

Figure 1. Sr composition dependencies of the electrical conductivity and oxygen self diffusion coefficient D for $La_{(1-x)}Sr_xFeO_{3-\delta}$, from Kim *et al.* [2].

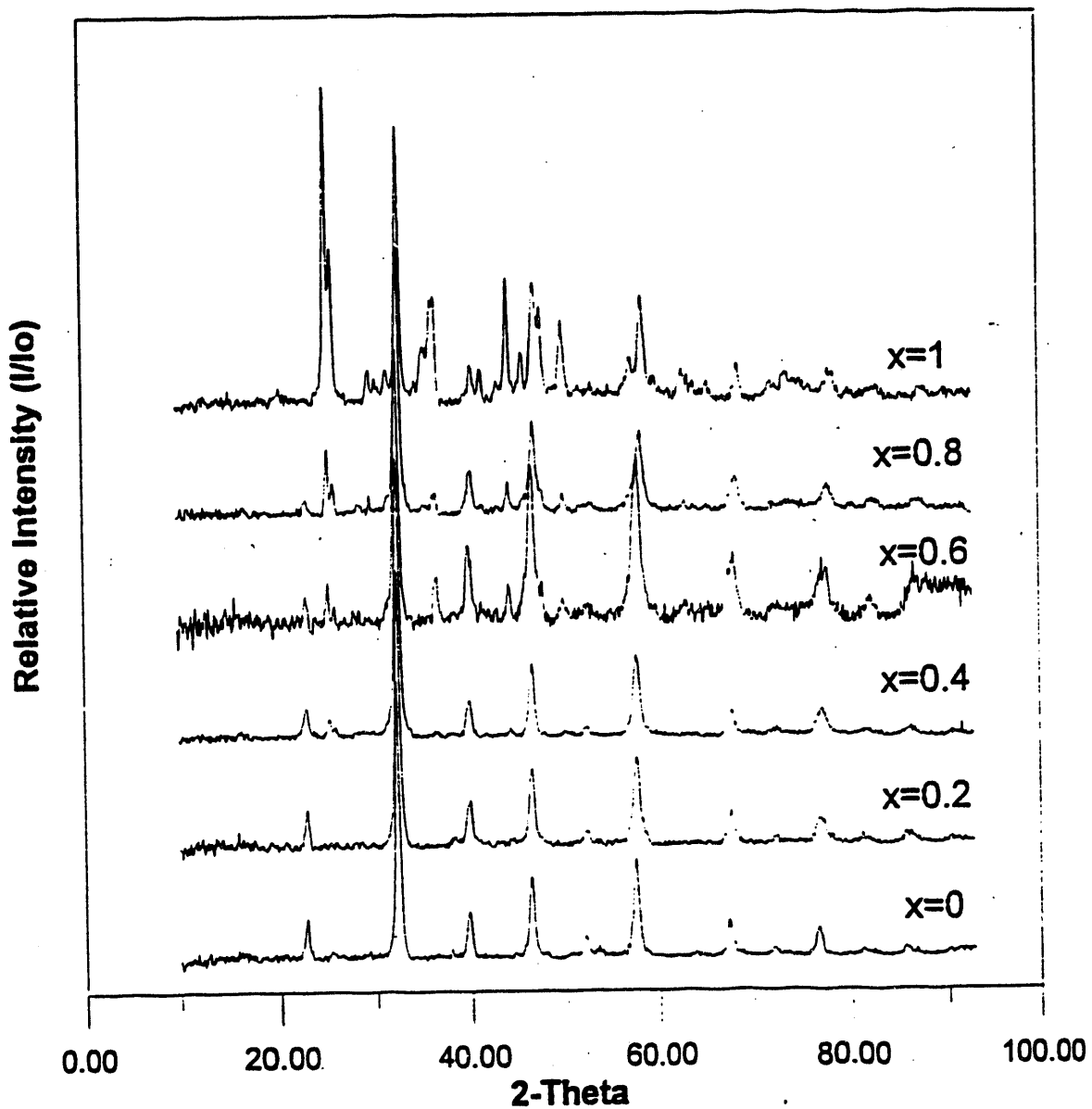


Figure 2 XRD spectra showing the crystallographic structure of Sr substituted perovskite-type oxide, $\text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}_3$, as a function of varying Sr composition.

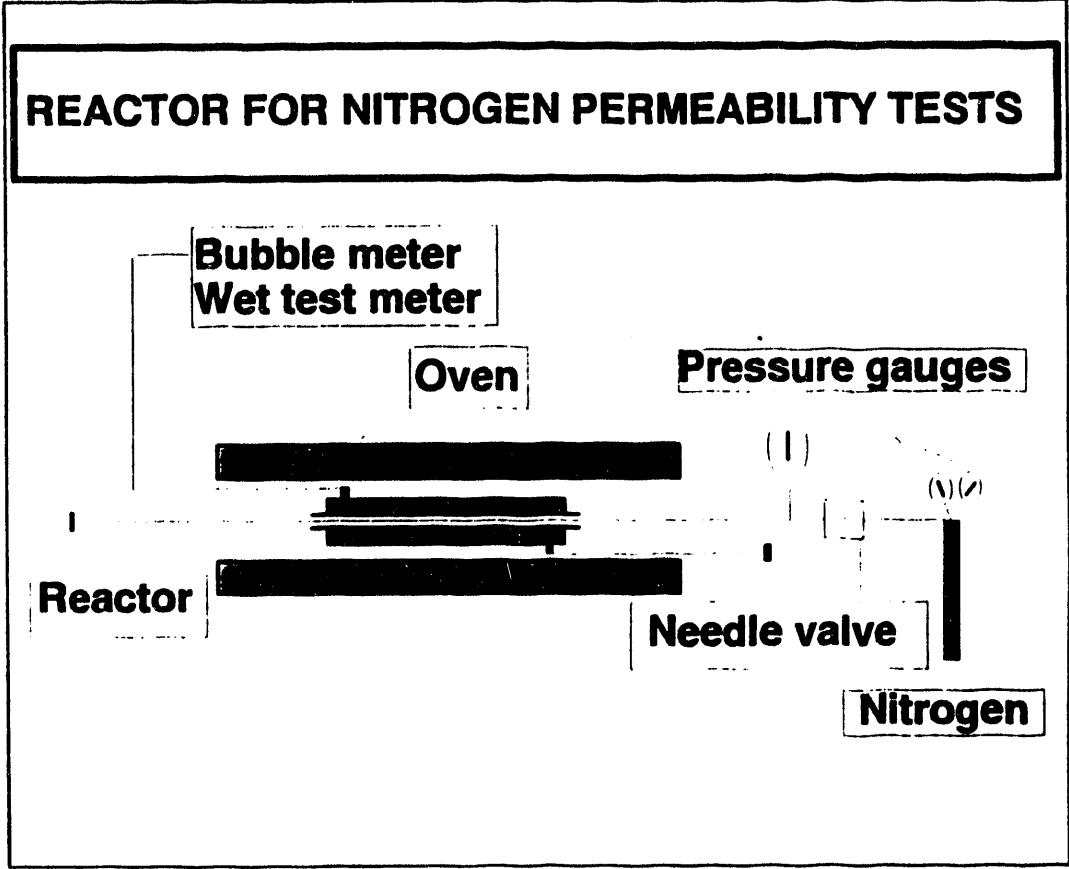


Figure 3. Schematic of the experimental setup showing the permeability measuring apparatus.

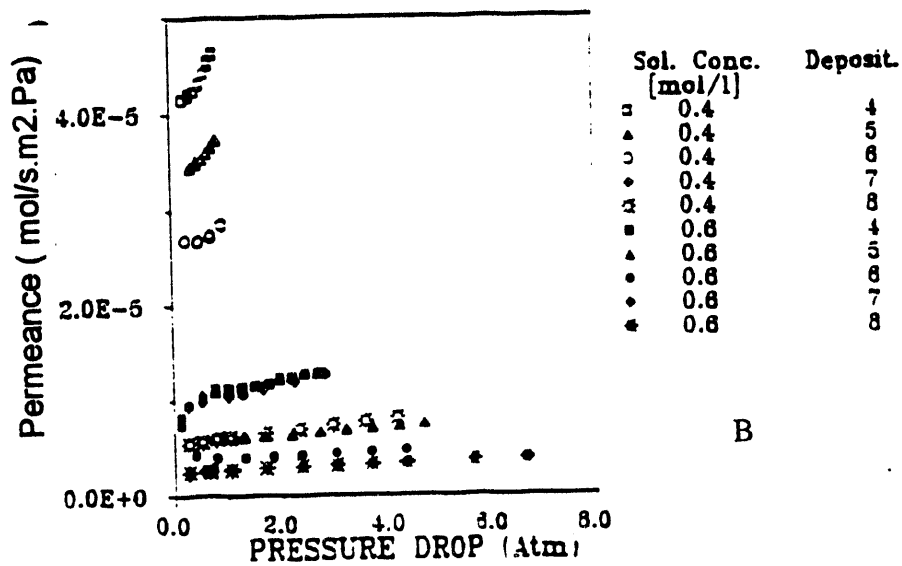
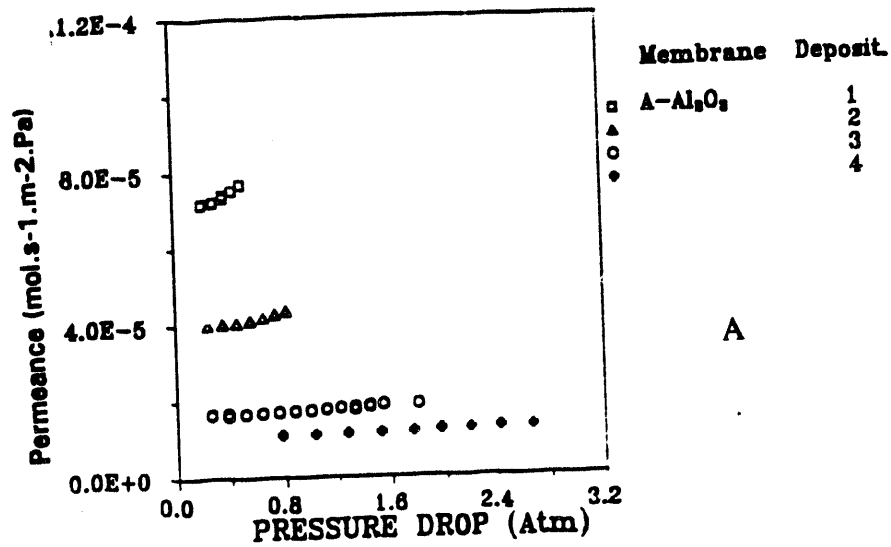


Figure 4. Effect of successive perovskite depositions on nitrogen permeance through alpha alumina and zirconia membranes. (A) 1-3 Deps. (B) 4-8 Deps.

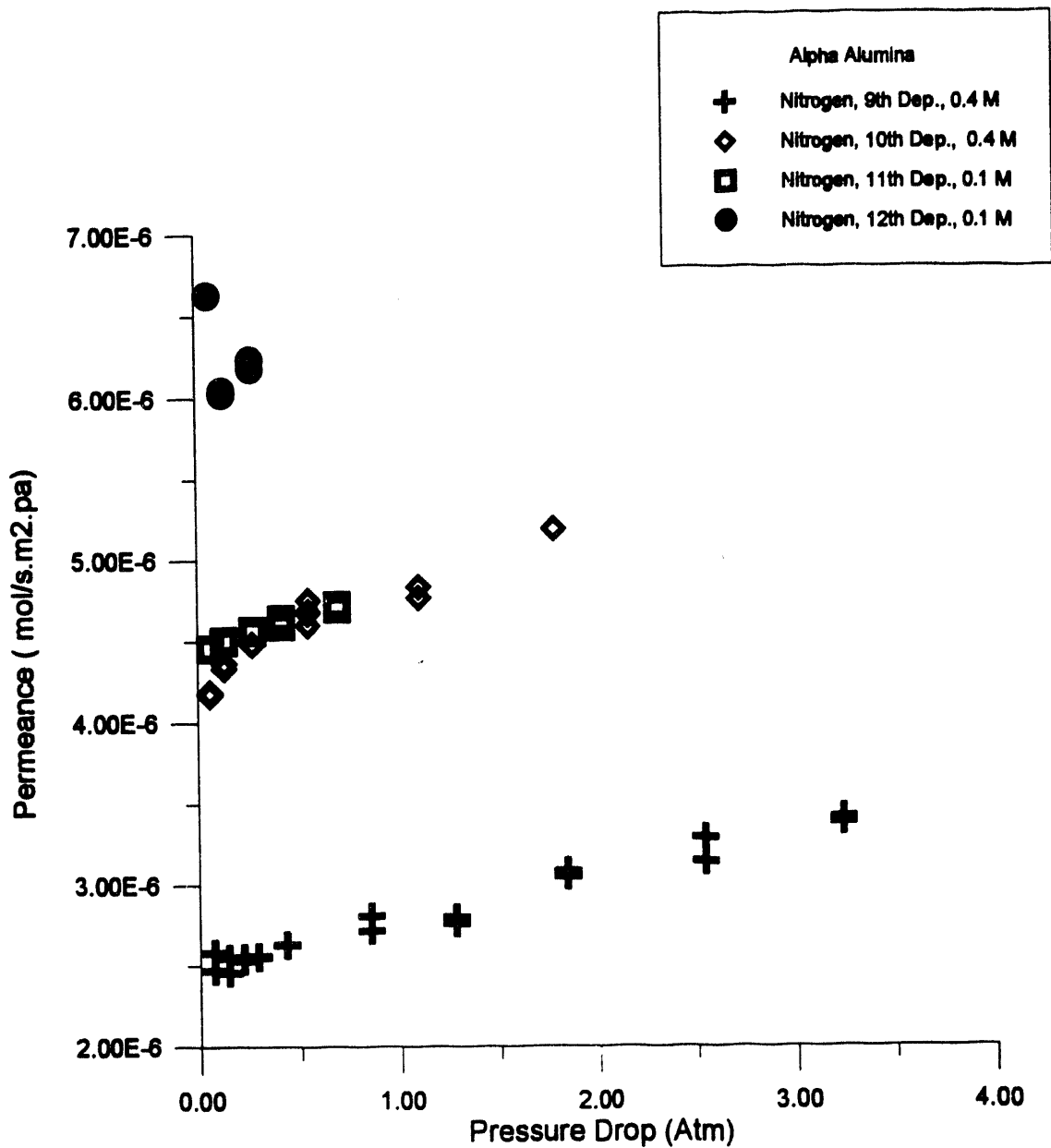


Figure 5. Change of Nitrogen permeance through alpha alumina with depositions at successively lower $\text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}_3$ solution concentrations.

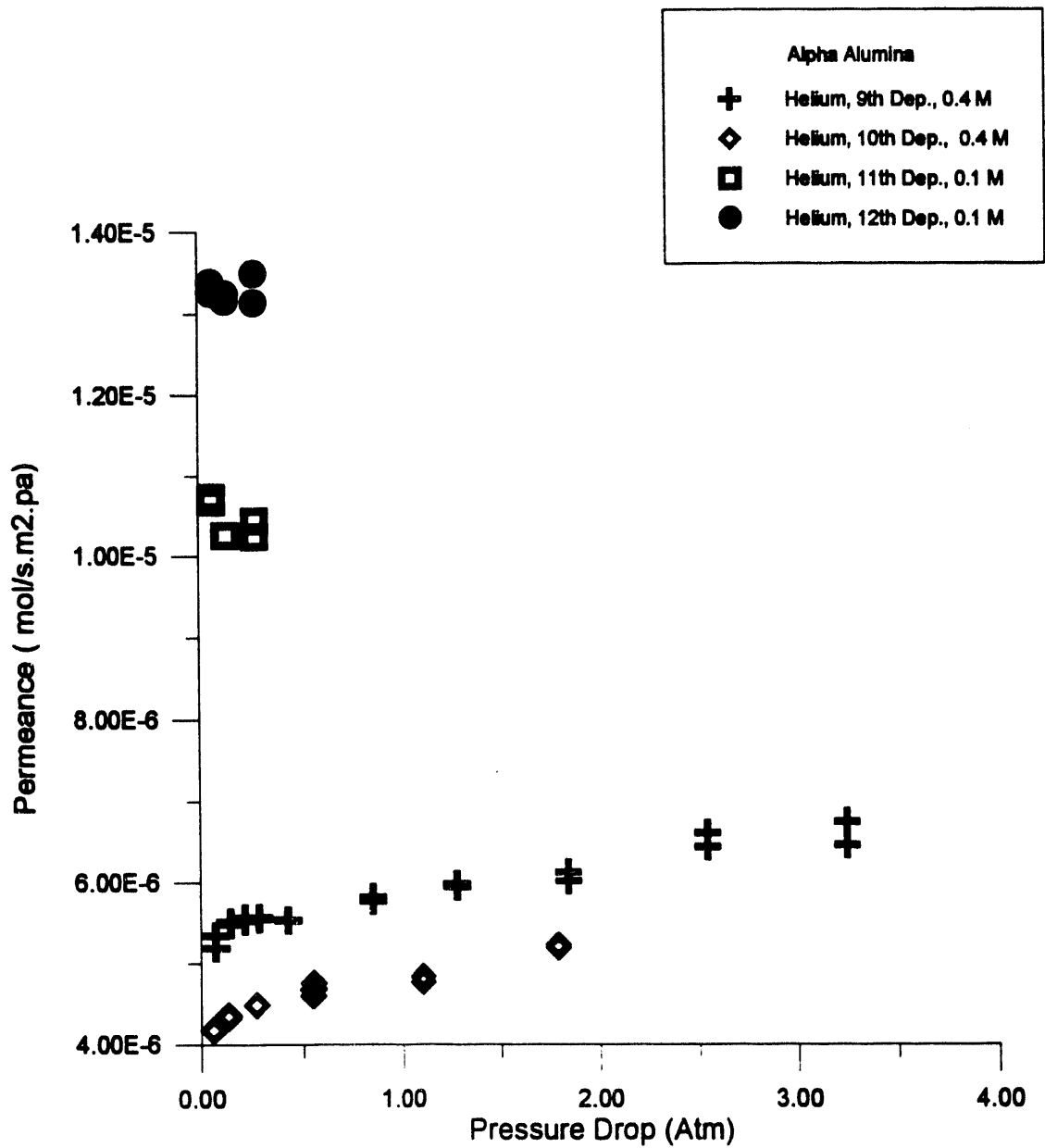


Figure 6. Change of Helium permeance through alpha alumina with depositions at successively lower $\text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}_3$ solution concentrations.

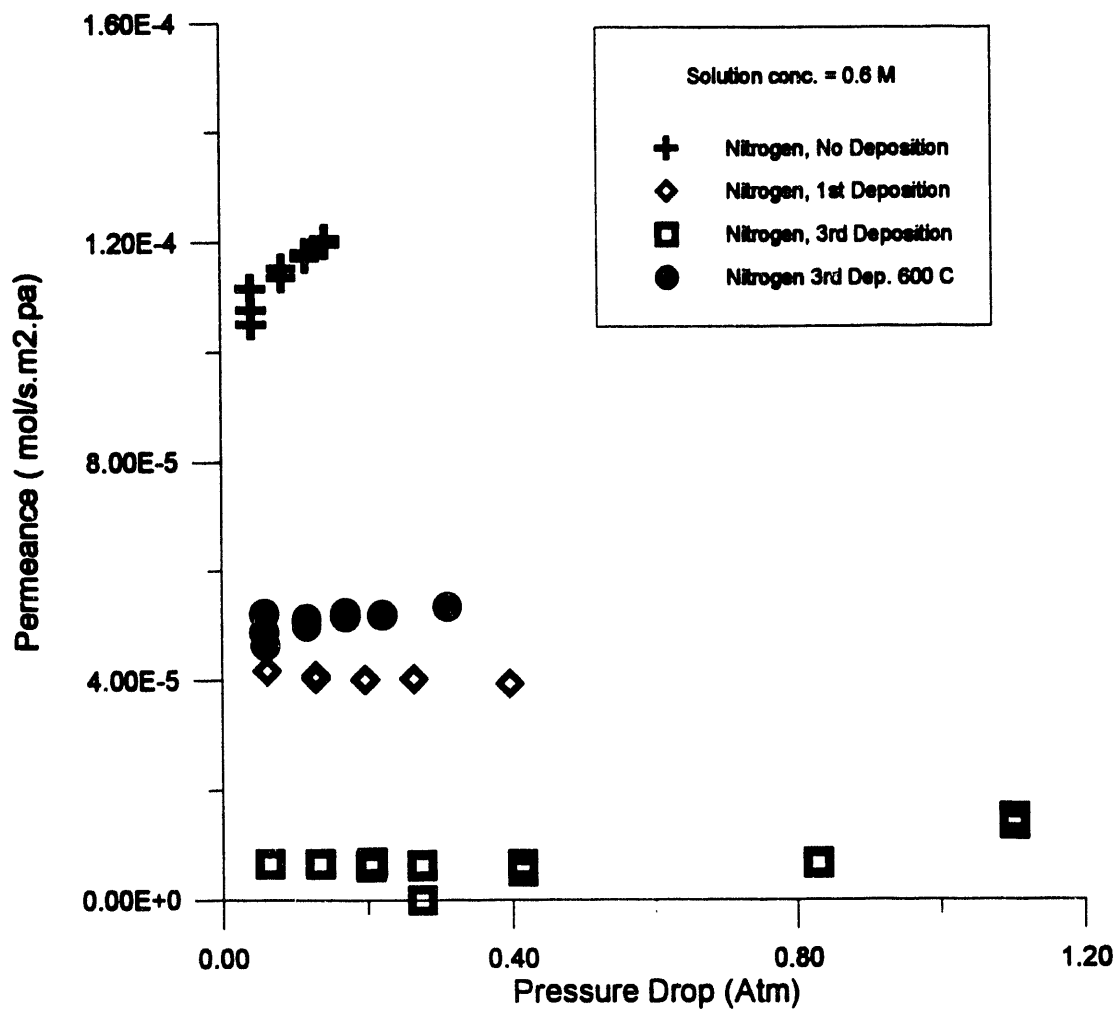


Figure 7. Change of Nitrogen permeance through modified alpha alumina on increasing temperature.

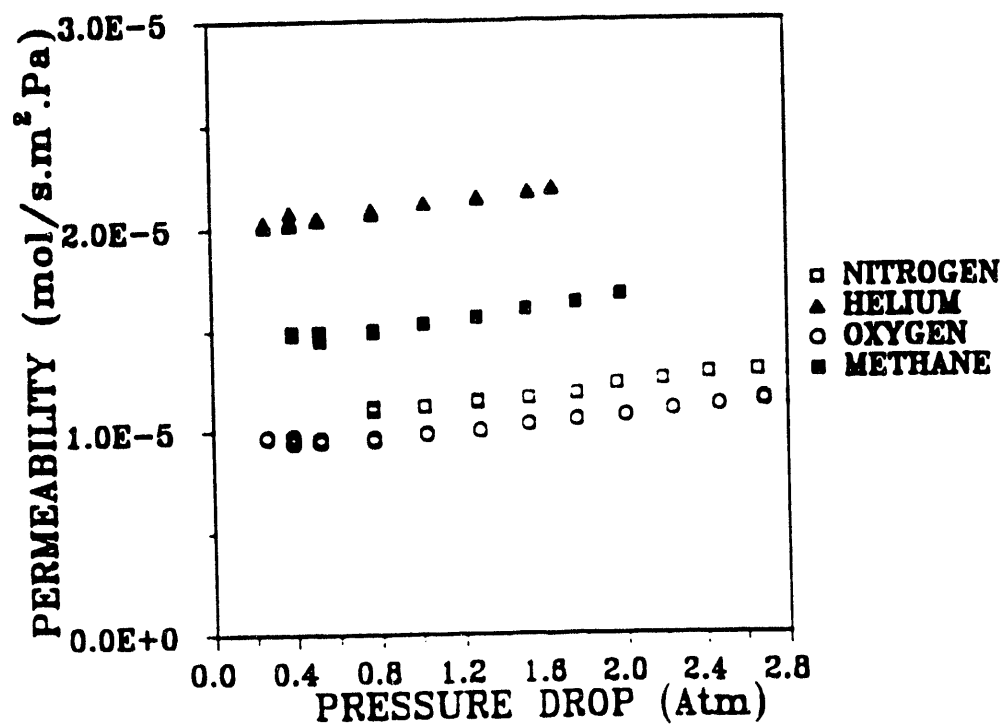


Figure 8. Permeance of various gases through a 2000 Angstrom alpha alumina membrane after 4th deposition of $\text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}_3$.

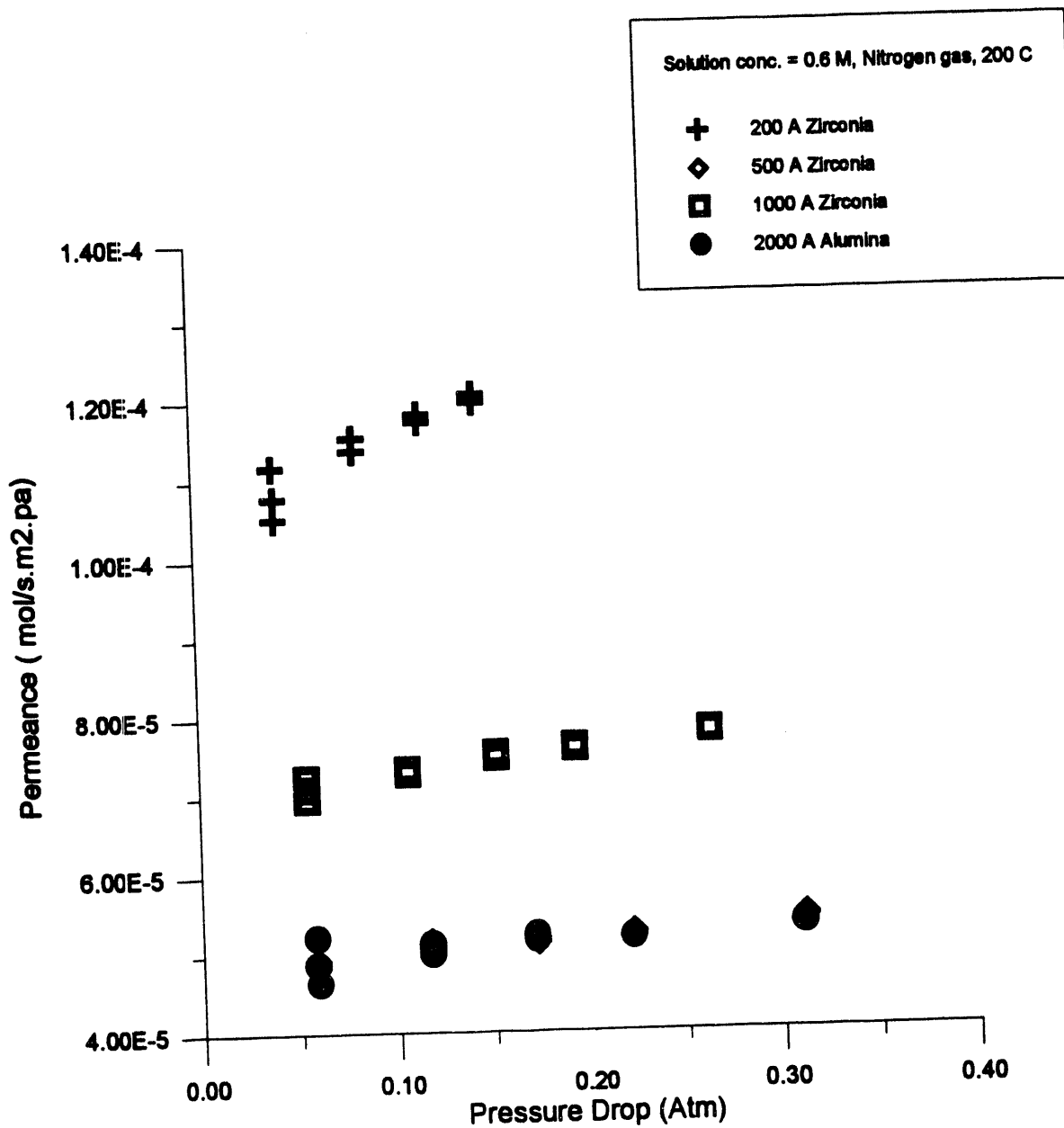


Figure 9. Comparison of nitrogen permeances through modified zirconia membranes of different pore sizes and 2000 Angstrom pore size alpha alumina membrane .

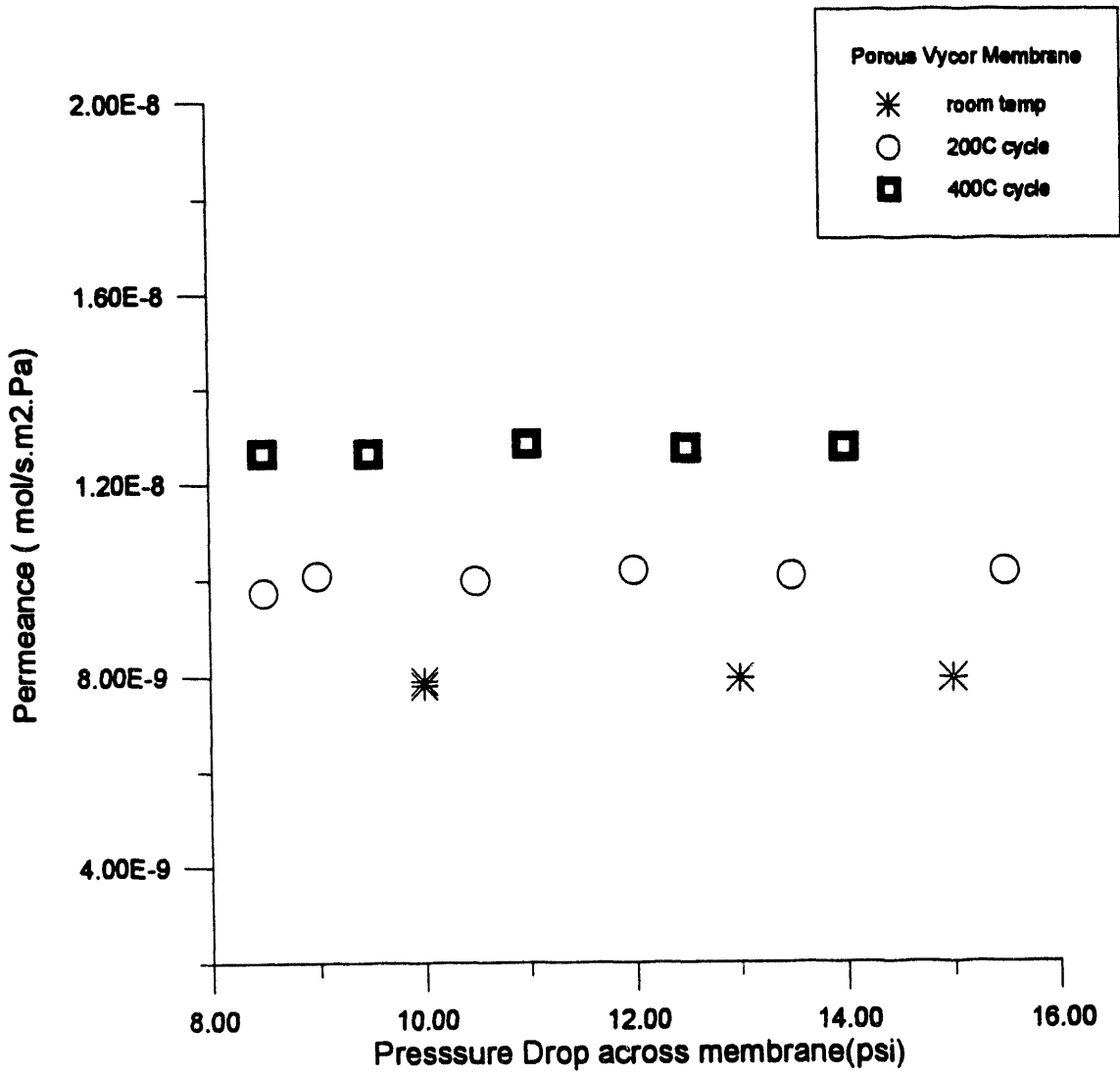


Figure 10. Permeance changes for nitrogen gas through porous VYCOR with temperature treatments.

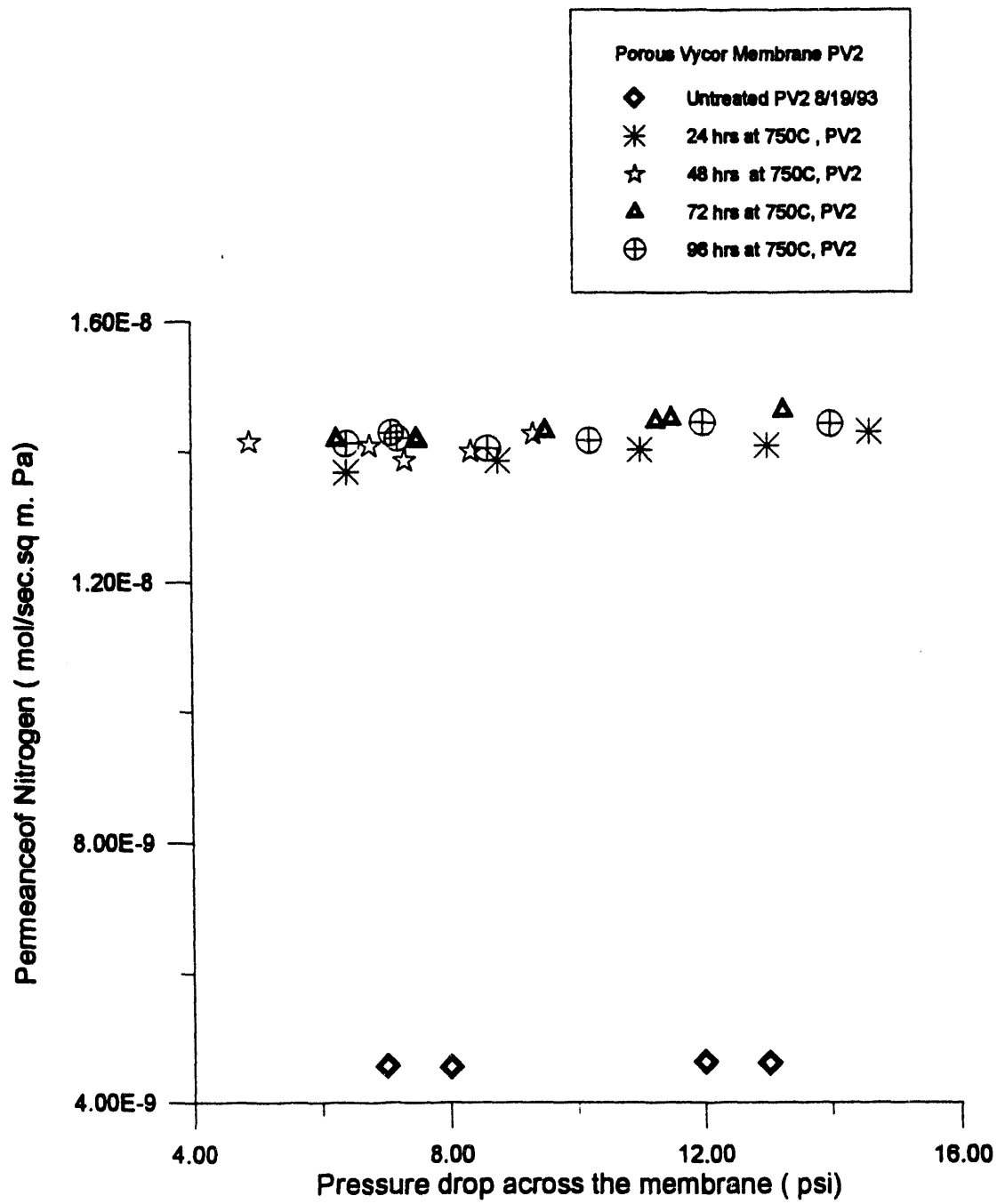


Figure 11. Permeance stabilization in Porous VYCOR at 750°C for extended times.

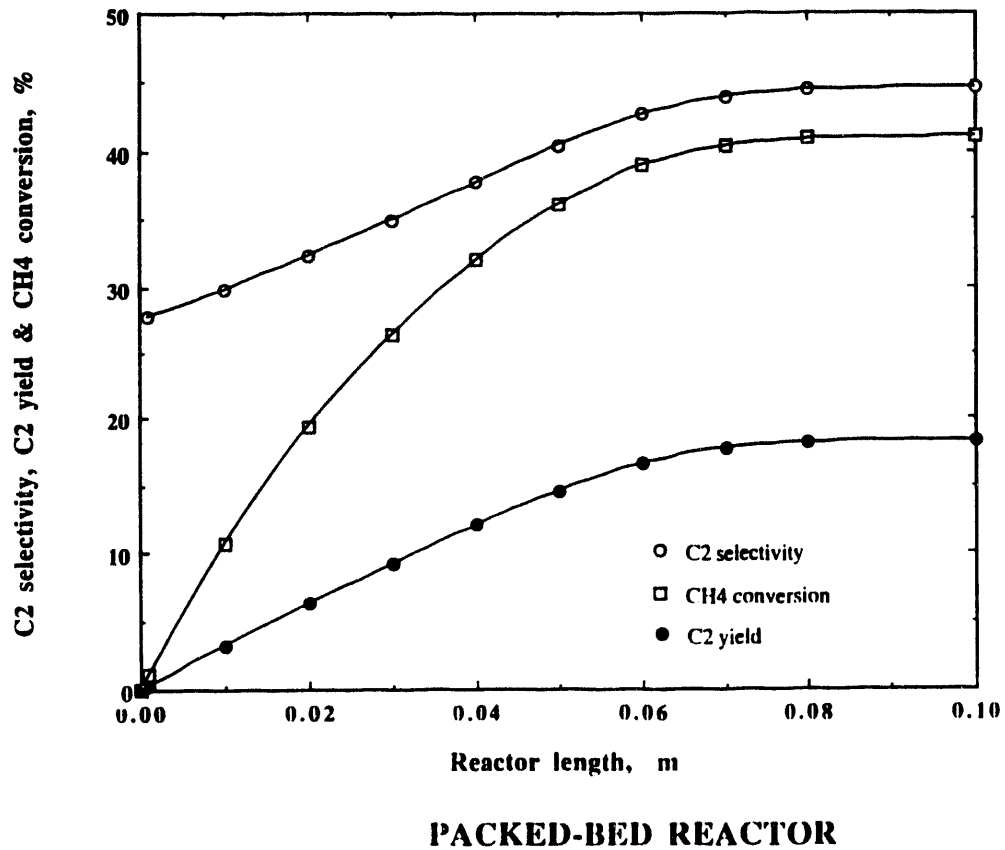


Figure 12. Modeling results for conventional packed bed reactor.

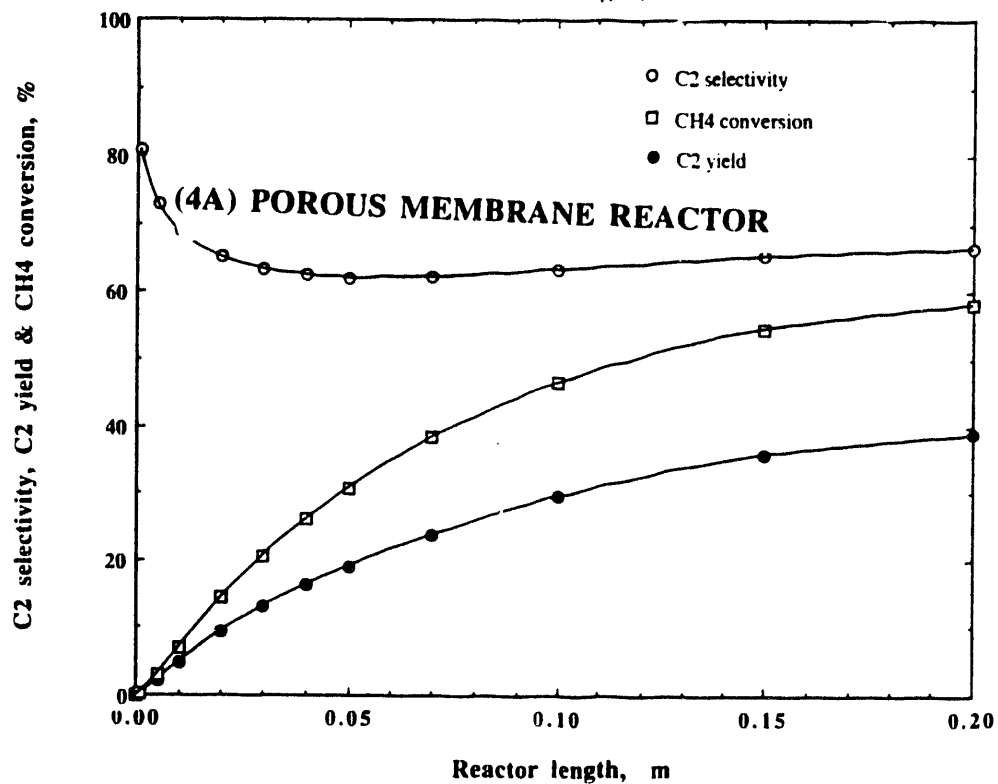
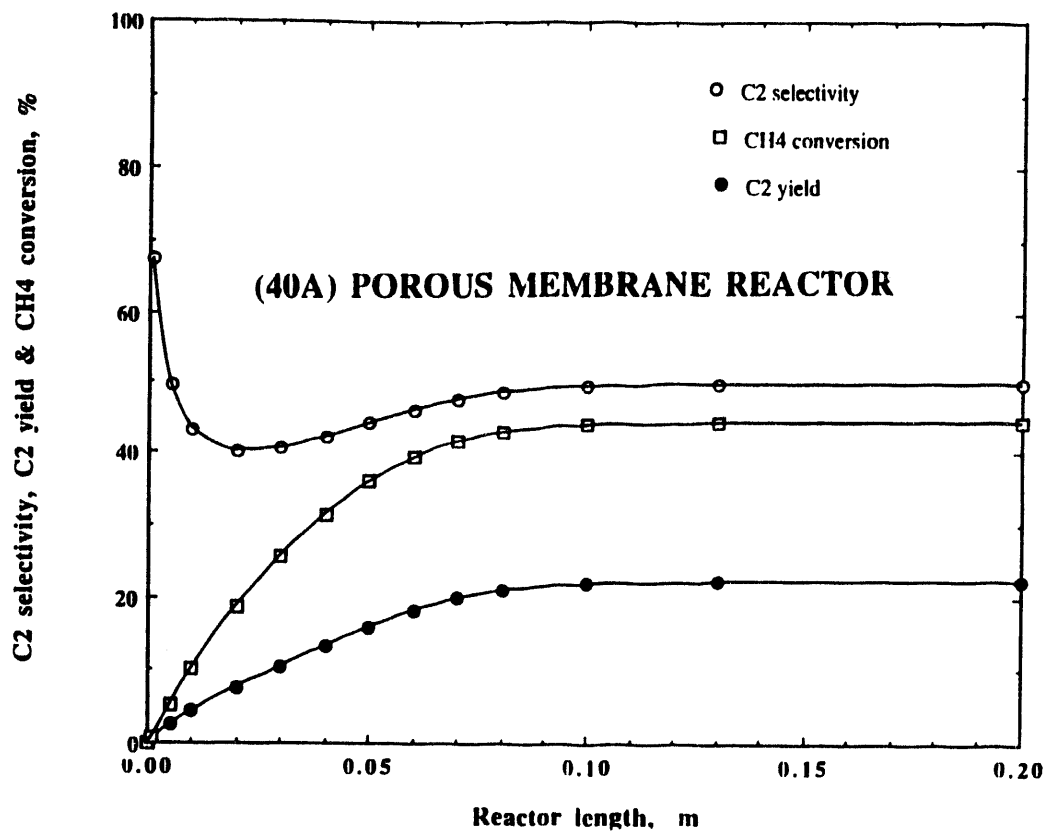


Figure 13. Modeling results for 40 Angstrom and 4 Angstrom pore size packed bed membrane reactor.

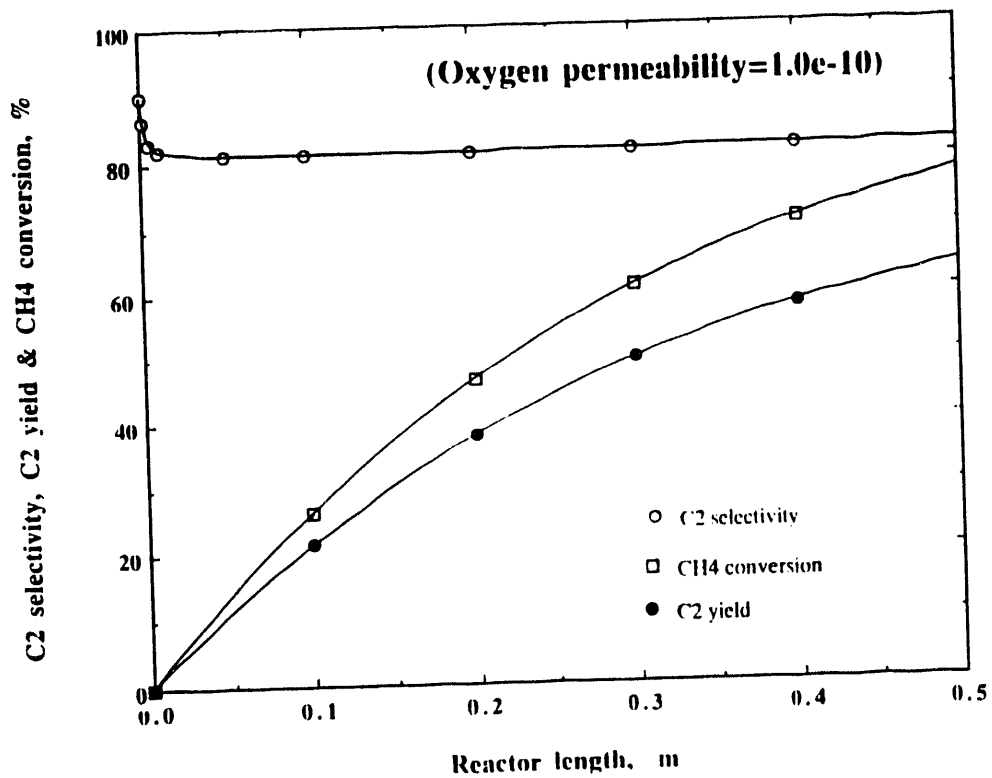
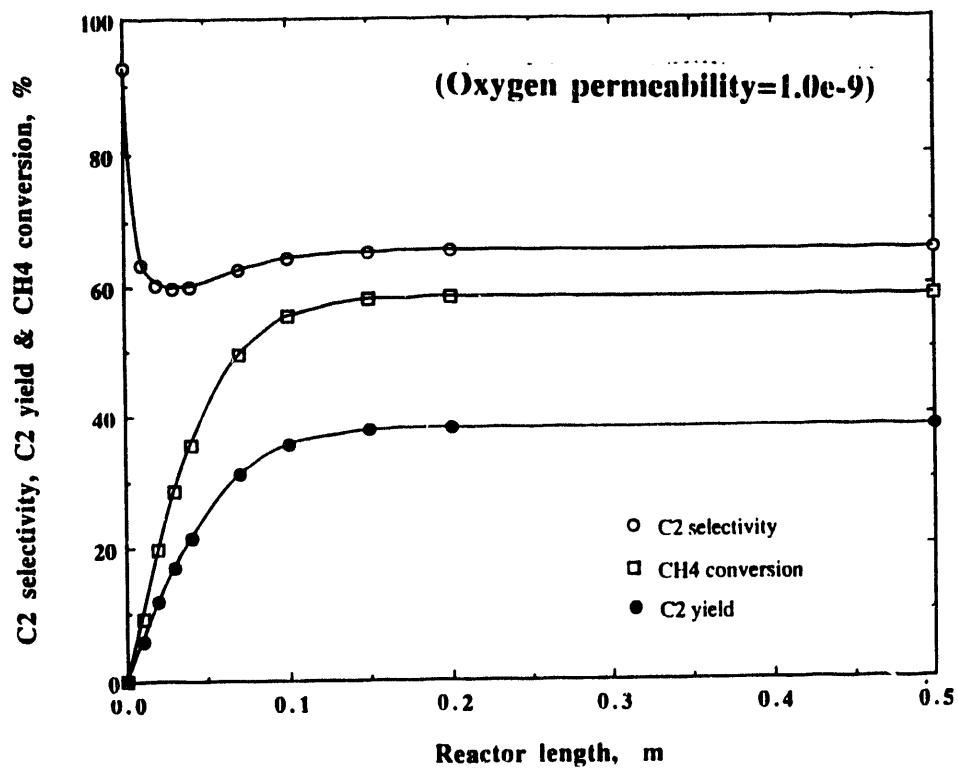


Figure 14. Model predictions for a dense membrane reactor.

Methyl Chloride via Oxyhydrochlorination of Methane

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Dow Corning Corporation

Contracts: DOE #DE-AC22-91PC91030 and GRI #5091-222-2300

Objective:

The purpose of this contract is to develop a process for converting light alkane gases to CH_3Cl via oxyhydrochlorination using highly selective, stable catalysts in fixed bed or fluid bed reactors designed to remove the large amount of heat generated, so as to control the reaction necessary for developing a commercially feasible process and to evaluate the economics of the process.

Accomplishments and Conclusions:

Laboratory effort and design work leading to the development of refined P&ID's for the process development unit (PDU) were the primary engineering activities undertaken during this stage of the contract effort. Concomitant chemical development of an optimized catalyst focused on the demonstration of a stable, selective Cu based catalyst for CH_4 oxyhydrochlorination was also undertaken.

The separation of CH_3Cl product from the unreacted non-condensable effluent stream is a major factor in the overall economics of this process. Significant effort this year was made in the evaluation and development of an absorption/stripping system for product recovery. Single and multicomponent absorption studies, comprehensive solvent testing and analysis, as well as laboratory scale demonstration of the technology were the key activities during this period. Other engineering development activities included fixed bed reactor design, material of construction evaluation, phase separator design and effluent profile modelling.

Catalyst optimization work has focused on the development of a catalyst that will give stable, highly selective formation of CH_3Cl . The impacts of several different promoters for a Cu based catalyst system have been evaluated. It has been found that the appropriate promoter can enhance both catalyst life and catalyst yield. This work has led to a significant improvement in the lifetime of our Cu oxyhydrochlorination catalyst, as measured in the limitations of non-isothermal non-adiabatic laboratory screening reactors.

Plans:

Detail engineering, procurement and construction leading to the start up of the PDU are currently underway. Start up will occur in early 1994. Optimization work focusing on catalyst selection for the PDU reactor is planned for the next 2 quarters.

Introduction

There are several key technology challenges associated with the development of a CH₄ oxychlorination process. Among these are the chemistry problems associated with development of a selective CH₃Cl catalyst, and in addition, the chemical engineering challenges associated with the operation of a process containing HCl and CH₃Cl. This contract effort has worked toward the goal of developing this technology by working on both the chemistry and the engineering challenges in a parallel and linked effort.

Process Development

Figure 1 shows the process chemistry that is operative in the oxyhydrochlorination of CH₄. As is shown, this complex system is a mixture of chlorination and combustion reactions that are particularly challenging to control due to the consecutive nature of the reaction kinetics.

The thermodynamics of these chemistries dictate the formation of the equilibrium favored CCl₄ as well as heavily oxidized byproducts. In addition, kinetic measurements, done both as part of our research and published previously,¹ show that the kinetics of chlorination also favor a fast succession of chlorination steps to the deeply chlorinated chloromethanes. Because of these facts, neither the kinetics or the thermodynamics of this chemical reaction system are driving this system to selective formation of CH₃Cl.

Comparisons of several apparent activation energies and enthalpies of reactions are shown in Table 1. These data show another challenge that needs to be faced to control the selectivity of the OHC reaction. First of all, the activation energies for the combustion reactions are significantly higher than those for the chlorination reactions. For reactant CH₄ the reaction to form CH₃Cl has an activation energy of 121 kJ/mol, this compares with 225 and 240 to form CO and CO₂ respectively. Clearly this dictates that the selectivity can be expected to be a function of temperature to a fairly significant extent, with higher temperatures favoring CO and CO₂ as a product. To compound this situation the heats of reaction for the combustion chemistries are significantly higher and as such any increase in temperature without an associated increase in heat transfer capability will likely add to the non-isothermal reactor profile that is common in laboratory experiments.

This rather straightforward analysis shows that the ideal condition for limiting the combustion side reaction will be one with adequate heat transfer capability to remove the heat of reaction. Thus, the ideal system will likely be an isothermal reactor. This key issue is one that has been central in determining both our reactor design and accordingly our catalyst activity.

Process Description

Figure 2 depicts the overall OHC process schematic for the oxyhydrochlorination of CH_4 . Without question the two most challenging unit operations are the reactor and the reactor effluent separation system. As such, it is these two unit operations that will be evaluated in the PDU that is currently under construction.

A significant amount of effort has been expended recently in the determination and design of these two unit operations. This work is finished and a list of key equipment for the PDU follows:

-Feed System

-OHC Reactor System

- OHC Reactor
- Hot Oil System

-Reactor Effluent Recovery

- Desuperheater
- Acid Condenser Separator
- Absorber Column
- Absorber Bottoms Separator
- Solvent Chiller
- Pumps and Tankage

-Steam Stripping

- Preheater
- Stripping Column
- Stripping Column Bottoms Separator
- Overhead Condenser
- Overhead Condenser Separator
- Pumps.

The definition of the separation unit operation was a key technical challenge in this project effort. Many different methods of product separation were evaluated. All indirect cooling methods looked both technically and economically non-feasible. The large amount of non-condensable gas simply made the separation impossible. Pressure Swing Adsorption was evaluated on paper as a possible alternative method for use in this application. While technically feasible, the economics of this method were unacceptable. It became clear that a direct contact absorption followed by a steam stripping operation was the only acceptable route to recover the product CH_3Cl . This approach however was highly dependent on the identification of an appropriate process solvent.

The key requirements for the OHC process solvent are:

- Low Volatility

- Strong absorption characteristics for C1 chlorocarbons
- Resistance to HCl(aq)
- Insoluble with H₂O
- Stable over temperature range of -20 C to 180 C.
- Preferably possess a low viscosity.

The approach used to identify this solvent was fairly empirical. A great deal of information was gathered on potential process solvents. Once this database was put together a list of potential solvents was identified and procured. A series of CH₃Cl single component saturation experiments was performed. Solvents that showed some promise were then evaluated for stability in acid. Finally, multicomponent absorption studies were performed on several potential candidates.

Figure 3 shows the initial % CH₃Cl absorbance for 6 of the potential solvents evaluated. These solvents had the highest CH₃Cl absorbance of those tested. The range in this group was from a high of 23% to a low of 12%. This testing was performed at 0 C at 15 PSI.

Figure 4 shows the Viscosity vs Temperature profile for 4 of the process solvents shown in Figure 3. Note that there is a wide range of response with solvents A and B showing significant increases in viscosity at low temperatures while solvents C and D showed very little change. Figure 5 shows a enlarged view of the data for solvents C and D. Note that solvent D gives a viscosity increase of only 20 cP when the temperature is lowered from 25 C to -25 C. This gives a very clear advantage in the performance of this material in a low temperature absorber column.

Further testing of solvent D was carried out to evaluate its stability in an hydrochloric acid environment. Extensive sealed tube exposures to acid at temperatures similar to those that will be found in the PDU showed no change in the GC-MS and FTIR spectra of this hydrocarbon solvent. No chlorination was noted. Figure 6 shows the % Wt. CH₃Cl absorbance for this solvent after being thermally aged for up to 30 hours. No decrease was seen from the virgin material. In fact, a small increase in the CH₃Cl saturation was noted.

Catalyst Development and Evaluation

The development of a highly selective OHC catalyst is a parallel objective to the process development described above. Several key catalysts have been described in the recent literature ^{2,3,4,5} regarding selective catalysis of the OHC reaction to CH₃Cl. The primary catalytic metals reported to be useful for the OHC reaction of CH₄ are Cu and Fe, with the PETC group also reporting the use of Co as a selectivity enhancing catalyst ⁵. Our work has primarily focused on the optimization of a Cu based catalyst.

Figure 7 shows a overview of the published results as well as previously unpublished Dow Corning results for Cu oxyhydrochlorination catalysts. This data represents a wide range of residence times, fluid velocities, stoichiometries and temperatures. The box with a lower left corner at 20% CH₄ conversion and 80% CH₃Cl selectivity represents the desired range of operation for this technology. As is shown, only the single point represented by the British Petroleum patent is currently in this desired range. However, all three other groups have data that is very close to this range. Figure 8 shows the same plot with a thick line indicating the range of recent Dow Corning results showing yields consistently at the edge of the target region.

Two key elements of catalyst development have been the focus of recent effort in this project. The first is to establish the deleterious impact of excess heat upon the product distribution. As shown earlier, the ability to control the combustion side reactions should be a key area in increasing the selectivity of the reaction. Figure 9 shows the internal bed temperature for two different Cu on silica catalysts. These data, taken under identical conditions by a thermocouple inserted directly into the catalyst bed, show quite clearly the extent of exotherm possible if a catalyst with too high of an activity is used without adequate heat transfer capability to remove the large heat of reaction. Note that Dow Corning catalyst #535 gives a nominally flat profile over 145 hours of reaction. By comparison, a PETC catalyst with very high Cu loading gives an exotherm of about 200 C over baseline conditions. A correlating degradation of selectivity was noted.

An additional verification of the impact of temperature upon selectivity is shown in Figure 10. In this case a Cu on Al₂O₃ catalyst was evaluated with a feed stoichiometry of 4.4/1/1.2 CH₄/O₂/HCl. The CH₃Cl and CH₂Cl₂ selectivities as well as the CO_x (oxygenated products) selectivity and CH₄ conversions are given by the Y axis. The X axis denotes reaction time. This reaction was conducted at a constant temperature of 340 C for 20 hours. At this point the temperature was lowered 5 C to 335 C. Note that the CH₄ conversion changed only very slightly, indicating that for this system a reactor temperature of 340 C was not necessary to obtain the target 20% conversion. The very interesting result however is that the CO_x products dropped from 18% to 8%. This was accompanied by a rise in the CH₃Cl selectivity from 68% to 78%. This is a fairly clear indication that the excess heat was serving only to further react product CH₃Cl via combustion to CO and CO₂.

The second key catalyst development issue is stability. A key reason for the use of very high metal loadings for some of the published catalysts is the fact that these catalysts deactivate. Primarily via Cu loss. The technical approach followed in the current catalyst development was to establish the minimum amount of Cu necessary to maintain adequate activity and develop a mechanism to stabilize the catalyst. In keeping with this, Figure 11 shows a simple Cu on SiO₂ catalyst that is not promoted in any way. The conditions used were a reaction temperature of 340 C, stoichiometry of CH₄/O₂/HCl 4/1/1.3. Note that the overall activity is very low with a CH₄ conversion of about 5%. Clearly this catalyst, with about 2% Cu loading, did not possess adequate activity to provide the targeted 20% CH₄ under these reaction conditions.

Figure 12 shows the impact of using a promoter in this Cu catalyst system. Note that the

activity increases to an initial value of about 20%, but declines over a period of 180 hours to less than half of the original activity. The reaction conditions were identical. The catalyst was the same with the promoter added by sequential impregnation. The Cu loading on the catalyst remained the same. This is a strong indication that large loadings of Cu are not necessary to yield an active OHC catalyst.

Figure 13 shows the impact of added another promoter sequentially. In this case the activity again starts at about 20% CH₄ conversion, but declines very slightly and is still about 17% after 180 hours of experimentation. This series of sequential impregnations shows the apparent strong impact that key promoters can have on the stability of Cu oxychlorination catalysts. The data indicates that a relatively low loading Cu OHC catalyst may be able to be modified by the appropriate promoters to have sufficient long term stability.

Conclusion

Recent effort on the development of a commercially feasible oxyhydrochlorination route to CH₃Cl has dealt with a variety of technical challenges. Work has proceeded on the engineering development of a PDU to evaluate the process. Several technical development issues have been associated with this development. The key results from our work on these issues over the past year have been two fold. First, a laboratory scale demonstration was completed of a product recovery system that has the potential to solve the engineering challenge of removing the product CH₃Cl from the large amount of non-condensable gases that are in the reactor effluent. This is an unavoidable situation in this relatively low conversion process. This recovery process is the key economic driver in process capital expenditure. This system will be demonstrated at the PDU scale.

Second, a promoted Cu based catalyst system with sufficient metal loading to achieve the desired activity was demonstrated. The technical advance with this catalyst is that it is a low metal loading catalyst. This has the impact of restricting the catalyst activity to the desired amount is to limit the selectivity and deactivation problems associated with the large exotherms found while using high metal loading catalysts under the conditions necessary for realistic process operation. It is of clear benefit to use the lower metal loading as long as necessary activity can be demonstrated and sustained. Future work will focus on long term stability improvements for this new catalyst.

Experimental Details

The OHC reactor setup consists of a feed system, a reactor system, analysis equipment, scrubber system and a control system.

The feed system is used to mix CH₄, HCl, and O₂ as well as inert gasses as necessary and provide them to the reactor at a usable pressure. Reactant used are Air Products USP grade O₂, Technical grade HCl, and a certified standard mixture of 2% Xe in CH₄. These gasses are piped through industry standard regulators, and stainless steel tubing to Tylan Model FC-280

AV Mass Flow Controllers. The controllers are factory certified at a range of 0-100 ml/min for the specified gas and merge together through a stainless steel manifold to one reactor feed line.

The reactants are fed through a teflon feed line to the reactor system. The furnace consists of an ATS series 3210 three zone furnace with a temperature controller. Reactor sizes change with desired fluid velocity conditions, heavy wall quartz tubes with quartz wool and low surface area ceramic bed supports on each end are used. All equipment after the entrance to the reactor must be constructed of a corrosion resistant material. Hastelloy C works best for metal components, but where possible quartz or teflon construction is used.

The analysis equipment consists of an HP 5890 Series II GC connected to a HP3396A integrator. The analysis is a two column analysis. The light gases are separated using a 12' x 1/8" 5A molecular sieve column, 80/100 mesh. The separation is conducted isothermally at 75C, then the column is heated to 200C and baked out for 15 minutes to prepare it for the next set of injections. The components eluting from this analysis include O₂, N₂, CH₄, CO, and Xe. The heavy ends are separated using a 12' x 1/8" Chromosorb 102 column, 80/100 mesh. The analysis is made isothermally at 75C for 6.5min, then programmed at 10°C to 180 where it remains for 16 min. Components separated on this column include O₂/N₂/CO, CH₄, CO₂, Xe, and Cl chlorocarbons. Each analysis takes about 30 minutes to complete, and the two analysis are combined to obtain selectivity and conversion data.

The scrubber system consists of two scrubbers in series. The first scrubber is a teflon container with a NaOH solution for the reactor effluent to sparge through. A secondary water scrubber is used to insure the complete scrubbing of any effluent HCl.

The control system consists of a Camile System 3000. This system provides PID control for the furnace power supplies, provides a control signal to the mass flow controllers, records multiple thermocouple readings, collects and analyzes data from the GC, and in addition provides an automated emergency shutdown protocol should a problem occur.

In order to initiate a catalyst screening run the reactor tube is packed with catalyst. Weights are obtained before and after the tube is packed, and the results are recorded. The loaded reactor is placed in the furnace, and dry N₂ is used to inert the reactor at 100 ml/min. While still under flowing N₂, the reactor is heated to pretreatment temperature for the required amount of time and desired pretreatment gas flow is initiated. The reactor is then brought to the first screening temperature, and allowed to equilibrate for 45 minutes. The pretreatment gas flow is shut off and the reactants are started in the following order: HCl, CH₄, and then O₂. The GC is started to collect data, and the run is allowed to proceed. Upon completion of the run, the gases are shut down in the reverse order that they were started, and the bed is again inerted with N₂. The bed is cooled and removed from the oven.

Acknowledgments

The authors would like to acknowledge the following individuals for their valuable assistance in this work: Steve Freeburne, Bob Smith, Wayne Ellegood, and David Miller. In addition the a special thanks to Bruce Crum who performed a significant portion of the laboratory work cited in this paper.

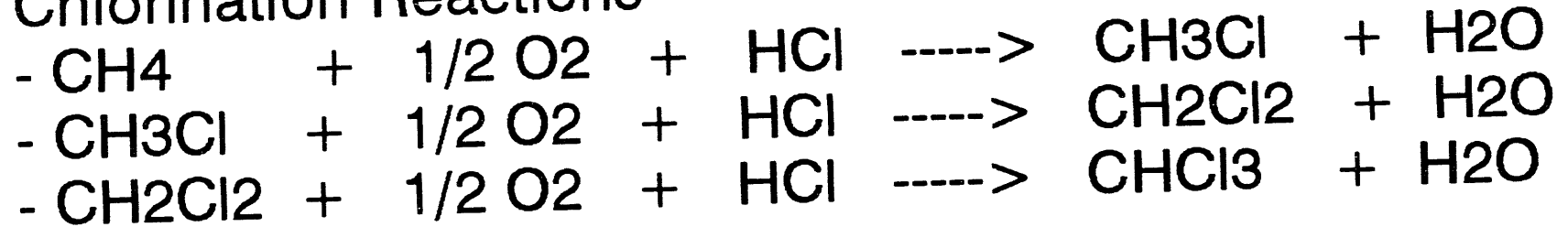
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1. Y.A. Treger and V.N. Rozanov, *Uspekhi Khimii*, Vol. 58 (1), (1989), pp. 138-164.
2. U.S. Patent 4,769,504. To R.D. Noceti,et.al., 06 Sept. 1988.
3. Int. Patent WO 84/ 03277. To J. Bromhead, Aug. 30, 1984.
4. V.N. Rozanov, *Khim. Prom.-st.*, 7 , (1989) , 495.
5. Taylor, C.E. and Noceti, R.P., *Proc. Int. Cong. Cat.*, 2, 990, (1988).

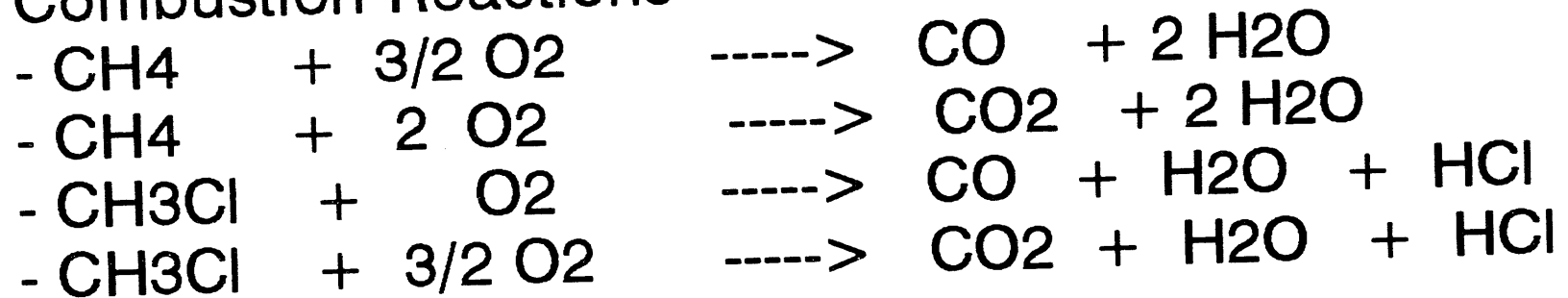
OXYHYDROCHLORINATION OF METHANE

Figure 1

- Chlorination Reactions



- Combustion Reactions



- Deacon Chemistry



Apparent Activation Energies for OHC Reactions

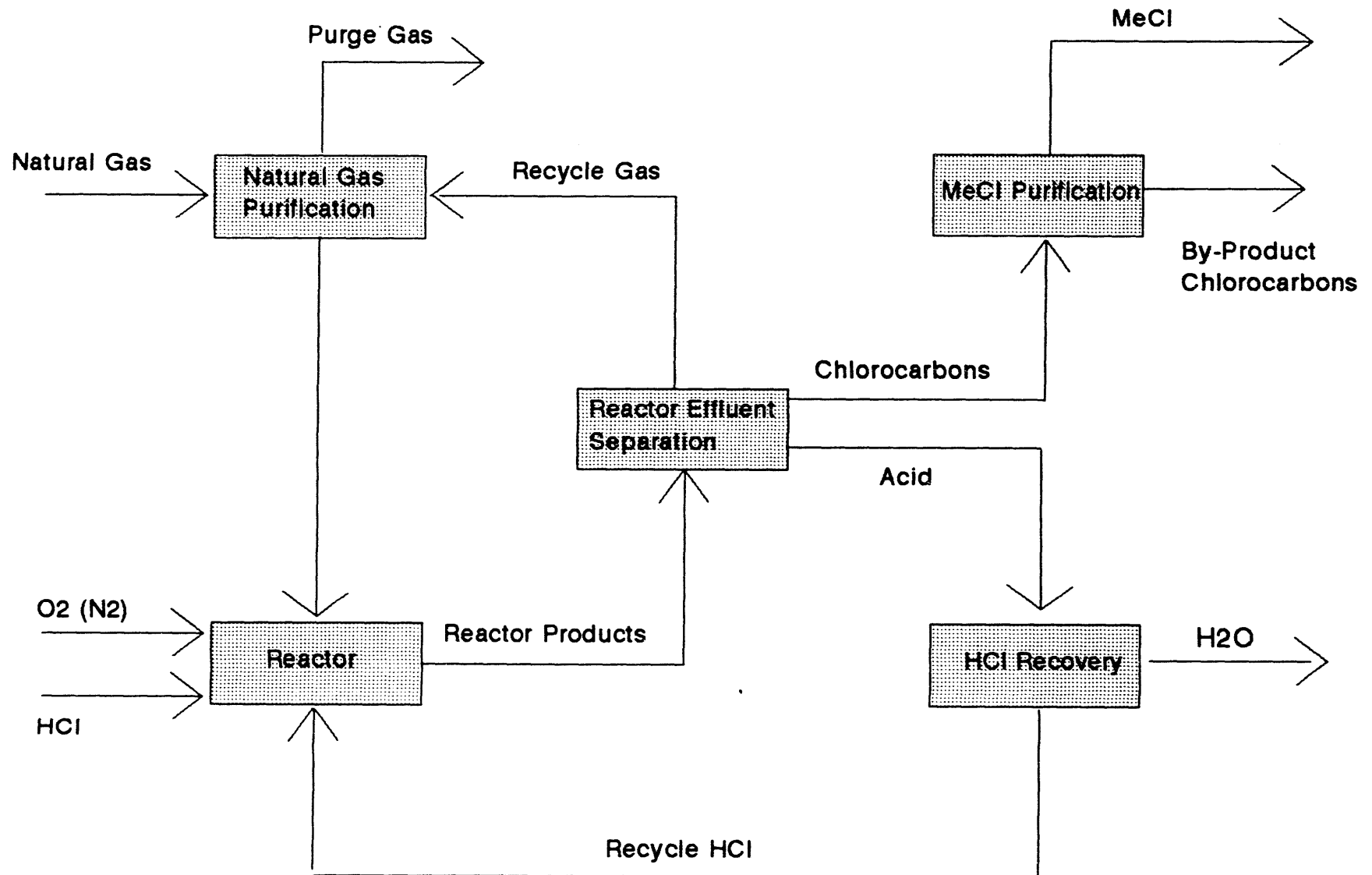
Table 1

Reactant	Product	E act	H rxn
CH ₄	CH ₃ Cl	121	-157
CH ₄	CO	225	-500
CH ₄	CO ₂	240	-781
CH ₃ Cl	CH ₂ Cl ₂	126	-153
CH ₃ Cl	CO	187	-343
CH ₃ Cl	CO ₂	197	-624

Values in kJ/mol

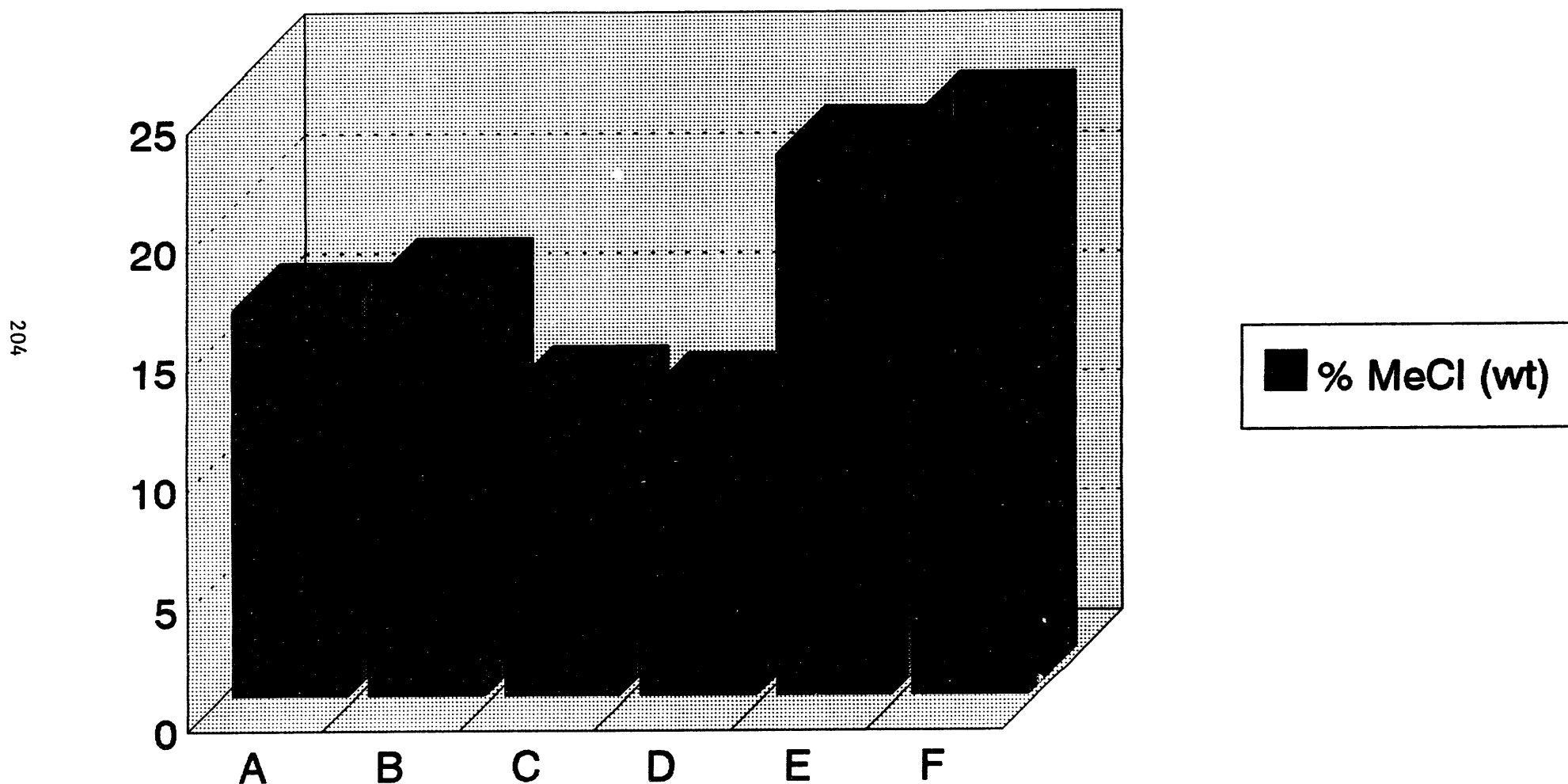
OHC PROCESS BLOCK FLOW DIAGRAM

Figure 2



Oxyhydrochlorination of Methane

Figure 3

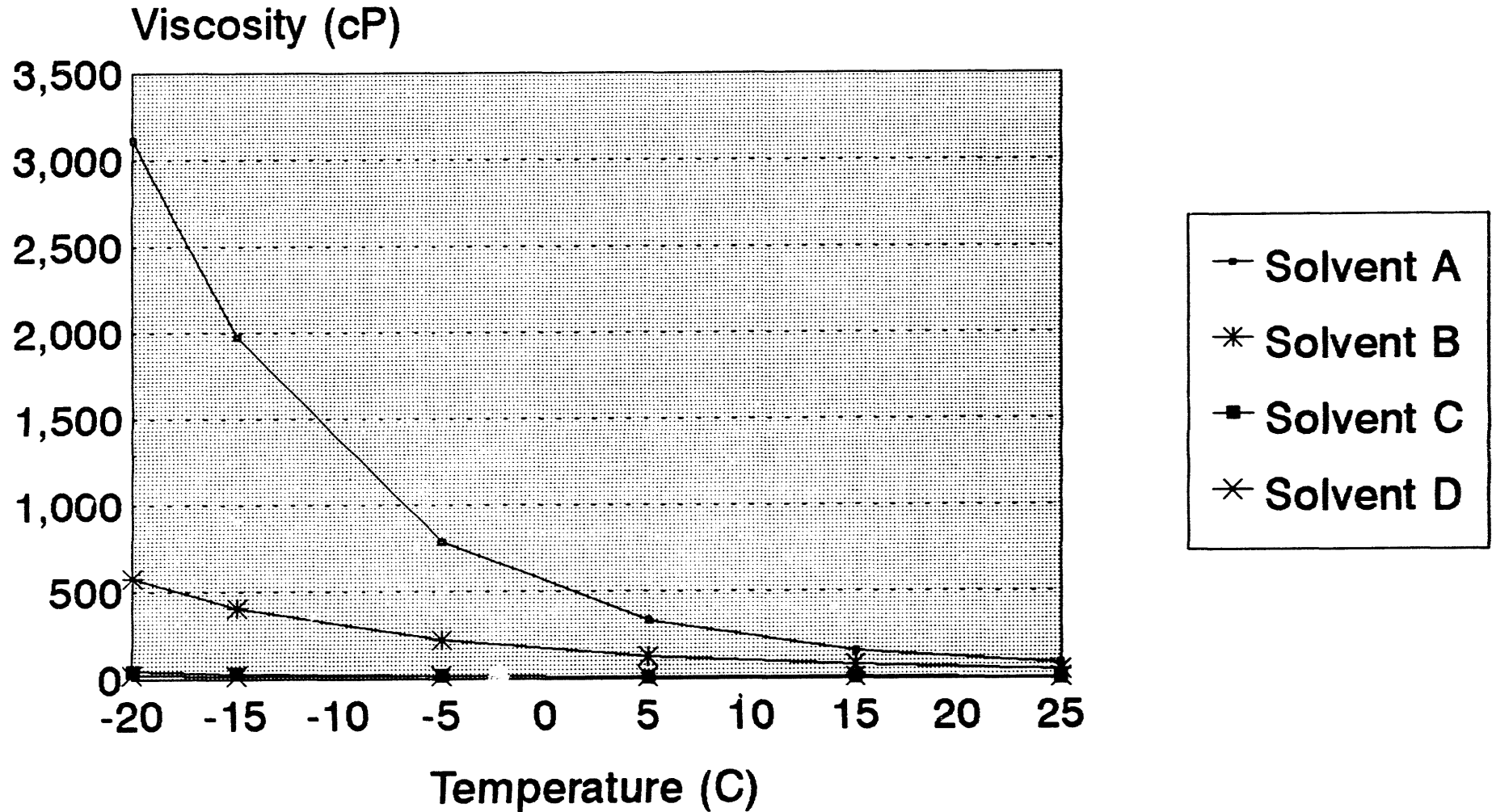


MeCl Absorbance

Absorber/Stripper Solvents

Figure 4

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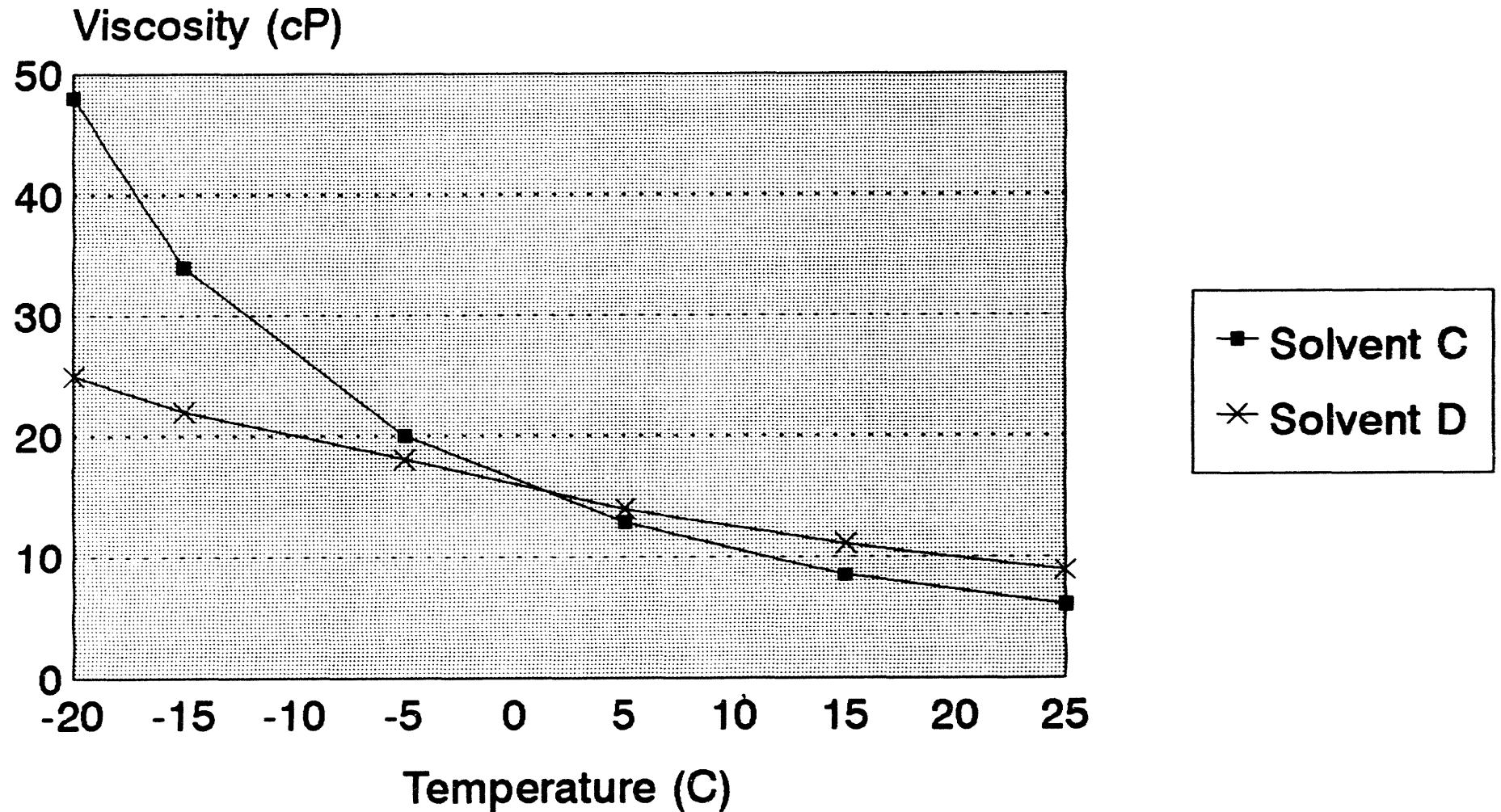


Temperature vs Viscosity

Absorber/Stripper Solvents

Figure 5

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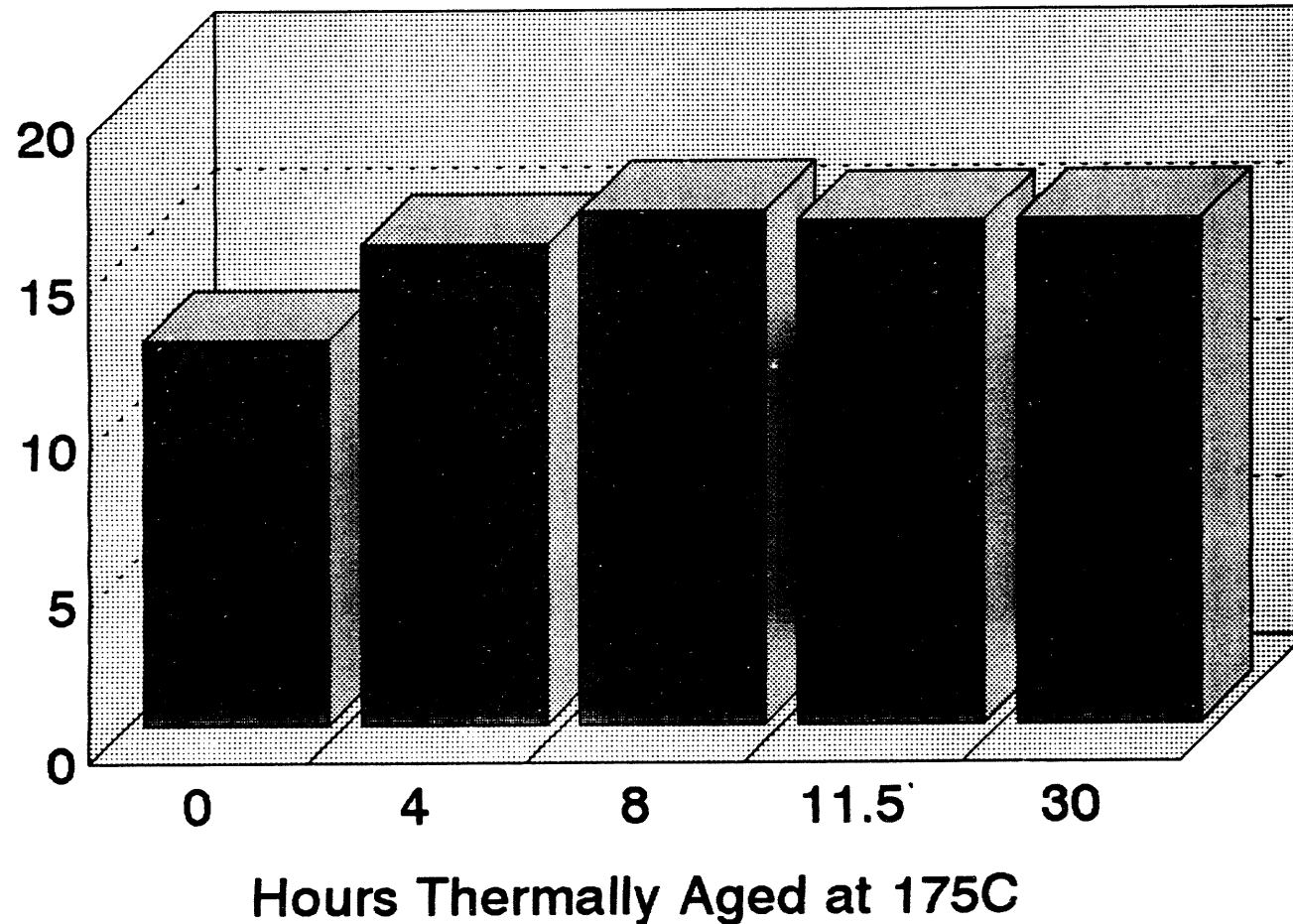


Temperature vs Viscosity

Thermally Aged Process Solvent

Figure 6

% Wt. MeCl Saturation



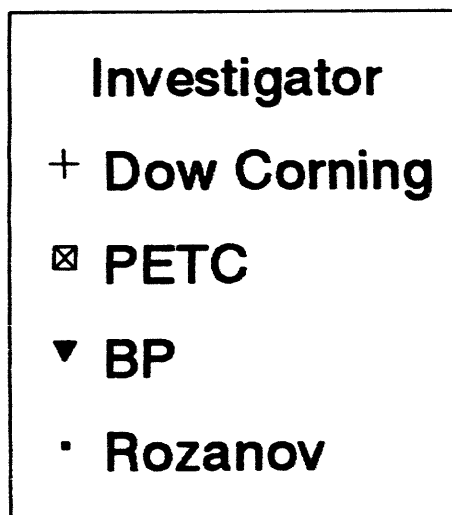
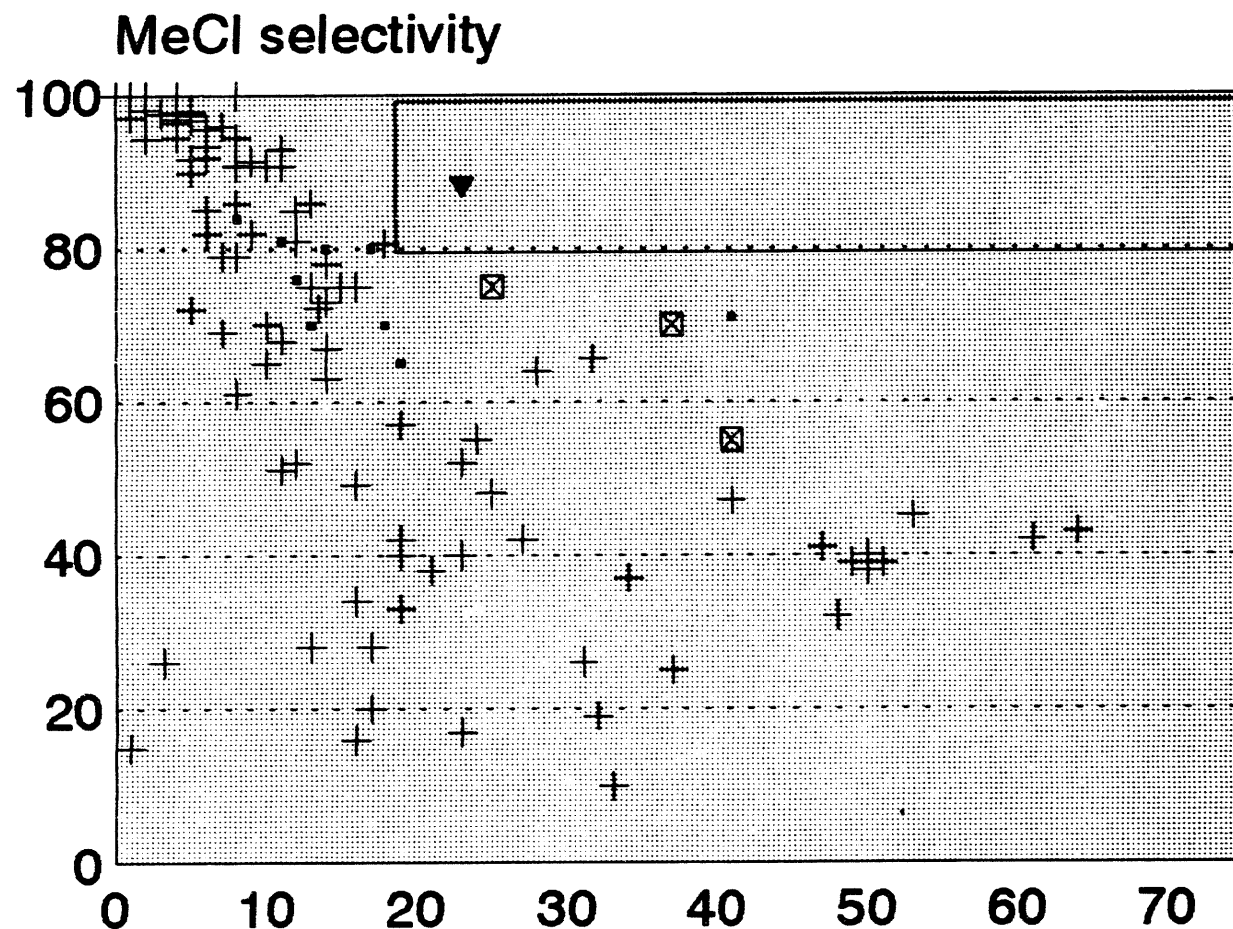
■ Solvent D

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Solvent Evaluation Data

Copper OHC Catalyst Evaluations

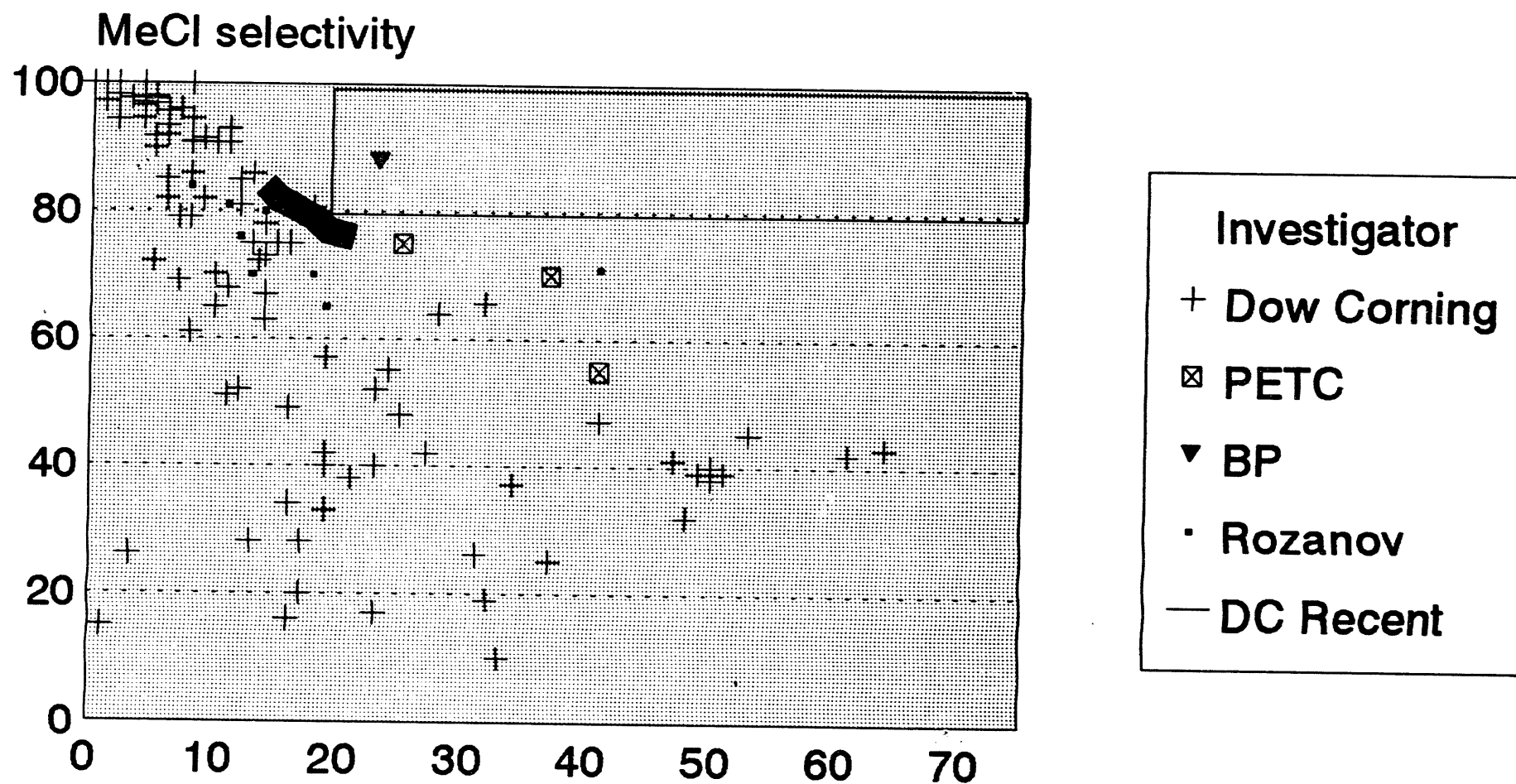
Figure 7



Variable residence time, fluid velocity, stoichiometry, temperature

Copper OHC Catalyst Evaluations

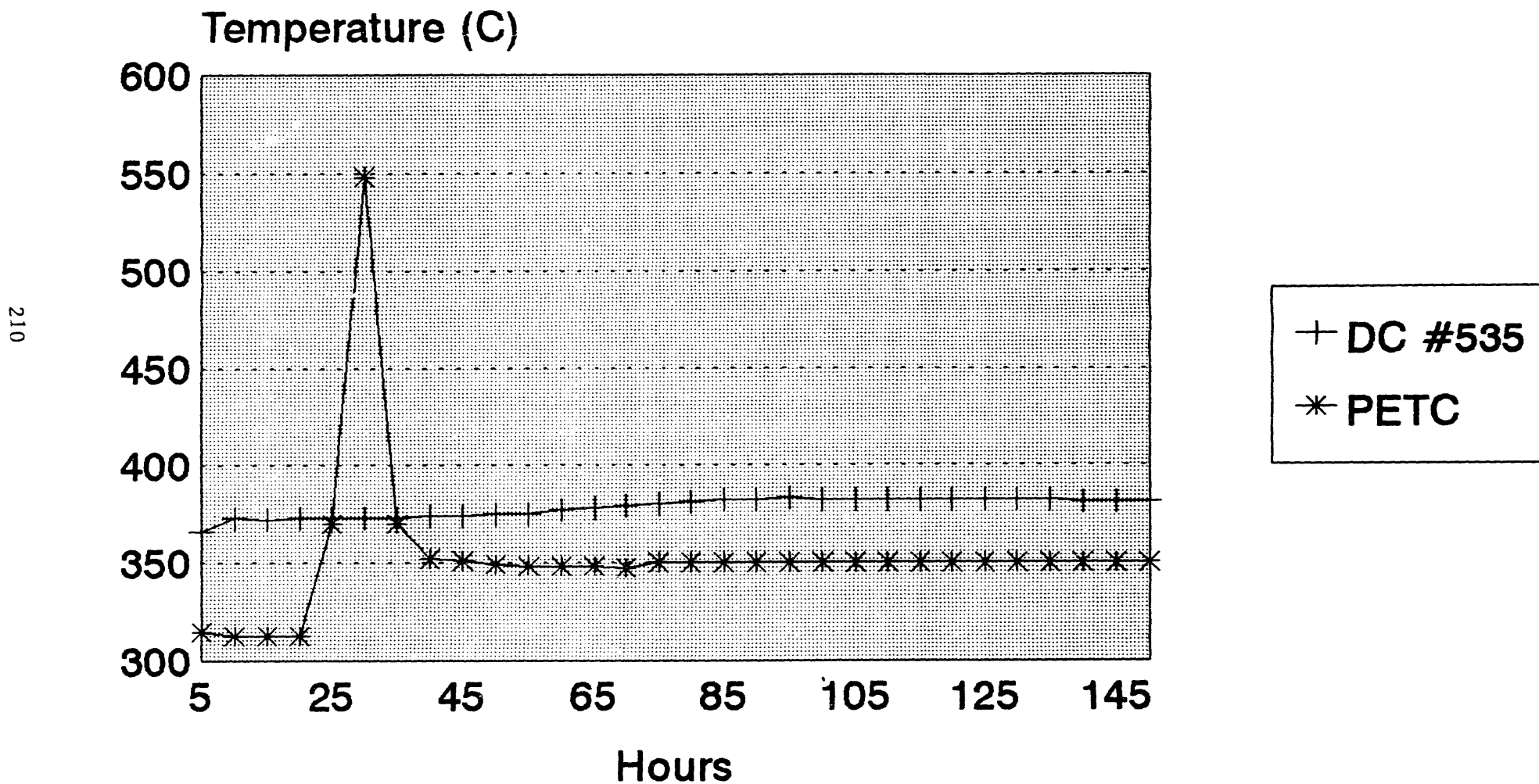
Figure 8



Variable residence time, fluid velocity, stoichiometry, and temperature

Internal Bed Temperature

Figure 9



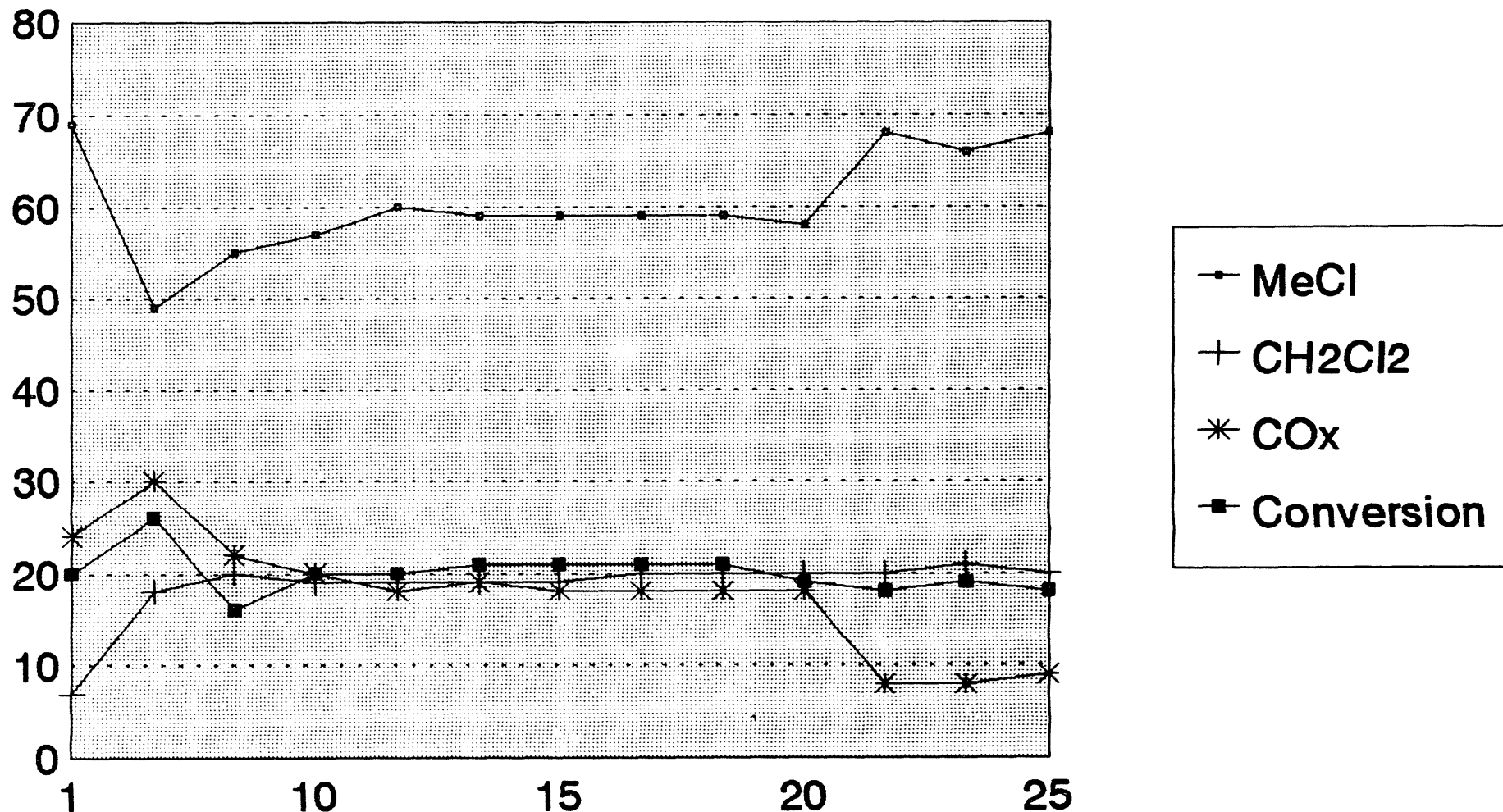
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Catalyst Comparison

Catalyst #539 Evaluation

Figure 10

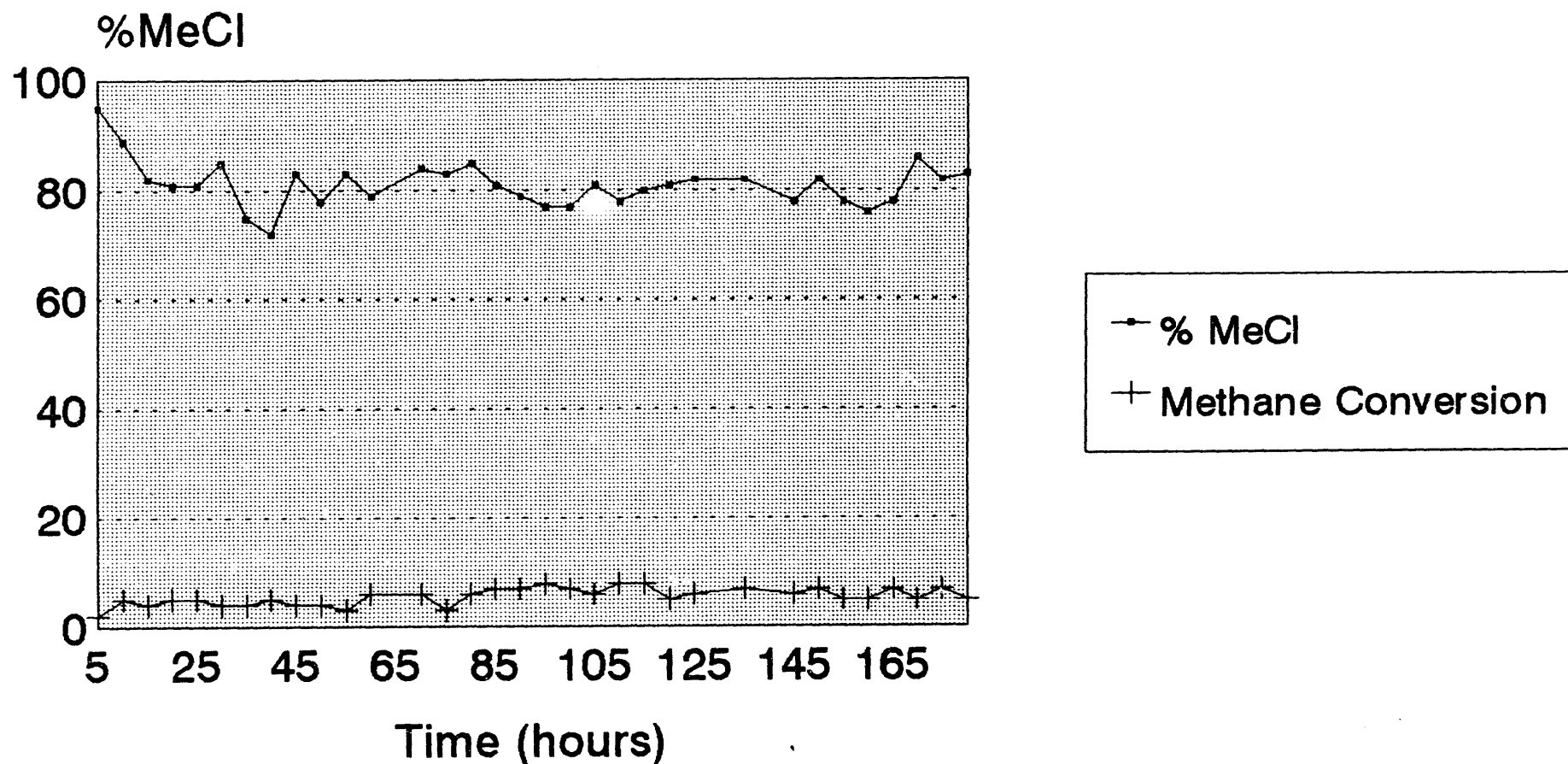
211



Stoichiometry 4.4/1/1.2 CH₄/O₂/HCl

Catalyst #538A Evaluation

Figure 11



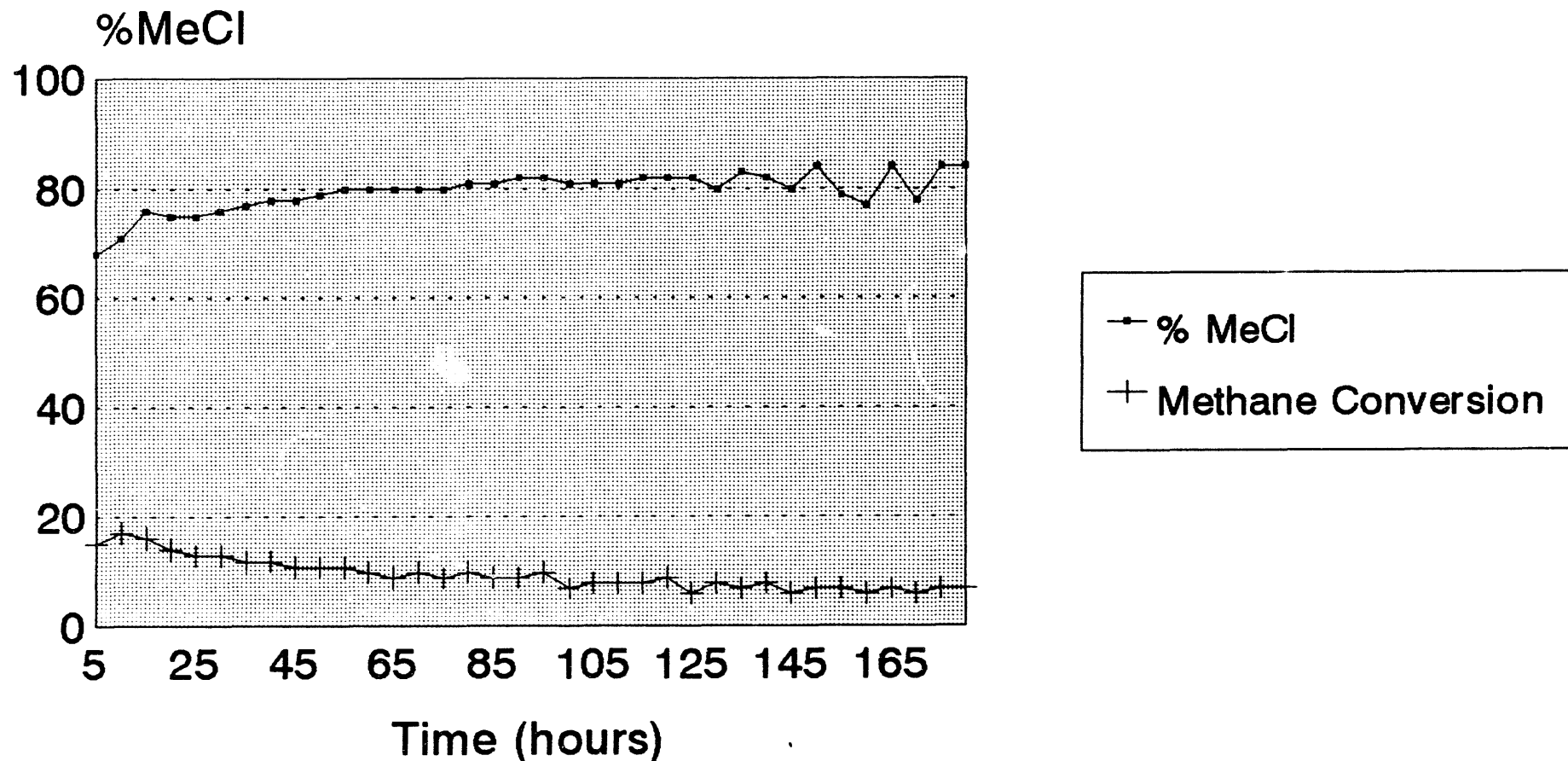
Temperature 340C

Stoichiometry CH₄/O₂/HCl 4:1:1.3

Experiment 11046002

Catalyst #538B Evaluation

Figure 12



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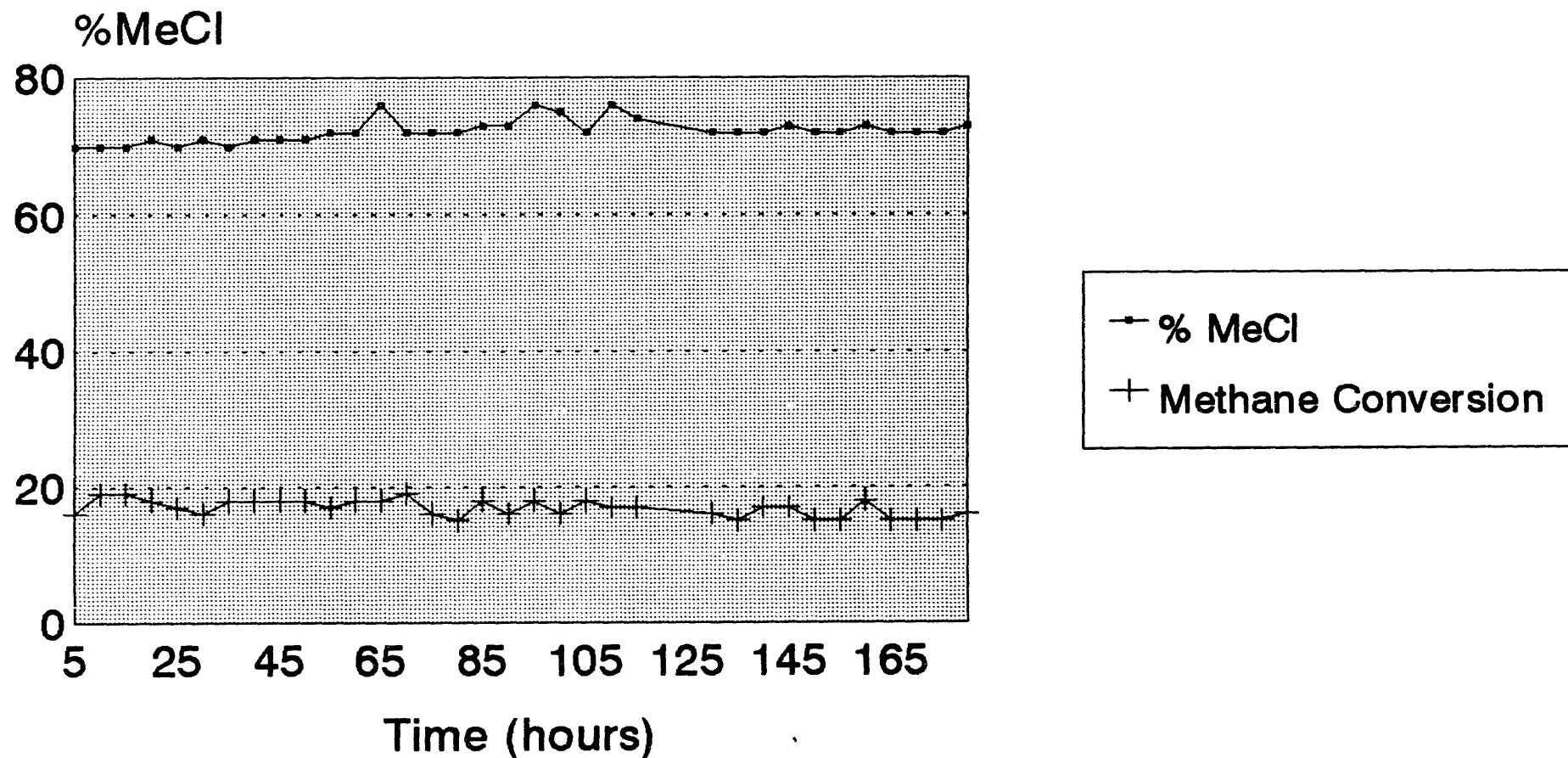
Temperature 340 C

Stoichiometry CH₄/O₂/HCl 4:1:1.3

Experiment 11046004

Catalyst #538D Evaluation

Figure 13



Temperature 340 C
Stoichiometry CH₄/O₂/HCl 4:1:1.3
Experiment 11046009

EXPLORATORY STUDIES OF OXIDATIVE CONVERSION OF METHANE TO METHANOL

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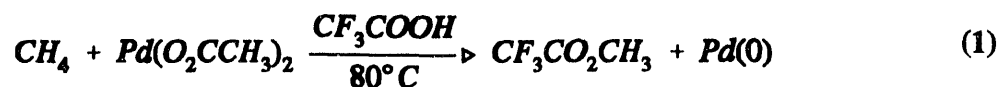
INTRODUCTION

Methane is produced as a by-product of coal gasification. Depending upon reactor design and operating conditions, up to 18% of total gasifier product may be methane. In addition, there are vast proven reserves of geologic methane in the world. Unfortunately, a large fraction of these reserves are in regions where there is little local demand for methane and it is not economically feasible to transport it to a market. There is a global research effort under way in academia, industry, and government to find methods to convert methane to useful, more readily transportable and storable materials. Methanol, the initial product of methane oxidation, is a desirable product of conversion because it retains much of the original energy of the methane while satisfying transportation and storage requirements. Methanol, a liquid at room temperature, could be transported to market utilizing the existing petroleum pipeline and tanker network and distribution infrastructure. Methanol may be used directly as a fuel or be converted to other valuable products (*i.e.* other transportation fuels, fuel additives, or chemicals). Currently, the direct oxidation of methane to methanol suffers from low methane conversion and poor methanol selectivity. A process for the direct oxidation of methane to methanol, in high yield and with high selectivity, is desirable.

GOALS AND OBJECTIVES

A long term goal of our research group is the exploration of novel pathways for the direct oxidation of methane to liquid fuels, chemicals, and intermediates.

Historically, reports have appeared in the literature describing the use of organometallic complexes to effect this transformation.^{1,2} Investigation of one of these reaction schemes in our laboratory has produced interesting results. Our research effort was an extension of work reported by Sen and co-workers³⁻⁴ The purported reaction occurs between methane (at 800 psig) and palladium(II) acetate in trifluoroacetic acid at 80°C (Equation 1). The product, methyl trifluoroacetate, is readily hydrolyzed to produce methanol and trifluoroacetic acid. The reported conversions, calculated on the basis of palladium(0) recovered, were about 60%.



As written, this reaction scheme requires stoichiometric amounts of the palladium(II)acetate. In addition, a second step, hydrolysis, is required to produce free methanol (Figure 1). Gretz *et al.*³ had speculated that it might be possible to make the reaction catalytic by including a co-oxidant, and, in fact, reported a catalytic reaction cycle using potassium peroxydisulfate, $\text{K}_2\text{S}_2\text{O}_8$, as a co-oxidant with the Pd(II) in the monotrifluoroacetoxylation of 1,4-dimethoxybenzene. Further, it was reported in this work that the hydrolysis step can usually be carried out quantitatively (100% yield of 2,5-dimethoxyphenol).⁴

Our objective was to investigate this reaction scheme, reproduce the results reported in the literature and explore the possibility of using this reaction pathway in a commercial process. On initial examination, this reaction scheme appears not to have much commercial application because of long reaction times (~150 hours) and batch mode operation. The reported conversions of 60% were intriguing, but were calculated on the amount of Pd(0) recovered from the reactor system. When conversions are calculated on the basis of methane consumed, they are on the order of about 3 percent, of which only 33 percent of the converted methane is methyl trifluoroacetate, a net conversion of methane to product of 1 percent. In spite of this and in light of the reported catalytic reaction, it was decided to examine this reaction in some detail. A reaction scheme similar to that shown in Figure 1 could be of commercial interest if all steps could be realized at reasonable conversions and with minimal side reactions. For purposes of discussion, the scheme may be separated into three major parts: (1) conversion of methane to methyl trifluoroacetate, (2) hydrolysis of methyl trifluoroacetate to methanol and trifluoroacetic acid, and (3) conversion of palladium(0) to palladium acetate.

Part 2 is a known hydrolysis reaction for conversion of the methyl trifluoroacetate to methanol in acidic solution. An unknown aspect of this part is the separation of products on a commercial scale.

Part 3 is a commercial preparation scheme for production of palladium(II) acetate. The reaction is conducted by boiling palladium(0) in glacial acetic acid to which a small amount of nitric acid has been added. All of the palladium(0) can be converted to the acetate by this method.

This leaves Part 1, the conversion of methane, as the only unknown reaction sequence to be examined.

EXPERIMENTAL

All reactions were conducted in a sealed, 0.5-in (1.27-cm) O.D. X 12-in (30.5-cm) silica-lined stainless-steel batch reactor (Figure 2). Total volume of the reactor system was <35 mL. The reactor was lined by Restek, Inc. In order to reproduce the earlier work, experimental conditions were the same as those reported by Sen and co-workers.³ The reactor was purged several times with helium, charged with reactants (typically 0.15 g of palladium(II) acetate dissolved in 5.00

g of trifluoroacetic acid). The reactor was then connected to the manifold, purged several times with helium, followed by several purges of methane with a final methane pressure of 800 psig, and isolated from the gas manifold. The reactor was heated in a bath of silicon oil to 80°C and the reaction was allowed to proceed for 5 days. The reactor pressure was monitored by a pressure transducer and recorded during the run. Blank runs followed the same procedure with the exception of helium replacing methane.

After removal of the reactor's liquid contents, the reactor was filled with deionized water, capped and placed in an 720-W ultrasonic cleaner for one hour. The solution was then passed through a preweighed .50- μm Teflon® filter and air dried. The contents of the filter were removed and identified by scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS).

The $^{13}\text{CH}_4$, rated by the supplier at 99+% isotopic purity, was supplied in 1 L cylinders at 20 psig pressure. The contents of two cylinders were required to obtain the necessary >800 psig pressure for reaction. The reactor was rinsed with 5.0 g (3.3 mL) of dry trifluoroacetic acid, purged several times with helium at 1000 psig, charged with reactants, and purged again several times with helium at 1000 psig. The reactor was then immersed in a liquid nitrogen bath. When the temperature had reached -190°C, the reactor was connected to a mechanical vacuum pump and evacuated. The reactor was then isolated from the vacuum pump and, while still immersed in liquid nitrogen, was connected to the cylinders of $^{13}\text{CH}_4$ to allow transfer of the cylinder's contents to the reactor. After transfer of the cylinder's contents, the reactor was sealed and placed in the silicone oil bath.

When necessary, the gases were dried prior to entering the reactor by passing through a 8-ft (2.44-m) X 1/4-in (0.64-cm) coil of stainless-steel tubing immersed in an acetone/dry ice bath.

Gaseous components were analyzed on a Hewlett-Packard 5730 gas chromatograph. Liquid samples were analyzed on a Hewlett-Packard 5988A GC/MS system.

RESULTS

The results reported by Sen and co-workers were reproduced; in Run 241 production of methyl trifluoroacetate was observed and a fine metallic powder was recovered. SEM and EDS analysis of the powder confirmed it to be palladium metal with crystallites of the order of 1 micron in size. Quantitative analysis of the palladium(0) gave >80% of the palladium acetate recovered as palladium(0). Methane conversion, calculated by the difference in pressure from the beginning to the end of the run, was ~3 mol% (Table I). Figure 3 shows a typical plot of temperature and pressure as a function of time during the course of the run. As shown in Figure 3, the majority (~93.5%) of the methane was consumed during the first 30 hours of the reaction.

Analysis of the reaction mixture from Run 241 (Table II) identified several other oxygenated compounds and water. To determine the source of these compounds, the palladium(II) acetate dissolved in trifluoroacetic acid for Run 242 was analyzed prior to introduction of methane. This revealed the presence of methyl trifluoroacetate, the product of methane oxidation, prior to introduction of methane, and the same components identified before.

The trifluoroacetic acid was analyzed to determine if the methyl trifluoroacetate and other compounds found in Runs 241 and 242 were present. All the unexpected compounds except methyl trifluoroacetate were detected including a significant quantity of water. A blank run (243) was conducted wherein the methane was replaced with helium at 800 psig. All reaction conditions and operations were identical to previous runs. This experiment resulted in the production of methyl trifluoroacetate and a 68.30% recovery of palladium metal. The only logical origin of the ester's methyl group is via decomposition of the starting material's acetate ligand.

After completion of the above experiments, the gas in the reactor was sampled prior to venting and recovery of liquid products. Analysis of the gas samples by GC (Table III) showed only the components present in the feed gas.

For use in the remaining experiments, dry, high purity trifluoroacetic acid was obtained in sealed ampules containing enough acid for a single use. Analysis of this trifluoroacetic acid revealed no detectable quantities of water or the other impurities previously detected. The blank run was repeated. After 150 hours at 80°C and 800 psig helium, the reactor was opened and the solution removed for analysis and comparison with the starting material. No difference in composition was detected between the two samples. Water (8×10^{-3} moles, a 10 fold excess) was then added to the mixture of Run 244, the reactor was charged with helium at 800 psig, and held at 80°C for 150 hours. Analysis of the products of reaction (Run 245) revealed the presence of methyl trifluoroacetate and methyl acetate. Since no methane was present in the system, the only source of the methyl group in the products is from the displaced acetate. This observation is inconsistent with that of Sen⁵ in that he did not observe any deuterium incorporation into the methyl trifluoroacetate when $\text{Pd}(\text{O}_2\text{CCD}_3)_2$ was used.

The first experiment (Run 246) to use both methane and the dry, high purity trifluoroacetic acid resulted in products similar to previous experiments with the exception that the amount of palladium metal recovered was only 39.20 mol%, a reduction of >50%. We attribute this decrease to the absence of side reactions caused by the water in the trifluoroacetic acid.

An experiment (Run 248) was conducted using methane that was isotopically enriched in carbon-13. Oxidation products arising solely from the labelled methane, determined by GC-MS, would eliminate the possibility of products arising from the acetate ligand on the palladium(II) acetate. The reactor was filled as described above. Operating under conditions similar to previous experiments resulted in similar methane conversions but a recovered palladium metal amount of only 7.88 mol%. Analysis of the product mixture revealed both $\text{CF}_3\text{C}(\text{O})\text{O}^{13}\text{CH}_3$ and $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$. Single Ion Monitoring (SIM) analysis of the isotopic ratio of the labeled products gave a $^{13}\text{C}/^{12}\text{C}$ ratio of 4.98. The composition of the labeled methane was determined by mass spectroscopy to be 93.5% $^{13}\text{CH}_4$ and 6.5% $^{12}\text{CH}_4$; a ratio of 14.38. This means that ~11% of the methyl carbon in the methyl trifluoroacetate comes from a source other than the labeled methane. This confirms our postulate that not all of the product arises from the methane introduced as a reactant.

To test the postulate that the presence of water in the reactor system was responsible for the observed decrease in palladium metal recovery, two experiments were conducted (Runs 250 and

252) where the gases were dried prior to entering the reactor as described above. The reactor was prepared as in the $^{13}\text{CH}_4$ experiment. After warming to room temperature, 4.8×10^{-3} grams (2.7×10^{-4} moles) of water was recovered from the drying trap. The result of these experiments is that the methane consumption and product distribution remained the same as previously observed, but that recovery of palladium metal was only 4.21 and 7.46 mol% respectively. This suggests that the presence of water in either the reactants or in the reactor system is responsible for the greater quantities of palladium metal reported in the literature. Water was not detected in the product mixture by GC/MS for these experiments.

Sen and co-workers postulated that the mechanism of this reaction is electrophilic attack on the methane by Pd(II), followed by reductive elimination to give Pd(0) and the alcohol derivative. This mechanism is supported only by the fact that palladium is a strong electrophile and a good two electron oxidant. Our observations do not support the original assumption that the reaction, as stated in Equation 1, is a 1:1 stoichiometric reaction between methane and palladium(II) trifluoroacetate. Table V lists the molar balance for the experiments. The last column of the table shows the ratio of methane consumed to palladium metal recovered. The data from the early experiments, when water was present, show that the molar ratio of methane consumed to palladium metal recovered is of the order of 10. In later experiments, when water was removed from the reactants, this ratio is an order of magnitude larger. These inconsistencies leave open the important questions about the reaction mechanism which is key to proper evaluation of this reaction as a method for direct oxidation of methane. If the methane is being consumed by some other reaction not involving palladium, is the palladium(0) being reoxidized to a palladium(II) complex, or are other impurities present in the system?

CONCLUSION

This study has shown that the reaction expressed in Equation 1 does occur, as confirmed by the production of $\text{CF}_3\text{CO}_2^{13}\text{CH}_3$ from $^{13}\text{CH}_4$, but that this reaction is not responsible for all product methyl trifluoroacetate. When a blank experiment was performed using the highest purity starting materials and replacing methane with helium, methyl trifluoroacetate was detected in the product if water was not excluded from the system. The presence of water in the reaction mixture appears to cause the palladium acetate/trifluoroacetate complex to decompose and produce methyl trifluoroacetate and account for the high yields of palladium metal reported in the literature.

FUTURE PLANS

Research during the next six months will be focused on completing this study. Of primary importance is quantitation of reaction products. This will be accomplished by the use of a gas chromatographic system. The majority of the products have already been identified. These components will be obtained commercially and used in the standard addition method to analyze the product mixture. An additional $^{13}\text{CH}_4$ experiment will be conducted to confirm the presence of non-labeled methyl group in the methyl trifluoroacetate. At the end of these experiments, the laboratory portion of this project will be completed. While our study will be completed there are several points which we will not address but are of scientific interest:

- 1). What is the reaction mechanism which accounts for the production of methyl trifluoroacetate in the absence of methane when water is present?
- 2). Is methane being consumed by some other reaction not involving palladium?
- 3). Is the palladium(0) being reoxidized to a palladium(II) complex?
- 4). Are other impurities present in the system responsible for the observations?
- 5). How is the displaced acetate ligand involved in the reaction scheme?

ACKNOWLEDGMENT

We would like to acknowledge the technical assistance of Joseph R. D'Este with construction and operation of the reactor unit and Donald V. Martello and Joseph P. Tamilia with the SEM/EDS analyses.

DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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**TABLE I. COMPARISON OF Pd
RECOVERED WITH CH₄ CONSUMED**

RUN	% Pd (0) RECOVERED	% CH₄ CONSUMED
241	83.50	3.00
242	77.00	3.13
243	68.30	N/A
244	0.00	N/A
245	83.20	N/A
246	39.20	6.42
248	7.88	4.08
250	4.21	4.01
252	7.46	10.30

**TABLE II. GC/MS ANALYSIS OF METHANE
OXIDATION REACTION MIXTURES**

COMPOUND IDENTIFIED	241	242 START	242 FINISH	242 FILTERED (NO CH₄)	243	CF₃COOH
AIR/CO₂	X	X	X	X	X	X
CH₃-O-CH₃		X	X	X		
CF₃C(O)OCH₃	X	X	X	X	X	
CH₃C(O)H	X	X	X	X	X	X
C₂H₅-O-C(O)H	X	X	X	X		
H₂O	X	X	X	X	X	X
CH₃COOH	X	X	X	X	X	X
C₂H₅COOH	X	X	X	X		X
CH₃(CH₂)₂COOH	X					X
CF₃COOH	X	X	X	X	X	X

TABLE III. GAS COMPOSITION (PERCENT)

SAMPLE	CH ₄	He	N ₂	C ₂ H ₆	O ₂	CO ₂
CH ₄	99.32		0.66	0.02		
He		100.00				
241	99.70	0.25				TRACE
242	93.19	0.11	5.28	0.02	1.39	0.02
243		100.00				TRACE
244		100.00				TRACE
¹³ CH ₄	93.5%	¹³ CH ₄	6.5%	¹² CH ₄		

TABLE IV. GC/MS ANALYSIS OF METHANE OXIDATION REACTION MIXTURES

COMPOUND IDENTIFIED	243 (NO CH4)	244 START	244 FINISH ▲ (NO CH4) ▲	245 (244 + H2O)	246	248 13CH4	250	252
AIR/CO2	X	X	X	X	X	X	X	X
CF3C(O)OCH3	X			X	X	X	X	X
CH3C(O)H	X	X	X	X	X			X
CH3C(O)OCH3				X	X	X	X	X
H2O	X			X				
CH3COOH	X	X	X	X	X			X
CF3C(O)CF3				X	X	X	X	X
CF3COOH	X	X	X	X	X	X	X	X

TABLE V. CH₄ AND Pd MOLAR BALANCE

RUN	Pd(2+) START (x 10 ⁴)	Pd(0) RECOVERED (x 10 ⁴)	CH ₄ START (x 10 ²)	CH ₄ END (x 10 ²)	CH ₄ CONSUMED (CALC x 10 ³)	CH ₄ _{CON.} Pd(0)
241	6.69	4.70	7.05	6.59	4.69	9.98
242	6.69	5.14	7.07	6.72	3.59	6.99
243	6.69	4.30	0.00	0.00	0.00	N/A
245	6.92	5.76	0.00	0.00	0.00	N/A
246	6.92	2.72	7.07	6.62	4.54	16.72
248	6.71	0.55	6.83	6.52	3.07	56.32
250	6.99	0.29	8.14	7.55	5.94	203.84
252	6.54	0.49	6.79	6.10	6.90	141.15

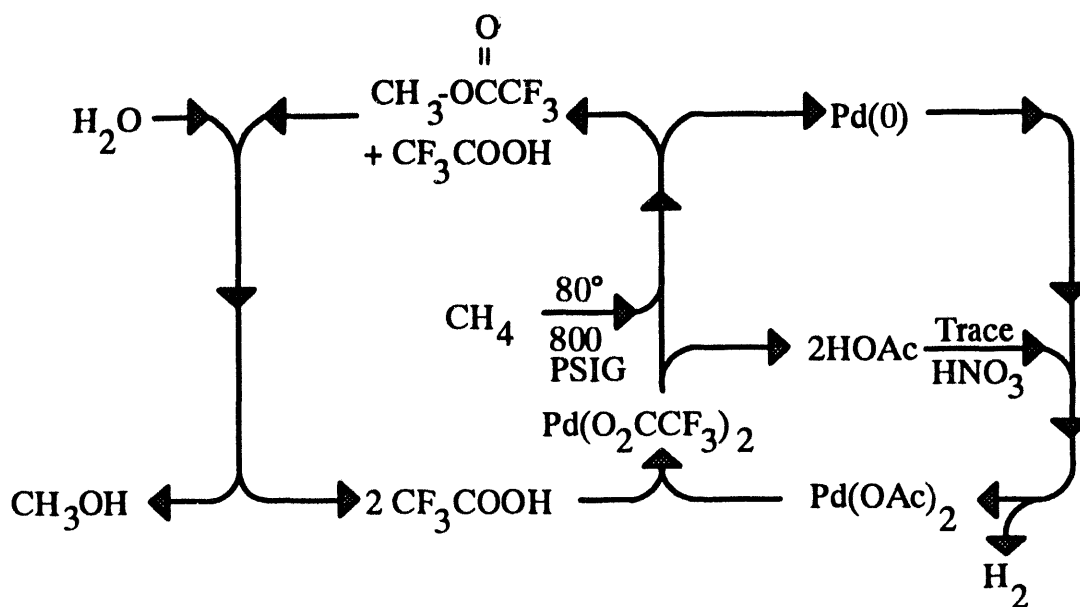


FIGURE 1. REACTION PATHWAY FOR THE DIRECT OXIDATION OF METHANE TO METHANOL

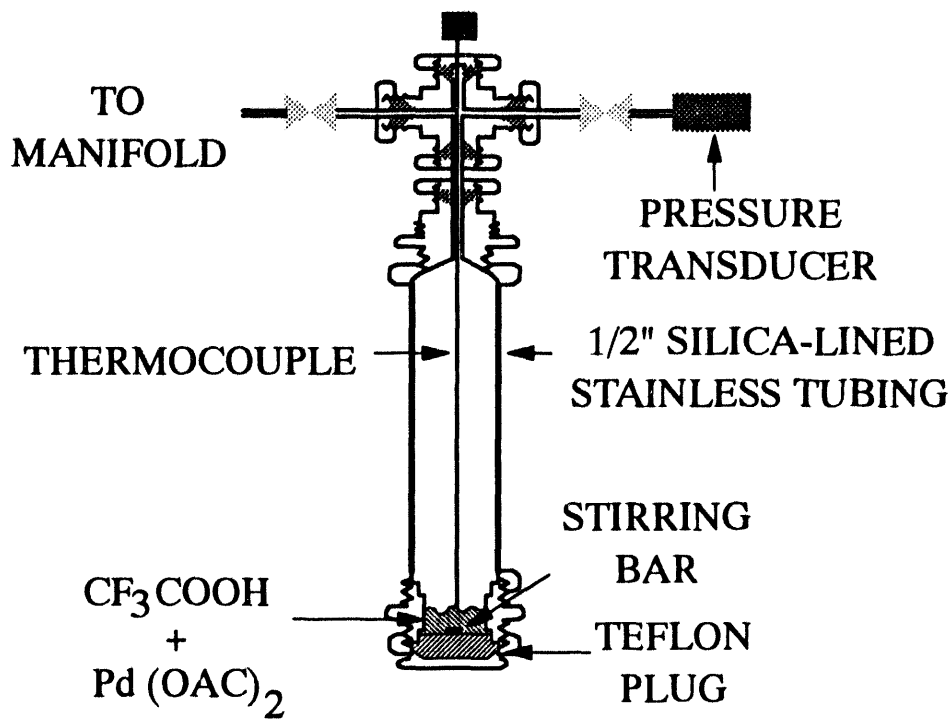
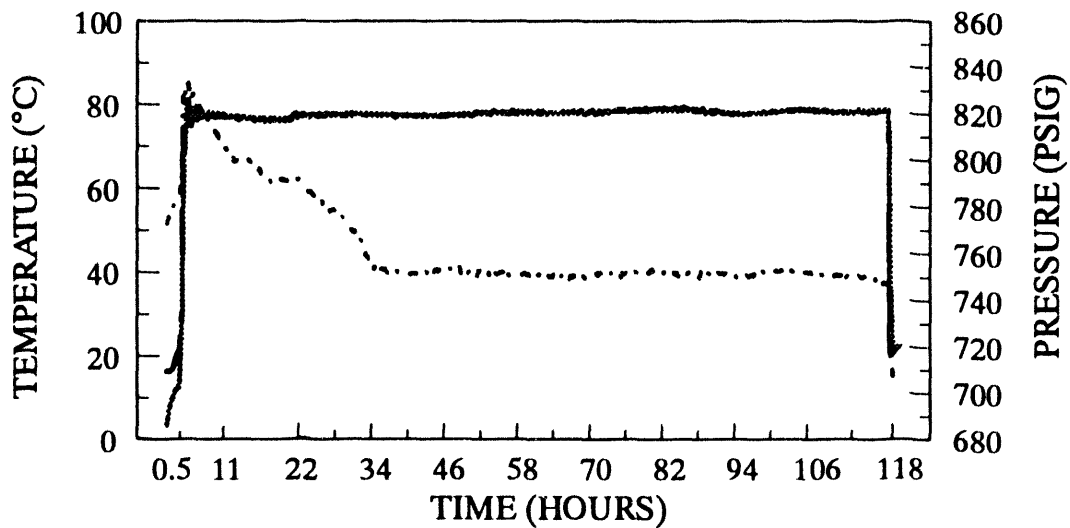


FIGURE 2. METHANE OXIDATION REACTOR



OUTSIDE TEMPERATURE (°C) REACTOR PRESSURE (PSIG)

REACTOR TEMPERATURE (°C)

FIGURE 3. TYPICAL PRESSURE-TEMPERATURE PROFILE OF OXIDATION RUN

**Conversion of Light Hydrocarbon Gases to Metal Carbides for
Production of Liquid Fuels and Chemicals**

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September 27, 1993

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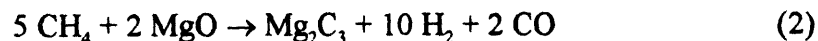
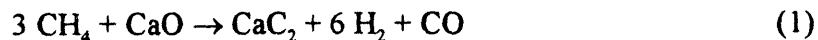
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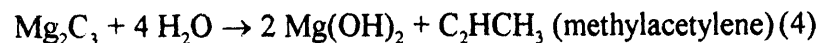
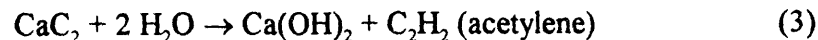
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1. Executive Summary

Pseudo stoichiometric (i.e. non-catalytic) reactions of methane with low cost, recyclable, alkaline earth metal oxides at temperatures above 2100 K



indicate technical and economic promise for upgrading natural gas to solid metal carbides that can be stored, transported, and hydrolyzed to acetylenes:



which can be subsequently converted to premium liquid fuels and petrochemicals. Earlier MIT work by Kim (1977) *et al.* (1979) demonstrated high (>95%) methane conversion to CaC_2 by passing pre-mixed suspensions of powdered CaO in CH_4 through a laboratory scale electrical arc

discharge reactor. The overall aim of the present project is to develop new scientific and engineering knowledge for improved technical and economic assessment of Reactions (1) and (2) as bases for gas-to-liquids upgrading. Our specific objectives are : (a) to assess the technical feasibility of achieving high conversions of CH_4 to Mg_2C_3 via Reaction (2) in a thermal plasma; (b) to identify plasma operating conditions of practical interest, showing high CH_4 conversions to CaC_2 and Mg_2C_3 via Reactions (1) and (2), respectively; (c) to determine the technical viability of implementing Reactions (1) and (2) thermally, i.e. without a thermal plasma; and (d) to shed light on the underlying chemical and physical mechanisms responsible for desired yield-selectivity behavior in Reactions (1) and (2).

Progress to date has concentrated on design, construction, and procurement of a new lab scale thermal plasma reactor and related accessories and on preliminary thermodynamic calculations of equilibrium compositions for the Ca-C-H-O and Mg-C-H-O systems. These calculations imply significant thermodynamic driving force for converting methane to CaC_2 and Mg_2C_3 at temperatures around 2500 and 2100 K, respectively, and thus, further support the importance of systematic experiments to determine if reactions (1) and (2) can be implemented thermally.

Future work will focus on: completing and testing the new thermal plasma reactor; use of this reactor to steady CH_4 conversion to CaC_2 and Mg_2C_3 ; and on studies of thermal (i.e. non-plasma) implementation of Reactions (1) and (2).

2. Introduction

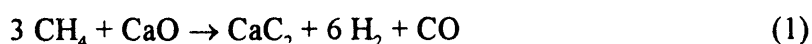
2.1 Background and Motivation

Diversification of the raw materials base for manufacturing premium fuels and chemicals offers U.S. and international consumers economic and strategic benefits (Longwell, 1993). Extensive reserves of natural gas in the world provide a valuable source of clean gaseous fuel and chemical feedstock. Assuming the availability of suitable conversion processes, natural gas thus offers the prospect of improving flexibility in liquid fuels and chemicals manufacture, and thus, the opportunity to complement, supplement, or displace petroleum-based production as economic and strategic considerations require. Many attractive deposits of natural gas are remotely located from key market sites. In order to utilize this remote resource commercially, natural gas must be transported to the market from the production site either via extensive sophisticated pipeline distribution networks under pressure or in specially designed ocean-going tankers as liquefied natural gas at low temperatures. Due to the state in which it exists at normal conditions, natural gas has a low energy content per unit volume compared to petroleum or coal. This relatively low energy density contributes to elevated transportation costs which exclude significant quantities of gas from commercial exploitation. Thus, there is considerable interest in developing new approaches to the volumetric energy densification of natural gas to enhance its marketability.

The composition of natural gas varies widely from reservoir to reservoir but the principal hydrocarbon constituent is always methane (CH_4). With its high hydrogen-to-carbon ratio, methane has the potential to produce hydrogen or hydrogen-rich products. However, methane is a

very chemically stable molecule and, thus, is not readily transformed to other molecules or easily reformed to its elements (H₂ and carbon). With the interest in upgrading natural gas to "value-added" products, several technologies for methane conversion to liquid fuel and chemical precursors currently exist at various stages of scientific and technical development. In many cases, further research is needed to augment selectivity to desired product(s), increase single-pass conversions, or improve economics (e.g. projections of ≥ 50\$/bbl for liquid products) before the full potential of these methodologies can be realized on a commercial scale. With the trade-off between gas conversion and product selectivity, a major challenge common to many of these technologies is to simultaneously achieve high methane single-pass conversions and high product selectivity.

Prior work at MIT (Kim, 1977; Kim *et al.*, 1979) has demonstrated that, by reacting methane with calcium oxide (CaO) in a laboratory-scale rotating d.c. arc reactor, high (>95%) methane single-pass conversions to molecular hydrogen (H₂) and calcium carbide (CaC₂) can be obtained, according to the reaction:



Hydrogen can be used as a fuel in thermal processes and in fuel cells to generate electricity at efficiencies which may approach 60%. It finds wide applications in petroleum refining and coal liquefaction where it is used to improve fuel quality, e.g. by increasing hydrogen-to-carbon ratio and lowering the fuel content of pollutant precursors such as sulfur, nitrogen, and heavy metals. Mixed with carbon monoxide (CO), hydrogen forms synthesis gas which is also valuable as a fuel, and which, by various catalytic processes, can be upgraded to a wide range of petroleum-like fuels, methanol, waxes, and other premium products. Calcium carbide, which exists as a solid at dry ambient conditions, is a particularly attractive product with significant commercial benefits in the present context: (a) being a solid, it can be separated from the gaseous products of Reaction (1) relatively easily; (b) it has an equivalent heating value (based on acetylene - see Reaction (3)) of about 8700 BTU/lb and thus, like low-rank coal, can be stored and transported over long distances at reasonable cost; and (c) by well-established hydrolysis processes, it can be converted to acetylene (C₂H₂) by the reaction:



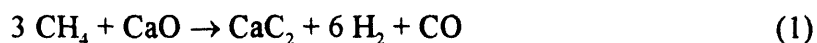
Acetylene, well-known for its reactivity and use as a basic raw material in the organic chemical industry, can be converted to a diverse array of chemicals and to high-grade liquid fuels.

In the light of the success of the previous work by Kim (1977), *et al.* (1979), there is incentive to investigate comparable reactions of methane with other alkaline earth metal oxides. In particular, magnesium oxide (MgO) undergoes an analogous reaction to produce hydrogen, carbon monoxide and magnesium sesquicarbide (Mg₂C₃) and/or magnesium dicarbide (MgC₂). Thermodynamic calculations imply that the sesquicarbide is strongly favored over the dicarbide above 2000 K. Of interest is the fact that magnesium is the only alkaline earth metal that forms a sesquicarbide, which, upon hydrolysis, yields methylacetylene (C₃H₄), effectively resulting in a C₁-to-C₃ conversion. Furthermore, methylacetylene offers a potential route to benzene by

condensation/dehydrocyclization. Concepts for synthesizing magnesium sesquicarbide from magnesium oxide and methane, with further upgrading of the sesquicarbide to C₃ hydrocarbons by hydrolysis, are described by Peters and Howard (1990). The earlier experimental work by Kim (1977), *et al.* (1979), together with more recent, though preliminary, cost estimates done at MIT (Peters and Howard, 1989) indicate that the metal carbide route offers sufficient potential for good thermal efficiency and for favorable economics, to warrant further systematic study of this approach to methane upgrading.

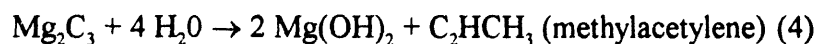
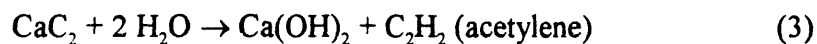
2.2 Description of Proposed Methane Upgrading Approach

In the proposed approach, methane would be reacted, essentially stoichiometrically (rather than catalytically), with relatively low cost and recyclable alkaline earth metal oxides such as calcium oxide (quicklime), magnesium oxide (magnesia) or mixtures of the two (calcined dolomite) to achieve very high (approaching 100%) conversion to hydrogen, carbon monoxide and the corresponding alkaline earth metal carbide, according to the reactions:



In order to carry out Reactions (1) and (2), the extreme chemical stability of methane would be overcome under high severity conditions, i.e. high temperature (>2000 K), in a thermal reactor or an electrical arc discharge (thermal plasma) reactor.

The carbides thus produced are solids at dry ambient conditions which can be more readily separated, stored and transported. Their value as fuel precursors and chemical intermediates is further enhanced when, upon reaction with water, they yield the valuable hydrocarbon gases acetylene and methylacetylene:



The acetylene and methylacetylene liberated from the carbides are virtually pure, thus eliminating the need for costly separation and purification steps inherent in hydrocarbon-based acetylene generation processes. Acetylenes can be upgraded to a wide range of chemicals or to premium-value liquid hydrocarbon fuels.

CaO and MgO for reuse in Reactions (1) and (2) can be regenerated from Ca(OH)₂ and Mg(OH)₂ according to:



and subsequently recycled back to the process.

A conceptual process wherein Reaction (1) [or (2)] is carried out under thermal plasma conditions followed by low temperature Reaction (3) [or (4)] to produce CO, H₂ and C₂H₂ (or C₃H₄) is estimated to have a reasonably high thermal efficiency. In the case of good heat integration where the plasma provides only the endothermicity of Reaction (1) or (2) and where CH₄ is used to generate electricity for driving the plasma reactor at 33% efficiency, Table 1 shows that the process thermal efficiencies are about 60%, which compare well with the 60% thermal efficiency of hydrogen manufacture by steam reforming of methane (Gary and Handwerk, 1984).

Table 1. Estimated Process Thermal Efficiency of Methane Conversion in a Thermal Plasma

Product LHV as a Percentage of Total CH ₄ Converted to Products and Converted to Electricity to Run Plasma at 33% Efficiency*					
Reaction	H ₂	CO	C ₂ H ₂	C ₃ H ₄	Total
(1) and (3)	32	6	28		66
(2) and (4)	29	7		22	58

*Assumes ideal heat integration so the plasma supplies only the endothermicity of Reactions (1) or (2).

2.3 Preliminary Cost Estimates

A study at MIT (Peters and Howard, 1989) on the economics of acetylene synthesis via metal carbide intermediates indicates that projected acetylene U.S. delivered costs from this approach can compare quite favorably with market prices. The study further suggests that, if the lower range of projected costs could be realized, acetylene from CaC₂ synthesized from remote natural gas could be economically competitive on a straight \$/BTU basis with remotely manufactured methanol or Fischer-Tropsch hydrocarbons, as shown in Table 2. The lower range of costs could be obtained by improving upon the CaO utilization efficiencies obtained by Kim (1977) *et al.* (1979), by achieving multiple recycles of CaO, and by use of low cost electricity or thermal (i.e. non-electrical discharge) processing. Table 3 shows how different costs for electricity are estimated to affect projected acetylene costs by arc discharge conversion of CaO and CH₄.

A major underlying assumption in this study is that the natural gas is converted to CaC₂ at the remote site and that the calcium carbide is then shipped to market sites for hydrolysis to acetylene. Without the need for long distance transport of the carbides or liquid products to the market site or the metal oxides to the gas site, metal carbide synthesis could offer an even more economically

promising route to the conversion of methane to liquid fuels, assuming that near-site methane costs are not significantly greater than the cost of remote gas.

Table 2. Estimated U.S. Delivered Costs of Products from Remote Site Conversion of Methane, 1986\$/10⁶ BTU (Peters and Howard, 1989)*

Product	Shipping Distance, Miles	
	6,200	12,400
LNG	4.3	5.8
Methanol	6	6.7
Fischer-Tropsch Liquid	8.8	9.1
Synthetic Gasoline or Distillate	8.25	8.6
Acetylene from CaC ₂ via		
Arc Discharge	5 - 36	6 - 38
Thermal Conversion	4 - 12	5 - 14
Acetylene Price in the U.S.	20 - 25	

*Estimated using information from Fox *et al.* (1988), Kim (1977), *et al.* (1979), and other sources given by Peters and Howard (1989).

The proposed approach shows good potential for high methane gas conversion and high product selectivity, economical energy storage and long-distance transport, relatively high thermal efficiency estimated at 60% even with electrical arc discharge processing and cost-competitiveness with other methane conversion routes and with domestic acetylene. If successful, this metal carbide synthesis approach will enhance technological options for the use of methane and, thus, of natural gas. This can lead to diversification of the raw materials base for fuels and chemicals manufacture since, by choosing the appropriate chemical reaction pathway for acetylene or methylacetylene, natural gas can be converted to particular products that respond to specific market opportunities, or to strategic situations calling for raw materials diversification.

Table 3. Estimated Market Site Costs of Acetylene from Electrical Arc Discharge or Thermal Conversion of Remote Gas to Calcium Carbide, 1986\$/10⁶ BTU*

		Carbide Shipping Distance, Miles			
		6,200		12,400	
		Specific Energy Consumption, kWh/lb Acetylene			
Electricity Cost, ¢/kWh		5	8.4-8.6	5	8.4-8.6
0.72		5-13	6-14	6-15	7-16
2.0		8-16	11-19	9-18	13-21
2.5		9-17	13-22	11-19	15-23
3.0		10-18	15-24	12-20	17-25
6.0		18-26	27-36	19-27	29-38
• Thermal Process		4 - 12		5 - 14	
• U.S. Domestic Price of Acetylene		20 - 25			

*Estimated using information from Fox *et al.* (1988), Kim (1977), *et al.* (1979), and other sources given by Peters and Howard (1989).

3. Objectives of Research Supported by U.S. DOE/PETC

The major goal of this research is to develop new scientific and engineering knowledge bases for assessing the technical and economic promise of converting methane to alkaline earth metal carbides by Reactions (1) and (2) for subsequent production of acetylenes, chemicals and premium-value liquid hydrocarbon fuels.

Specific objectives are:

- (1) To determine the technical feasibility of converting CH₄ and MgO to Mg₂C₃, H₂ and CO, according to Reaction (2), under thermal plasma conditions to achieve high single-pass CH₄ conversions and strong selectivity to these three products;
- (2) To define preferred ranges of commercially practical plasma operating conditions for converting CH₄ and CaO and/or MgO selectively to CaC₂ and/or Mg₂C₃, H₂ and CO according to Reactions (1) and (2), with high yields and at sustainable rates;
- (3) To determine, if, as implied by thermodynamic calculations, Reactions (1) and (2) can be made to proceed "thermally", e.g. at temperatures of 2000 to 3000 K, without the need for a thermal plasma (electrical arc discharge) within reasonable time scales; and

- (4) To develop better understanding of the underlying chemical and physical mechanisms by which this approach gives desired methane conversion, product selectivity and kinetics behavior.

4. Research Plan and Approach

4.1 Introduction

The proposed research is being conducted as two tasks. Task 1 mainly addresses Objectives (1) and (2) while Task 2 is primarily concerned with Objectives (3) and (4). The work is outlined briefly in Table 4.

Table 4. Tasks and Objectives to be Addressed

Task 1: Industrial Chemistry and Applied Kinetics

- Technical Feasibility of Mg_2C_3 Synthesis from CH_4 and MgO via Reaction (2) in a thermal plasma reactor
- Measurement of Product Yields and Selectivities, CH_4 Conversion and Global Kinetics under Thermal Plasma Conditions for Reactions (1) and (2)
- Identification of Plasma Conditions for Desired Methane Conversion and Product Selectivity Behavior

Task 2: Mechanistic Foundations

- Technical Viability of Thermal Approach for CaC_2 and Mg_2C_3 Synthesis from CH_4 with CaO and MgO
 - Thermodynamic Calculations and Chemical Kinetics Models
 - Important Chemical and Physical Phenomena Underlying Desired Behavior
-

4.2 Task 1: Industrial Chemistry and Applied Kinetics of Methane Conversion to Metal Carbides, H₂, and CO

4.2.1 Laboratory-Scale Electric Arc Discharge (Thermal Plasma) Studies

A laboratory-scale electrical arc discharge (thermal plasma) reactor will be used to systematically investigate the effects of variations in thermal plasma operating conditions on the conversion of methane to metal carbides. The experimental apparatus will consist of a commercial plasma torch as the reactor, a post-plasma cooling chamber for thermally quenching the plasma effluent, and a sample collection system. A premixed suspension of CaO and/or MgO in CH₄ will be passed through the inter-electrode region of the plasma gun, as schematically depicted in Figure 1. Methane conversion, product yields and, to the extent feasible, product formation rates will be measured as functions of independent variations in operating conditions of practical interest such as temperature, power input, residence time, quench time, CaO/CH₄ and MgO/CH₄ ratios, initial particle size of CaO and MgO, methane partial pressure and partial pressure of a diluent such as hydrogen in a thermal plasma reactor. Table 5 gives the design basis for the proposed experimental work together with the range of operating conditions examined by Kim (1977). The overall layout of the experimental apparatus is shown in Figure 2.

A product quenching and collection system will be fabricated and will consist of a movable, cooled cylindrical collection probe that can be mounted at the bottom of the cooling chamber. This probe will be designed so that the distance of separation between the end tip of the plasma "flame" and the entrance to the probe can be varied in a controlled manner. The time necessary to quench the products (and unreacted feed) from the plasma reactor depends on the temperature and enthalpy content of the reactor effluent, the final temperature desired, and the rates at which enthalpy can be removed from the effluent stream. The length of the cooling zone, which will consist of the region between the plasma tip and the entrance to the collector, will then depend on the exit gas flowrate and the necessary quench time. Gas samples will be collected either with an evacuated sampling can or with a sampling loop with multiple valves. Solid samples will be collected in fritted disk filters. In addition to sampling through the probe, the rest of the solid effluent from the reactor will be collected on sintered bronze filters at the bottom of the cooling chamber.

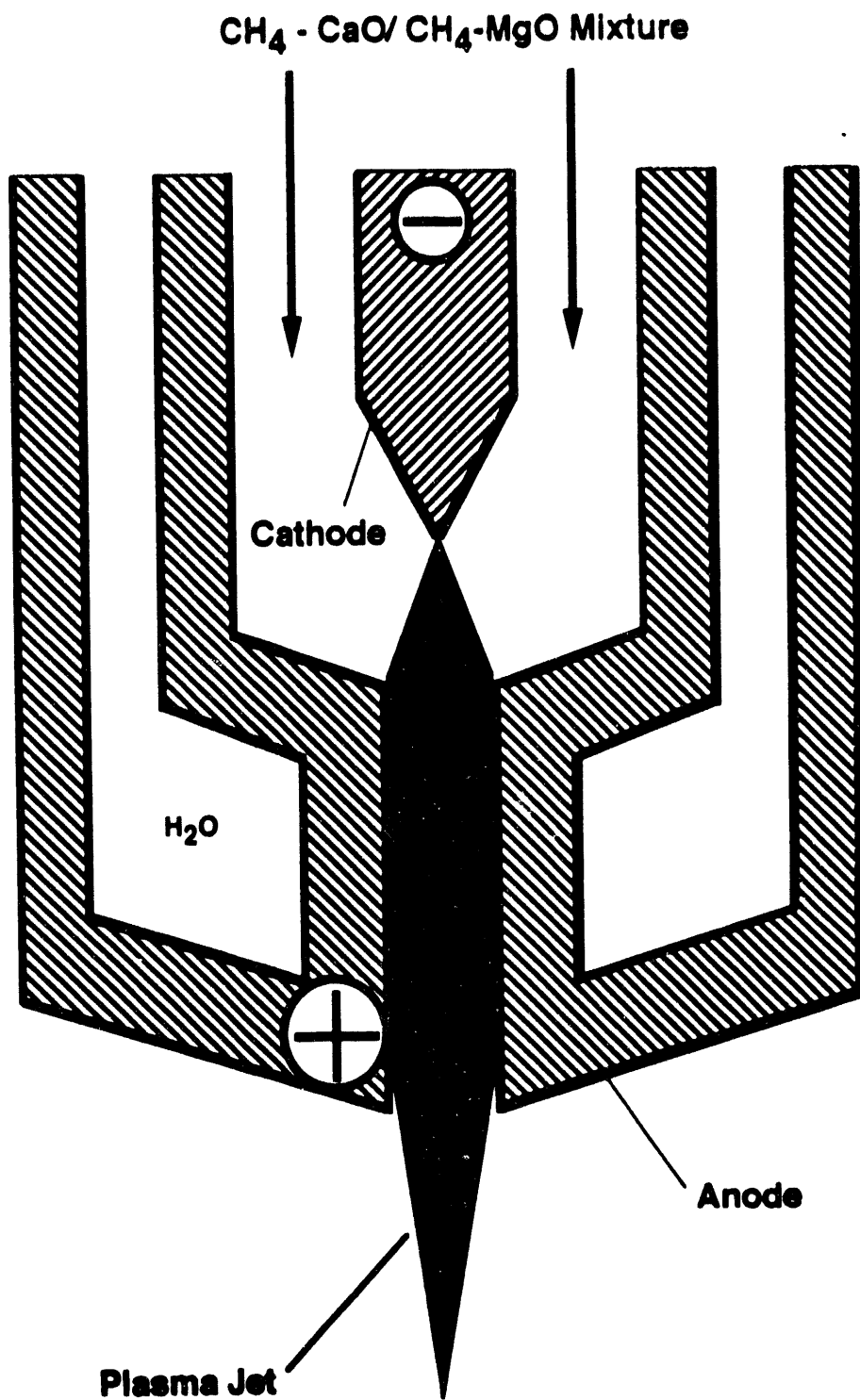


Figure 1. Schematic Representation of Plasma Gun Internals

Table 5. Experimental Design Basis

	<u>Kim's Study (1977)</u>	<u>Proposed for Present Study</u>
Power Input, kW	10 - 26	10 - 60
Methane Flowrate, L/min @ 70°F (294 K) and 1 atm	16 - 48	10 - 150
Powder Feedrate, g/min		
CaO	1.5 - 38 (0.12-1.4 times stoich. amt based on moles C in CH ₄)	1.5 - 116.1 (0.2-1.5 times stoich. amt based on C moles in CH ₄)
MgO		1.3 - 100.1 (0.2-1.5 times stoich. amt based on C moles in CH ₄)
Particle Size, μm	<8, <44, <74	1 - 100
Residence Time	- diff. anode lengths	- diff. anode lengths - cathode-anode gap - change in power and gas flow
Quench Distance, in (probe to anode nozzle exit)	5, 15	5 - 15

4.2.2 Physical and Chemical Analysis of Products

Metal carbide yield will be determined by hydrolysis of the solid sample and subsequent gas chromatographic measurement of the acetylene/methylacetylene gas evolved. Since the solid sample will contain unreacted CaO and/or MgO, the total calcium and/or magnesium content in the hydrolyzed sample will be determined by complexometric titration (Snell and Ettore, 1969). The calcium and/or magnesium in carbide form as a percentage of the total calcium and/or magnesium content is also the conversion of the metal oxide to the corresponding carbide. Analysis of gas samples will be done by gas chromatography.

Solid samples will be analyzed for bulk and surface properties using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Reactant and product particle size ranges will be determined by sieving, when feasible. Product morphology at various degrees of methane conversion will be examined to gain insight into the stages of product formation. Techniques such as X-ray diffraction, X-ray Photoelectron Spectroscopy and High Pressure Liquid Chromatography can be accessed to identify components of the solid product or in its solvent extracts.

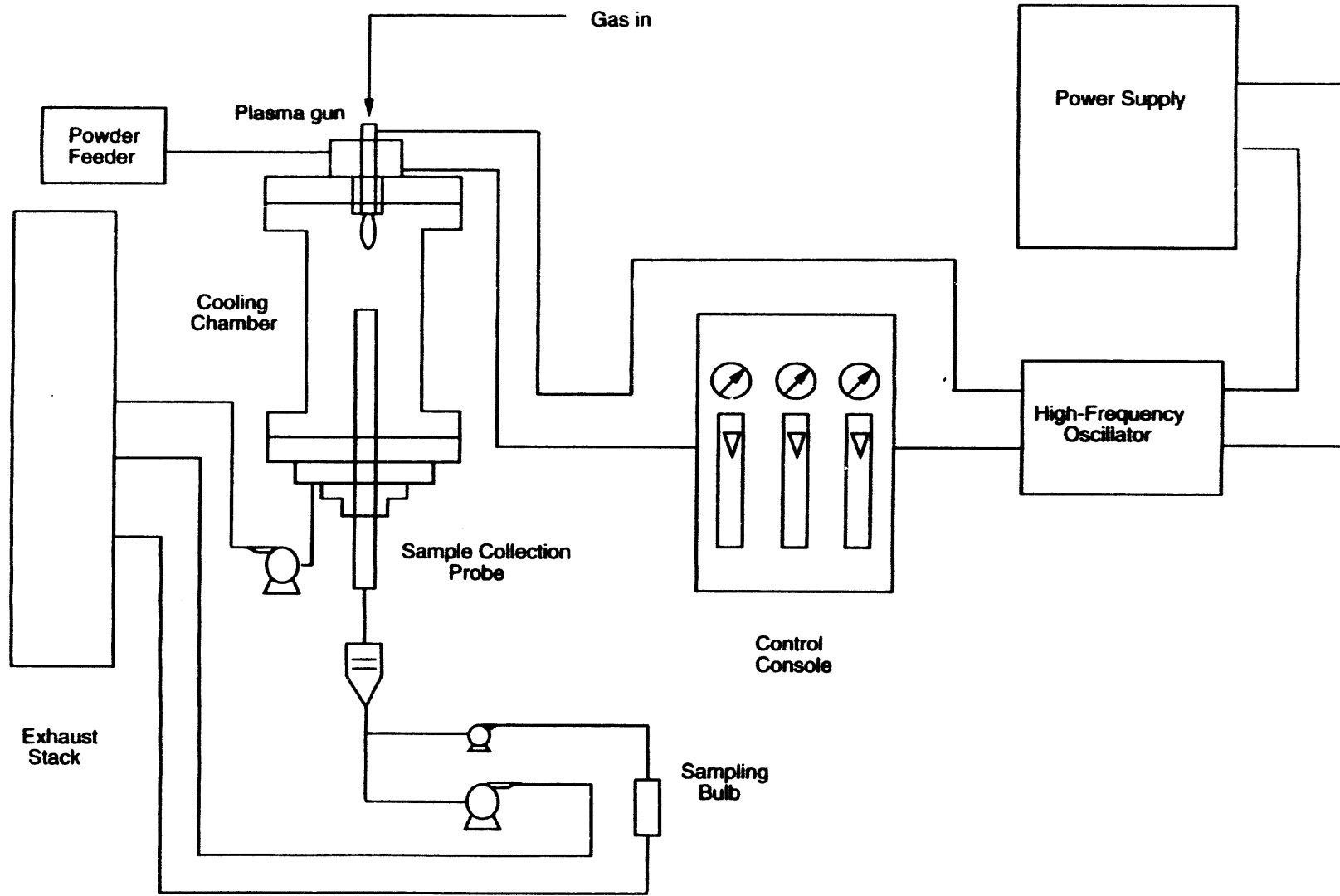


Figure 2. Overall Layout of Experimental Apparatus

4.3 Task 2: Mechanistic Foundations for Methane Conversion to Metal Carbides, H₂, and CO

The technical feasibility of carrying out Reactions (1) and (3) thermally (2000 - 3000 K), rather than under thermal plasma conditions, will be examined experimentally. To facilitate kinetics interpretation, these experiments should promote excellent CH₄-CaO contacting, avoid CH₄ consumption by pyrolysis, and allow temperature and residence time to be reliably determined. Candidate apparatus includes electrical screen heaters, low pressure thermal reaction chambers, electrically heated tungsten tubular reactors, shock tubes or bubbling cauldron reactors. Alternatively, the thermal plasma reactor under Task 1 may be utilized in experiments where the plasma arc is used to generate high temperature (2000 - 3000 K) argon flows for rapid contacting with initially cool CH₄-CaO mixtures. The extent and global rates of methane conversion as well as yields and production rates of CaC₂, Mg₂C₃, H₂, and CO will be measured by subjecting mixtures of methane and CaO and/or MgO to high temperatures and controlled residence times. Hypothesis-testing of possible mechanistic pathways will be conducted with selected experiments. Global and possibly more detailed reaction models will be investigated to better understand the underlying chemical and physical processes that could influence process design and scale-up possibilities.

4.3.1 Thermodynamic Calculations

In addition to previous thermodynamic calculations indicating that the thermal conversion approach is thermodynamically feasible at tractable temperatures, equilibrium compositions for the Ca-C-H-O and Mg-C-H-O systems for ranges of temperature, pressure and CaO/CH₄, MgO/CH₄ ratios of practical interest for thermal conversion will be calculated to gain insight on potential reaction pathways contributing to desired methane conversion and product selectivity behavior. Programs such as CHEMKIN will be used and supplemented with thermodynamic data on CaC₂ and Mg₂C₃. From a mechanistic standpoint, the thermodynamic favorability of different candidate pathways for vaporization of calcium metal (or magnesium metal) from their corresponding oxides and for carbide formation from the elemental vapor will be assessed.

4.3.2 Thermochemical Kinetics and Fluid-Solid Reaction Modeling

Thermochemical kinetic calculations and global and more refined kinetics models of gas conversion and product formation will be investigated to gain mechanistic understanding of the underlying chemical and physical rate phenomenon. Representative mechanistic questions include:

- (1) What are the roles of methane and of the CaO and MgO in carbide formation? Do the reactants (or just one) require conversion to reactive intermediates and, if so, what are those active species: free radicals, atoms, solids defects, super- or sub-stoichiometric compounds (CaO₂), etc.?
- (2) Is a thermal plasma required for reasonable rates of carbide synthesis and, if so, what are the principal functions of the plasma? Possible plasma contributions are: provision of high reaction

temperatures to overcome chemical or transport barriers or to allow favorable reaction pathways to dominate over alternatives; creation of critical inventories of active species; or shock fracturing or evaporative decomposition of solid oxide into more reactive particle sizes or vapor phase moieties.

(3) What is the chemistry of carbide formation and what are the pathways for carbide nucleation as a solid?

4.3.3 Laboratory-Scale Thermal Reactor Studies

Goals are to subject premixed suspensions of CaO and/or MgO in methane to elevated temperatures (2000 - 3000 K) and rapid heating rates (100 - 10,000 K/sec) for various prescribed contact times (10 - 100 ms) under various methane partial pressures in a category of candidate apparatus for carrying out a purely thermal reaction. Criteria for selecting reactor(s) will include their ability to allow adequate contacting between methane and the CaO and/or MgO, and independent variations in CaO/CH₄, MgO/CH₄ ratios, treatment time and temperature. Temperatures can be measured with thermocouples or by optical pyrometry. Residence times will be calculated based on inlet flowrates of feed, reactor volume and reaction stoichiometry. Product yields and the amount of unreacted feed material will be determined to close material balances and to quantify feed conversion and product selectivity. Kinetic parameters will be deduced from the temperature-time profile, feed conversion and product yields using a suitable reactor model.

4.3.4 Laboratory-Scale Experiments for Hypothesis-Testing and Model Parameterization

Selected experiments are of interest to test specific hypotheses on how carbide formation proceeds and to provide best-fit parameters for proposed kinetic models of products formation and methane depletion. Experiments designed for independent study and simulation of critical features of high-temperature or plasma reactions of methane with CaO and/or MgO are of interest. For example, localized inventories of nascent species (e.g. free radicals, ions) can be generated in selected runs by creating an arc discharge in the vicinity of the reactor heating stage with a tesla coil. Also, if rapid heating of tiny CaO or MgO particles are of particular interest, an electrical screen heater reactor might be used to investigate the effects of intense heating on particles of different initial sizes on their morphology.

Typical domains of more fundamental investigation may include:

(1) Shock-heating pre-sized CaO/MgO particles under an inert atmosphere to determine the effect of heating rate, temperature, time at final temperature and quench rate on particle size distribution and morphology as well as surface and bulk chemical and physical properties.

(2) Repeating (1) at known initial methane partial pressures and examining the products for metal carbides and carbon deposits and the gaseous products for stable species like CO and H₂ and trace hydrocarbons such as acetylene.

- (3) Repeating (1) with a small arc discharge at the particle heating stage.
- (4) Repeating (2) with a small arc discharge at the hot stage.
- (5) Repeating (1) and (3) but without exposing the metal oxide to air and admitting methane to the reactor at certain partial pressures and then subjecting the metal oxide-methane mixture to a prescribed temperature-time history including conditions less severe than those of a plasma reactor and comparing the product yield, composition and properties to those in (1) and (3).

5. Accomplishments for the Period October 1, 1992 - September 20, 1993

Under Task 1 (Industrial Chemistry), progress to date has concentrated on the design, construction, and procurement of a thermal plasma reactor and related accessories. The proposed experimental equipment is being constructed using a thirty-year-old AVCO plasma generator system consisting of a plasma gun (AVCO Model PG-041), a high frequency oscillator (for initiating the arc), a control console and an AIRCO d.c. power supply unit rated by the manufacturer at up to 83 kW, which was successfully revitalized. The system was test-fired with Argon as the plasma-forming gas and was found to be in good working order. A steel, post-plasma cooling chamber system, with a water-cooled wall (Figure 3) has been developed to allow for cooling of the plasma effluent and to facilitate rapid quenching and recovery of solid and gaseous reaction products. The main chamber body for this system was one component of a now dismantled coal pyrolysis/hydrolysis reactor. This chamber was revitalized for service in the present system. A steel flange with a water-cooled channel on which the plasma gun is mounted forms the top part of this chamber (Figure 3). The bottom part consists of a steel flange welded to the bottom of the chamber, a matching steel flange which rests on a supporting aluminum plate, a removable brass flange for sample collection and a smaller brass flange for supporting the sample collection probe (Figure 3). The chamber is mounted inside a fragmentation containment room that was built to house the plasma reactor assembly. This room is vented to a steel-cased chimney and is designed with enough air flow to dilute hydrogen gas to 25% of its Lower Explosive Limit at 1 atm pressure.

The sample collection system is currently under construction. A commercial unit will be employed to feed powder to the plasma gun and various options are being investigated.

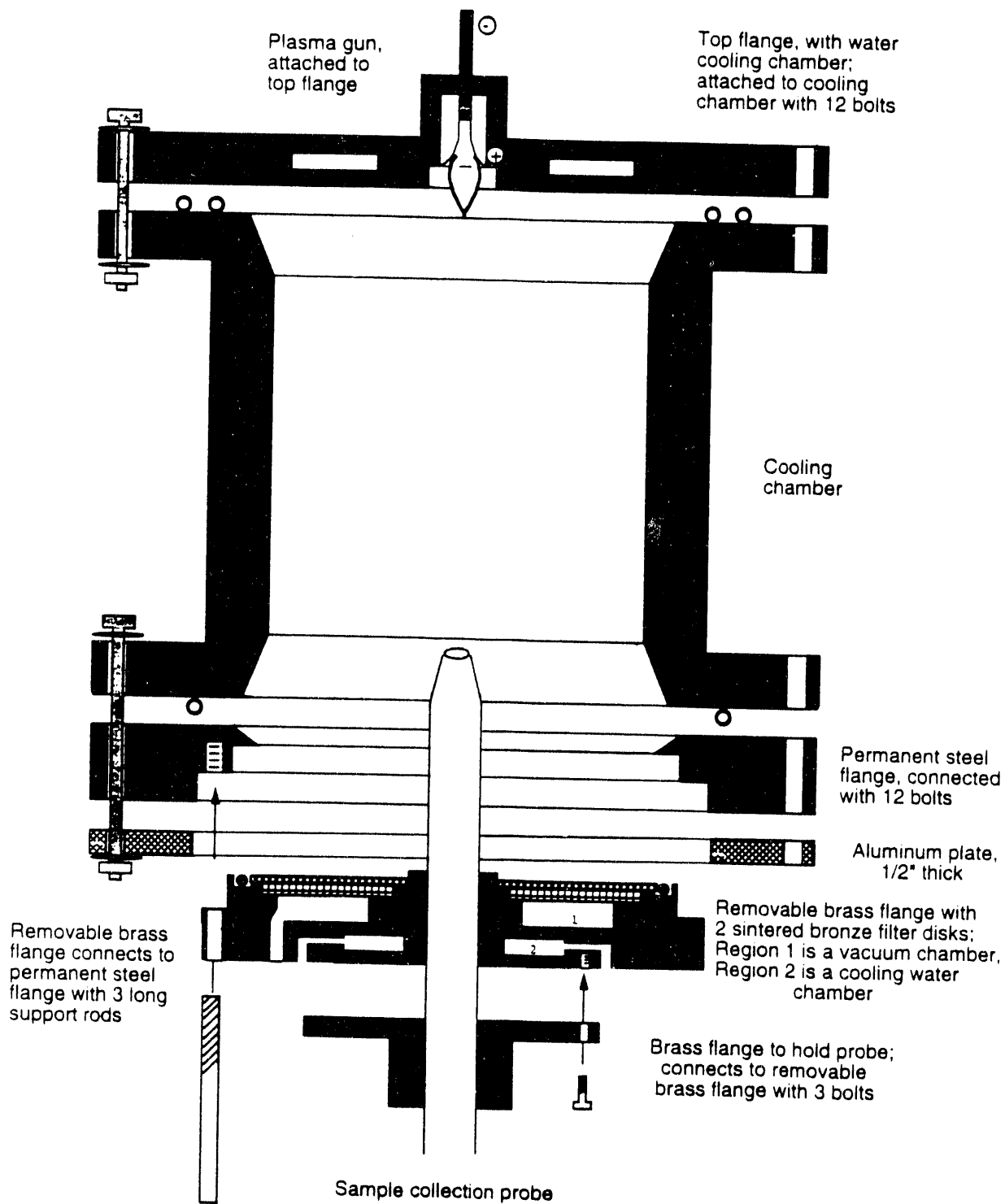
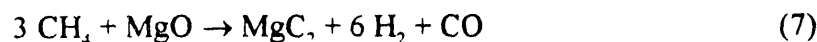


Figure 3. Cooling Chamber Assembly

Under Task 2 (Mechanistic Foundations), thermodynamic calculations show strong support for a tractable thermal (non-plasma) approach to converting methane to CaC_2 and Mg_2C_3 . The $\text{Log}_{10} K_p$ values for Reactions (1) and (2) are plotted against the reciprocal of absolute temperature in Figure 4. In addition, a similar plot is shown for the formation of magnesium dicarbide:



The plots suggest strong thermodynamic driving force for the formation of calcium carbide and magnesium sesquicarbide from high temperature reactions of methane with CaO and MgO above 1600 K and 1740 K, respectively, corresponding to $\text{Log}_{10} K_p$ values above 5. Furthermore, Mg_2C_3 formation is thermodynamically preferred over MgC_2 formation at 1740 K and becomes increasingly favored at even higher temperatures. However, the kinetics behavior of these reactions needs to be determined in order to assess whether desired conversions and selectivities can be achieved at commercially sustainable rates.

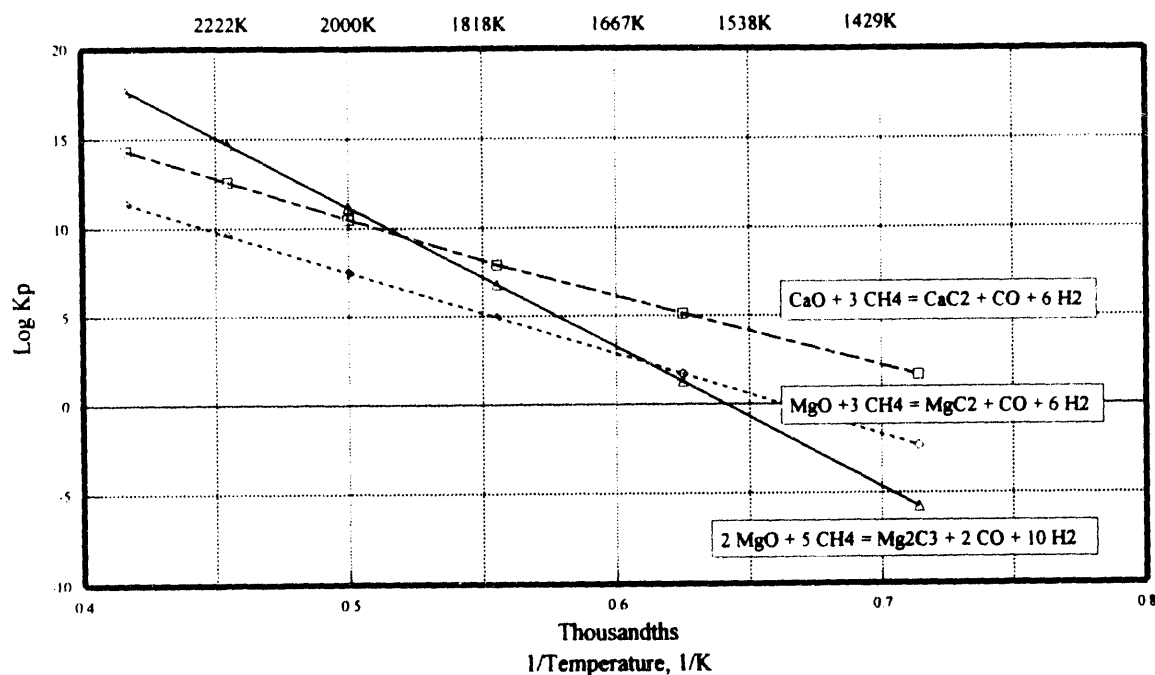
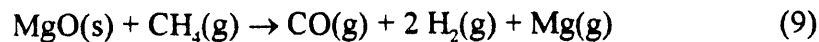
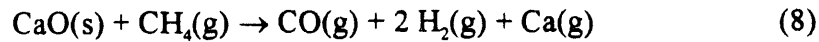


Figure 4. $\text{Log} K_p$ Values for Methane Conversion to Alkaline Earth Metal Carbides

Preliminary thermodynamic calculations using CHEMKIN were performed for the Ca-C-H-O and Mg-C-H-O systems. Figures 5 and 6 show the equilibrium diagrams predicted for the two systems at 1 atm pressure in the 1500 - 3500 K temperature range with 1:3 Ca:CH₄ and 2:5 Mg:CH₄ ratios, respectively. These are the stoichiometric ratios corresponding to Reactions (1) and (2). These plots give the equilibrium mole fractions of the reaction products. Interestingly, when converted to

percentage molar conversion of CaO to CaC₂, these calculations reveal a CaO molar conversion of 71% at 2900K, which corresponds very well with the 70 ± 15% reported by Kim (1977) *et al.* (1979). The molar conversion of MgO to Mg₂C₃ is calculated to be 50% at 2100 K. Furthermore, there appears to be a high elemental vapor concentration, suggesting possible pathways involving metals vaporization.

Assessment of the thermodynamic favorability of different candidate pathways for vaporization of calcium metal and magnesium metal from their corresponding oxides was performed and results are presented in Figures 7 and 8, respectively. These plots indicate strong thermodynamic driving force for metals vaporization via reaction with CH₄, according to:



A similar assessment for carbide formation from the elemental vapor is given in Figures 9 and 10, suggesting support for metal-CH₄ reaction pathways:

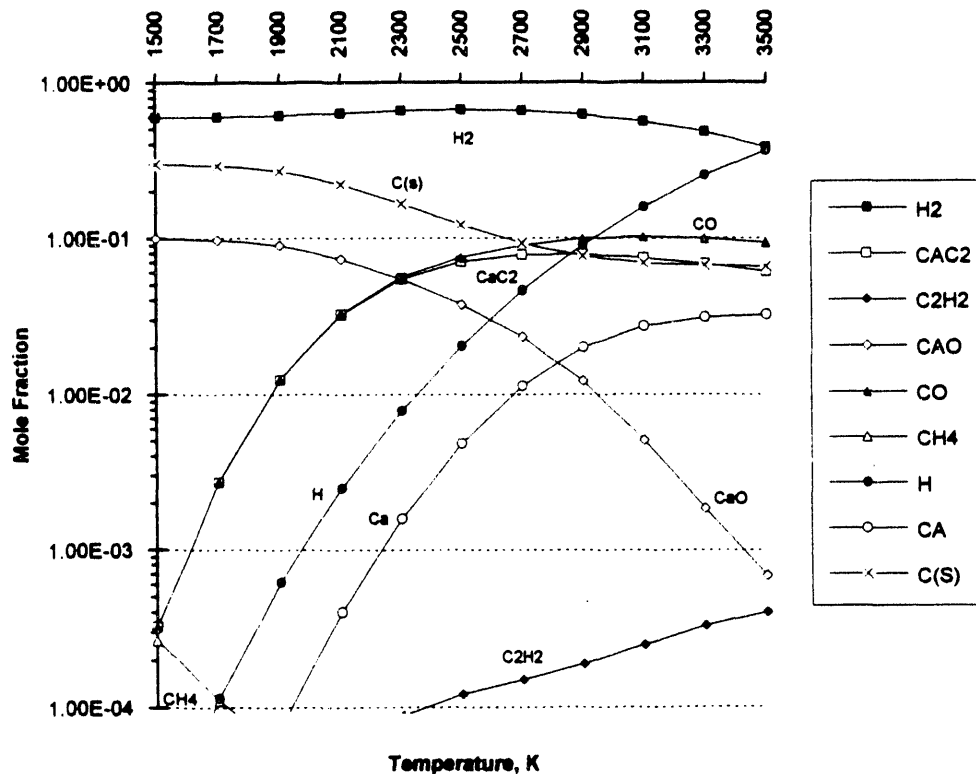
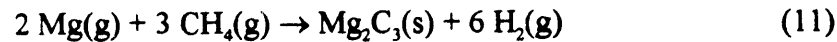
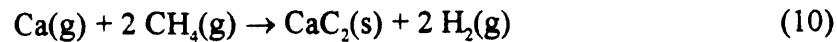


Figure 5. Equilibrium Diagram for Ca-C-H-O System at 1 Atm and 1:3 Ca/CH₄ Ratio

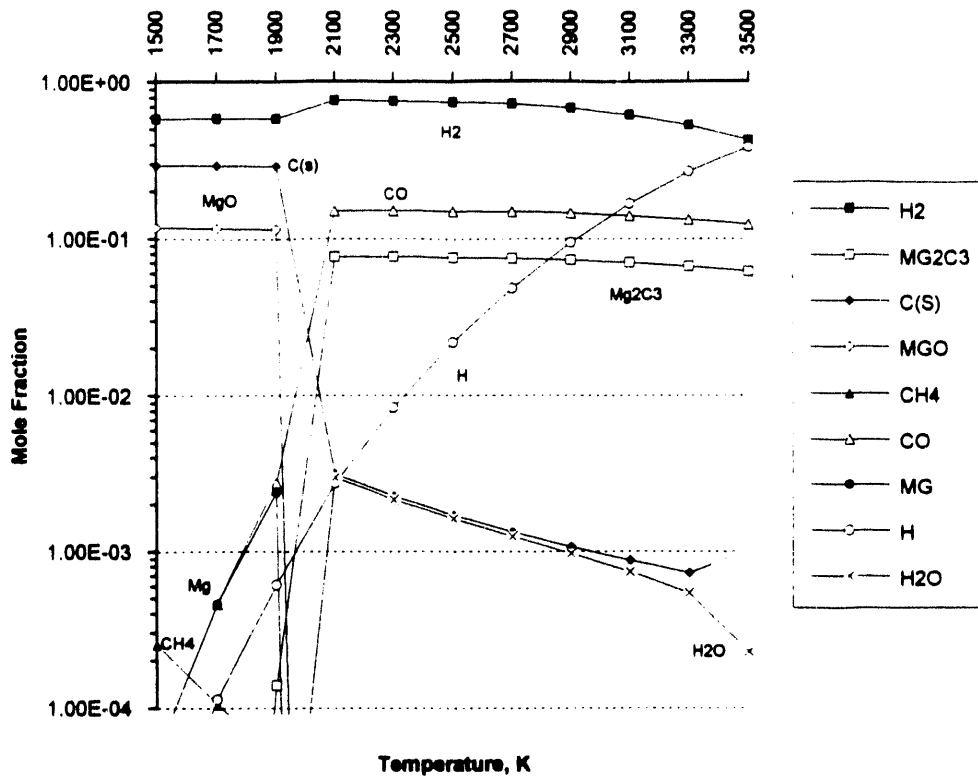


Figure 6. Equilibrium Diagram for Mg-C-H-O System at 1 Atm and 2.5 Mg/CH₄ Ratio

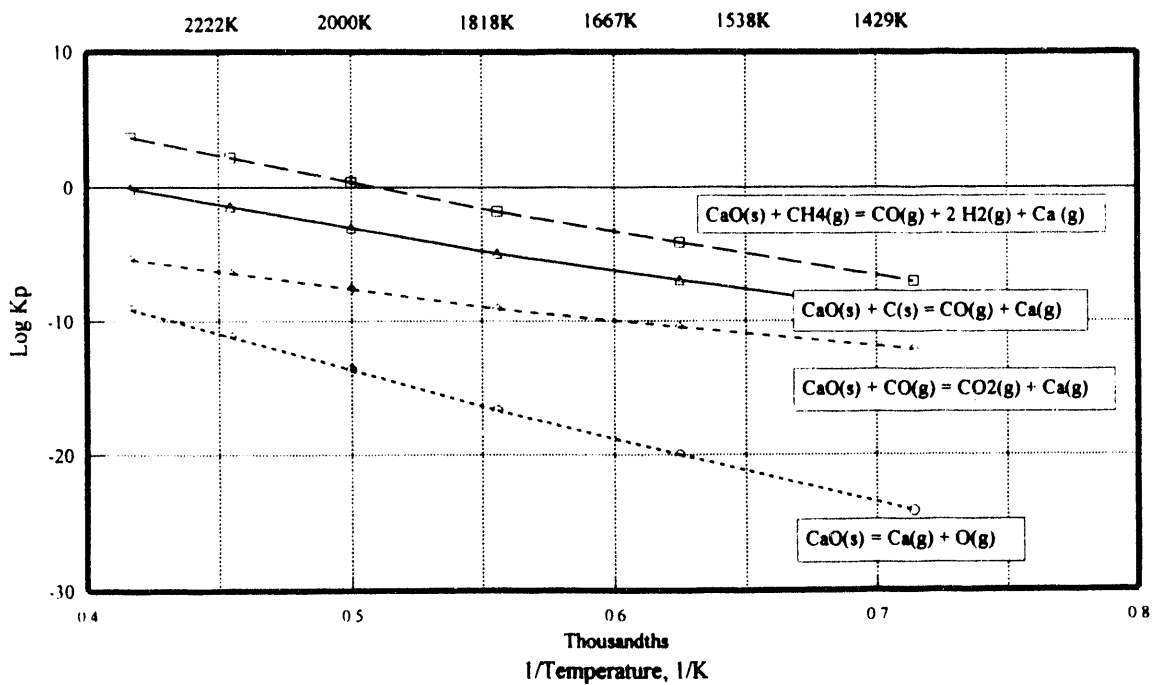


Figure 7. Log K_p Values for Calcium Metal Vaporization Pathways

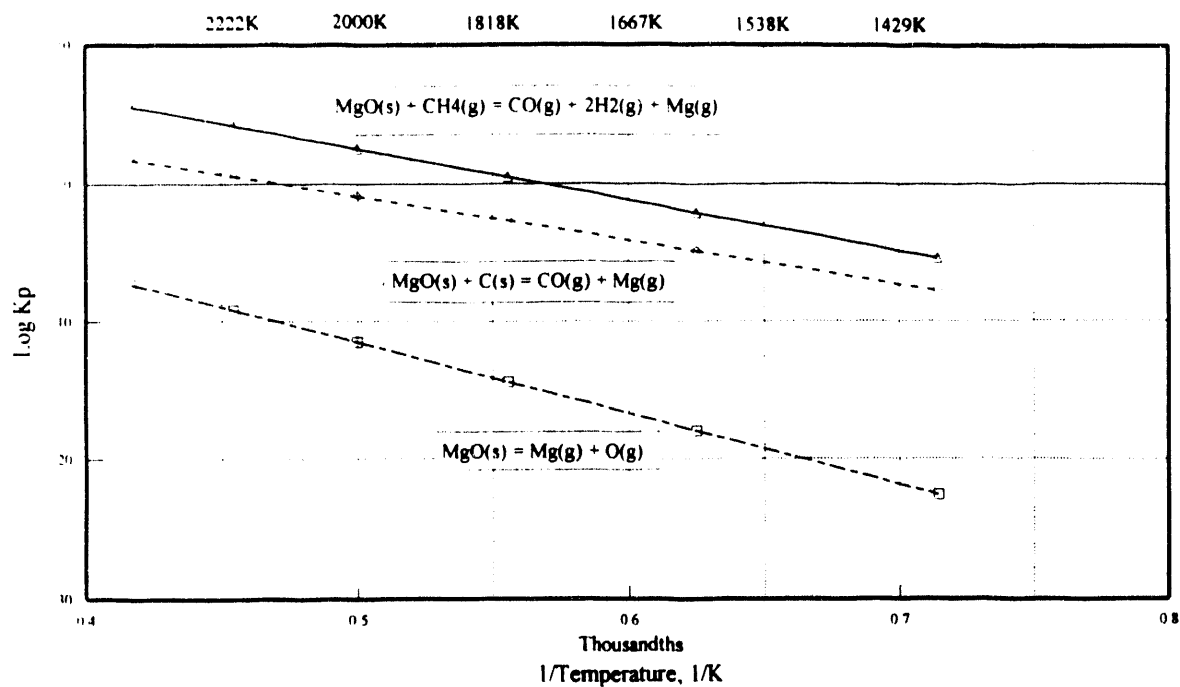


Figure 8. Log K_p Values for Magnesium Metal Vaporization Pathways

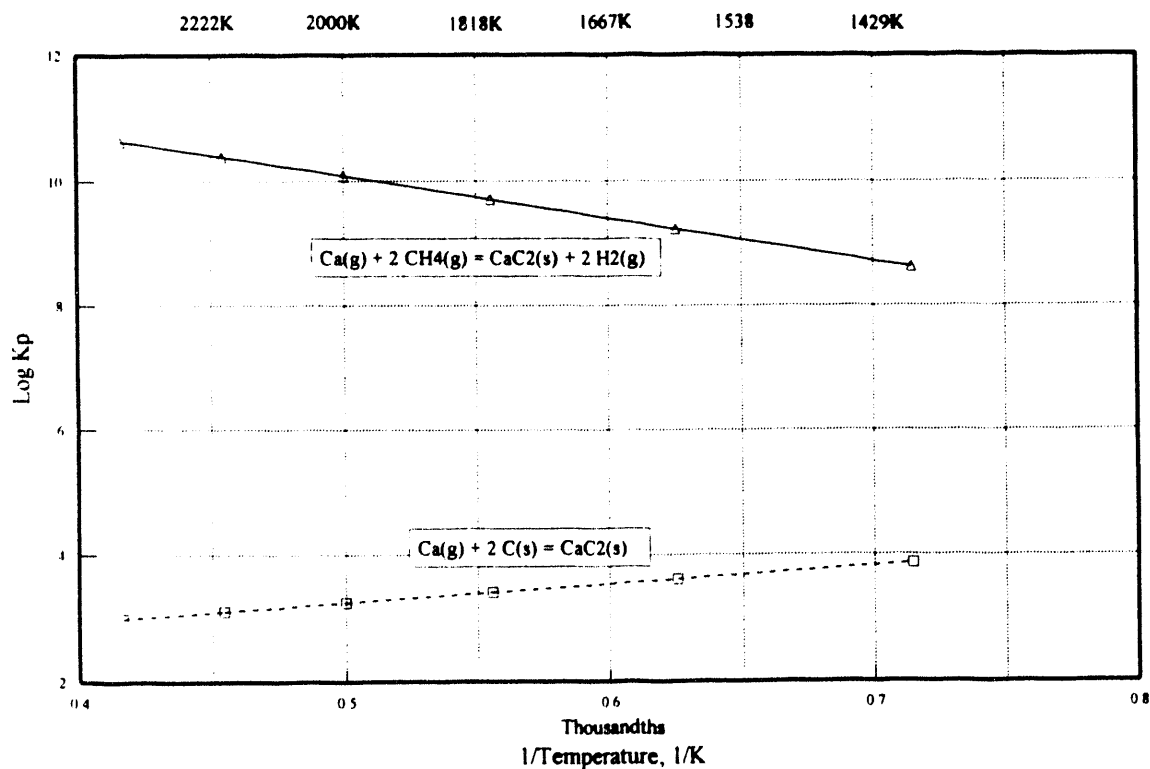


Figure 9. Log K_p Values for Calcium Carbide Formation Pathways via Calcium Vapor

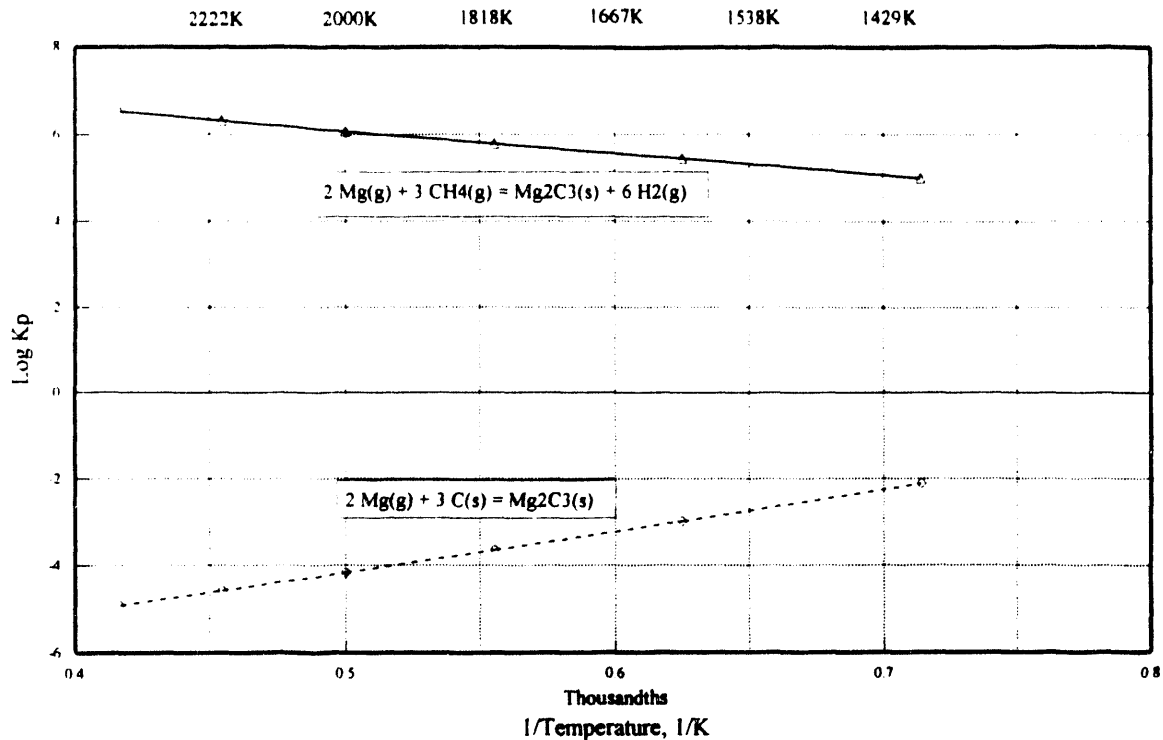


Figure 10. Log K_p Values for Magnesium Sesquicarbide Formation Pathways via Magnesium Vapor

Figures 9 and 10 also show, respectively, that CaC_2 and Mg_2C_3 formation by reaction of $\text{Ca}(\text{g})$ or $\text{Mg}(\text{g})$ with solid carbon (taken here as β -graphite) is far less favored thermodynamically compared to Reactions (10) and (11).

6. Conclusions

The proposed metal carbide route to CH_4 conversion has sound experimental and theoretical foundations. This methodology is well-matched to current and projected policy and technology demands on the energy and environmental sectors, with specific advantages that include near stoichiometric conversion of CH_4 , a range of premium products including liquid transportation fuels and molecular hydrogen, and suitability to all forms of natural gas including remote gas. Laboratory-scale studies are needed to determine the technical feasibility of thermal processing for the CaO/CaC_2 conversion route, and of both thermal and electrical discharge processing for the $\text{MgO}/\text{Mg}_2\text{C}_3$ conversion pathway. These studies will be carried out with a plasma reactor, which is nearing completion and with a thermal reactor, which needs to be developed. Detailed thermodynamic calculations continue to support the technical viability of the thermal chemical route at tractable temperatures (i.e. temperatures attainable by methane or H_2 combustion in

preheated air or oxygen) and also indicate that metals vaporization and metal-CH₄ reactions may play significant roles in metal carbide formation.

7. Future Plans

Under the Industrial Chemistry and Applied Kinetics Task, work will focus on the completion of the thermal plasma reactor and subsequent shakedown testing of the total system. With a working experimental set-up, systematic study of CaO/CH₄ and MgO/CH₄ conversion can then be undertaken. Conditions and feed characteristics giving desired yield and selectivity behavior will be identified.

Under the Mechanistic Foundations Task, more detailed thermodynamic equilibrium composition calculations under different CaO/CH₄ and MgO/CH₄ ratios and pressure conditions will be performed. A thermal reactor competent for kinetics studies will be developed and used to generate data for kinetics modeling and identification of major reaction pathways and kinetics hurdles.

8. Acknowledgements

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