

THE EFFECTS OF MOLAR FLUX, PRESSURE, AND
PRODUCT GASES ON THE STABILITY OF
MOLYBDENUM CARBIDE DURING STEAM
METHANE REFORMING

By
ROBERT LOWRY MCCAULEY

A thesis submitted in partial fulfillment
of the requirement for the degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

WASHINGTON STATE UNIVERSITY
Department of Chemical Engineering

DECEMBER 2005

To the Faculty of Washington State University:

The members of the Committee appointed to examine the thesis of ROBERT
LOWRY MCCAULEY find it satisfactory and recommend that it be accepted.

Chair

ACKNOWLEDGEMENT

Without a doubt I would not have gotten to this point without the love and support of my wife Melody. She has stood at my side through this whole process and deserves the main credit for my accomplishments. I thank my children Logan, Kalyn, and Brayden for their love and encouragement. My wife and I plunged into the challenges of children and education at the same time and have emerged happier and stronger on the other end. I am grateful for the counsel and support of my advisor William J. Thomson. He is a great teacher and he has helped me to grow as a chemical engineer and as a person. I am proud to be his final grad student. I recognize all of my fellow lab mates past and present. I have learned from all of them. I thank the Washington State Chemical Engineering department that has given me courage and confidence to face any new problem. I thank my mother for her love and example. She has always taught me the importance of earning an education. I appreciate my in-laws for their kind support of my family and me during this process. I thank my brothers, sister and extended family that have all taught me and loved me through out my life. Finally I recognize my Heavenly Father's hand in my life. He has blessed me with more than I could ask for. I am grateful for his son Jesus Christ, the Master Teacher, and hope to be His student for the rest of my life.

THE EFFECTS OF MOLAR FLUX, PRESSURE, AND PRODUCT GASES ON THE STABILITY OF MOLYBDENUM CARBIDE DURING STEAM METHANE REFORMING

ABSTRACT

Robert Lowry McCauley, MS

Washington State University

December 2005

Chair: William J. Thomson

The oxidation resistance of bulk Mo_2C was tested in a plug flow reactor during steam methane reforming (SMR) at varied molar fluxes, pressures and product co-fed compositions. Lowering the total molar flux caused the oxidation temperature of Mo_2C to be reduced; oxidation deactivates Mo_2C . Increasing the pressure also decreased the oxidation temperature until a pressure of 5 bar is reached. Raising the pressure beyond this point yielded no further decrease in the oxidation temperature. Low molar flux and high pressure are both lower the mass transfer signifying that Mo_2C is stabilized for SMR when the mass transfer is lowered. SMR product gases have been found to stabilize Mo_2C . During low mass transfer conditions the concentrations of the SMR products would be expected to increase near the catalyst particles thus increasing stability. The lowest observed oxidation temperature due to molar flux and pressure effects was 875 ± 5 °C at $0.131 \text{ mol/cm}^2\text{-hr}$ and 5 bar. Co-feeding H_2 and CO was also found to lower the stable operating temperature for SMR. At low concentrations of H_2 and CO, 6% to 26 %,

there was a distinct deactivation temperature that was not a result of oxidation. Elevated H₂ concentrations during these deactivations suggest that coke formation due to the cracking of CH₄ was the cause of deactivation. An additional effect of co-feeding H₂ and CO, was a depressed conversion when compared to a product free feed. This loss of conversion was due to both thermodynamic and kinetic reasons. At higher concentrations of co-fed H₂ and CO, 47% and 46% respectively, there was no deactivation temperature at all. This allowed SMR to be conducted at 850 °C. That temperature is considered an important industrial benchmark because it allow for the use of conventional reactor materials. The best conversion at 850 °C was .53 +/- .0075 with 47% co-fed H₂, 5 bar, and a molar flux of 0.173 mol/cm²-hr.

TABLE OF CONTENT

ACKNOWLEDGEMENT	iii
ABSTRACT.....	iv
LIST OF TABLES.....	viii
LIST OF FIGURES	ix
1 INTRODUCTION	1
1.1 Background.....	1
1.2 Previous work	2
1.3 Current study.....	5
2 EXPERIMENTAL.....	6
2.1 Catalyst characterization.....	6
2.2 Equipment.....	6
2.3 Methods.....	8
3 RESULTS	13
3.1 Equilibrium considerations	13
3.2 Blank experiments	15
3.3 Molar flux experiments.....	15
3.4 Pressure experiments	17
3.5 Co feeding H ₂ and CO	17
4 DISCUSSION AND CONCLUSIONS	23
4.1 Comparison to previous results.....	23

4.2	Effects from co-feeding	24
4.3	Future work.....	26
5	REFERENCES	45
	APPENDIX.....	46
A.	Equipment	47
B.	Run catalogs	49
C.	Thermodynamic equilibrium calculations in MathCad.....	52

LIST OF TABLES

	Page
1. Operating conditions for molar flux experiments	9
2. Operating conditions for pressure experiments	11
3. Concentrations of H ₂ and CO used during experiments	12
4. The thermodynamic conversion and actual conversion at the lowest stable temperatures	14
5. Normalized H ₂ /CO ratios during deactivation of co-fed and non co-fed experiments.....	19
6. CO/CO ₂ ratios at 870 °C for 46% CO.....	22

LIST OF FIGURES

	Page
Figure 1. SMR oxidation deactivation experiment and the equilibrium conversions.....	29
Figure 2. Typical molar flux experiment.....	30
Figure 3. Photograph of oxidized Mo ₂ C bed after a SMR experiment.....	31
Figure 4. XRD scan comparison of Mo ₂ C and MoO ₂ to an oxidized Mo ₂ C bed.....	32
Figure 5. Molar flux deactivation map.....	33
Figure 6. Pressure deactivation map.....	34
Figure 7. Comparison of co-fed H ₂ experiments.....	35
Figure 8. Comparison of co-fed H ₂ experiments.....	36
Figure 9. Carbon conversions at various H ₂ and CO concentrations compared to the thermodynamic equilibrium at 890 °C.....	37
Figure 10. Deactivation temperatures at various levels of H ₂ and CO.....	38
Figure 11. XRD scan comparison of Mo ₂ C and MoO ₂ to a deactivated Mo ₂ C bed.....	39
Figure 12. 23% H ₂ co-fed experiment to test long term stability.....	40
Figure 13. High concentration CO and H ₂ experiment that did not deactivate.....	41
Figure 14. 46% CO experiment with long term stability test.....	42
Figure 15. Comparison of DMR and SMR molar flux maps.....	43

	Page
Figure 16. Comparison of DMR and SMR pressure maps.....	44
Figure A1. Experimental packed bed reactor system.....	47
Figure A2. View of quartz reactor tube inside of the heater and pre-heater from Figure A1.....	48

1 INTRODUCTION

1.1 Background

Historically the world has been moving towards increasingly hydrogen rich fuels¹. A progression can be seen in moving from wood (hydrogen to carbon ratio H:C = .1), to coal (H:C = 1), to oil (H:C = 2), and most recently to natural gas (H:C = 4)². This progression has led to the current push for a hydrogen energy economy. A large portion of the fuel in the world is used to produce electricity. With the world's growing demand for electricity the fuel cell has gained prominence as the ideal way to use hydrogen fuel. One of the greatest challenges in using hydrogen as a fuel is determining the best way to generate it. Ideas on this topic range from thermal decomposition of water with nuclear energy to hydrolysis of water with solar power to the reforming of hydrocarbons with steam. Currently the most practical and least expensive way to produce hydrogen comes from reforming.

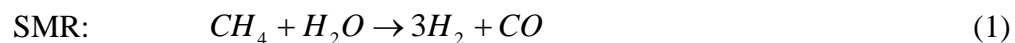
If reforming is to be used for producing hydrogen, there is an underlying question that must be answered first. Are there economic benefits from making hydrogen from hydrocarbons instead of simply burning hydrocarbons for energy needs? This is a complex question that needs to be approached on many fronts. One place where hydrogen fuel may be beneficial is in motor vehicles. Car engines are not nearly as efficient with gasoline as fuel cells are using hydrogen³. The other side of this choice is that it takes more energy to make hydrogen than it does to make gasoline. The best choice is found in

weighing both factors together. For hydrogen fuel to be practical fuel cell efficiency must be maximized and the cost of reforming hydrocarbons must be reduced.

Nickel is the major catalyst used in industry for reforming⁴. The major disadvantages of nickel as a reforming catalyst, is that it is very susceptible to coking and poisoning by sulfur compounds. In order to prevent coking, three to four times the stoichiometric requirement of steam must be used. To prevent sulfur poisoning, the hydrocarbon feed stock must be stripped of sulfur prior to being reformed. Both of these procedures add to the cost of the reforming process. A catalyst that is resistant to coking and sulfur poisoning would create a more cost effective process. Noble metals have shown high activity for reforming⁵⁻⁶, while being resistant to coking and sulfur⁷. However, they are so expensive that using them would offset any economic benefit⁸. Recently, molybdenum carbide (Mo_2C) has been shown to have reforming activity^{7,9-15}, in addition to being able to resist coking with only stoichiometric amounts of steam^{7,9-10, 13-15} and tolerate sulfur in the feed⁷. It also has about the same cost as nickel⁸. Therefore, it has promise to bring down the cost of generating hydrogen.

1.2 Previous work

In 1997, Mo_2C was discovered to be active for steam methane reforming (SMR)⁹. The SMR reaction is shown here:



In a follow up study, Claridge et al¹⁰ concluded that Mo₂C was only active at high pressures, whereas the catalyst were converted to MoO₂ at atmospheric pressure by the general oxidation reaction shown below:

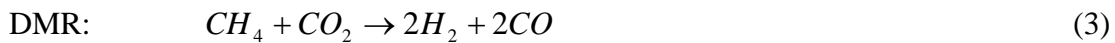


The oxidant in this case was steam. Oxidation is detrimental because MoO₂ is not active for reforming. It was proposed that the oxidation was due to kinetic effects where carburization was faster than oxidation at high pressure but slower at low pressure¹⁰. However, in the same paper however it was shown that oxidation took place faster while increasing space velocity at a constant pressure¹⁰. This was a curious observation because the space velocity should have no separate effect on the deactivation kinetics (space velocity is defined in Appendix B). Later, a group at Haldor-Topsoe found that it was possible to have stable reforming, no deactivation with respect to time, with Mo₂C by back mixing the products into the reactor at a very high recycle ratio of about 360¹². Follow-up work by Darujati et al. took the next step by studying the effect of various gas compositions on the oxidation of Mo₂C using a dynamic X-ray diffraction system¹⁴. The various gases (CH₄, CO₂, CO, H₂, and steam) were added in situ while varying the temperature. From this study¹⁴ it was discovered that there is an oxidation stability ratio between reforming products and oxidants as shown here:

$$\frac{P_{H_2} + P_{CO}}{P_{H_2O} + P_{CO_2}} = \text{stability_ratio} = R_s \quad (1)$$

It was found that, if the stability ratio was greater than 0.8 then Mo_2C would not oxidize regardless of the temperature or pressure. This showed conclusively that the reforming product gases are necessary for stability. It was also found that CH_4 did not play a role in the prevention of the oxidation of Mo_2C ¹⁴.

This was followed by an investigation to understand the effects of sulfur poisoning on Mo_2C ⁷. In this study it was found that sulfur does poison Mo_2C , but not catastrophically. Using auto thermal dry reforming conditions in the presence of 250-ppm dimethylsulfide (DMS), the catalyst suffered only a 10% loss of conversion. At dry methane reforming (DMR) conditions, the DMS caused a greater deactivation; approximately 35% below sulfur free conversion, but this deactivation was reversible. The DMR reaction is shown here:



This was the first evidence that Mo_2C is resistant to sulfur poisoning during reforming⁷.

Due to Claridge's and Darujati's work, LaMont and Thomson undertook a study of the effects of mass transfer on the stability of Mo_2C ¹⁵. To do this they conducted DMR experiments where either the molar flux or pressure was varied while holding the other parameters constant. From this set of experiments, they were able to show that mass transfer-limited conditions improved the stability of Mo_2C by preventing oxidation. This was attributed to the fact that under mass transfer limited conditions, the local

concentration of products is higher around the Mo_2C particles thus preventing oxidation¹⁵.

1.3 Current study

The purpose of the study reported here was to further the progress of Mo_2C as a reforming catalyst by studying the requirements for stable reforming under SMR conditions. SMR is known to be more prone to Mo_2C oxidation than DMR¹³⁻¹⁴. This topic is important to understand because SMR produces a higher hydrogen yield than DMR. All of Lamont's studies were done with DMR and while Darujati's work used steam, the concentrations were not under optimal reforming conditions. Claridge's group also conducted SMR experiments but they were only able to find one stable SMR condition because they did not understand the essential stabilizing action of the product gases. The goal of this study was to determine the conditions (molar flux, pressure, temperature) under which the Mo_2C catalysts would remain stable during SMR. A secondary consideration was to find out if Mo_2C could be used for SMR at a target temperature of 850 °C. This is a temperature typically used in nickel catalyzed reformers and is an important benchmark because it is low enough to allow for the use of conventional reactor material. Additionally, the effect of co-feeding H_2 or CO during SMR was also explored.

2 EXPERIMENTAL

2.1 Catalyst characterization

The molybdenum carbide used in this study was a bulk catalyst purchased from Alfa Aesar, lot #K17J11 (99.5% metals purity, <325 mesh). Prior characterization of this catalyst, via X-Ray powder diffraction, shows it to be pure β -Mo₂C and to have an average crystallite size of 40 nm, as determined by the Debye-Scherrer method¹⁴. The BET surface area was <5 m²/g, and the carbon content was 6.200 ± 0.001 wt% (the stoichiometric value is 5.9 wt%). This low surface area catalyst was chosen based on earlier work in our laboratory. It has been shown that high surface area Mo₂C yields no better reforming performance than the low surface area catalyst mentioned above¹³. All experiments were conducted with a bed of pure Mo₂C.

2.2 Equipment

All reforming reactions were performed in a bench scale packed bed reactor, which can be seen in Figure A1 in Appendix A. The reactor consisted of a quartz tube (ID = 7.0 mm, OD = 9.0 mm, L = 57.2 cm), that was electrically heated using a preheater, an oversized quartz tube wrapped with heating tape and insulation, and a 12" 850 W Watlow ceramic fiber heater that was insulated and wrapped in tin foil. The heating tape was controlled using an Electrothermal heating tape controller and the Watlow heater was controlled with a Cole Parmer Digi-Sense temperature controller. The control temperature was measured at the bottom of the Mo₂C bed with a high temperature type K thermocouple. A secondary thermocouple was placed on the outside of the quartz reactor,

located at the top of the bed. The pre-heater was operated at 280 °C and the main heater was operated from 820 to 980 °C. A bed of silicon carbide (SiC) was placed in the preheating zone to facilitate vaporization of the water and mixing with the CH₄. The Mo₂C bed was held in place by quartz wool plugs with Mo₂C loadings ranging from 1.5 to 2.9 g. A detailed picture of how the reactor tube was loaded can be seen in Figure A2 in Appendix A.

The inlet gas flow rates were set using a bubble flow meter and controlled with Brooks 5850 E series mass flow controllers. The water was introduced using a Cole Parmer syringe pump and a 5 ml or 2.5 ml Hamilton Gastight syringe. The reactor pressure was controlled using a Tescom backpressure regulator. The outlet gas stream from the reactor was run through an ice bath before entering the gas chromatograph (GC). The effluent gas was analyzed using a Carle GC that was outfitted with a Hayesep D column held at 50 °C and operated in a 10% H₂ 90% He carrier gas. The output from the GC is a characteristic peak for each species in the gas that is sampled. The peak area for a species is proportional to the mole fraction of that species in the sample. A 4-point calibration was done for each SMR reactant and product species, except for H₂O which could not be measured by the GC. This calibration was done using a standard gas cylinder and a CH₄ cylinder. The error in the calibrations was +/- .00325 mole fraction. The source of the error was from taking the flow rate measurements with a bubble flow meter during the calibration.

X-Ray diffraction was used to determine any bulk crystalline changes in the spent catalyst samples. This was accomplished in a Phillips X'Pert XRD System (Co K α source) that was equipped with a RAYTECH Position Sensitive Detector. The scans were conducted at ambient pressure and temperature in air through a range of 20 °2 Θ to 100 °2 Θ .

2.3 Methods

The Mo₂C was loaded into the quartz tube at a height of 8 inches above the ultra-torr fitting. It was supported on the top and bottom by a layer of quartz wool. The SiC was then loaded into the top of the reactor tube on a layer of quartz wool. The quartz reactor was then placed in the heaters and pressurized with CH₄ for two hours during the molar flux and pressure experiments. During the co-feeding experiments, the reactor was pressurized and purged with CH₄ and either H₂ or CO. Once oxygen was no longer observed with the GC, the heater was started and ramped to the desired temperature at a rate of 20 °C per minute. When the temperature was within 25 °C of the set point temperature the steam was introduced into the system. This procedure was common to all of the experiments.

One set of experiments was conducted in which the molar flux was varied while holding the space velocity and pressure constant. The molar flux was varied by changing the input flow rate or by changing the inner reactor diameter (ID). It was not possible to change the molar flux by only varying the flow rate because it would cause an excessive pressure drop across the bed. The space velocity was held constant at 3000 hr⁻¹, by

adjusting the catalyst loading to match the input flow rate. The pressure was held constant at 5 bars and the CH₄/steam ratio in the feed was 1.06 for all of the experiments. The specific flow rates (CH₄ and steam), catalyst loading and reactor ID are listed in Table 1:

Table 1. Operating conditions for molar flux experiments

Molar flux (mol/cm ² *hr)	Reactor ID (mm)	Total flow rate feed (SCCM)	Mo ₂ C loading (grams)
.131	7	18.8	1.52
.173	7	24.8	2.0
.25	7	35.9	2.9
.355	5	26	2.1

For these experiments it was desired to determine a deactivation temperature for the catalyst. In this case deactivation means the oxidation of Mo₂C. For clarity, the term oxidation temperature will be used when oxidation was the source of deactivation. The term deactivation temperature will be used when the deactivation was caused by some other mechanism such as coking. The reactor was ramped to a stable SMR temperature and then held for about an hour. At this point the temperature was then lowered, in 5 °C to 20 °C increments, depending on the desired resolution for the deactivation temperature and length of the experiment. The temperature step size was not always constant through an experiment. Typically larger steps were used at higher temperatures with smaller steps being taken near the oxidation temperature. The temperature was held constant for about 50 minutes while taking two to three GC scans and flow readings. This procedure was repeated until deactivation was observed from oxidation or other causes. The reaction

was considered to be deactivating when the carbon conversion dropped steadily throughout the 50 minute time period. The carbon conversion was calculated using a carbon balance on the GC measurements with the following equation:

$$\text{Carbon_Conversion} = \frac{y_{CO} + y_{CO_2}}{y_{CO} + y_{CO_2} + y_{CH_4}} \quad (2)$$

This equation assumes that CO was formed during the SMR reaction and that some of that CO is converted to CO₂ through the water gas shift reaction (WGS) that is shown here:



It was determined that error from the GC measurements was an order of magnitude larger than the repeatability of the experiments. The propagated error from the GC measurements gives a maximum error in the carbon conversion of +/- 0.0075.

During some of the experiments, there was coke deposited on the walls of the reactor tube. This loss of carbon is not accounted for in the conversion calculation. However, this carbon loss is considered to be small because the calculated carbon conversions were not noticeably different than the expected results. From not being able to close the carbon balance, it is estimated that the error in the carbon conversion is +/- 0.01 at most.

The actual oxidation temperature falls somewhere between the last stable temperature and the temperature where deactivation was observed. The oxidation temperature was defined to be the midway point between the two temperatures and the error bars were one half of the final step size. The step sizes that were used introduced the most significant source of error in the oxidation temperature. Once the deactivation was confirmed with GC measurements, the experiments were shut down by turning the steam away from the reactor and turning off the heater while the CH₄ was still flowing.

Another set of experiments was conducted where the pressure was varied from 1 to 7 bar while holding the space velocity at 3000 hr⁻¹, and the molar flux at 0.173 mol/cm²-hr with a CH₄/steam ratio in the feed of 1.06. The experimental conditions can be seen in

Table 2:

Table 2 Operating conditions for pressure experiments

Pressure (bar)	Reactor ID (mm)	Total flow rate feed (SCCM)	Mo ₂ C loading (grams)
1	7	24.8	2.0
3.5	7	24.8	2.0
5	7	24.8	2.0
7	7	24.8	2.0

The oxidation temperatures were determined in the same manner as in the molar flux experiments.

Experiments were conducted to test the effects of adding CO, H₂ or both into the feed. In these co-fed experiments, the reactor was ramped up in both CH₄ and the selected product gas.

The experiments were conducted at 5 bar while holding the space velocity at 3000 hr⁻¹, the molar flux at 0.173 mol/cm²-hr with a CH₄/steam ratio in the feed of 1.06. The temperature was lowered in the same manner as in the previous experiments and carbon conversion was calculated with equation (2). The mole fractions used in the equation were adjusted to account for the excess H₂ or CO in the feed. A unique occurrence for some of these experiments was an absence of deactivation. These latter experiments were terminated when the carbon conversion had dropped below 10% to 20%. Table 3 shows the various concentrations of H₂ and CO that were used for these experiments.

Table 3. Concentrations of H₂ and CO used during experiments

Molar percentage of H₂ or CO
No - CO and No - H ₂
6% - CO and 6% - H ₂
18% - H ₂
23% - H ₂
25% - H ₂
47% - H ₂
19% - CO
26% - CO
46% - CO

3 RESULTS

3.1 Equilibrium considerations

The overarching purpose of this research was to determine the conditions required to operate stable SMR with high conversions at practical temperatures. In practice there are trade offs between high conversions and realistic operating temperatures. In the case of SMR, higher temperatures result in greater stability and higher conversions because the kinetics are improved and the thermodynamic conversion ceiling is raised. The problem is that higher temperatures create greater expense and in this case they are so high that they would prohibit the use of cheap reactor materials. Lowering the temperature has the disadvantage of dropping the thermodynamic conversion ceiling, decreasing the kinetics and eventually the deactivation of the catalysts through oxidation. The experiments carried out in this study allow for a consideration of this topic.

Figure 1 compares the thermodynamic limits on conversion as a function of temperature for one of the molar flux experiments at $.173 \text{ mol/cm}^2\text{-hr}$. The method for calculation of the thermodynamic equilibrium compositions is found in Appendix C. As can be seen, the conversion is essentially at equilibrium at $900 \text{ }^\circ\text{C}$. It is less than the equilibrium conversions as the temperature is lowered to $875 \text{ }^\circ\text{C}$, at which point the catalyst deactivates. This demonstrates the kinetic as well the deactivation issues facing this catalyst. While lower temperatures are desirable, the catalyst activity suffers and may deactivate through oxidation.

Table 4 shows the thermodynamic conversion and the actual conversion at the last stable temperature, for each experiment. In the two experiments that did not deactivate (noted by an asterisk in Table 4) the target temperature of 850 °C was chosen as the comparison temperature.

Table 4. The thermodynamic conversion and actual conversion at the lowest stable temperatures.

Type of experiment	Defining parameter	Temperature +/- 0.5 (°C)	Thermodynamic Conversion	Actual Conversion +/- 0.01
<i>Molar Flux</i>	.131 mol/cm ² -hr	880	0.84	0.55
<i>Molar Flux</i>	.173 mol/cm ² -hr	880	0.84	0.69
<i>Molar Flux</i>	.25 mol/cm ² -hr	890	0.85	0.69
<i>Molar Flux</i>	.355 mol/cm ² -hr	940	0.91	0.72
<i>Pressure</i>	7 bar	890	0.80	0.56
<i>Pressure</i>	5 bar	880	0.83	0.69
<i>Pressure</i>	3.5 bar	910	0.91	0.70
<i>Pressure</i>	1 bar	965	0.99	0.83
<i>Co-Feed</i>	6% CO and 6% H ₂	870	0.81	0.65
<i>Co-Feed</i>	18% H ₂	875	0.81	0.65
<i>Co-Feed</i>	25% H ₂	870	0.80	0.56
<i>Co-Feed*</i>	47% H ₂	850	0.71	0.53
<i>Co-Feed</i>	19% CO	870	0.79	0.62
<i>Co-Feed</i>	26% CO	870	0.78	0.37
<i>Co-Feed*</i>	46% CO	850	0.70	0.32

3.2 Blank experiments

In order to insure that the reforming activity was due to the Mo_2C and no other factors, a blank experiment was conducted using a quartz reactor tube that only contained SiC in the preheating/mixing zone. This experiment was carried out at 950 °C, a space velocity of 3000 h^{-1} , molar flux of $.11 \text{ mol/cm}^2\text{-hr}$, pressure of 4.4 bar and a CH_4/steam ratio of 1.06. At these conditions, a carbon conversion of 3 % was observed which was attributed to cracking of the CH_4 and gasification of coke by the steam. Large deposits of coke were observed on the tube walls after the experiment was cooled to room temperature. This conversion is considered negligible because coking to this extent is never observed when Mo_2C is present.

3.3 Molar flux experiments

For this set of experiments it was desired to determine an oxidation temperature at various molar fluxes. This was done as noted in the methods section above by lowering the reactor temperature in 5 °C to 20 °C steps until oxidation was observed. It was considered that oxidation was occurring, when the carbon conversion was steadily decreasing over the 50 minute period. The results of a typical experiment can be seen in Figure 2. As can be seen, the conversion drops as a function of temperature, but is still stable with time until 875 °C is reached. The conversion then steadily drops as a function of time. The upward swing in conversion at the end of the 880 °C period, is attributed to temperature and pressure oscillations due to the imposed temperature change. The deactivation is due to oxidation of the Mo_2C catalyst, which could be seen visually as well as with XRD scans of the spent catalyst. A bed that has been partially oxidized has a

moving front at the top of the bed that is distinctly purple (MoO_2), instead of the light gray of the Mo_2C . A picture of this can be seen in Figure 3. XRD scans of the spent catalyst corroborated this observation, and can be seen in Figure 4. These experiments at four different molar fluxes constitute a stability map, which is shown in Figure 5. The lowest molar flux experiments ($0.131 \text{ moles/cm}^2\text{-hr}$) were considered the hardest to conduct, the low flow rate are difficult to control, and were repeated three times. Each time the result showed an oxidation temperature of $875 \pm 5 \text{ }^\circ\text{C}$. This shows high precision and gives evidence that the largest cause of error in the deactivation temperature is the experimental temperature step size. From this map, it can be seen that the catalyst will remain stable to oxidation at temperatures above $930 \text{ }^\circ\text{C}$, when the molar flux is highest ($0.36 \text{ moles/cm}^2\text{-min}$) but the catalyst can operate stably at lower temperatures if the molar flux is lower. This is consistent with LaMont and Thomson's conclusions for DMR¹⁵. While lower temperatures are desirable from an operational point of view, equilibrium conversions are lower and the reaction can become kinetically limited at this space velocity. Table 4 lists the equilibrium and measured carbon conversions at the lowest stable temperature for all of the experiments. It is observed that actual conversions for the molar flux experiments are about 20% to 30% lower than the thermodynamic limits and only marginally acceptable for practical applications. Additionally, all of the lowest stable temperatures are higher than the target of $850 \text{ }^\circ\text{C}$, although the $880 \text{ }^\circ\text{C}$ temperature for the two lowest molar fluxes is getting much closer. Overall, it appears that reducing the molar flux alone is not enough to make Mo_2C a practical SMR catalyst.

3.4 Pressure experiments

Due to Claridge's¹⁰ observation that higher pressures promote oxidation stability, the results of similar experiments as a function of pressure are shown in Figure 6. On the basis of these results it can be concluded that there is little advantage in operating at pressures higher than 5 bar. In fact when the thermodynamics shown in Table 4 are considered, it can be seen that further increases in pressure will reduce the conversion. Thus over the molar flux and pressure ranges utilized in this study, the lowest stable temperature is 880 °C. This occurs at the two lowest molar fluxes examined.

3.5 Co feeding H₂ and CO

Since the reaction products, H₂ and CO increase the stability ratio (Equation 1), the effect of adding H₂ and CO to the feed was also examined. One of the first results of co-feeding H₂ or CO was that the conversion was depressed. This trend can be seen in Figures 7 and 8, where the decrease in conversion at a given temperature is seen to be proportional to increasing H₂ or CO concentration. This is apparently due to both thermodynamics and kinetics as shown in Figure 9. While thermodynamics predicts decreasing conversions as the concentration of H₂ or CO in the feed is raised, it is obvious that the addition of these two species into the feed also results in decreased kinetics.

As expected, it was observed that adding CO or H₂ created greater oxidation stability during SMR. Concentrations of CO and H₂ from 6% to 26 % resulted in lower

deactivation temperatures than under identical reaction conditions with no H₂ or CO, as can be seen in Figure 10. From the data in Figure 10, it appears that 6% H₂ and CO is sufficient to lower the minimum stability temperature by about 25 °C. However, this lowered stability temperature appears to be over shadowed by the deleterious effect on the kinetics (Fig. 9) caused by co-feeding low concentrations of CO and H₂.

After running the CO or H₂ experiments there was no visual appearance of oxidation of the catalyst but there was obviously some type of deactivation occurring. The top half of the catalyst bed for these experiments was scanned in the Philips XRD instrument to look for a cause of the deactivation. An example of a scan is shown in Figure 11 where a co-fed experiment with 26% CO was compared to a fresh Mo₂C sample and a sample of MoO₂. As can be seen, the scan of the experimental sample is virtually identical to the fresh Mo₂C scan, with no evidence of the formation of crystalline MoO₂.

It was then thought that the oxidation may have been very slight and not detected via XRD because the Mo₂C was only held at the deactivation temperature for about an hour. Consequently, an additional experiment was conducted to repeat the conditions, but with the initial deactivation temperature being held for 8 hours. Figure 12, shows the conversion data for this the 23% H₂ co-fed experiment, which indicates that the deactivation at 855 °C was initially rapid but then proceeded at a much slower rate. Once again, the XRD scan of the spent catalyst gave no evidence of oxidation, but there was a slight difference in the color of these deactivated samples when compared to a fresh sample of Mo₂C. The deactivated samples were a darker gray color.

In searching for the cause of the deactivation, a comparison of the normalized H₂/CO ratios was made between the 23 % H₂ co-fed deactivation experiment and an experiment that was known to deactivate by oxidation. Subtracting the excess H₂ normalized the H₂/CO ratio. As can be seen in Table 5 the H₂/CO ratio is higher in the H₂ co-fed experiment than in H₂ free feed experiment.

Table 5. Normalized H₂/CO ratios during deactivation of co-fed and non co-fed experiments; experimental conditions 5 bar, space velocity 3000 h⁻¹, molar flux .173 mol/cm²-hr, CH₄/H₂O = 1.06

23% H₂		No H₂	
Time	H ₂ /CO	Time	H ₂ /CO
0	3.61	0	3.66
.34	5.24	0.30	3.76
0.69	5.74	0.53	3.50
1.73	6.09	0.7	4.29
2.93	6.05	1.06	4.07
3.33	6.64		
3.66	6.63		
8.30	6.31		
8.51	6.92		
8.87	6.42		

The likely cause of the extra H₂ is from the cracking of CH₄. Additional H₂ could have been produced if the unreacted steam was gasifying some of the coke that was created during the cracking of CH₄. This evidence suggests that coking is the cause of for the unknown deactivation because carbon deposition on the Mo₂C would physically block the active sites on the catalyst.

A final comment on the 23% H₂ experiment was that the initial conversion at the deactivation temperature is below the conversion of the 47% H₂ co-fed experiment. This is an apparent contradiction to the behavior observed in Figure 7. The figure shows that higher concentrations of H₂ result in lower conversions. The low initial conversion is an artifact of when it was measured and the large temperature drop. The large temperature drop caused the system to take longer than normal to reach a stable temperature. During this time no GC samples were taken and the opportunity to record the actual initial conversion was lost. The initial conversion was likely higher than what is shown in Figure 12. This alone cannot explain the difference between the two conversions. An additional contribution could have come from the large undershoot for this experiment. In this experiment the catalyst experienced temperatures 10 °C lower than desired for about 4 to 6 minutes. This may have caused increased deactivation, which further decreased the conversion.

For the co-fed sets of experiments, there were two experiments that showed no sign of deactivation. One was with H₂ and the other was with CO at 47% and 46% respectively. A plot of the conversion versus temperature for these results can be seen in Figure 13. It should be noted that both of these experiments are stable at 850 °C for SMR with H₂ having the higher conversion of 0.53. Something to be mentioned here is that this same behavior was observed in two preparatory experiments of 59% and 61 % co-fed H₂. They were conducted at 0.26 mol/cm²-hr and 0.13 mol/cm²-hr respectively and at 2 bar. At 850 °C, they had conversions higher than the 47% H₂ experiment. The 61% H₂ was 0.72 and the 59% H₂ was 0.76. These would be considered terrific results if they did not

require such high levels of H₂. The 47% H₂ condition is bordering on requiring too much H₂ in the feed to be applied practically so these two initial experiments are definitely excessive. For this reason the 47% H₂ experiment should be considered the most promising result for all of the SMR experiments that were conducted.

The experiment with 46% CO was conducted in two parts. The first part concentrated on the result of lowering the temperature to 850 °C (Fig 13) and the second part explored stability over time at 850 °C for 6 hours. At the end of the 6 hours the temperature was then raised to 870 °C and held for another 6 hours. A plot showing the time behavior for this experiment can be seen in Figure 14. At 850 °C, the temperature at which the lower concentration CO and H₂ experiments deactivated (Fig. 12), the conversion is stable and actually rose slightly. In fact, after the temperature was raised back to 870 °C, the conversion was higher than the previous conversion at 870 °C. This suggests some hysteresis behavior for Mo₂C during the reforming reaction. Part of the difference can be explained by looking at the conversion for the first 870 °C case in Figure 13. The conversion rose over time. This behavior was common in a number of experiments and was a result of the temperatures being stepped down. The temperature oscillated slightly around the new set point and some of the pressure was lost. With time, the temperature stabilized and the pressure built back up. Both of these factors caused the conversion to increase with time. If the first 870 °C was held for a longer time the conversion presumably would have climbed higher but considering the patterns observed in previous experiments it would not have reached the conversion levels of recorded at the second 870 °C. This would require an additional explanation to account for the difference

between the two conversions. Another observation was that the CO/CO₂ ratios at the two different times were not the same. This data is shown in Table 6.

Table 6. CO/CO₂ ratios at 870 °C for 46% CO. In one case 870 °C was reached by lowering the temperature 20 °C and in second case the temperature reached by being raising 20 °C; experimental conditions 5 bar, space velocity 3000 h⁻¹, molar flux .173 mol/cm²-hr, CH₄/H₂O = 1.06

870 °C	870 °C
Lowered	Raised
CO/CO ₂	CO/CO ₂
7.8	12.5
8.5	12.2
9.1	12.4
	11.9
	12.1
	11.2
	11.4
	11.8
	12.1
	12.1

This ratio was higher at the raised 870 °C, which suggests that the WGS reaction had been depressed and the SMR enhanced, thus improving the conversion. A reason for this may be that the WGS reaction is improved at lower temperatures so that there may be one steady state point going down in temperature and a different steady state point going up.

4 DISCUSSION AND CONCLUSIONS

4.1 Comparison to previous results

One of the objectives of the experimental design was to allow comparisons with the DMR results published by LaMont and Thomson¹⁵; in particular, the effect of molar flux and pressure on catalytic stability. Figure 15 compares the flux stability map generated for SMR to that of DMR. However, there are differences between the two sets of experiments. The space velocities are slightly different, they are at different pressures (5 bar vs. 8.3 bar) and the molar fluxes examined by LaMont and Thomson were lower than those used here. The pressure difference was unimportant because as seen in Figure 6 the deactivation temperature does not change significantly once 5 bar is reached. In the one data point that overlaps the two sets of experiments, the results are statistically identical. On the linear portion of the maps, (molar flux values less than or equal to $0.25 \text{ mol/cm}^2\text{-hr}$), the slopes of the two data sets show some variation. It would appear that dry reforming receives a slightly greater benefit from lower molar fluxes than steam reforming but there is not enough data from LaMont to confirm this.

A comparison of the effect of pressure on deactivation can be seen in Figure 16. In order to compare the two sets of results, it was necessary to back-extrapolate the molar flux in the SMR results to $0.08 \text{ moles/cm}^2\text{-hr}$, which was the molar flux employed by LaMont and Thomson for their examination of the effect of pressure. This is a reasonable approach since the effect of molar flux on steam reforming is linear at low fluxes

(Fig. 5). In this case it is clear that DMR has a broader range of stable reforming conditions. This confirms that steam is a stronger oxidant than CO₂.

4.2 Effects from co-feeding

An interesting finding was that the distinct deactivation temperatures for the low concentration co-fed experiments were not caused by oxidation. An additional experiment was conducted with 23% H₂ in the feed and held at a previously observed deactivation temperature for 8 hours. Again no oxidation was observed but analysis of the product gases during deactivation showed that the normalized H₂/CO ratio was higher for the 23% H₂ case than the H₂ free experiment. This was evidence that the elevated levels of H₂ were not from SMR and WGS but from another reaction, presumably the cracking of methane. It should also be noted that for this experiment, the initial conversion at 855 °C was lower than expected. This was attributed to the large temperature step down to reach 855 °C. The temperature drop caused a larger than normal undershooting and required more time than normal to stabilize, preventing rapid GC data collection.

Another finding was that at high concentrations, H₂ and CO, 47% and 46% respectively, prevented any type of deactivation, allowing SMR to be run at the bench mark temperature of 850 °C. The 47% H₂ experiment had a significantly higher conversion than the 46% CO at 850 °C, 0.53 and 0.32 respectively. The thermodynamic equilibrium for the two cases are nearly the same so the difference in conversion must be due to the

kinetics. The 47% H₂ experiment represented the very best SMR operation conditions that were found considering the reactor temperature, conversion, and stability.

At the end of this study it can be said that some more of the practical aspects of using Mo₂C as a reforming catalysts are clearer. The molar flux and pressure deactivation maps can be a jumping off point for future researchers. It can also be seen that DMR and SMR behave very similarly and that steam is a somewhat stronger oxidant for Mo₂C. The benefits of adding CO and H₂ have been shown for steam reforming. Even with as little as 6 % CO and 6% H₂ the possible reforming temperature range is lowered between 5 °C to 25 °C. This comes with the cost of a conversion depression that is about 17 % below the thermodynamic limit. This alone would bring the reforming temperature down to 870 °C, which is very near current industrial conditions. With even higher concentrations of H₂ or CO, deactivation can be prevented all together and SMR can be conducted at the benchmark temperature of 850 °C. For the 47% H₂ case, the fraction carbon conversion of 0.53 is not too far away from being practical for industrial applications.

This new understanding combined with the work from future researchers can make Mo₂C a viable reforming catalyst to lower the production cost of H₂ from hydrocarbons. As mentioned in the introduction, catalyst improvement is an important part in making H₂ applications economical. Historical trends¹ point to H₂ as the fuel of the future and it will be interesting to see how scientific discoveries, especially in catalysis, will make this possible.

4.3 Future work

As with any research project there have been unexpected questions that fall outside the scope of the current work. One of the first questions would be, what is the exact cause of the deactivation of Mo_2C at the low concentrations of co-fed CO and H_2 ? An attempt has been made to discover the cause by looking at a scan of the bulk crystal structure of the deactivated Mo_2C . The suspected cause is coking but this was not proven conclusively. It is possible that a change is taking place on the surface of the Mo_2C . Surface x-ray photospectroscopy analyses of the spent catalysts may be able to detect surface carbon or other changes on the surface and conclusively prove the reason for the deactivation.

It should be possible to surpass the conversions obtained at the best reaction conditions in this study, by lowering the pressure, finding out if less H_2 can be used to achieve the same stability, and by using a supported Mo_2C to increase the activity. The most favorable results from this study were found at 5 bar, but even better results may be found at lower pressures. The two preliminary H_2 experiments run at 2 bar suggest this should be the case. The equilibrium conversion at 1 bar and at 850 °C with the same parameters as the 47% H_2 case is 0.94. This is 23% higher the equilibrium conversion for 47% H_2 . If pressures below 5 bar were found to be stable then these lower pressures should result in conversions higher than 0.53. There is an untested region between 26% and 46% H_2 or CO concentrations that may fully stabilize Mo_2C like the 46% to 47% H_2 or CO experiments. It has been shown in this study, that lower concentrations of H_2 and CO will have higher conversions due to both thermodynamic and kinetic reasons. For all of these experiments a bulk low surface area Mo_2C was used. Supporting the Mo_2C would

increase the surface area and could likely push the conversion closer to the thermodynamic ceiling.

Using a fluidized bed reactor instead of a packed bed reactor may be a useful way to employ Mo_2C for SMR. In an industrial packed bed reactor the co-feeding of H_2 and CO would come from a recycle stream that would increase the equipment and operational costs. A fluidized bed would have the same stability benefits of a recycle, but the equipment and operational costs would be lower. The disadvantage would be a reduced conversion because a fluidized bed would operate with higher local concentrations of products than a recycled packed bed reactor.

Another interesting finding was the hysteresis observed for Mo_2C during the 46% CO co-fed experiment. Is this hysteresis unique to this experiment or could it be found at other conditions? It would also be useful to know if this hysteresis could be used practically to increase the conversion at a given temperature by following a particular temperature pathway. It may also be helpful to know if there is a physical change that happens to the surface of the Mo_2C while moving through the hysteresis. If there was a surface change found perhaps an improved method could be developed for making Mo_2C for reforming.

An interesting side issue to explore, would be to see if the sulfur tolerance observed by Prichard et al⁷. exists at lower temperatures and higher pressures. For example, is Mo_2C still sulfur tolerant at lower temperatures? In Prichard's study, the reforming temperature was 1050 °C, which is too high to be economical or practical. This current study found a number of stable reforming conditions with high conversions at temperatures 100 °C to

180 °C lower than was employed in the sulfur study. Prichard proposed that the reversibility of the sulfur poisoning was a result of the sulfur being only chemisorbed to the surface of the Mo₂C. If this were true, then the chemisorbed sulfur would be less mobile at lower temperatures and would cause a more severe deactivation. The effect of pressure in the presence of sulfur would also be interesting to look at because increased pressure would result in a higher local concentration of sulfur around the catalyst. Would the reforming stability gained from higher pressures be offset or worsened due to higher local concentrations of sulfur? Mo₂C would have to be tested with sulfur at practical conditions to fully compare its sulfur tolerance to other reforming catalysts such as nickel.

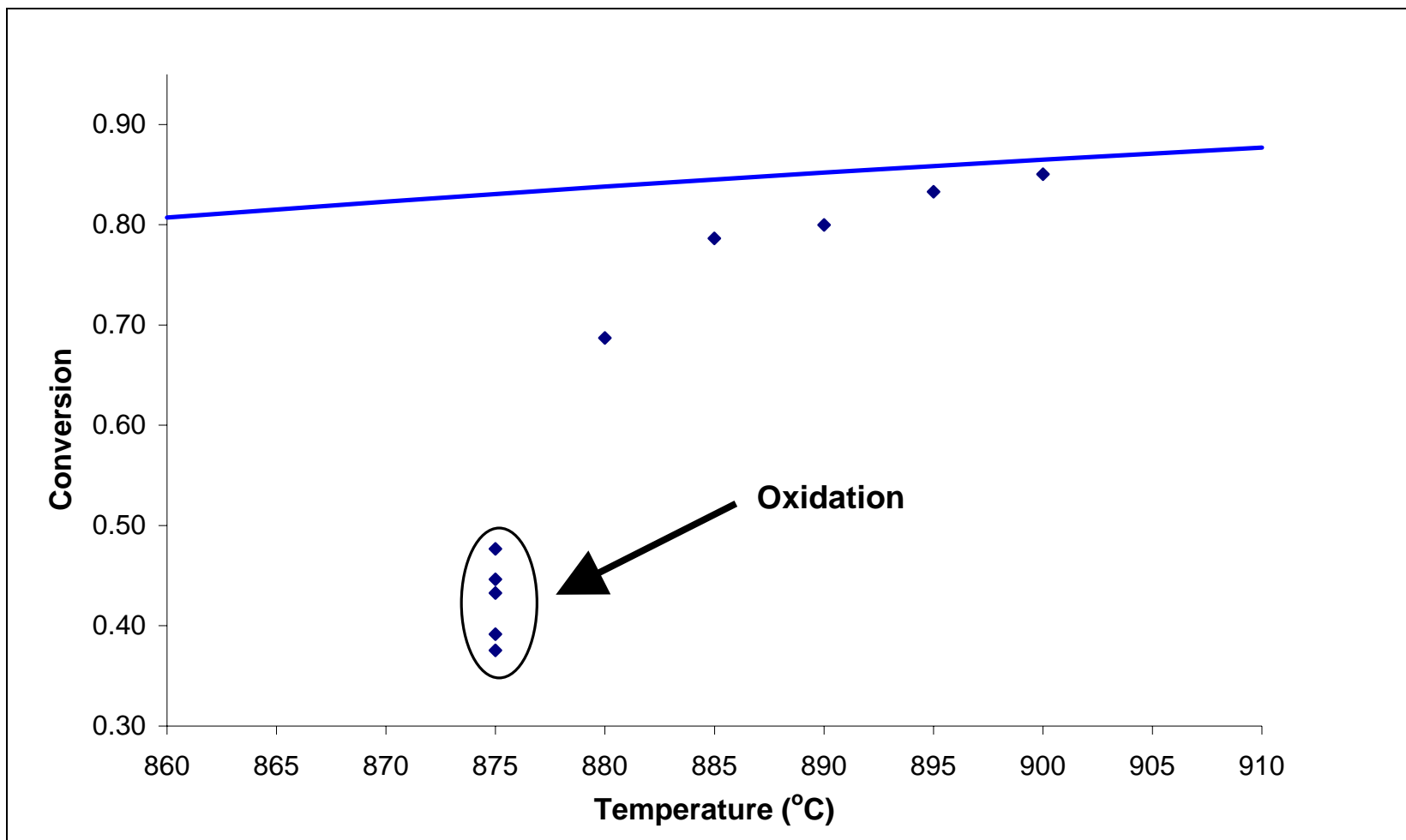


Figure 1. SMR oxidation deactivation experiment and the equilibrium conversions; (♦) experimental data at 5 bar, space velocity 3000 h^{-1} , molar flux $.173 \text{ mol/cm}^2\text{-hr}$; (—) thermodynamic equilibrium at 5 bar, space velocity 3000 h^{-1} , molar flux $.173 \text{ mol/cm}^2\text{-hr}$, $\text{CH}_4/\text{H}_2\text{O} = 1.06$

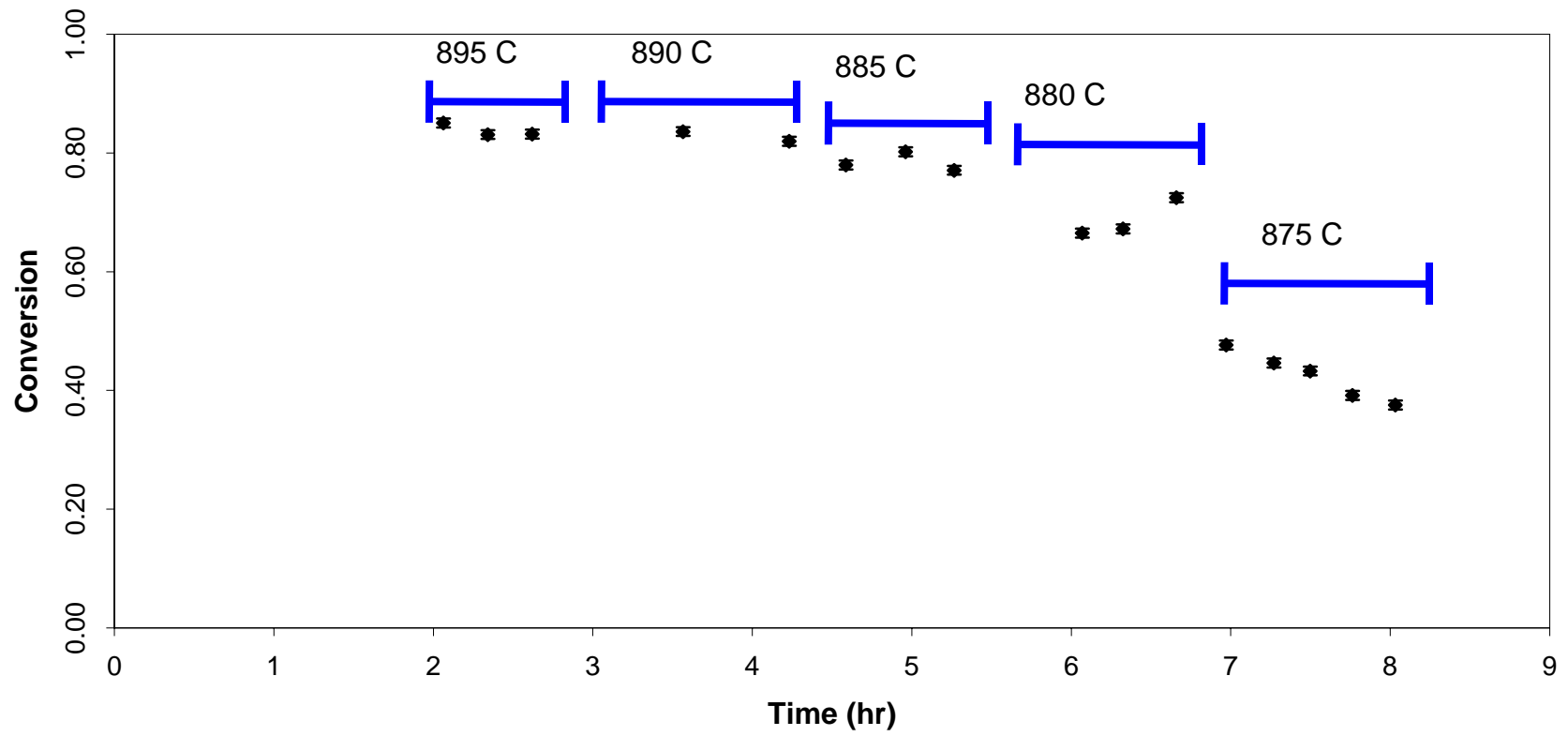


Figure 2. Typical molar flux experiment; 5 bar, space velocity 3000 h^{-1} , molar flux $.173 \text{ mol/cm}^2\text{-hr}$, $\text{CH}_4/\text{H}_2\text{O} = 1.06$

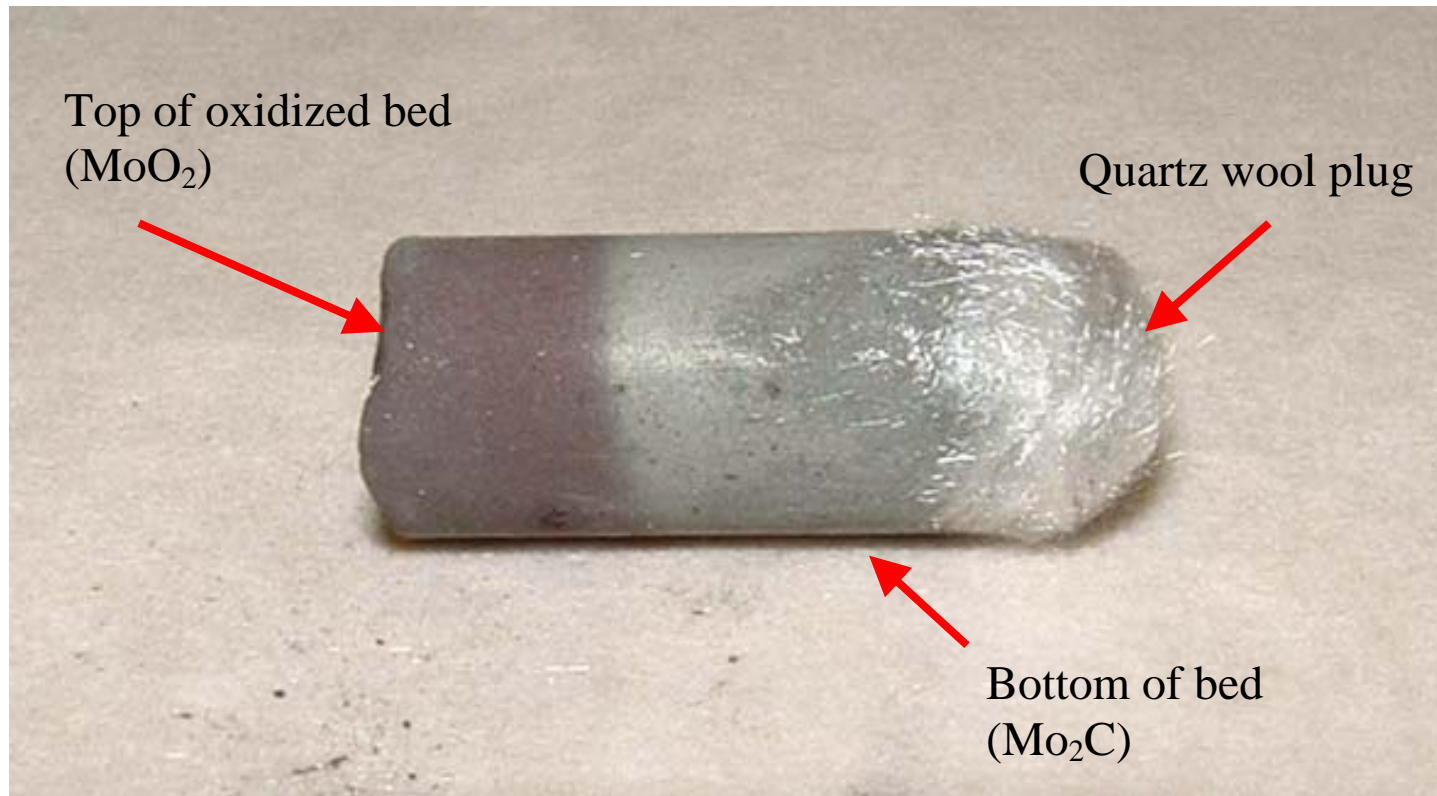


Figure 3. Photograph of oxidized Mo_2C bed after a SMR experiment; experiment at molar flux $.173 \text{ mol/cm}^2\text{-hr}$ and oxidized at $877.5 \pm 5 \text{ }^\circ\text{C}$

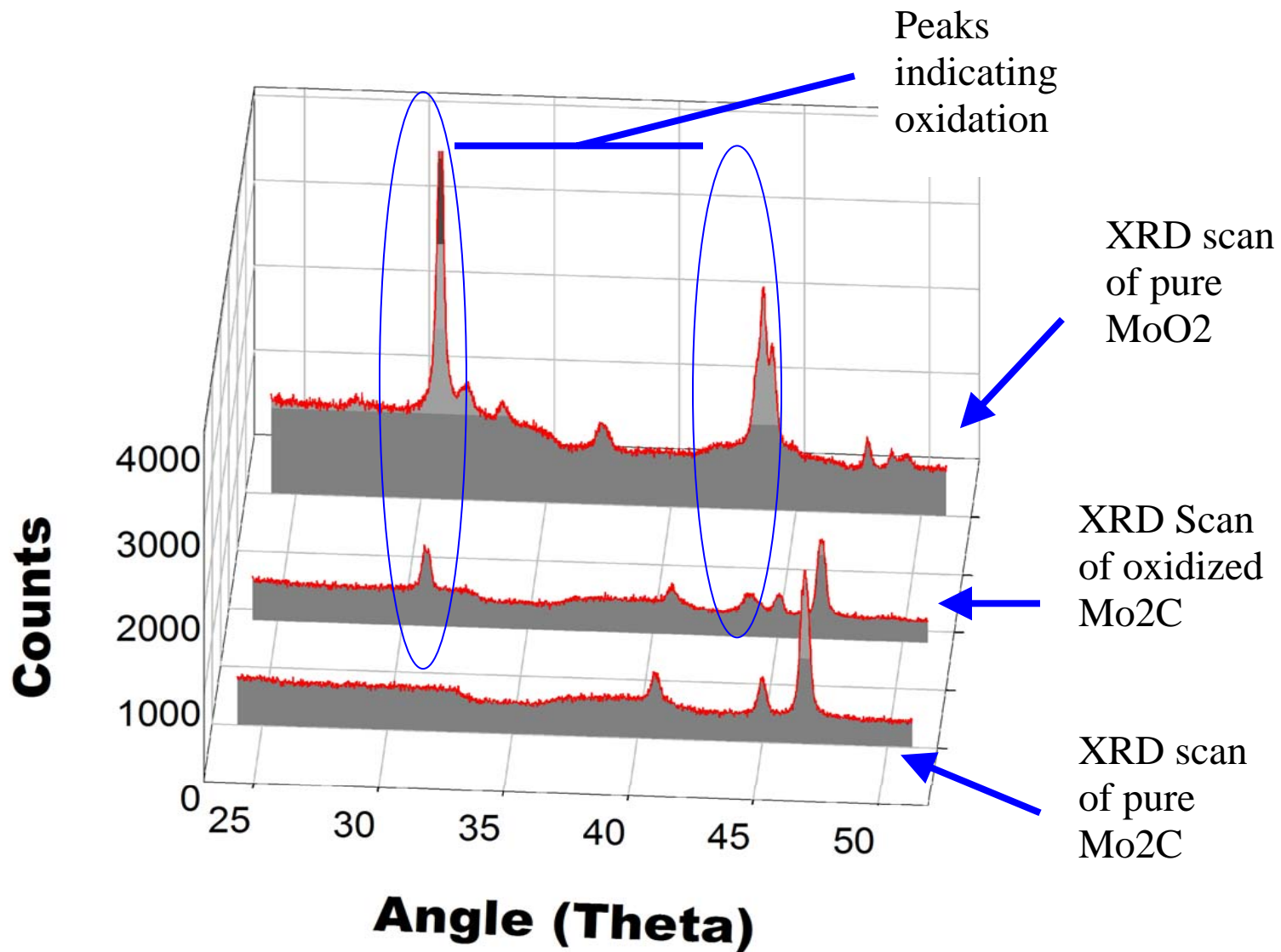


Figure 4. XRD scan comparison of Mo₂C and MoO₂ to an oxidized Mo₂C bed; experimental conditions 5 bar, space velocity 3000 h⁻¹, molar flux .173 mol/cm²-hr, CH₄/H₂O = 1.06 deactivated at 877.5 +/- 5 C

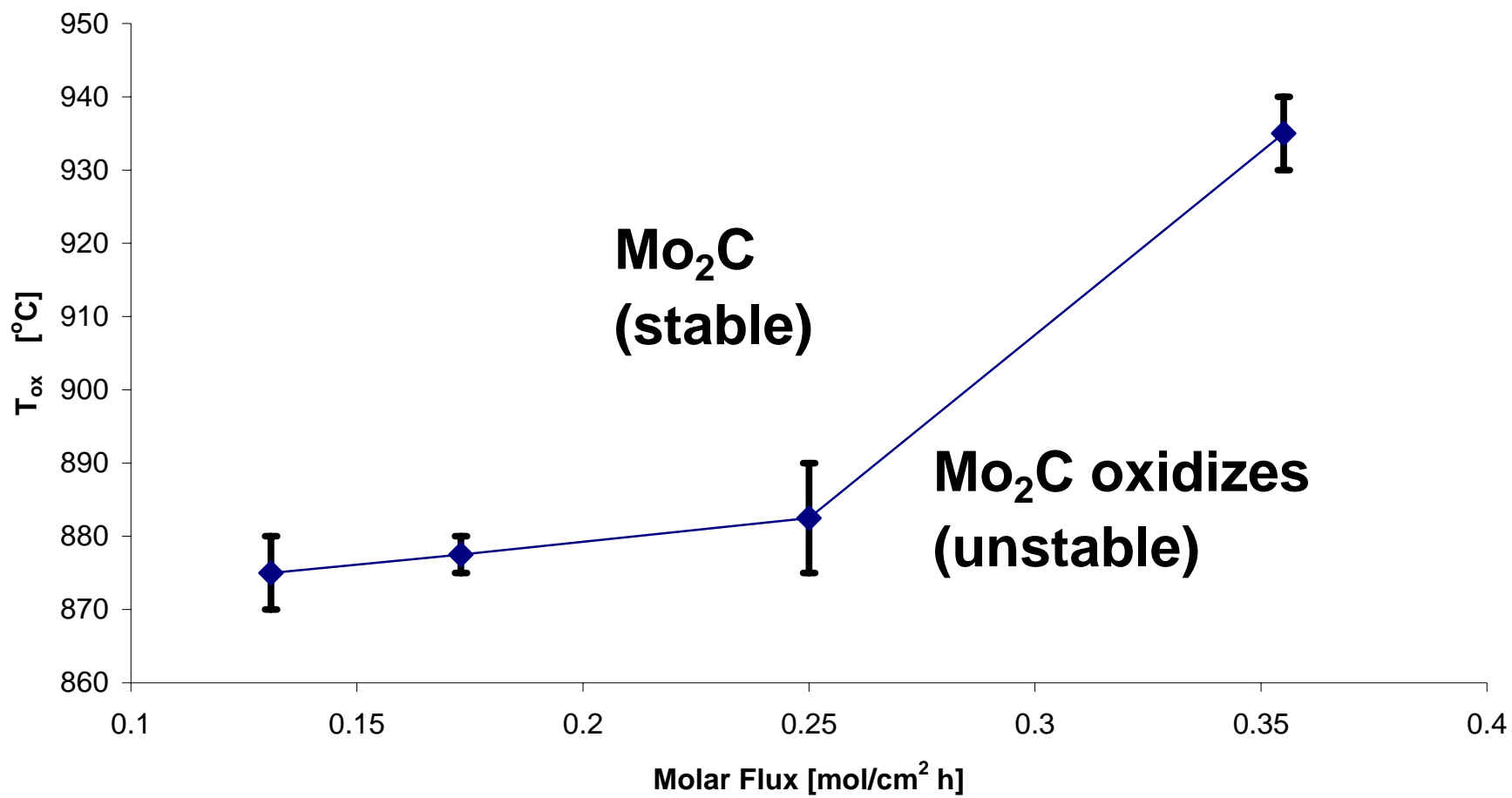


Figure 5. Molar flux deactivation map; 5 bar, space velocity $3000 h^{-1}$, $CH_4/H_2O = 1.06$

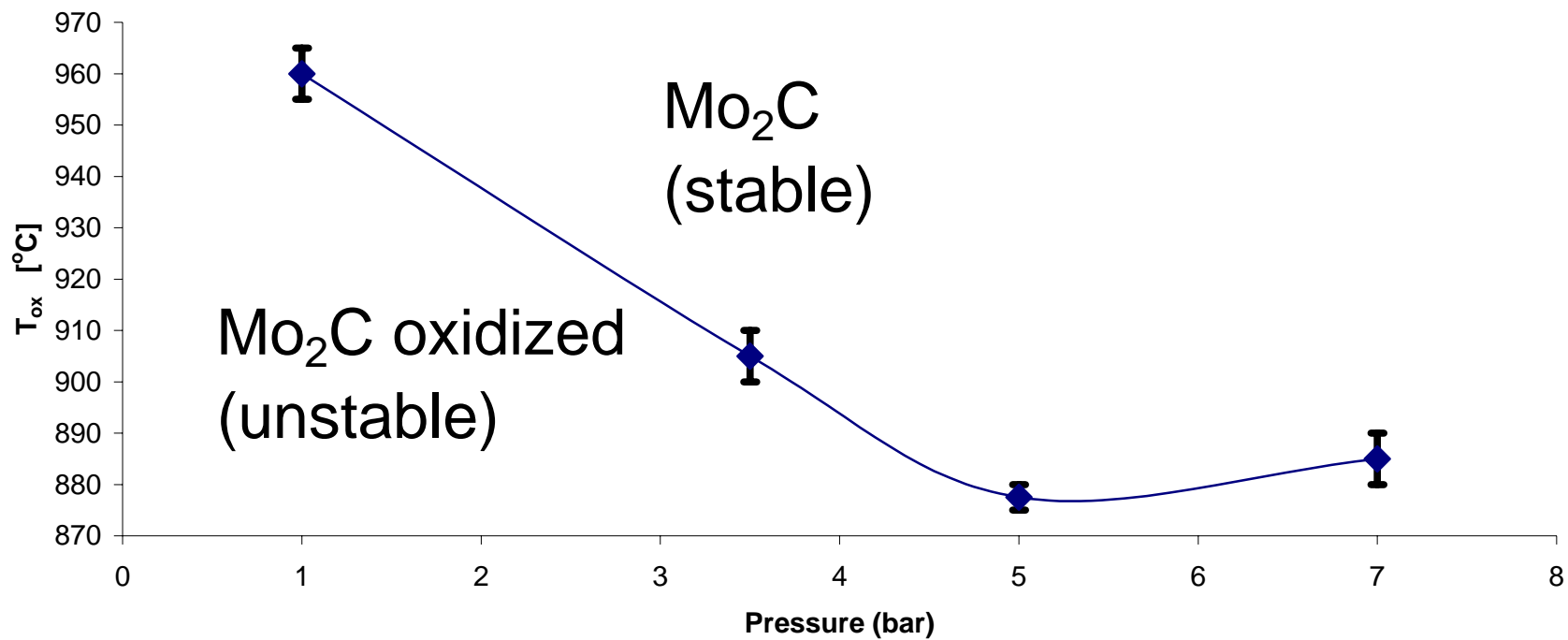


Figure 6. Pressure deactivation map; space velocity 3000 h^{-1} , molar flux $.173\text{ mol/cm}^2\text{-hr}$, $CH_4/H_2O = 1.06$

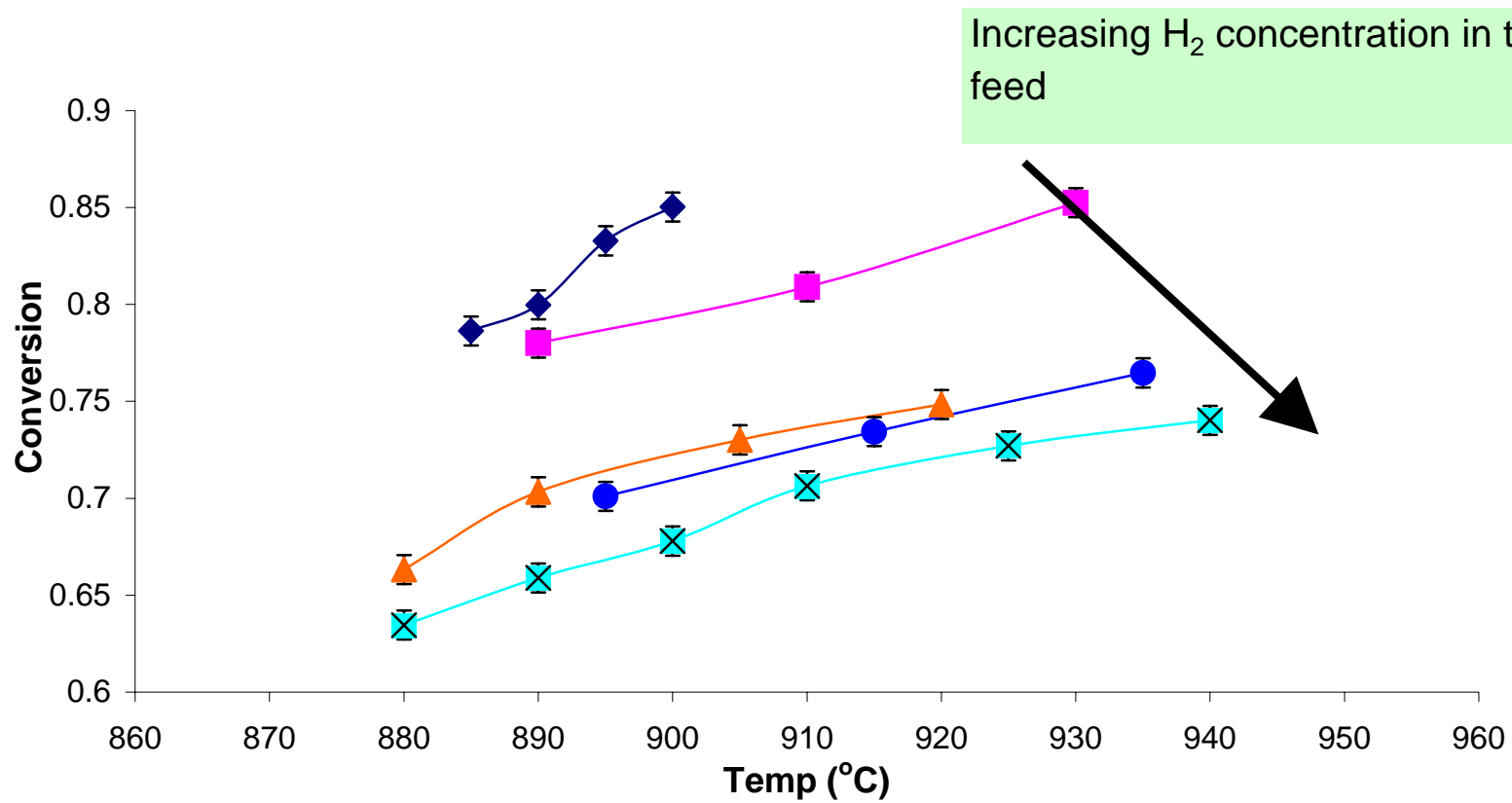


Figure 7. Comparison of co-fed H₂ experiments; 5 bar, space velocity 3000 h⁻¹, molar flux .173 mol/cm²-hr, CH₄/H₂O = 1.06; (—●—) No H₂, (—■—) 6% H₂ and 6% CO, (—●—) 18% H₂, (—○—) 25% H₂, (—x—) 47% H₂

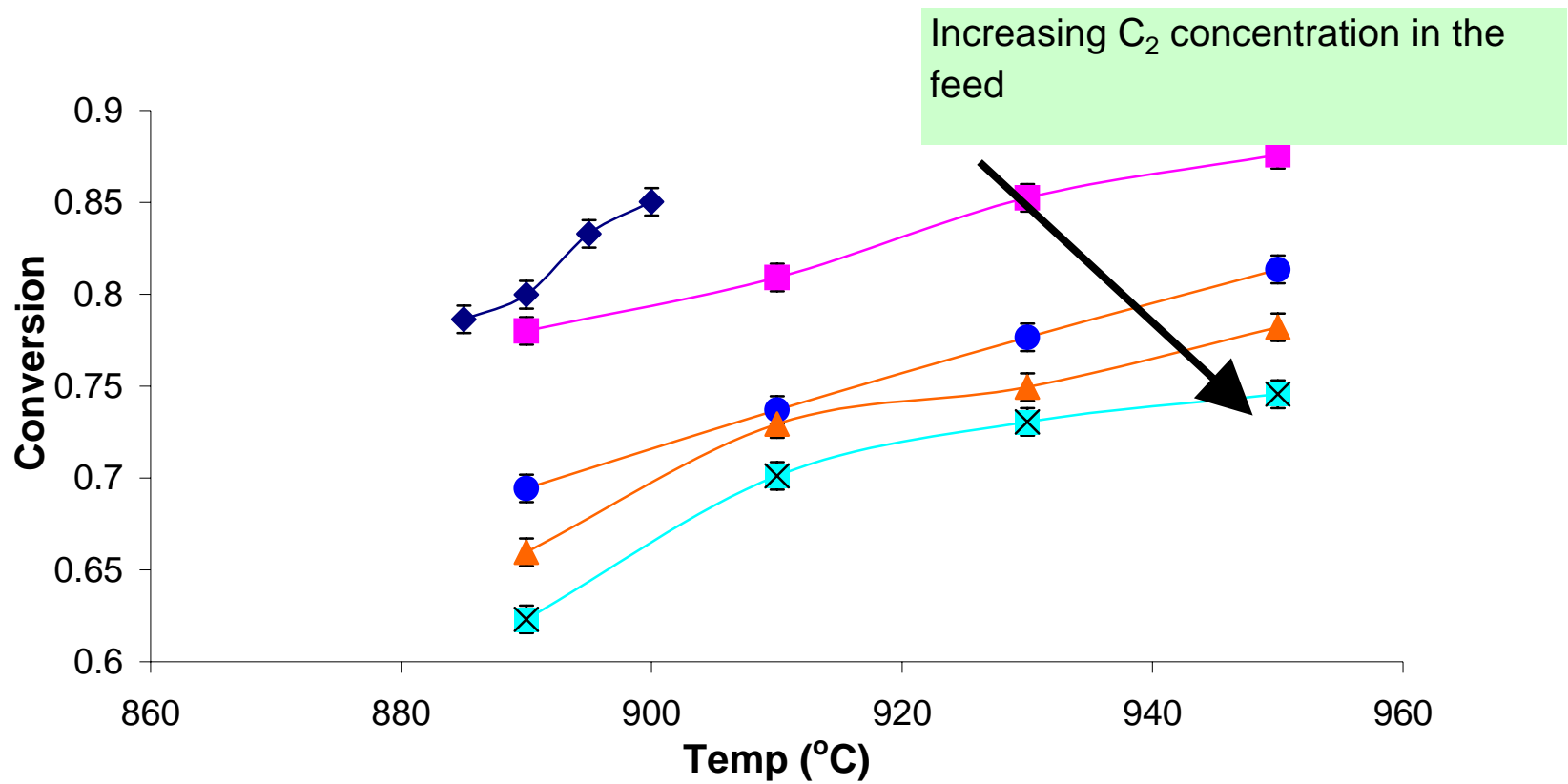


Figure 8. Comparison of co-fed H_2 experiments; 5 bar, space velocity 3000 h^{-1} , molar flux $.173\text{ mol/cm}^2\text{-hr}$, $CH_4/H_2O = 1.06$;
 (—♦—) No H_2 , (—■—) 6% H_2 and 6% CO, (—●—) 19% CO, (—▲—) 26% CO, (—×—) 46% CO

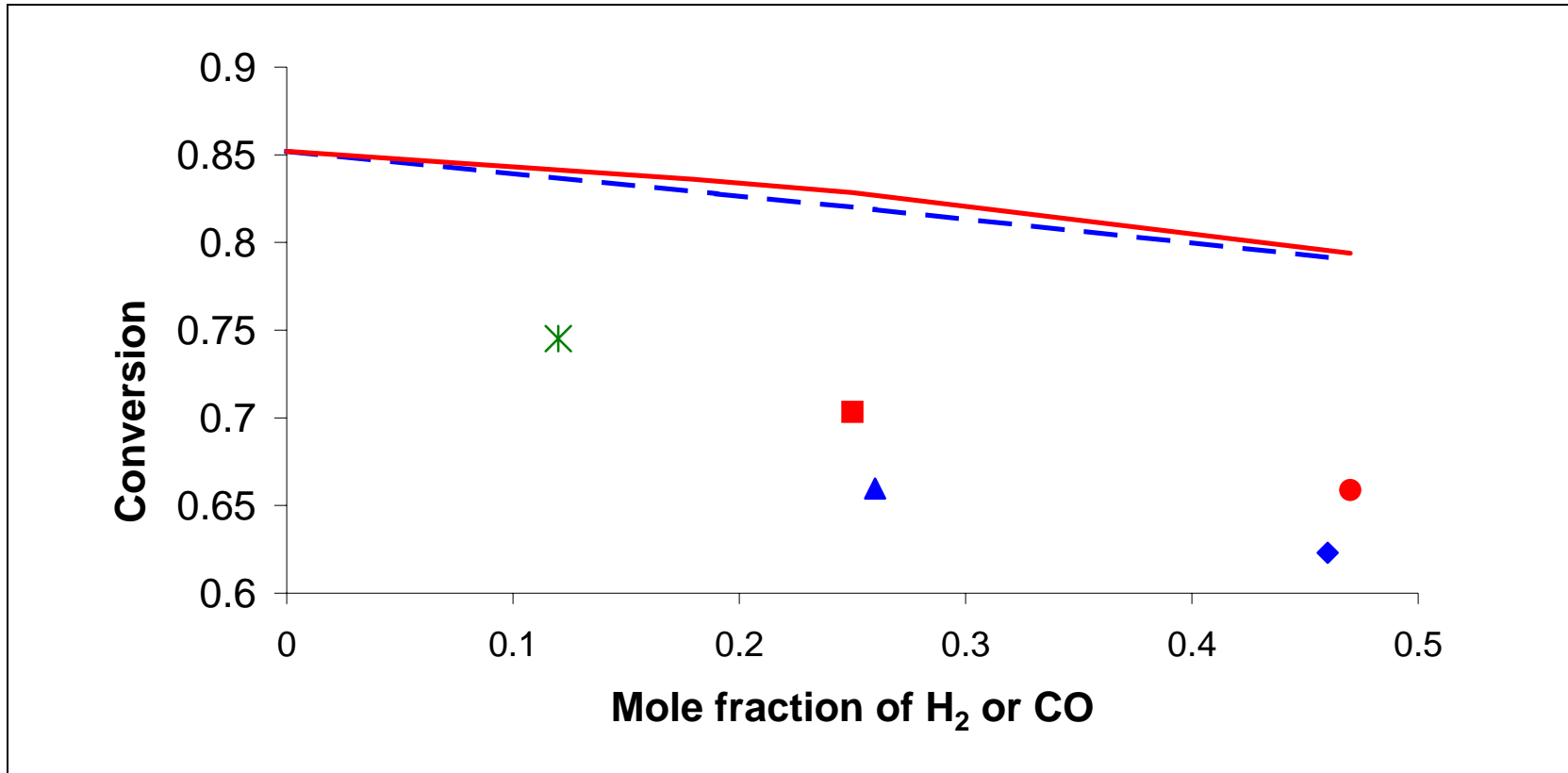


Figure 9. Carbon conversions at various H₂ and CO concentrations compared to the thermodynamic equilibrium at 890 °C, 5 bar, space velocity 3000 h⁻¹, molar flux .173 mol/cm²-hr, CH₄/H₂O = 1.06; (—) H₂ thermodynamic equilibrium; (---) CO thermodynamic equilibrium; (●) H₂ 6 % and CO 6%; (●) H₂ 25 %; (●) H₂ 47 %; (●) CO 26 %; (●) CO 46 %

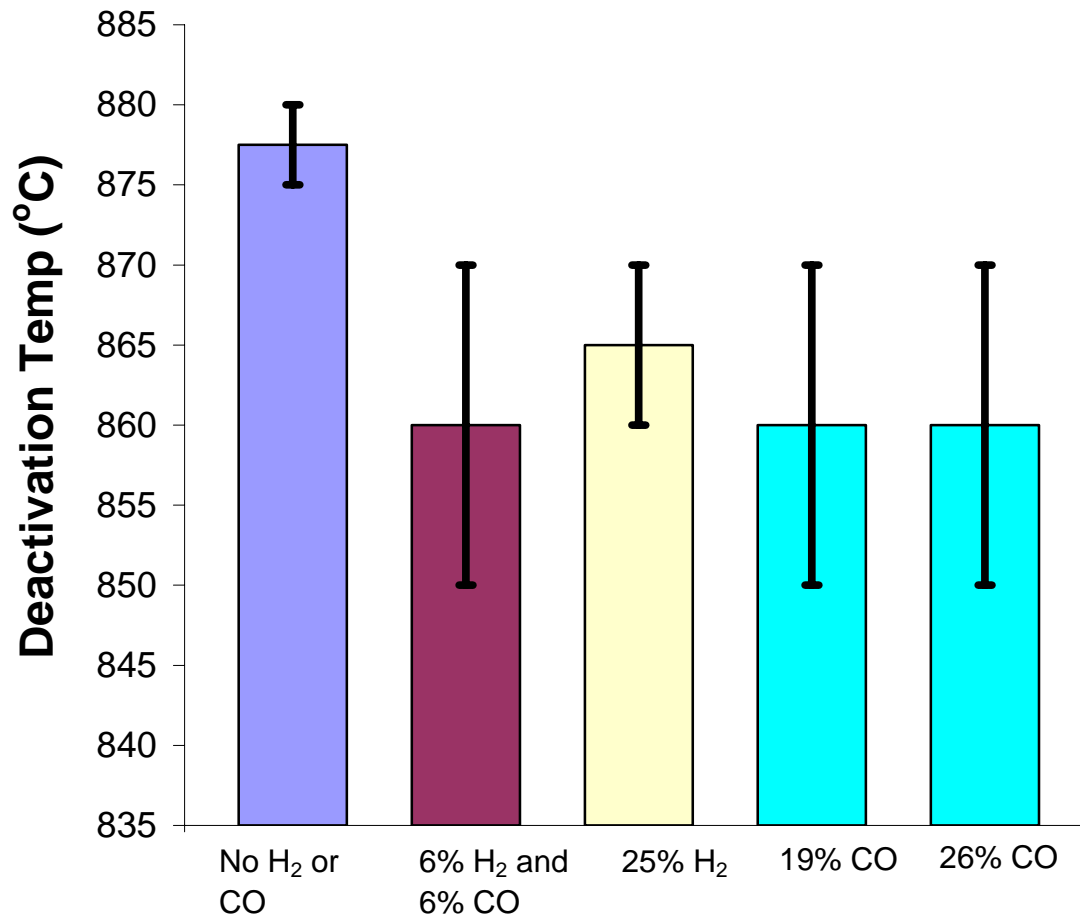


Figure 10. Deactivation temperatures at various levels of H₂ and CO; experimental conditions 5 bar, space velocity 3000 h⁻¹, molar flux .173 mol/cm²-hr, CH₄/H₂O = 1.06

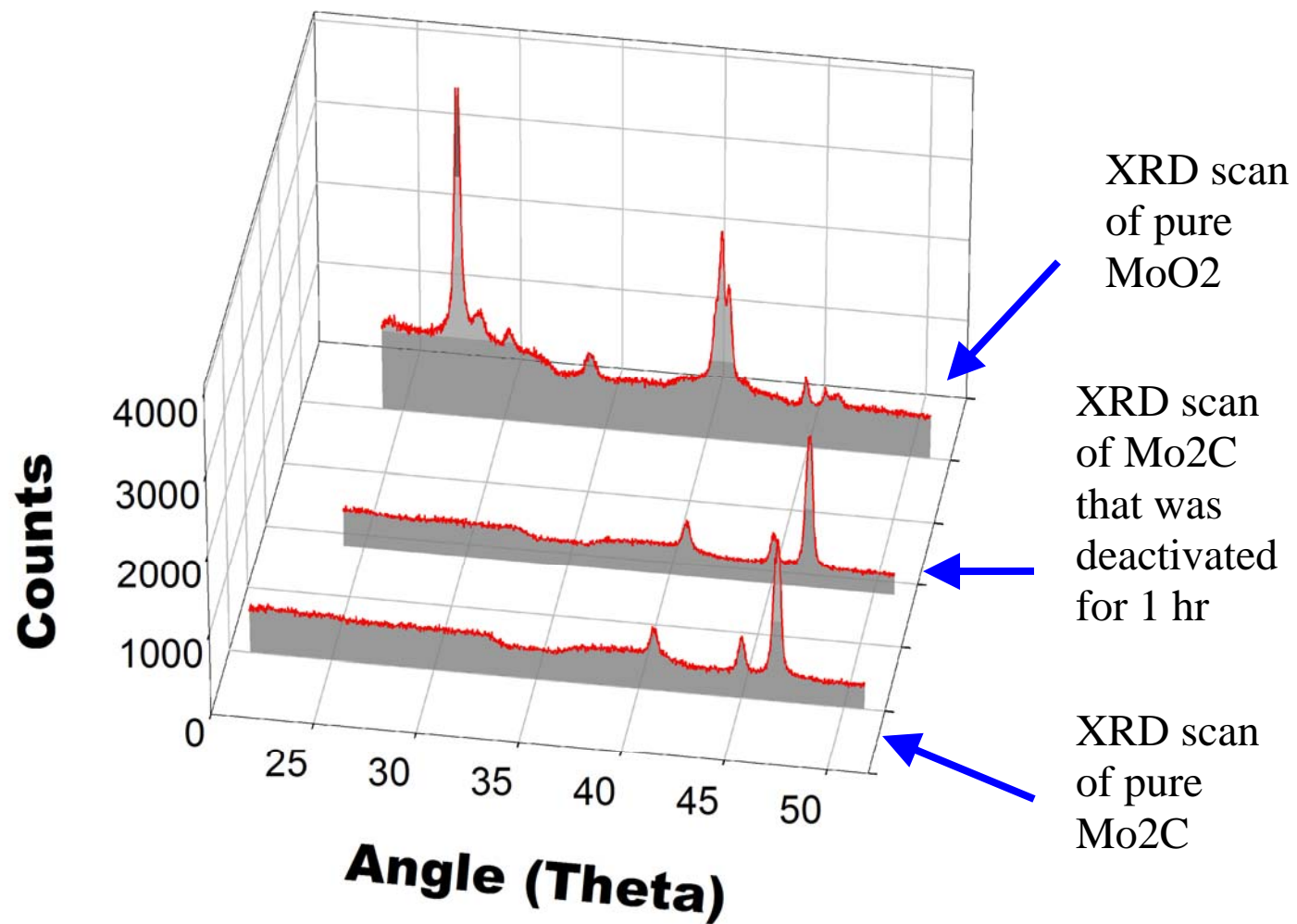


Figure 11. XRD scan comparison of Mo₂C and MoO₂ to a deactivated Mo₂C bed; experimental conditions 5 bar, space velocity 3000 h⁻¹, molar flux .173 mol/cm²-hr, CH₄/H₂O = 1.06, 26% CO, deactivated at 860 +/- 10 °C for 1 hr

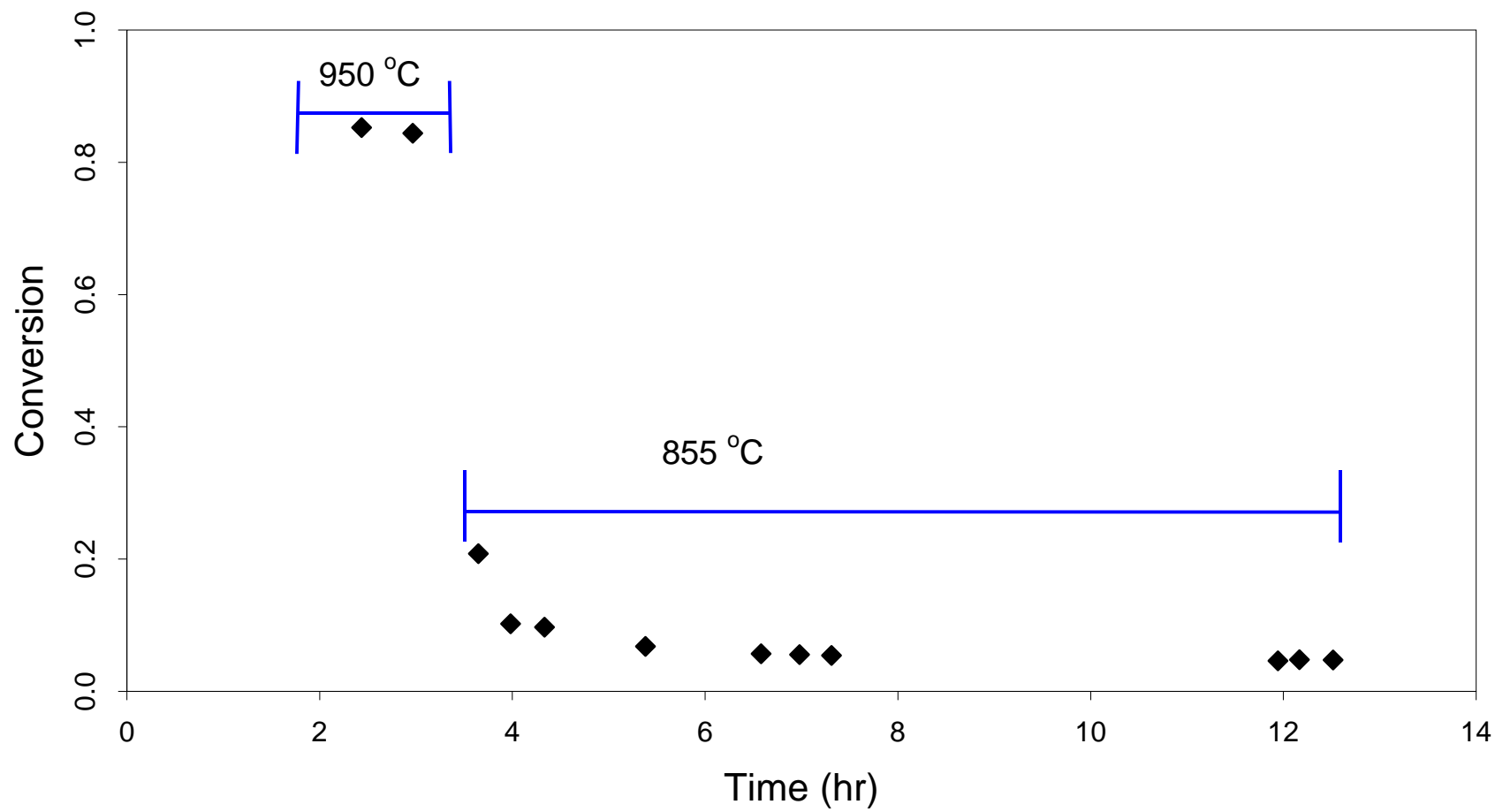


Figure 12. 23% H₂ co-fed experiment to test long term stability; 5 bar, space velocity 3000 h⁻¹, molar flux .173 mol/cm²-hr, CH₄/H₂O = 1.06, deactivated for 8 hrs

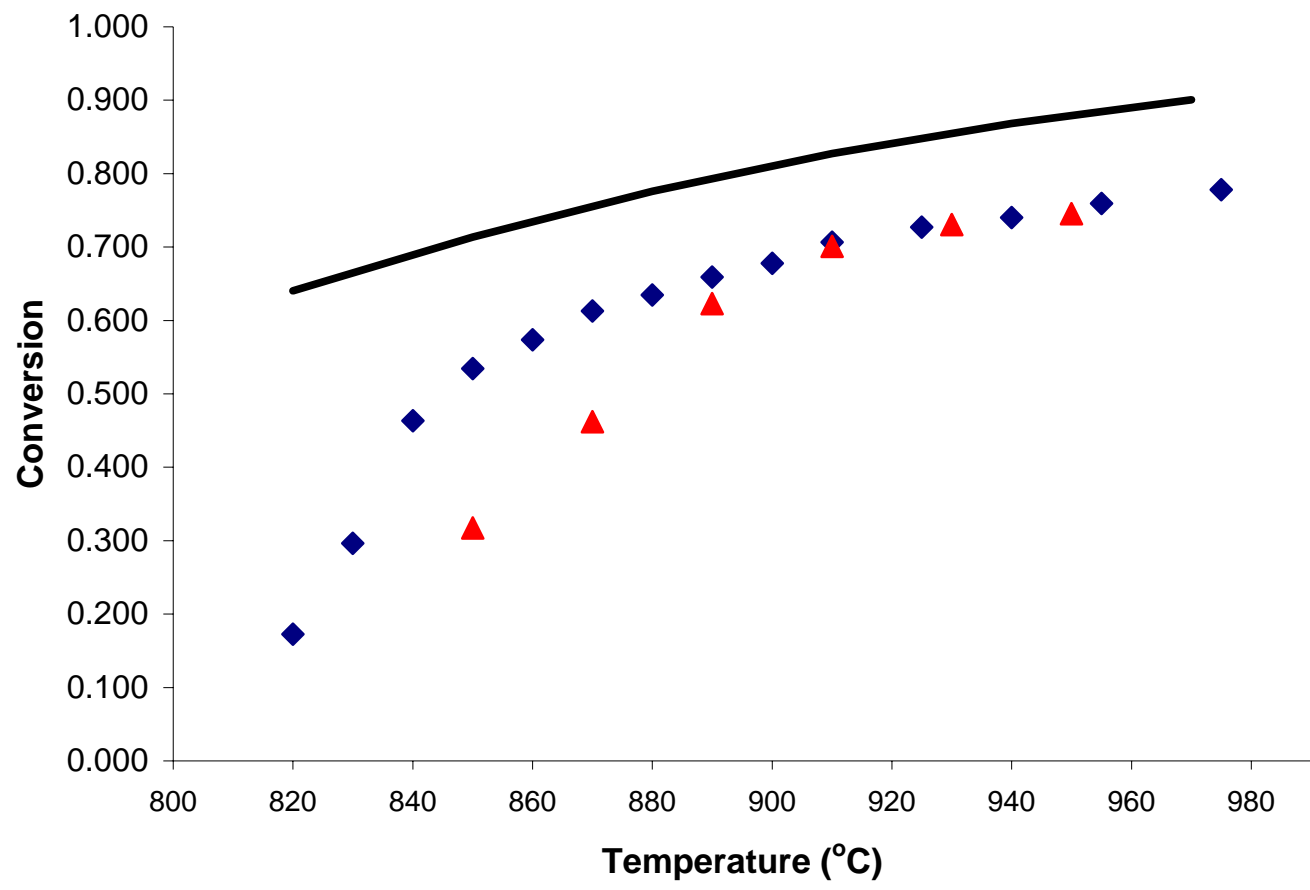


Figure 13. High concentration CO and H₂ experiment that did not deactivate; experimental conditions 5 bar, space velocity 3000 h⁻¹, molar flux .173 mol/cm²-hr, CH₄/H₂O = 1.06; (●) 47% H₂, (▲) 46% CO, (—) 47% H₂ equilibrium

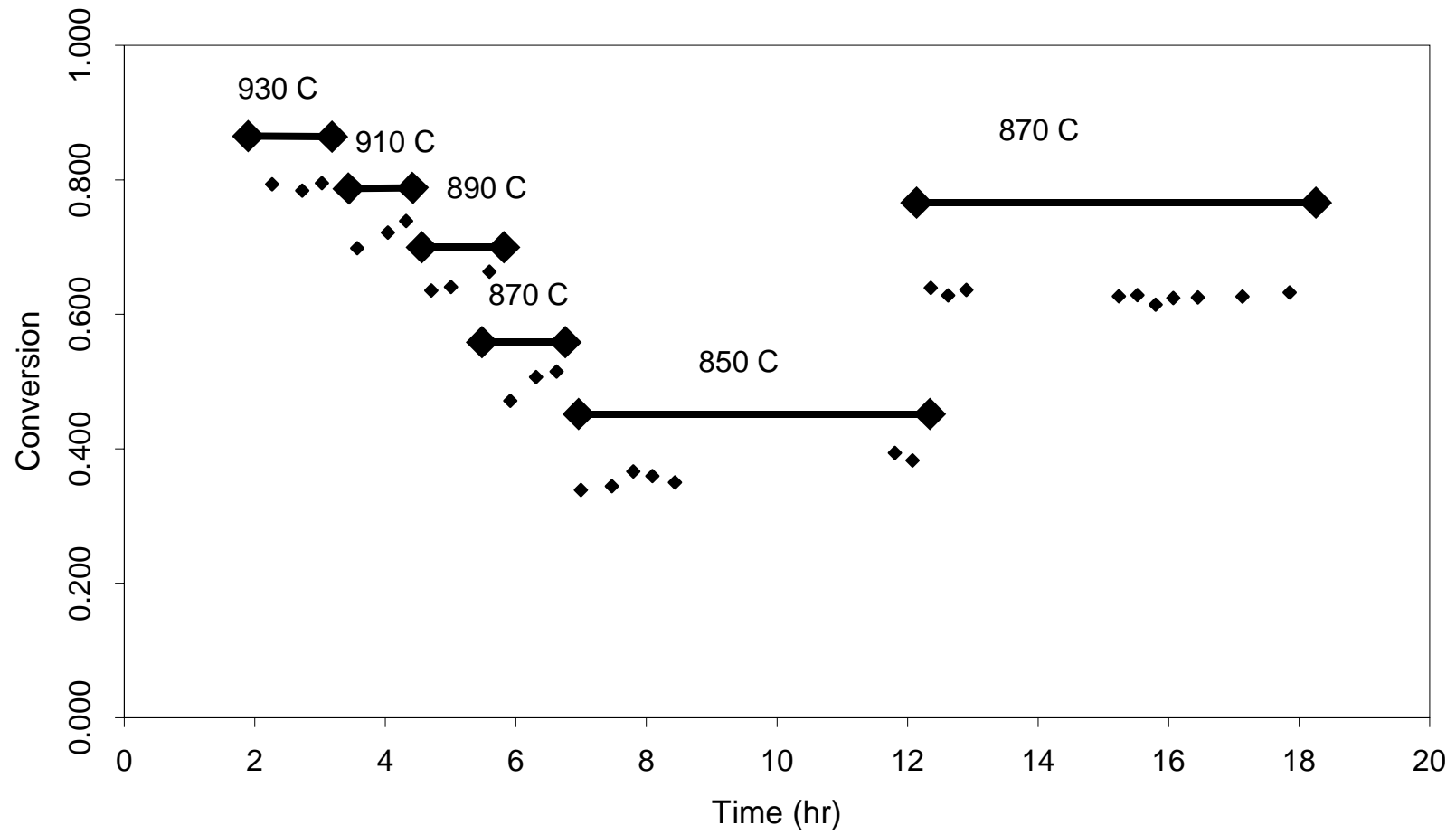


Figure 14. 46% CO experiment with long term stability test; 5 bar, space velocity 3000 h^{-1} , molar flux $.173 \text{ mol/cm}^2\text{-hr}$, $\text{CH}_4/\text{H}_2\text{O} = 1.06$, 46% CO

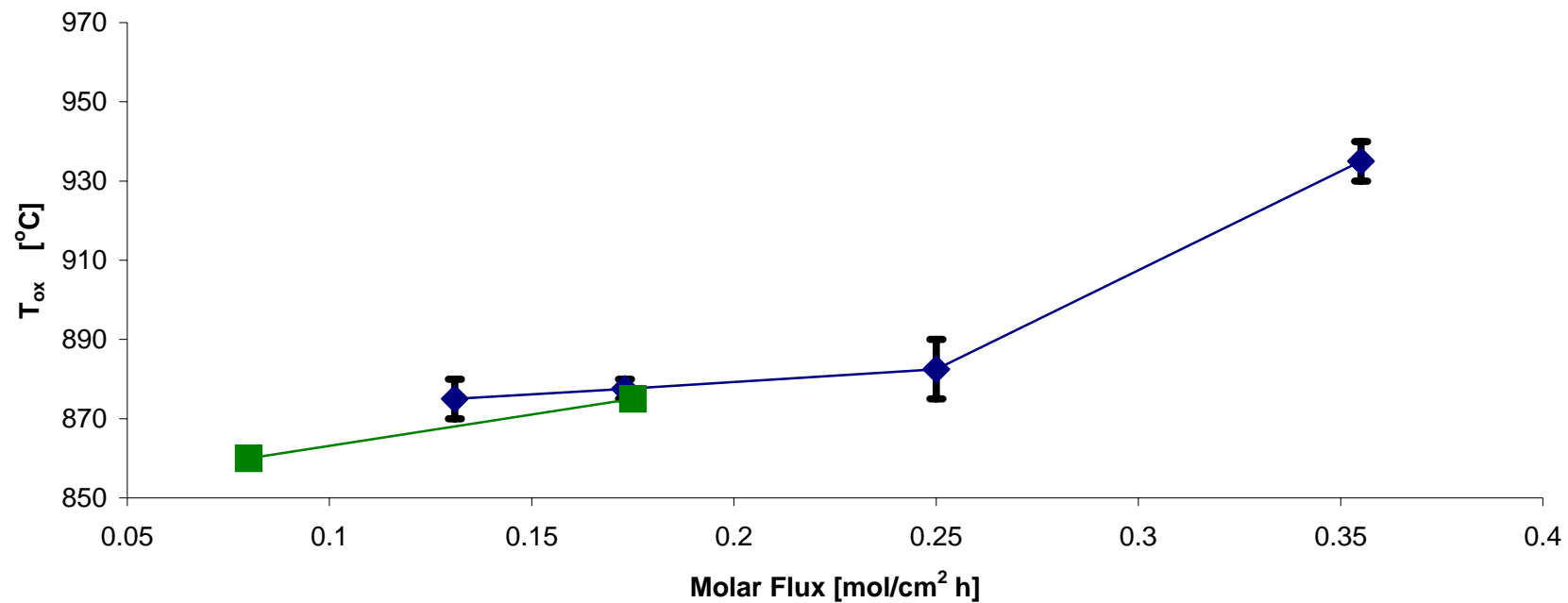


Figure 15. Comparison of DMR and SMR molar flux maps; (— • —) SMR experiments at 5 bar, space velocity 3000 h^{-1} , $\text{CH}_4/\text{H}_2\text{O} = 1.06$; (— • —) DMR experiments at 8.3 bar, space velocity 2900 h^{-1} , $\text{CH}_4/\text{H}_2\text{O} = 1.0$

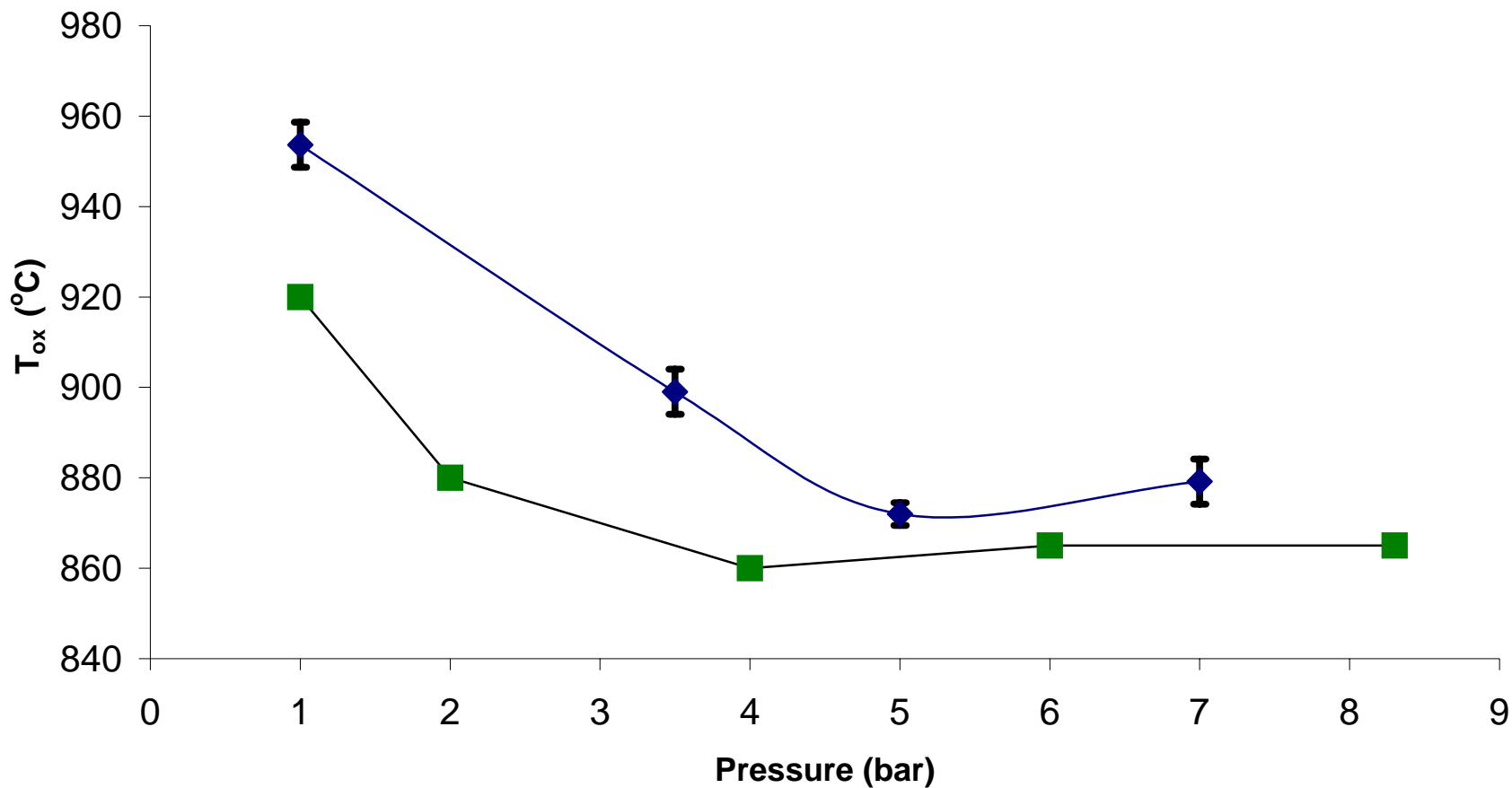


Figure 16. Comparison of DMR and SMR pressure maps; (— • —) SMR experiments extrapolated to molar flux of $.08 \text{ mol/cm}^2\text{-hr}$, space velocity 3000 h^{-1} , $\text{CH}_4/\text{H}_2\text{O} = 1.06$; (— • —) DMR experiments at molar flux of $.08 \text{ mol/cm}^2\text{-hr}$, space velocity 2900 h^{-1} , $\text{CH}_4/\text{H}_2\text{O} = 1.0$

5 REFERENCES

- [1] Ausubel, Jesse H. “Decarbonization: The Next 100 Years” 50th Anniversary Symposium of the Geology Foundation Jackson School of Geosciences, U. of Texas Austin, Texas 25 April 2003 <http://phe.rockefeller.edu/AustinDecarbonization/>
- [2] J. H. Ausubel, Can Technology Spare the Earth? *American Scientist* 84(2):166-178, 1996
- [3] S.E. Wright, *Renewable Energy* 29 (2004) 179–195
- [4] R.J. Farrauto, C.H. Batholomew, *Fundamentals of Industrial Catalytic Process*, Chapman and Hall, London, 1997.
- [5] P. Ferreira-Aparicio, A. Guerrero-Ruiz, I. Rodriguez-Ramos, *Appl. Catal.* 170 (1998) 177.
- [6] H.Y. Wang, E. Ruckenstein, *Appl. Catal.* 204 (2000) 143.
- [7] M L. Pritchard, R L. McCauley, B N. Gallaher, W J. Thomson, *Applied Catalysis A: General* 275 (2004) 213–220
- [8] United States Geological Survey (USGS) website “Metal prices in the United States until 1998”, last modification 8 September 2004, http://minerals.usgs.gov/minerals/pubs/metal_prices/
- [9] A.P.E. York, J.B. Claridge, A.J. Brungs, S.C. Tsang, M.L.H. Green, *Chem. Commun.* 1 (1997) 39.
- [10] J.B. Claridge, A.P.E. York, A.J. Brungs, C. Marquez-Alvarez, J. Sloan, S.C. Tsang, M.L.H. Green, *J. Catal.* 180 (1998) 85.
- [11] A.J. Brungs, A.P.E. York, M.L.H. Green, *Catal. Lett.* 57 (1999) 65.
- [12] J. Sehested, C.J.H. Jacobsen, S. Rokni, J.R. Rostrup-Nielsen, *J. Catal.* 201 (2001) 206.
- [13] D.C. LaMont, A.J. Gilligan, A.R.S. Darujati, A.S. Chellappa, W.J. Thomson, *Appl. Catal.* 255 (2003) 239.
- [14] A.R.S. Darujati, D.C. LaMont, W.J. Thomson, *Appl. Catal.* 253 (2003) 397.
- [15] D.C. LaMont, W.J. Thomson, *Applied Catalysis A: General* 274 (2004) 173–178

APPENDIX

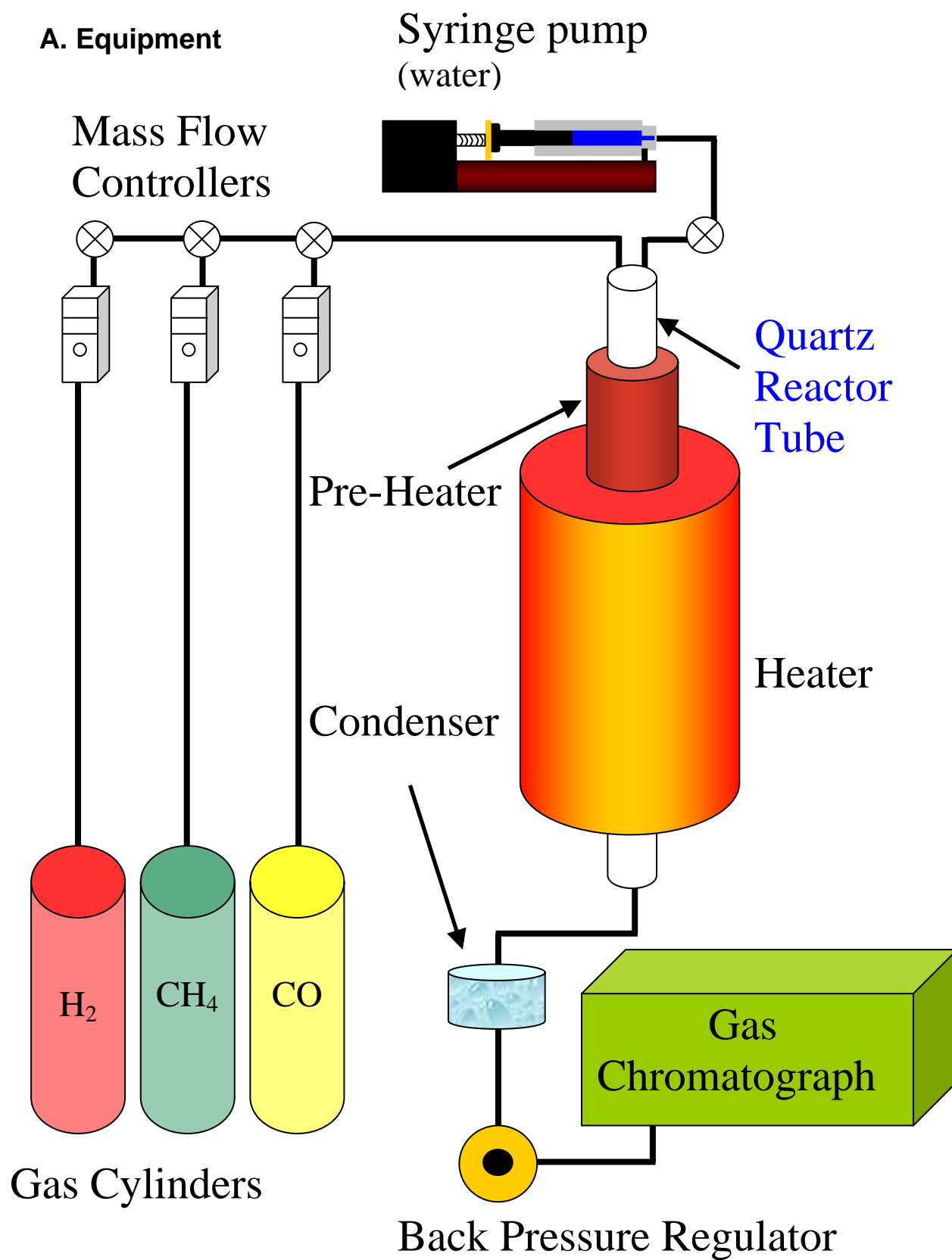


Figure A1. Experimental packed bed reactor system

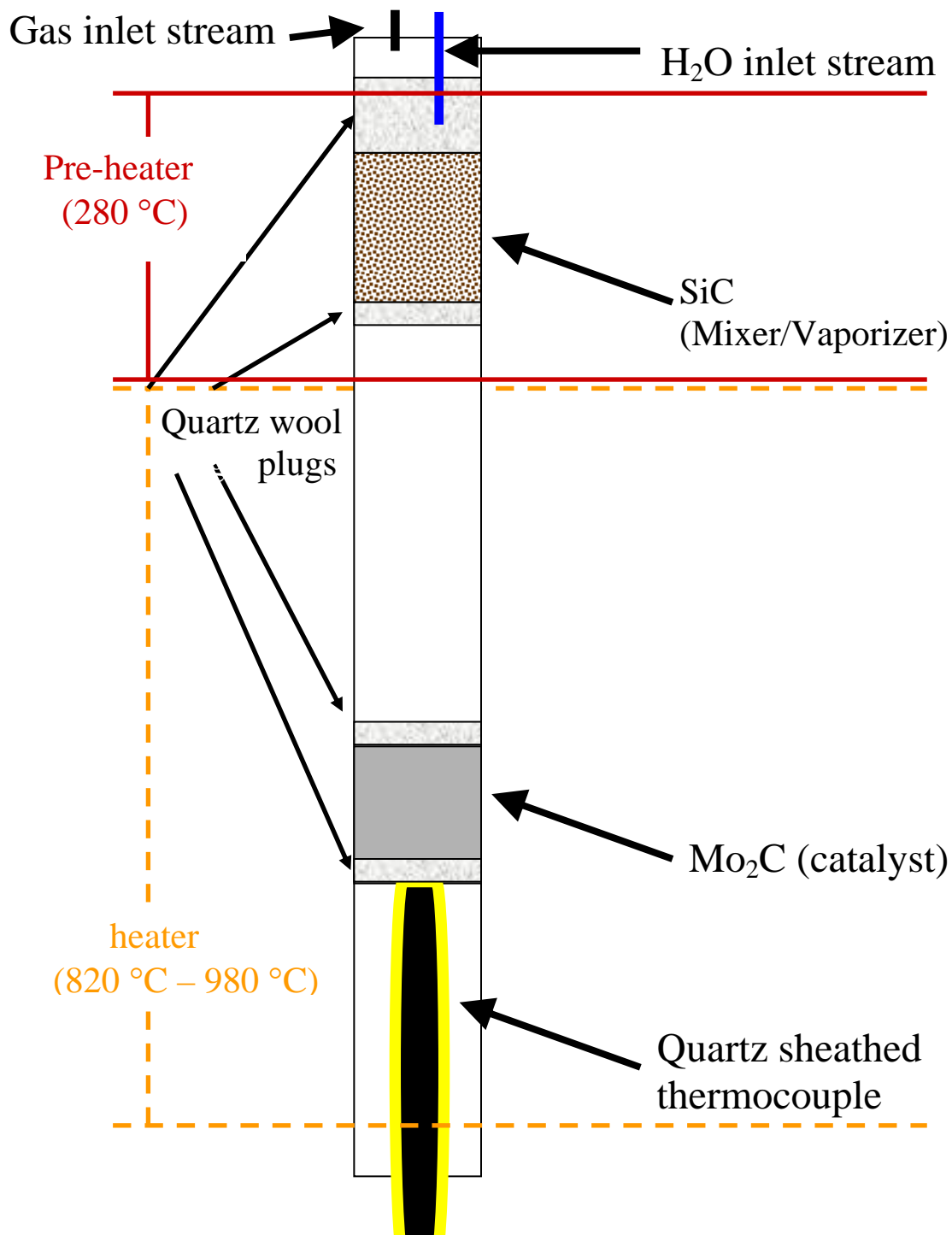


Figure A2. View of quartz reactor tube inside of the heater and pre-heater from Figure A1

B. Run catalogs

Tables B1, B2, B3, and B4 show the run catalog for all runs that were considered essential for analysis and discussion. Table B5 is a run catalog of runs that failed, were not at comparable conditions, and the blank. All these runs had a space velocity (SV) of 3000 hr⁻¹. The SV was calculated using the total volumetric feed flow rate and volume of packed catalyst. The equation for SV can be seen below:

$$SV = \frac{\text{total_volumetric_flow_rate}}{\text{volume_of_catalyst}} = \frac{\text{total_volumetric_flow_rate}}{\text{mass_of_catalyst}} * \text{density_of_catalyst}$$

The CH₄/steam ratio for all of the experiments was 1.06. The molar flux for each experiment is included in the catalog and was calculated by the following equation:

$$\text{Molar_flux} = \frac{\text{total_molar_flow_rate}}{\text{cross_sectional_bed_area}}$$

The reasons why an experiment failed or was not included are compiled in the following list. The given abbreviations will be used in Table B5.

NM – Some experiments were not represented because they had different parameters than those that were chosen for the master experiment.

PD – Excessive pressure drop across the catalyst bed caused the experiment to fail.

SU – There was a mistake at start up that caused the experiment to be terminated.

PUL – The supply of steam to the reactor was pulsing. This happened when the water feed tube was not covered by quartz wool when inserted into the reactor.

☠ - A part of the reactor broke

Table B1. Run catalog for molar flux experiments

Name	Date	Molar Flux (mol/cm ² -hr)	Pressure (bar)	Co-fed products	Deactivation Temp (°C)	Misc
rmsr51305	5/13/2005	0.25	5	no	880 +/- 10	
rmsr51705	5/17/2005	0.131	5	no	875 +/- 5	
rmsr51805	5/18/2005	0.131	5	no	875 +/- 10	Repeat
rmsr51905	5/19/2005	0.173	5	no	877.5 +/- 2.5	Master experiment
rmsr62105	6/21/2005	0.131	5	no	875 +/- 5	Repeat
rmsr62305	6/23/2005	0.355	5	no	935 +/- 10	

Table B2. Run catalog for pressure experiments

Name	Date	Molar Flux (mol/cm ² -hr)	Pressure (bar)	Co-fed products	Deactivation Temp (°C)	Misc
rmsr51905	5/19/2005	0.173	5	no	877.5 +/- 2.5	Master experiment
rmsr63005	6/30/2005	0.173	3.5	no	905 +/- 10	
rmsr7205	7/2/2005	0.173	1	no	960 +/- 10	
rmsr72805	7/28/2005	0.173	7	no	885 +/- 10	

Table B3. Run catalog for H₂ experiments

Name	Date	Molar Flux (mol/cm ² -hr)	Pressure (bar)	Co-fed products	Deactivation Temp (°C)	Misc
rmsr51905	5/19/2005	0.173	5	no	877.5 +/- 2.5	Master experiment
rmsr81805	8/18/2005	0.173	5	25% H ₂	865 +/- 5	
rmsr4705	8/22/2005	0.173	5	47% H ₂	none	
rmsr9305	9/3/2005	0.173	5	18% H ₂	865 +/- 10	
rmsr9505	9/5/2005	0.173	5	6% H ₂ and 6% CO	860 +/- 5	
rmsr92205	9/22/2005	0.173	5	23% H ₂	NA	

Table B4. Run catalog for CO experiments

Name	Date	Molar Flux (mol/cm ² -hr)	Pressure (bar)	Co-fed products	Deactivation Temp (°C)	Misc
rmsr51905	5/19/2005	0.173	5	no	877.5 +/- 2.5	Master experiment
rmsr9505	9/5/2005	0.173	5	6% H ₂ and 6% CO	860 +/- 5	
rmsr9605	9/6/2005	0.173	5	19% CO	860 +/- 10	
rmsr9805	9/8/2005	0.173	5	26% H ₂	860 +/- 10	
rmsr91505	9/15/2005	0.173	5	46% H ₂	none	

Table B5. Run catalog for blank, failed runs and excluded runs

Name	Date	Molar Flux (mol/cm ² -hr)	Pressure (bar)	Co-fed products	Deactivation Temp (°C)	Misc
rmsr122704	12/27/2004	0.131	2.5	no	875 +/- 5	NM
rmsr122905	12/29/2004	0.451	>7	no	-	PD NM
rmsr123004	12/30/2004	0.25	3.5	no	not clear	NM
rmsr1305	1/3/2005	0.131	2	no	875 +/- 5	NM
rmsr1505	1/5/2005	0.25	2	no	912.5 +/- 7.5	NM
rmsr1805	1/8/2005	0.13	2	61% H ₂	none	NM conversion at 850 °C 72%
rmsr12905	1/29/2005	0.26	2	59% H ₂	none	NM
rmsr2305	2/3/2005	0.26	2	59% H ₂	none	NM conversion at 850 °C 76%
rmsr21705	2/17/2005	0.4	>7	no	-	PD NM
rmsr22405	2/24/2005	0.3	5	no	865 +/- 10	NM
rmsr53105	5/31/2005	0.131	5	no	-	SU
rmsr6205	6/2/2005	0.131	5	no	-	SU
rmsr6905	6/9/2005	0.131	5	no	-	PUL
rmsr61605	6/16/2005	0.131	5	no	-	PUL
rmsr62005	6/20/2005	0.131	5	no	-	PUL
rmsr62905	6/29/2005	0.355	5	no	-	☀ Broken heater
rmsr72705	7/27/2005	0.173	7	no	-	SU
rmsr8905	8/9/2005	0.173	5	6% H ₂	-	SU
rmsr81705	8/17/2005	0.173	5	6% H ₂	-	☀ Broken thermocouple
rmsr91705	9/17/2005	0.11	4.4	no	NA	Blank (lots of coke on tube walls)
rmsr92105	9/21/2005	0.173	5	23% H ₂	-	SU

C. Thermodynamic equilibrium calculations in MathCad

Method for calculating the thermodynamic equilibrium compositions for steam methane reforming. This method will take into account the water gas shift reaction and the dry reforming reaction that may occur simultaneously with steam reforming.

Methane gibbs free energy calculations for various temperatures

$\text{data} := \begin{pmatrix} 0 & -66911 \\ 298 & -50768 \\ 500 & -32741 \\ 1000 & 19492 \\ 2000 & 130802 \\ 3000 & 242332 \end{pmatrix}$	<p>Gibbs free energy data from: Physical Chemistry 3rd ed. Silbey, Alberty 2001 Table C.3 pgs 901-903</p>	
	$\Delta G_{\text{ch4}} := (\text{data})^{(1)} \quad \text{units J/mol}$	$T := (\text{data})^{(0)} \quad \text{units K}$

$$\text{vs}_1 := \text{cspline}(T, \Delta G_{\text{ch4}}) \quad \Delta G_{\text{CH4}}(T_{\text{val}}) := \text{interp}(\text{vs}_1, T, \Delta G_{\text{ch4}}, T_{\text{val}})$$

$$\Delta G_{\text{CH4}}(1000) = 1.949 \times 10^4$$

H2O gibbs free energy calculations for various temperatures

$\text{data} := \begin{pmatrix} 0 & -238921 \\ 298 & -228582 \\ 500 & -219051 \\ 1000 & -192590 \\ 2000 & -135528 \\ 3000 & -77163 \end{pmatrix}$	<p>Gibbs free energy data from: Physical Chemistry 3rd ed. Silbey, Alberty 2001 Table C.3 pgs 901-903</p>	
	$\Delta G_{\text{h2o}} := (\text{data})^{(1)} \quad \text{units J/mol}$	$T := (\text{data})^{(0)} \quad \text{units K}$

$$\text{vs}_2 := \text{cspline}(T, \Delta G_{\text{h2o}}) \quad \Delta G_{\text{H2O}}(T_{\text{val}}) := \text{interp}(\text{vs}_2, T, \Delta G_{\text{h2o}}, T_{\text{val}})$$

$$\Delta G_{\text{H2O}}(1000) = -1.926 \times 10^5$$

CO gibbs free energy calculations for various temperatures

$$\text{data} := \begin{pmatrix} 0 & -113805 \\ 298 & -137163 \\ 500 & -155414 \\ 1000 & -200275 \\ 2000 & -286034 \\ 3000 & -367816 \end{pmatrix}$$

Gibbs free energy data from:
Physical Chemistry 3rd ed.
Silbey, Alberty 2001
Table C.3 pgs 901-903

$$\Delta G_{\text{CO}} := (\text{data})^{\langle 1 \rangle} \quad \text{units J/mol} \quad T := (\text{data})^{\langle 0 \rangle} \quad \text{units K}$$

$$\text{vs}_3 := \text{cspline}(T, \Delta G_{\text{CO}}) \quad \Delta G_{\text{CO}}(T_{\text{val}}) := \text{interp}(\text{vs}_3, T, \Delta G_{\text{CO}}, T_{\text{val}})$$

$$\Delta G_{\text{CO}}(1000) = -2.003 \times 10^5$$

CO2 gibbs free energy calculations for various temperatures

$$\text{data} := \begin{pmatrix} 0 & -393151 \\ 298 & -394389 \\ 500 & -394939 \\ 1000 & -395886 \\ 2000 & -396333 \\ 3000 & -395461 \end{pmatrix}$$

Gibbs free energy data from:
Physical Chemistry 3rd ed.
Silbey, Alberty 2001
Table C.3 pgs 901-903

$$\Delta G_{\text{CO}_2} := (\text{data})^{\langle 1 \rangle} \quad \text{units J/mol} \quad T := (\text{data})^{\langle 0 \rangle} \quad \text{units K}$$

$$\text{vs}_4 := \text{cspline}(T, \Delta G_{\text{CO}_2}) \quad \Delta G_{\text{CO}_2}(T_{\text{val}}) := \text{interp}(\text{vs}_4, T, \Delta G_{\text{CO}_2}, T_{\text{val}})$$

$$\Delta G_{\text{CO}_2}(1000) = -3.959 \times 10^5$$

The following method is from Perry's Chemical Engineering Handbook 7th ed. section 4-34

$$\text{Temp} := 1.183 \times 10^3 \quad \text{in K}$$

$$\Delta G_1 := \Delta G_{\text{CH}_4}(\text{Temp}) \quad \Delta G_1 = 3.958 \times 10^4 \quad R_g := 8.314 \quad \text{Gas constant}$$

$$\Delta G_2 := \Delta G_{\text{H}_2\text{O}}(\text{Temp}) \quad \Delta G_2 = -1.824 \times 10^5 \quad p := 1 \quad \text{pressure of standard gibbs free energy (bar)}$$

$$\Delta G_3 := \Delta G_{\text{CO}}(\text{Temp}) \quad \Delta G_3 = -2.163 \times 10^5 \quad p := 5 \quad \text{pressure of the experiment (bar)}$$

$$\Delta G_4 := \Delta G_{\text{CO}_2}(\text{Temp}) \quad \Delta G_4 = -3.961 \times 10^5 \quad T_K := (\text{Temp})$$

$A_C := .27295$	Moles of C in feed	Mol fraction in feed
		$y_{CH_4} = .27295$
$A_O := .25705$	Moles of O in feed	
		$y_{H_2O} = .25705$
$A_H := 4 \cdot .27295 + 2 \cdot .25705 + 2 \cdot .47$	Moles of H in feed	
		$y_{H_2} = .47$
		Basis 1 mol of gas in feed

The main equation used to solve for the equilibrium compositions.
 One of these equations is required for each species present.

$$\frac{\Delta G_{f_i}^{\circ}}{RT} + \ln \frac{n_i}{\sum_j n_j} + \sum_k \frac{\lambda_k}{RT} a_{ik} = 0$$

Initial guesses for the solve block

moles of the various gases

$n_{CH_4} := .5$ $n_{H_2O} := 1$ $n_{CO} := 1$ $n_{CO_2} := 1$ $n_{H_2} := .8$

$f_i = \frac{\lambda_k}{R \cdot T} \cdot a_{ik}$ This term can just be considered a constant that must be solve for to get the moles of each species.

$f_c := 1$ $f_o := 5$ $f_h := 5$

Start of the solve block

Given

$$\frac{\Delta G_1}{R_g \cdot T_K} + \ln \left(\frac{n_{CH_4}}{n_{CH_4} + n_{H_2O} + n_{CO} + n_{CO_2} + n_{H_2}} \cdot \frac{P}{p} \right) + f_c + 4 \cdot f_h = 0 \quad \text{Methane}$$

$$\frac{\Delta G_2}{R_g \cdot T_K} + \ln \left(\frac{n_{H_2O}}{n_{CH_4} + n_{H_2O} + n_{CO} + n_{CO_2} + n_{H_2}} \cdot \frac{P}{p} \right) + 2 \cdot f_h + f_o = 0 \quad \text{Steam}$$

$$\frac{\Delta G_3}{R_g \cdot T_K} + \ln \left(\frac{n_{CO}}{n_{CH_4} + n_{H_2O} + n_{CO} + n_{CO_2} + n_{H_2}} \cdot \frac{P}{p} \right) + f_c + f_o = 0 \quad \text{CO}$$

$$\frac{\Delta G_4}{R_g \cdot T_K} + \ln \left(\frac{n_{CO_2}}{n_{CH_4} + n_{H_2O} + n_{CO} + n_{CO_2} + n_{H_2}} \cdot \frac{P}{p} \right) + f_c + 2 \cdot f_o = 0 \quad \text{CO}_2$$

$$\ln \left(\frac{n_{H_2}}{n_{CH_4} + n_{H_2O} + n_{CO} + n_{CO_2} + n_{H_2}} \cdot \frac{P}{p} \right) + 2 \cdot f_h = 0 \quad \text{H}_2$$

$$n_{CH_4} + n_{CO} + n_{CO_2} = A_c \quad \text{Carbon balance}$$

$$n_{CO} + 2 \cdot n_{CO_2} + n_{H_2O} = A_o \quad \text{Oxygen balance}$$

$$4 \cdot n_{CH_4} + 2 \cdot n_{H_2O} + 2 \cdot n_{H_2} = A_H \quad \text{Hydrogen balance}$$

$$\text{vec} := \text{Find}(n_{CH_4}, n_{H_2O}, n_{CO}, n_{CO_2}, n_{H_2}, f_c, f_o, f_h)$$

$$\text{vec} = \begin{pmatrix} 0.057 \\ 0.036 \\ 0.211 \\ 5.175 \times 10^{-3} \\ 1.122 \\ 0.319 \\ 21.983 \\ -0.683 \end{pmatrix}$$

Mole fraction calculations

$$y_{CH_4} := \frac{\text{vec}_0}{\text{vec}_0 + \text{vec}_1 + \text{vec}_2 + \text{vec}_3 + \text{vec}_4} \quad y_{CH_4} = 0.04$$

$$y_{\text{H}_2\text{O}} := \frac{\text{vec}_1}{\text{vec}_0 + \text{vec}_1 + \text{vec}_2 + \text{vec}_3 + \text{vec}_4}$$

$$y_{\text{H}_2\text{O}} = 0.025$$

$$y_{\text{CO}} := \frac{\text{vec}_2}{\text{vec}_0 + \text{vec}_1 + \text{vec}_2 + \text{vec}_3 + \text{vec}_4}$$

$$y_{\text{CO}} = 0.147$$

$$y_{\text{CO}_2} := \frac{\text{vec}_3}{\text{vec}_0 + \text{vec}_1 + \text{vec}_2 + \text{vec}_3 + \text{vec}_4}$$

$$y_{\text{CO}_2} = 3.615 \times 10^{-3}$$

$$y_{\text{H}_2} := \frac{\text{vec}_4}{\text{vec}_0 + \text{vec}_1 + \text{vec}_2 + \text{vec}_3 + \text{vec}_4}$$

$$y_{\text{H}_2} = 0.784$$