. A picture of the 1st generation reactor assembly prior to installation can be seen in Figure 4. After installation, the reactor assembly was insulated with high temperature insulation to minimize heat loss to the environment.

Heating Element Control

Heating elements were controlled remotely by a computer in conjunction with data acquisition hardware and a power distribution unit (PDU). Computer software utilized temperature data from the rig to determine the desired status (on/off) of any given heating element. A digital output module controlled the operation of the heating elements through the power distribution unit. A schematic of the control setup is shown in Figure 5. The power distribution unit, shown in Figure 6, housed a bank of solid state relays, with a specific relay controlling each heating element. Each relay was energized by a 5V-power source, while the switch side connected a 120VAC circuit to each heating element. In order to measure the power input to each heating element, a power meter was installed in the heating element circuit. A switchboard allowed for a single meter to monitor any one of the heating elements at a time. Figure 7 shows the configuration of the heating element control circuit.

CO₂ Purge System

One additional feature of the experimental rig was a CO₂ purge system that was used to purge hydrogen from the system after use as well as maintain the catalyst bed in a non-oxidizing environment. Implementation of this system was straightforward and is shown in schematic form in Figure 8.

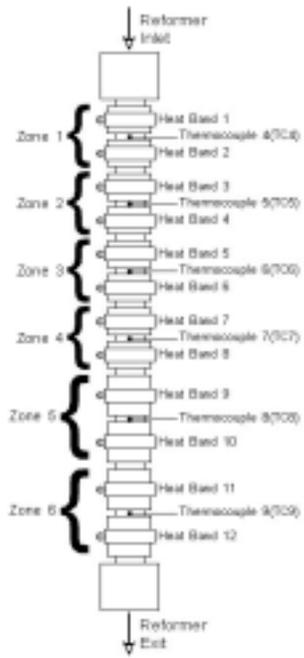


Figure 3: 1st Generation Reactor Schematic



Figure 4: 1st Generation Reactor Assembly

Figure 5: Control System Setup

Figure 6: Power Distribution Unit (PDU)

Figure 7: Heating Element Control Circuit

Figure 8: CO₂ Purge System

(not available electronically)

Summary

The 1st generation rig was a useful tool in determining the feasibility of reforming stabilized methanol using standard methanol steam-reforming operating conditions and catalysts. Attempts to reform stabilized methanol under standard conditions in the 1st generation rig were unsuccessful in the context of use in a fuel cell. It quickly became apparent that additional research should be conducted in order to determine the cause(s) of, and possible solution(s) to, the lack of ability to reform stabilized methanol at standard operating conditions. However, the existing rig was limited in its capability to modify certain parameters, particularly increasing the reaction temperature. Therefore, it was proposed that an improved rig be built (2nd generation rig) that would be a modification of the 1st generation rig with some new components, and would allow for increased flexibility with respect to operating conditions compared to the 1st rig.

2nd Generation Rig

For the 2nd generation rig, the basic premise of the 1st generation design was left unchanged- two identical flow paths, one running chemical grade methanol, the other running some form of contaminated methanol, were used to compare the reforming characteristics of two types of feedstock. In this manner, a relative “performance” level could be characterized for a contaminated feedstock relative to an uncontaminated feedstock.

Design of the 2nd generation reforming rig involved modifying the existing rig as well as adding new components to improve the functionality of the unit. A schematic of the 2nd generation experimental rig is shown in Figure 9.

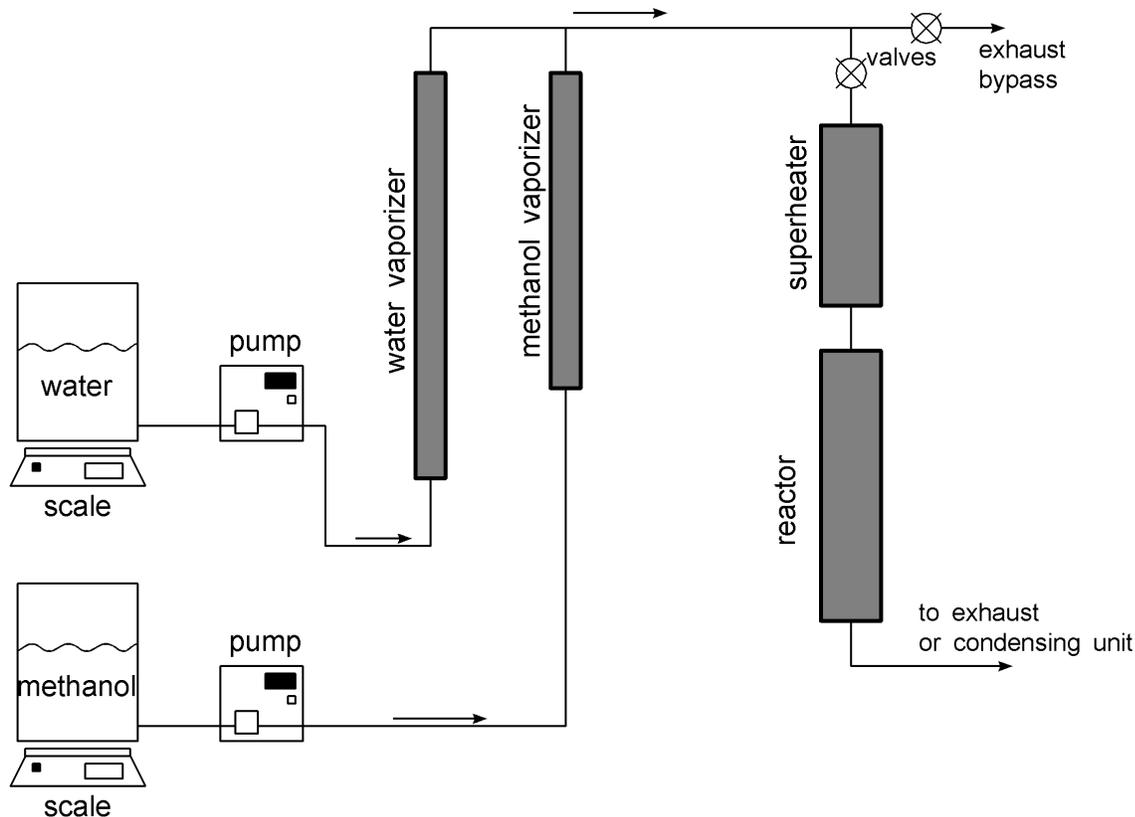


Figure 9: 2nd Generation Experimental Methanol Steam-Reformer Rig Schematic
(one of two parallel flow paths)

1st Generation Minor Modifications

Several components of the 1st generation rig were left essentially unchanged. Control hardware was for the most part identical to the 1st generation rig, with only slight modifications in some hardware components. The pumping system was changed only slightly, as the 2nd generation rig had the ability to monitor the flow rate of the liquid directly through the use of a digital scale that measured the weight of each reservoir. In addition, in the 2nd generation rig pumps were set up for remote operation and monitoring. A schematic of the pumping system used is shown in Figure 10, and a picture of the pumping sub-system is shown in Figure 11.

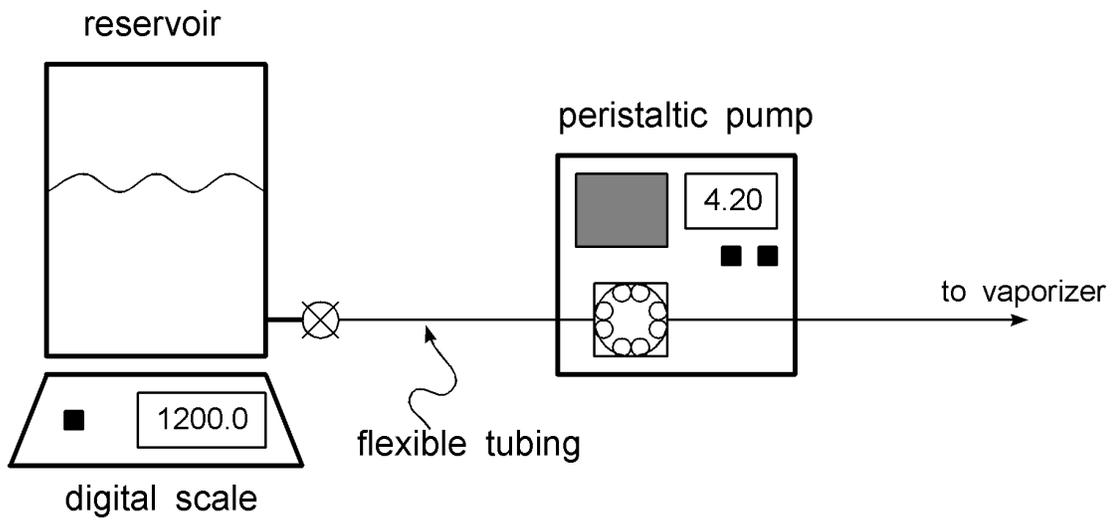


Figure 10: Pumping System Schematic



Figure 11: Pumping Sub-System Assembly

Vaporizer Design

Liquid methanol and water were pumped to separate vaporizers that vaporized and superheated the fluid to a maximum temperature of approximately 300°C. The 1st generation design for the vaporizers was found to work well, so an identical design was used in the 2nd generation rig.

Superheater Design

The superheater was a new component for the 2nd generation design. Upon leaving the vaporizers, the mixed methanol and water vapor were piped to the superheater, which was located immediately prior to the reactor assembly. The purpose of the superheater section was to raise the temperature of the methanol-water vapor to the desired operating temperature of the reactor, with a maximum temperature of 450°C. The design of the superheater was similar to that of the vaporizers, and can be seen in Figure 12. The superheater section was 15” in length, and utilized an electrically resistive ceramic beaded heater to supply heat. The surface temperature of the superheater was monitored at the approximate location shown on Figure 12 to ensure the heating element was below its maximum operating temperature. The superheater heating element was controlled based on the inlet temperature to the reactor assembly. In this way, the inlet temperature to the reactor could be controlled by the superheater assembly upstream, ensuring a predictable reactor inlet temperature. The entire superheater assembly was insulated using high temperature insulation.

Reactor Design

The reactor portion of the rig was completely redesigned compared to the 1st generation model. This was necessary due to the use of a different type of heating band

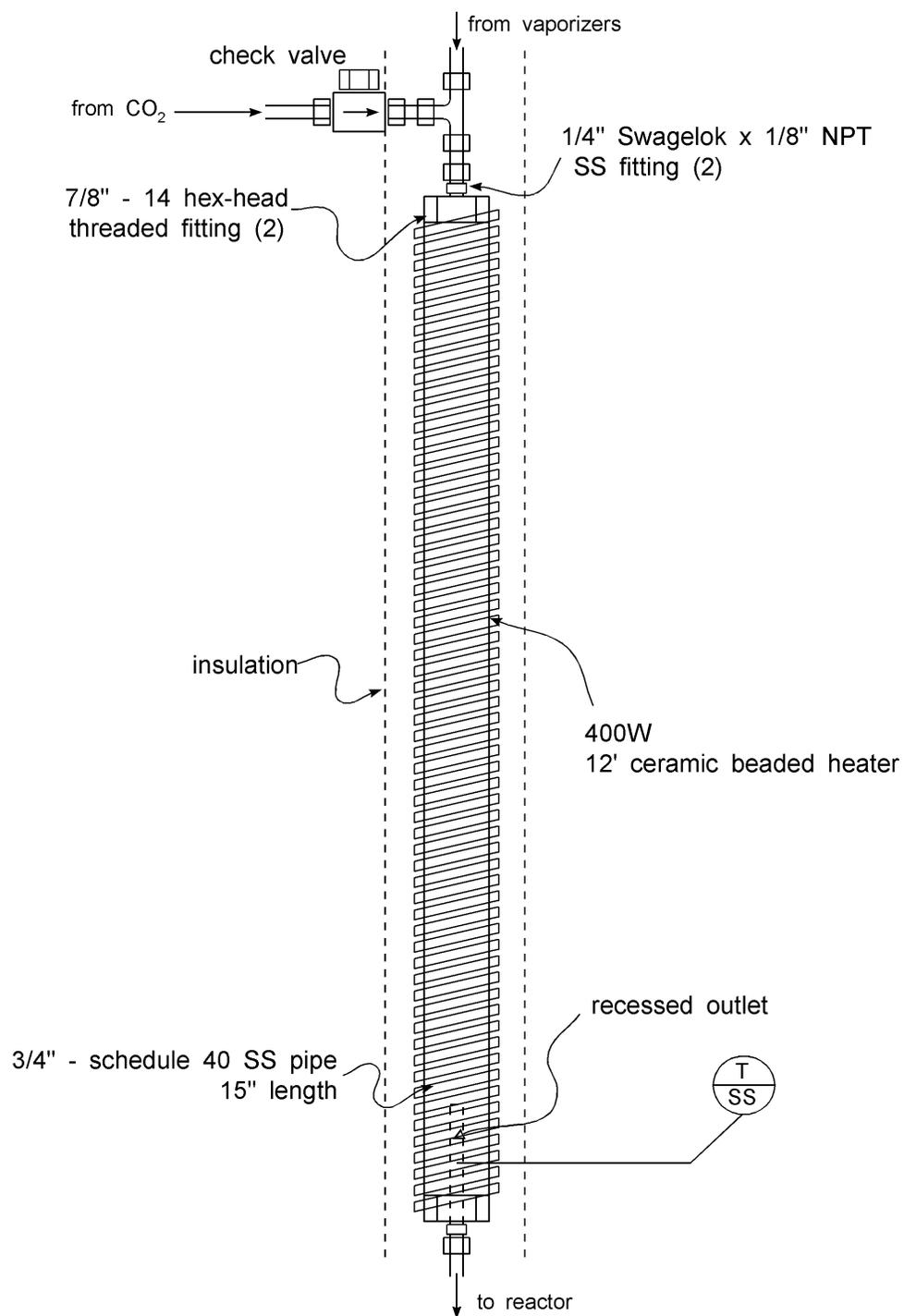


Figure 12: Superheater Assembly Schematic

that allowed for higher operating temperatures. These heaters had a maximum temperature rating of over 800°C, which was about 300°C higher than in the 1st design. A schematic of the reactor is shown in Figure 13, and a photograph of the completed reactor prior to installment on the rig can be seen in Figure 14. Six heat bands were used on each reactor, resulting in six reaction “zones”. Heat could be supplied to each of these zones individually, allowing for nearly isothermal operation. Thermocouple probes at the reactor core, as well as surface thermocouples at the outer surface of the reactor were used to collect temperature data that could be used to control heat band operation. An additional feature of the 2nd generation design was the ability to take gas samples at multiple locations throughout the reformer bed. The locations of the gas ports are shown on Figure 13, and plug valves that could be opened or closed manually controlled operation.

Condensing Unit

A condensing unit was required to cool reformat product gas. This process was necessary to condense excess water, as well as non-reacted hydrocarbons, out of the product stream. The condensing unit consisted of a condensing coil submerged in an ice water bath. This ice water bath was contained in a refrigeration unit to delay melting as long as possible. The temperature of the dry product gas exiting the condensing unit was monitored to ensure adequate cooling had occurred to condense a majority of the “condensable” products. Condensable products accumulated in a liquid trap and were collected for analysis. Figure 15 shows a schematic of the condensing unit assembly.

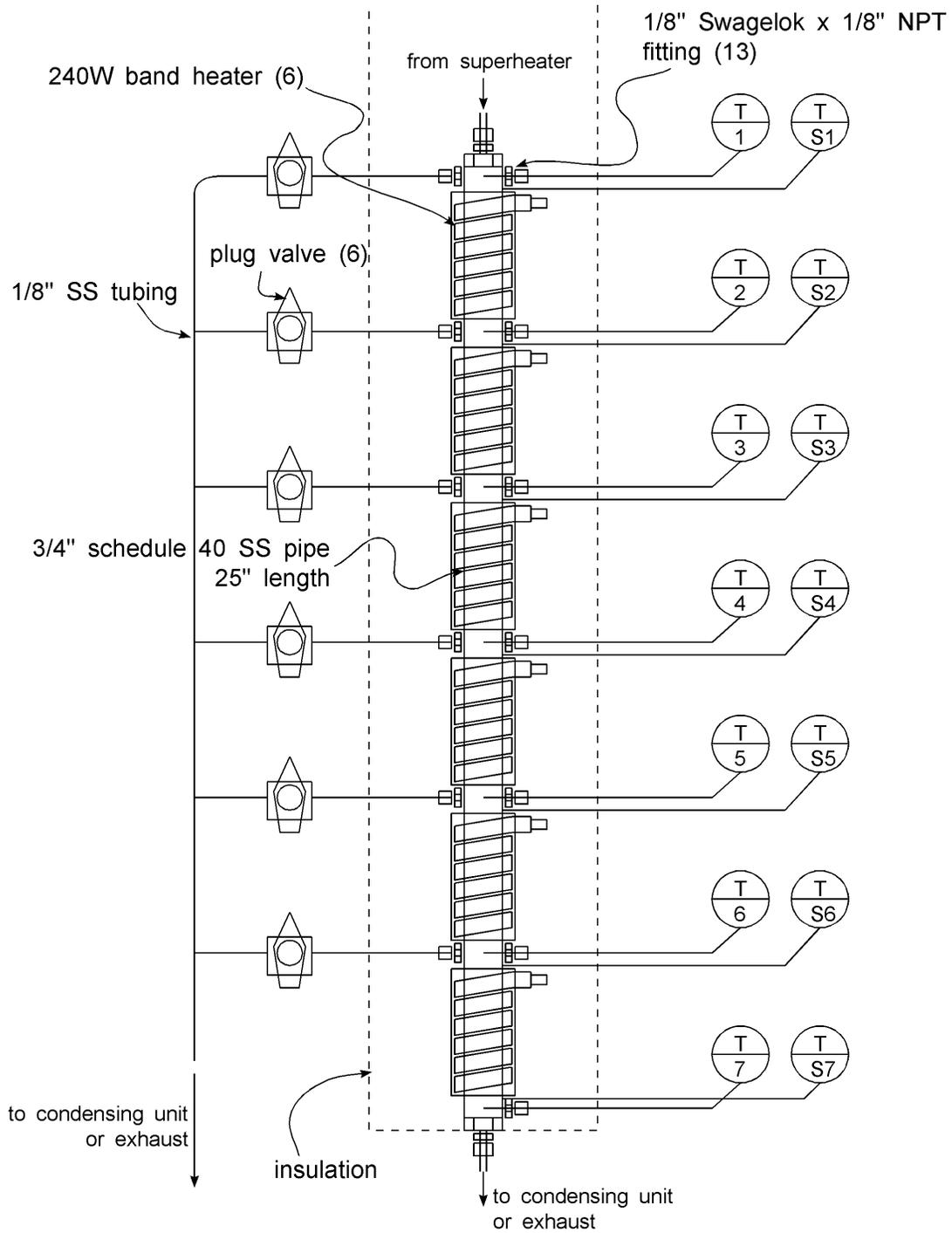


Figure 13: Reactor Sub-System Schematic



Figure 14: 2nd Generation Reactor Assembly

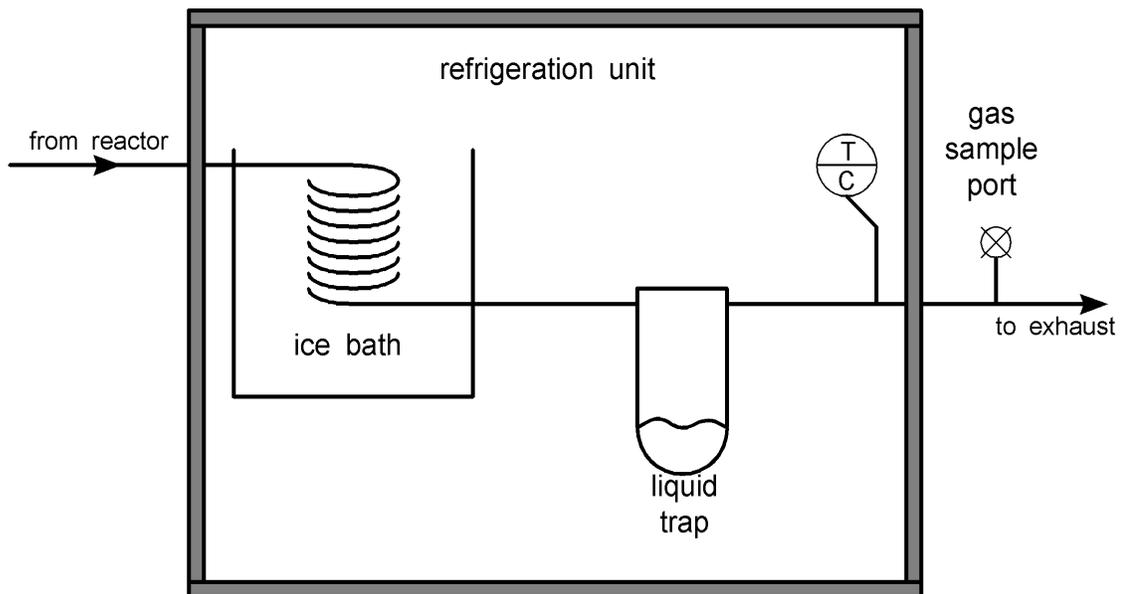


Figure 15: Condensing Unit Schematic

Control Software

Computer control programming was developed using Labview® software. This program allowed for data input in the form of thermocouple signals, and data output in the form of digital signals to rig components. In addition, data logging and storage was done automatically by the control program. For several items, including pump and exhaust fan operation, switch (on/off) logic was all that was required. Heating elements, however, could be controlled manually or automatically by control logic.

The automatic control of the heat bands utilized several different techniques in an attempt to maintain nearly isothermal operation. The first control parameter was a simple thermostatic control. Temperature settings for each of the thermocouple inputs were adjustable and controlled the operation of respective heating elements. Each heating element was controlled by two separate thermocouple readings. One thermocouple monitored the outer surface temperature of the rig, another thermocouple monitored the fluid temperature at the core of the reactor. The allowable temperature for each heating band limited the surface temperature, while the fluid temperature was set at the desired reaction temperature. Table 2 lists the thermocouple control signals for each respective heating element. Nomenclature is referred to Figure 2, Figure 12, and Figure 13. Note that OR logic was used for the surface temperature of heat bands 1 through 6, as either one of the two signals could indicate an overheating problem.

Table 2: Thermocouple Control Assignments

Heating Element	A. Fluid TC Control	B. Surface TC Control
W	W	SW
M	M	SM
S	1	SS
1	2	S1 & S2
2	3	S2 & S3
3	4	S3 & S4
4	5	S4 & S5
5	6	S5 & S6
6	7	S6 & S7

Summary

The 2nd generation rig is an experimental rig that is both versatile and practical. Figure 16 shows the complete experimental rig. The design allows for a wide range of operating conditions, yet allows for repairs and maintenance to be timely in the event of component failure. In many ways, the steam reforming system described is ideal for performing a parametric study of operational variables that might impact the steam reforming process, including the presence of hydrocarbon impurities as is the case with stabilized methanol.



Figure 16: 2nd Generation Experimental Rig

Results

Results obtained during experimentation can be divided into two categories, namely, 1st generation rig results and 2nd generation rig results. The 1st generation rig was primarily used to evaluate the feasibility of reforming stabilized methanol under standard methanol steam-reforming conditions. The 2nd generation rig was used for two purposes, first, to investigate using a higher temperature process with a different catalyst to reform stabilized methanol, and second to perform a parametric study regarding the effect of several hydrocarbon impurities on the methanol steam-reforming process.

1st Generation Rig Results

Commercial Grade Methanol Results

Initially, experimentation using commercial grade methanol was necessary to prove the functionality of the experimental rig. The results of this work were favorable, as the rig appeared to reform the methanol and water input into a hydrogen-rich gas product according to design expectations. This was evidenced by several indicators, including the following:

- i) analysis of collected condensate indicated a very low level of methanol present, corresponding to a high level of feedstock conversion
- ii) input energy required to maintain the reaction temperature was near ($\pm 10\%$) values predicted by thermodynamic calculations
- iii) dry product analyzed in gas chromatograph consisted of predicted species in near predicted quantities

These observations indicated that the experimental rig was indeed capable of reforming methanol at high conversion levels under standard process operating conditions.

Stabilized Methanol Results

During stabilized methanol experimentation, one side of the rig was used to reform stabilized methanol, while the other was used to reform commercial grade methanol. The results of experimentation were immediate and obvious. The first indication of a difference in the reforming potential of the two feedstocks was the difference in power usage by each reactor. The stabilized methanol showed a significant decrease in power consumption, which indicated a decrease in overall conversion of methanol. Further analysis of reformat obtained from the stabilized methanol process showed a decrease in carbon monoxide levels, which is consistent with more incomplete conversion. Finally, the condensable products of the reaction were analyzed and shown to have high concentrations of methanol relative to the commercial grade methanol feedstock. These observations led to the conclusion that with the current configuration (operating conditions and catalyst), the reforming process using stabilized methanol was unsatisfactory, especially for fuel cell applications. In order to ensure the validity of this conclusion, a re-evaluation was conducted under the same operating conditions using a fresh catalyst bed.

Stabilized Methanol Re-Evaluation

Each reactor was dismantled, cleaned and loaded with fresh catalyst prior to a re-evaluation of the stabilized methanol feedstock. Using the same procedure as previous experimentation, similar results were obtained during the second attempt at reforming stabilized methanol. These results seemed to confirm the conclusion that the stabilized methanol as-produced is unsuitable for reforming under standard methanol steam-reforming conditions.

Conclusions based on 1st Generation Results

At the time, it was theorized that the oil present in the stabilized methanol might act to somehow deactivate the catalyst, resulting in a reduction of feedstock conversion in the reactor. It was possible that at least some of the oil remained in liquid form at rig operating temperatures (due to its relatively high boiling point), resulting in the physical deposition of oil on the catalyst, effectively blocking catalytic sites and reducing active surface area. Development of a 2nd generation experimental rig was intended to allow for experimentation that would either support or refute this hypothesis, as well as allow for a parametric investigation that could determine acceptable levels (if any) of oil in the feedstock fuel.

2nd Generation Rig Results

Two different lines of investigation were explored using the 2nd generation experimental rig. First, higher reforming temperatures and a different catalyst were used to determine the feasibility of reforming stabilized methanol at higher temperatures than those typically associated with methanol steam-reforming. Second, a parametric study was conducted using commercial grade methanol feedstock that had been contaminated with controlled quantities of “mineral” oil and other contaminants.

Higher Temperature Reforming Results

Initial experimentation conducted on the 2nd generation rig was completed using commercial grade methanol and a standard high-temperature water-gas shift catalyst. The catalyst used was iron oxide-chromium oxide in composition and was intended for use in the range of 350°C to 450°C. In this case, the reaction temperature selected was 400°C, with all other operating conditions (including space velocity) similar to standard methanol steam-reforming conditions (as in 1st generation rig experimentation).

Results obtained during the higher temperature experimentation were (as expected) markedly different than those obtained using lower temperatures and the Cu-Zn catalyst. A summary of some results is presented in Table 3, which shows some typical results for each case (high and low temperature) under similar operating conditions (except for temperature).

Table 3: Typical Reforming Results w/ Commercial Grade Methanol

Reforming Method	Methanol Conversion	C. Dry Reformate Analysis		
		(% by volume)		
		CO	CO ₂	CH ₄
Low Temp(275°C) Cu-Zn catalyst	>99%	1-2%	23.5-24.5%	<100ppm
High Temp(400°C) Fe-Cr catalyst	94-98%	4-5%	21-23%	10-12%

Experimentation using stabilized methanol was conducted under identical conditions compared to the commercial grade feedstock. Gas chromatograph results indicated that product species were nearly identical for the two cases. However, there was a slight difference in species concentration. The concentration of methane was about 1% higher in the case of stabilized methanol, while the concentration of carbon monoxide was approximately 1% lower. The conversion level of the stabilized methanol was nearly identical to that of the commercial grade methanol. Experimentation was continued over several days for a total of approximately 20 hours of run time. Over this period, there was no noticeable change in the product gas composition or conversion level of the higher temperature stabilized methanol reforming process.

During the condensation process, some type of oil film was evident on the surface of the condensate, presumably mineral oil. This indicated that at least a small portion of the oil passed

unreacted through the reactor in vapor form. If used in a PEM fuel cell, this oil could contaminate the fuel cell anode, possibly in a very short amount of time.

Results from higher temperature reforming research seem to indicate that the reaction temperature is a significant factor when considering the effect of hydrocarbon impurities on the steam-reforming process. It is possible that raising the reaction temperature above the boiling point of the potential contaminant species is at least partially effective in reducing the contaminating effect of the offending species. However, while raising the temperature of the reaction may ensure the species will remain in vapor form, it does not necessarily result in the decomposition of the contaminant in question.

Parametric Study of Contaminated Methanol Feedstock

Experimentation conducted using stabilized methanol indicated that some type of contamination in the methanol results in an almost immediate degradation of the catalyst bed, severely limiting the ability to reform the methanol into a hydrogen rich gas. It was proposed that the “mineral” oil present in the stabilized methanol was the probable cause of the observed catalyst deactivation, although a parametric study was required to confirm this hypothesis.

Experimentation proceeded along two lines of investigation. One plan was developed to test only commercial grade methanol and establish a database that could be compared to data obtained using contaminated feedstock. A second plan was developed to research the effect of several specific contaminants on the reforming process.

Commercial grade experimentation. All commercial grade methanol experimentation was conducted using a 1.5:1 molar ratio of water to methanol feedstock. ICI-Katalco 51-3 low-temperature shift catalyst was used during all phases of investigation. Two different reaction temperatures were examined, 255 and 275 degrees centigrade. Since methanol is a liquid at room

temperature and pressure, determining a standard for the gas phase of methanol is problematic. Because of this, a space velocity based on the volumetric flow rate of liquid methanol was utilized. The range of space velocities used during the course of experimentation was roughly 0.5hr^{-1} to 3.0hr^{-1} . It was found that this range of flow rates corresponded to the region where methanol conversion begins to “drop off” for the reaction temperatures indicated. That is, at a space velocity less than 0.5hr^{-1} , the conversion of methanol is very near 100%, above 0.5hr^{-1} , conversion levels begin to diminish. Since future evaluation would presumably require some measurable change in performance, it was desirable to conduct experimentation in a region where any degradation effect would be readily apparent.

Contaminated feedstock experimentation. The operating conditions used during experimentation using contaminated feedstock were similar to those using commercial grade feedstock. There were no changes in the type of catalyst used, the temperature range used, the flow rates applied, or the water to methanol molar ratio. Three different types of contaminants were used, including a lightweight (Drakeol-10) mineral oil supplied by Air Products, isooctane, and kerosene. Each contaminant was evaluated over a range of concentrations. The mineral oil was tested in the range of 0.05% to 0.5% by weight. This concentration was determined based on the mass of methanol only, not a premix of methanol and water. Isooctane and kerosene were tested in the range of 0.1% to 1.0% by weight. In order to reduce the necessity of catalyst replacement and reduction, a single catalyst load was used over the course of experimentation for any specific contaminant. For this reason, experimentation was initiated at a relatively low concentration so that any affect on the catalyst would be gradual in occurrence. After completing experimental runs using each of the contaminants, a series of commercial grade runs were used to evaluate the potential removal of contamination from the catalyst bed. Upon completion of

experimental runs for each contaminant, the reactor was dismantled, cleaned, and charged with a fresh load of catalyst.

Parametric Study Results

One of the important issues regarding a parametric study of a chemical reaction is the control and monitoring of reaction temperature. The reaction temperature is exponentially related to the reaction rate as expressed by the Arrhenius reaction model. This emphasizes the necessity of accurately monitoring and controlling reaction temperature in order to determine reaction rates based on conversion of the reactant species. Since a perfectly isothermal reactor is not possible to obtain, changes in the temperature of the reactor in time and space must be considered in an analysis of experimental results.

Temperature

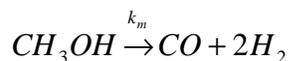
Over the course of experimentation, the uncertainty in the actual temperature from point to point and instant to instant within the reactor was probably the single largest contributing factor to uncertainty in experimental results. Figures 17 and 18 show how the temperature at one of the seven reactor thermocouple locations (along the centerline of the reactor) would change with time during a typical experimental run. In the case shown, the temperature setpoint for the reactor was 250°C, and the space velocity was 1.57hr⁻¹ (based on the liquid flow rate of methanol). Other operating conditions produced similar results with respect to the range of temperatures about the set-point. In general, the measured temperature remains between 245°C and 260°C for a majority of the run, with an exceptional spike up to near 270°C or down to 240°C in some cases.

Commercial grade results

Evaluation of commercial grade (no contaminant) feedstock was conducted at two different reaction temperatures, 255°C and 275°C. Data obtained at 255°C is presented in Figures 19 and 20.

Figure 19 shows the measured fractional methanol conversion level for separate experimental runs at varying space velocities. A linear curve fit to the data is included to emphasize the drop off in feedstock conversion as the space velocity (and therefore flow rate) increases past a certain point. For fuel cell applications, a conversion level of 0.99 (99%) would be the absolute minimum allowable conversion level without risking damage to the fuel cell stack. The dotted line on Figure 19 is intended to indicate this limit in terms of space velocity for the given reaction temperature.

Figure 20 presents a solution for the rate constant of the methanol decomposition reaction,



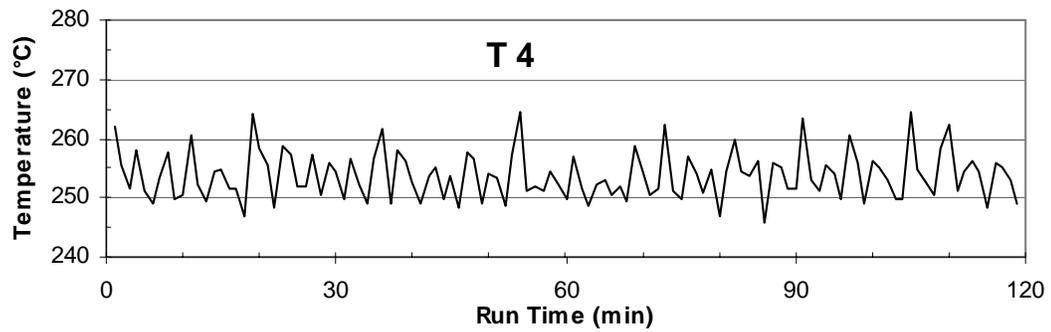
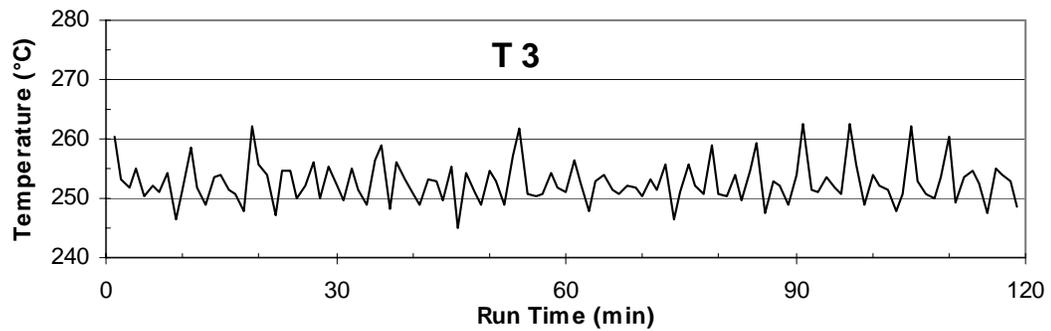
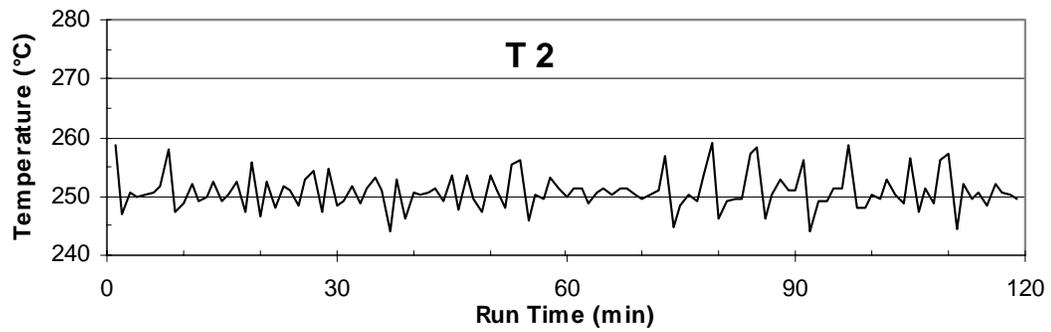
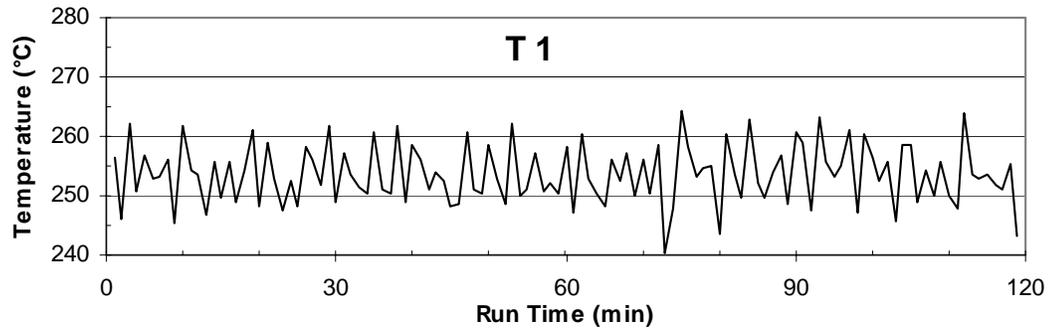


Figure 17: Typical Instantaneous Temperature Measurements over Duration of Experimental Run for Thermocouples 1 through 4

Figure 18: Typical Instantaneous Temperature Measurements over Duration of Experimental Run for Thermocouples 5 through 7

Figure 19: Fractional Methanol Conversion Using Chemical Grade Feedstock at 255°C

Figure 20: Rate Constant Solution Using Chemical Grade Feedstock over Duration of Experimental Run at 255°C

(not available electronically)

which is considered the rate limiting reaction for the methanol steam-reforming process. The solution for the rate constant was obtained using a plug flow model that was developed for this research. The rate constant could be solved numerically using fractional conversion data and the space velocity coupled with chemical equilibrium calculations. In Figure 20, the rate constant is plotted with respect to run time, which is the total time that the catalyst bed had been operational. Presumably, any degradation in the catalyst would be seen as a decrease in the rate constant over the course of operation. For the commercial grade feedstock there does not appear to be any degradation over the time period shown. This was expected, as catalyst deactivation using commercial grade feedstock is gradual and is only observed after hundreds of hours of operation.

Figures 21 and 22 show similar data as the previous figures, with the only difference being the reaction temperature of 275°C. Notice that, in general, the space velocity at 99% conversion level is nearly double that at 255°C, which emphasizes the effect of temperature on reaction rate. In addition, the slope of the linear curve fit is smaller in magnitude at the higher temperature, indicating a more gradual decrease in conversion level “drop off” with increasing space velocity. Figure 22 indicates that the rate constant is higher in the higher temperature case, as expected. Again, there is no discernible degradation of the catalyst over the time period of experimentation.

Mineral oil contaminant

Figures 23 and 24 show results obtained from experimentation using methanol contaminated with small quantities of mineral oil at a reaction temperature of 255°C. Data is presented in similar form to commercial grade data with the following exceptions:

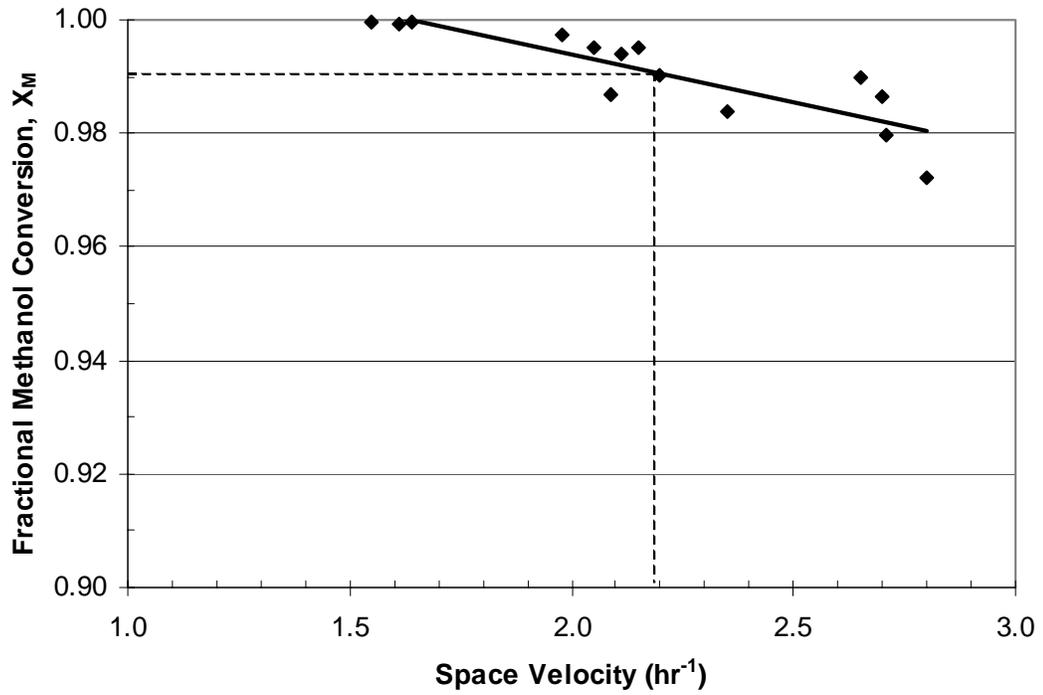


Figure 21: Fractional Methanol Conversion Using Chemical Grade Feedstock at 275°C

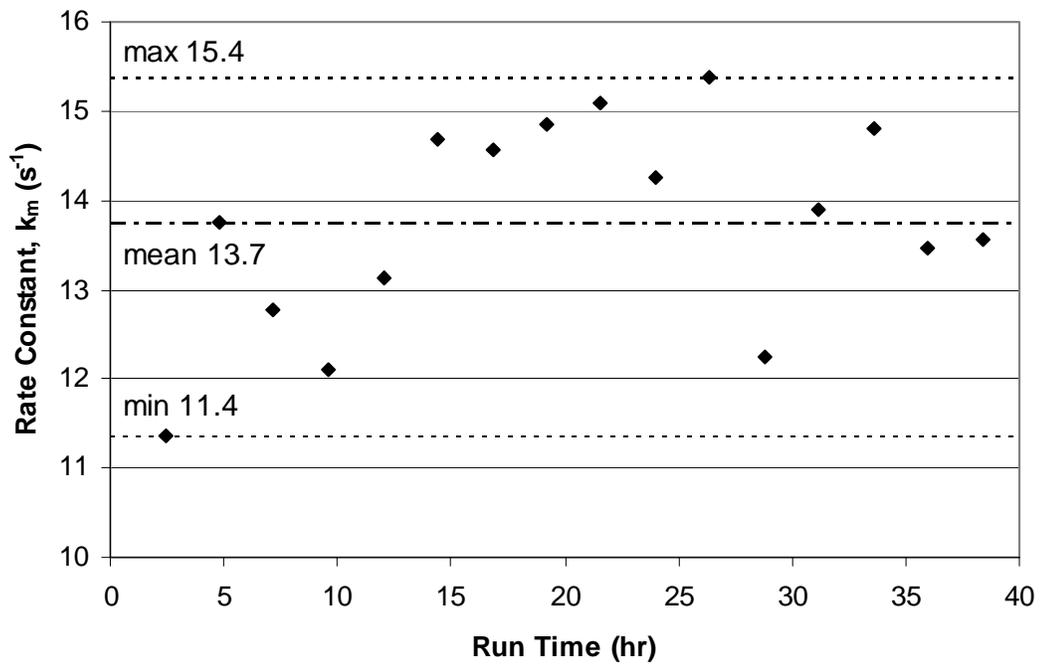


Figure 22: Rate Constant Solution Using Chemical Grade Feedstock over Duration of Experimental Run at 275°C

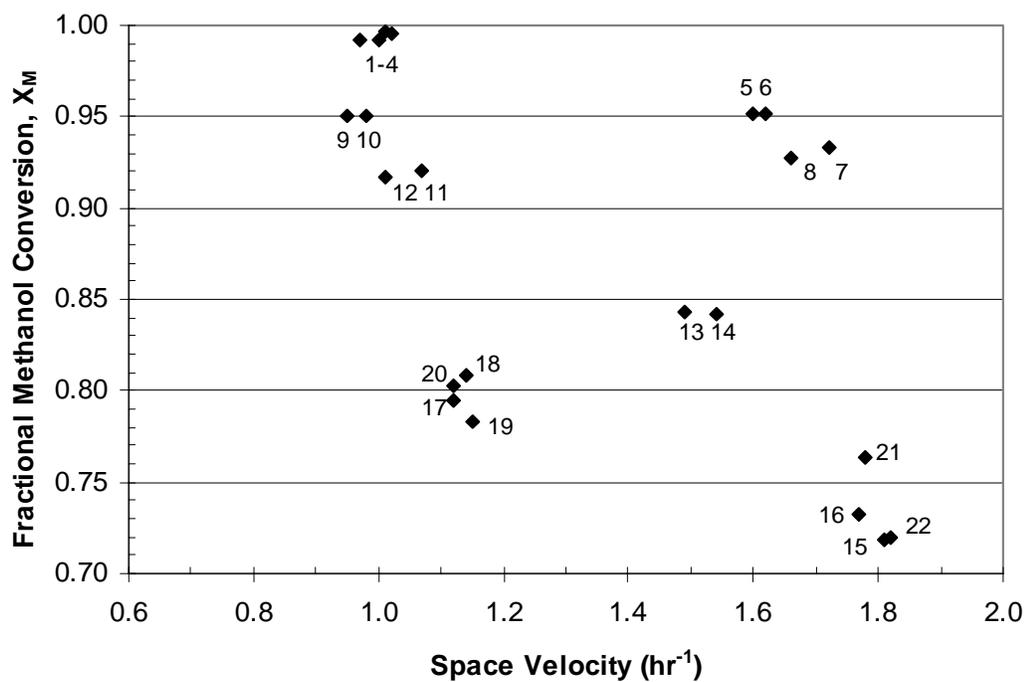


Figure 23: Fractional Methanol Conversion with Mineral Oil Contaminant at 255°C

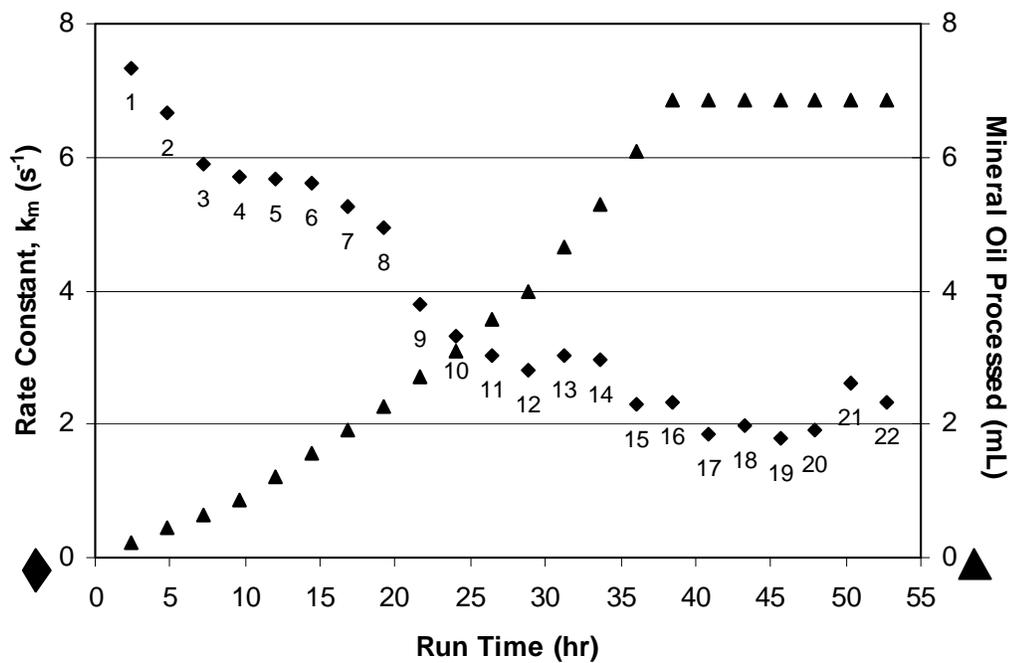


Figure 24: Rate Constant Solution and Total Volume of Mineral Oil Processed over Duration of Experimental Run at 255°C

- i) The number associated with each data point matches data between the two figures.
- ii) Figure 24 has a secondary y-axis, which shows the total amount (volume) of contaminant processed by the reactor. The term “processed” is used loosely here, as it is probable that the oil passed through the reactor unreacted.

The effect of the mineral oil on the reaction rate is immediate and apparent. The rate constant appears to be similar to the commercial grade case initially (about 8s^{-1}), but it decreases quickly over time. By approximately 20 hours of run time (runs 1-8) at a very low oil concentration (0.05%, or 0.5 grams of oil per 1000 grams of methanol) and nominal space velocities the rate constant had been reduced by nearly 50%. The data indicates that there is an additional 50% drop (75% total) in the rate constant by the 40 hour mark (runs 9-16) using similar flow rates and slightly elevated oil concentrations (0.1% and 0.5%). After completing experimentation using contaminated feedstock, non-contaminated, commercial grade methanol was used in an attempt to “clean” the catalyst (runs 17-22). Over a period of 10-15 hours of run time, there was no noticeable increase in the reaction rate constant, indicating that any positive effect this process might have is either not measurable using this rig or is very gradual in occurrence.

Figures 25 and 26 show results similar to those shown in the previous two figures, only at a higher reaction temperature. The results are very similar qualitatively, although the values are different due to the change in experimental conditions. A similar decrease in the reaction rate constant is seen over a relatively short amount of time. This indicates that over the range of temperatures examined, the contaminating effect of the mineral oil is relatively independent of temperature.

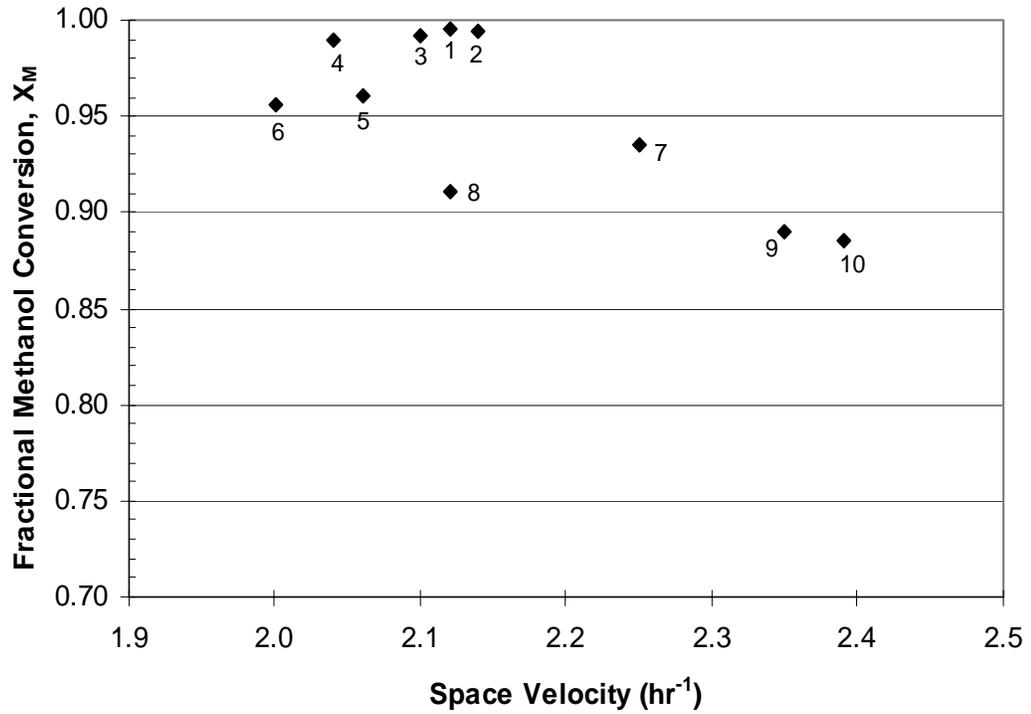


Figure 25: Fractional Methanol Conversion with Mineral Oil Contaminant at 275°C

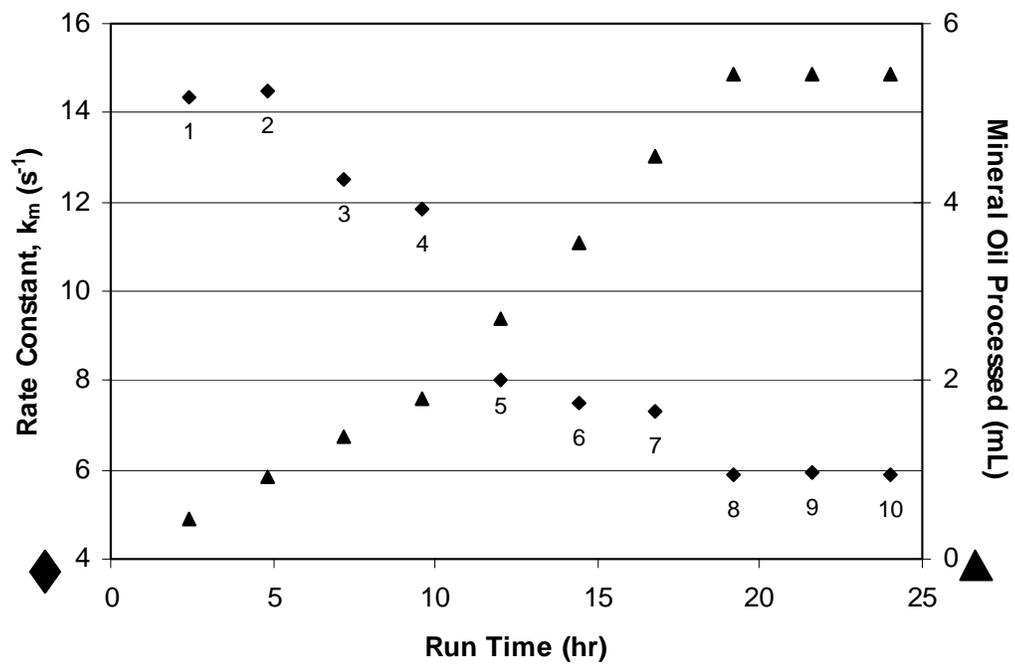


Figure 26: Rate Constant Solution and Total Volume of Mineral Oil Processed over Duration of Experimental Run at 275°C

Kerosene and isooctane contaminants

The results obtained during kerosene and isooctane experimentation are shown in Figures 27 and 28, and Figures 29 and 30, respectively.

The kerosene data seems to indicate a slight reduction in the reaction rate constant over time, although it is not as pronounced as the mineral oil case. Note also that the concentration of kerosene in the methanol was considerably higher (0.1% to 1.0%) than for the mineral oil, resulting in a much higher total quantity of kerosene “processed” for the same amount of run time. As in the mineral oil case, the use of commercial grade methanol does not appear (at least over the time period indicated) to replenish the activity of the catalyst to its original state.

The isooctane results were inconclusive. Any effect that the isooctane might have on the reforming process is either too small to measure using the existing rig, or occurs over a more gradual time scale than the experimentation conducted for this research. This is evidenced by the data shown in Figure 30, which is very similar to data obtained during commercial grade experimentation with respect to the values obtained and the “scatter” observed.

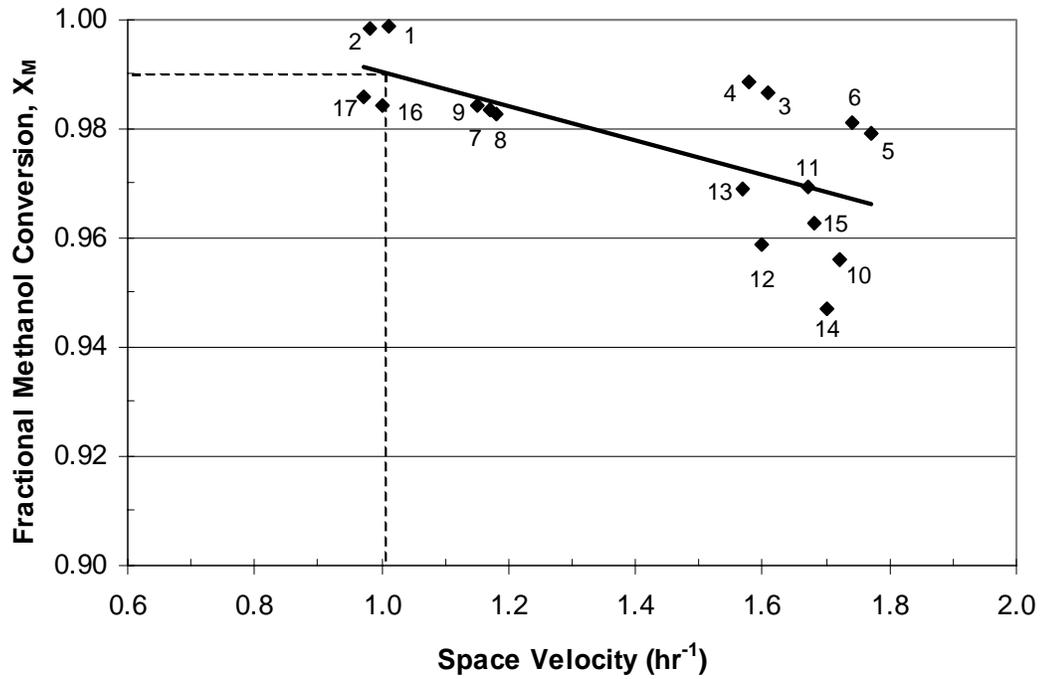


Figure 27: Fractional Methanol Conversion with Kerosene Contaminant at 255°C

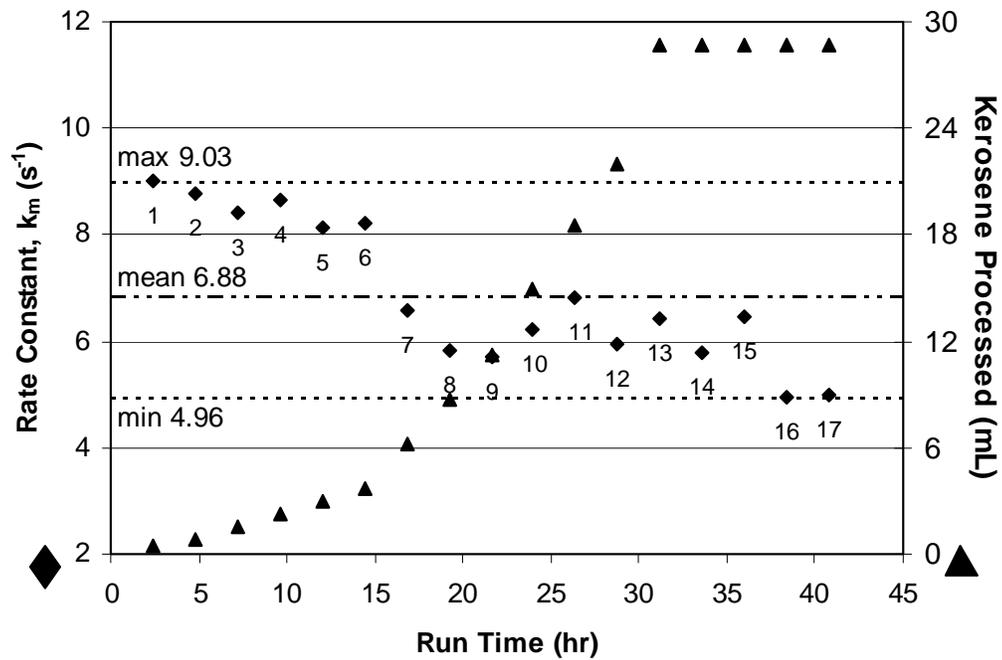


Figure 28: Rate Constant Solution and Total Volume of Kerosene Processed over Duration of Experimental Run at 255°C

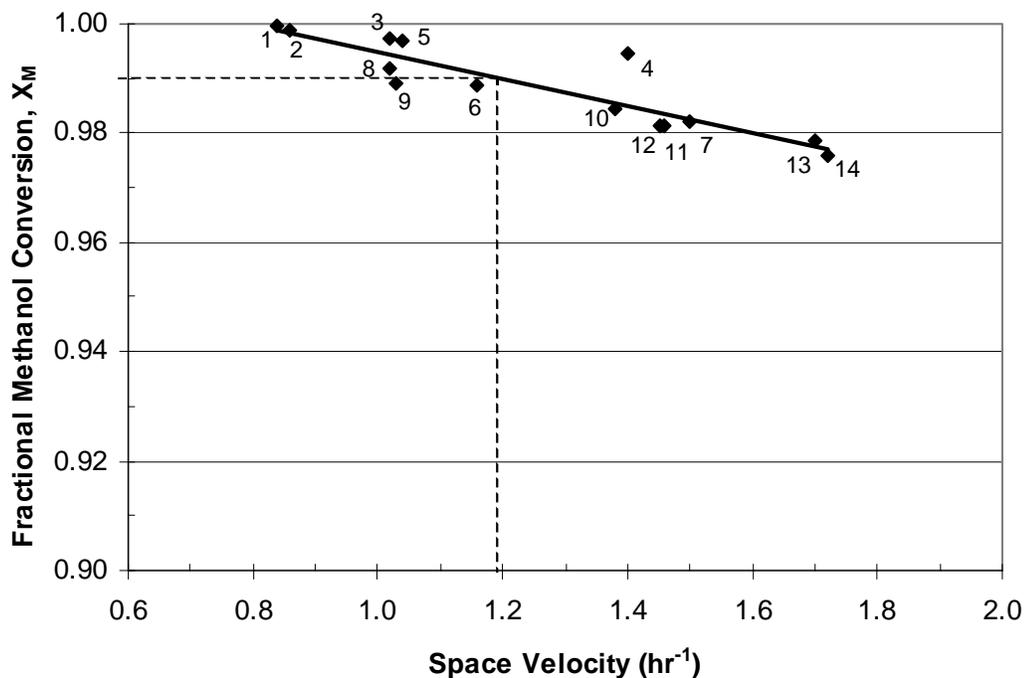


Figure 29: Fractional Methanol Conversion with Isooctane Contaminant at 255°C

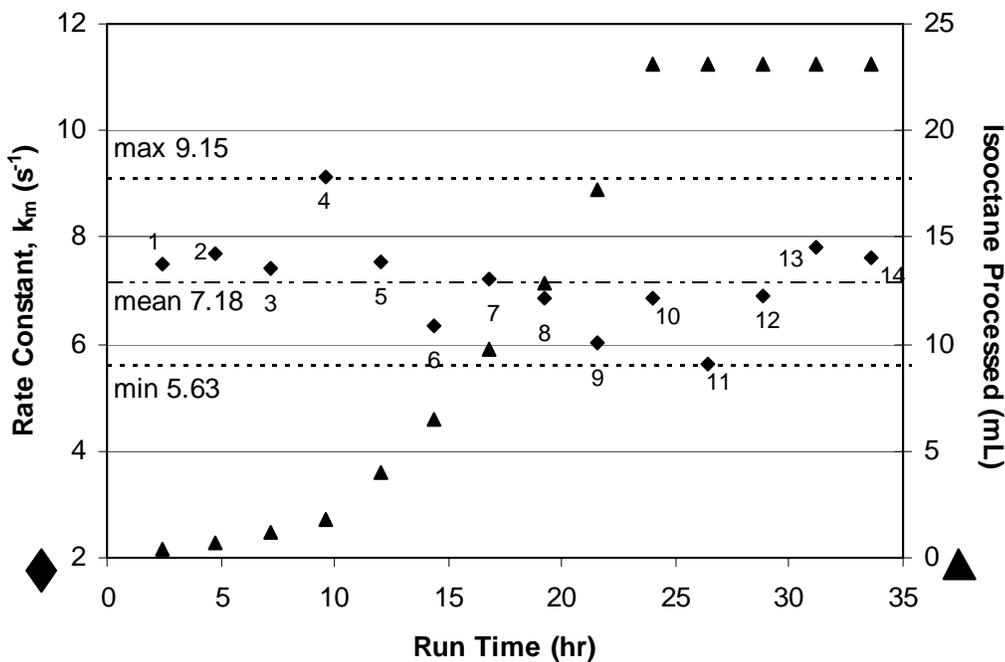


Figure 30: Rate Constant Solution and Total Volume of Isooctane Processed over Duration of Experimental Run at 255°C

Conclusions

Stabilized methanol produced by Air Products, Inc. was evaluated by the University of Florida as a candidate fuel for certain fuel cell systems. Analysis of samples of this methanol showed that

1) the stabilized methanol is over 97% pure methanol, but contains a small amount of water, small amounts of various hydrocarbons, and negligible quantities of sulfur and chlorine compounds.

2) one of the hydrocarbons contained in the stabilized methanol is an oil similar to mineral oil, apparently utilized in the methanol production process. The analyzed samples indicated that the “mineral” oil represented from 0.2% to 0.5% of the methanol by weight.

An experimental rig was successfully designed and fabricated to allow accurate temperature control as well as determination of energy input distribution for the endothermic steam reforming of methanol. The rig also allowed for the simultaneous evaluation of steam reforming of commercial grade and stabilized methanol. Results from the test rig showed that

3) at a normal steam reforming temperature (~275-285°C) for methanol using a typical low-temperature water-gas shift catalyst, the catalyst quickly became deactivated on the side processing the stabilized methanol, while the side processing commercial grade methanol proceeded without apparent deactivation.

4) the deactivation of the catalyst was caused by the physical deposition (coating) of the contaminant “mineral” oil on the catalyst pellets.

5) the “mineral” oil coating was apparently due to the incomplete vaporization of the oil at the reformer temperatures used, thus passing essentially as an unreacted liquid through the reformer catalyst bed.

A subsequent modification to the test rig involved replacing the CuO/ZnO (low temperature) catalyst with an Fe-Cr (high-temperature shift) catalyst that could be operated at higher temperatures (up to 450°C). Results from this experimentation showed that

6) at the higher temperatures, most of the mineral oil passed through the catalyst bed in vapor form with little evidence of catalyst degradation.

7) even though the reformer catalyst was relatively unaffected by the oil, there was some evidence of oil in the condensate downstream of the reformer, suggesting that at least some of the oil was passing through the reformer unreacted.

8) any remaining unreacted oil in the reformat would likely condense out at the operating temperature of a phosphoric acid fuel cell stack (~200°C), and would surely condense in a PEM system stack (<100°C). Such oil condensation in the stack would be extremely detrimental.

9) at the higher reforming temperature (~400°C) using the Fe-Cr catalyst, some of the advantages of typical methanol steam-reforming are lost resulting in a lower hydrogen yield as well as a greater concentration of carbon monoxide in the reformat.

With respect to the primary issue of the suitability of Air Products stabilized methanol as a suitable fuel for fuel cell systems, the following conclusions can be reached:

10) With the blend of specie as received and evaluated by the University of Florida, stabilized methanol is not an acceptable fuel for typical low temperature steam reforming systems.

11) Using a higher temperature catalyst and operating at approximately 400°C, the stabilized methanol might be an acceptable fuel. Additional investigation as well as system modifications (provide a more suitable catalyst and/or additional treatment of the reformat) to reduce the CO concentration and improve the H₂ yield would be required. It would also be necessary to ensure that no oil reached the fuel cell stack.

12) A higher temperature steam reforming configuration as described above would also require additional overall system analyses and optimization studies to determine if the system could be competitive with a low temperature reforming system on an energy utilization and economic basis.

13) Although no experimentation other than for steam reforming was conducted, based on those observations it seems likely that the stabilized methanol could be (possibly) used satisfactorily in an autothermal reformer for phosphoric acid or a PEM fuel cell system. At the even higher temperatures of partial oxidation (POX) reformers, no problems due to fuel composition would be expected.

14) There is no reason to believe that there would be fuel composition issues when using stabilized methanol in high temperature applications such as molten carbonate or solid oxide fuel cell systems.

Recommendations

Methanol has been shown to be an excellent fuel for transportation applications of phosphoric acid and PEM fuel cell systems. A primary reason for this is that methanol can be reformed at much lower temperatures than other hydrocarbon fuels, thus providing a lower CO concentration and a more favorable H₂/CH₄ balance in reformat. The result is less aftertreatment (typically none for a phosphoric acid stack), and a more efficient fuel processing system.

Clearly, as-produced stabilized methanol will require a higher processing temperature to avoid catalyst contamination. It is therefore important to determine whether the higher processing temperature will cause stabilized methanol to lose its advantages over other hydrocarbon fuels. To accomplish this, it is recommended that the following actions be taken:

- 1) Perform additional experimentation with steam reformation of the stabilized methanol with reformer temperature, steam/methanol ratio and catalyst composition as primary independent variables. The purpose of this research would be to determine the combination of variables that would yield no oil downstream of the reformer while providing the best H₂ yield and lowest CO concentration in the reformat.

- 2) Perform systems studies to determine the effect of higher temperatures and appropriate reformat aftertreatment on the potential advantages of methanol as compared to other hydrocarbon fuels.

3) Air Products should investigate the feasibility (and additional cost) of removing the mineral oil from the stabilized methanol, at least for the portion that would be used for PEM and phosphoric acid fuel cell system applications.

Appendix A

The following appendix contains copies of the analysis of stabilized methanol from three different sources.

- Pages 48-49 Atlantic Analytical Laboratory, Inc.
Whitehouse, N.J
- Pages 50-51 Intertek Testing Services
Seabrook, TX
- Page 52 LaPorte, TX Process Demonstration Unit
(supplied by Air Products)

(not available electronically)

Appendix B

This appendix contains results taken from the gas chromatograph and are typical of the following experimental conditions:

Page 54	TCD chromatogram Low-Temperature Operation using Commercial Grade Methanol
Page 55	FID chromatogram Low-Temperature Operation using Commercial Grade Methanol
Page 56	TCD chromatogram High-Temperature Operation using Commercial Grade Methanol
Page 57	FID chromatogram High-Temperature Operation using Commercial Grade Methanol

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