



Environmentally-Preferred
Advanced Generation

A NOVEL STEAM REFORMING REACTOR FOR FUEL CELL DISTRIBUTED POWER GENERATION

Gray Davis, Governor

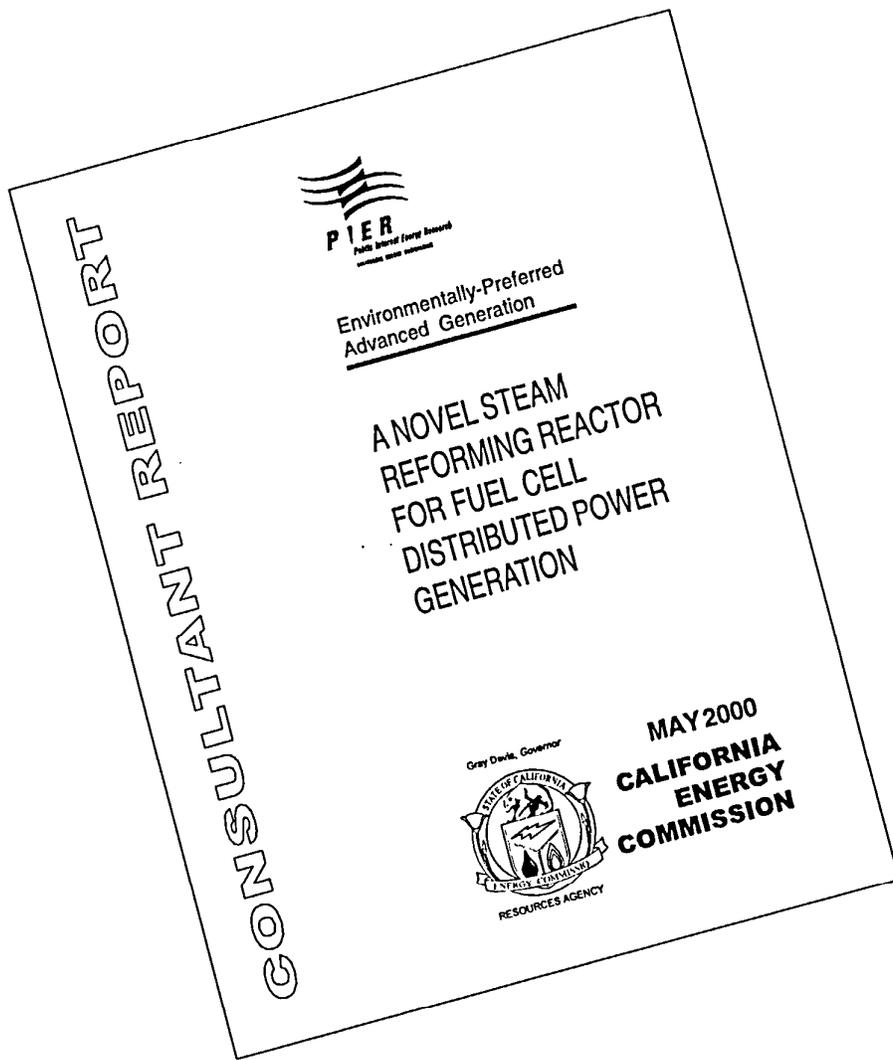


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Preface

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million to conduct the most promising public interest energy research by partnering with Research, Development, and Demonstration (RD&D) organizations, including individuals, businesses, utilities, and public or private research institutions.

PIER funding efforts are focused on the following six RD&D program areas:

- Buildings End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research.

What follows is the final report for the Public Interest Energy Research contract, 500-97-038, conducted by the GE Energy and Environmental Research Corporation. The report is entitled A Novel Steam Reforming Reactor for Fuel Cell Distributed Power Generation. This project contributes to the Environmentally-Preferred Advanced Generation program.

For more information on the PIER Program, please visit the Commission's Web site at: <http://www.energy.ca.gov/research/index.html> or contact the Commission's Publications Unit at 916-654-5200.

Executive Summary

GE Energy and Environmental Research Corporation (EER) is developing a novel steam reforming process to convert natural gas to hydrogen for use in polymer electrolyte membrane (PEM) fuel cells. As part of the effort, the California Energy Commission sponsored development of catalysts and selection of materials for use in a prototype reactor to be tested on a pilot reforming facility. The purpose of this project was to further develop the novel reforming process by studying catalyst and absorber materials with the goal of identifying materials with lifetimes in excess of 5,000 hours. EER ultimately intends to commercialize this reforming technology to provide a convenient and local source of hydrogen fuel for distributed fuel cell applications, thereby removing a significant barrier to the commercialization of PEM fuel cells.

Objectives

The overall objective of this project was to identify catalyst and absorber materials with extended lifetimes. To this end, EER obtained support from Phillips Petroleum to develop catalysts and absorber materials. These materials were tested to identify promising materials and operating conditions to advance the demonstration of the pilot reforming facility.

The specific objectives upon which this project's success were evaluated include:

- Identification of catalyst/absorber materials with projected lifetimes in excess of 2000 hours
- Use of catalyst per cycle of the process: >50 percent
- Absorber's carbon dioxide (CO₂) absorption capacities: ~50 percent of theoretical
- Volume of hydrogen produced: > 25,000 cubic feet per day
- Power output from reactor: >35 kWe¹ (target 50 kWe)
- Total cycle efficiency: >35 percent based on lower heating value (LHV) of fuel
- Conversion efficiencies: 75-85 percent based on LHV of fuel and hydrogen produced
- Emissions of NO_x, carbon monoxide (CO), methane (CH₄) at 7 percent oxygen (O₂): 0.1 ppm NO_x, <10 ppm CO, <50 ppm CH₄
- Catalyst/absorber cost/durability trade-off to result in a leveled incremental cost of electricity production equal to or less than that for centralized power production using California Energy Commission cost basis guidelines (including cogeneration credit).

We evaluated catalyst and absorber materials in three stages of bench-scale experiments: preliminary screening tests, detailed parametric testing, and accelerated durability testing. Preliminary screening tests were conducted at baseline reforming conditions to

¹ kWe refers to kW of equivalent electric power when the reformer is integrated with a PEM fuel cell.

quickly ascertain material suitability for the process. Fifteen catalyst materials were screened. Four catalysts did not meet the screening criteria and were excluded from further testing.

In the early screening stage, secondary reactions were identified that caused catalyst deactivation and poor catalyst regeneration. Continued catalyst development efforts, led by Phillips Petroleum, achieved a breakthrough with the discovery of a durable catalyst, designated P10, which met the performance requirements of the reforming process. One of the main areas of improvement was the reduced CH₄ slip during the fuel regeneration part of the reforming step. The CH₄ slip for catalyst P10 is much lower than for catalyst P3, and is comparable to the performance of commercial reforming catalysts.

Materials that met the performance requirements were selected for further parametric tests. Parametric testing identified potential operating limitations and generated a database of benchmark catalyst performance. Selected catalysts were tested through a range of conditions suitable for the reforming process. Changes in performance were recorded and evaluated. During this testing stage, two materials were identified as promising: catalysts C3 and P10. Catalyst C3, shown to be a highly active commercial catalyst, was selected for use in the prototype reactor tests on the pilot facility. Catalyst P10 was prepared with nickel and other proprietary promoters on a durable substrate. Phillips Petroleum specifically engineered the substrate for hydrothermally stressful environments. While still in an early state of development, this catalyst showed the ability to inhibit secondary reactions and produced comparable performance to commercial catalysts. Because of its specific material formulation and acceptable performance, catalyst P10 was selected for further accelerated durability testing.

Outcomes

The following performance outcomes were demonstrated:

- EER and Phillips Petroleum developed a catalyst material that demonstrated projected lifetimes exceeding 4,350 hours under reforming operation.
- The catalyst used in the pilot test facility achieved a 61 percent utilization, exceeding the technical objective of 50 percent utilization.
- Only one absorber, commercial dolomite, was identified as currently suitable for the reforming process based on the CO₂ acceptor concentrations.
- As tests were conducted at reduced capacity, the volume of hydrogen-produced objective could not be demonstrated.
- The power output objective could not be demonstrated because the tests were conducted at reduced capacity during the catalyst tests.
- From the current pilot test results and engineering assessment of the planned full capacity operation, a net electrical efficiency of 37 and up to 41 percent is projected.
- Fuel conversion was acceptable during the reforming process; however, the conversion during the fuel regeneration step was poor specifically due to the absence of steam.

- EER plans to assess the emission levels of the system based on the operation of the reformer and the capabilities of catalytic oxidizers to convert CH₄ and CO. Currently the untreated emissions of CH₄ and CO are expected to reach 1,000 and 51 ppm, respectively. NO_x emissions were not measured.
- Our preliminary economic assessment of the commercial reformer demonstrates its capability to meet California ratepayers' incremental electricity cost of 4.4 cents/kWh.

The assessed performance for the prototype reactor on the Pilot Test Facility was:

- Power Output (Electrical Equivalent) -- 50 kWe
- Conversion Efficiency -- 68 percent
- Total Cycle Efficiency (Electrical) -- 37 percent
- Total Thermal Efficiency -- 79 percent
- H₂ Production -- 30,500 cubic feet per day
- Catalyst Utilization -- 61 percent
- Absorption Capacity -- 65 percent

Conclusions

- More durable catalysts could be developed to meet the economic cost/durability trade-off. This will result in better technology acceptance in the short-term and lower costs in the long-term.
- The identification of a durable catalyst was a significant discovery for this project. This was made possible by the application of promoters that inhibited undesirable reactions. While the efforts to date have not exhausted or even scratched the surface of all possible catalyst enhancement techniques, the relatively significant improvement made with this experimental catalyst is a positive indication of future potential.
- Based on the current tests at a 20 kW electrical output equivalent and a calculated hydrogen production volume of 12,400 cubic feet per day, a hydrogen production volume of 25,000 cubic feet per day will be achieved at an operating capacity of 41 kWe. EER intends to demonstrate the ability to achieve this production level through upcoming tests conducted under the DOE program.
- Once EER has completed the pilot test facility reconfiguration, operation at 50 kW electrical output equivalent is expected to be achieved.
- The expansion in the industrial and commercial market sectors will initially be filled primarily by existing DPG technologies due to their commercial availability and proven track records. However, short, mid and long-term markets do exist for emerging technologies, such as EER's reformer based power system, that have improved efficiency and substantial environmental benefits relative to existing DPG technology.
- EER projects that the proposed DPG system will be:
 - cost competitive in the 2-300 kW (kW of electric power) size range

- net electrical system efficiencies exceeding 35 percent will be easily achieved
- total system efficiency, which includes the recoverable cogeneration heat, can be as high as 83 to 88 percent
- the engineering analysis also indicates that the system can operate cyclically with turndown as low as 10 percent of the design electric power output with a nominal increase in electric production efficiency.

Benefits to California

- Air Quality Improvement: The reforming process, when combined with fuel cell technology and with complete system integration, is estimated to produce total pollutant emissions at least 50 percent lower on average than the best technology for centralized electric power generation.
- Energy Savings: If the reforming technology was used to accommodate growth for target applications in California, it could reduce costly infrastructure improvements and provide a relatively inexpensive source of electricity estimated at 4 cents/kWh.
- Landfill Space Conservation: Only the spent substrates from the catalysts would need to be disposed. Catalyst metals are recovered. Increasing catalyst lifetime reduces the replacement frequency.
- Water Quality: The reforming process is not expected to have a significant impact on water quality.
- Increased Employment: Commercialization of the reforming technology will create several thousand jobs in the manufacture, sales, export, and maintenance of these DPG systems.
- Other Economic Benefits: Reduced health costs and ecological restoration costs.

Recommendations

Recommendations for future work to address the commercialization challenges and take the next steps for reforming commercialization include:

- continued development of materials, hardware, and manufacturing designs as well as identifying government and industry sources of support
- additional development of catalyst and absorber to significantly improve the commercial viability of the process
- development of hardware components to reduce the cost of the system
- the technology will require prototype development based on manufacturing and value engineering to optimize form and function
- testing conducted on absorber materials identified new methods for manufacture of absorbers using durable substrates. The material development conducted as part of this project verified that the deposition of calcium carbonate on durable substrates produces effective absorbers. Additional development is needed to enhance the absorber capacities to those appropriate for the reforming process.

Abstract

GE Energy and Environmental Research Corporation (EER) has advanced the technology of distributed power generation using fuel cells by developing a novel steam reforming process to convert fossil fuels to hydrogen. The process advances fuel cell technologies that are being hampered by the lack of hydrogen distribution and production systems.

This novel steam reforming process is a breakthrough in small-scale conventional steam reforming, which up to now has not been economically feasible for applications less than one million cubic feet per day. EER's process boasts higher efficiencies than competing small-scale hydrogen production technologies such as Partial Oxidation. When combined with polymer electrolyte membrane fuel cells, the process significantly reduces pollutant emissions from electricity production. The emissions are even substantially lower than those from conventional power plants, microturbines and reciprocating engines. In addition, waste heat from exhaust gases, used for cogeneration, further increases overall plant efficiency.

Recent support for this reforming technology from the California Energy Commission Public Interest Energy Research Program and Phillips Petroleum has furthered the understanding of the catalysis process. Under the current project, EER has developed and evaluated catalysts and carbon dioxide absorber materials and applied material and process discoveries to the advancement of a prototype reforming reactor evaluated on a pilot test facility. The key technical issue addressed by this project was developing catalysts with extended lifetimes and optimizing the use of these catalysts in the reforming process. This effort filled a vital link in a broader program supported by the United States Department of Energy and Edison Technology Solutions to demonstrate a distributed hydrogen generation power plant.

The accelerated durability test subjected the materials to a high frequency of the cyclic stresses that occur under normal operation in EER's reforming process. The test's purpose was to estimate the operational lifetime of the catalyst. The durability of catalyst P10 was demonstrated to exceed the target of 2,000 hours and has currently been demonstrated for an equivalent of 4,350 hours with no evidence of failure. The material exhibited an initial drop in activity, but once in service, the catalyst was able to maintain its performance over the lifetime test. The material is experimental in nature and through further development of preparation procedures and use of promoters, further improvement in material activity is likely.

Catalyst C3 demonstrated promising activity and because of the timing of this discovery, the material was selected for use in the prototype reactor. Two prototype reactors were installed on a preliminary configuration of the pilot test facility. The preliminary pilot plant configuration was restricted to low operating capacity, reduced steam feed and lower reactant preheating. These restrictions are being addressed by a plant reconfiguration as part of the broader DOE program scheduled for completion later this year. However, the objective of prototype reactor testing—to guide the development of the pilot facility and assess the extent to which the technology can demonstrate the technical objectives—was successful. Testing of the prototype reactors

provided guidance in the reconfiguration effort and based on current pilot test results, EER has already met many of the technical objectives of this technology. The remaining technical objectives were also assessed and, based on realistic improvements resulting from the pilot reconfiguration, EER expects to meet these objectives in continuing demonstrations later this year.

Several improvements in the pilot facility will be implemented based on findings of the bench-scale catalyst studies. Chief among these findings was an alteration to the fuel regeneration process that significantly improved performance in bench-scale testing. Apart from hardware reconfigurations, the primary issue affecting pilot plant performance is the fuel regeneration kinetics. In an assessment of the pilot plant performance, EER used current test results with adjusted fuel regeneration performance levels representative of those achieved in bench-scale tests. The results of this assessment are provided in Table E-1, and show that all remaining technical objectives can be met by improving the fuel regeneration performance. Therefore, the primary challenge remaining in this continuing program is demonstration of improved fuel regeneration performance.

1.0 Introduction

1.1 Purpose of Report

This report summarizes and reviews the project entitled: “A Novel Steam Reforming Reactor for Fuel Cell Distributed Power Generation”. This work was conducted by GE Energy and Environmental Research Corporation (EER), a fully owned subsidiary of General Electric Company, and by their subcontractor, Phillips Petroleum. The California Energy Commission under Public Interest Energy Research (PIER) I Contract No. 500-97-038, the U.S. Department of Energy (DOE) and Phillips Petroleum funded the project.

1.2 Actual Project Expenditures (PIER and Match Funds)

Actual project expenditures in the amount of \$ 648,644 were made for this project. This total includes \$ 342,310 of PIER funds and \$ 308,223 of matching funds.

1.3 Purpose of Project

EER has developed a novel steam reforming process that efficiently converts natural gas to fuel cell-grade hydrogen (H_2). The purpose of this project was to further develop the reforming process by evaluating catalyst/absorber materials for suitability and durability in the reforming process, with the goal of identifying materials with lifetimes in excess of 5,000 hours in reforming service.

A variety of materials were tested at a range of operating parameters to assess their ability to maintain desired levels of physical stability, activity and effectiveness over extended service lifetimes. In addition, testing was performed on a prototype reactor to improve process performance. EER ultimately intends to commercialize this reforming process to provide a convenient and local source of hydrogen fuel for distributed power applications. The commercialization of this technology will remove a significant barrier to the commercialization of polymer electrolyte membrane (PEM) fuel cells: the need for a hydrogen distribution system.

1.4 Project Goals and Objectives

1.4.1 Overall Project Goals

The overall goal of this project was to develop a less-costly process for producing small volumes of fuel cell-grade hydrogen from natural gas. It contributes to the PIER program objective of improving the energy cost/value of California’s electricity by raising acceptance and reducing maintenance costs of the reforming technology. The overall technical goal of this project was to develop and evaluate catalyst/absorber systems with expected lifetimes in excess of 5,000 hours and with an ultimate target lifetime of 30,000 hours.

1.4.2 Technical Objectives

The specific technical objectives upon which this project’s success were evaluated include:

- Identification of catalyst/absorber materials with projected lifetimes in excess of 2000 hours
- Use of catalyst per cycle of the process: >50 percent
- Absorber's carbon dioxide (CO₂) absorption capacities: ~50 percent of theoretical
- Volume of hydrogen produced: > 25,000 cubic feet per day
- Power output from reactor: >35 kWe² (target 50 kWe)
- Total cycle efficiency: >35 percent based on lower heating value (LHV) of fuel
- Conversion efficiencies: 75-85 percent based on LHV of fuel and hydrogen produced
- Emissions of NO_x, carbon monoxide (CO), methane (CH₄) at 7 percent oxygen (O₂): 0.1 ppm NO_x, <10 ppm CO, <50 ppm CH₄

1.4.3. Economic Objective

The overall economic goal of this project is to produce electricity through a distributed power generation system based on fuel cell technology at rates competitive with existing central generation systems. The specific economic performance objective of this project was:

- Catalyst/absorber cost/durability trade-off to result in a levelized incremental cost of electricity production equal to or less than that for centralized power production using California Energy Commission cost basis guidelines (including cogeneration credit).

² kWe refers to kW of equivalent electric power when the reformer is integrated with a PEM fuel cell.

2.0 Background

2.1 Reforming Technology Concept

The reforming process is a thermodynamically efficient way to produce high purity hydrogen from natural gas and steam at small scales. The reforming reactions that produce hydrogen from natural gas and steam are endothermic and require a source of heat to sustain the process. In industrial hydrogen production processes, that heat is transferred by a high temperature source such as a burner.

Use of a burner is efficient at large industrial scales, but at small scales, high heat loss to the surroundings reduces the efficiency. The reforming process addresses the inefficiency at small scale by heating the process directly using chemical energy stored on the reactor bed in lieu of a high temperature heat source. This is done by conducting the reforming process in a cyclic fashion wherein the catalyst is heated directly by chemical reactions during a catalyst regeneration step. This heat is then used by the endothermic reforming reactions in the reforming step.

To better understand the reforming technology, consider.

Error! Not a valid bookmark self-reference., **which schematically illustrates the process**

Figure 1. The (A) Unmixed Reforming Reactor Produces a Hydrogen Rich Product Gas in (B) a Cyclic Process that Removes Carbon Dioxide from the Product and Releases It with the Air Vent.



Three steps make up the reforming process: the reforming step, the air regeneration step, and the fuel regeneration step. During the reforming step, steam and natural gas pass over the heated catalyst and ceramic support matrix. The endothermic steam reforming reaction draws energy directly from the sensible heat of the ceramic support matrix. As the reaction proceeds, the ceramic support matrix cools until the kinetics of the process become unfavorable. At that point, the natural gas and steam feeds are stopped and the reactor is fed with air to initiate the air regeneration step.

During the air regeneration step, air oxidizes the nickel (Ni) in a highly exothermic (heat-releasing) reaction to form nickel oxide (NiO). Since nickel and nickel oxide are both solids, there are no gaseous products of this oxidation reaction to carry heat away. This enables the oxidation to very effectively heat the bed. Then the introduction of natural gas during the fuel regeneration step reduces the nickel oxide to nickel and the catalyst is once again in its active state for reforming.

An additional aspect of the reforming process involves the introduction of a CO₂ acceptor such as calcium oxide (CaO) into the packed bed. The acceptor material (calcium oxide) absorbs CO₂ formed during the reforming step. During the regeneration step, heat released by oxidation of nickel is used to decompose the absorber to calcium oxide and CO₂.

The absorber serves three functions in the process. First, it provides additional thermal mass to transfer sensible heat from the oxidation step to the reforming step of the process. The decomposition of calcium carbonate, an endothermic reaction, substantially moderates the temperature rise of the system, reducing parasitic heat losses. Secondly, the absorption of CO₂ by the calcium oxide to produce calcium carbonate is an exothermic chemical reaction that also delivers energy to the reforming process *in situ* during reforming. This is a far more efficient means of transferring energy to the reforming process than relying solely on the sensible heat stored in the ceramic catalyst support matrix. Third, the presence of the CO₂ acceptor material improves the gas-phase equilibrium, leading to increased hydrogen yield. By removing CO₂ from the products of the steam reforming process, equilibrium is shifted toward greater hydrogen production and reduced CO concentrations.

2.2. Project Approach

The objective of this project was to identify catalyst and absorber materials with extended lifetimes. To this end, EER enlisted the support of Phillips Petroleum to develop catalyst and absorber materials. These materials were tested to identify promising materials for use in the reforming process.

The evaluation of catalyst and absorber materials was performed in three stages. Preliminary screening tests were the first stage of evaluation. During this stage, materials were tested at baseline conditions to quickly ascertain their suitability for the reforming process. Fifteen catalyst materials were screened. Catalysts that met the screening criteria were submitted to the next stage of evaluation: detailed parametric testing.

The detailed parametric tests were used to identify the envelope of operating conditions where satisfactory performance was achieved. Selected catalysts were tested through a range of conditions centered around the baseline condition of the preliminary screening tests. Changes in performance were recorded and evaluated. These tests served two purposes: to identify additional unsuitable materials, and to provide a database of performance as a function of changes in experimental parameters. The performance database was used in the subsequent evaluation stage. Materials selected in the parametric testing stage were submitted to accelerated durability testing.

Accelerated durability testing provided a means of estimating the lifetime of materials. The accelerated test was designed to subject the materials to cyclic stresses that occur under normal reforming operation and to do so at increased frequency. The intent was to identify material for later evaluation in the prototype reactor in EER's pilot test facility.

As part of the project, a prototype reactor was designed for the pilot test facility. Testing was conducted on this reactor using selected catalysts to improve the performance of the reforming process through operational evaluation. The DOE is sponsoring continuing development and testing of the pilot test facility.

3.0 Project Outcomes

3.1 Technical Objectives

EER and their subcontractor Phillips Petroleum have completed efforts to develop a durable catalyst for the reforming process. In the initial catalyst development stage, secondary reactions were identified that caused catalyst deactivation and poor catalyst regeneration. During this initial test period a highly active commercial catalyst was identified and then tested on the pilot test facility. Continued catalyst development efforts, led by Phillips Petroleum, achieved a breakthrough with the discovery of a durable catalyst that met the performance requirements of the reforming process. This discovery came later in the project and did not allow sufficient time to test this material on the pilot facility. The testing of this catalyst is anticipated to occur later this year under the continuing development of the pilot test facility sponsored by the DOE.

The extent to which the project technical objectives were met will be discussed based on the completed catalyst development efforts and the prototype reactor testing conducted to date. Optimization of the pilot test facility is in progress. EER plans to continue testing and demonstration of the technical objectives with the newly discovered catalysts, however, the extent to which the stated objectives have been met to date are assessed based on the preliminary pilot test results.

The specific technical objectives upon which this project's success are evaluated include:

1. Identification of catalyst/absorber materials with projected lifetimes in excess of 2,000 hours
2. Use of catalyst/cycle of the process: >50 percent
3. Absorber's CO₂ absorption capacities: ~50 percent of theoretical
4. Volume of hydrogen produced: > 25,000 cubic feet per day
5. Power output from reactor: >35 kWe (target 50 kWe)
6. Total cycle efficiency: >35 percent based on lower heating value (LHV) of fuel
7. Conversion efficiencies: 75-85 percent based on LHV of fuel and hydrogen produced
8. Emissions of NO_x, CO, CH₄ at 7 percent O₂: 0.1 ppm NO_x, <10 ppm CO, <50 ppm CH₄

1. Identification of catalyst/absorber materials with projected lifetimes in excess of 2,000 hours: EER and Phillips Petroleum have developed a catalyst material and demonstrated projected lifetimes exceeding 4,350 hours under reforming operation. This major achievement represents a significant improvement over previously tested catalysts that have only exhibited approximately 1,000 hour lifetimes. The newly developed material comprises a proprietary blend of nickel catalyst and promoters deposited on a durable catalyst substrate.

EER has also developed a CO₂ absorber that may prove to have improved durability. The material comprises a CO₂ acceptor deposited on a durable catalyst substrate. Currently, additional development is needed to increase the CO₂ acceptor concentration

to make the material suitable for the reforming process. Because the material was unsuitable, definitive lifetimes of the new absorber material were not studied.

2. Use of catalyst/cycle of the process: >50 percent: During the pilot tests, 61 percent of the catalyst was involved in the catalyst oxidation and reduction reactions. The heat release from these reactions is essential for the autothermal process. The extent to which the catalyst participates in the oxidation and reduction reactions dictates how much excess catalyst must be loaded in the bed. The catalyst used in the pilot test facility exceeds the technical objective of 50 percent utilization.

Comparison of bench-scale results for the newly discovered catalyst P10 and C3 shows that both materials exhibit similar catalyst utilization over parametric and accelerated lifetime testing. Therefore, the performance of catalyst P10 is anticipated to be comparable when pilot testing of this material is conducted.

3. Absorber's CO₂ absorption capacities: ~50 percent of theoretical: Only one absorber was identified as currently suitable for the reforming process based on the CO₂ acceptor concentrations. This material is commercial dolomite.

The pilot facility testing was conducted at reduced capacity, with excess absorber material in the bed. The absorption CO₂ capacity was much greater than the CO₂ formed. Under this reduced capacity and also operating through non-optimized thermal cycles, 1.6 percent of the absorber material participated in the cyclic CO₂ absorption and desorption process. This corresponds to approximately 65 percent of the theoretical absorption capacity and meets the target performance objective.

4. Volume of hydrogen produced: > 25,000 cubic feet per day: Tests were conducted at reduced capacity, so this objective could not be demonstrated. However, EER has assessed the capability of the system to meet these hydrogen production levels when testing on the reconfigured facility resumes later this year. Based on the current tests at a 20 kW electrical output equivalent and a calculated hydrogen production volume of 12,400 cubic feet per day, a hydrogen production volume of 25,000 cubic feet per day will be achieved at an operating capacity of 41 kWe. EER intends to demonstrate the ability to achieve this production level through upcoming tests conducted under the DOE program.

5. Power output from reactor: >35 kWe (target 50 kWe): As stated above, the pilot test facility was operated at reduced capacity during catalyst tests. The operation was restricted to low capacity by hardware components and low steam production. The facility is being reconfigured for 50 kWe operation. Based on the unit's operational characteristics, the reconfigured pilot test facility will achieve 50 kW electrical output equivalent. Note that a fuel cell is not planned for integration with the unit, and electrical power output is calculated on a hydrogen equivalence basis utilizing actual PEM fuel cell performance for a commercially targeted fuel cell.

Apart from the hardware and boiler efficiency issues that limited the previous test's operating capacity, another issue that can limit operating capacity is excessive pressure drop on either the natural gas or compressed air process lines. A pressure drop analysis was conducted. The pressure drop coefficients through the system were determined for

current operating conditions. Using these coefficients, the pressure drop at increased capacity was calculated to be well below the maximum line pressures available.

Once EER has completed the pilot test facility reconfiguration, operation at 50 kW electrical output equivalent is expected to be achieved.

6. Total cycle efficiency: >35 percent based on lower heating value (LHV) of fuel: From the current pilot test results and engineering assessment of the planned full capacity operation, a net electrical efficiency of 37 and up to 41 percent is projected. This is based on a PEM fuel cell integrated into the system that operates at a vendor-reported 62 percent efficiency. Currently the pilot testing has not demonstrated this level of efficiency and this can be attributed to lower fuel conversion during the fuel regeneration step. Fuel conversion limitations were impacted by low reactant preheat temperatures and insufficient steam production. These issues are being addressed in the reconfiguration of the pilot test facility and, based on engineering assessment, a total cycle efficiency between 37 and 41 percent will be demonstrated.

7. Conversion efficiencies: 75-85 percent based on LHV of fuel and hydrogen produced: Fuel conversion was acceptable during the reforming process; however, the conversion during the fuel regeneration step was poor specifically due to the absence of steam. One very significant discovery of the California Energy Commission sponsored effort was that steam is necessary during fuel regeneration. Previously, steam was only used during the fuel-reforming step to increase hydrogen production by the water-gas shift reaction. However, bench-scale tests showed that a steam to carbon molar ratio of 1 significantly improved conversion during the fuel regeneration step. During the reforming step a steam to carbon molar ratio of 3 is used and this produced good fuel conversion. With the reconfiguration of the pilot facility to provide increased steam production and reactant feed temperatures, improved fuel conversion is expected.

An assessment of the fuel conversion for a properly preheated reactant stream with sufficient steam indicates that conversion efficiencies of 68 percent will be readily achieved. Further process optimization, to be conducted during the DOE program, is expected to raise fuel conversion as high as 77 percent. In later tests of the reconfigured pilot test facility, EER plans to demonstrate these conversion levels.

8. Emissions of NO_x, CO, CH₄ at 7 percent O₂: 0.1 ppm NO_x, <10 ppm CO, <50 ppm CH₄: Ultimately, EER plans to assess the emission levels of the system based on the operation of the reformer and the capabilities of catalytic oxidizers to convert CH₄ and CO. Currently the untreated emissions of CH₄ and CO are expected to reach 1,000 and 51 ppm, respectively. To meet the target emissions involves 1) improving the fuel conversion during regeneration and 2) assessing the capability of catalytic oxidizers. Based on the planned integration of a catalytic oxidizer the untreated emission levels currently demonstrated will be reduced to target levels.

NO_x emissions were not measured. Based on the planned pilot test facility operation and current bench-scale performance results, EER anticipates non-detectable NO_x emissions in testing later this year. The emission objectives of this technology are planned for demonstration later this year.

3.2. Economic Objective

The specific economic performance objective of this project is:

- Catalyst/absorber cost/durability trade-off to result in a levelized incremental cost of electricity production equal to or less than that for centralized power production using California Energy Commission cost basis guidelines (including cogeneration credit).

The cost of the newly developed catalyst is not yet established, however, the durability of the material has been tested in this project and has been demonstrated to exceed the durability target of 2,000 hours (currently demonstrated 4,350 hours). Based on the preliminary economic assessment of the commercial reformer, the system has the capability to meet California ratepayers' incremental electricity cost of 4.4 cents/kWh. The benefits of increasing the catalyst durability will be seen in extended maintenance periods and improved acceptability of the technology. It is hoped that these benefits will not come at the expense of higher electricity costs. Therefore it is necessary to offset any increase in catalyst cost with reduced maintenance costs. Based on the projected cost savings for extending a catalyst life from 2,000 to 4,350 hours, the newly developed catalyst can cost twice that of current commercial catalyst and still meet the project's economic objectives.

Phillips Petroleum has assured EER that these materials can be readily made with standard commercial catalyst manufacturing processes. The durable substrate is also available for mass production and is being developed for a number of markets, so costs of this material will be kept low. Use of substrate of the purity grade provided by Phillips Petroleum will result in only a moderate increase in catalyst cost. Optimization of the catalyst composition may later find that a lower grade is also acceptable. Based on this initial assessment, the newly developed catalyst meets the economic cost/durability trade-off objective of this project.

3.3. Discussion

EER's reforming process is unique in its use of reforming catalysts and CO₂ absorber materials. It is a cyclic process with two steps: reforming and regeneration. In the reforming step, the nickel on the catalyst is reduced to its active catalytic state, hydrogen is produced, and the CO₂ produced by reforming reactions is absorbed. In the regeneration step, the nickel on the catalyst is oxidized and the previously absorbed CO₂ is released into the vent gases. The nickel on the catalyst must be repeatedly oxidized and reduced, in addition to having high activity for the reforming reactions. To our knowledge, there are currently no commercially available catalysts designed for these purposes since conventional steam reforming is a continuous process eliminating repeated catalyst oxidation and reduction.

The CO₂ absorber materials suitable for the reforming process are generally either naturally occurring minerals containing calcium (Ca) such as dolomite, or materials prepared by depositing calcium carbonate on a substrate. The repeated absorption and desorption of CO₂ by the absorber material poses a unique challenge for reforming material selection. Dolomite undergoes a physical breakdown in the presence of the high temperature steam required for the reforming process, while the CO₂ absorbing capacity of substrates with calcium deposited on them is limited by the amount of calcium present that can be utilized for absorption.

Development of materials, sponsored by the California Energy Commission PIER I Program, is intended to identify suitable materials for the reforming process. Catalyst and absorber material development was identified as an area in which advances could have a significant impact on the commercial viability of the process. The development of the reforming process is part of a broader program supported by the DOE.

EER teamed with Phillips Petroleum to use their expertise in high-temperature catalytic processes to address the catalyst and absorber issues unique to the reforming process. EER also considered several commercial catalysts that, although not designed for the reforming process, may coincidentally be suitable.

The approach taken to develop and identify suitable materials involves three steps: screening tests, parametric testing, and accelerated durability testing.

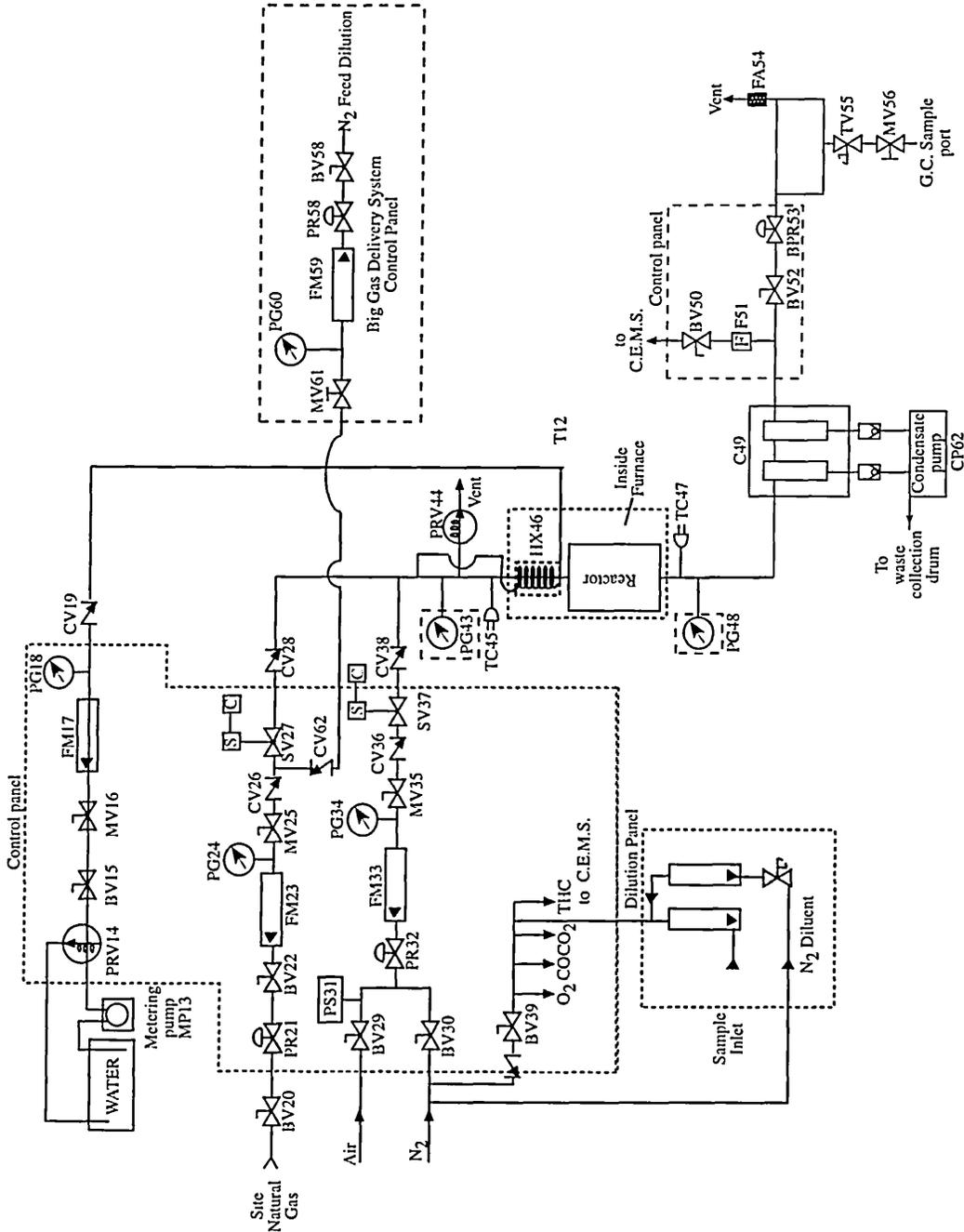
3.4. Screening Tests and Results

The first step in materials development for the reforming process was to screen catalyst and absorber materials. These tests involve short-term testing of catalyst and absorber materials under a set of baseline operating conditions. The objective of the screening tests was to eliminate unsuitable materials from more detailed testing and evaluation. Screening tests were designed to be brief evaluations of material performance under baseline reforming conditions.

3.4.1. Catalyst Screening Test System Design

The screening tests were performed on the bench-scale experimental system (Figure 2). This system was designed to allow detailed characterization of catalyst/absorber performance during the reforming and regeneration operating cycle.

Figure 2. Bench-Scale reforming Experimental System



3.4.2. Screening Test Operation

A set of baseline experimental parameters was selected for the screening tests based on the DOE Phase I process development efforts that were supported by previous studies. Table 1 provides the baseline parameters. From these experimental parameters, the baseline operating conditions for a selected catalyst were calculated following the method presented in the Test Plan³. The baseline operating conditions are shown in Table 2. Tests run at these conditions provide a consistent basis for comparison of different catalyst/absorber materials.

Table 1. Selected Baseline Experimental Parameters for Preliminary Screening Tests

Ca:Ni Ratio (mol/mol)	Reforming Gas Hourly Space Velocity (GHSV) (h ⁻¹)	Regeneration Oxygen to Nickel (O ₂ :Ni) Ratio (mol/mol)	Reforming Steam to Carbon (S:C) Ratio (mol/mol)	Reactor Temperature (°C)
3	3500 and 5000	1	3	700

Table 2. Sample Baseline Operating Conditions for Preliminary Screening Tests

Cycle Time	Flow Rates		
	Natural Gas	Water	Air
10 min	2.9 scfh	3.1 ml/min	6.3 scfh

Calculations of Testing Results

The measurements taken during screening tests were used to calculate three performance indicators: percent O₂ consumed, percent converted carbon absorbed, and percent CH₄ conversion. These performance indicators are related to the performance of the catalyst and absorber during the regeneration and reforming steps as described below.

Percent Oxygen Consumed: The percent O₂ consumed is defined as:

$$\text{Percent O}_2 \text{ consumed} = \frac{(\text{O}_2 \text{ fed [mol]} - \text{O}_2 \text{ exiting [mol]})}{\text{O}_2 \text{ fed [mol]}} \times 100 \text{ percent (1)}$$

³ A Novel Steam Reforming Reactor for Fuel Cell Distributed Power Generation: Test Plan, February 11, 1999.

The percent O₂ consumed is a measure of the amount of oxygen that reacts with the nickel on the catalyst to form nickel oxide. As oxygen is consumed, the packed bed is heated by the exothermic nickel oxidation process. Oxygen consumption indicates the amount of nickel that is participating in the oxidation and reduction cycle during the regeneration and reforming steps. This is useful in identifying materials that are able to maintain catalytic activity for reforming after cycling through the oxidized state.

Percent Converted Carbon Absorbed: The percent converted carbon absorbed is defined as the percent of reacted CH₄ absorbed as CO₂, as follows:

$$\text{Percent converted carbon absorbed} = \frac{\text{CO}_2 \text{ released in regeneration step [mol]}}{\text{reacted CH}_4 \text{ in reforming step [mol]}} \times 100 \text{ percent} \quad (2)$$

The absorption capacity of the dolomite material is measured as the amount of CO₂ released in the regeneration step. The basis for carbon absorption is the moles of carbon fed during the reforming step that react to form CO or CO₂. To decouple the impact of catalyst activity, the percent converted carbon absorbed is based only on reacted CH₄.

Percent CH₄ Conversion: The CH₄ conversion is measured as the amount of CH₄ reacted. The percent CH₄ conversion is defined as:

$$\text{Percent CH}_4 \text{ conversion} = \frac{\text{CH}_{4\text{in}} \text{ [mol]} - \text{CH}_{4\text{out}} \text{ [mol]}}{\text{CH}_{4\text{in}} \text{ [mol]}} \times 100 \text{ percent} \quad (3)$$

The percent CH₄ conversion is an indication of the amount of natural gas fed that reacts to form products such as hydrogen, CO, and CO₂.

3.4.3. Catalysts Evaluated

Phillips Petroleum provided two sets of materials: catalysts P1 through P7 and P8 through P10. Phillips Petroleum sent substrate materials early in the program, and EER used these materials to prepare catalysts P1 through P7. After these materials were tested, EER and Phillips Petroleum discussed results and Phillips Petroleum conducted analyses of the spent catalysts. Based on the initial catalyst results, Phillips Petroleum prepared and sent catalysts P8 through P10.

In addition to the materials provided by Phillips Petroleum, several commercial steam reforming catalysts were screened. The commercial catalysts were obtained from several catalyst manufacturers. All were designed for continuous steam reforming, and not for the cyclic oxidation and reduction of the nickel catalyst. Commercial catalysts are known to contain proprietary blends of promoters to enhance performance. EER prepared catalyst E1 with a blend of promoters following guidelines obtained through literature review.

Table 3 lists all of the catalyst materials studied in this program, along with some of their characteristics. Catalysts P1, P2, and P5 were made with calcium as well as nickel. These materials were tested as absorbers as well as catalysts. A total of 18 catalysts were tested.

Table 3. Screening Test Catalyst Materials

Catalyst ID	percent Ni	Substrate Type	Other
P1	14	Extrudate	8.5 percent Ca
P2	7	Extrudate	10.5 percent Ca
P3	9	Extrudate	
P4	15	Extrudate	
P5	13	Pellets	7 percent Ca
P6	10	Pellets	
P7	12	Pellets	
P8	15	Pellets	
P9	15	Pellets	
P10	15	Pellets	Promoter
C1	13	Wheels	
C2	14	Pellets	
C3	12	Rings	
C4	14	Pellets	
C5	10	Pellets	
C6	14	Wheels	
C7	14	Crushed	
E1	14	Pellets	Various promoters

3.4.4. Catalyst Screening Test Results and Discussion

The primary evaluation criteria for the screening tests were the CH₄ conversion, O₂ consumed, and converted carbon absorbed. These criteria are performance indicators of the materials' suitability for the reforming process. The absorber used for screening tests was dolomite. Table 4 summarizes the test results for the materials screened.

Table 4 shows that of the original Phillips Petroleum materials, catalysts P3 and P5 showed the most promise. Catalysts P3 and P5 had the highest combination of CH₄ conversion and O₂ consumed. The oxygen consumption of catalyst P3 was relatively low, as was the CH₄ conversion of catalyst P5.

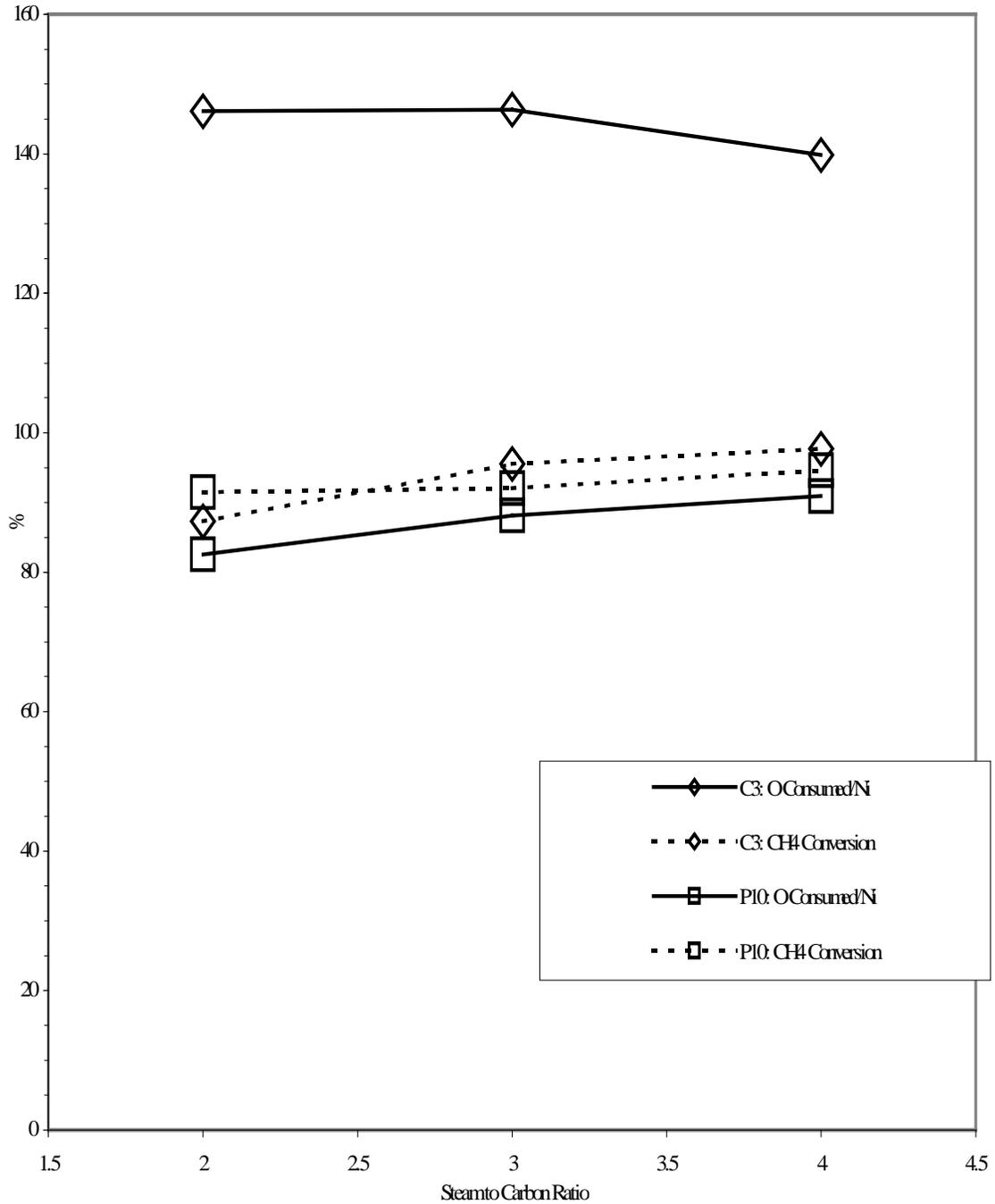
Table 4. Selected Results Of Screening Tests

Material ID	percent O ₂ Consumed	percent CH ₄ Conversion	percent Converted Carbon Absorbed	Reforming GHSV
P1 ^(a)	13	75	15	3500
P2 ^(a)	0.25	42	6	3500
P3	31	84	14	3500
P4	11	71	15	3500
P5	44	58	9	3500
P6	43	41	3	3500
P7 ^(a)	33	54	1	3500
P8 ^(a)	16	78	NA	5000
P9	39	85	NA	3500
P10	50	86	NA	3500
E1	12	94	NA	3500
C1	48	87	10	5000
C3	69	91	12	5000
C4	40	94	9	5000
C5 ^(a)	0	35	6	5000

^(a) Catalyst eliminated from further testing.

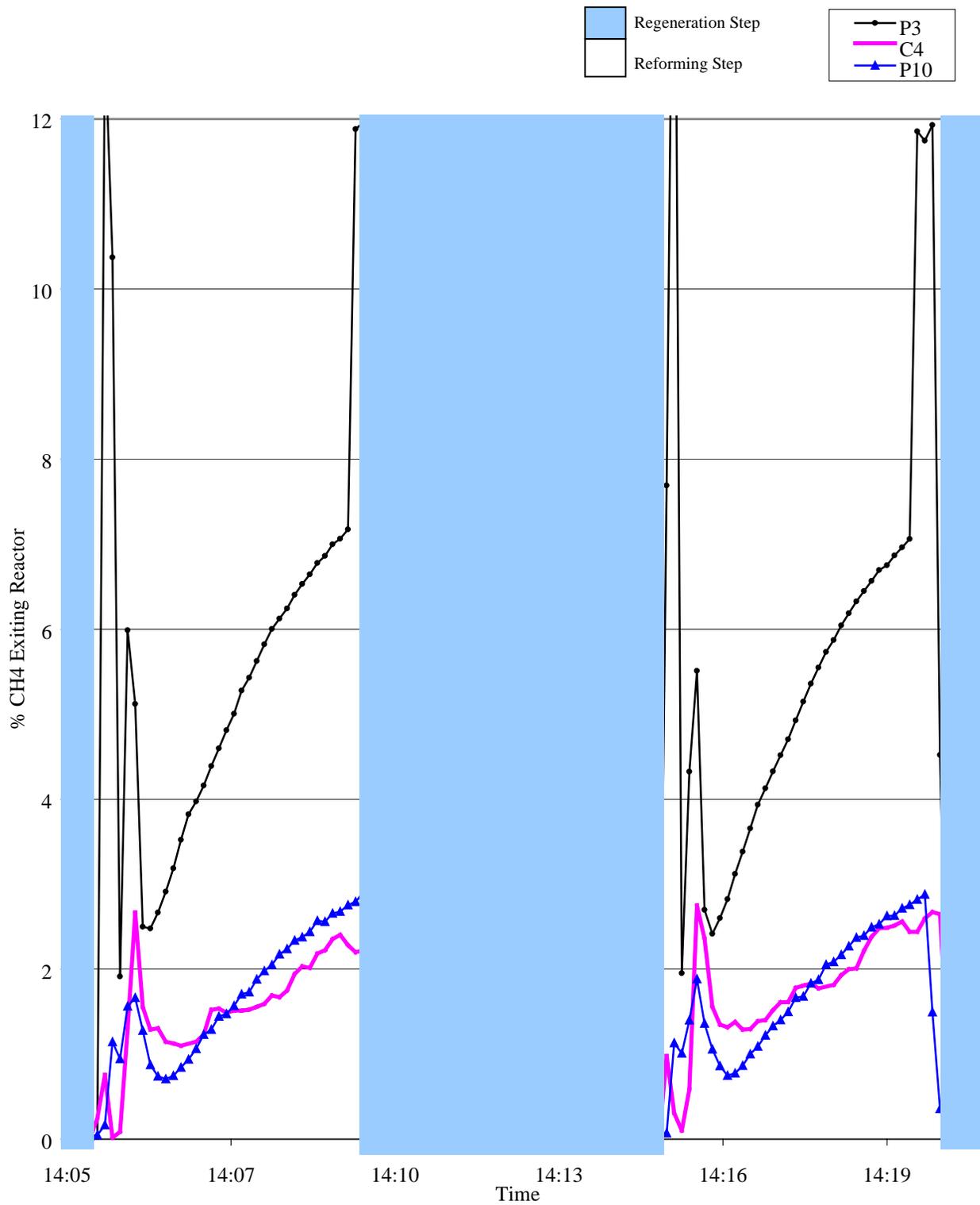
Catalysts P8, P9 and P10 were developed by Phillips Petroleum based on screening results of earlier catalysts. These materials demonstrated improved CH₄ conversion. Catalyst P10 was especially promising, with its high oxygen consumption and low breakthrough of CH₄ at the beginning of the reforming step

(Fig 3). This figure shows the CH₄ concentration profile for P10, along with those of catalysts P3 and C4. The level of CH₄ breakthrough is less than two percent at its peak.



Catalyst P10 overcame a limitation that previous Phillips Petroleum catalysts such as catalyst P3 had demonstrated. The initial CH₄ spike occurs during the fuel regeneration performance, most noticeably during fuel regeneration.

Figure 3. Unreacted CH₄ Levels Exiting the Reactor for Catalysts P3, C4 and P10 During Two Reforming Steps



The combination of low O₂ consumed and low CH₄ conversion led to the elimination of catalysts P1, P2, P7, and P8 from further testing. All of the commercial catalysts had high CH₄ conversion, and high O₂ consumed except for catalyst C5. Catalyst C3 had exceptionally high oxygen consumption. The EER-prepared catalyst E1 had very high conversion of CH₄, but very low oxygen consumption. Both catalysts C5 and E1 were found to be unsuitable for the reforming process. Catalyst E1 had very low oxygen consumption, and catalyst C5 had low oxygen consumption and CH₄ conversion.

3.4.5. Absorbers Screened

Separate tests were conducted to measure the CO₂ absorption capacities of various absorber materials. Phillips Petroleum provided absorbers that consisted of calcium oxide supported on different thermally stable substrates. Some of the catalyst materials provided by Phillips Petroleum contained both nickel and calcium oxide. These materials were screened separately for absorption capacity and reforming catalytic activity. Table 5 lists the absorber materials tested. Absorbers D1 and D2 were dolomite from different mines, one of which was received in a calcined state.

Table 5. Screening Test Absorber Materials

Absorber Materials	percent Ca	Form	Other
D1	22	Crushed	
D2	22	Crushed	Calcined
PA1	8.5	Extrudate	14 percent Ni
PA2	10.5	Extrudate	7 percent Ni
PA3	8.5	Extrudate	
PA4	7	Pellets	
PA5	7	Pellets	13 percent Ni

3.4.6. Absorber Test Setup

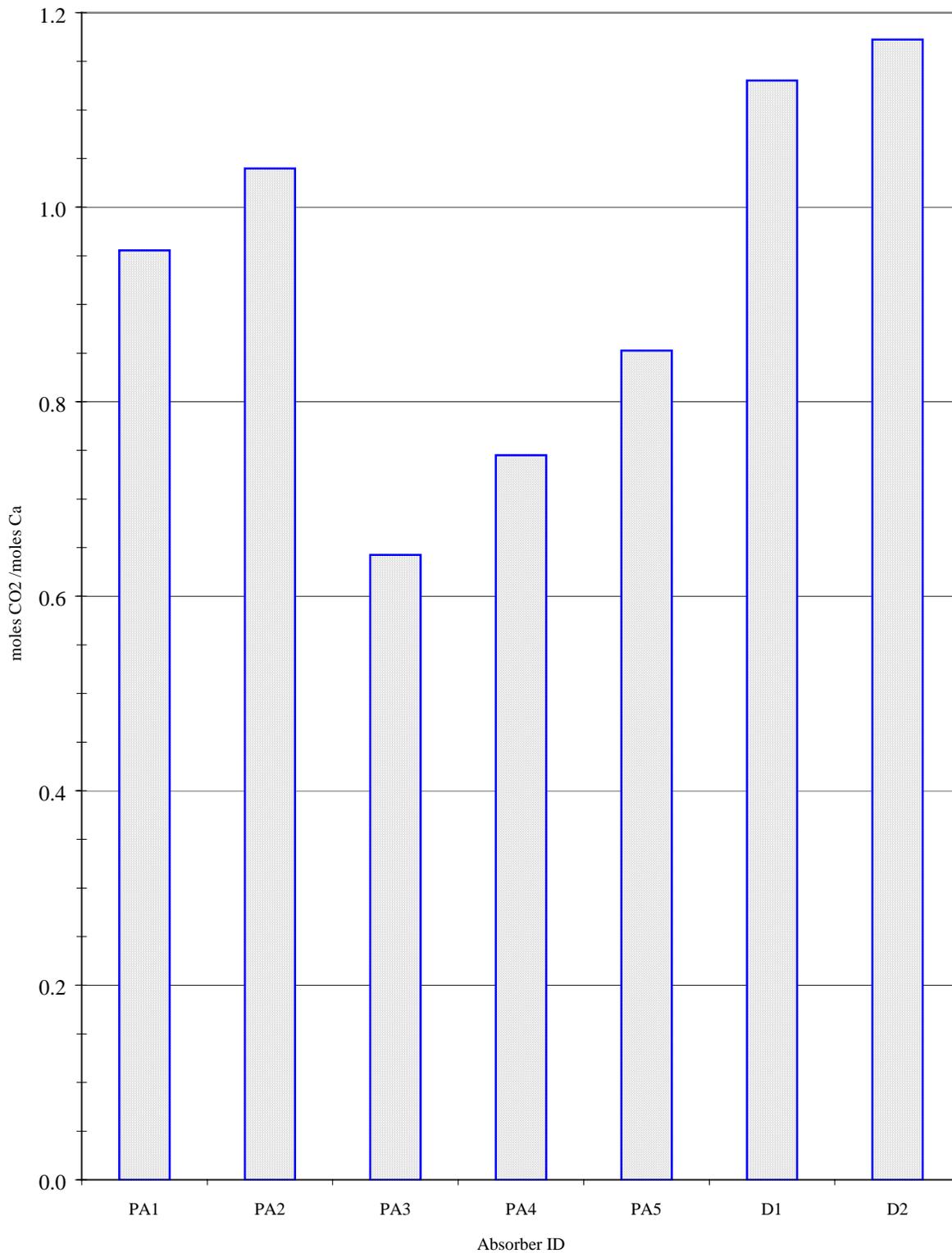
The CO₂ absorption tests were performed by placing a known mass of absorber into a plug flow reactor located inside a controlled-temperature furnace. Pure CO₂ was passed over the absorber for several hours at room temperature. After allowing for saturation of the absorber materials, the flow of CO₂ was stopped, and pure nitrogen carrier gas was passed over the absorber bed. The temperature of the furnace was then slowly increased to cause the absorbed CO₂ to be released. The concentration of CO₂ in the gas exiting the reactor was recorded and the total amount of CO₂ released was determined.

3.4.7. Absorber Screening Test Results and Discussion

The capacity of the materials to absorb CO₂ was used as a screening criterion. The reforming process requires high CO₂ absorption capacity as well as the ability to release the CO₂ in the specific temperature range of 750-850°C. The absorber screening test was designed solely to measure the CO₂ absorption capacity of the materials. The dolomite materials, D1 and D2, had higher calcium concentrations than the Phillips Petroleum absorbers.

On a molar basis (Fig 4), the dolomite materials, D1 and D2, had higher capacities than the Phillips Petroleum absorbers. Although the Phillips Petroleum absorbers were able to absorb CO₂, their low loadings and thus low capacities made them unsuitable for the reforming process at this time.

Figure 4. CO₂ Absorption by Various Commercial and Phillip Petroleum Absorber Materials Tested in the Absorber Test Facility



None of the Phillips Petroleum absorber materials were found to be promising for use in the reforming process. Absorber D1, commercial dolomite, was used for parametric testing. All of the other absorber materials were excluded from further testing due to their low absorption capacities.

3.5. Parametric Testing and Results

Parametric testing is the second step in materials development for the reforming process. The parametric tests were conducted to develop a classical database of important parameter effects on process performance. The tests identified the range of operating conditions at which the catalyst materials are effective and the individual effects of each variable on overall performance. Parametric testing provided a more complete picture of the catalyst activity and oxygen consumption capacity and identified limitations in performance.

3.5.1. Experimental System Design

The same bench-scale experimental system used for screening tests was used for parametric testing.

3.5.2. Selection of Operating Parameters and Procedures

Four variables were selected for parametric testing. These include the GHSV, the O₂:Ni molar ratio, the S:C molar ratio, and the reactor temperature. Values both above and below the baseline condition were selected for testing and are shown in Table 6.

Table 6. Detailed Parametric Test Parameters

Test Description	Reforming GHSV	Regeneration O ₂ :Ni Ratio (mol/mol)	S:C Ratio (mol/mol)	Reactor Temperature (°C)
Baseline Test Conditions for All Catalysts*	3500	1	3	700
Variation of Reforming GHSV	2500	1	3	700
	5000	1	3	700
Variation of Regeneration O ₂ /Ni Ratio	3500	0.625	3	700
	3500	1.5	3	700
Variation of Steam to Carbon Ratio	3500	1	2	700
	3500	1	4	700
Variation of Reactor Temperature	3500	1	3	650
	3500	1	3	750
	3500	1	3	800

* Repeat tests were performed to determine process repeatability and measurement precision

The operating procedure used for parametric testing was the same as that used for the screening tests⁴. A typical set of parametric tests was conducted over two test days, with the specified conditions set and allowed to stabilize, then run at stable conditions for several complete cycles. Repeat tests were conducted at the baseline conditions for each catalyst.

3.5.3. Calculation of Parametric Testing Results

Measurements taken during parametric testing were used to calculate three performance indicators: percent O consumed/Ni, percent converted carbon absorbed, and percent CH₄ conversion. The methods for calculating percent converted carbon absorbed and percent CH₄ conversion were presented in 3.1.4. The calculation method for percent O consumed/Ni is provided below.

During parametric testing, the O₂:Ni ratio was varied, so the oxygen consumption was normalized by the amount of nickel in the bed to provide a consistent basis for comparison as shown in Equation 4.

$$\text{Percent O Consumed/Ni} = \frac{(2 \text{ mol O/mol O}_2) * (\text{moles of O}_2 \text{ fed} - \text{moles of O}_2 \text{ exiting})}{(\text{moles of Ni})} 100 \quad (4)$$

The percent O consumed/Ni is a measure of the elemental oxygen (O) that reacts with the nickel on the catalyst to form nickel oxide.

3.5.4 Results of Parametric Tests

While parametric testing was conducted on a variety of catalysts, only results for the most promising catalysts, C3 and P10, are discussed in this final report. Results from the testing of other catalysts can be found in the parametric test report⁴ appended to this final report. In general, no limitations of these catalysts were observed over the wide range of operating conditions evaluated. The results suggest that catalysts C3 and P10 are suited for the UMR process, as they demonstrated consistently good performance across the selected range of UMR conditions.

Reactor Temperature Variation

Figure 8 presents the performance of catalyst C3 and P10 at different temperatures. The results show that increasing the reactor temperature had no significant impact on CH₄ conversion for either of the catalysts. Also shown in Figure 8, increasing the reactor

⁴ A Novel Steam Reforming Reactor for Fuel Cell Distributed Power Generation: Screening Test Report, February 29, 2000.

temperature resulted in slightly increased oxygen consumption for catalyst C3, but did not impact the oxygen consumption of catalyst P10.

Steam to Carbon Ratio Variation

As the S: C ratio is increased; CH₄ conversion can increase because of decreased fuel concentrations. On the other hand, oxygen consumption would not be expected to change much unless S: C ratio had a significant impact on the state of the catalyst bed. Since S: C ratio of 1 provides sufficient steam to avoid choke formation and enhance nickel reduction, the state of the catalyst bed and hence, oxygen consumption, should not be impacted. Figure 5 represents the CH₄ conversion and O consumed/Ni for catalysts C3 and P10. This data shows that S: C ratio had no significant impact in performance.

Oxygen to Carbon Ratio Variation

The effect of varying O₂:Ni ratio on catalyst C3 performance is shown in Figure 6. The stoichiometric O₂:Ni ratio is 0.5, so excess air was present for all tests. If increasing excess air improves the oxygen consumption, then the nickel on the catalyst is not being oxidized efficiently. Increasing the O₂:Ni ratio above 0.635 did not have a significant impact on the performance of catalyst C3, demonstrating that this catalyst participates in nickel oxidation efficiently at these conditions and does not require much excess air. O₂:Ni ratio tests were not conducted on catalyst P10.

Reforming Gas Hourly Space Velocity Variation

For catalysts C3 and P10, increasing the GHSV did not change the CH₄ conversion or O consumed/Ni. The impact of GHSV on these performance indicators is shown in Figure 7. It should be noted that CH₄ conversion was relatively high at all the space velocities tested. This suggests that the conversation may deteriorate only at a much higher space velocities. Because the reforming space velocity did not impact CH₄ conversion, no impact would be expected for the oxygen consumption and this is borne out in the data.

The results shown in Figures 5 through 8 showed that catalysts C3 and P10 were not significantly impacted by the different parametric testing conditions. This suggests that these materials were within a suitable operating range, and should have good performance around the target reforming conditions.

3.5.5 Selection of Materials for Accelerated Durability Testing

The baseline parametric testing results are summarized in Figure 9. Many of the catalysts showed high CH₄ conversion, although the oxygen consumption varied substantially from catalyst to catalyst. Catalyst C3 had very high oxygen consumption, while catalyst P10 had high CH₄ conversion and oxygen consumption.

Figure 5. Steam to Carbon Ratio Variation for Catalysts C3 and P10

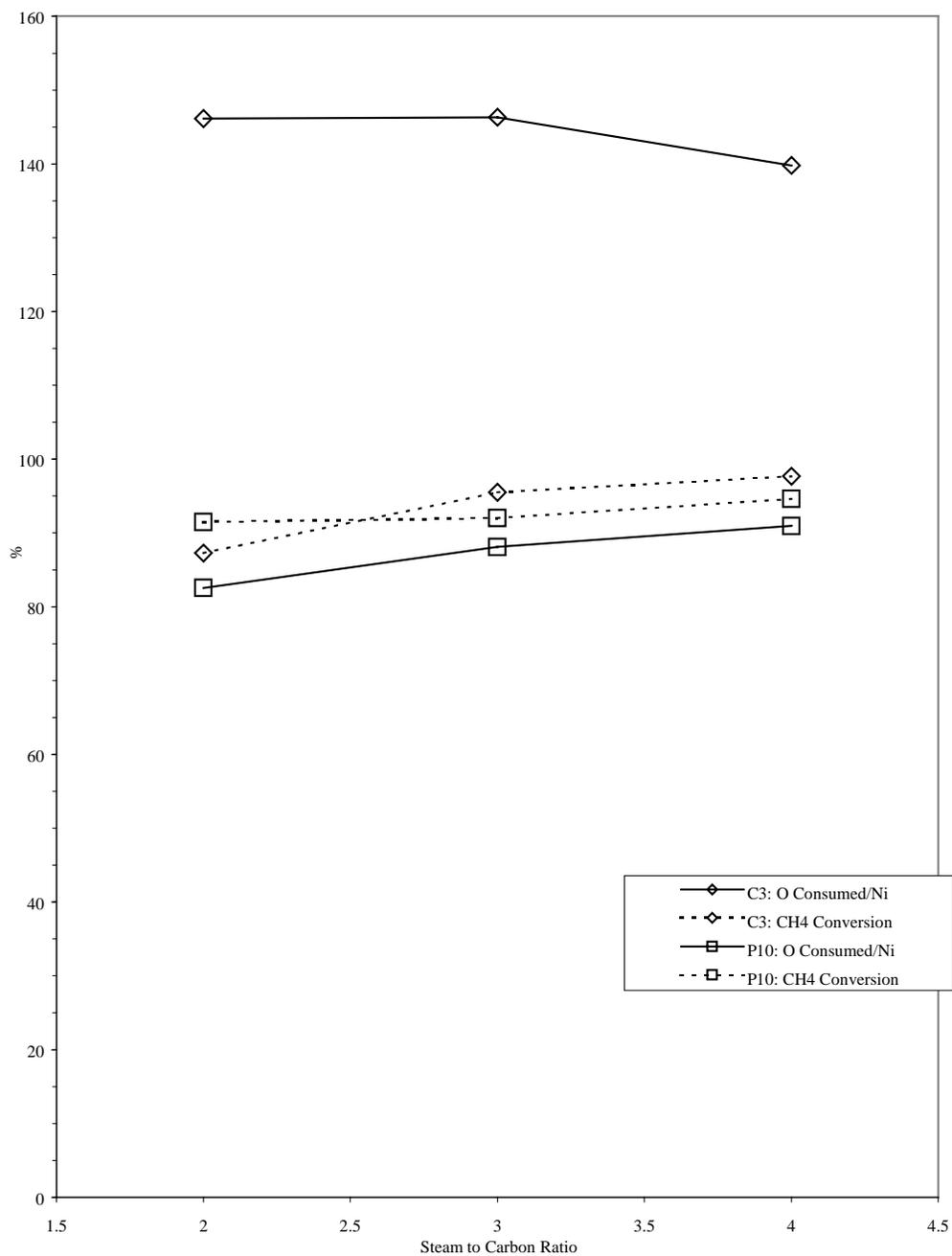


Figure 6. Oxygen to Nickel Ratio Variation for Catalyst C3

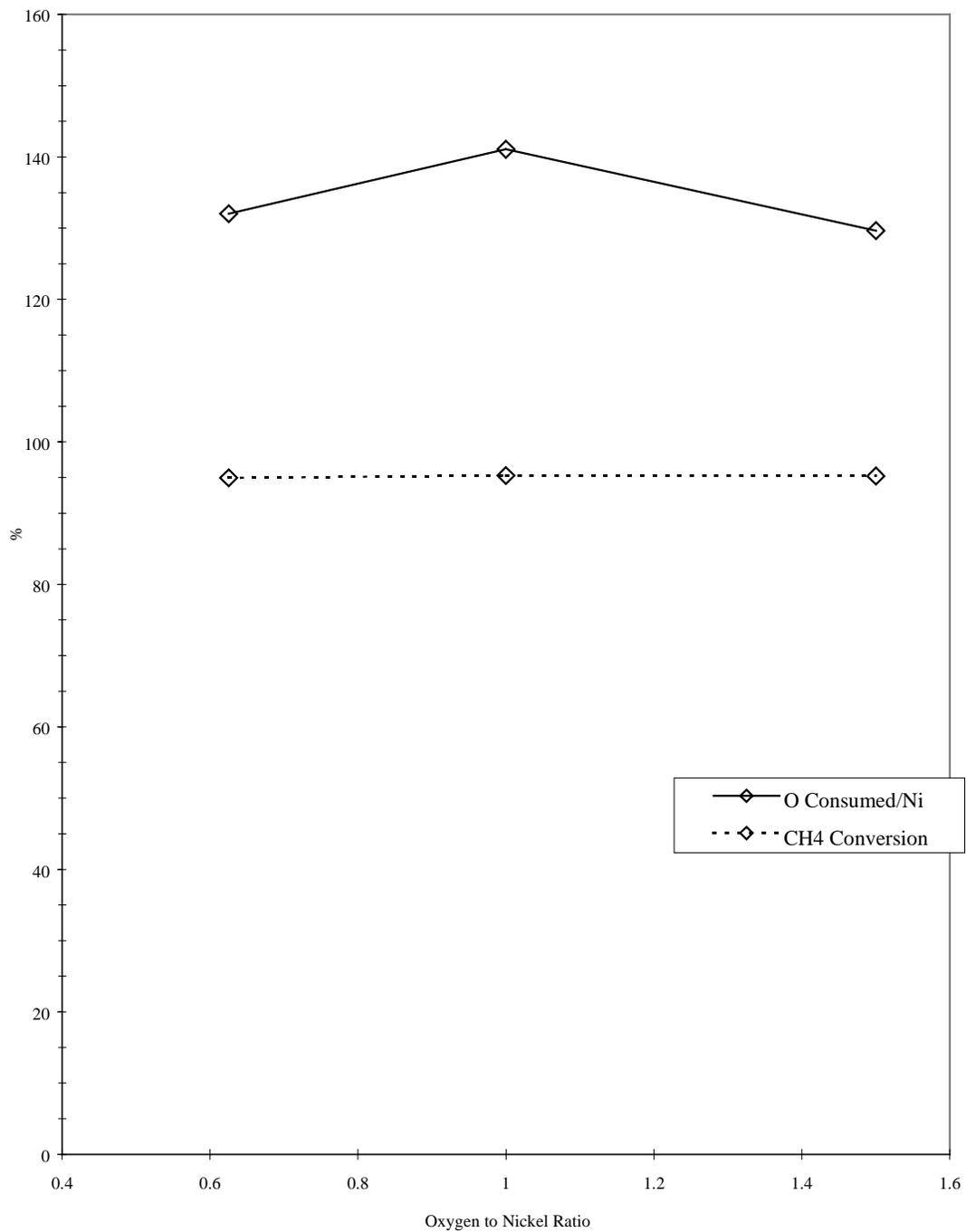


Figure 7. Gas Hourly Space Velocity Variation for Catalysts C3 and P10

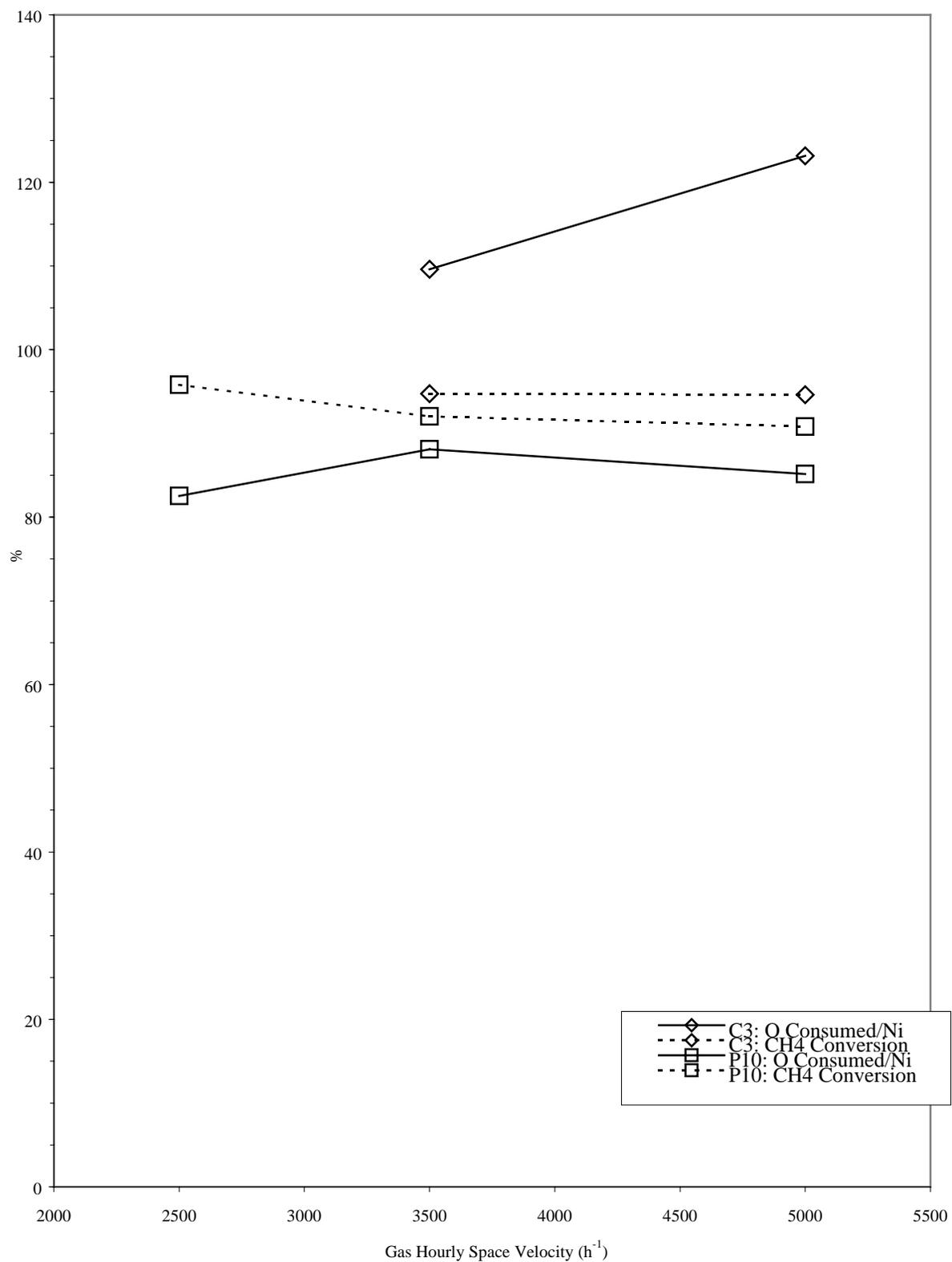
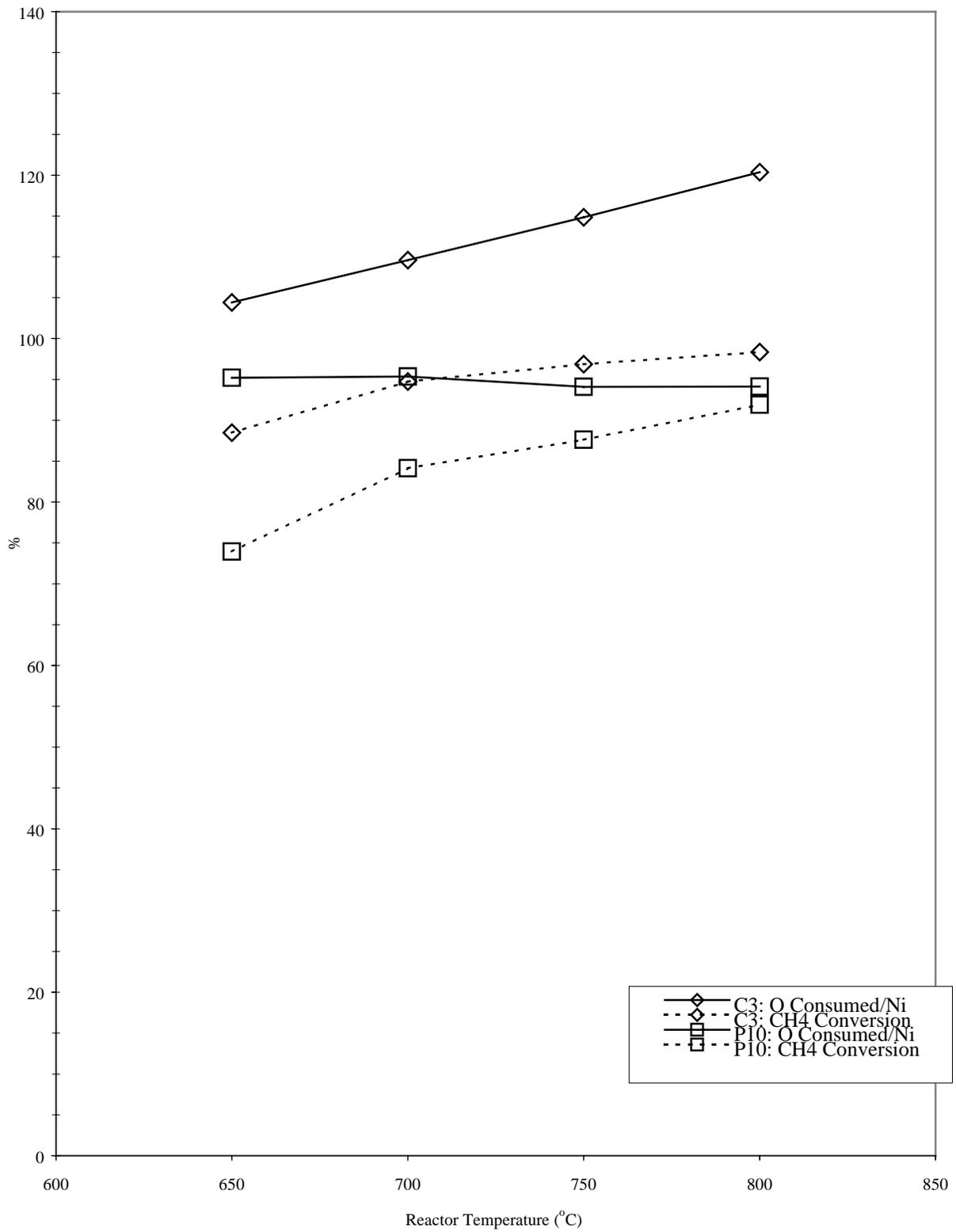


Figure 8. Reactor Temperature Variation for Catalysts C3 and P10



Based on the results of parametric testing, catalyst C3 was selected for prototype reactor testing and was used in accelerated durability protocol development. Catalyst C3 is a promising commercial catalyst primarily because of its high oxygen consumption, indicative of its ability to participate in the nickel oxidation/reduction cycle. It also had high CH₄ conversion.

Catalyst P10 was selected for accelerated durability testing because it exhibited good performance, especially with regard to its ability to reduce nickel rapidly in the fuel regeneration step. Phillips Petroleum developed the substrate for catalyst P10 to be an especially durable and physically stable material.

3.6. Accelerated Durability Testing and Results

Accelerated durability testing was performed on catalysts that were selected based on the results of parametric testing. The accelerated durability test was designed to estimate catalyst lifetime under conditions that simulate reforming operation. Several stresses influence catalyst performance in reforming service. These include thermal cycling and oxidation/reduction cycling. The purpose of the accelerated durability test was to estimate catalyst lifetimes by subjecting the catalyst to accelerated frequencies of the stresses that lead to failure. The development of a protocol for accelerated durability testing was a significant part of this effort. Significant discoveries were made during development of the protocol that also assisted in optimization of the reforming process.

3.6.1. Accelerated Durability Testing Protocol

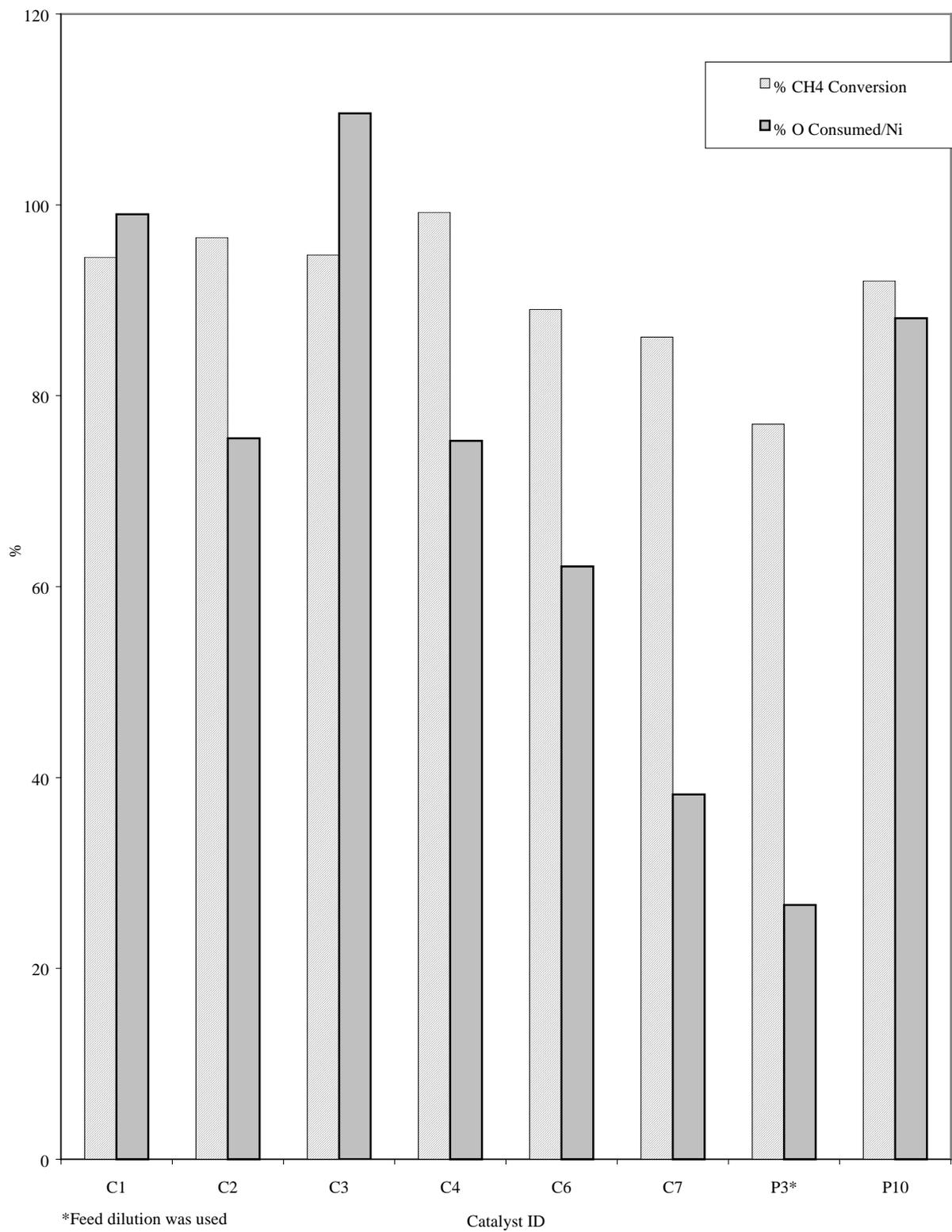
Due to the importance of accurately assessing catalyst lifetime, a significant effort was devoted to development of a protocol for accelerated durability testing. Accelerated durability testing can provide accurate lifetime assessments when the stresses that lead to failure under typical operating conditions are identified and reproduced for accelerated durability testing. A protocol⁵ was developed for accelerated durability testing based on a review of the literature and knowledge of the reforming process and typical catalyst failure modes. This protocol was developed

The accelerated durability testing replicated reforming stresses. The three stresses identified as causing material failure were: thermal cycling, oxidation/reduction cycling, and CO₂ absorption/release cycling. Initial testing focused on reproducing all three of these stresses. However, after testing that included analysis of weight loss due to attrition of the particles, it was identified that the dolomite absorber material degraded early in the tests, losing significant mass due to attrition. In addition, the gentle sieving used to separate powder from the material seemed to cause comminution of dolomite to powder. This led to the decision to perform accelerated testing on the catalysts only, as new CO₂ absorber materials suitable for the reforming process had not been identified.

⁵ A Novel Steam Reforming Reactor for Fuel Cell Distributed Power Generation: Test Plan Appendix F. Accelerated Durability Test Protocol Summary, June 30, 1999.

Another change made in the original testing protocol was the use of steam during the reforming step. Testing showed that steam was necessary to prevent the formation of coke, which was oxidized during the regeneration step and created an unwanted stress on the catalyst that would not be present in typical reforming operation.

Figure 9. Summary of Baseline Parametric Test Results



Testing catalysts without absorbers reduced the number of stresses needed to two: thermal cycling and oxidation/reduction cycling. Figure 10 shows several steps of an accelerated test. The shaded areas of the chart are the regeneration steps. Because the steps were so brief, there was significant lag in analyzer response, which did not impact the results. A qualitative assessment showed that durability testing produced the types of oxidation/reduction cycling and therefore temperature cycling stresses expected in typical reforming operation.

Figure 10. Accelerated Test Results for Catalyst P10

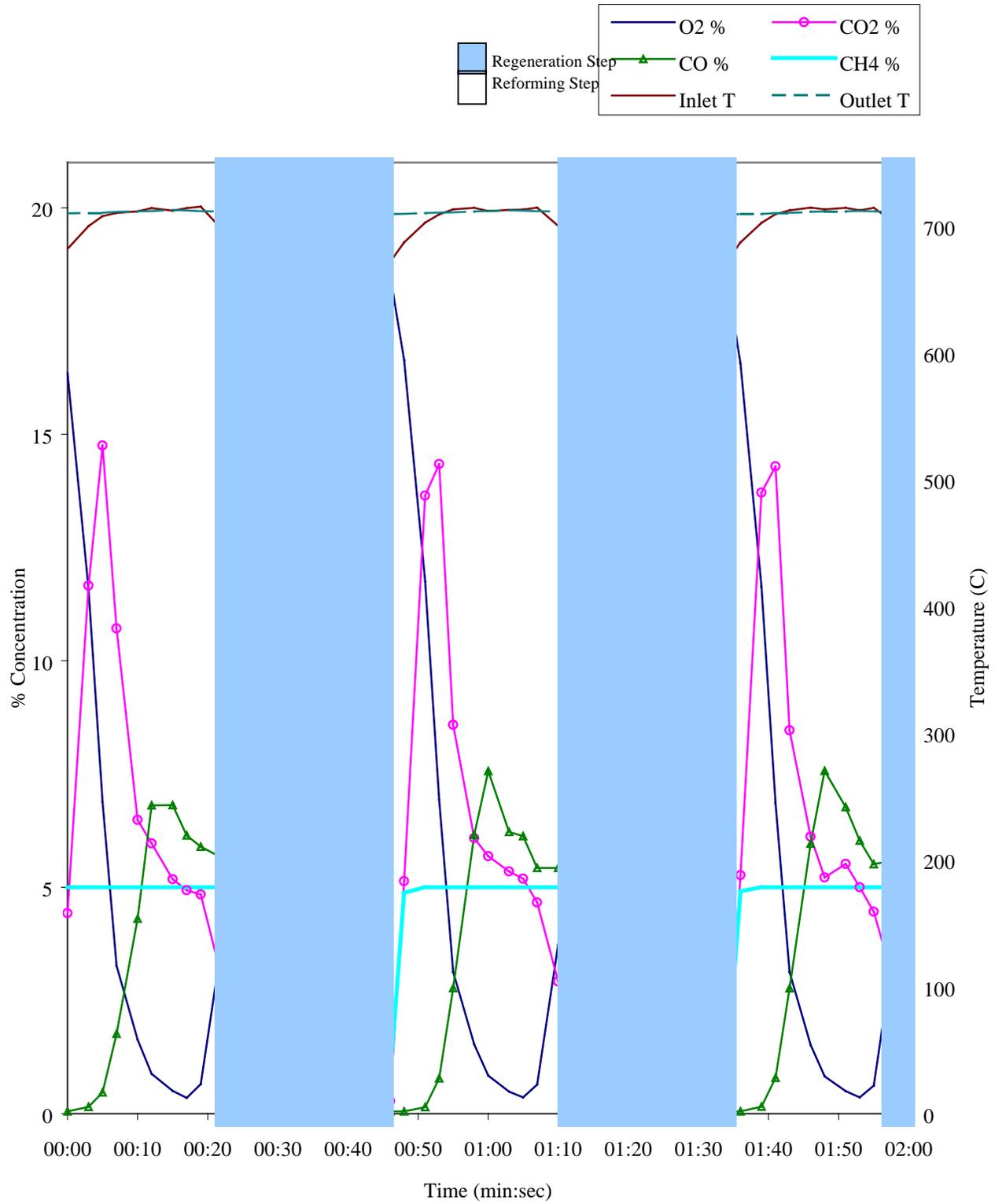


Figure 10 also shows that the CO₂ concentration reached a peak value at the beginning of the reforming step, consistent with the formation of CO₂ during the nickel reduction reaction. The concentrations of CO, CO₂, and CH₄ all dropped to zero during the regeneration step, which verified that coke oxidation was not taking place during the regeneration step. An estimate of the O consumed/Ni showed that approximately 35 percent of the nickel was being oxidized in each 20-second regeneration step. The oxidation of nickel generates significant heat, which leads to local temperature cycling.

The accelerated durability test was designed to subject the catalysts to the normal cyclic stresses of the reforming process at accelerated frequencies. Catalyst performance was measured intermittently to identify degradation of performance. Thus, the accelerated durability testing protocol included two modes of operation: performance characterization and accelerated testing.

The performance characterization test was used to make an initial characterization of material performance, and then check the performance intermittently over the catalyst life span. The performance test was conducted by running one reforming step and one regeneration step at 700 °C.

The accelerated test was run at 700 °C, and involved cycling between reforming and regeneration steps every 20 seconds. The 20-second steps provided an acceleration factor of 15 relative to the standard 300-second reforming and regeneration steps of the reforming process. Steam and natural gas were fed during the reforming step, and air was fed during the regeneration step.

The accelerated test was stopped periodically to conduct performance characterization tests and to observe the physical changes in the catalyst. After the performance characterization, accelerated testing was resumed.

3.6.2. Experimental Facility Setup

Accelerated durability testing was performed on a modified version of the bench-scale experimental system shown previously in Figure 2. The system was modified to accommodate the unique operating conditions of the accelerated durability tests.⁶ The modifications included a change to the steam preheater system, the addition of low-flow rotameters for the natural gas and air, and the use of a syringe pump for water delivery.

The use of short cycles required that the lag times between cycle switching and the delivery of the reactants to the reactor be minimized. The system was modified so that steam was generated continuously, and vented during the air regeneration step.

During accelerated durability performance testing, small quantities of catalyst were tested. This required the use of much lower reactant flow rates than had been used in

⁶ A Novel Steam Reforming Reactor for Fuel Cell Distributed Power Generation: Accelerated Durability Test Report, February 29, 2000.

the screening or parametric tests. Thus, the addition of reduced capacity rotameters to the system for both the natural gas and the air was required. A syringe pump was also added to provide the low flow rates of water required for these tests.

The low flow rates of steam and natural gas during the performance tests did not produce enough product gas for all of the CEMS analyzers, and the nature of the test ensured high, unreacted CH₄ levels. Thus, it was decided to dilute the reactants with nitrogen during the performance tests. A calibrated mixture of 4.5 percent CH₄ in nitrogen was used, along with steam, as the feed for the reforming step of the performance tests.

3.6.3. Calculations of Performance Indicators

The CH₄ conversion during reforming and the O consumed/Ni are the performance indicators for the performance tests. These were calculated according to the same procedure used for the parametric tests.

3.6.4. Results of Accelerated Durability Tests

Extensive testing was performed on catalyst C3 in evaluation and development of the accelerated durability testing protocol. After the protocol was finalized, an accelerated durability test was conducted on catalyst C3. However, a mechanical malfunction ended the test prematurely and the material had totally disintegrated. The cause of failure could not be identified. Accelerated durability testing was also performed on catalyst P10.

Catalyst P10 was tested for 290 hours, equivalent to a 4,350-hour lifetime. Catalyst P10 showed a step change in conversion level after initial accelerated durability testing (Figure 11). However, the level of conversion achieved after 20 hours of testing was maintained for the remainder of the 290-hour test. Figure 12 shows the oxygen consumption. The oxygen consumption showed a slight drop initially and then remained adequate for the remainder of the test.

Figure 11. Accelerated Durability Testing Results for Catalyst P10: percent CH₄ Conversion

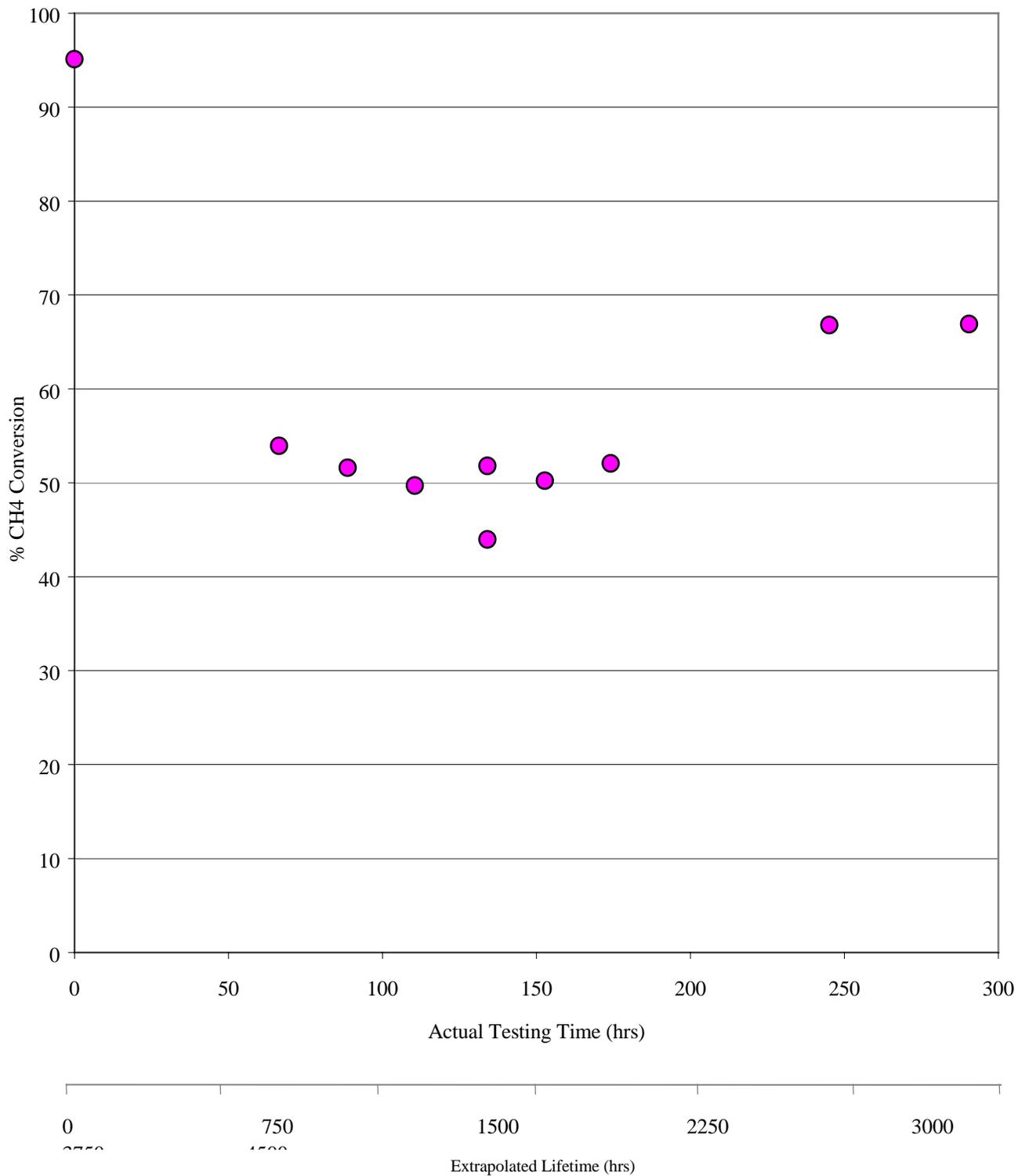
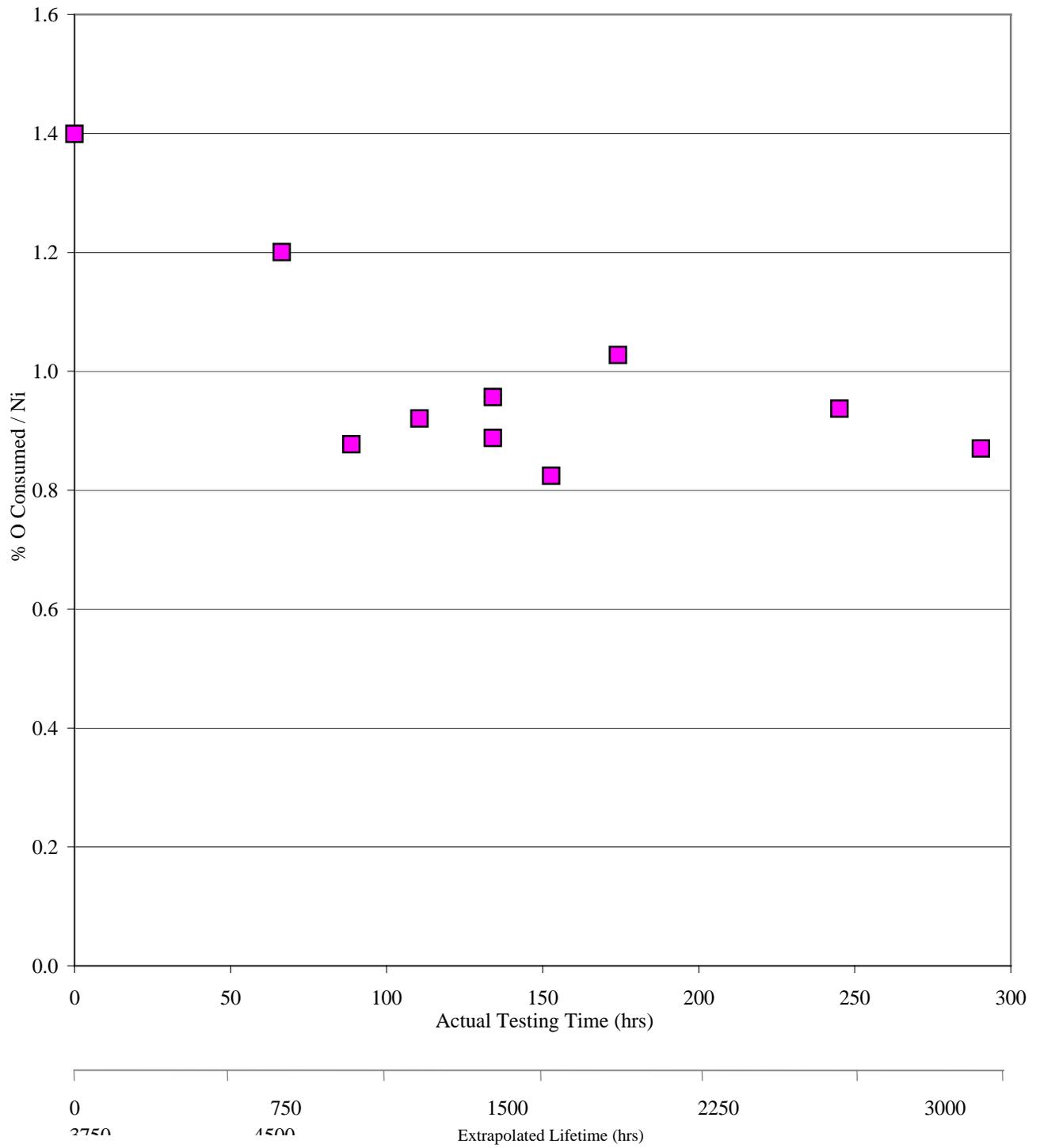


Figure 12. Accelerated Durability Testing Results for Catalyst P10: percent O Consumed/Ni



The physical properties of the catalyst P10 substrate are well suited to the reforming conditions. This material was designed by Phillips Petroleum to be an especially durable material at high temperatures and in the presence of high temperature steam. This was verified during testing, as even after 4,350 hours of equivalent lifetime, no evidence of attrition or phase changes were reported. The lower conversion for this catalyst may be overcome by judicious selection of operating conditions such as GHSV and temperature. Further development of this catalyst may involve the addition of promoters that would allow it to maintain its initial activity to a greater extent.

3.6.5. Selection of Materials for Prototype Reforming Reactor Testing

Within the original timeframe of this project, only catalyst C3 was seen to meet the reforming performance requirements in time for testing on the pilot facility. Several of the catalysts developed by Phillips Petroleum had nickel reduction issues that caused poor performance. The screening and parametric testing identified specific aspects of catalyst behavior that limited performance, and these were discussed with Phillips Petroleum.

Later in the program, a significant discovery occurred that led to the development of a catalyst that minimized previous reactivation issues of the fuel regeneration step. This led to the development of catalyst P10. Catalyst P10 was subjected to accelerated durability testing and found to be extremely durable and have a suitable level of activity that was maintained during testing. EER is currently pursuing the use of this catalyst in the pilot test facility during the course of the DOE program.

3.7. Prototype Reforming Reactor Design, Construction and Testing

EER is currently conducting a program to design, assemble and operate a pilot test facility for reforming natural gas to produce fuel cell grade hydrogen. The facility comprises a fully integrated autothermal process for natural gas reforming and hot water cogeneration system. Under this project, reforming catalysts are being developed for testing in prototype reforming reactors installed on the pilot test facility.

Later in the catalyst development effort, a modified formulation of nickel catalyst and catalyst promoters was produced which substantially overcame the activity issues. Unfortunately, this material was discovered too late in the project to allow testing on the pilot facility. However, EER did identify a very active commercial catalyst that was tested on an early configuration of the pilot facility. EER is continuing the optimization of the pilot test facility and is planning continued testing of catalyst materials identified under this project as suitable for the reforming process.

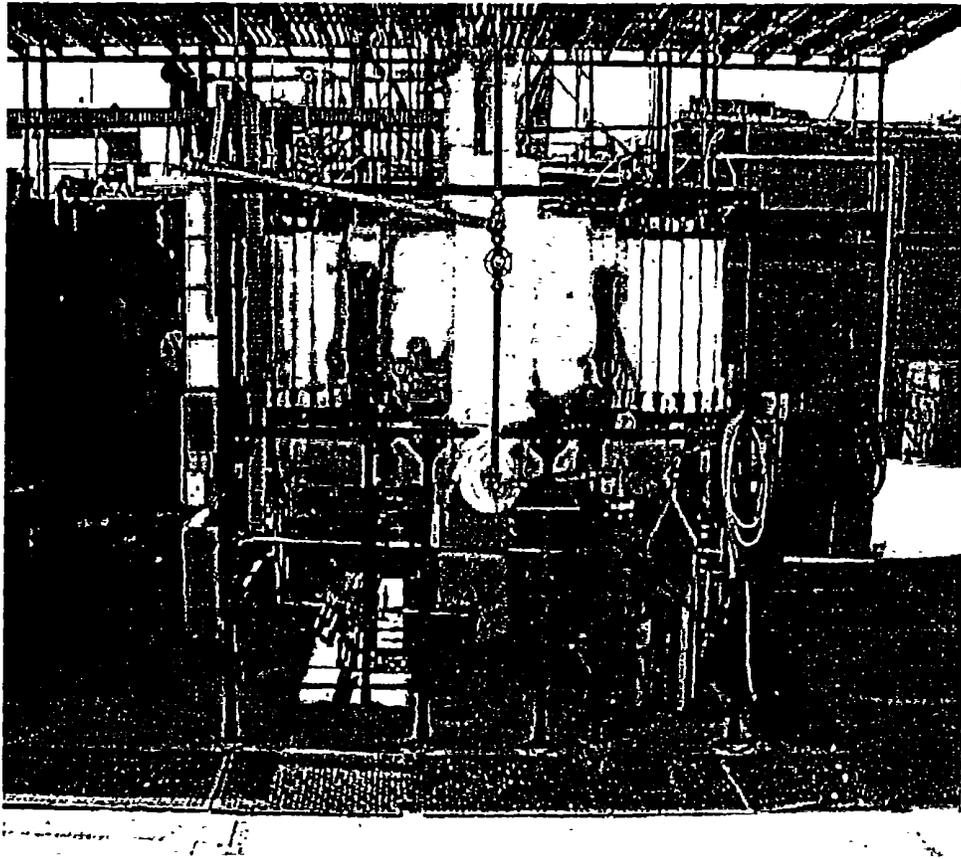
The purpose of this section is to describe the prototype reactor design for the selected commercial catalyst and to present results of the pilot facility tests on commercial reforming catalyst C3.

3.7.1. Pilot Test Facility Description

The pilot test facility is a breadboard design that allows component evaluation and reconfiguration for process optimization. Figure 13 is a process flow diagram of the pilot test facility. The reforming reactors are the heart of the pilot facility, around which various heat exchangers are integrated for heat recuperation and steam production. The reformat product gases from the reactors are delivered to polishing systems including low temperature shift and CO removal reactors to produce PEM fuel cell grade hydrogen. The reactor vent gas from the regeneration cycle is treated in a catalytic oxidizer to reduce CO and CH₄ emissions prior to the gas being used for cogenerated water heating.

The pilot testing is currently focused on autothermal operation of the reforming reactors, thus the reformate polishing systems and the vent gas emission components are not yet integrated. The performance of the integrated system is therefore assessed based on the actual reactor performance and the design performance of the peripheral components. Figure 14 shows the pilot test facility with the breadboard component assembly supported on a truss framework.

Figure 13. Photograph of the Pilot Test Facility



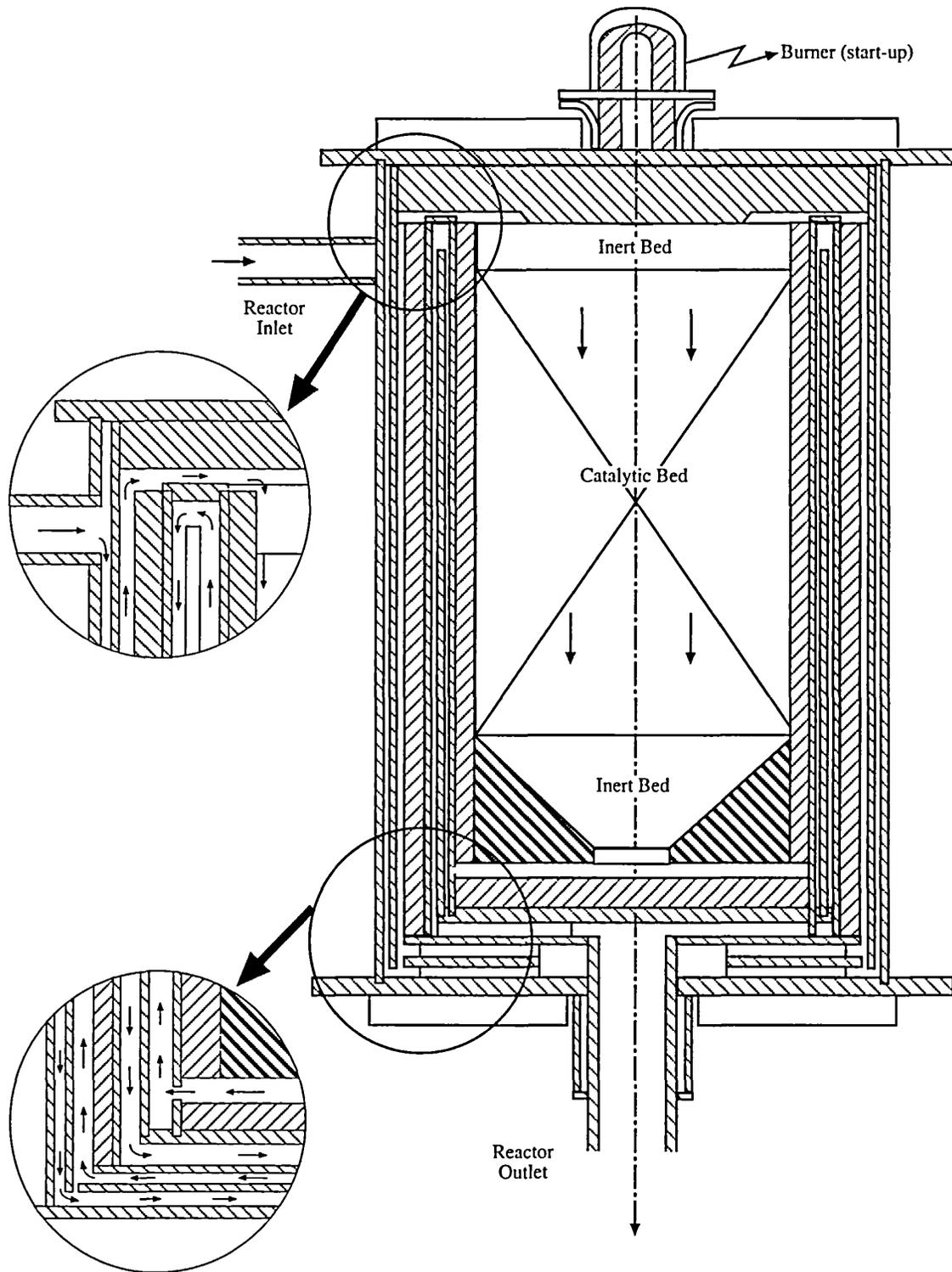
3.7.2. Prototype Reactor

Unmixed reforming is a cyclic process requiring at least two reactors for continuous hydrogen production. The reactor designed and used for testing of the selected catalyst consists of a packed catalyst bed in an axial flow reactor. The reforming and regeneration feeds flow downward along the axis of reactor. The reactor specifications are presented in Table 7. The reactor comprises multiple concentric channels around the internal catalyst bed (Figure 15).

Table 7. Prototype Reactor Specifications

Specification	Units	Value	
Reactor Capacity (Electrical Equivalence)	kWe	50	
Process Parameters:		Reforming Step	Regeneration Step
Feed		Fuel+Steam	Air
Reactor Feed Rate	kg/hr	28	152
GHSV	hr ⁻¹	2000	7000
Reactor Pressure Drop	bar	0.05	0.5
Inlet/Outlet Temperature (max.)	°C	570/900	
Design Pressure	bar	3	
Packed Catalytic Bed Specifications:			
Composition		Ni+CaO+Substrate	
Mean Particle Size	mm	3	
Bed Volume	Liters	27	
Bed Diameter	cm	28	
Bed Length	cm	44	
Reactor Vessel Specifications:			
Outer Wall Temperature	°C	150	
Heat Loss	kW	1.0	
Inner Refractory	Alumina Silica		
Outer Insulation	3" Kao-wool Blanket		
Reactor Flow Dispersion Plates	Reticulated Ceramic		
Reactor Weight	kg	100	

Figure 15. Illustration of the Prototype Reactor Internal Multi-Channel Design



Reactants enter along the outer wall and flow downward and then back up the inside wall before entering the bed from above. After passing through the bed, the reformat gases flow up along the outer bed wall and then down, exiting from the bottom of the reactor.

The multi-channel design accomplishes internal heat recuperation by preheating the reactants, and achieves a more uniform bed thermal profile. By reducing radial temperature gradients in the axial flow reactor, lower slip at the wall boundary can be achieved. Figure 16 is a photograph of the reactor outer housing and internal liners that make up the various channels.

Figure 146. Prototype Reactor Housing and Internal Liners



The outer housing (Figure 17) is enclosed top and bottom by reactor lids sealed with high temperature gasket material. Several gasket materials have been evaluated for sealing the reforming reactors. Interam^{TM7} when coated with Silver Seal II paste sealant⁸ has met performance requirements at pressures up to 3 bar. Also shown in Figure 17 are the natural gas burners on the reactor that are used for startup.

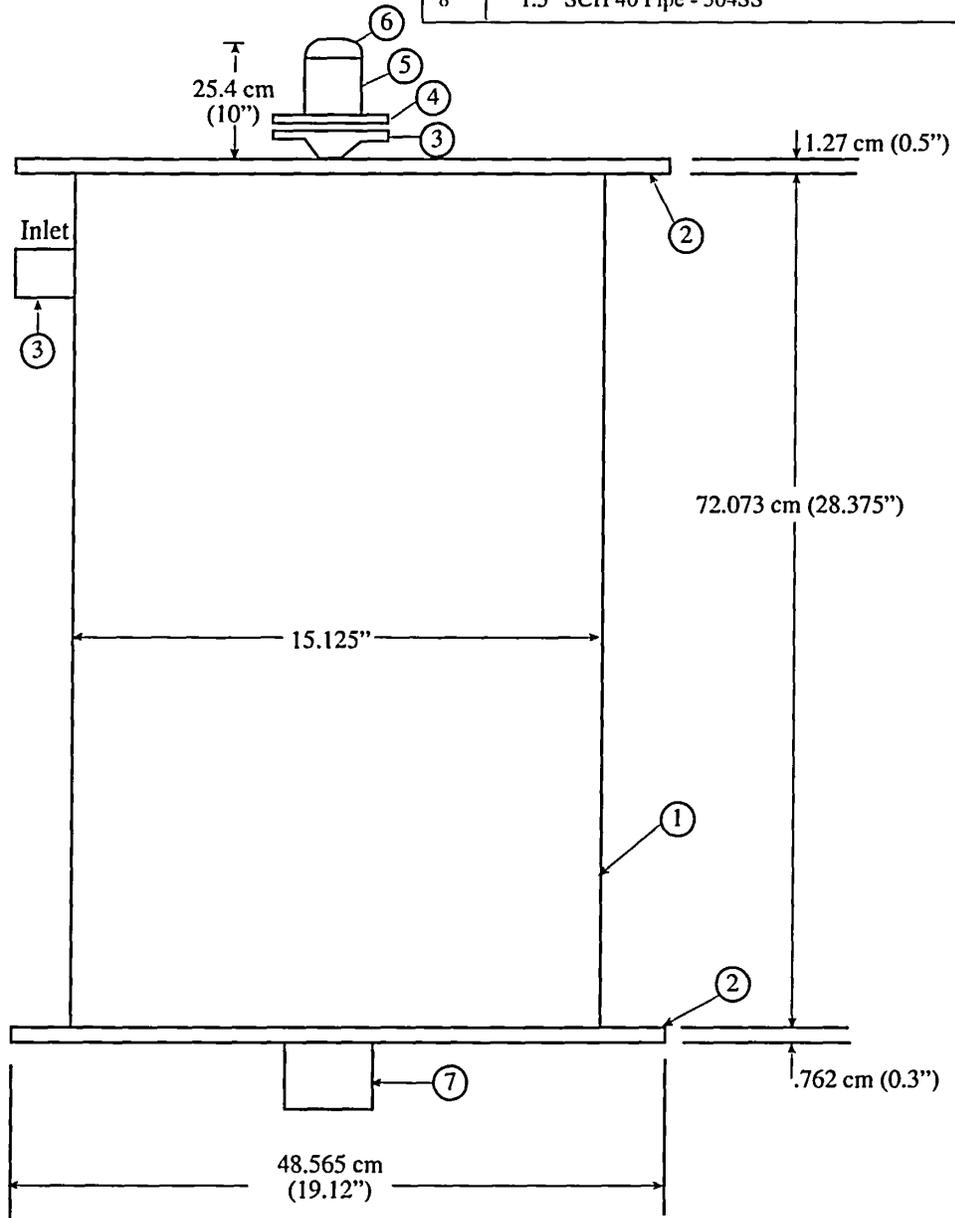
⁷ 3M, St. Paul, Minnesota

⁸ IGS sealant Technology Group, Meadow Lands, PA

Figure 15. Prototype Reactor Housing

GE Energy and Environmental
 Research Corporation
 UMR Close Coupled Heat
 Exchanger
 MAWP 50 PSI@1800°F

Item	Description	Qty.
1	15.125"OD x .1875 wall x 28.375" LG-304SS	1
2	19.125"OD x 1.5" th - 304SS	2
3	3" Flange, 300lb - Weldneck - 304SS	1
4	3" Flange, 300 lb - Slip on - 304SS	1
5	3" SCH 40 Pipe x 10" lg - 304SS	1
6	3" SCH 40 Cap Butt Weld - 304SS	1
7	2" SCH 40 Pipe - 601 Alloy	1
8	1.5" SCH 40 Pipe - 304SS	1



3.7.3.

Pilot Facility Controls

The pilot test facility is equipped with complete process monitoring and control for automatic and manual operation. It is also equipped with process monitoring for real-time performance analysis at a component-by-component level and for feedback control of the entire process. The control system is run from a Microsoft Windows NT™ computer running National Instruments' LabView™ software.

A cascade control system was developed to control the reforming reactor temperatures. The control system determines the set points for the steam and natural gas flow rates to maintain the process within a thermally acceptable window and then regulates the steam and natural gas flow by automatically actuated valves.

The control system for determining the set points for the steam and natural gas flow rates has two modes: manual and feed-back control. In manual control, the user enters the steam and natural gas flow rate set points. In feedback control these set points are determined by an algorithm based on the cycling time-temperature profile of the reactor bed and the boiler steam pressure. In cases where boiler steam pressure reaches the maximum allowable pressure, the steam flow is increased to maintain boiler pressure.

Additionally, the steam and natural gas valves can be manually set to a percent open or can be placed into proportional integral derivative (PID) control, where the control system will continually adjust the valve position to maintain the desired flow set point. The valve control must be in PID control mode when the reformer control system is in feedback control mode.

3.7.4. Prototype Reactor Tests

The development of the prototype reactors was accomplished with bench top testing of the reactors prior to installation and operation on the pilot test facility. The bench top tests allowed independent operation of the reactors on preheated reactant streams and did not rely on process subcomponents for steam production and reactant preheating. Later testing on the pilot test facility was carried out with integrated heat recuperation and steam generation.

Testing on the Bench Top System

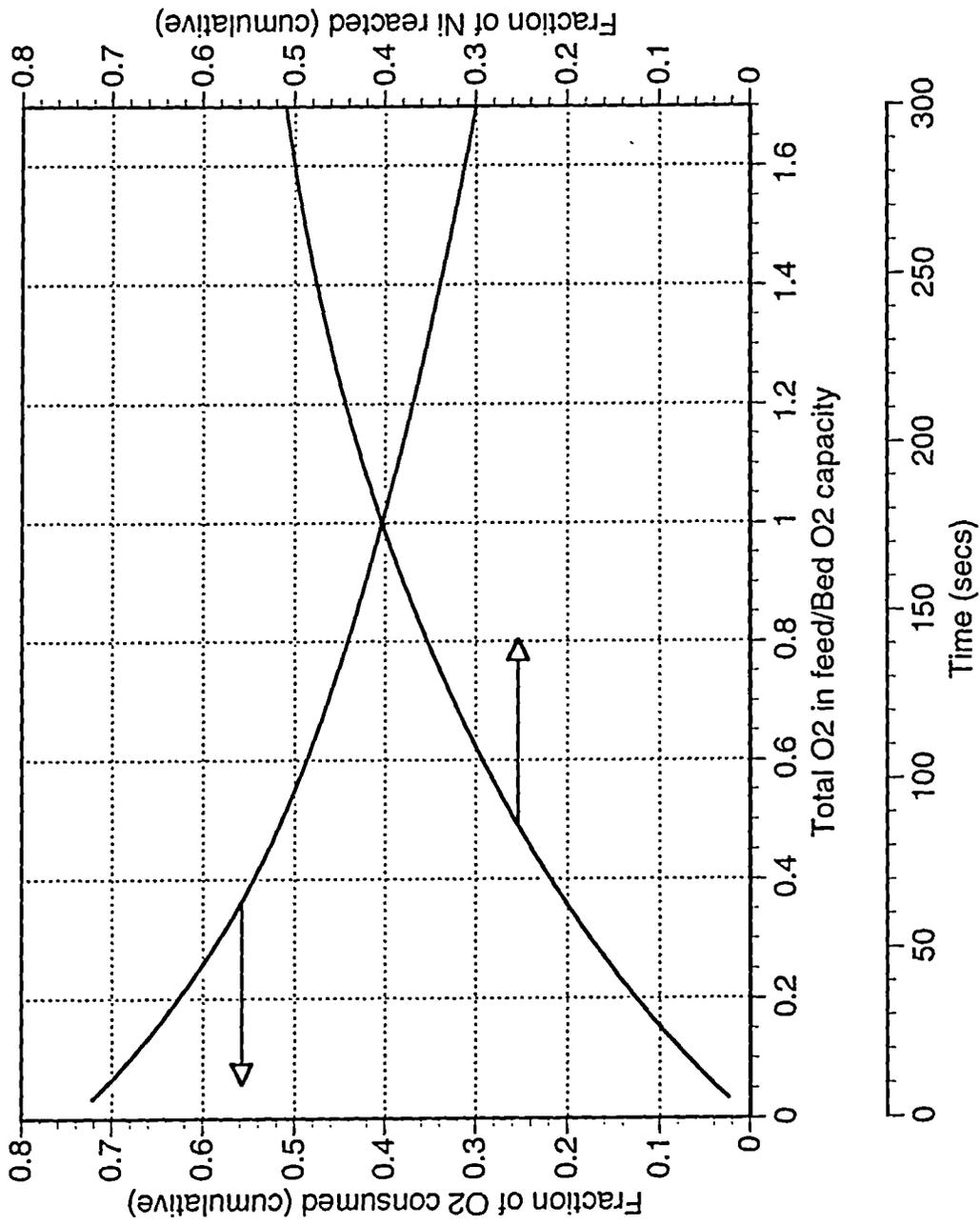
The prototype reactor was tested on the bench top system, which had been configured specifically for evaluating new reactor designs. Three reforming catalysts and two bed configurations were independently evaluated in the prototype reactor. In the first bed configuration the catalyst and the CO₂ absorber, dolomite, were mixed uniformly throughout the bed. In the second bed configuration, ten alternating layers of catalyst and dolomite were loaded. The catalyst bed with the mixed configuration was the most effective in bench top tests. The reforming data for the mixed catalyst C3 and dolomite is presented in Table 8. The catalyst was effective in converting over 80 percent of the CH₄, and the reformat stream contained 5 percent CH₄ and 8 percent CO. These levels meet the design target for the concentrations of these impurities exiting the reactors. The CO₂ level at 14 percent is slightly above the target of 10 percent but should be effectively optimized to target levels.

Table 8. Reforming Step Average Data for the Prototype Reactor on the Bench Top System

CH₄ conversion during reforming:		81.6 percent
Dry composition of the syngas:	CO₂	14.2 percent
	CO	7.8 percent
	CH₄	4.6 percent
	H₂	73.4 percent

Intrinsic to the reforming process is the oxidation and reduction reactions of the nickel catalyst. The oxidation reaction provides the heat for the endothermic reforming reactions. The fractions of nickel oxidized and reduced during each cycle can impact the overall efficiency of the process. Figure 18 presents the fractions of oxygen consumed and nickel reacted over a single air regeneration step.

Figure 18. Bench Top System Data for the Fraction of Oxygen Consumed and Nickel Reacted During the Air Regeneration Step of the Reforming Process



The period of the air regeneration step is 300 seconds. The ratio of oxygen fed to nickel's oxygen capacity is 1.7, corresponding to 70 percent excess oxygen. During the regeneration step, 30 percent of the oxygen fed was consumed and 51 percent of the nickel was oxidized. Increasing the fraction of nickel oxidized with minimal air feed can increase the overall efficiency of the process. Efforts are planned to identify the optimal operating conditions and catalyst material for increasing the effectiveness of the nickel oxidation and reduction.

The bench top tests provided some preliminary shakedown performance information on the prototype reactor, which demonstrated suitable high temperature operation, heat recuperation and reforming chemistry. The prototype reactors were then installed on the pilot test facility.

Testing on the Pilot Test Facility

The breadboard system was designed to test and integrate all of the fuel processor components. The data collected on reactor performance included reactant feed rates, process stream temperatures, line pressures, component skin temperatures, and product and vent gas compositions. This unit was operated in a preliminary configuration, subject to operating restrictions resulting from excessive heat recuperation and low steam boiler heat exchanger effectiveness. The high heat recuperation of the reactor's external heat exchangers reduced the enthalpy of the vent gas to the boiler, which, coupled with a steam boiler not meeting specifications, caused low steam production. Therefore, the pilot facility was limited to low capacity operation and only minimal reactant preheating. Under these conditions, the promising catalyst C3 identified in California Energy Commission bench-scale experiments was evaluated in the prototype reactors.

EER is currently reconfiguring the pilot test facility to increase steam production and reactant preheating and plans to demonstrate reforming process performance at the target capacity of 50 kWe. The following sections present performance results of the prototype reactors operating with catalyst C3 on the pilot test facility.

Operating Capacity: As the pilot facility is reconfigured to increase steam production and reactant preheating, the only issue that should impact operating capacity is the system pressure drop. The pressure drop through the prototype reactor and external heat exchanger has been measured experimentally operating at 20 kWe. The pressure drop was then scaled to 50 kWe conditions using the relationship:

$$\Delta P = K \rho V^2 \quad (5)$$

Where:

ΔP is pressure drop

ρ is the gas density

V is the gas velocity

K is the pressure drop coefficient.

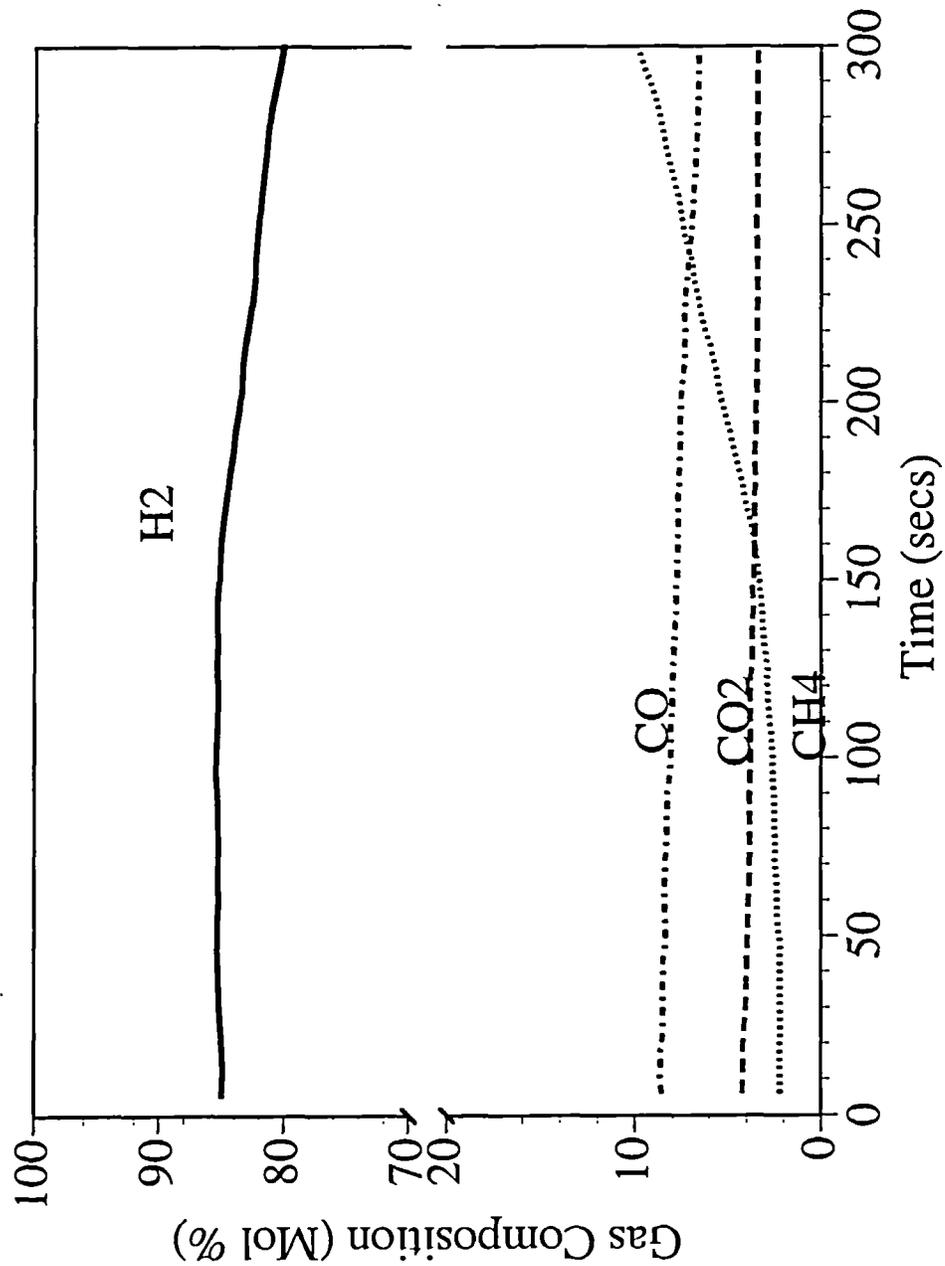
The predicted pressure drops through the prototype reactor and external heat exchanger at 50 kWe during the reforming and regeneration steps are 0.1 and 1.8 bar, respectively. The available pressure drop during reforming and regeneration is estimated at 0.7 and 3.5 bar, respectively. Therefore, an operating capacity of 50 kWe is achievable.

Pilot Facility Thermal Profile: The pilot facility was operated at 20 kW electrical equivalent. The steam was superheated to 210°C and blended with natural gas prior to entering the external heat exchanger. The reactants exiting the heat exchanger were preheated to 273°C and delivered to the reactors. The reactant feed temperature of 273°C was considerably below the design preheat of 640°C as a result of the facility limitations discussed earlier. The product gas temperature from the reactor was controlled to 800°C, which is within the reaction sustaining temperature window of 700 to 1000°C.

From skin temperature measurements of the reactors, the reactor heat loss is comparable to 3 kW out of a total input heat value of 60 kW. The heat loss is three times the desired level but was necessary to reduce thermal stress and sealing difficulties. To reduce heat loss in a fully integrated unit, the external heat exchanger will be replaced by additional internal recuperation so that the reactor shell can operate at low temperatures, thereby reducing heat loss and thermal design issues. However, these levels of heat loss are acceptable within the framework of component-by-component evaluation of a breadboard system.

Reformate Product: The prototype reactors were again operated at 20 kWe with a reactor exit temperature of 790°C and pressure of 2.0 bar absolute. The S: C was maintained at a 3:1 molar ratio and the reactor GHSV was 1400 hr⁻¹. Figure 19 shows the composition of the syngas produced during the reforming step. Here the hydrogen concentration exceeds 80 percent. The CO averages 8 percent and CO₂ is around 4 percent. CH₄ concentrations are likewise low at 4.5

Figure 19. The Experimentally Measured Composition of the Syngas from the Pilot Test Facility



At these operating conditions the hydrogen production was calculated at 350 cubic meters per day (12,400 standard cubic feet per day). Therefore at 50 kWe, a hydrogen production level of 875 cubic meters per day (31,000 standard cubic feet per day) is achievable.

Oxidation/Reduction of Nickel: The fractions of oxygen consumed and nickel reacted over a cycle are presented in Table 9 for various maximum bed temperatures. The breadboard system was operated at 20 kWe. The table shows that the nickel particles are most reactive at a bed temperature of 790°C and that the reactivity is reduced at lower and higher temperatures. The significant activity loss at 890°C was not recoverable in subsequent tests at 800°C. This activity loss may have resulted from coking. We investigated this further by removing catalyst samples from the bed and conducting Loss on Ignition (LOI) tests.

During the LOI tests the catalyst particles from one reforming reactor lost 0.1 percent (by weight) and from the other reforming reactor lost 2.3 percent (by weight). This indicates that there might have been coke deposition on the catalysts. Later experiments at the bench-scale indicated that coking occurs during the nickel reduction step if steam is not present in at least equal molar concentrations to carbon. All prototype reactor tests on the pilot facility to date were conducted without steam flow during the nickel reduction step. The reconfigured pilot facility will provide sufficient steam for the nickel reduction step and may potentially improve the efficiency of the reforming process by increasing the oxidation and reduction of nickel.

Table 9. Effect of Maximum Bed Temperature on Oxygen Consumed and Nickel Reacted

Maximum bed temperature during each cycle	630°C	790°C	890°C
Fraction of Ni reacted in one cycle	0.28	0.61	0.12
Fraction of O ₂ consumed in one cycle	0.19	0.44	0.28

Since the pilot plant did not allow sufficient operational control to optimize the reforming process, a parametric evaluation of the catalyst oxidation and reduction performance was conducted. Prior bench-scale experiments indicated that the fuel regeneration chemistry to reduce nickel is slow and results in significant CH₄ slip through the reactor. The effect of the fuel regeneration step GHSV on the nickel oxidation and reduction process was experimentally investigated. Table 10 provides the results. The results showed that oxygen, fuel and nickel reactions increased at low GHSV. This test was also conducted at a bed temperature of 600°C and without steam, which is recognized to improve the nickel reduction process. As a result, the overall fuel conversion was low in all cases. The test did show that use of a lower GHSV improved the fuel regeneration chemistry.

Table 10. Effect of GHSV During the Fuel Regeneration Step on the Unmixed Combustion Process

GHSV during fuel regeneration step	385 hr ⁻¹	162 hr ⁻¹
Fraction of O ₂ consumed in one cycle	0.193	0.263
Fraction of fuel reacted in one cycle	0.162	0.208
Fraction of Ni reacted in one cycle	0.278	0.374
<ul style="list-style-type: none"> The reactor was fed with 43 percent excess air relative to total Ni (not just reactive Ni) and 90 percent excess fuel relative to total Ni. GHSV during air step is 2776 hr⁻¹. Temperature of bed is approximately 600°C. 		

In later pilot facility tests, the steam feed and GHSV during fuel regeneration will be optimized to reduce unconverted CH₄. It should be noted that any unconverted CH₄ is recycled within the total plant and does not represent a significant efficiency penalty.

Absorption/Release of CO₂: The pilot facility was operated at 20 kWe for 15 cycles. The average bed temperature was 794°C, the GHSV was 1400 hr⁻¹ and the reforming step and regeneration step reactor pressures were 2.2 and 1.8 bar, respectively. Under these conditions the dolomite absorbed 65 percent of the CO₂ exiting the reactor and thus separated this CO₂ from the reformat product stream and vented it with the regeneration vent gas. The removal of CO₂ *in-situ* represents a significant advantage in increased hydrogen production. The removal of CO₂ allows additional water-gas shift reactions where increased hydrogen is produced from the reaction of CO and water. Additionally, the removal of CO₂ from the product stream increases the hydrogen purity and this will increase the PEM fuel cell efficiency.

Overall and Project Performance: The pilot plant was operated under reduced capacity and with insufficient steam flow and reactant preheat. Despite these restrictions the prototype reactors have demonstrated the capability to meet or exceed many of the performance targets. Table 11 presents the current performance of the pilot facility and projected performance for improved fuel regeneration performance corresponding to performance already demonstrated in California Energy Commission bench-scale tests. The projected performance does not consider process optimization efforts that may increase performance above those demonstrated to date.

The overall performance shows that improvements in the fuel regeneration chemistry, impacted by steam flow and temperature, are sufficient to raise the conversion efficiency to 68 percent. This is still slightly below the target of 75 percent, however, other process optimization efforts have not been considered. The total cycle efficiency can exceed the 35 percent target and hydrogen production can exceed the 25,000 cubic feet per day level. The current testing has shown that catalyst utilization and the absorber's CO₂ capacity meets the target performance. The CO and CH₄ are reported based on actual measurements of untreated vent gas. The vent gas will be integrated with a catalytic oxidizer that can effectively reduce the emissions to the target levels of 10 ppm CO and 50 ppm CH₄. Because of the high levels of CH₄ in the vent gas, NO_x levels were not

measured. Based upon previous laboratory measurements the reactor NOx levels are expected to be below the 1 ppm detection limit of the chemiluminescent analyzer.

Table 11. Prototype Reactor Performance on the Pilot Test Facility

Objective	Units	Limited Operation	Projected Operation
Power Output (Electrical Equivalent)	kWe	20	50
Conversion Efficiency	percent	42	68
Total Cycle Efficiency (Elec.)	percent	19	37
Total Thermal Efficiency	percent	42	79
H₂ Production	ft ³ /day	12,400	30,500
Catalyst Utilization	percent	61	61
Absorption Capacity	percent	65	65
NOx Emissions	ppm	NM	NM
CO Untreated Levels	ppm	87	51
CH₄ Untreated Levels	percent	3.8	0.1

NM - not measured

3.8. Economic Analyses, Results, and Interpretations of Findings

Currently, the domestic market for DPG relies on proven technologies such as diesel engines and gas turbines, which are less efficient, yet economical and reliable. Internal combustion engines have low capital costs because of the significant amount of development work funded by the transportation industry. They are reliable but relatively costly to maintain and operate. In order for emerging technologies to penetrate the DPG market, they must be cost competitive and reliable and provide benefits over the existing technologies. These benefits could include reduced costs for operation and maintenance and less expensive environmental compliance.

The deregulation of the utility industry is changing the face of power generation and distribution in the United States. According to the Gas Research Institute (GRI), the future trend will shift towards distributed power technologies that can replace large central power plants. Ultimately DPG provides an economically attractive alternative to capital intensive and risky central power plants for the newly deregulated utility industries. Advancements in DPG will allow more companies to enter the power market and could in the long run lead to lower-cost power generation.

3.8.1. Market Evaluation

Forty-five percent of U.S. commercial electricity use is consumed by facilities with base load power requirements in the range of 10-200 kW representing a significant market for DPG. This market exists across all sectors; industrial, commercial and residential with specific needs for each sector being significantly different.

Industry often negotiates the best energy rates and therefore DPG must be highly cost competitive with central power stations. This can be accomplished with cogeneration systems and by reducing large scale investment and infrastructure costs.

In the commercial sector the distributed power needs are for backup generation, peak shaving, premium quality power, heating and hot water. Some portions of the commercial sector require reliable backup generation. Typically for backup generation the commercial user is not willing to pay premium capital costs for high efficiency systems since the power systems are not intended for high capacity operation, and this means fuel costs are less significant than capital cost. Here the less efficient but proven technologies are hard to displace with emerging technologies unless significant market drivers such as very high fuel costs or strict environmental regulations essentially prohibit the use of low efficiency DPG.

The residential sector has always borne the greatest share of energy costs largely because of the thousands of individual metering and distribution systems required and the inability to collectively bargain lower rates. Therefore, distributed generation technologies that are uneconomical to industry may still prove to be economical for residential markets⁹. The challenge to DPG is producing a small generator at low costs. Generally the cost per kW increases exponentially with decreasing size. Hence penetration of the residential market will potentially be served by a larger generator supplying the electricity and hot water/heating needs of several homes.

The expansion in these market sectors, specifically industrial and commercial, will initially be filled primarily by existing DPG technologies due to their commercial availability and proven track records. However, short, mid and long-term markets do exist for emerging technologies, such as EER's reforming based power system, that have improved efficiency and substantial environmental benefits relative to existing DPG technology.

Short-Term Market

Only a small market is thought to exist for high efficiency DPG in the short-term. The market is essentially restricted to military applications that stress high efficiency, due to the cost of delivering fuel to remote staging areas. In the short-term, technology costs may still be high due to low production levels and high development costs. However, the emerging reforming technology, at 36 to 40 percent electrical efficiency, can cut fuel consumption by 33 to 44 percent over existing diesel generators that operate at 25 to 30 percent average duty cycle efficiency. The military estimates that it takes on average 4 gallons of fuel to deliver 1 gallon of fuel to staging areas. Therefore high capital costs are more than offset by lower fuel cost. With fuel cost dominating the electricity production costs, reducing the fuel consumption by 44 percent can drastically lower energy costs but equally important to the military, it reduces the exposure of front line personnel to possible harm while protecting fuel delivery equipment and personnel.

⁹Preston, G.T. and Rastler, D.M.; "Distributed Generation: Competitive Threat or Opportunity?" Public Utilities Fortnightly, pp13. August 1996.

EER has seen significant interest in developing higher efficiency DPG systems for military applications and has demonstrated reforming of diesel fuel for Defense Advance Research Program Agency (DARPA). In fact initial financial investment in the technology is expected to come primarily from the military and far sighted government agencies. Government agencies' support for this technology is in recognition of the depletion of natural fuel resources and increased global environmental impacts resulting from energy production.

Mid-Term Market

Three potential markets exist for DPG in the mid-term. These include developing nations, specific domestic industrial and commercial applications and remote rural applications. According to a study by Southern California Edison (now Edison Capital) and the World Bank, the first major civilian market for distributed power systems will be in central Africa, with China and Southeast Asia following shortly thereafter. The market in North America will probably be small for at least a decade, except where distributed power provides advantages other than low cost (witness the slow market acceptance of the ONSI PC25, which cannot be explained solely by the high installed cost.)

It has been estimated that there are now 2 billion people in the world without access to electricity. These roughly 500 million households represent an initial market for 500 million kilowatts of installed electrical capacity. For each one percent of these households that are initially served by DPG, the market just for installed equipment is \$5.4 billion. The majority of this market is expected to be captured by distributed power. Of course, market penetration of fuel cell based technologies such as reforming will depend on commercial availability and its capabilities for fuel flexibility, reliability, and cost competitiveness. Much of the initial market in developing nations may be served by existing DPG systems that are established and have low initial capital costs. However, in regions with high fuel costs, the benefits of reforming power systems may secure a significant market share. Southern California Edison estimated that two percent of that market could be captured by fuel cell based DPG if the technology is ready. This represents \$11 billion in initial sales starting in 2004 or \$720 million annually assuming a 15-year equipment life span.

The second market includes domestic industrial and commercial applications that have high cogeneration heating demands, are in regions with high electricity rates and fuel costs, and in certain commercial sectors where high reliability and premium service will be valued highly enough to warrant the initial capital investment in DPG. DPG is likely to be used by medium to small-sized facilities to provide reliably high-quality power. In addition, DPGs have the potential to be used by utilities to assist in meeting peak demand and for standby "reliability" power. Fuel cell technologies can penetrate this market in environmentally sensitive areas and areas with high fuel costs. Further penetration of the market will depend on environmental drivers that are likely to generate long-term rather than mid-term markets.

The third mid-term market includes domestic remote and rural areas. When considering remote and rural areas, the electricity infrastructure does not always exist, is costly to

install and has high operating costs because of distribution power losses and infrastructure maintenance. Current central power generation and network distribution requires an expensive and often prohibitive capital outlay, raising the cost of electricity for everyone. DPG will allow providers to avoid or delay expensive capacity expansions and electricity supply can grow as the local demand increases. Fuel cell technologies are more likely to penetrate this remote and rural market where fuel costs are high. The reforming system has an advantage because the technology can be configured to operate on regional fuel supplies and on renewable energy sources such as landfill gas, methanol, and methane digester gas.

Long-term Market

Several issues favor the use of DPG in the short to long-term and these include the risk of large-scale power outages and the costs of expanding and maintaining infrastructure. Other issues, in the long-term, favor the development of environmentally friendly and efficient DPG and these include offsetting rising fuel costs, reducing environmental impacts and maintaining strategic fuel diversity options.

One of the main reasons for delay in immediate commercialization of PEM fuel cells is the lack of small-scale hydrogen production where it is needed. Installation of a hydrogen distribution system is costly and inefficient, hence the need for technologies such as reforming that can generate hydrogen locally from available fuels using, for example, the existing natural gas, gasoline, and diesel distribution infrastructure or even renewable landfill gas sites. Currently, there are no economically viable technologies that can generate hydrogen on-site from fossil fuels at the scales of interest (<2 MWe). However, the long-term prospect for fuel cells and related technologies is positive. The fuel cell and reformer costs are expected to be driven down by the intense development underway in the automotive industry, which is driven by the U.S. Environmental Protection Agency (EPA) regulations. This development will also reduce the cost of stationary power generators in the long-term.

The reforming technology market in the U.S. is expected to have initial penetration in high electrical cost and environmentally sensitive regions. A current analysis shows that nationally, the annual electricity market is 900×10^9 kWh and of this market, 260×10^9 kWh are in environmentally sensitive areas with high electricity costs, above 8 cents/kWh¹⁰. Also in the U.S., sites with base load power requirements of 10-200 kW such as small offices, hotels, and multifamily residential units, represent 45 percent of the electric power market. If we assume reforming/fuel cell technologies can address half of the environmentally sensitive, high electricity cost market and has a 10 percent market penetration, then the current U.S. market translates to at least 7,500 DPG units (assuming a 50 kWe size) with a projected sales revenue of over \$405 million in equipment costs.

¹⁰Source: Energy Information Administration, Form EIA-826, "Monthly Electric Utility Sales and Revenue Report with State Distributions." 1996.

The U.S. Energy Information Administration predicts 153×10^{12} kWh of additional domestic generation by 2010 for the industrial sector. An Interstate Natural Gas Association of America (INGAA) study has shown that DPG has the potential to meet 20 percent of additional power generating capacity in the U.S. over the next two decades. If 20 percent comes from DPG, DPG could account for 3.07×10^{11} kWh¹¹. Much of the industrial growth occurs in densely populated regions that provide the needed labor force but these regions have more strict environmental regulations and often higher fuel costs. Therefore a substantial portion of this market can be served by efficient fuel cell technologies. Even a modest one percent penetration of the DPG market represents 3×10^9 kWh annually across a range of DPG sizes. At an average industry electricity cost of 4 cents/kWh, the annual electricity market for fuel cell DPG can be over 120 million dollars.

3.8.2. Commercial Feasibility

Commercial feasibility requires a market and a mechanically viable technology. Many companies are developing PEM fuel cells for automotive and stationary applications and are developing the reforming technologies to make PEM fuel cells possible. EER is developing a promising novel steam reforming technology that demonstrates high efficiency at small scale. Compared with other reforming technologies, EER's technology is capable of achieving efficiencies comparable with even large scale reforming while most reforming technologies at small scale are being developed for the automotive applications where efficiency targets are low. Unmixed Reforming is capable of significant market penetration in the stationary DPG market provided it is economical and mechanically feasible to build and operate. This section describes the mechanical and economic feasibility of the technology and discusses the implications of other market and technology drivers.

3.8.3. Mechanical Feasibility

EER has demonstrated the reforming technology in a pilot-scale reformer and developed the methodology for operation and control. The technology faces two major challenges. First, the catalyst life must be improved to decrease operating and maintenance (O&M) costs. Currently the catalyst life is about 1000 hours while 2000 hours is a desired economic life, and any increase in life beyond 2000 hours will relate to increased consumer acceptability. The second issue involves the manufacturing cost and maintenance of the reforming system components. For the capital cost to be acceptable, durable low cost mass produced components are preferred. Here EER is looking to the automotive and refrigeration technologies, which utilize similar components. EER expects that very few new components will be specifically developed for commercialization of reforming.

¹¹Hennagir T.; "Distributed Generation Hits Market." Power Engineering, pp 19. October 1997.

In terms of the interface with end-users, the power system would be an enclosed unit of small footprint and weight. The unit is potentially capable of replacing commercial water heater footprints in commercial applications and will provide both the electricity and hot water needs. Noise would be limited to compressor operation, which can be effectively soundproofed to below 65 dB. The reactor's heat recovery and insulation provide low surface temperatures that would be further shielded by the enclosure. The low pressure system means that the system is safe for building applications. The utility input requirements include water and fuel feed similar to those of water heaters. The byproducts include excess water that can be drained and vitiated air that can be vented through existing water heating vents.

The technology, unlike internal combustion engines, has low complexity and very few moving parts except for process valves. This will translate into longer equipment life than internal combustion engines and 15-year life spans can be achieved readily. The lower complexity will also mean that reforming can demonstrate greater reliability and lower maintenance. O&M requirements will likely include periodic catalyst recharging and longer term (2-5 years) component maintenance for pumps, valves, etc.

3.8.4. Economic Feasibility

DPG based on EER's fuel processor and Plug Power's PEM fuel cell can generate power (electric) at 35 percent efficiency and heat at 50 percent efficiency leading to a total system efficiency of 85 percent. If central power generation is used, power and heat are generated separately at efficiencies of 40 percent and 90 percent respectively. This implies that a net fuel savings of 29 percent can be achieved when the proposed DPG technology is used instead of central power generation.

The economics of DPG will be determined by a large number of factors. However, for fuel cell-based DPG, three factors will always dominate the cost of electricity production. These are levelized capital costs, O&M costs and fuel costs. Maintaining low fuel costs for fuel cell operation means providing high efficiency conversion of the original fuel to fuel cell grade hydrogen. An advantage of the reforming technology is that it is suited to various liquid and gaseous fuels, which can lower fuel costs. The reforming process is at heart a steam reforming process and it is estimated that conversion efficiencies as high as 77 percent will be achieved. Table 12 shows estimated large scale production (5,000 units/yr) capital costs of \$216 per kWe for the fuel processor system and \$1,080 per kWe for the complete power system. Due to the early stage of development, the reforming fuel processor costs were estimated based on similar industrial ammonia based refrigeration system costs. Costs for PEM fuel cells are based on vendor's projected costs for mass production once the units are commercially available.

Baseline electricity costs using reforming with PEM fuel cells are also shown in Table 12. The costs were levelized over 15 years with a 3.5 percent inflation rate. The costs shown in Table 12 indicate that the reforming and PEM fuel cell technology can be competitive with current electrical production costs. Fixed electricity costs to residential consumers are on the order of 8 cents/kWh and include hard costs for infrastructure while incremental costs are 4.4 cents/kWh and are associated with less tangible costs such as

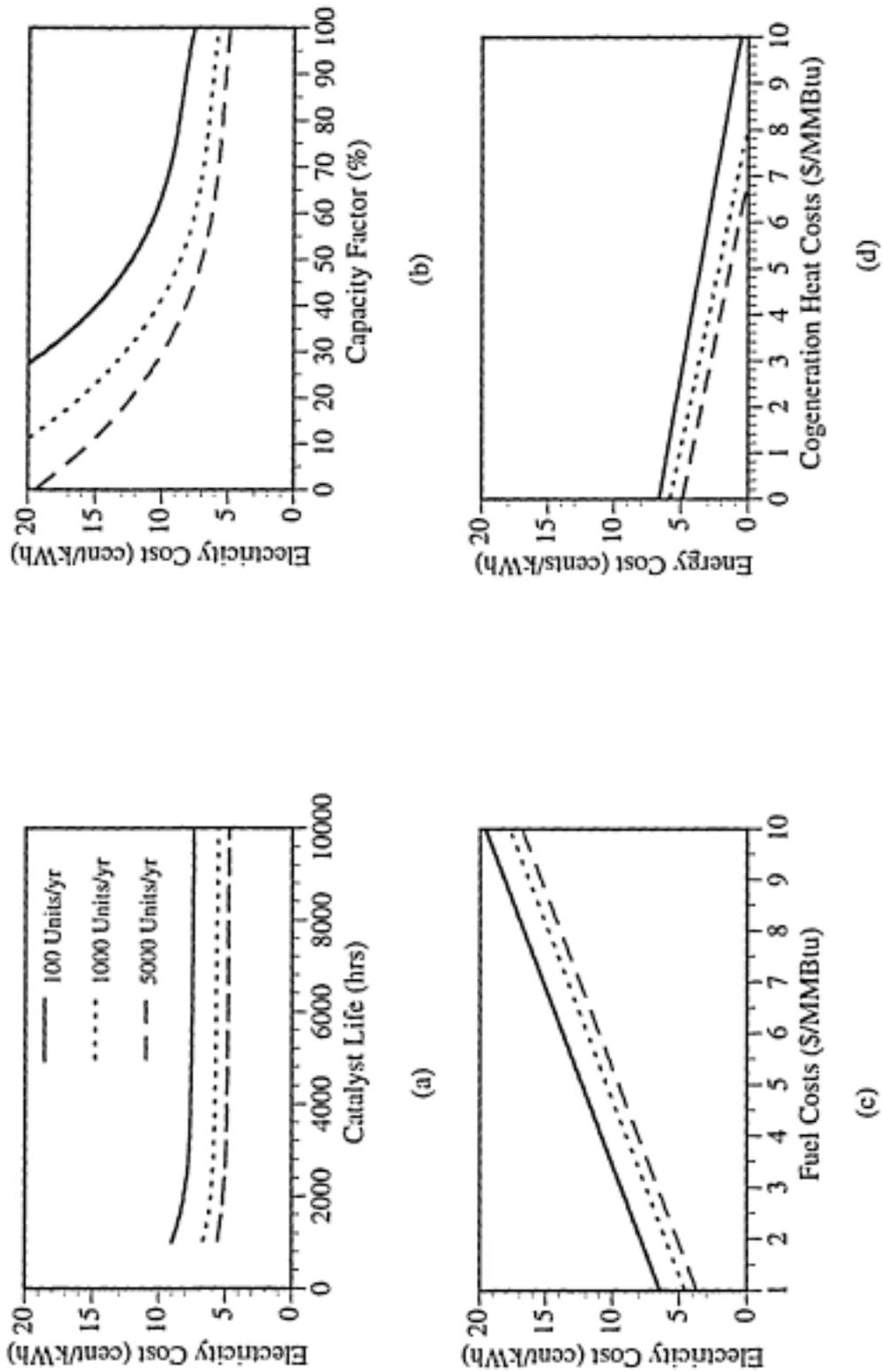
those for fuel price fluctuations¹². For a utility to cost effectively add additional power generators to their existing infrastructure, it must have electricity generation costs on the order of 4.4 cents/kWh. Table 12 shows that reforming can better the incremental costs for base load applications (100 percent capacity factor). These costs assume a 4,000 hour catalyst life span, a projected 37 percent electrical efficiency based on higher heating value, a favorable \$1.82 per MMBtu fuel cost and a \$6 per MMBtu cogeneration heat credit. The use of cogenerated heat can substantially lower total energy costs to the consumer. The lower value for the total electricity incremental cost, shown in Table 12, assumes 100 percent usage of the available cogeneration heat and the higher value assumes no cogeneration usage. The table indicates that reforming can better the current incremental costs for buildings with cogeneration needs even at a modest production capacity of 1000 units per year. Since the technology is still several years from commercialization, these costs represent a preliminary economic estimate that shows the capability of the technology to maintain ratepayer electricity costs, while improving environmental benefits.

Impact of Catalyst Lifetime, System Capacity , Fuel Cost and Electrical Efficiency on reforming Baseline Electricity Cost

Figure 20 presents a cost sensitivity analysis of (a) catalyst life span, (b) annual capacity factor, and (c) fuel cost impacts on baseline electricity costs. The last plot (d) illustrates the total energy cost (electricity cost minus cogeneration heating costs) when factoring in the value of cogeneration heating credit assuming 100 percent cogeneration heat utilization.

¹²Conversation with representative of Edison Technology Solutions, 24 April 1998.

Figure 20. Impact of (A) Catalyst Life, (B) Capacity Factor and (C) Fuel Cost on reforming Power System Baseline Electricity Costs (Excludes Cogen Credit). The Impact of (D) Cogeneration Credit on Total Energy Cost



The baseline electricity and total energy costs were presented in Table 12. The baseline conditions highlighted in each of the figures are: catalyst life 4,000 hours; capacity factor 100 percent; fuel cost \$1.82/MMBtu and for Figure 20(d) a cogeneration heat value of \$6/MMBtu. Development of a catalyst for reforming with lifetimes two times the current experimentally determined levels (2,000 hours) can substantially impact both system reliability and O&M costs (Figure 20(a)). Catalyst life increases above 2,000 hours will be most noticed in terms of plant reliability and customer satisfaction.

Figure 20(b) illustrates the impact of operating capacity factor on electricity cost. As with most technologies, operating at high capacity is important for recovering capital investment. However, these levelized costs do not reflect the potential life span increases of units operated at lower capacity. Ideally, the initial market for this technology will be base load applications with capacity factors over 70 percent. As the technology matures, the power system may be suited to distributed residential applications that have lower capacity factors. Figure 20(c) shows the effect of primary fuel costs on the cost of electricity production. For high fuel cost applications, catalyst life and O&M costs become a less significant portion of the total cost. However, at utilities' current fuel rates of about \$1.82/MMBtu for natural gas, reducing maintenance costs can have a significant impact on electricity costs. At \$6/MMBtu, which is the current cost of residential natural gas, the electricity costs are less competitive. This will be one factor that may keep DPG under electricity provider control rather than control of the individual end-users. The last plot (d) in Figure 20, shows the impact of cogeneration water heating costs on total energy cost. Total energy cost is the electricity cost minus the cost of cogenerated hot water. A baseline cost of \$6/MMBtu generates a significant credit to the electricity cost and reduces the energy cost to very competitive levels even if natural gas prices are higher than the favorable industry rate of \$1.82/MMBtu.

EER projects that the proposed DPG system will be cost competitive in the 2-300 kW (kW of electric power) size range. The goal to achieve net electrical system efficiencies of 35 percent is easily exceeded. The total system efficiency, which includes the recoverable cogeneration heat, can be as high as 83 to 88 percent. The engineering analysis also indicates that the system can operate cyclically with turndown as low as 10 percent of the design electric power output with a nominal increase in electric production efficiency. However, under reduced load operation the system will incur a substantial increase in levelized electricity cost (expressed as \$/kWh) due to the impact of fixed installed capital costs.

3.8.5. Market and Technology Drivers

The reforming technology appears to meet the mechanical and economic feasibility requirements for commercialization. The actual acceptance of the technology and capture of market share is likely to improve with further drivers such as material advances, stricter environmental regulations, rising fuel costs, along with market expansion and remote area development.

It is increasingly likely with utility deregulation that many smaller utility providers will continue to supply electricity to consumers rather than consumers being directly responsible for the purchase, operation and maintenance of their own systems. The consumer's prevailing attitude is that they don't want to know where the electricity comes from; just that it's there when they need it. Therefore it may be reasonable to assume that the utility providers will continue to obtain favorable fuel rates. However, for remote applications fuel costs are the most significant cost of electricity, and in these applications, which includes much of the developing nations, higher efficiency can mean significantly lower fuel costs. For fuel costs at \$10/MMBtu, an efficiency increase from 25-36 percent can lower electricity costs 40 percent and provide a return on investment in 3 years. A 5-year return on investment can be realized with fuel costs at \$6/MMBtu. The current low fuel costs in the U.S. may be one barrier to rapid emergence of DPG in small residential and commercial sectors.

On the other hand, environmental drivers are more likely to lead the push to higher efficiency systems. There is a growing concern about global warming as a result of the world's increased energy consumption during this century. This has prompted agreements by individual nations to reduce greenhouse gas emissions back to 1990 levels by the year 2010, even while population and industry are growing at historic levels. This plainly means higher efficiency and reduced consumption are necessary.

Unmixed reforming can compete effectively with other DPG systems and show short-term payback in regions where fuel costs are high. Therefore reforming markets in developing nations and remote U.S. regions will exist. The U.S. domestic market will be much more challenging to enter. Here, regulatory and fuel cost pressures are key to market penetration and this is likely only in the long-term (10-20 years).

3.8.6. Other Technical Results

In addition to the results described above, several other findings have contributed to the goal of the project to develop a database of catalyst performance and identify operational limitations. These include the identification of the optimum steam to carbon ratio for the fuel regeneration step, an assessment of EER's capability to manufacture absorbers, insight into the use of promoters to enhance catalyst performance, and an overall increase in process understanding.

During bench-scale testing, observations of catalyst behavior led to a brief study of the effect of steam to carbon ratio on the fuel regeneration step. Previous tests on the pilot facility were conducted without steam during fuel regeneration, but bench-scale testing showed that there was significant potential for coking in the absence of steam. Testing

showed that a steam to carbon ratio of 1 was sufficient to prevent coking during the fuel regeneration step. This information was used to modify the operation of the pilot test facility to enhance performance during the fuel regeneration step.

Testing conducted on absorber materials has identified new methods for manufacture of absorbers using durable substrates. The material development conducted as part of this project verified that the deposition of calcium carbonate on durable substrates produces effective absorbers. Additional development is needed to enhance the absorber capacities to those appropriate for the reforming process.

The identification of a durable catalyst was a significant discovery for this project. This was made possible by the application of promoters that inhibited undesirable reactions. While the efforts to date have not exhausted or even scratched the surface of all possible catalyst enhancement techniques, the relatively significant improvement made with this experimental catalyst is a positive indication of future potential. EER is currently planning additional catalyst development utilizing sophisticated combinatorial chemistry methods to systematically enhance the catalysts prepared with durable substrates.

The testing conducted to date has provided detailed information on the behavior of the reforming system. Because of the flexibility of the bench-scale system, it was easy to conduct brief parametric tests on the effect of steam to carbon ratio, regeneration step time, nitrogen and hydrogen dilution, etc. These tests have provided insight into the reforming catalytic process, and have guided modifications of the pilot test facility. In addition, calculation methods used to analyze bench-scale testing data have been adapted as a benchmark for reforming performance assessments.

4.0 Conclusions and Recommendations

4.1. Conclusions

In addition to the results described above, several other findings have contributed to the goal of the project to develop a database of catalyst performance and identify operational limitations. These include the identification of the optimum steam to carbon ratio for the fuel regeneration step, an assessment of EER's capability to manufacture absorbers, insight into the use of promoters to enhance catalyst performance, and an overall increase in process understanding.

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4.2. Benefits to California if Technology were Commercialized

4.2.1. Air Quality Impacts

The reforming process, when combined with fuel cell technology, and with complete system integration, is estimated to produce total pollutant emissions at least 50 percent lower on average than the best technology for centralized electric power generation.

This emissions level is perhaps an order of magnitude lower than the best anticipated alternative for distributed power generation (DPG). The reforming technology is capable of essentially zero NO_x emissions, very low CO emissions (< 10 ppm), and very low total organic emissions (other than CH₄). Although CH₄ emissions (< 50 ppm @ 7 percent O₂) represent an incremental increase in greenhouse emissions, the total greenhouse gas emissions can be reduced due to the higher system efficiencies achieved with DPG

4.2.2. Energy Savings Due to Increased Efficiency

The annual electricity market in California across all sectors is 20.5 billion dollars with an average electricity cost of 9.3 cents/kWh¹³. If the reforming technology was used to accommodate growth for target applications in California, it could reduce costly infrastructure improvements and provide a relatively inexpensive source of electricity estimated at 4 cents/kWh. When combined with modest infrastructure maintenance costs to ensure electricity service or to provide peak demand and with distribution and administration costs, the final electricity cost for expanding capacity could be reduced by 3 cents/kWh from current levels of 9.3 cents/kWh in California. If this technology were to address 2.5 percent of the California market, this would result in an average California ratepayer savings of 165 million dollars annually.

4.2.3. Landfill Space Conserved

The reforming technology generates no solid wastes other than spent catalyst and absorber materials. The purpose of this project was to increase the lifetime of the catalyst materials so that they would be replaced less frequently. Current development has increased the lifetime from monthly replacement to approximately every six months. Catalyst metals would be recovered, and only the spent substrates would be placed in a landfill. This project may serve to further conserve landfill space for disposal of spent catalyst.

4.2.4. Water Quality Impacts

The reforming process is not expected to have a significant impact on water quality. The reforming process uses water to produce hydrogen. Most of the unutilized water from the process is recycled or filtered to remove particulates, resulting in low volumes of relatively clean water for disposal.

4.2.5. California Employment Impacts

Commercialization of the reforming technology will create jobs in the manufacturing industry. Many of these jobs are expected to be created in California. In addition, the continuing development and licensing of this technology will be performed by EER, a California-based company.

¹³ Source: Energy Information Administration, Form EIA-826, "Monthly Electric Utility Sales and Revenue Report with State Distributions."

The manufacture, sales, export and maintenance of these DPG systems is estimated to generate several thousand jobs ranging from medium to high quality. Additionally, the increased jobs and equipment sales will increase wage and sales tax revenue to the state. Nationally, the electricity market is 900×10^9 kWh and of this market, 260×10^9 kWh are in environmentally sensitive areas with high electricity costs, above 8 cents/kWh¹⁴. If we assume this technology addresses 50 percent of the market and has a 10 percent market penetration, the total market translates to 7,500 units per year (assuming a 50 kWe size). This would provide sales revenues of 405 million dollars and potential state sales tax revenues of 30 million dollars. If half the cost of production/distribution is for wages averaging \$35,000, then this market represents an employment expansion of 5,700 jobs.

In addition to the direct electricity market job sector, job creation is also likely in fields of distributed and mobile hydrogen production for automotive applications. In the future, a hydrogen-based economy may exist which would drastically shift the current work force.

4.2.6. Other Benefits

Other less tangible economic benefits to California may arise out of reduced environmental impacts that 1) reduce health costs and 2) reduce ecological restoration costs.

In future development, the reforming system could be adapted for the processing of renewable fuels. Very little market currently exists for processing of renewable fuels such as landfill gas. However, the development of the reforming technology for multi-fuel use that includes renewable fuels expands the potential market to include environmentally sensitive areas and areas where natural fuel resources are scarce. Once a potential use is established for these renewable fuels, Californians can expect to reap benefits in both waste management and energy production.

It has been estimated that there are now two billion people in the world without access to electricity. These roughly 500 million households represent an initial market for 500 million kilowatts of installed electricity capacity. For each one percent of these households that are initially served by DPG, this market represents \$5.4 billion just for installed equipment. If the technology is made available soon enough, the majority of this market is expected to be captured by distributed power. If this market is effectively penetrated by fuel cell technology, then EER's reforming technology stands to capture two percent of the total market value. As a company based in California, EER's gains would then be contributing substantially to the state economy.

¹⁴ Source: Energy Information Administration, Form EIA-826, "Monthly Electric Utility Sales and Revenue Report with State Distributions."

4.3. Recommendations

4.3.1. Next Steps for Commercialization

Work performed on the prototype reactor and pilot test facility to date has identified some of the next steps for commercialization. These include reconfiguration and testing of the pilot test facility, development of absorber materials, and further catalyst development and lifetime testing. Future steps will include the development of a first generation fully integrated system. To eliminate CO poisoning issues for PEM fuel cells, a cost-effective and robust CO clean-up system, such as a reforming-based technology EER is developing, will be needed. A preliminary estimate of the amount of funds required for commercialization of the Unmixed Reforming process is provided in this section.

The continued development of the pilot test facility is a step toward commercialization. The pilot test facility was designed to allow component-by-component evaluation and independent process optimization while still demonstrating self-sustaining thermally efficient power generation. Thus, use of the pilot test facility makes it possible to address some of the issues related to integration of the components into one system. EER is currently reconfiguring the pilot unit to increase steam production, minimize bypassing in the reactor, and increase hydrogen production capacity.

Another area identified for targeted resource development is the further development of CO₂ absorber materials to enhance the commercial readiness of the process. Development that focuses on the need for increased CO₂ acceptor concentrations on more durable substrates provides the benefit of reduced absorber replacement costs over the lifetime of the system.

The encouraging results of this project with regard to identification of a durable catalyst suggests that continuation of catalyst development and lifetime testing will provide additional benefits for commercialization. Catalyst development may include optimization of the catalyst composition to further improve catalyst activity and prevent catalyst deactivation. This may allow the reforming process to run more efficiently and/or at higher capacities.

The measurement of catalyst activity and durability may be more accurately gauged by conducting actual lifetime tests to compare with the results of accelerated durability tests. Catalyst and absorber development that focuses on meeting a goal of 30,000-hour lifetimes in the long-term may offer additional commercialization benefits in terms of reduced catalyst replacement costs over the lifetime of the system.

EER expects that a first generation prototype of the fully integrated reforming/fuel cell power plant with cogeneration capabilities will follow successful demonstration of the pilot test facility. Demonstration of this prototype system will be another important step toward commercialization. Since the prototype will not be designed for component-by-component analysis, several heat loss and material stress concerns will be eliminated. The prototype system will then address manufacturing and value engineering issues which, integrated into the prototype design, can have a significant impact on the

manufacturing cost of the system. The detailed prototype system design will provide a more clear assessment of both market entry and potential.

An important component of the integrated system is the CO clean-up system. Several technologies are available or in development. EER has proposed a method to reduce the CO levels in the hydrogen product gas to 10 ppm, as currently required for fuel cell operation. This component is currently being developed under a parallel program with the South Coast Air Quality Management District (SCAQMD) and the DOE.

Technical issues related to PEM fuel cells that could enhance commercialization readiness include easing the restrictions on the composition of the hydrogen feed. Current restrictions require a number of gas polishing steps prior to the fuel cell. Increasing the fuel tolerance for CO would lower the cost of the fuel processor.

The investment threshold to launch the commercial product has been estimated to be on the order of \$100 million. EER estimates that this includes an initial \$10 million to reach the point of preproduction prototype. An additional investment of about \$90 million in capital would then be needed to develop the necessary production facilities and tooling to handle the estimated initial production demand of 100,000 units per year.

It should be recognized that these figures are ballpark estimates provided by EER and EER's partners in the overall development program. Since the technology is still at least four years from commercial entry (PEM fuel cells are still several years away by most estimates) there is not enough information on either the hardware or the process to develop more accurate estimates for the investment threshold to production.

4.3.2. Commercialization Challenges and Recommendations

The commercialization challenges facing the reforming technology likely involve market factors and the tandem development of both reforming and fuel cell technologies.

In terms of market acceptance, the reformer technology has value-added features such as low emissions and superior reliability that make it more attractive than other distributed power sources. It is important to identify the markets where the environmental and reliability benefits are drivers for commercialization. Environmental subsidies in environmentally sensitive areas may provide the impetus for adoption of these systems over other competing technologies.

Another key challenge is the tandem development of both the reformer and fuel cell technologies. One of the key challenges to commercialization of the fuel cell technologies is the lack of an economical hydrogen distribution system, while on the other hand, the lack of economical fuel cell systems will inhibit commercialization of distributed hydrogen production. EER has worked closely with PEM fuel cell developers such as Ballard and Plug Power to push both reforming technology and fuel cell technology development in tandem. EER's reforming technology is much more efficient and is cleaner than competing technologies such as partial oxidation. However, the technologies that are ready for commercialization when fuel cells are ready will have the greatest potential for market penetration.

Other technical and economic challenges for reforming commercialization are related to fuel cell capabilities and cost. Recently, great advances have been made in fuel cell development. Outside of the transportation market, economic investment has come primarily from government sources, while private investment capital is still targeted to traditional electrical generation systems. However, as investments in the automotive market, such as those of Daimler Benz and Ford Motor Company, begin to take hold, the resulting economies of scale and mass production are expected to transition to the distributed power generation market.

Recommendations for future work to address the commercialization challenges and take the next steps for reforming commercialization include continued development of materials, hardware, and manufacturing designs as well as identifying government and industry sources of support.

The progress made in catalyst and absorber development in this project has been substantial, and has laid the groundwork for optimization of the catalyst and absorber compositions using methods such as combinatorial chemistry. Additional development of catalyst and absorber materials is recommended because it has great potential to significantly improve the commercial viability of the process. Development of hardware components is also recommended to reduce the cost of the system. Finally, the technology will require prototype development based on manufacturing and value engineering to optimize form and function.

4.3.3. Recommendations

Recommendations for future work to address the commercialization challenges and take the next steps for reforming commercialization include continued development of materials, hardware, and manufacturing designs as well as identifying government and industry sources of support.

Additional development of catalyst and absorber materials is recommended because it has great potential to significantly improve the commercial viability of the process. Development of hardware components is also recommended to reduce the cost of the system. Finally, the technology will require prototype development based on manufacturing and value engineering to optimize form and function.

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5.0 Glossary

Accelerated Durability Tests	Tests in which cyclic stresses are placed on a catalyst through rapid regeneration and reforming steps to predict the catalyst's useful lifetime
Air Regeneration Step	The introduction of air into the reactor to generate heat by the exothermic reaction of the O ₂ in the air with the Ni catalyst to form NiO
Al₂O₃; Alumina	Aluminum oxide; used as a catalyst support/substrate
Autothermal	Pertaining to a process in which sufficient energy is generated by chemical reactions in the system so that energy is not required to be added to the system
Ca	Calcium
CaCO₃	Calcium carbonate; the product of the absorption of CO ₂ by CaO; the addition of sufficient heat to CaCO ₃ results in its decomposition into CaO and CO ₂
CaO	Calcium oxide; the CO ₂ absorbing material
Catalyst	A substance that hastens a chemical reaction or reduces the reaction's energy requirements without being consumed
CEMS	Continuous emissions monitoring system
Central power generation	The generation of electrical power through several power generation facilities none of which are dedicated to a specific geographic area, but rather are part of a power generation network dedicated to a large geographical area
CH₄	Methane; the major component of natural gas
Chemical energy	Energy that is stored in a substance's internal bonds and is released when that substance participates in a chemical reaction
CO	Carbon monoxide; a product of reforming that is undesirable because of its negative effects on fuel cells
CO₂	Carbon dioxide; a desired product of reforming that is absorbed by CaO forming CaCO ₃
CO₂ absorber	A substance containing calcium CaO that reacts with CO ₂ to form CaCO ₃
Cogeneration	Pertaining to the simultaneous production of electricity and useful thermal energy
Conversion	The transformation of one or more substances into one or more substances through a chemical reaction

DARPA	Defense Advance Research Program Agency
DAS	Data acquisition system
Distributed power generation (DPG)	The generation of electrical power through several power generation facilities each of which is dedicated to its own geographic region
DOE	Department of Energy
EER	Energy and Environmental Research
EPA	Environmental Protection Agency
Endothermic	Pertaining to a chemical reaction which absorbs heat, or requires the addition of heat
Exothermic	Pertaining to a chemical reaction which liberates heat
Fuel Cell	A battery-like energy source that uses hydrogen as its fuel
Fuel cell grade hydrogen	High-purity hydrogen suitable for use in fuel cells
Fuel Regeneration Step	The introduction of natural gas into the reactor to reduce the NiO to Ni for the following reforming step
GRI	Gas Research Institute
H₂	Hydrogen; the principal desired product of reforming; used as a fuel for fuel cells
INGAA	Interstate Natural Gas Association of America
Kinetics	Pertaining to the rate at which a chemical reaction occurs
KWe	The power of the electrical energy, in kilowatts, obtained from the fuel cell in the integrated fuel cell/reformer system
Levelized cost	The average cost over the lifetime of a facility, with future costs discounted by the time value of money
LHV	Lower heating value; a heating value associated with a fuel assuming that its combustion yields gaseous water (steam) as a product instead of liquid water
LOI	Loss on ignition
MMBtu	Million British thermal unit
MWe	Megawatts electricity
N₂	Nitrogen; a major component of air; used as a diluent of the natural gas feed and as a diluent of the product stream to the

	CEMS; used as a carrier gas during the CO ₂ absorber tests
Ni	Nickel; a reforming catalyst
NiO	Nickel (II) oxide; the product of air regeneration
NO_x	One or more of the oxides of nitrogen
O&M	Operating and Maintenance
O₂	Oxygen; a major component of air; reacts with Ni in an exothermic reaction to form NiO
Parametric Tests	Tests in which certain parameters are varied to determine if that parameter variation has effects
Parasitic Heat Losses	The unrecoverable loss of heat energy from a system
PEM	Polymer electrolyte membrane
ppm	Parts per million
Reactants	Substances that when heated, pressurized, and/or combined with other substances transform into other substances
Reactor	A container or vessel in which a chemical reaction takes place
Reforming Step	The introduction of steam and CH ₄ into the reactor resulting in the production of CO ₂ , CO and H ₂
SCAQMD	South Coast Air Quality Management District
Screening Tests	Tests conducted to eliminate unsuitable catalysts and absorbers from detailed testing
scfh	Standard cubic feet per hour
Substrate	A non-reactive substance with which a catalyst is integrated; a primary factor in substrate selection is its durability; also known as a support
Thermodynamics	Pertaining to transformations of energy from one form to another
Thermodynamic efficiency	A measure of the amount of energy retained by a system relative to the amount of energy put into the system
Unmixed Reforming	A cyclic process in which hydrogen is produced from natural gas and steam through a catalyst air regeneration step and an endothermic reforming step

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SCREENING TEST REPORT

APPENDIX II

PARAMETRIC TESTING REPORT

APPENDIX III

ACCELERATED DURABILITY TESTING REPORT

APPENDIX IV

PROTOTYPE REACTOR TESTING ON THE PILOT TEST FACILITY

APPENDIX I:

SCREENING TEST REPORT

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1.0 INTRODUCTION

Energy and Environmental Research (EER)'s Unmixed Reforming (UMR) process is unique in its use of reforming catalysts and carbon dioxide (CO₂) absorber materials. It is a cyclic process with two steps: reforming and regeneration. In the reforming step, the nickel (Ni) on the catalyst is reduced to its active catalytic state, hydrogen is produced, and the CO₂ produced by reforming reactions is absorbed. In the regeneration step, the Ni on the catalyst is oxidized and the previously absorbed CO₂ is released into the vent gases. The Ni on the catalyst must be repeatedly oxidized and reduced, in addition to having high activity for the reforming reactions. To our knowledge, there are currently no commercially available catalysts designed for these purposes since conventional steam reforming is a continuous process eliminating repeated catalyst oxidation.

The CO₂ absorber materials suitable for the UMR process are generally either naturally occurring minerals containing calcium (Ca) such as dolomite or materials prepared by depositing calcium carbonate on a substrate. The repeated absorption and desorption of CO₂ by the absorber material poses a unique challenge for UMR material selection. Dolomite undergoes a physical breakdown in the presence of the high temperature steam required for the UMR process, while the CO₂ absorbing capacity of substrates with calcium deposited on them is limited by the amount of calcium present that can be utilized for absorption.

Development of materials for the UMR process, sponsored by the California Energy Commission (CEC) PIER I Program, is intended to identify suitable materials for the UMR process. Catalyst and absorber material development was identified as an area in which advances could have a significant impact on the commercial viability of the process. The development of the reforming process is part of a broader program supported by the U.S. Department of Energy (DOE).

EER teamed with Phillips Petroleum to utilize their expertise in high-temperature catalytic processes to address the catalyst and absorber issues unique to the UMR process. EER also considered several commercial catalysts that, although not designed for the UMR process, may coincidentally be suitable.

EER built on the lessons learned in earlier UMR development efforts with commercial steam reforming catalysts to efficiently guide catalyst and absorber development. The selection of baseline operating conditions for the screening tests was simplified by earlier work that identified a reasonable set of operating conditions for the UMR process.

The approach taken to develop and identify suitable materials involves three steps: screening tests, parametric testing, and accelerated durability testing. This report presents the results of the screening tests.

The first step in materials development for the UMR process was screening of catalyst and absorber materials. These tests involved short-term testing of catalyst and absorber materials under a set of baseline operating conditions. The objective of the screening tests was to

eliminate unsuitable materials from more detailed testing and evaluation. Screening tests were designed to be brief evaluations of material performance under baseline UMR conditions.

2.0 CATALYST SCREENING SETUP

The screening tests were performed on the bench-scale UMR reactor system depicted in Figure 1. This system was designed to allow detailed characterization of catalyst/absorber performance during the UMR reforming and regeneration operating cycle.

The major system components are the reactant feed system, the reactor and the product gas process system. The reactor was situated in a controlled-temperature electric furnace. The reactor housed the packed bed of catalyst/absorber material. Water, natural gas and air were fed to the reactor, and the product gases from the reactor were analyzed by continuous emission monitoring system (CEMS) gas composition analyzers. Measurements were taken on the experimental system using an automated data acquisition system.

The UMR process is a cyclic process involving reforming and regeneration steps. During the reforming step, natural gas and steam were fed to the reactor in order to reduce the Ni and produce hydrogen via the reforming reaction. During the regeneration step, air was fed to the reactor. The oxidation of Ni by air increases the catalyst/absorber bed temperature and releases CO₂ from the CO₂ absorber material. The reforming and regeneration steps repeat in this manner.

2.1 Baseline Operating Conditions

A set of baseline experimental parameters was selected for the screening tests based on the DOE Phase I process development efforts that were supported by previous studies. The baseline parameters are presented in Table 1. From these experimental parameters, the baseline operating conditions for a selected catalyst were calculated following the method presented in the Test Plan¹. The baseline operating conditions are shown in Table 2. Tests run at these conditions provide a consistent basis for comparison of different catalyst/absorber materials.

TABLE 1. SELECTED BASELINE EXPERIMENTAL PARAMETERS FOR PRELIMINARY SCREENING TESTS

Ca:Ni Ratio (mol/mol)	Reforming Gas Hourly Space Velocity (GHSV) (h ⁻¹)	Regeneration O ₂ :Ni Ratio (mol/mol)	Reforming Steam to Carbon (S:C) Ratio (mol/mol)	Reactor Temperature (°C)
3	3500 and 5000	1	3	700

¹ A Novel Steam Reforming Reactor for Fuel Cell Distributed Power Generation: Test Plan, February 11, 1999.

TABLE 2. SAMPLE BASELINE OPERATING CONDITIONS FOR PRELIMINARY SCREENING TESTS

Cycle Time	Flow Rates		
	Natural Gas	Water	Air
10 min	2.9 scfh	3.1 ml/min	6.3 scfh

Initially a gas hourly space velocity (GHSV) of 5000 h⁻¹ was chosen. For certain catalysts this resulted in very high methane (CH₄) slip so a lower GHSV of 3500 h⁻¹ was subsequently used. The screening test results include operation at GHSV's of 3500 h⁻¹ and 5000 h⁻¹.

2.2 Calculations of Testing Results

The measurements taken during screening tests were used to calculate three performance indicators: % oxygen (O₂) consumed, % converted carbon absorbed, and % CH₄ conversion. These performance indicators are related to the performance of the catalyst and absorber during the regeneration and reforming steps as described below.

% O₂ Consumed

Oxygen consumption is measured as the difference between the amount of oxygen fed to the reactor and the amount of oxygen leaving the reactor during the air regeneration step. The % O₂ consumed is defined as:

$$\% \text{ O}_2 \text{ consumed} = \frac{\text{O}_2 \text{ fed [mol]} - \text{O}_2 \text{ exiting [mol]}}{\text{O}_2 \text{ fed [mol]}} \times 100\% \quad (1)$$

The % O₂ consumed is calculated as:

$$\% \text{ O}_2 \text{ consumed} = \frac{0.21 \times F_{\text{REG}_f} [\text{mol/hr}] - \% \text{O}_{2v} \times F_{\text{REG}_v} [\text{mol/hr}]}{0.21 \times F_{\text{REG}_f} [\text{mol/hr}]} \times 100\% \quad (2)$$

Where:

F_{REG_f} is the molar flow rate of air fed during the regeneration step.

%O_{2v} is the average measured concentration of oxygen in the regeneration vent stream.

F_{REG_v} is the molar flow rate leaving the reactor during the regeneration step.

The % O₂ consumed is a measure of the amount of oxygen that reacts with the nickel on the catalyst to form nickel oxide. As oxygen is consumed, the packed bed is heated by the exothermic nickel oxidation process. Oxygen consumption indicates the amount of nickel that is participating in the oxidation and reduction cycle during the regeneration and reforming steps. This is useful in identifying materials that are able to maintain catalytic activity for reforming after cycling through the oxidized state.

% Converted Carbon Absorbed

The absorption capacity of the dolomite material is measured as the amount of CO₂ released in the regeneration step. The % converted carbon absorbed is defined as the percent of reacted CH₄ absorbed as CO₂, as follows

$$\% \text{ converted carbon absorbed} = \frac{\text{CO}_2 \text{ released in regeneration step [mol]}}{\text{reacted CH}_4 \text{ in reforming step [mol]}} \times 100\% \quad (3)$$

The % converted carbon absorbed is calculated as:

$$\% \text{ converted carbon absorbed} = \frac{F_{\text{CO}_{2\text{rel}}} \text{ [mol/hr]}}{F_{\text{NGREF}_f} \text{ [mol/hr]} - \text{AvgCH}_4\% \times F_{\text{REF}_p} \text{ [mol/hr]}} \times 100\% \quad (4)$$

Where:

$F_{\text{CO}_{2\text{rel}}}$ is the molar flow rate of CO₂ released during the regeneration step.

F_{NGREF_f} is the molar flow rate of natural gas fed during the reforming step.

AvgCH₄% is the average CH₄ mole percent in the product gas during the reforming step.

F_{REF_p} is the product flow rate during the reforming step.

The basis for carbon absorption is the moles of carbon fed during the reforming step that react to form carbon monoxide (CO) or CO₂. To decouple the impact of catalyst activity, the % converted carbon absorbed is based only on reacted CH₄.

% CH₄ Conversion

The CH₄ conversion is measured as the amount of CH₄ reacted. The % CH₄ conversion is defined as:

$$\% \text{ CH}_4 \text{ conversion} = \frac{\text{CH}_4\text{in [mol]} - \text{CH}_4\text{out [mol]}}{\text{CH}_4\text{in [mol]}} \times 100\% \quad (5)$$

The % CH₄ conversion is calculated as:

$$\% \text{ CH}_4 \text{ conversion} = \frac{F_{\text{NGREF}_f} \text{ [mol/hr]} - \text{AvgCH}_4\% * F_{\text{REF}_p} \text{ [mol/hr]}}{F_{\text{NGREF}_f} \text{ [mol/hr]}} \times 100\% \quad (6)$$

The % CH₄ conversion is an indication of the amount of natural gas fed that reacts to form products such as hydrogen, CO, and CO₂.

2.3 Data Quality

To effectively enhance our diagnostic capabilities, nitrogen diluent was added to the CH₄ analyzer sample gas. Catalysts that required significant dilution of the CH₄ analyzer sample are by definition poor performers. The catalyst activities, as represented by CH₄ conversion, were low. The uncertainty introduced by this procedure is significant; therefore the results are only qualitative.

3.0 CATALYSTS EVALUATED

Phillips Petroleum provided two sets of materials: catalysts P1 through P7, and P8 through P10. Substrate materials were sent by Phillips Petroleum early in the program, and EER used these materials to prepare catalysts P1 through P7. After these materials were tested, EER and Phillips Petroleum discussed results, and Phillips Petroleum conducted analyses of the spent catalysts. Based on the initial catalyst results, Phillips Petroleum prepared and sent catalysts P8 through P10.

In addition to the materials provided by Phillips Petroleum, several commercial steam reforming catalysts were screened. The commercial catalysts were obtained from several catalyst manufacturers. All were designed for continuous steam reforming, and not for the cyclic oxidation and reduction of the Ni catalyst. Commercial catalysts are known to contain proprietary blends of promoters to enhance performance. EER prepared catalyst E1 with a blend of promoters following guidelines obtained through literature review.

Table 3 lists all of the catalyst materials studied in this program, along with some of their characteristics. Catalysts P1, P2, and P5 were made with Ca as well as Ni. These materials were tested as absorbers as well as catalysts. A total of 18 catalysts were tested.

TABLE 3. SCREENING TEST CATALYST MATERIALS

Catalyst ID	% Ni	Substrate Type	Other
P1	14	Extrudate	8.5% Ca
P2	7	Extrudate	10.5% Ca
P3	9	Extrudate	
P4	15	Extrudate	
P5	13	Pellets	7% Ca
P6	10	Pellets	
P7	12	Pellets	
P8	15	Pellets	
P9	15	Pellets	
P10	15	Pellets	Promoter
C1	13	Wheels	
C2	14	Pellets	
C3	12	Rings	
C4	14	Pellets	
C5	10	Pellets	
C6	14	Wheels	
C7	14	Crushed	
E1	14	Pellets	Various promoters

4.0 RESULTS OF CATALYST SCREENING TESTS

The primary evaluation criteria for the screening tests were the CH₄ conversion, O₂ consumed, and converted carbon absorbed. These criteria are performance indicators of the materials' suitability for the UMR process. The absorber used for screening tests was dolomite. Table 4 summarizes the test results for the materials screened.

TABLE 4. SELECTED RESULTS OF SCREENING TESTS

Material ID	% O ₂ Consumed	% CH ₄ Conversion	% Converted Carbon Absorbed	Reforming GHSV
P1 ^(a)	13	75	15	3500
P2 ^(a)	0.25	42	6	3500
P3	31	84	14	3500
P4	11	71	15	3500
P5	44	58	9	3500
P6	43	41	3	3500
P7 ^(a)	33	54	1	3500
P8 ^(a)	16	78	NA	5000
P9	39	85	NA	3500
P10	50	86	NA	3500
E1	12	94	NA	3500
C1	48	87	10	5000
C3	69	91	12	5000
C4	40	94	9	5000
C5 ^(a)	0	35	6	5000

^(a) Catalyst eliminated from further testing.

Detailed examination of the test data for these screening tests showed that there were significant differences in the concentration profiles obtained during testing of different catalysts. An effort was made to compare different materials and relate the behavior to catalyst characteristics. The relationship between CH₄ conversion and oxygen consumption can be explained by the oxidation state of the Ni on the catalyst. Only Ni in its reduced state is catalytically active and promotes the conversion of CH₄ to hydrogen. The oxygen consumed by Ni oxidation is proportional to the amount of Ni that was present in its reduced state at the end of the previous reforming step. If oxygen consumption is low, this indicates incomplete reduction of the Ni, suggesting the presence of Ni in an unreactive state.

Figure 2 presents the CH₄ concentrations for catalysts P3 and C4 during the UMR process cycle. As discussed above, the reduction of Ni is an important part of the reforming step. It was not uncommon for higher levels of CH₄ to be present in the product gas early in the reforming step, as very little Ni is in its active state for reforming. This situation generally improves with time as the system reaches a steady state between cycles. The concentration profiles shown in Figure 2 vary greatly in the amount of CH₄ breakthrough early in the reforming step. Catalyst C4 behaves more favorably, with only a minor peak of approximately 3% CH₄ during the fuel regeneration step, and quickly levels out around 2%. The CH₄ peak early in the reforming step

of catalyst P3 exceeds 12%, and again rises during the remainder of the reforming step from 3% to 7%, and peaks above 12%.

Figure 3 illustrates the relative performance of Phillips Petroleum catalysts P1 through P10. Of the original Phillips Petroleum materials, catalysts P3 and P5 showed the most promise. Catalysts P3 and P5 had the highest combination of CH₄ conversion and oxygen consumption. However, the oxygen consumption of catalyst P3 was relatively low, as was the CH₄ conversion of catalyst P5.

Catalysts P8, P9 and P10 were developed by Phillips Petroleum based on screening results of earlier catalysts. Figure 3 shows that these materials demonstrated improved CH₄ conversion. Catalyst P10 was especially promising, with its high oxygen consumption and low breakthrough of CH₄ at the beginning of the reforming step, as illustrated in Figure 4. This figure shows the CH₄ concentration profile for P10, along with those of catalysts P3 and C4. The level of CH₄ breakthrough is less than 2% at its peak. Catalyst P10 overcame a limitation that previous Phillips Petroleum catalysts such as catalyst P3 had demonstrated.

The combination of low oxygen consumption and low CH₄ conversion led to the elimination of catalysts P1, P2, P7, and P8 from further testing. The screening test results of select commercial catalysts and catalyst E1 are reported in Figure 5. All of the commercial catalysts had high CH₄ conversion, and high oxygen consumption, except for catalyst C5. Catalyst C3 had exceptionally high oxygen consumption. The EER-prepared catalyst E1 had very high conversion of CH₄, but very low oxygen consumption. Both catalysts C5 and E1 were found to be unsuitable for the UMR process and were eliminated from further testing. Catalyst E1 had very low oxygen consumption, and catalyst C5 had low oxygen consumption and CH₄ conversion.

5.0 ABSORBERS SCREENED

Separate tests were conducted to measure the CO₂ absorption capacities of various absorber materials. Phillips Petroleum provided absorbers that consisted of CaO supported on different thermally stable substrates. Some of the catalyst materials provided by Phillips Petroleum contained both Ni and CaO. These materials were screened separately for absorption capacity and UMR catalytic activity. Table 5 lists the absorber materials tested. Absorbers D1 and D2 were dolomite from different mines, one of which was received in a calcined state.

TABLE 5. SCREENING TEST ABSORBER MATERIALS

Absorber Materials	% Ca	Form	Other
D1	22	Crushed	
D2	22	Crushed	Calcined
PA1	8.5	Extrudate	14% Ni
PA2	10.5	Extrudate	7% Ni
PA3	8.5	Extrudate	
PA4	7	Pellets	
PA5	7	Pellets	13% Ni

6.0 ABSORBER TEST SETUP

The CO₂ absorption tests were performed by placing a known mass of absorber into a plug flow reactor located inside a controlled-temperature furnace. Pure CO₂ was passed over the absorber for several hours at room temperature. After allowing for saturation of the absorber materials, the flow of CO₂ was stopped, and pure nitrogen (carrier gas) was passed over the absorber bed. The temperature of the furnace was then slowly increased to cause the absorbed CO₂ to be released. The concentration of CO₂ in the gas exiting the reactor was recorded and the total amount of CO₂ released was determined.

7.0 ABSORBER SCREENING TEST RESULTS

The capacity of the materials to absorb CO₂ was used as a screening criterion. The UMR process requires high CO₂ absorption capacity as well as the ability to release the CO₂ in a specific temperature range. The absorber screening test was designed solely to measure the CO₂ absorption capacity of the materials. As seen in Table 5, the dolomite materials, D1 and D2 had higher Ca concentrations than the Phillips Petroleum absorbers.

The UMR process requires the use of an absorber that is efficient on a mass basis, as the reactor size is limited and the potential for bypassing of the Ni increases as the amount of absorber exceeds the amount of catalyst required. The presence of excessive amounts of absorber materials in the catalyst/absorber bed also has a negative impact on the heat transfer from Ni to Ca during the regeneration step, which affects the efficiency of CO₂ release.

On a molar basis, as shown in Figure 6, the dolomite materials (D1 and D2) had higher capacities than the Phillips Petroleum absorbers. Although the Phillips Petroleum absorbers are able to absorb CO₂, their low loadings and thus low capacities made them unsuitable for the UMR process at this time.

None of the Phillips Petroleum absorber materials were found to be promising for use in the UMR process. Absorber D1, commercial dolomite, was used for parametric testing. All of the other absorber materials were excluded from further testing due to their low absorption capacities.

8.0 EXCLUSION OF MATERIALS FROM PARAMETRIC TESTING

Only one commercial catalyst, C5, was excluded from further testing due to its low CH₄ conversion and oxygen consumption. It should be noted that some commercial catalysts were chosen for parametric testing without performing screening tests. These materials were catalysts C2, C6, and C7. Several of the Phillips Petroleum catalysts (catalysts P1, P2, P7, P8, and P9) were excluded from further testing due to a combination of low CH₄ conversion and oxygen consumption. The catalyst prepared by EER (catalyst E1) was excluded from further testing because of its low oxygen consumption. Absorber D1, the baseline commercial dolomite, was used for parametric testing. All of the other absorber materials were excluded from further testing due to their low CO₂ absorption capacities.

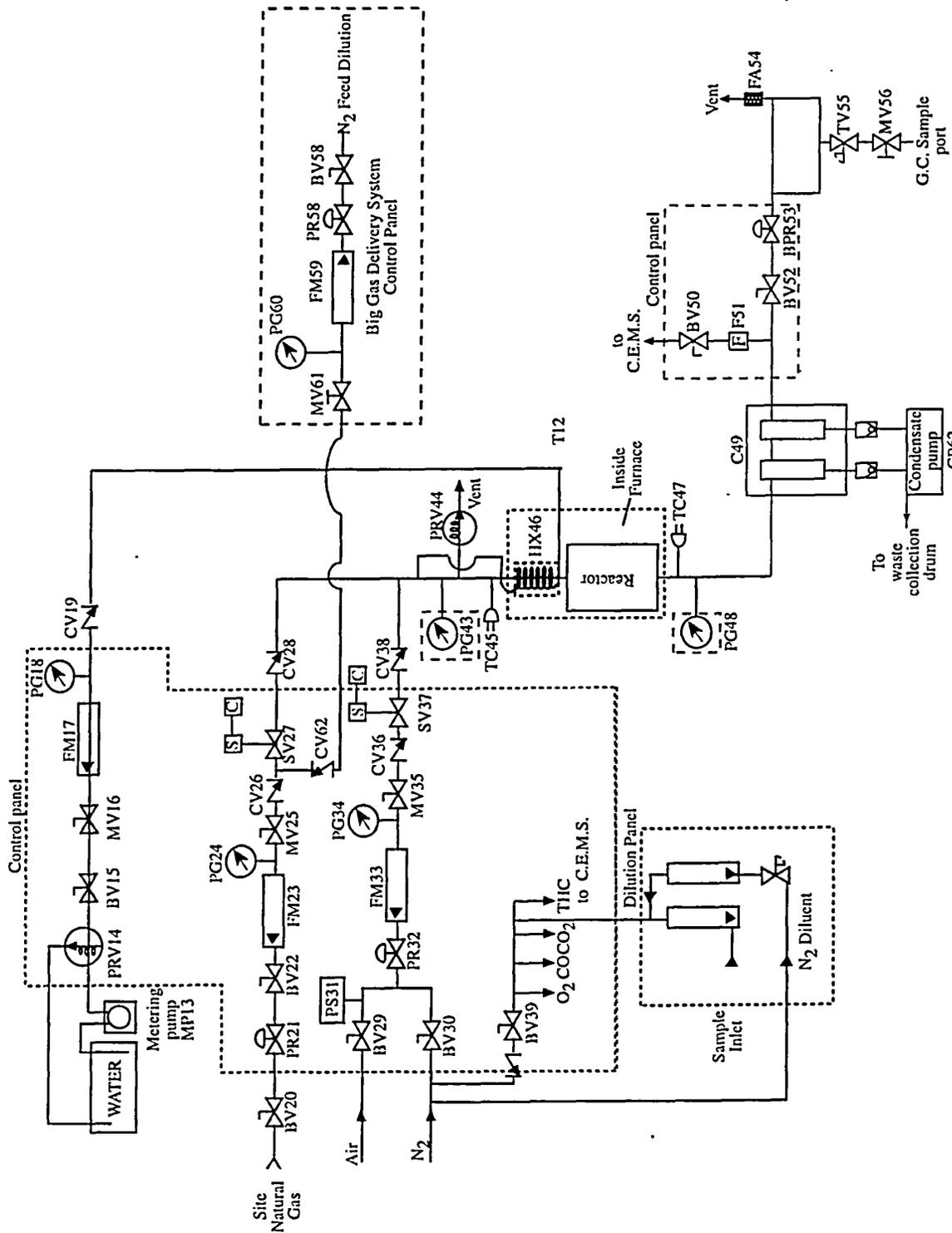


Figure 1. Bench-scale UMR experimental system.

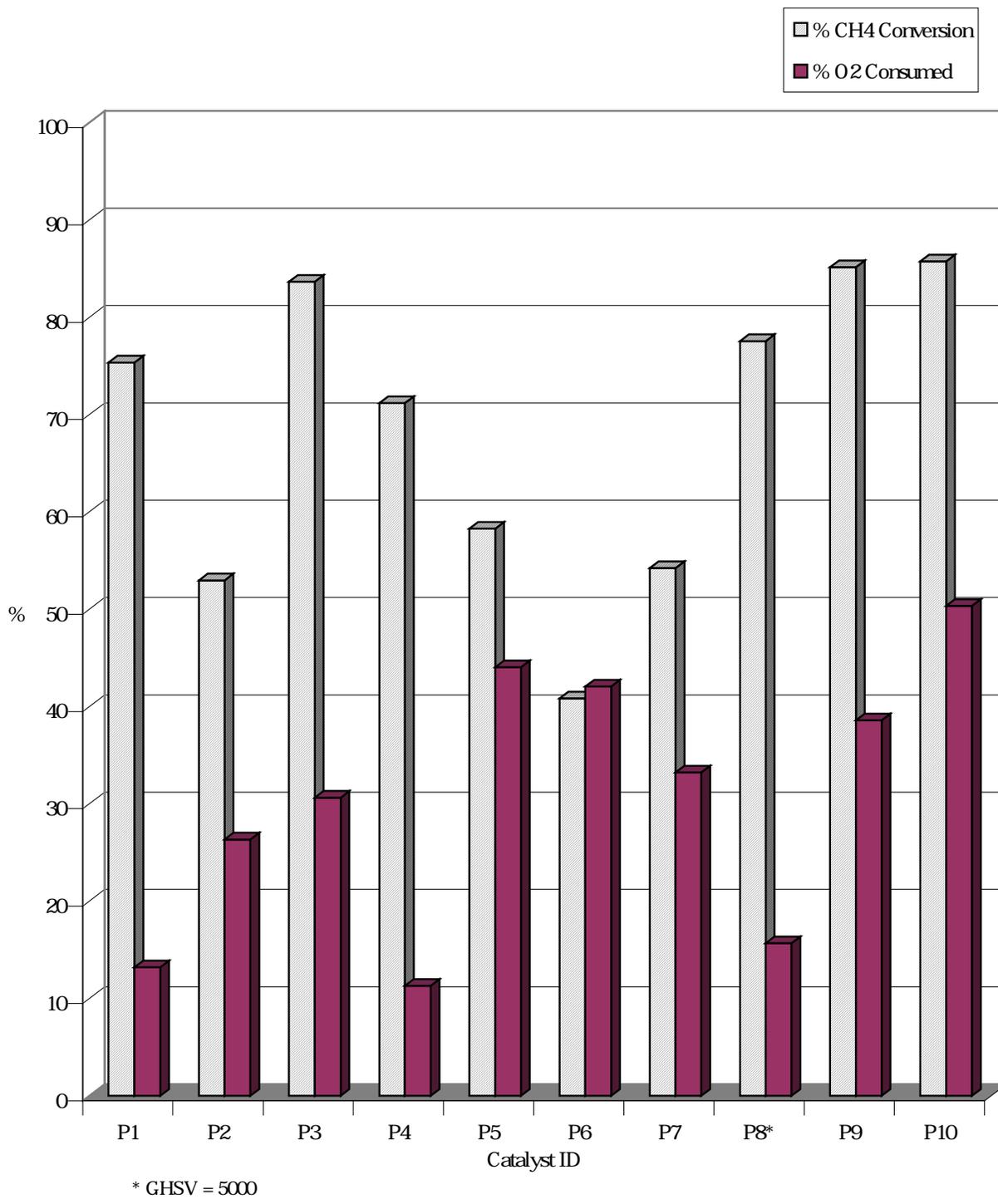


Figure 3. Screening test results for Phillips Petroleum catalysts.

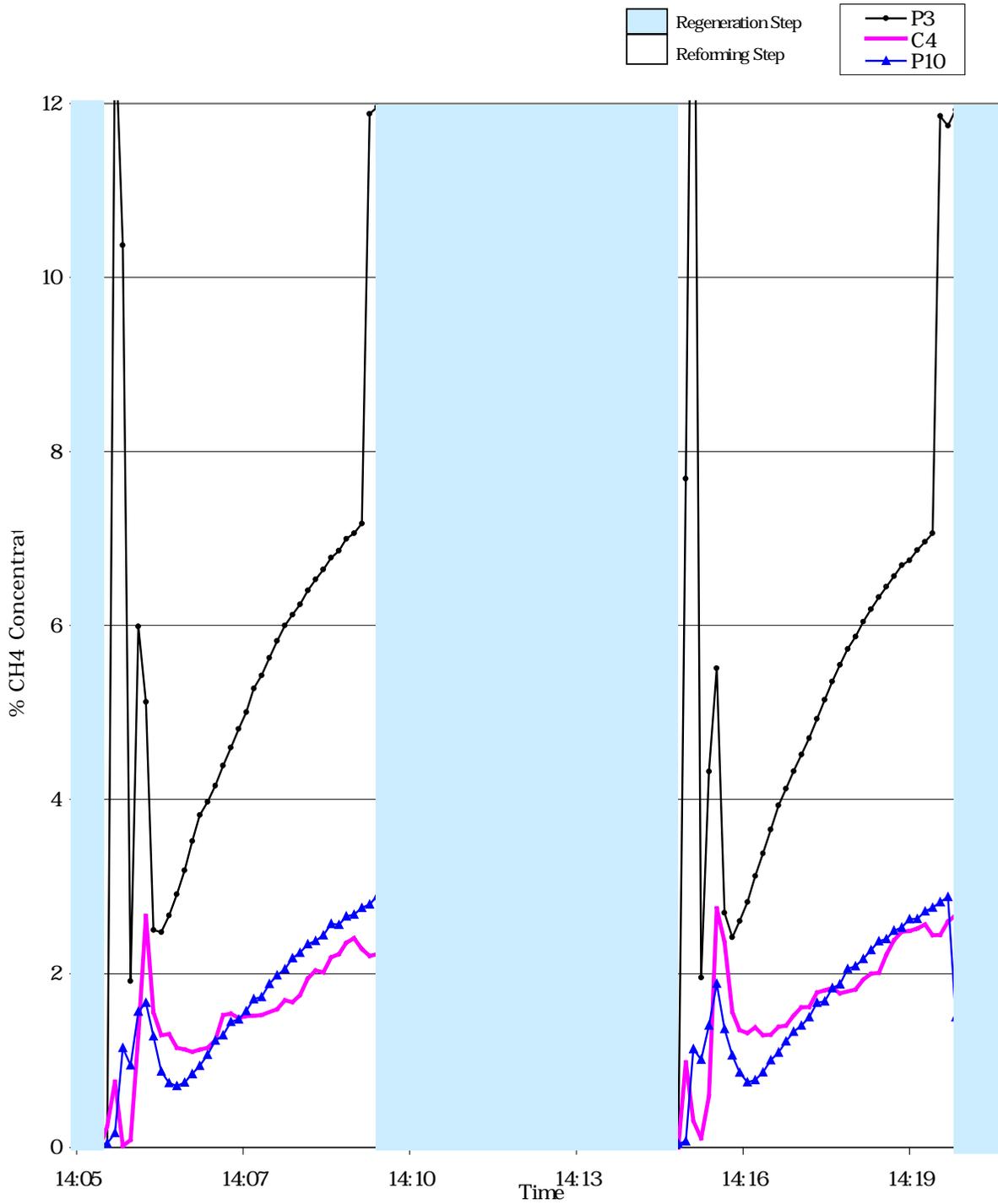


Figure 4. Illustration of the unreacted CH₄ levels exiting the reactor for catalysts P3, C4 and P10 during two reforming during the fuel regeneration process. Catalyst P10 demonstrates a significant improvement in the CH₄ conversion performance, n

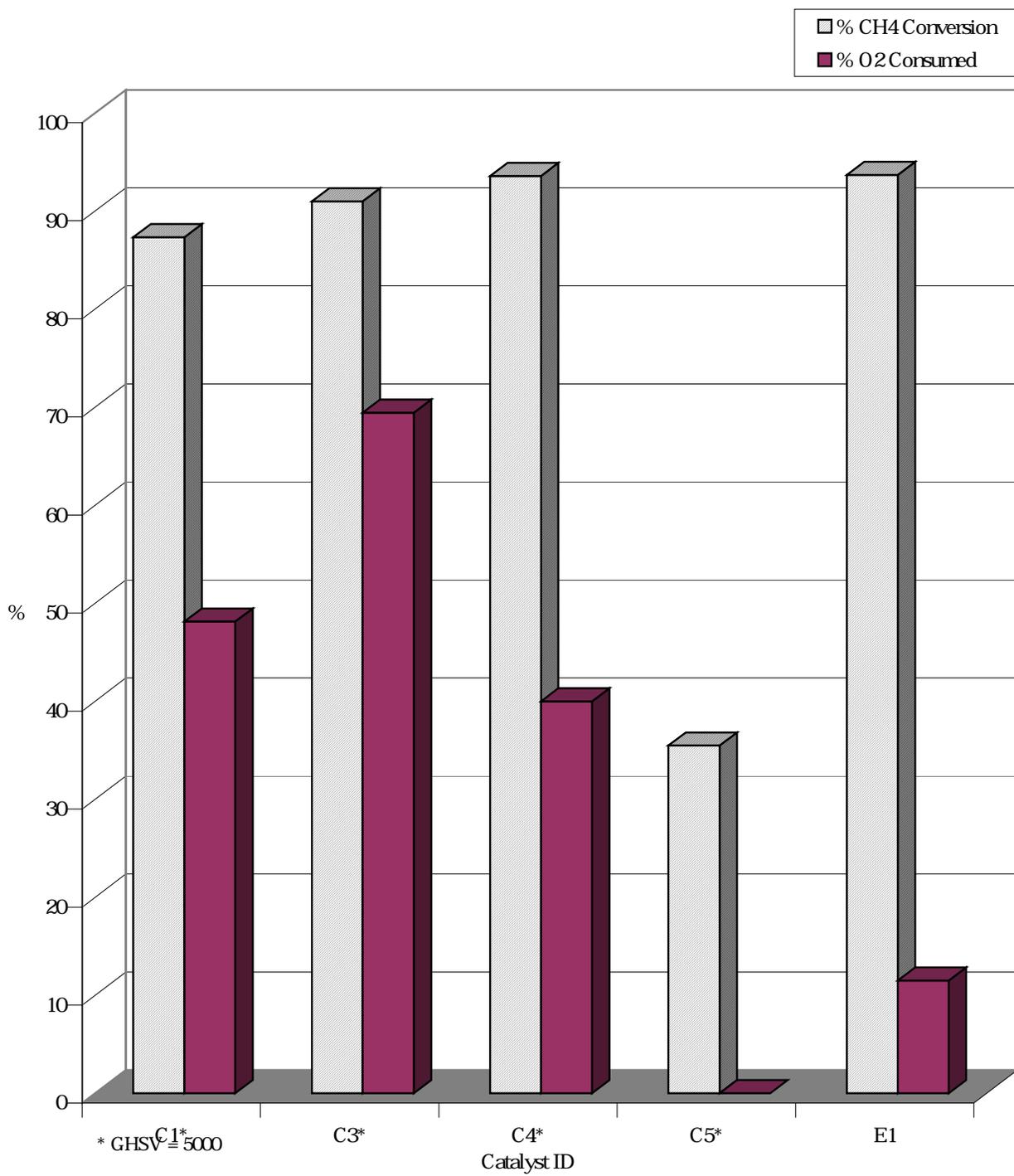


Figure 5. Screening test results for select commercial catalysts and catalyst E1.

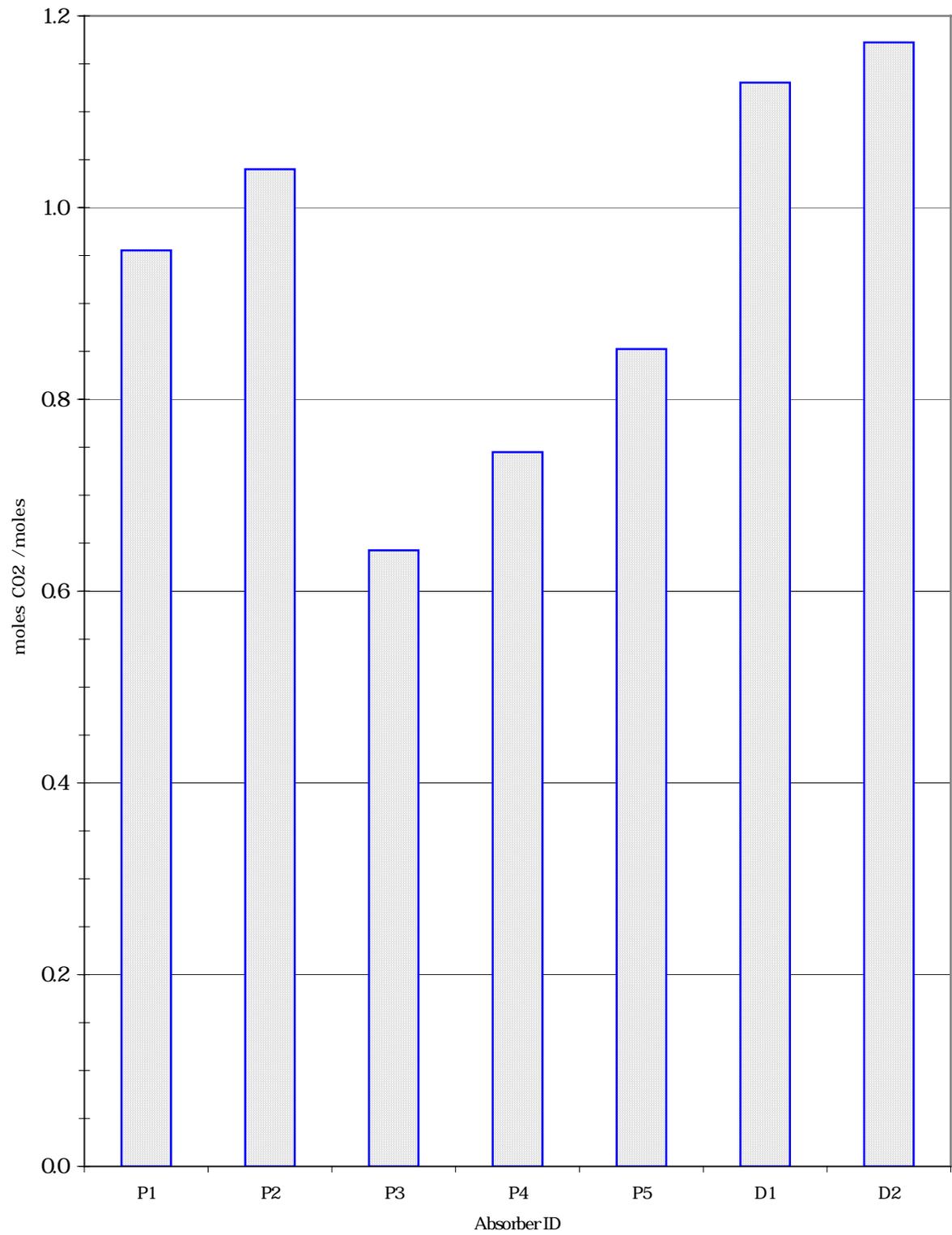


Figure 6. CO₂ absorption by various commercial and Phillips Petroleum absorber materials tested in the absorber test facility.

APPENDIX II:

PARAMETRIC TESTING REPORT

A Novel Steam Reforming Reactor for Fuel Cell Distributed Power Generation

Parametric Testing Report

California Energy Commission PIER I
Contract No. 500-97-038

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1.0 INTRODUCTION

EER's Unmixed Reforming (UMR) process is unique in its use of reforming catalysts and carbon dioxide (CO₂) absorber materials. It is a cyclic process with two steps: reforming and regeneration. In the reforming step, the nickel (Ni) on the catalyst is reduced to its active catalytic state, hydrogen is produced, and the CO₂ produced by reforming reactions is absorbed. In the regeneration step, the nickel on the catalyst is oxidized and the previously absorbed CO₂ is released into the vent gases. The nickel on the catalyst must be repeatedly oxidized and reduced, in addition to having high activity for the reforming reactions. To our knowledge, there are currently no commercially available catalysts designed for these purposes since conventional steam reforming is a continuous process eliminating repeated catalyst oxidation.

The CO₂ absorber materials suitable for the UMR process are generally either naturally occurring minerals containing calcium (Ca) such as dolomite or materials prepared by depositing calcium carbonate on a substrate. The repeated absorption and desorption of CO₂ by the absorber material poses a unique challenge for UMR material selection. Dolomite undergoes a physical breakdown in the presence of the high temperature steam required for the UMR process, while the CO₂ absorbing capacity of substrates with calcium deposited on them is limited by the amount of calcium present that can be utilized for absorption.

Development of materials for the UMR process, sponsored by the California Energy Commission (CEC) PIER I Program, is intended to identify suitable materials for the UMR process. Catalyst and absorber material development was identified as an area in which advances could have a significant impact on the commercial viability of the process. The development of the reforming process is part of a broader program supported by the U.S. Department of Energy (DOE).

EER teamed with Phillips Petroleum to utilize their expertise in high-temperature catalytic processes to address the catalyst and absorber issues unique to the UMR process. EER also considered several commercial catalysts that, although not designed for the UMR process, may coincidentally be suitable.

The approach taken to develop and identify suitable materials involves three steps: screening tests, parametric testing, and accelerated durability testing. This report presents the results of parametric testing.

Parametric testing is the second step in materials development for the UMR process. The parametric tests were conducted to develop a classical database of important parameter effects on process performance. The tests identified the range of operating conditions at which the catalyst materials are effective and the individual effects of each variable on overall performance. Parametric testing provides a complete picture of the catalyst activity and oxygen (O₂) consumption capacity and identifies any limitations in performance.

2.0 EXPERIMENTAL FACILITY SETUP

The same bench-scale experimental system used for screening tests was used for parametric testing. This system is described in detail in the Test Plan¹ and the Screening Test Report².

3.0 SELECTION OF PARAMETRIC PROCESS OPERATING CONDITIONS

Four variables were selected for parametric testing. These include the reforming gas hourly space velocity (GHSV), the oxygen to nickel molar ratio (O₂:Ni), the steam to carbon molar ratio (S:C), and the reactor temperature. Brief descriptions of the significance of these parameters to the UMR process are provided below.

3.1 Reforming GHSV

The reforming GHSV is a normalized factor that is independent of scale. Systems with the same GHSV tend to produce similar product purity, regardless of scale, while reactor scale affects product capacity. If the GHSV is too high, the reactions do not reach kinetic equilibrium, and some of the natural gas fed can exit the reactor without reacting, a situation described as breakthrough. For low GHSV's, the system production capacity is decreased. Very active catalysts are likely to perform as well at high GHSV's as they do at low GHSV's.

For parametric testing, the reforming GHSV was varied by varying the feed flow rates of steam and natural gas.

3.2 Oxygen to Nickel Molar Ratio

The oxidation of nickel by air during the regeneration step is important to the thermodynamic efficiency of the UMR process. This highly exothermic reaction ($2\text{Ni} + \text{O}_2 \rightarrow 2\text{NiO}$) provides *in situ* heat for the packed bed that aids both the release of CO₂ during the regeneration step and the endothermic reforming reactions during the reforming step. The oxidation of nickel is limited by diffusion in many cases, so more oxygen is needed than the stoichiometric requirement. The stoichiometric O₂:Ni ratio equals 0.5. The baseline O₂:Ni ratio for the parametric tests is 1.0.

The O₂:Ni ratio was varied experimentally by changing the air flow rate during the regeneration step. The amount of nickel in the catalyst bed remained constant.

¹ A Novel Steam Reforming Reactor for Fuel Cell Distributed Power Generation: Test Plan, February 11, 1999.

² A Novel Steam Reforming Reactor for Fuel Cell Distributed Power Generation: Screening Test Report, February 29, 2000.

3.3 Steam to Carbon Molar Ratio

The S:C ratio is effectively the ratio of the two feeds: water and natural gas, during the reforming step. The stoichiometric S:C ratio is approximately 2.0, but reaction equilibrium and coking considerations make higher S:C ratios desirable. At the temperatures of interest, the presence of excess steam prevents side reactions from occurring and also prevents coking from occurring. The baseline S:C ratio for the parametric tests is 3.0.

The S:C ratio was varied for parametric testing by changing the relative flow rates of steam and natural gas while keeping the desired GHSV constant.

3.4 Reactor Temperature

Higher reactor temperatures usually result in improved activity and higher conversion. However, at higher temperatures the CO₂ absorber capacity decreases. In addition, at higher temperatures and CO₂ concentrations, the equilibrium of the exothermic water-gas shift reaction is unfavorable, resulting in high carbon monoxide (CO) concentrations.

Catalyst conversion efficiency can change with temperature. This can be due to structural changes that occur at elevated temperatures, such as the conversion of alumina (Al₂O₃) catalyst substrates from the more active γ - Al₂O₃ form to the lower-surface area and less active α - Al₂O₃ form. It is also possible that at higher temperatures, other reactions become more significant, and may result in the presence of higher concentrations of undesirable products. Higher temperatures decompose calcium carbonate (CaCO₃) to CaO and CO₂. The higher temperature is desirable during the exothermic air regeneration step but would hinder the absorption of CO₂ during the reforming step.

The temperature was varied by changing the furnace controller settings. The controller was set to provide the desired temperatures at both the inlet and outlet of the reactor. The controller settings were not necessarily the same as the desired temperatures.

3.5 Test Matrix

The values of the parameters selected for parametric testing are provided in a test matrix in Table 1. Values both above and below the baseline conditions were selected for testing and are shown in bold in Table 1. The Ca:Ni ratio was not used for parametric testing in this program, as only one absorber was selected for parametric testing, and the Ca:Ni ratio is primarily a measure of absorber performance. It was not deemed useful to separately measure absorber performance for each catalyst at this stage of absorber development.

TABLE 1. DETAILED PARAMETRIC TEST PARAMETERS

Test Description	Reforming GHSV	Regeneration O ₂ :Ni Ratio (mol/mol)	SCR (mol/mol)	Reactor Temperature (°C)
Baseline Test Conditions for All Catalysts*	3500	1	3	700
Variation of Reforming GHSV	2500	1	3	700
	5000	1	3	700
Variation of Regeneration O ₂ /Ni Ratio	3500	0.625	3	700
	3500	1.5	3	700
Variation of Steam to Carbon Ratio	3500	1	2	700
	3500	1	4	700
Variation of Reactor Temperature	3500	1	3	650
	3500	1	3	750
	3500	1	3	800

* Repeat tests were performed to determine process repeatability and measurement precision

It was planned that each material selected for parametric testing undergo each of the parametric test sequences, however, intermediate performance indicators and test scheduling sometimes precluded completion of all of the parametric tests. In cases where all of the parametric tests were not conducted, enough information was gathered to gain insight into the performance of the materials and indicate areas for further development.

4.0 SYSTEM OPERATING PROCEDURES

The bench-scale experimental system used in the screening tests was also used for parametric testing. The operating procedure used for the parametric tests was the same as that used for the screening tests³. A typical set of parametric tests was conducted over two test days, with the specified conditions set and allowed to stabilize, then run at stable conditions for several complete cycles. Repeat tests were conducted at the baseline conditions for each catalyst.

5.0 CALCULATION OF PARAMETRIC TESTING RESULTS

The measurements taken during parametric testing were used to calculate three performance indicators: % O consumed/Ni, % converted carbon absorbed, and % methane (CH₄) conversion. Each performance indicator is discussed below.

³ A Novel Steam Reforming Reactor for Fuel Cell Distributed Power Generation: Screening Test Report, February 29, 2000.

5.1 % O Consumed/Ni

Oxygen consumption is measured as the difference between the amount of oxygen fed to the reactor and the amount of oxygen leaving the reactor during the air regeneration step. During parametric testing, the O₂:Ni ratio was varied, so the oxygen consumption was normalized by the amount of nickel in the bed to provide a consistent basis for comparison. The % O Consumed/Ni is defined as:

$$\% \text{ O Consumed/Ni} = \frac{2 \text{ O}[\text{mol}]}{\text{O}_2 [\text{mol}]} \times \frac{(\text{O}_2 \text{ fed} [\text{mol}] - \text{O}_2 \text{ exiting} [\text{mol}])}{\text{Ni}[\text{mol}]} \times 100\% \quad (1)$$

The % O Consumed/Ni ratio is calculated as:

$$\% \text{ O Consumed/Ni} = \frac{2 \times t_{\text{REG}} \times (0.21 \times F_{\text{REG}f} [\text{mol/hr}] - \% \text{O}_{2v} \times F_{\text{REG}v} [\text{mol/hr}])}{\text{Ni} [\text{mol}]} \times 100\% \quad (2)$$

Where:

t_{REG} is the regeneration step time (hrs)

$\% \text{O}_{2v}$ is the average measured concentration of oxygen in the regeneration vent stream.

$F_{\text{REG}v}$ is the molar flow rate leaving the reactor during the regeneration step.

Ni is the moles of nickel present in the catalyst bed.

The % O consumed/Ni is a measure of the amount of elemental oxygen (O) that reacts with the nickel on the catalyst to form nickel oxide (NiO). This also indicates the amount of nickel that is participating in the oxidation and reduction cycle during the regeneration and reforming steps. This is useful in identifying materials that are able to maintain catalytic activity for reforming while cycling between the regeneration and reforming steps, one of the unique aspects of the unmixed reforming process. Another unique aspect is the use of the exothermic nickel oxidation reaction to provide heat to the bed during the regeneration step. The amount of oxygen consumed by nickel oxidation is an indicator of the extent to which this occurs, which is important for the intended autothermal use of the unmixed reforming technology.

5.2 % Converted Carbon Absorbed

The absorption capacity of the dolomite material is measured as the amount of CO₂ released in the regeneration step. The % converted carbon absorbed is defined as the percent of reacted methane absorbed as CO₂, as follows

$$\% \text{ converted carbon absorbed} = \frac{\text{CO}_2 \text{ released in regeneration step} [\text{mol}]}{\text{reacted CH}_4 \text{ in reforming step} [\text{mol}]} \times 100\% \quad (3)$$

The % converted carbon absorbed is calculated as:

$$\% \text{ converted carbon absorbed} = \frac{F_{\text{CO}_2\text{rel}} [\text{mol/hr}]}{F_{\text{NGREF}_f} [\text{mol/hr}] - \text{AvgCH}_4\% \times F_{\text{REF}_p} [\text{mol/hr}]} \times 100\% \quad (4)$$

Where:

$F_{\text{CO}_2\text{rel}}$ is the molar flow rate of CO_2 released during the regeneration step.

F_{NGREF_f} is the molar flow rate of natural gas fed during the reforming step.

AvgCH₄% is the average CH₄ mole percent in the product gas during the reforming step.

F_{REF_p} is the product flow rate during the reforming step.

The basis for carbon absorption is the moles of carbon fed during the reforming step that react to form CO or CO_2 . To decouple the impact of catalyst activity, the % converted carbon absorbed is based only on reacted methane.

5.3 % CH₄ Conversion

The CH₄ conversion is measured as the amount of CH₄ that leaves the catalyst bed unreacted. The % CH₄ conversion is defined as:

$$\% \text{ CH}_4 \text{ conversion} = \frac{\text{CH}_4\text{in} [\text{mol}] - \text{CH}_4\text{out} [\text{mol}]}{\text{CH}_4\text{in} [\text{mol}]} \times 100\% \quad (5)$$

The % CH₄ conversion is calculated as:

$$\% \text{ CH}_4 \text{ conversion} = \frac{F_{\text{NGREF}_f} [\text{mol/hr}] - \text{AvgCH}_4\% * F_{\text{REF}_p} [\text{mol/hr}]}{F_{\text{NGREF}_f} [\text{mol/hr}]} \times 100\% \quad (6)$$

The % CH₄ conversion is an indication of the amount of natural gas fed that reacts to form products such as hydrogen, CO, and CO_2 .

6.0 DATA VARIABILITY

Figure 1 shows the performance of catalyst C1 at the baseline conditions. The precision, illustrated with vertical error bars, is calculated as the standard deviation of repeat tests. The precision of four baseline tests on catalyst C1 are $\pm 4\%$ for converted carbon absorbed, $\pm 1.78\%$ for CH₄ conversion, and $\pm 1.43\%$ for O₂ consumed. These tests were conducted on separate days and the precision value is representative of catalyst, operating and measurement variability. The error bars shown in figures in this report are based on repeat tests of the baseline operating conditions for the same catalyst.

7.0 RESULTS OF PARAMETRIC TESTS

The purpose of the detailed parametric evaluation was to identify the individual effects of each variable on overall performance. Results presented in Figures 1 through 23 are for parametric tests performed at different steam to carbon molar ratios, oxygen to nickel molar ratios, gas hourly space velocities, and reactor temperatures. For each catalyst test series, three responses are presented: the % O consumed/Ni, the % converted carbon absorbed, and the % CH₄ conversion. For tests of catalyst P10, the % converted carbon absorbed is not reported because no absorber was used.

In addition to the test results provided, several other parametric tests were performed. Due to the low conversions that required the dilution of the reactant feed stream to keep the CH₄ concentrations within the range of the analyzer, there was a high degree of uncertainty associated with the results of these tests, so their results are not reported here. Qualitative information on the material performance was obtained and will be summarized.

7.1 Steam to Carbon Ratio Variation

The results of S:C ratio variation on various catalysts are shown in Figures 1 through 7. As the S:C ratio is increased, CH₄ conversion can increase because of decreased fuel concentrations. On the other hand, oxygen consumption would not be expected to change much with S:C ratio unless S:C ratio had a significant impact on the state of the catalyst bed. Since a S:C ratio of 1 provides sufficient steam to avoid coke formation and enhance nickel reduction, the state of the catalyst bed and hence, oxygen consumption, should not be impacted. Only the oxygen consumption of catalyst C2 was impacted by the S:C ratio, which decreased with increasing S:C ratio. The expected increase in CH₄ conversion with increasing S:C ratio was seen in catalysts C2, C4, C6, and C7. Catalysts C1, C3, and P10 were not significantly impacted by the S:C ratio.

The converted carbon absorbed was expected to increase as the S:C ratio was increased because of increased CO₂ production resulting from increased CH₄ conversion. This was seen in catalysts C2 and C4. No impact of S:C ratio on carbon absorption was observed in the other catalysts. This indicator was not relevant for catalyst P10 since it was not tested with an absorber.

7.2 Oxygen to Nickel Ratio Variation

The results of the O₂:Ni variation on various catalysts are presented in Figures 8 through 13. O₂:Ni ratio is varied in the air regeneration step and should have no effect on the CH₄ conversion in the reforming step. This was confirmed for all the tests. Like CH₄ conversion, no effect was expected for converted carbon absorbed. This was observed in all the tests.

The ability of the catalysts to undergo oxidation and reduction is indicated by the extent to which the catalysts consumed oxygen for nickel oxidation. The stoichiometric O₂:Ni is 0.5, so excess air was present for all of these tests. If increasing excess air improves the oxygen consumption, then the nickel on the catalyst is not being oxidized efficiently. Increasing the O₂:Ni ratio above 0.625 did not have a significant impact on catalysts C1, C3, and P3, demonstrating that these catalysts participate in nickel oxidation efficiently at these conditions and does not require much

excess air. However, the oxygen consumption capacities of catalysts C2 and C6 seemed to be inhibited by additional excess air. Catalyst C7 showed optimum oxygen consumption at the baseline condition.

7.3 Gas Hourly Space Velocity Variation

The results of the gas hourly space velocity variation on various catalysts are displayed in Figures 14 through 19. For catalysts C1, C3, C4, and P10, increasing the gas hourly space velocity resulted in little effect on the CH₄ conversion. For catalyst C6 there was a decreasing trend, as would be expected due to the lower residence time in the reactor. Catalyst P3 showed an increase in conversion with increased GHSV.

Oxygen consumption was not expected to be impacted by the GHSV. This expected result was seen in catalysts C3, C6, and P10. An increasing trend was observed in catalyst C1. High variability led to inconclusive results for catalysts C4 and P3.

The converted carbon absorbed for catalysts C1, C3, and P3 were effected little by gas hourly space velocity variation. Decreasing trends were observed for catalysts C4 and C6, which seem to be more sensitive to the reduced residence time at higher GHSV. This indicator was not relevant for catalyst P10 since it was not tested with an absorber.

7.4 Reactor Temperature Variation

The results of the reactor temperature variation on various catalysts are shown in Figures 20 through 23. Increasing the reactor temperature had little effect on CH₄ conversion for the tests shown, since the conversions were high at all temperatures.

Increasing the reactor temperature resulted in increasing oxygen consumed for catalysts C2 and C3. There were also increasing trends for catalysts C1 and C4, although high variability was present in each of those tests. The other catalysts were not affected by temperature variation.

The results of the reactor temperature variation on the converted carbon absorbed are inconclusive.

7.5 Other Tests

Additional parametric tests not included in the above discussions were performed on catalysts P3, P4 and P6. Their exclusion was based on the high variability and uncertainty of the results of these tests. Catalysts P4 and P6 both had consistently low oxygen consumption, and catalyst P6 also had low conversion. Catalysts P3 had significant degradation of performance at high S:C ratios. The degradation of performance at parametric testing conditions is an indicator of the sensitivity of the materials to the range of operating conditions tested.

8.0 SELECTION OF MATERIALS FOR ACCELERATED TESTING

The baseline parametric testing results are summarized in Figure 24.. Many of the catalysts showed high CH₄ conversion, although the oxygen consumption varied substantially from catalyst to catalyst. Catalyst C3 had very high oxygen consumption, while catalyst P10 had high CH₄ conversion and oxygen consumption.

The results showed that catalysts C3 and P10 were not significantly impacted by the different parametric testing conditions. This suggests that these materials are within a suitable operating range, and should have good performance around the target UMR conditions.

Based on the results of parametric testing, catalyst C3 was selected for prototype reactor testing and was used in accelerated durability protocol development. Catalyst C3 is a promising commercial catalyst primarily because of its high oxygen consumption, indicative of its ability to participate in the nickel oxidation/reduction cycle. It also had high CH₄ conversion.

Catalyst P10 was selected for accelerated durability testing because it exhibited good performance, especially with regard to its ability to reduce nickel rapidly in the fuel regeneration step. Phillips Petroleum developed the substrate for catalyst P10 to be an especially durable and physically stable material.

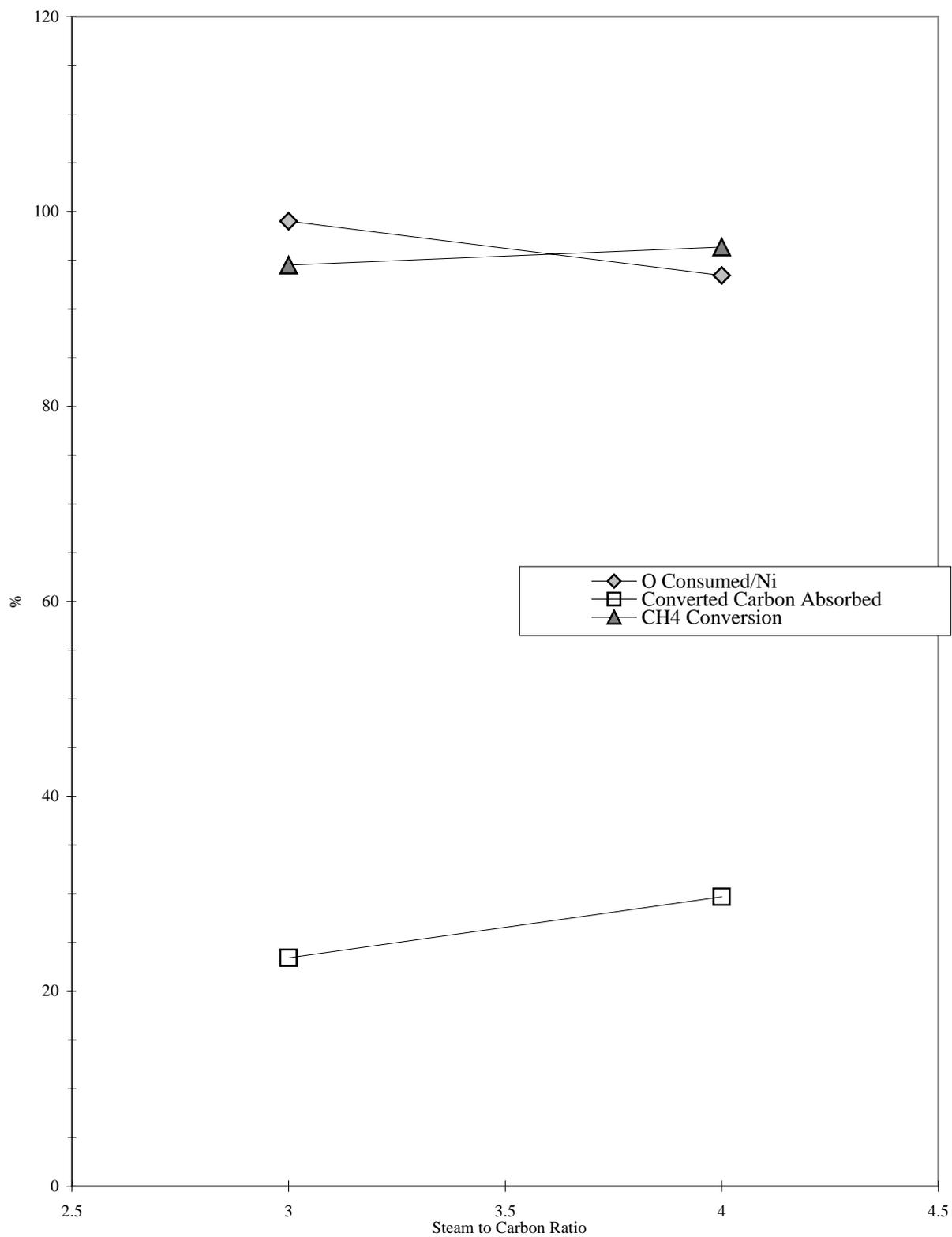


Figure 1. Steam to carbon ratio variation for catalyst C1.

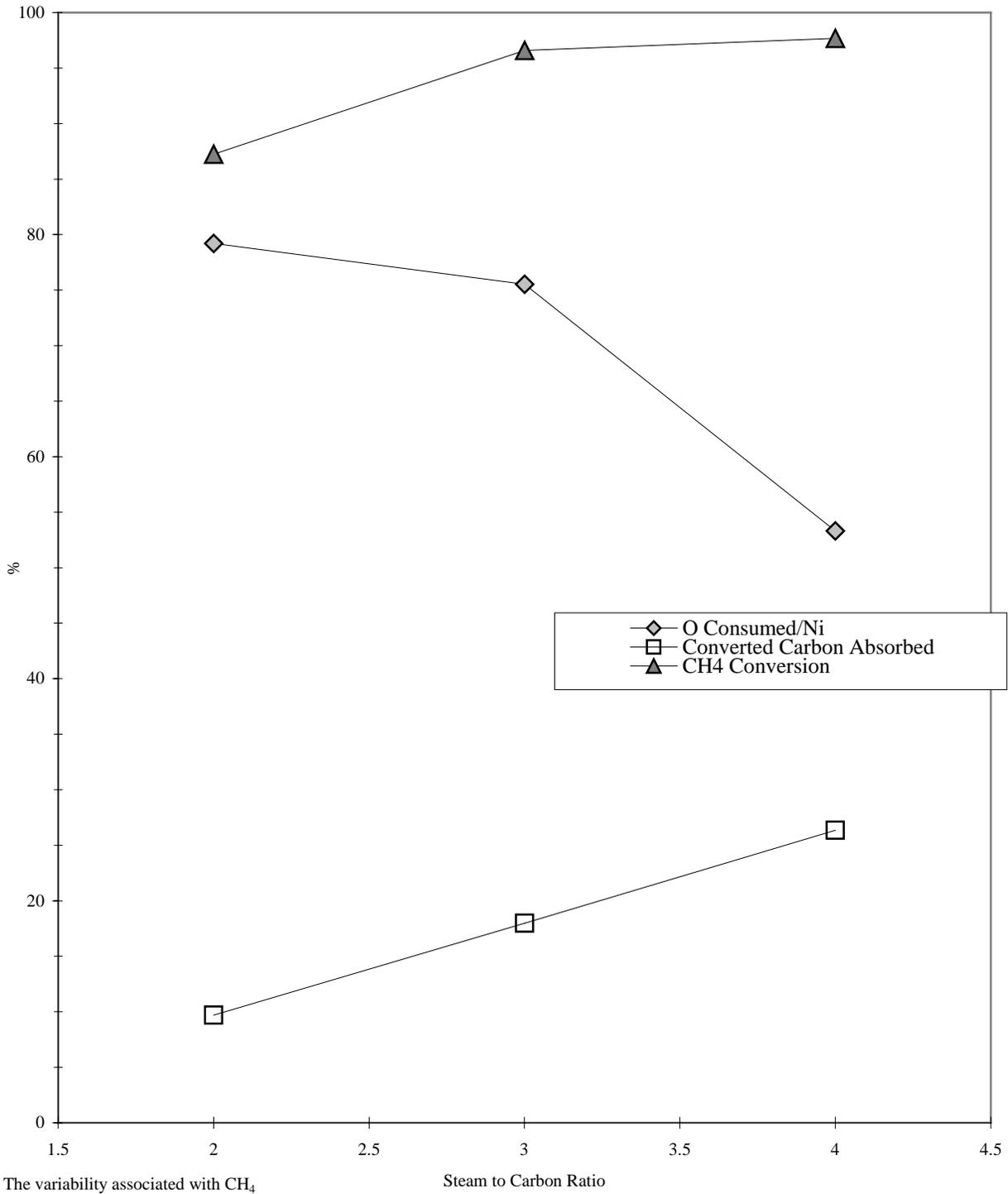
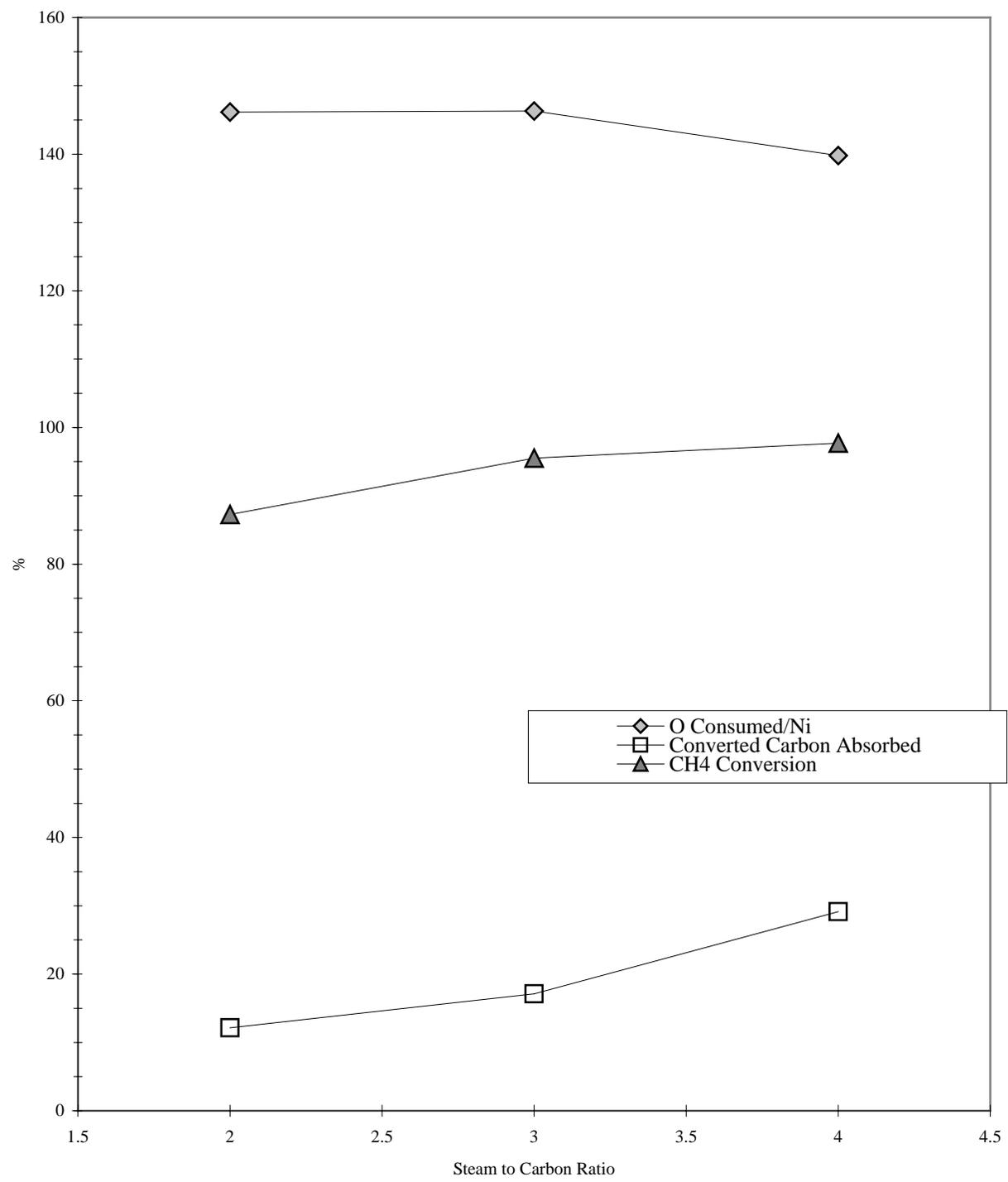


Figure 2. Steam to carbon ratio variation for catalyst C2.



GHSV = 5000 h⁻¹; O₂:Ni = 1.167

Figure 3. Steam to carbon ratio variation for catalyst C3.

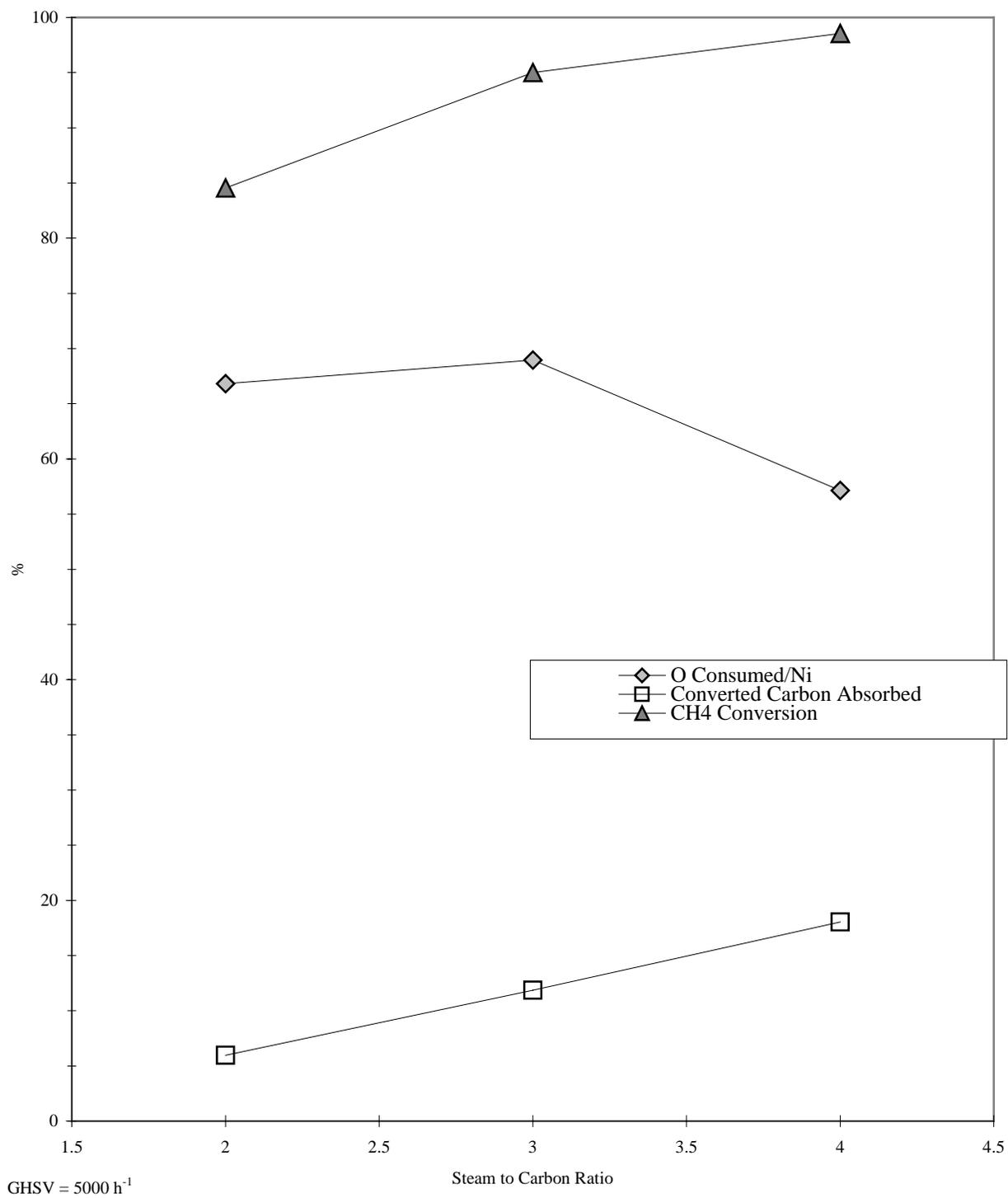


Figure 4. Steam to carbon ratio variation for catalyst C4.

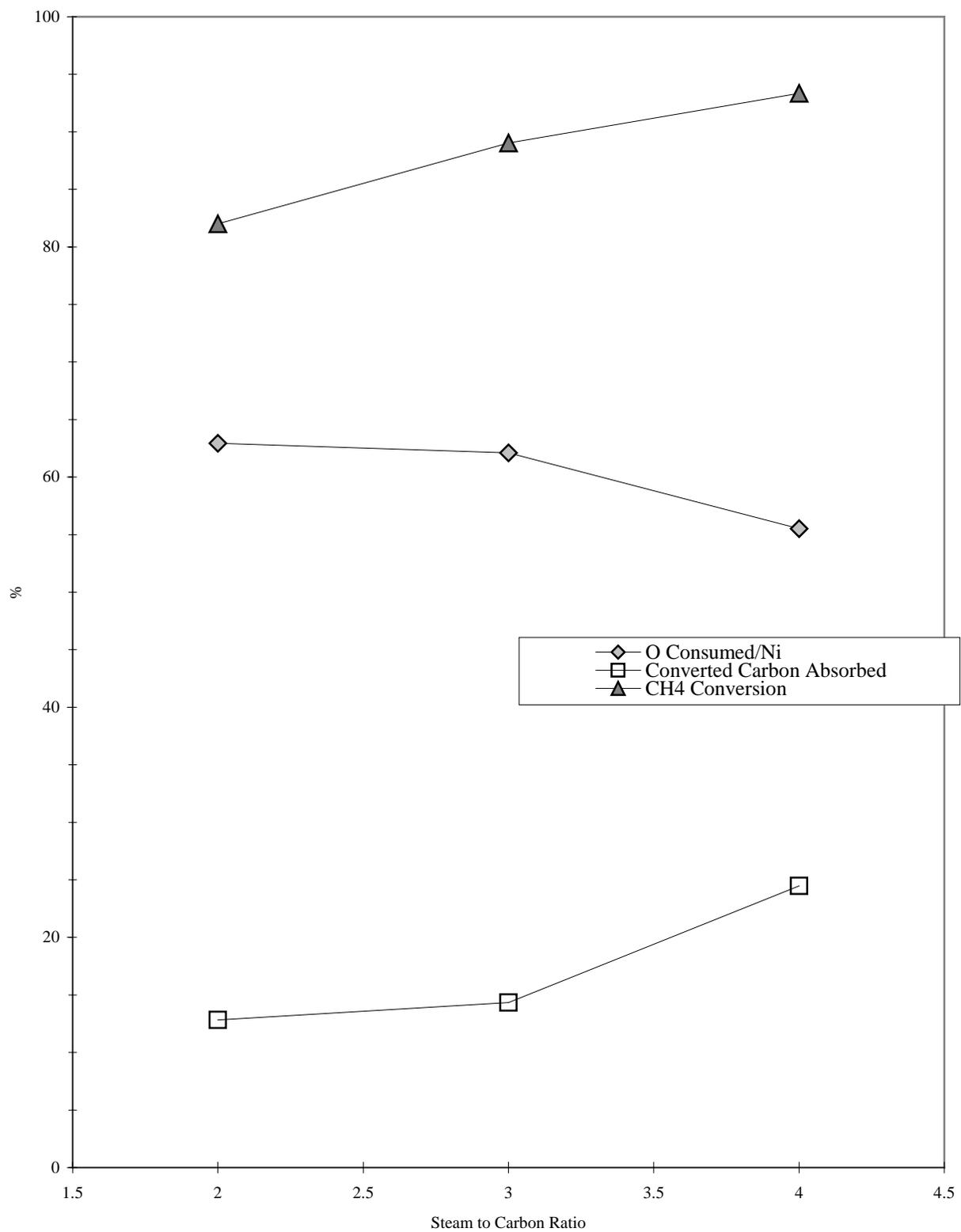


Figure 5. Steam to carbon ratio variation for catalyst C6.

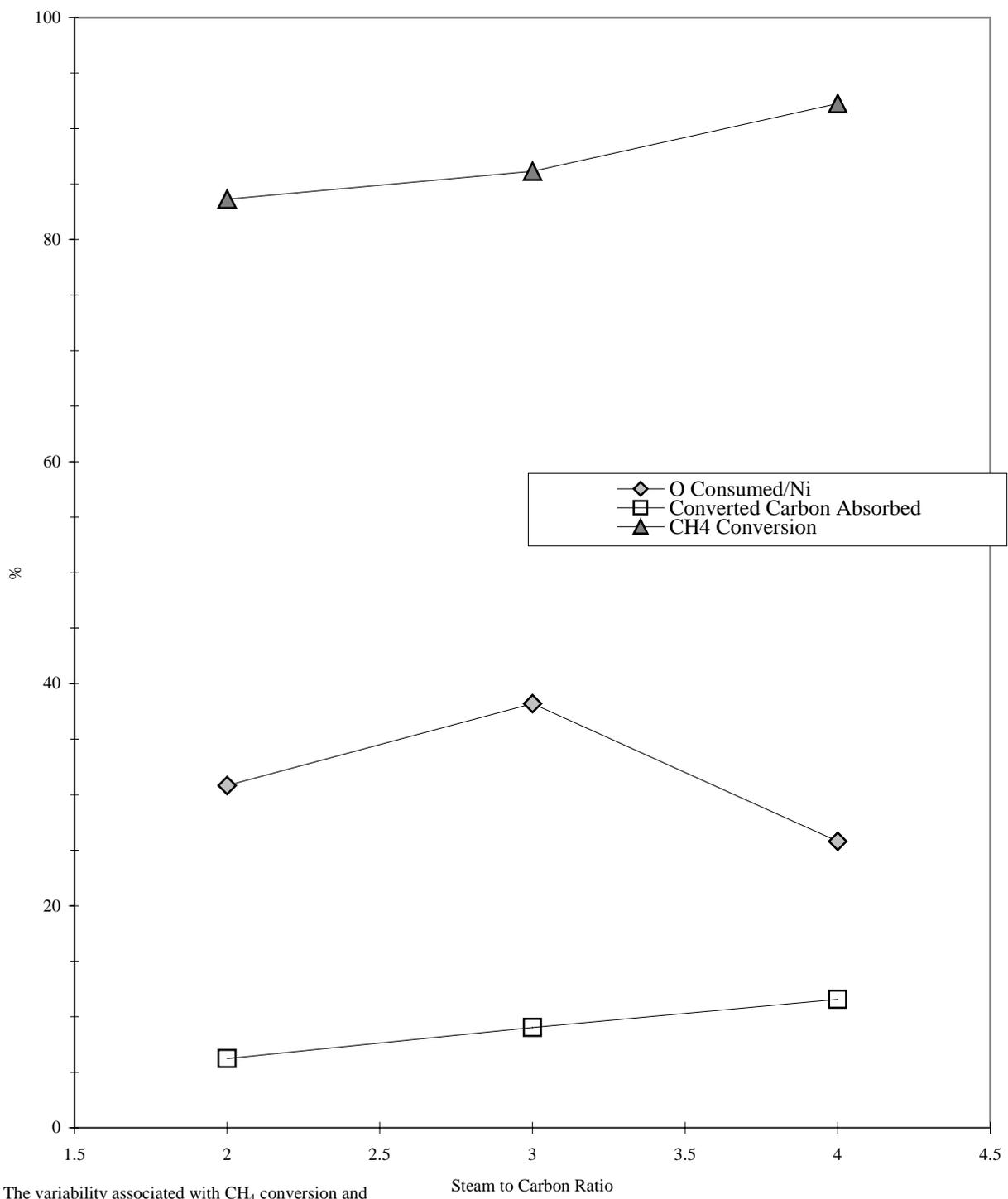
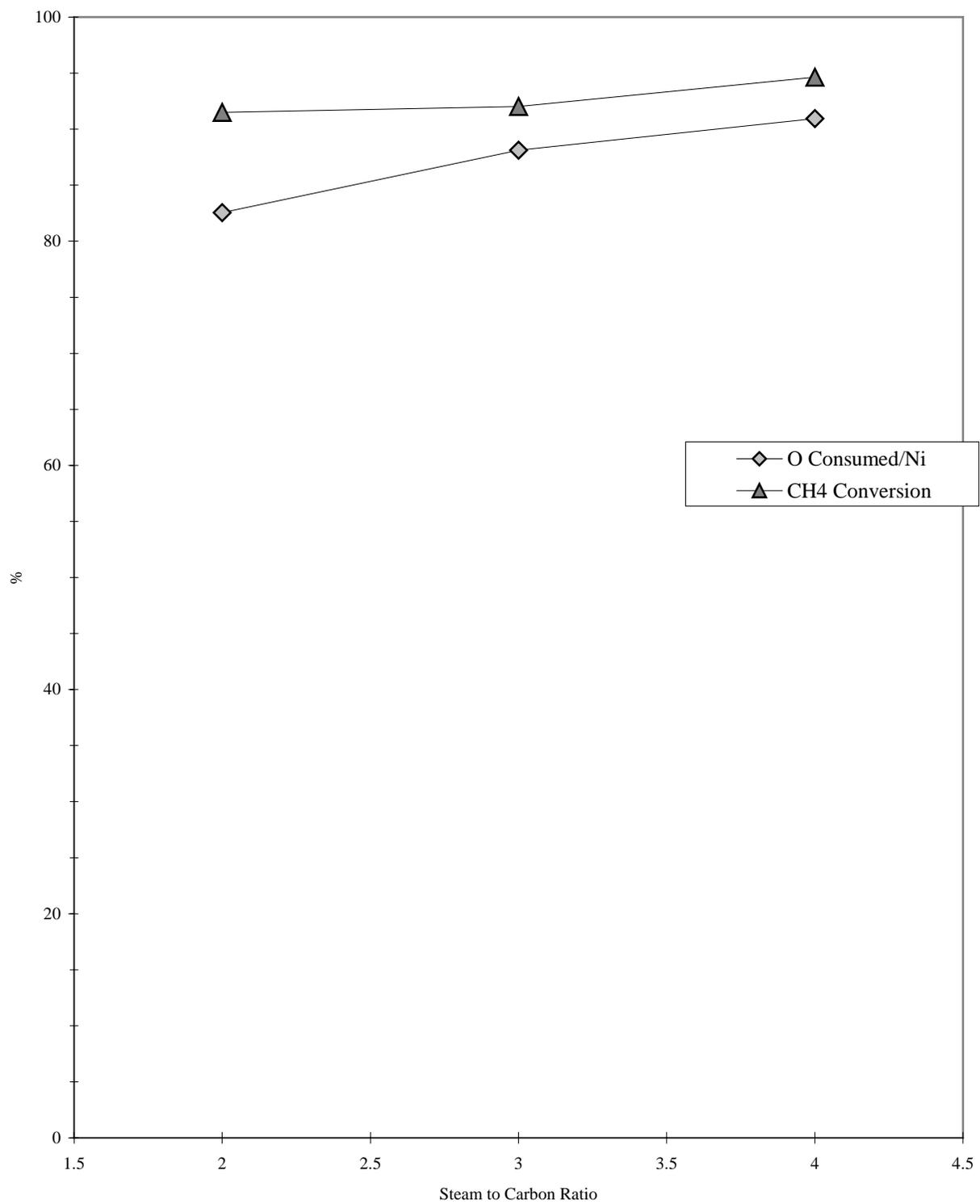


Figure 6. Steam to carbon ratio variation for catalyst C7.



Analyzer dilution was used for all conditions.

Figure 7. Steam to carbon ratio variation for catalyst P10.

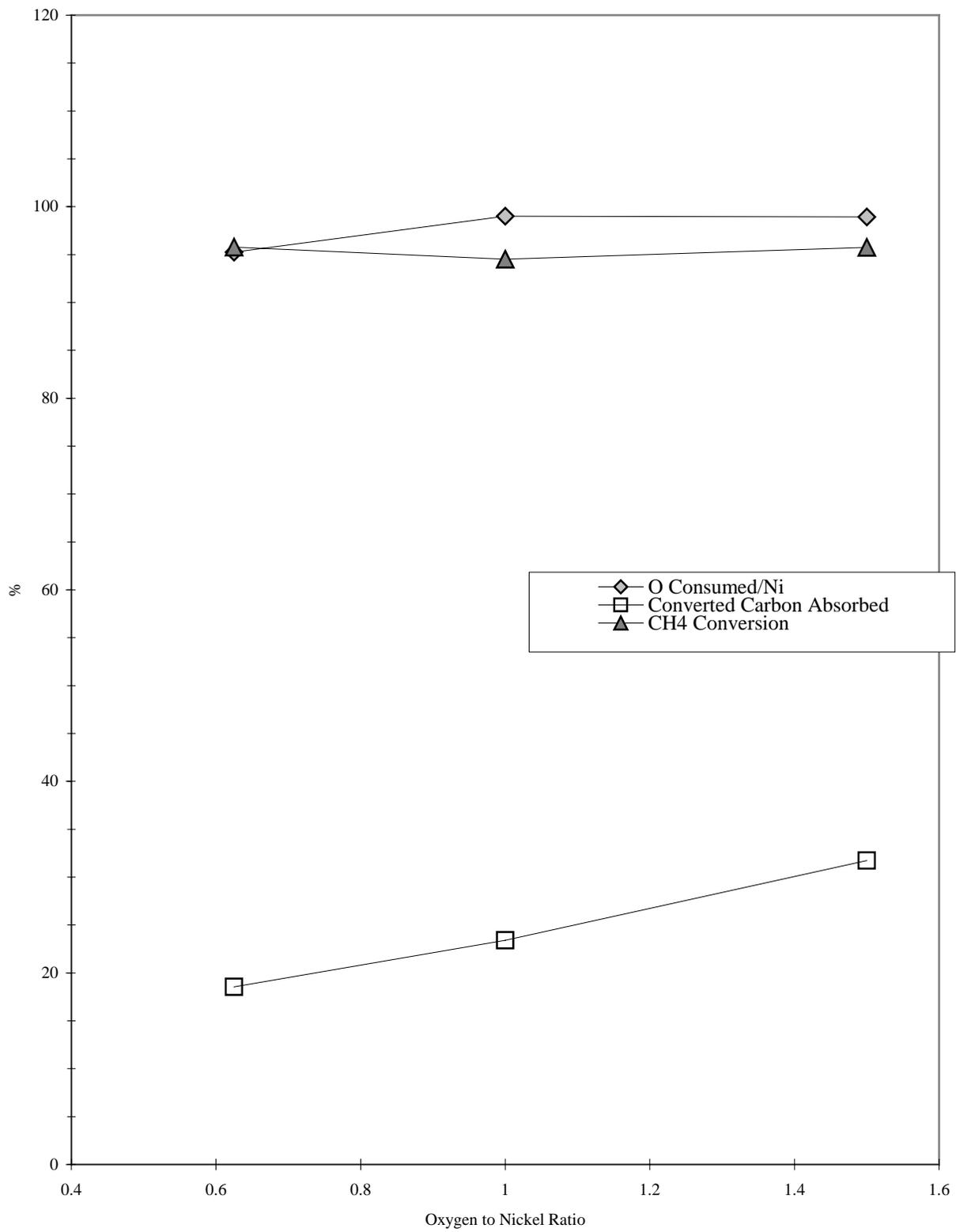
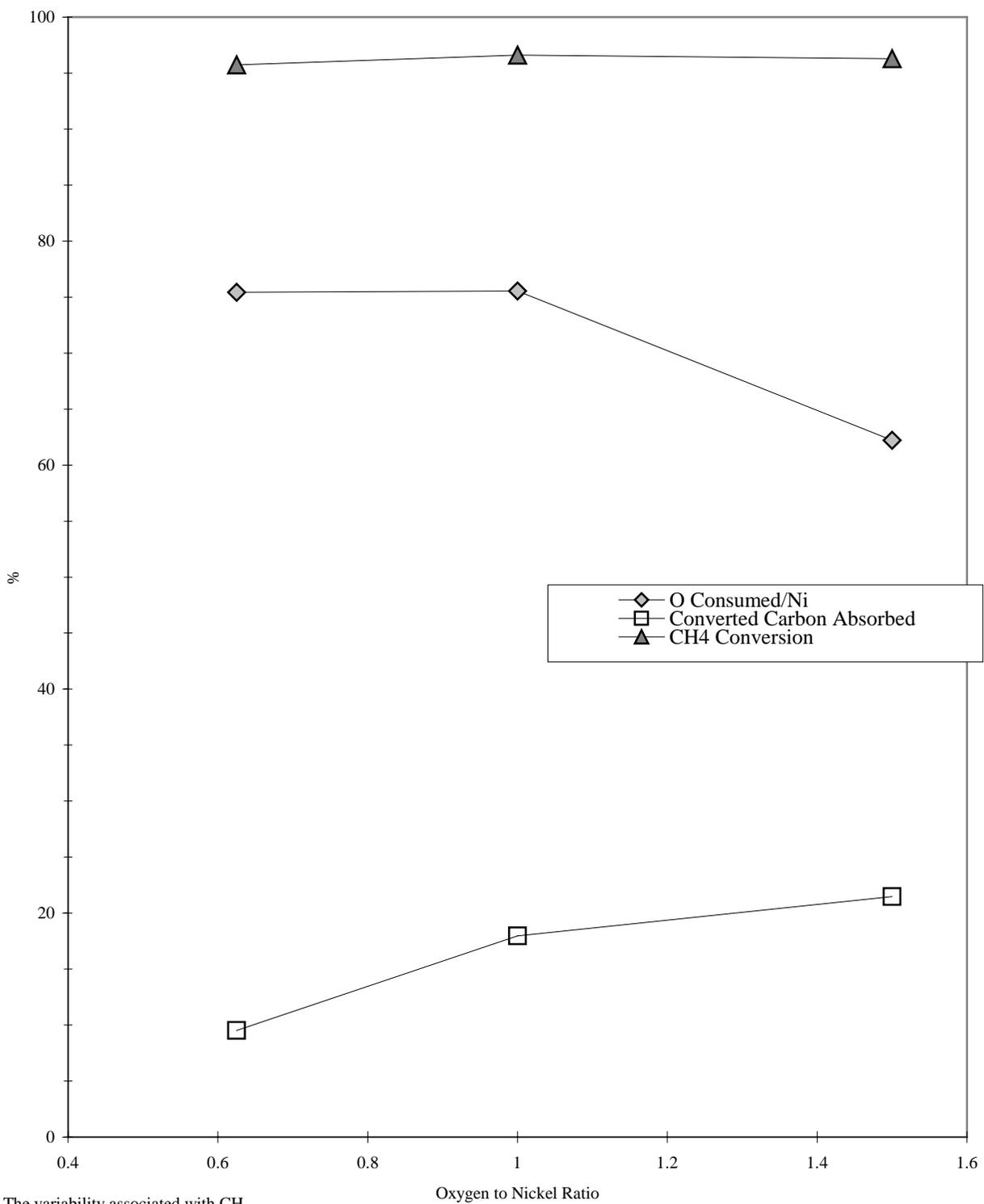


Figure 8. Oxygen to nickel ratio variation for catalyst C1.



The variability associated with CH₄ conversion is very small (0.02%).

Figure 9. Oxygen to nickel ratio variation for catalyst C2.

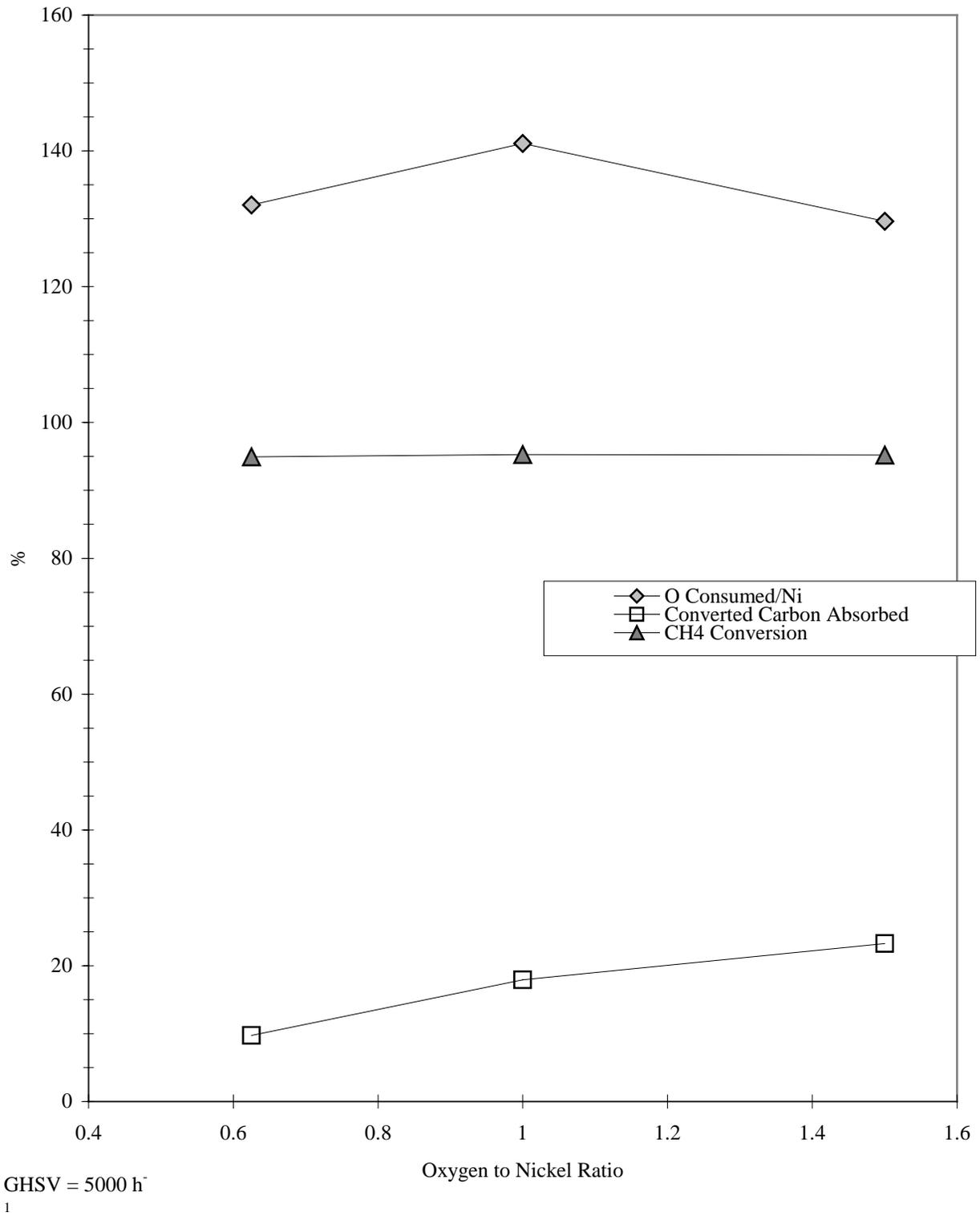


Figure 10. Oxygen to nickel ratio variation for catalyst C3.

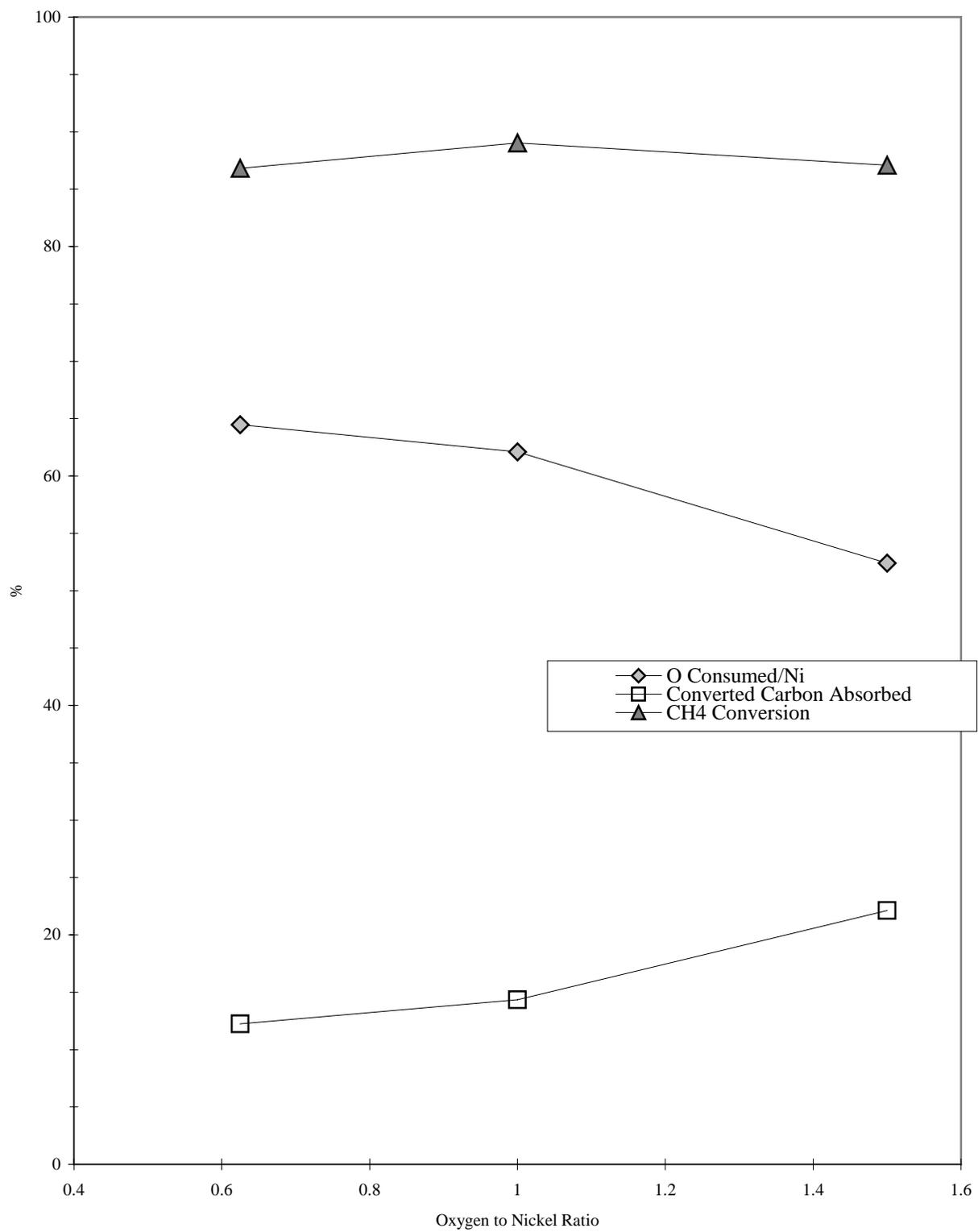
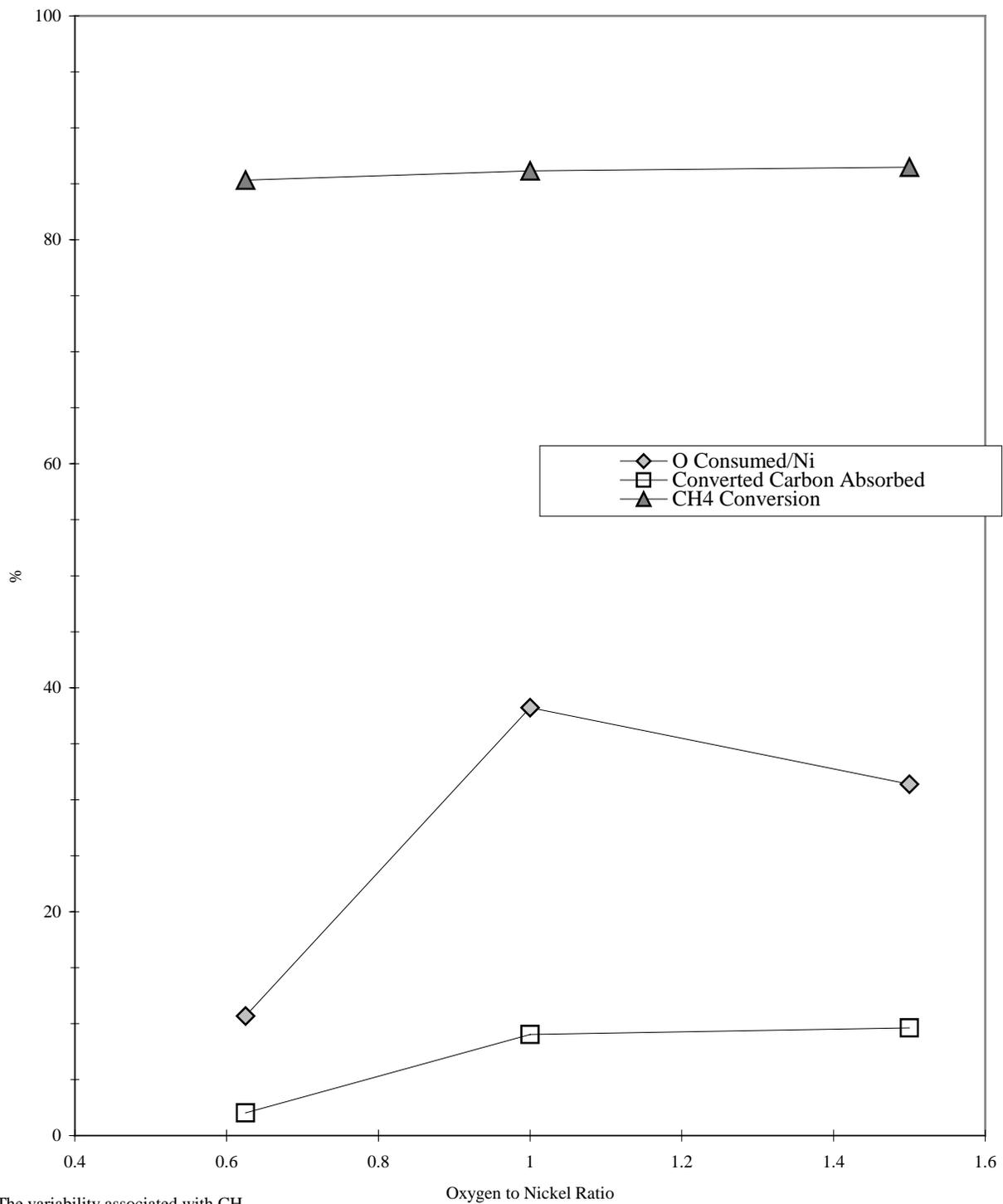
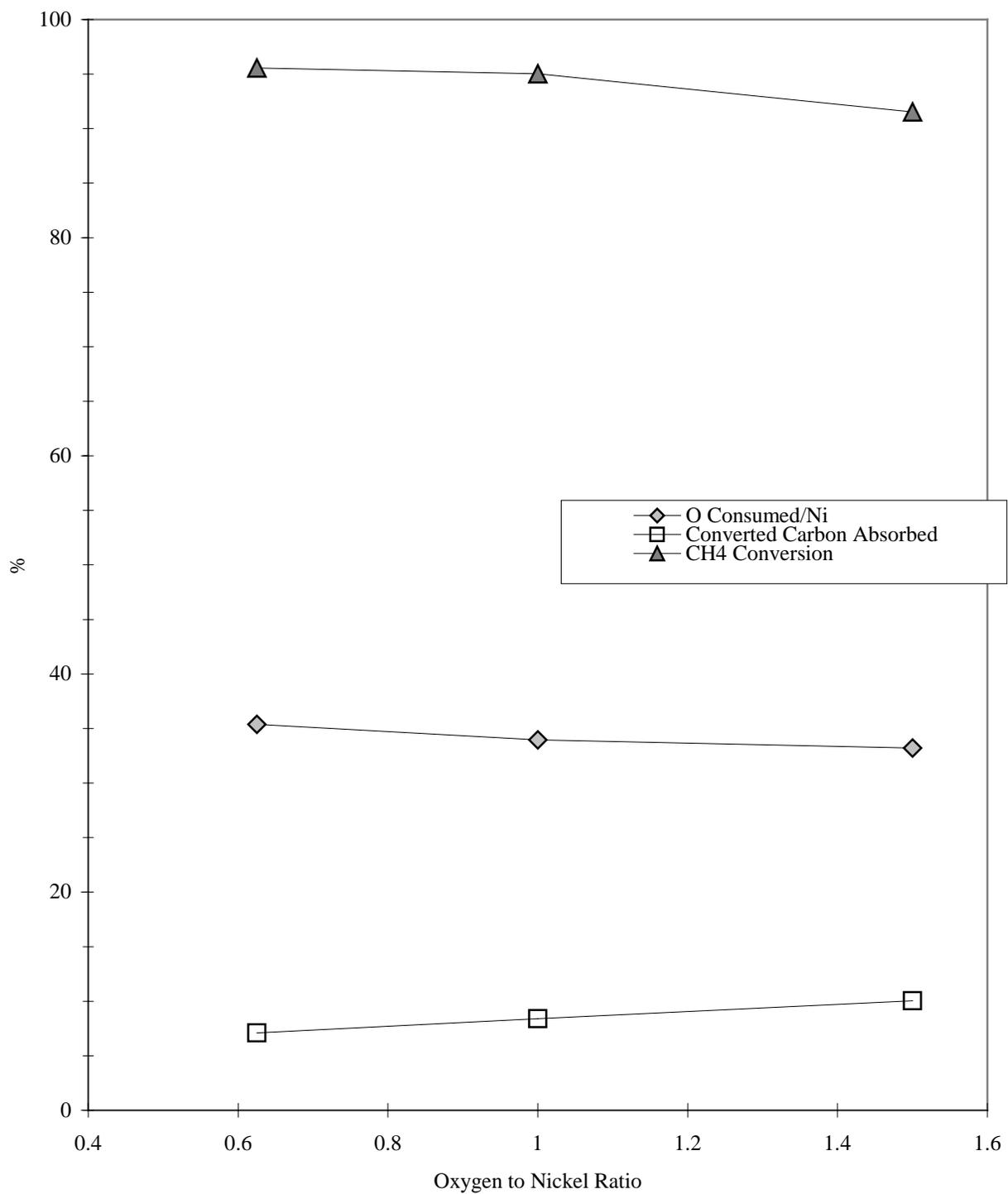


Figure 11. Oxygen to nickel ratio variation for catalyst C6.



The variability associated with CH₄ conversion and converted carbon adsorbed is very small (0.08% and 0.5%).

Figure 12. Oxygen to nickel ratio variation for catalyst C7.



Feed dilution was used for all conditions;
 GHSV = 5000 h⁻¹

Figure 13. Oxygen to nickel ratio variation for catalyst P3.

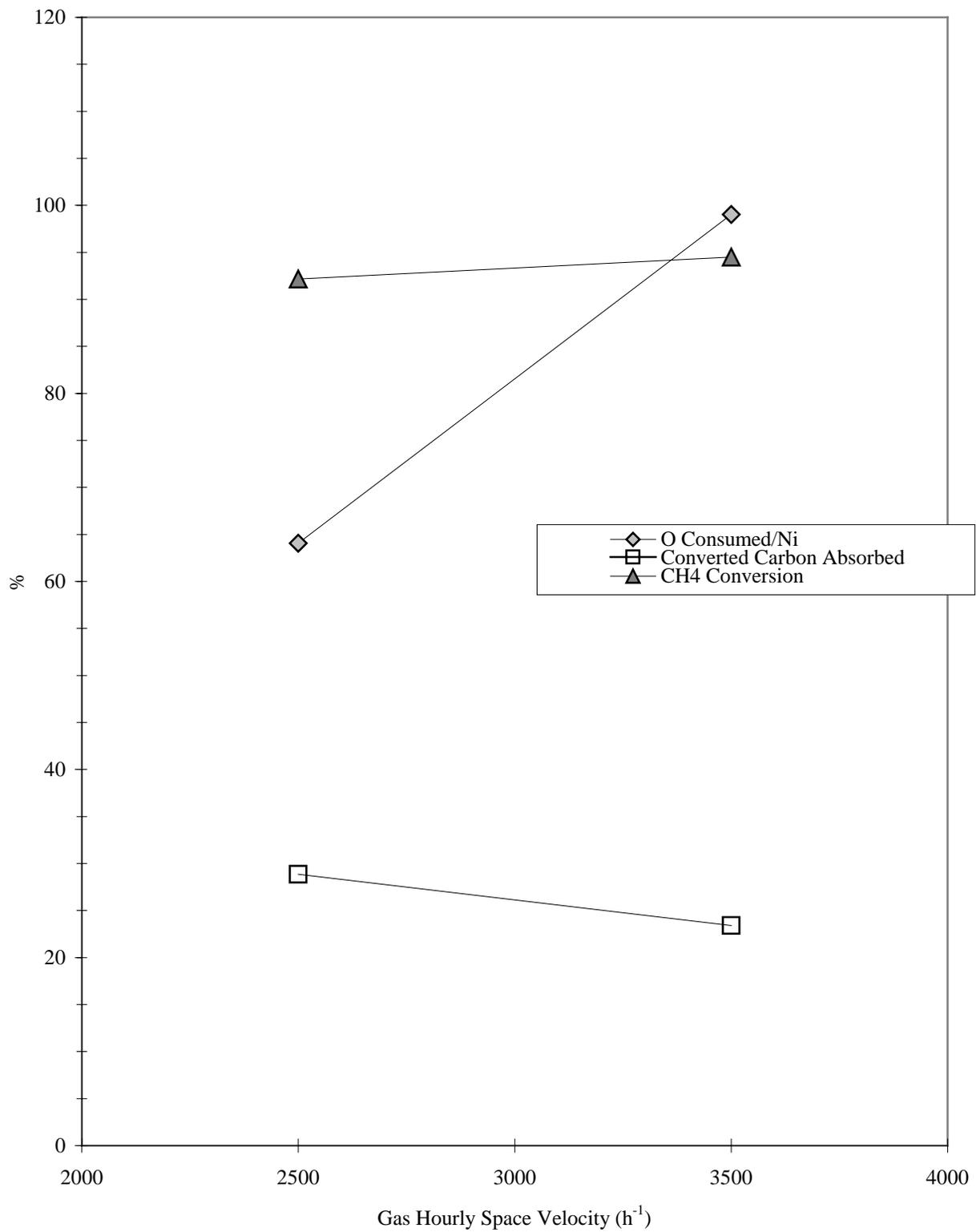


Figure 14. Gas hourly space velocity variation for catalyst C1.

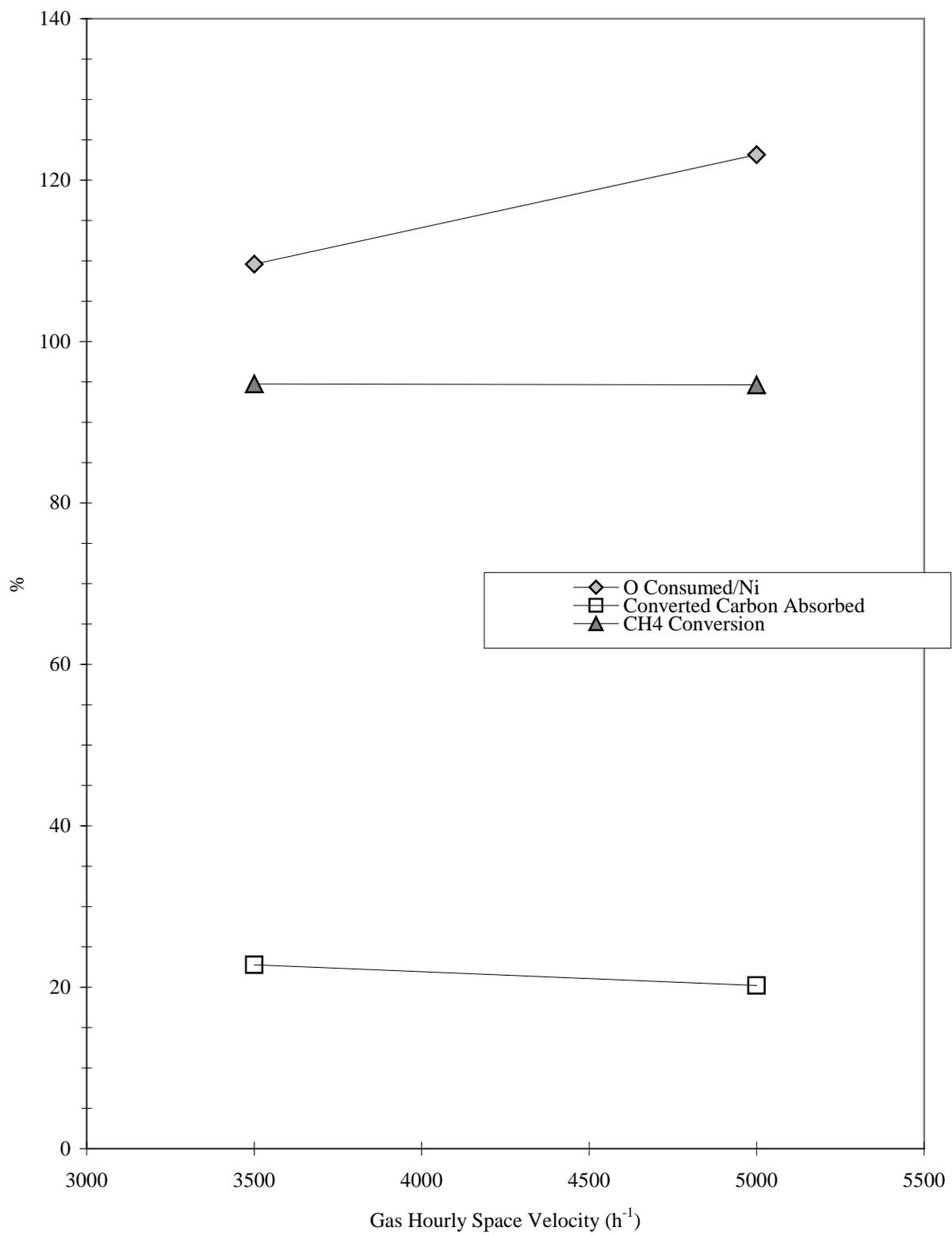


Figure 15. Gas hourly space velocity variation for catalyst C3.

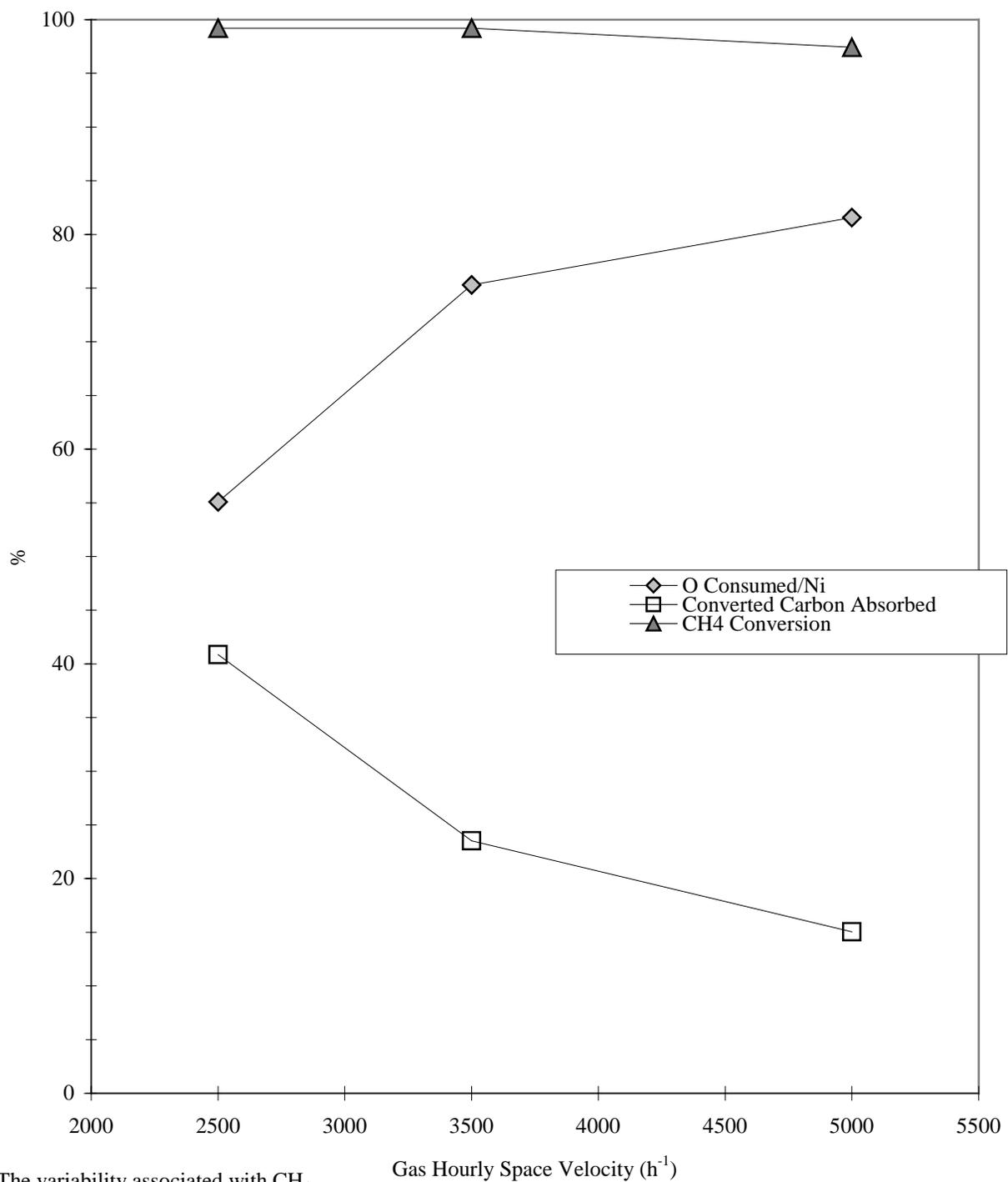
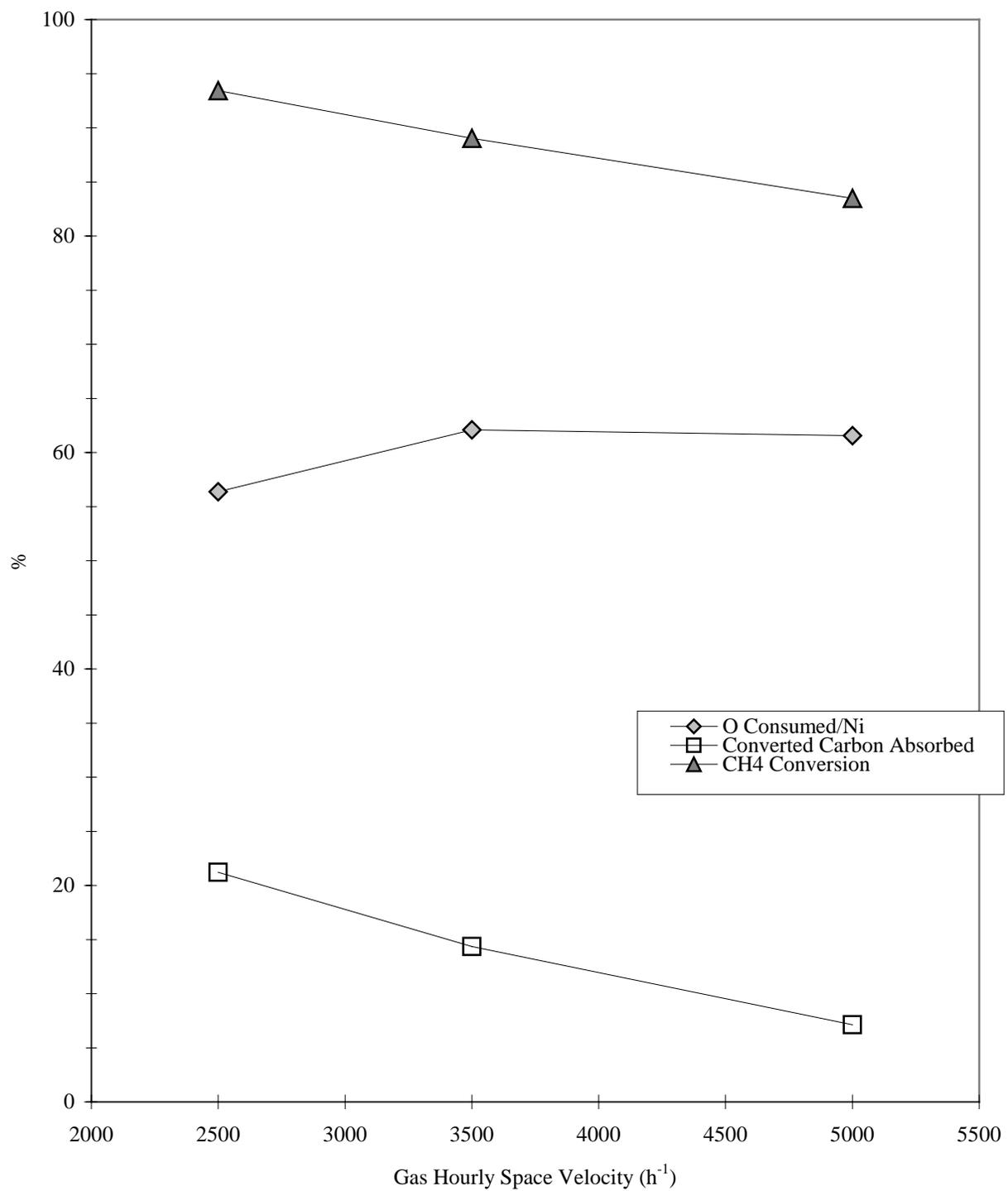


Figure 16. Gas hourly space velocity variation for catalyst C4.



Analyzer dilution was used for
 GHSV = 2500 h⁻¹ and 5000 h⁻¹.

Figure 17. Gas hourly space velocity variation for catalyst C6.

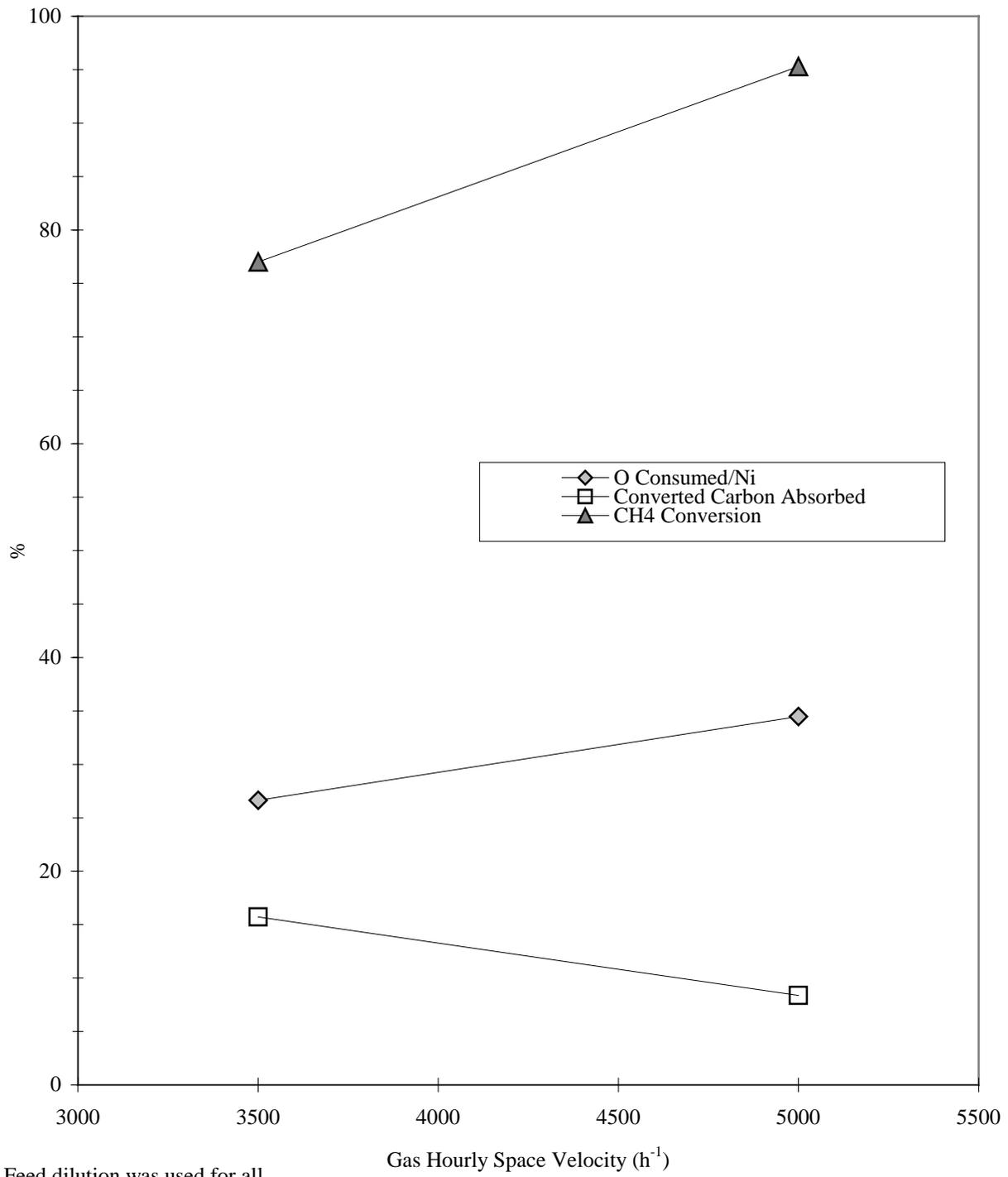


Figure 18. Gas hourly space velocity variation for catalyst P3.

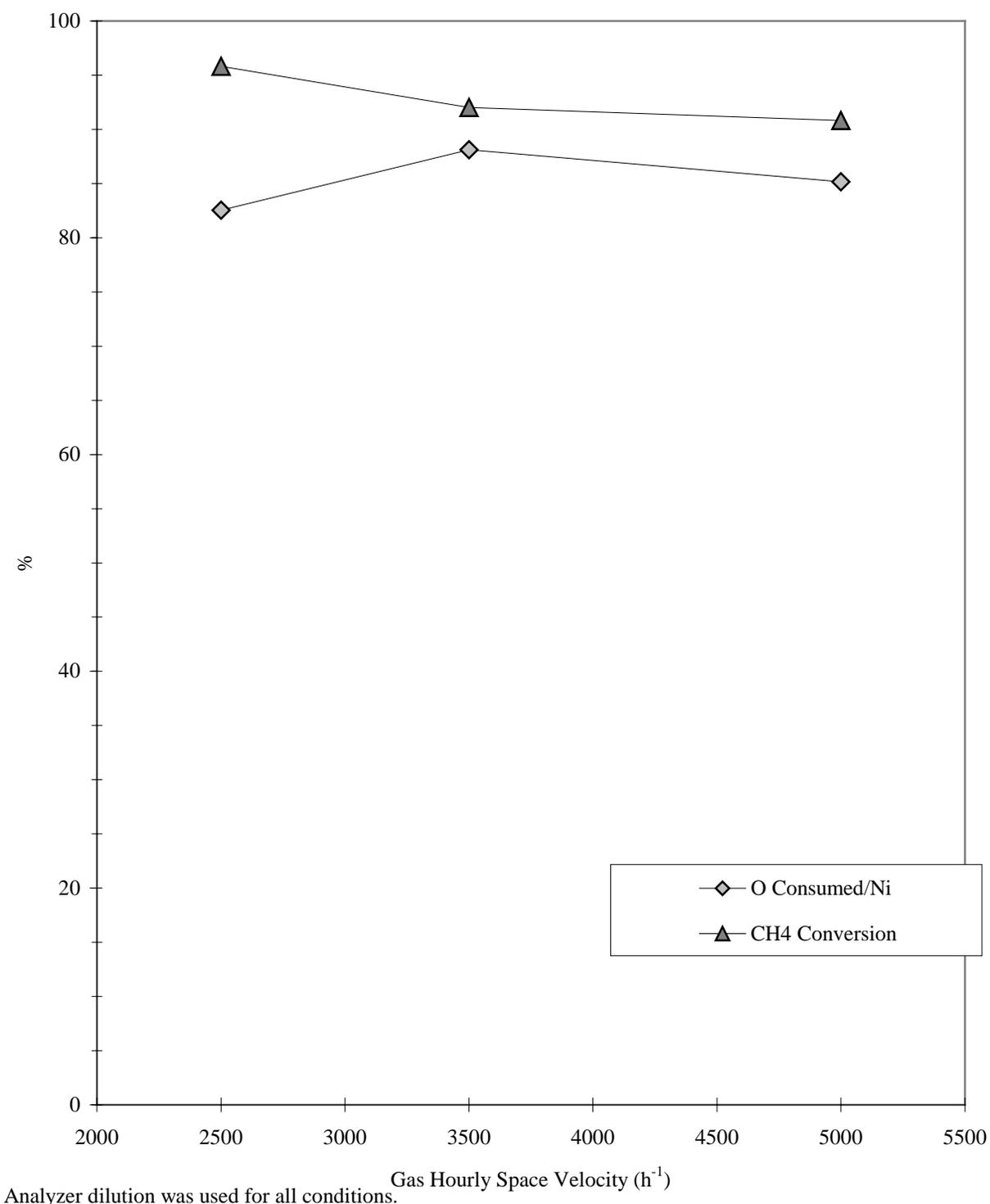


Figure 19. Gas hourly space velocity variation for catalyst P10.

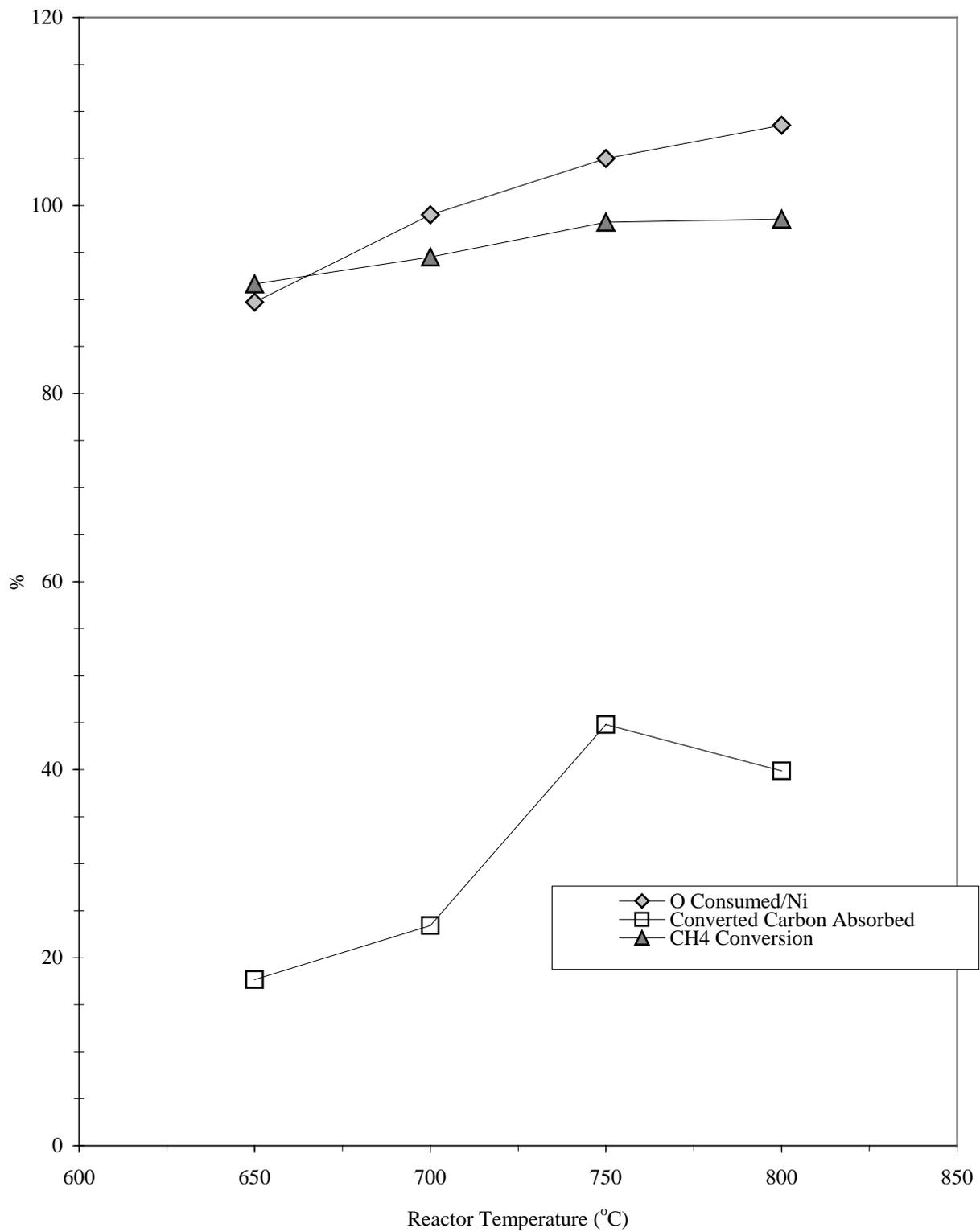
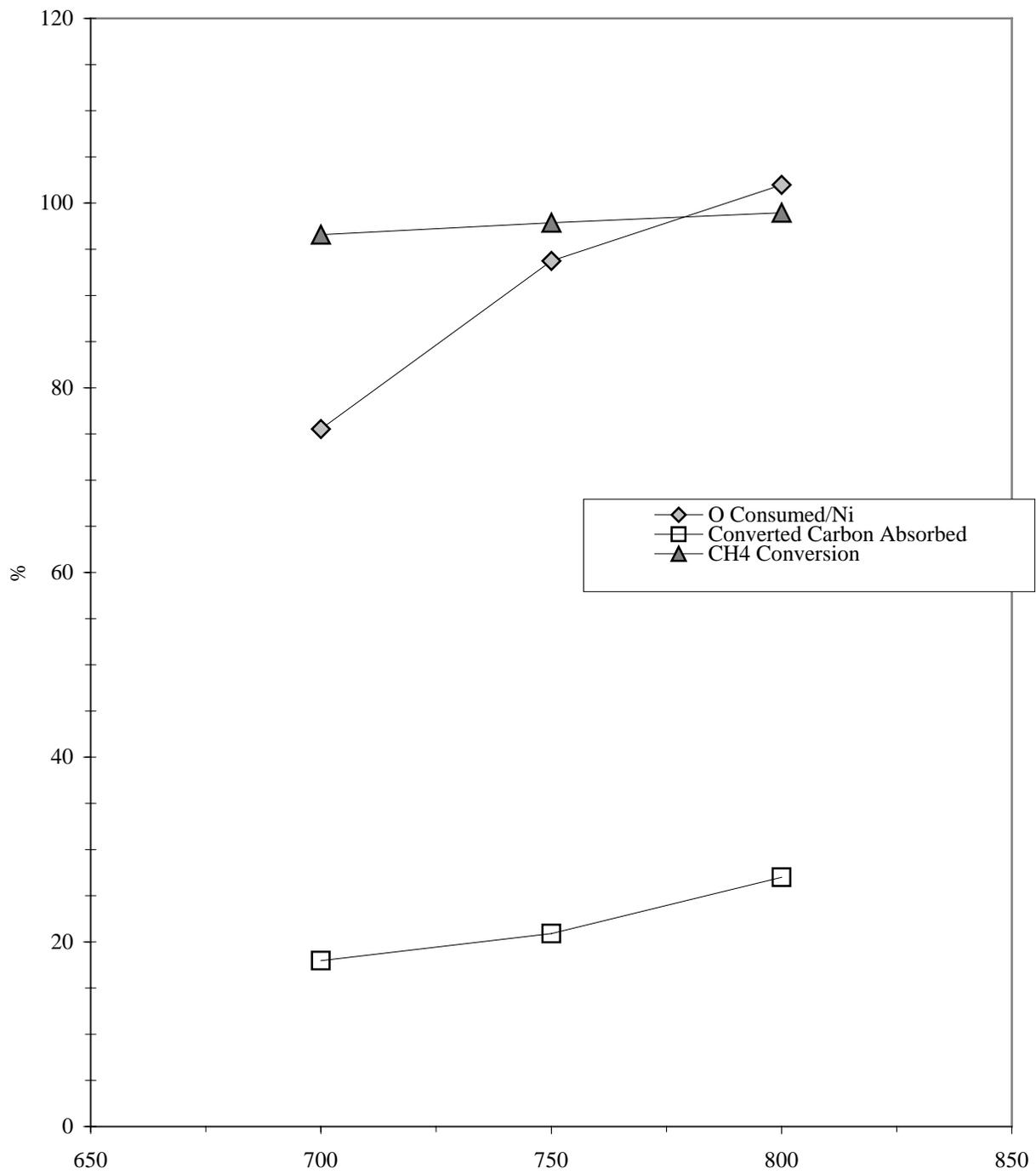


Figure 20. Reactor temperature variation for catalyst C1.



The variability associated with CH₄ conversion is very small (0.02%).

Figure 21. Reactor temperature variation for catalyst C2.

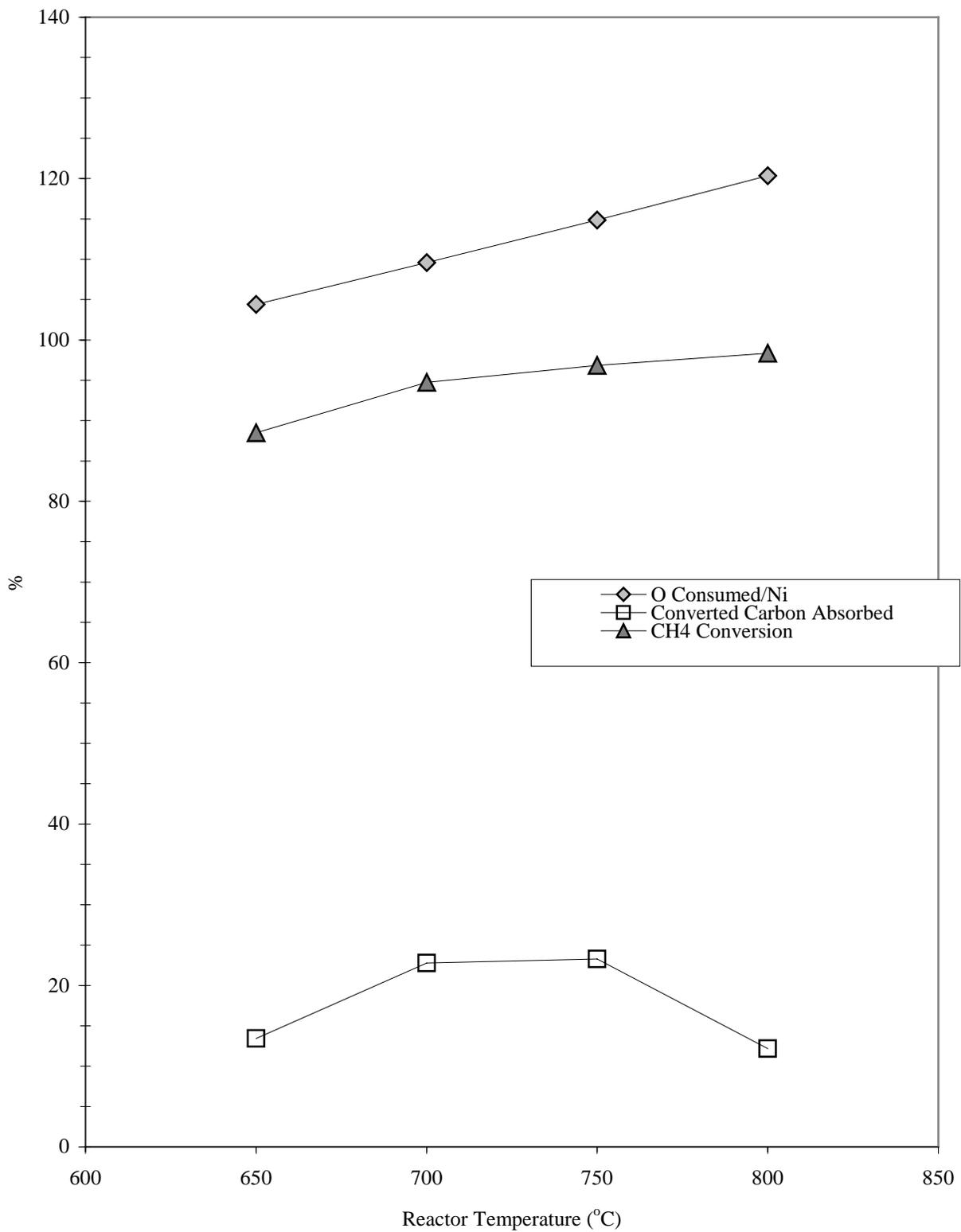
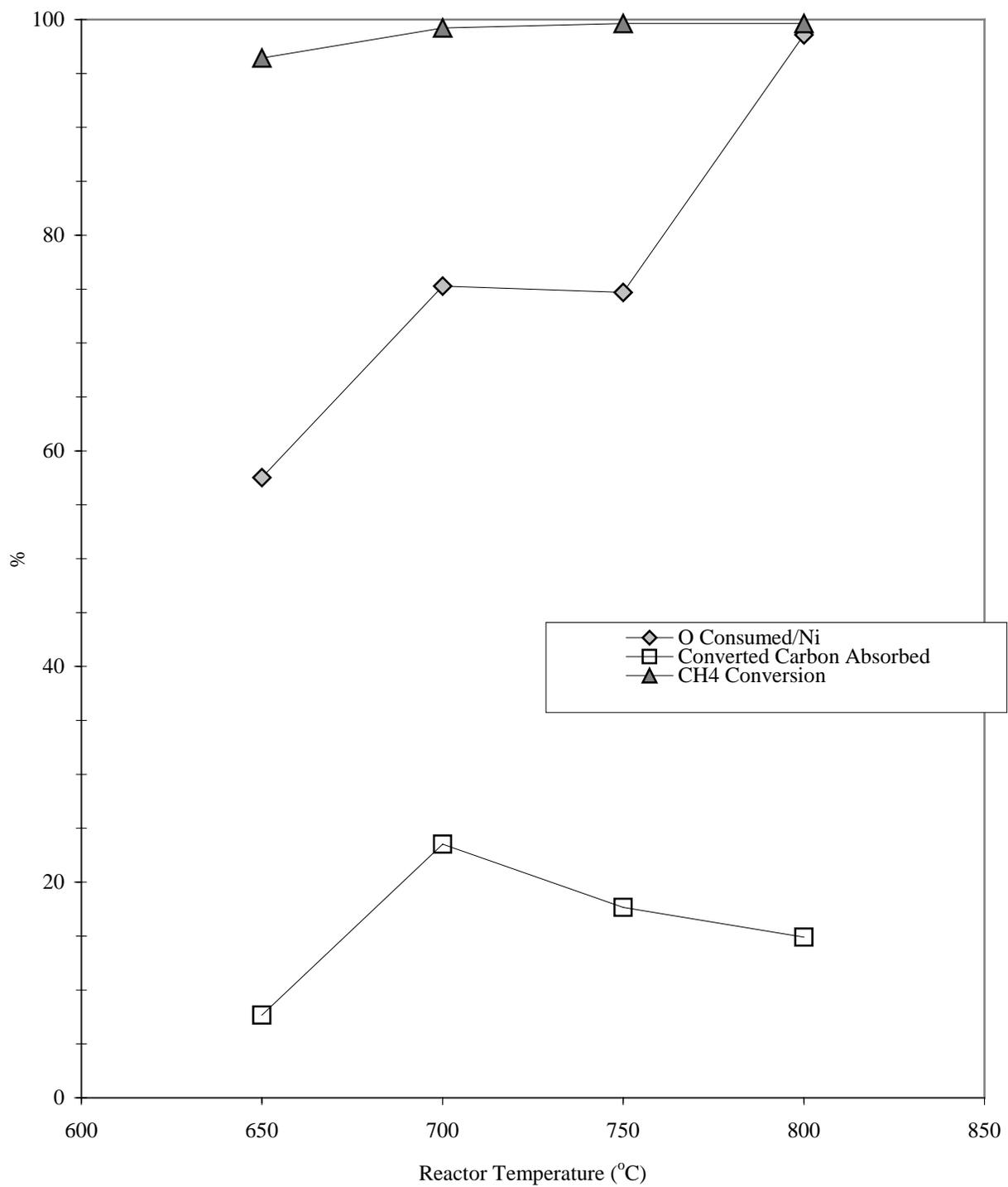


Figure 22. Reactor temperature variation for catalyst C3.



The variability associated with CH₄ conversion is very small (0.3%).

Figure 23. Reactor temperature variation for catalyst C4.

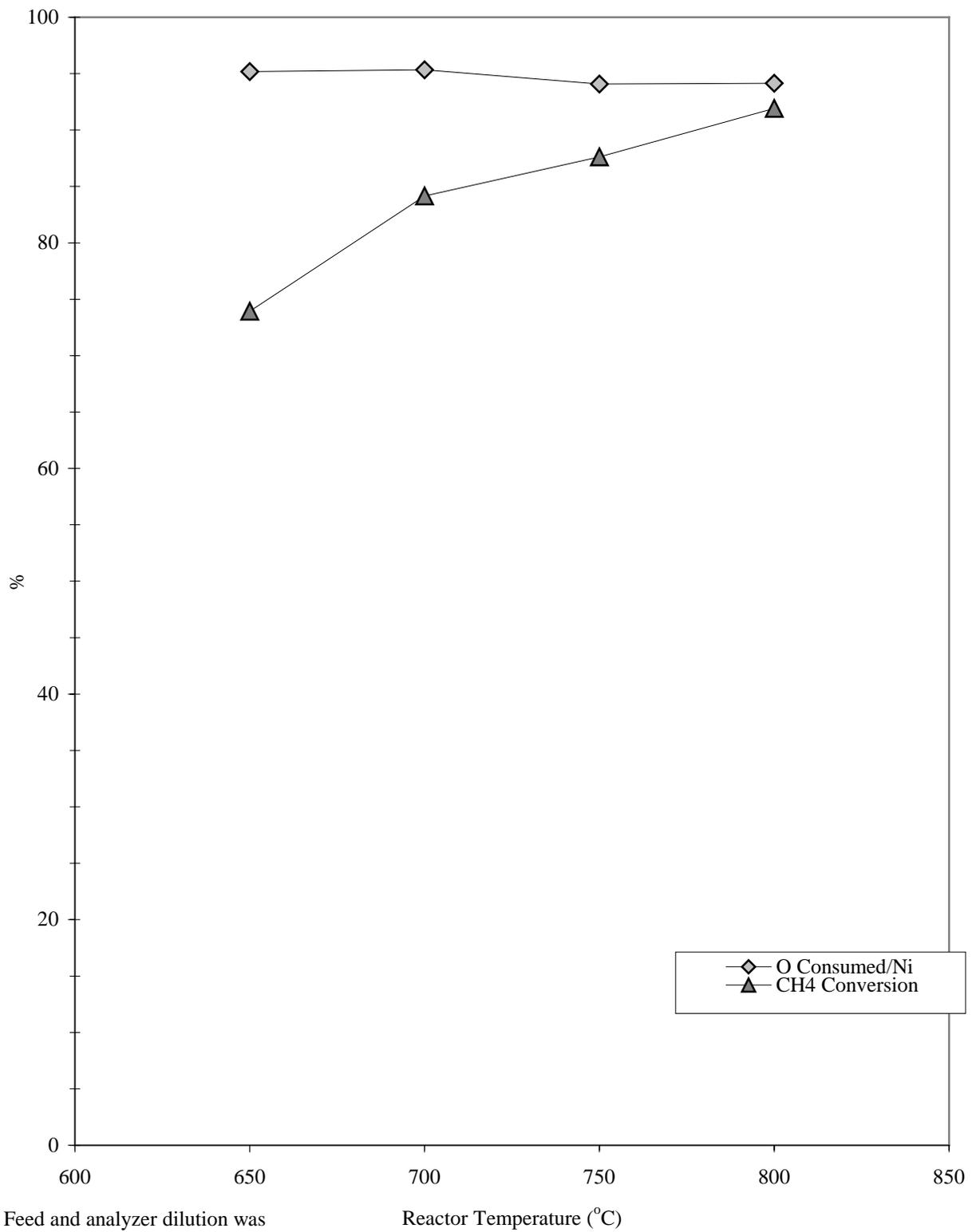


Figure 24. Reactor temperature variation for catalyst P10.

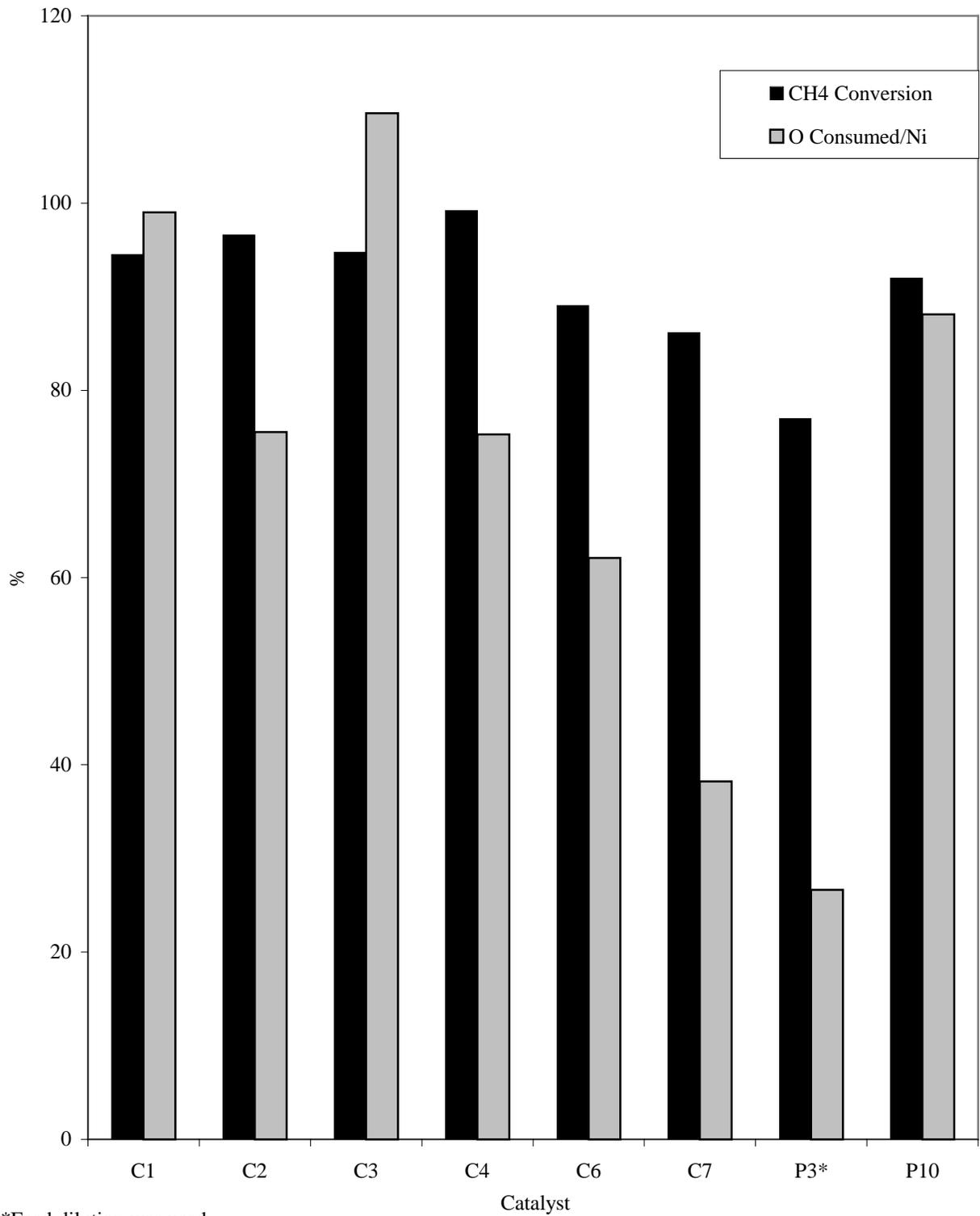


Figure 25. Summary of baseline parametric test results.

APPENDIX III:

ACCELERATED DURABILITY TESTING REPORT

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1.0 INTRODUCTION

EER's Unmixed Reforming (UMR) process is unique in its use of reforming catalysts and carbon dioxide (CO₂) absorber materials. It is a cyclic process with two steps: reforming and regeneration. In the reforming step, the nickel (Ni) on the catalyst is reduced to its active catalytic state, hydrogen is produced, and the CO₂ produced by reforming reactions is absorbed. In the regeneration step, the nickel on the catalyst is oxidized and the previously absorbed CO₂ is released into the vent gases. The nickel on the catalyst must be repeatedly oxidized and reduced, in addition to having high activity for the reforming reactions. To our knowledge, there are currently no commercially available catalysts designed for these purposes since conventional steam reforming is a continuous process eliminating repeated catalyst oxidation.

The CO₂ absorber materials suitable for the UMR process are generally either naturally occurring minerals containing calcium (Ca) such as dolomite or materials prepared by depositing calcium carbonate on a substrate. The repeated absorption and desorption of CO₂ by the absorber material poses a unique challenge for UMR material selection. Dolomite undergoes a physical breakdown in the presence of the high temperature steam required for the UMR process, while the CO₂ absorbing capacity of substrates with calcium deposited on them is limited by the amount of calcium present that can be utilized for absorption.

Development of materials for the UMR process, sponsored by the California Energy Commission (CEC) PIER I Program, is intended to identify suitable materials for the UMR process. Catalyst and absorber material development was identified as an area in which advances could have a significant impact on the commercial viability of the process. The development of the reforming process is part of a broader program supported by the U.S. Department of Energy (DOE).

EER teamed with Phillips Petroleum to utilize their expertise in high-temperature catalytic processes to address the catalyst and absorber issues unique to the UMR process. EER also considered several commercial catalysts that, although not designed for the UMR process, may coincidentally be suitable.

The approach taken to develop and identify suitable materials involves three steps: screening tests, parametric testing, and accelerated durability testing. This report presents the results of accelerated durability testing.

Accelerated durability testing was performed on catalysts that were selected based on the results of parametric testing. The accelerated durability test was designed to estimate catalyst lifetime under conditions that simulate UMR operation. Several stresses influence catalyst performance in UMR service. These include thermal cycling and oxidation/reduction cycling. The purpose of the accelerated durability test was to estimate catalyst lifetimes by subjecting the catalyst to accelerated frequencies of the stresses that lead to failure. The development of a protocol for accelerated durability testing was a significant part of this effort. Significant discoveries were made during development of the protocol that also assisted in optimization of the UMR process.

2.0 ACCELERATED DURABILITY TESTING PROTOCOL

Due to the importance of accurate assessment of catalyst lifetime, a significant effort was devoted to development of a protocol for accelerated durability testing. Accelerated testing provides accurate lifetime assessments when the stresses that lead to failure under typical operating conditions are identified and reproduced for accelerated testing. A protocol¹ was developed for accelerated durability testing based on a review of the literature and knowledge of the UMR process and typical catalyst failure modes. This protocol was further developed and refined using catalyst C3. The Durability Test Report² summarized the development of the protocol and presented the comprehensive accelerated durability test protocol.

The accelerated durability testing replicates UMR stresses. The three stresses identified as causing material failure are: thermal cycling, oxidation/reduction cycling, and CO₂ absorption/release cycling. Initial testing focused on reproducing all three of these stresses. However, after testing that included analysis of weight loss due to attrition of the particles, it was identified that the dolomite absorber material used in the tests degraded early in the tests, losing significant mass due to attrition. In addition, the gentle sieving used to separate powder from the material seemed to cause comminution of dolomite to powder. This led to the decision to perform accelerated testing on the catalysts only, as new CO₂ absorber materials suitable for the UMR process had not been identified.

Testing catalysts without absorbers reduced the number of stresses needed to two: thermal cycling and oxidation/reduction cycling. Air and fuel are the only feeds required to produce these stresses. The earlier testing protocol did not include the use of steam. After testing, the importance of steam to the fuel regeneration reactions was identified, and steam was again used in the system.

The importance of steam to the fuel regeneration reactions was identified after detailed evaluation of the accelerated tests. Tests conducted without dolomite were not expected to have significant concentrations of CO₂ during the air regeneration step, since CO₂ was not being released from the dolomite. However, significant concentrations of CO₂ and carbon monoxide (CO) were present during the air regeneration step, especially early in the step. After detailed evaluation of this phenomena, it was concluded that the absence of steam during the fuel regeneration step caused coking to occur, and this coke was being oxidized during the regeneration step to form CO and CO₂. Coke oxidation created an unwanted stress that would not be present in typical UMR operation. Tests were conducted to determine the amount of steam that was needed to prevent coking during the fuel regeneration step. A steam to carbon ratio of one provided enough steam to prevent coking during the accelerated test fuel regeneration/reforming step. This information was used to modify the typical operating conditions of the pilot test facility as well as the accelerated durability tests.

The stresses that the accelerated test is designed to reproduce are the thermal cycling and the oxidation/reduction cycling. Figure 1 shows several steps of an accelerated test. The shaded

¹ A Novel Steam Reforming Reactor for Fuel Cell Distributed Power Generation: Test Plan Appendix F. Accelerated Durability Test Protocol Summary, June 30, 1999.

² A Novel Steam Reforming Reactor for Fuel Cell Distributed Power Generation: Durability Test Report, October 11, 1999.

areas of the chart are the regeneration steps. Because the steps were so brief, there was significant lag in analyzer response, although it did not impact the results. A qualitative assessment showed that durability testing produced the types of oxidation/reduction cycling and therefore temperature cycling stresses expected in typical UMR operation

Figure 1 also shows that the CO₂ concentration reached a peak value at the beginning of the reforming step, consistent with the formation of CO₂ during the nickel reduction reaction. The concentrations of CO, CO₂, and methane (CH₄) all dropped to zero during the regeneration step, which verified that coke oxidation was not taking place during the regeneration step. An estimate of the O consumed/Ni showed that approximately 35% of the nickel was being oxidized in each 20-second regeneration step. The oxidation of nickel generates significant heat that leads to local temperature cycling.

The accelerated test was designed to subject the catalysts to the normal cyclic stresses of the UMR process at accelerated frequencies. Catalyst performance was measured intermittently to identify degradation of performance. Thus, the accelerated testing protocol includes two modes of operation: performance characterization tests and accelerated tests.

The performance characterization test was used to make an initial characterization of material performance, and then check the performance intermittently over the catalyst life span. The performance test was conducted by running one reforming step and one regeneration step at 700 °C. Each step was run for approximately 20 minutes.

The accelerated test was run at 700 °C, and involved cycling between reforming and regeneration steps every 20 seconds. The 20-second steps provided an acceleration factor of 15 relative to the standard 300-second reforming and regeneration steps of the UMR process. Steam and natural gas were fed during the reforming step, and air was fed during the regeneration step.

The accelerated test was stopped periodically to conduct performance characterization and to observe the physical changes in the catalyst. After the performance characterization, accelerated testing was resumed.

3.0 EXPERIMENTAL FACILITY SET-UP

Accelerated durability testing was performed on the modified bench-scale experimental system as shown in Figure 2. The system was modified to accommodate the unique operating conditions of the accelerated durability tests. The modifications included a change to the steam preheater system, the addition of low-flow rotometers for the natural gas and air, and the use of a syringe pump for water delivery.

The use of short cycles required that the lag times between cycle switching and the delivery of the reactants to the reactor be minimized. The need to preheat steam, which was not flowing during the regeneration step, was identified as an aspect of the system that needed modification. Since it was not desired to feed steam to the reactor during the air regeneration step, it was

decided to vent steam during the air regeneration step. This required the installation of a high-temperature three-way solenoid valve between the steam preheater and the reactor inlet. The valve was wired to the cycle switching controller so that the steam raised in the preheater was vented during the air regeneration step and fed to the reactor during the reforming step.

During accelerated durability performance testing, small quantities of catalyst were tested. This required the use of much lower reactant flow rates than had been used in the screening or parametric tests. Thus, the addition of reduced capacity rotameters to the system for both the natural gas and the air was required. A syringe pump was also added to provide the low flow rates of water required for these tests.

The low flow rates of steam and natural gas during the performance tests did not produce enough product gas for all of the continuous emissions monitoring system (CEMS) analyzers, and the nature of the test ensured high unreacted CH₄ levels. Thus, it was decided to dilute the reactants with nitrogen during the performance tests. A calibrated mixture of 4.5% CH₄ in nitrogen was used, along with steam, as the feed for the reforming step of the performance tests.

4.0 CALCULATIONS OF PERFORMANCE INDICATORS

The CH₄ conversion during reforming and the moles of elemental oxygen (O) consumed per mole of nickel present in the catalyst are the performance indicators for the performance tests. It was desired to know the ultimate steady state reforming performance, so an average outlet concentration was obtained after the system had stabilized, as shown by the lightly shaded region in Figure 3. These average reforming concentrations were then used to calculate the CH₄ conversion. The regeneration performance calculations were based on the data from the beginning of the air regeneration step, as shown by the more darkly shaded region in Figure 3. A nitrogen purge was used between reforming and regeneration steps to minimize overlapping.

During performance testing, the O₂:Ni ratio varied with the length of the regeneration step, so the oxygen consumption was normalized by the amount of nickel in the bed to provide a consistent basis for comparison.

4.1 % CH₄ Conversion

The CH₄ conversion is measured as the amount of CH₄ that leaves the catalyst bed unreacted. The % CH₄ conversion is defined as:

$$\% \text{ CH}_4 \text{ conversion} = \frac{\text{CH}_4\text{in} [\text{mol}] - \text{CH}_4\text{out} [\text{mol}]}{\text{CH}_4\text{in} [\text{mol}]} \times 100\% \quad (1)$$

The % CH₄ conversion is calculated as:

$$\% \text{ CH}_4 \text{ conversion} = \frac{F_{\text{NGREF}_f} [\text{mol/hr}] - \text{AvgCH}_4\% * F_{\text{REF}_p} [\text{mol/hr}]}{F_{\text{NGREF}_f} [\text{mol/hr}]} \times 100\% \quad (2)$$

The % CH₄ conversion is an indication of the amount of natural gas fed that reacts to form products such as hydrogen, CO, and CO₂.

4.2 % O Consumed/Ni

Oxygen consumption is measured as the difference between the amount of oxygen fed to the reactor and the amount of oxygen leaving the reactor during the air regeneration step. The % O consumed/Ni is defined as:

$$\% \text{ O Consumed/Ni} = \frac{2 \text{ O [mol]}}{\text{O}_2 \text{ [mol]}} \times \frac{\text{O}_2 \text{ fed [mol]} - \text{O}_2 \text{ exiting [mol]}}{\text{Ni [mol]}} \times 100\% \quad (3)$$

The % O Consumed/Ni ratio is calculated as:

$$\% \text{ O Consumed/Ni} = \frac{2 \times t_{\text{REG}} \times (0.21 \times F_{\text{REGf}} \text{ [mol/hr]} - \% \text{O}_{2v} \times F_{\text{REGv}} \text{ [mol/hr]})}{\text{Ni [mol]}} \times 100\% \quad (4)$$

Where:

t_{REG} is the regeneration step time (hrs)

F_{REGf} is the molar flow rate of air fed during the regeneration step.

$\% \text{O}_{2v}$ is the average measured concentration of oxygen in the regeneration vent stream.

F_{REGv} is the molar flow rate leaving the reactor during the regeneration step.

C_L is an experimentally determined constant to account for the time lag in the oxygen analyzer

mol Ni is the moles of nickel present in the catalyst bed.

The % O consumed/Ni is a measure of the amount of elemental oxygen that reacts with the nickel on the catalyst to form nickel oxide (NiO). This also indicates the amount of nickel that is participating in the oxidation and reduction cycle during the regeneration and reforming steps. This is useful in identifying materials that are able to maintain catalytic activity for reforming while cycling between the regeneration and reforming steps, one of the unique aspects of the unmixed reforming process. Another unique aspect is the use of the exothermic nickel oxidation reaction to provide heat to the bed during the regeneration step. The amount of oxygen consumed by nickel oxidation is an indicator of the extent to which this occurs, which is important for the intended autothermal use of the unmixed reforming technology.

5.0 RESULTS OF ACCELERATED DURABILITY TESTS

Extensive testing was performed on catalyst C3 in evaluation and development of the accelerated testing protocol. After the protocol was finalized, an accelerated durability test was conducted on catalyst C3. However, a mechanical malfunction ended the test prematurely and the material

had totally disintegrated. The cause of failure could not be identified. Accelerated testing was also performed on catalyst P10.

Catalyst P10 was tested for 290 hours, equivalent to a 4350-hour lifetime. Catalyst P10 showed a step change in conversion level after initial accelerated testing, as illustrated in Figure 4. However, the level of conversion achieved after 20 hours of testing was maintained for the remainder of the 290-hour test. The oxygen consumption is shown in Figure 5. The oxygen consumption showed a slight drop initially and then remained adequate for the remainder of the test.

The physical properties of the catalyst P10 substrate are well suited to the UMR conditions. This material was designed by Phillips Petroleum to be an especially durable material at high temperatures and in the presence of high temperature steam. This was verified during testing, as even after 4350 hours of equivalent lifetime, no evidence of attrition or phase changes were reported. The lower conversion for this catalyst may be overcome by judicious selection of operating conditions such as GHSV and temperature. Further development of this catalyst may involve the addition of promoters that would allow it to maintain its initial activity to a greater extent.

6.0 SELECTION OF MATERIALS FOR PROTOTYPE UMR REACTOR TESTING

Within the original timeframe of the CEC project, only catalyst C3 was seen to meet the UMR performance requirements in time for testing on the pilot facility. Several of the catalysts developed by Phillips Petroleum had nickel reduction issues that caused poor performance. The screening and parametric testing identified specific aspects of catalyst behavior that limited performance, and these were discussed with Phillips Petroleum.

Later in the CEC program, a significant discovery occurred that led to the development of a catalyst that minimized previous reactivation issues of the fuel regeneration step. This led to the development of catalyst P10. Catalyst P10 was subjected to accelerated durability testing and found to be extremely durable and have a suitable level of activity that was maintained during testing. EER is currently pursuing the use of this catalyst in the pilot test facility during the course of the DOE program.

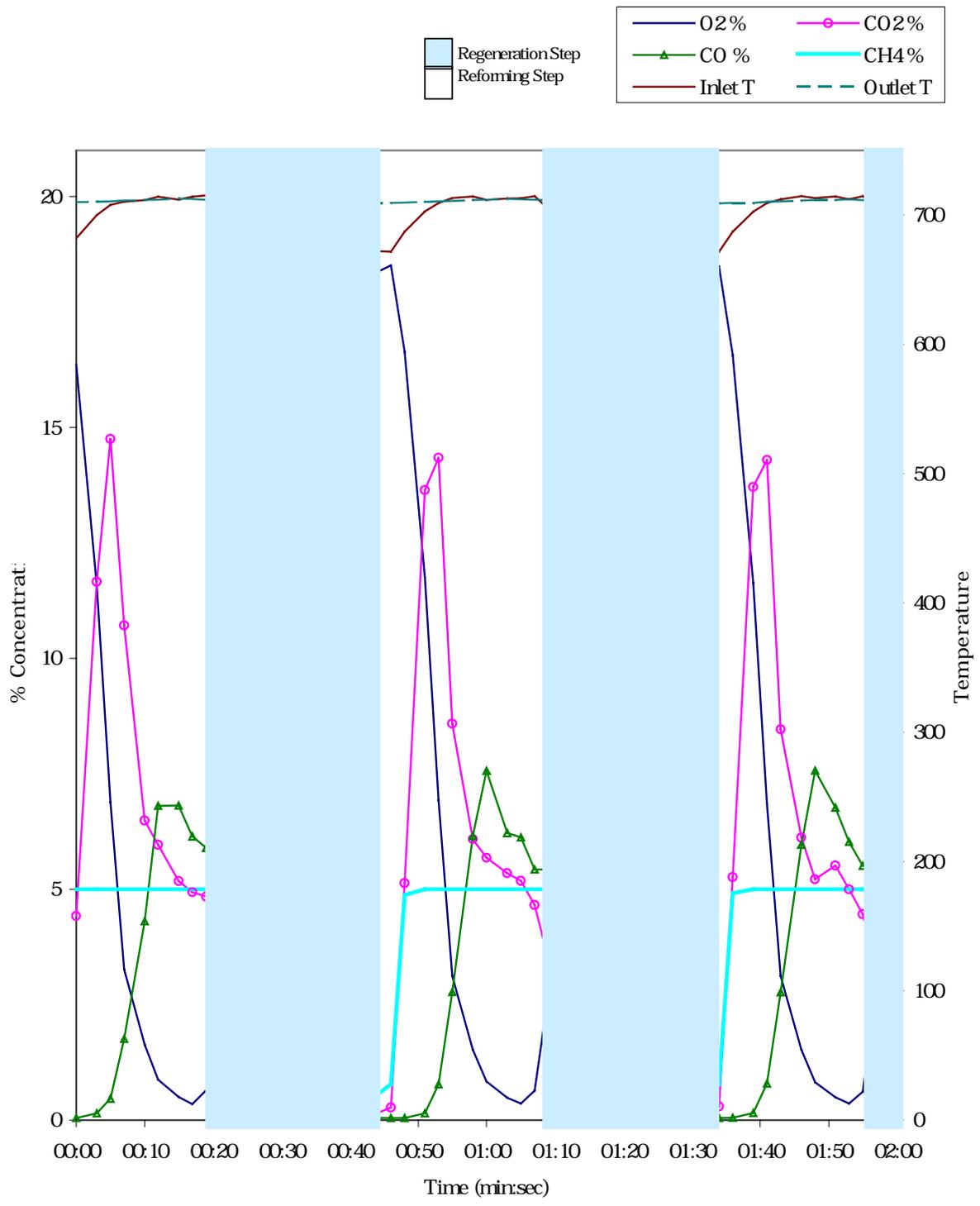


Figure 1. Accelerated testing results for catalyst P10.

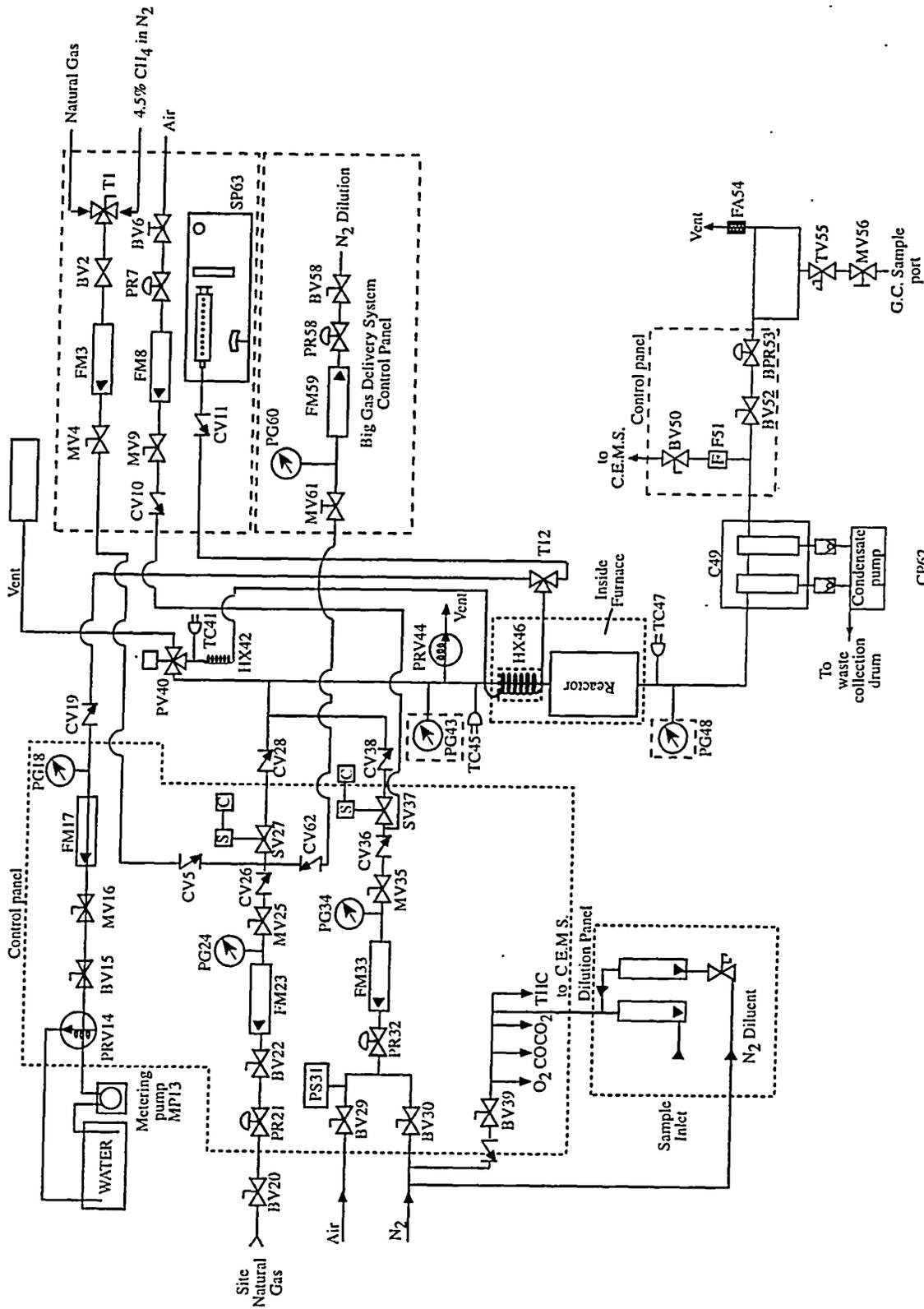


Figure 2. Bench-scale UMR experimental system modified for accelerated durability testing.

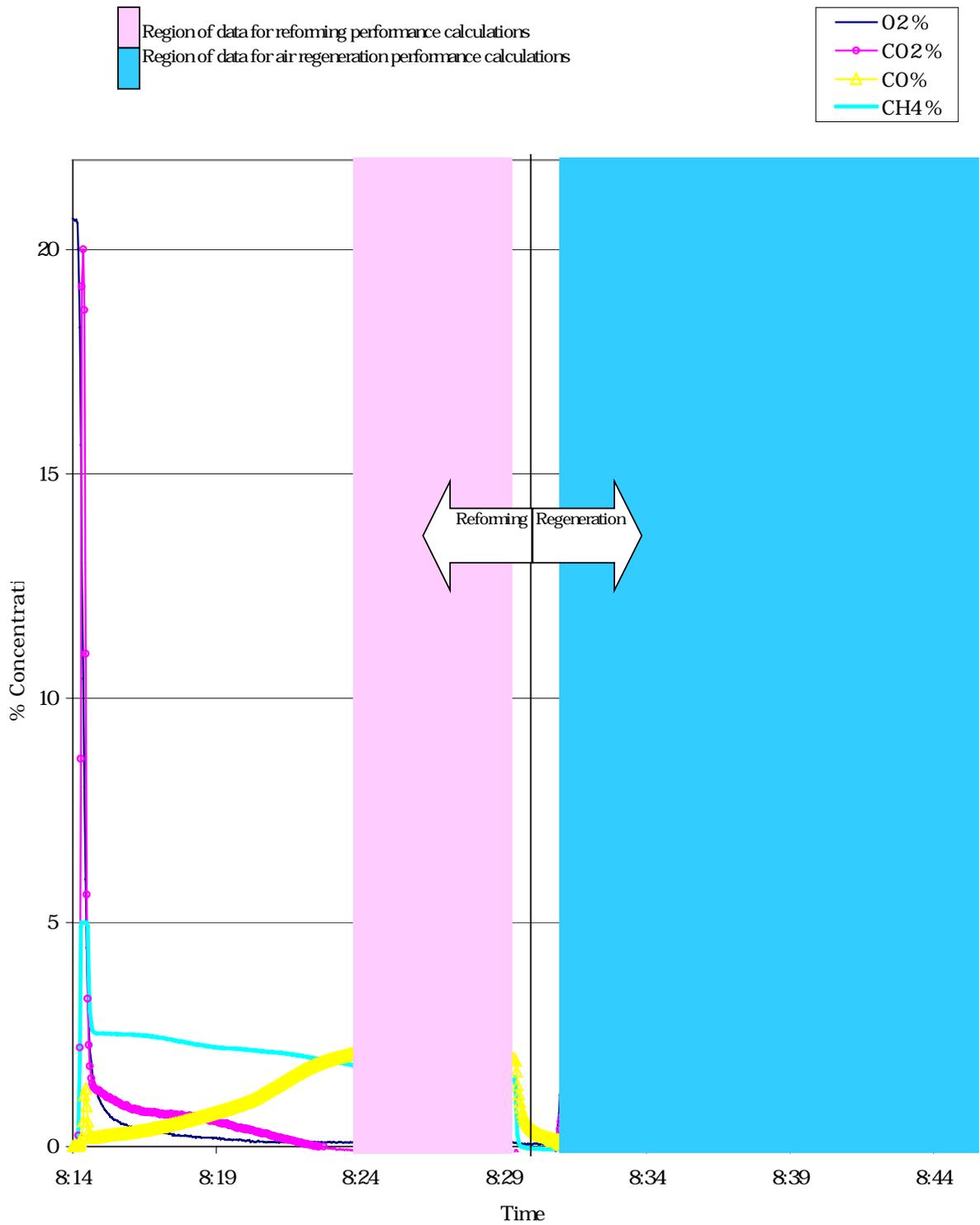


Figure 3. Accelerated durability performance test for catalyst P10.

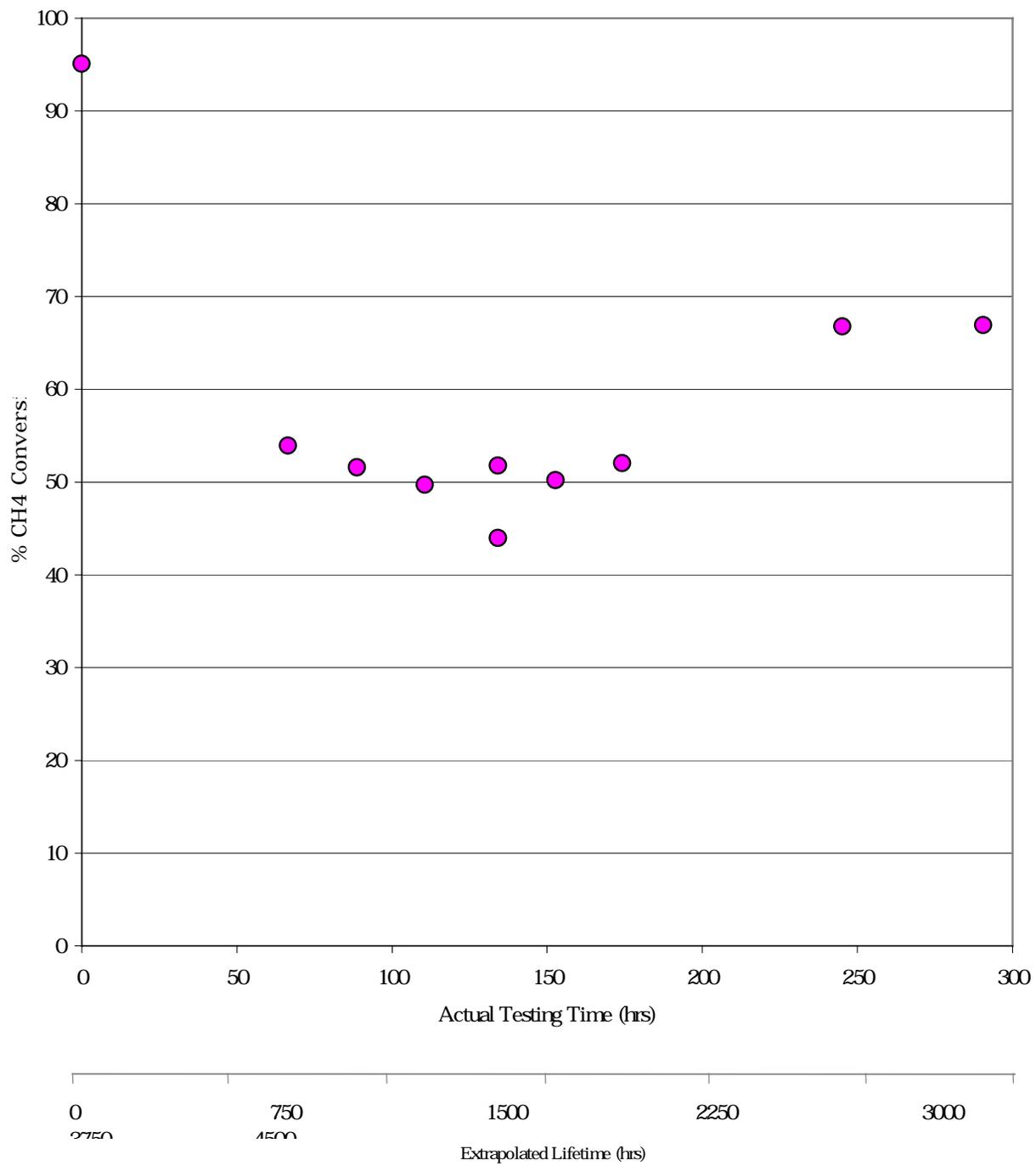


Figure 4. Accelerated durability test results for P10: % CH4 conversion.

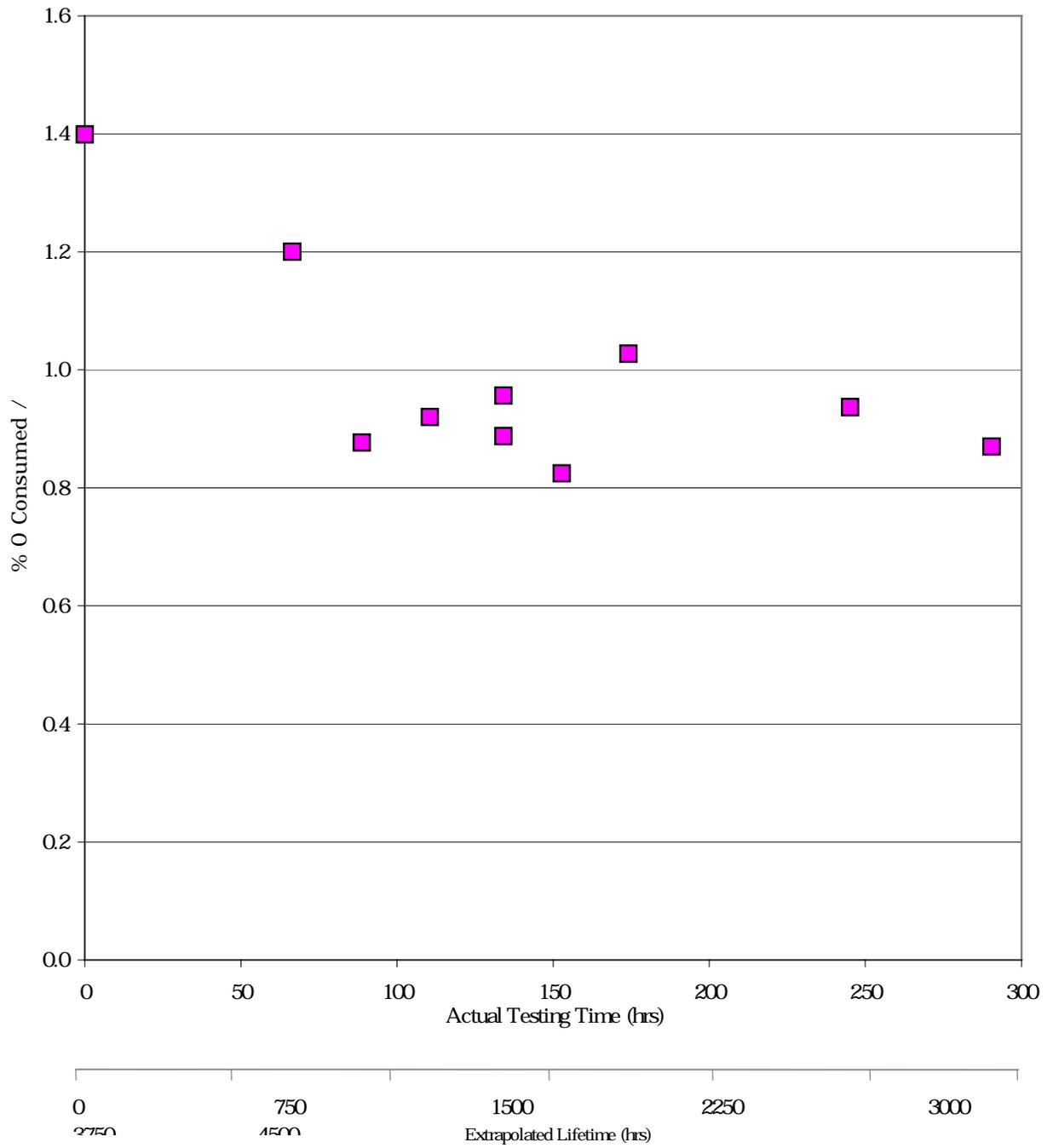


Figure 5. Accelerated durability testing results for P10: % O consumed /Ni.

APPENDIX IV:

**PROTOTYPE REACTOR TESTING
ON THE PILOT TEST FACILITY**

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1.0 INTRODUCTION

Energy and Environmental Research Corporation (EER) is currently conducting a program to design, assemble and operate a pilot test facility for reforming natural gas to produce fuel cell-grade hydrogen (H_2). The facility comprises a fully integrated autothermal process for natural gas reforming and hot water cogeneration system. Under this project, reforming catalysts are being developed for testing in prototype reforming reactors installed on the pilot test facility.

The intent of the catalyst development effort was to identify catalysts for testing on the pilot facility. The main focus of the catalyst development effort was to develop active catalyst comprised of thermally stable supports formulated by Phillips Petroleum. Initially, the catalyst formulations from Phillips Petroleum performed unsatisfactorily. The activity of the new materials rapidly dropped after regeneration and this was attributed to possible secondary reactions between the reactive nickel (Ni) catalyst and the catalyst support.

Later in the catalyst development effort, a modified formulation of nickel catalyst and catalyst promoters was produced which substantially overcame the activity issues. Unfortunately, this material was discovered too late in the California Energy Commission (CEC) project to allow testing on the pilot facility. However, EER did identify a very active commercial nickel catalyst that was tested on an early configuration of the pilot facility. EER is continuing the optimization of the pilot test facility and is planning continued testing of catalyst materials identified under the CEC project as suitable for the Unmixed Reforming (UMR) process.

The purpose of this section is to describe the prototype reactor design for the selected commercial catalyst and to present results of the pilot facility tests on commercial reforming catalyst C3.

2.0 PILOT TEST FACILITY DESCRIPTION

The pilot test facility is a breadboard design that allows component evaluation and reconfiguration for process optimization. A process flow diagram of the pilot test facility is included in Figure 1. The reforming reactors are the heart of the pilot facility, around which various heat exchangers are integrated for heat recuperation and steam production. The reformate product gases from the reactors are delivered to polishing systems including low temperature shift and carbon monoxide (CO) removal reactors to produce PEM fuel cell grade hydrogen. The reactor vent gas from the regeneration cycle is treated in a catalytic oxidizer to reduce CO and (CH_4) emissions prior to the gas being used for cogenerated water heating.

The pilot testing is currently focussed on autothermal operation of the reforming reactors so the reformate polishing systems and the vent gas emission components are not yet integrated. The performance of the integrated system is therefore assessed based on the actual reactor performance and the design performance of the peripheral components. The pilot test facility is illustrated in Figure 2 showing the breadboard component assembly supported on a truss framework.

3.0 PROTOTYPE REACTOR

UMR is a cyclic process requiring at least two reactors for continuous hydrogen production. The reactor designed and used for tested of the selected catalyst consists of a packed catalyst bed in an axial flow reactor. The reforming and regeneration feeds flow downward along the axis of reactor. The reactor specifications are presented in Table 1. The reactor comprises multiple concentric channels around the internal catalyst bed (Figure 3).

Reactants enter along the outer wall and flow downward and then back up the inside wall before entering the bed from above. After passing through the bed, the reformat gases flow up along the outer bed wall and then down, exiting from the bottom of the reactor.

The multi-channel design accomplishes internal heat recuperation by preheating the reactants, and achieves a more uniform bed thermal profile. By reducing radial temperature gradients in the axial flow reactor, lower slip at the wall boundary can be achieved. A photograph of the reactor outer housing and internal liners that make up the various channels is presented in Figure 4.

TABLE 1. PROTOTYPE REACTOR SPECIFICATIONS

Specification	Units	Value	
Reactor Capacity (Electrical Equivalence)	kWe	50	
Process Parameters:		Reforming Step	Regeneration Step
Feed		Fuel+Steam	Air
Reactor Feed Rate	kg/hr	28	152
Gas Hourly Space Velocity	hr ⁻¹	2000	7000
Reactor Pressure Drop	bar	0.05	0.5
Inlet/Outlet Temperature (max.)	°C	570/900	
Design Pressure	bar	3	
Packed Catalytic Bed Specifications:			
Composition		Ni+CaO+Substrate	
Mean Particle Size	mm	3	
Bed Volume	Liters	27	
Bed Diameter	cm	28	
Bed Length	cm	44	
Reactor Vessel Specifications:			
Outer Wall Temperature	°C	150	
Heat Loss	kW	1.0	
Inner Refractory		Alumina Silica	

Specification	Units	Value
Outer Insulation		3" Kao-wool Blanket
Reactor Flow Dispersion Plates		Reticulated Ceramic
Reactor Weight	kg	100

The outer housing (Figure 5) is enclosed top and bottom by reactor lids sealed with high temperature gasket material. Several gasket materials have been evaluated for sealing the UMR reactors. Interam^{TM1} when coated with Silver Seal II paste sealant² has met performance requirements at pressures up to 3 bar. Also shown in Figure 5 are the natural gas burners on the reactor that are used for startup.

4.0 PILOT FACILITY CONTROLS

The pilot test facility is equipped with complete process monitoring and control for automatic and manual operation. It is also equipped with process monitoring for real-time performance analysis at a component by component level and for feedback control of the entire process. The control system is run from a Microsoft Windows NTTM computer running National Instruments' LabViewTM software.

A cascade control system was developed to control the UMR reactor temperatures. The control system determines the set points for the steam and natural gas flow rates to maintain the process within a thermally acceptable window and then regulates the steam and natural gas flow by automatically actuated valves.

The control system for determining the set points for the steam and natural gas flow rates has two modes: manual and feed-back control. In manual control, the steam and natural gas flow rate set points are entered by the user. In feed-back control these set points are determined by an algorithm based on the cycling time-temperature profile of the reactor bed and the boiler steam pressure. In cases where boiler steam pressure reaches the maximum allowable pressure, the steam flow is increased to maintain boiler pressure.

Additionally, the steam and natural gas valves can be manually set to a percent open or can be placed into proportional integral derivative (PID) control, where the control system will continually adjust the valve position to maintain the desired flow set point. The valve control must be in PID control mode when the reformer control system is in feedback control mode.

5.0 PROTOTYPE REACTOR TESTS

The development of the prototype reactors was accomplished with bench top testing of the reactors prior to installation and operation on the pilot facility. The bench top tests allowed

¹ 3M, St. Paul, Minnesota

² IGS sealant Technology Group, Meadow Lands, PA

independent operation of the reactors on preheated reactant streams and did not rely on process subcomponents for steam production and reactant preheating. Later testing on the pilot test facility was carried out with integrated heat recuperation and steam generation.

5.1 Testing on the Bench Top System

The prototype reactor was tested on the bench top system, which had been configured specifically for evaluating new reactor designs. Three UMR catalysts and two bed configurations were independently evaluated in the prototype reactor. In the first bed configuration the catalyst and the carbon dioxide (CO₂) absorber, dolomite, were mixed uniformly throughout the bed. In the second bed configuration, ten alternating layers of catalyst and dolomite were loaded. The catalyst bed with the mixed configuration was the most effective in bench top tests. The reforming data for the mixed catalyst C3 and dolomite is presented in Table 2. The catalyst was effective in converting over 80 percent of the CH₄, and the reformat stream contained 5 percent CH₄ and 8 percent CO. These levels meet the design target for the concentrations of these impurities exiting the reactors. The CO₂ level at 14 percent is slightly above the target of 10 percent but should be effectively optimized to target levels.

TABLE 2. REFORMING STEP AVERAGE DATA FOR THE PROTOTYPE REACTOR ON THE BENCH TOP SYSTEM

CH ₄ conversion during reforming:		81.6 %
Dry composition of the syngas:	CO ₂	14.2 %
	CO	7.8 %
	CH ₄	4.6 %
	H ₂	73.4 %

Intrinsic to the UMR process is the oxidation and reduction reactions of the nickel catalyst. The oxidation reaction provides the heat for the endothermic reforming reactions. The fractions of nickel oxidized and reduced during each cycle can impact the overall efficiency of the process. Figure 6 presents the fractions of oxygen consumed and nickel reacted over a single air regeneration step. The period of the air regeneration step is 300 seconds. The ratio of oxygen fed to the nickel's oxygen capacity is 1.7, corresponding to 70 percent excess oxygen. During the regeneration step, 30 percent of the oxygen feed was consumed and 51 percent of the nickel was oxidized. The overall efficiency of the process can be increased by increasing the fraction of nickel oxidized with minimal air feed. Efforts are planned to identify the optimal operating conditions and catalyst material for increasing the effectiveness of the nickel oxidation and reduction.

The bench top tests provided some preliminary shakedown performance information on the prototype reactor, which demonstrated suitable high temperature operation, heat recuperation and reforming chemistry. The prototype reactors were then installed on the pilot test facility.

5.2 Testing on the Pilot Test Facility

The breadboard system was designed to test and integrate all of the fuel processor components. The data collected on reactor performance included reactant feed rates, process stream temperatures, line pressures, component skin temperatures, and product and vent gas compositions. This unit was operated in a preliminary configuration, subject to operating restrictions resulting from excessive heat recuperation and low steam boiler heat exchanger effectiveness. The high heat recuperation of the reactor's external heat exchangers reduced the enthalpy of the vent gas to the boiler, which, coupled with a steam boiler not meeting specifications, caused low steam production. Therefore, the pilot facility was limited to low capacity operation and only minimal reactant preheating. Under these conditions, the promising catalyst C3 identified in the CEC bench-scale experiments was evaluated in the prototype reactors.

EER is currently reconfiguring the pilot test facility to increase steam production and reactant preheating and plans to demonstrate UMR process performance at the target capacity of 50 kWe¹. The following sections present performance results of the prototype reactors operating with catalyst C3 on the pilot facility.

5.2.1 Operating Capacity

As the pilot facility is reconfigured to increase steam production and reactant preheating, the only issue that should impact operating capacity is the system pressure drop. The pressure drop through the prototype reactor and external heat exchanger has been measured experimentally operating at 20 kWe. The pressure drop was then scaled to 50 kWe conditions using the relationship:

$$\Delta P = K \rho V^2 \quad (1)$$

Where:

- ΔP is the pressure drop
- ρ is the gas density
- V is the gas velocity
- K is the pressure drop coefficient.

The predicted pressure drops through the prototype reactor and external heat exchanger at 50 kWe during the reforming and regeneration steps are 0.1 and 1.8 bar, respectively. The available pressure drop during reforming and regeneration is estimated at 0.7 and 3.5 bar, respectively. Therefore, an operating capacity of 50 kWe is achievable.

5.2.2 Pilot Facility Thermal Profile

The pilot facility was operated at 20 kW electrical equivalent. The steam was superheated to 210°C and blended with natural gas prior to entering the external heat exchanger. The reactants exiting the heat exchanger were preheated to 273°C and delivered to the reactors. The reactant feed temperature of 273°C was considerably below the design preheat of 640°C as a result of the

¹ kWe refers to kW of equivalent electric power when the reformer is integrated with a PEM fuel cell.

facility limitations discussed earlier. The product gas temperature from the reactor was controlled to 800°C, which is within the reaction sustaining temperature window of 700 to 1000°C.

From skin temperature measurements of the reactors, the reactor heat loss is comparable to 3 kW out of a total input heat value of 60 kW. The heat loss is three times the desired level but was necessary to reduce thermal stress and sealing difficulties. To reduce heat loss in a fully integrated unit, the external heat exchanger will be replaced by additional internal recuperation so that the reactor shell can operate at low temperatures, thereby reducing heat loss and thermal design issues. However, these levels of heat loss are acceptable within the framework of component-by-component evaluation of a breadboard system.

5.2.3 Reformate Product

The prototype reactors were again operated at 20 kWe with a reactor exit temperature of 790°C and pressure of 2.0 bar absolute. The S:C was maintained at a 3:1 molar ratio and the reactor GHSV was 1400 hr⁻¹. The composition of the syngas produced during the reforming step is shown in Figure 7. Here the hydrogen concentration exceeds 80 percent. The CO averages 8 percent and CO₂ is around 4 percent. CH₄ concentrations are likewise low at 4.5 percent. The CH₄ concentration is seen to increase during the reforming process because the temperature of the bed decreases. Further optimization of the CH₄ levels can be accomplished by adjusting the reforming step period or increasing the reactant preheat temperature to delay bed cooling.

At these operating conditions the hydrogen production was calculated at 350 cubic meters per day (12,400 standard cubic feet per day(ft³/day)). Therefore at 50 kWe, a hydrogen production level of 875 cubic meters per day (31,000 standard ft³/day) is achievable.

5.2.4 Oxidation/Reduction of Nickel

The fractions of oxygen consumed and nickel reacted over a cycle are presented in Table 3 for various maximum bed temperatures. The breadboard system was operated at 20 kWe. The table shows that the nickel particles are more reactive at a bed temperature of 790°C and that the reactivity is reduced at lower and higher temperatures. The significant activity loss at 890°C was not recoverable in subsequent tests at 800°C. This activity loss may have resulted from coking. This was investigated further by removing catalyst samples from the bed and conducting Loss on Ignition (LOI) tests. During the LOI tests the catalyst particles from one UMR reactor lost 0.1 percent (by weight) and from the other UMR reactor lost 2.3 percent (by weight). This indicates that there might have been coke deposition on the catalysts. Later experiments at the bench scale indicated that some coking will occur during the nickel reduction step if steam is not present in at least equal molar concentrations to carbon. All prototype reactor tests on the pilot facility to date were conducted without steam flow during the nickel reduction step. The reconfigured pilot facility will provide sufficient steam for the nickel reduction step and may potentially improve the efficiency of the UMR process by increasing the oxidation and reduction of nickel.

TABLE 3. EFFECT OF MAXIMUM BED TEMPERATURE ON OXYGEN CONSUMED AND NICKEL REACTED

Maximum bed temperature during each cycle	630°C	790°C	890°C
Fraction of Ni reacted in one cycle	0.28	0.61	0.12
Fraction of O ₂ consumed in one cycle	0.19	0.44	0.28

While the pilot plant did not allow sufficient operational control to optimize the reforming process, a parametric evaluation of the catalyst oxidation and reduction performance was conducted. Prior bench-scale experiments indicated that the fuel regeneration chemistry to reduce nickel is slow and results in significant CH₄ slip through the reactor. The effect of the fuel regeneration step GHSV on the nickel oxidation and reduction process was experimentally investigated and the results are presented in Table 4. The results showed that oxygen, fuel and nickel reactions increased at low GHSV. This test was also conducted at a bed temperature of 600°C and without steam, which is recognized to improve the nickel reduction process. As a result the overall fuel conversion was low in all cases. The test did show that use of a lower GHSV improved the fuel regeneration chemistry.

TABLE 4. EFFECT OF GHSV DURING THE FUEL REGENERATION STEP ON THE UNMIXED COMBUSTION PROCESS

GHSV during fuel regeneration step	385 hr ⁻¹	162 hr ⁻¹
Fraction of O ₂ consumed in one cycle	0.193	0.263
Fraction of fuel reacted in one cycle	0.162	0.208
Fraction of Ni reacted in one cycle	0.278	0.374
<ul style="list-style-type: none"> • The reactor was fed with 43% excess air relative to total Ni (not just reactive Ni) and 90% excess fuel relative to total Ni. • GHSV during air step is 2776 hr⁻¹. • Temperature of bed is approximately 600°C. 		

In later pilot facility tests, the steam feed and GHSV during fuel regeneration will be optimized to reduce unconverted CH₄. It should be noted that any unconverted CH₄ is recycled within the total plant and does not represent a significant efficiency penalty.

5.2.5 Absorption/Release of CO₂

The pilot facility was operated at 20 kWe for 15 cycles. The average bed temperature was 794°C, the GHSV was 1400 hr⁻¹ and the reforming step and regeneration step reactor pressures were 2.2 and 1.8 bar, respectively. Under these conditions the dolomite absorbed 65 percent of the CO₂ exiting the reactor and thus separated this CO₂ from the reformat product stream and vented it with the regeneration vent gas. The removal of CO₂ *in-situ* represents a significant

advantage in increased hydrogen production. The removal of CO₂ allows additional water-gas shift reactions where increased hydrogen is produced from the reaction of CO and water. Additionally, the removal of CO₂ from the product stream increases the hydrogen purity and this will increase the PEM fuel cell efficiency.

5.3 Overall and Project Performance

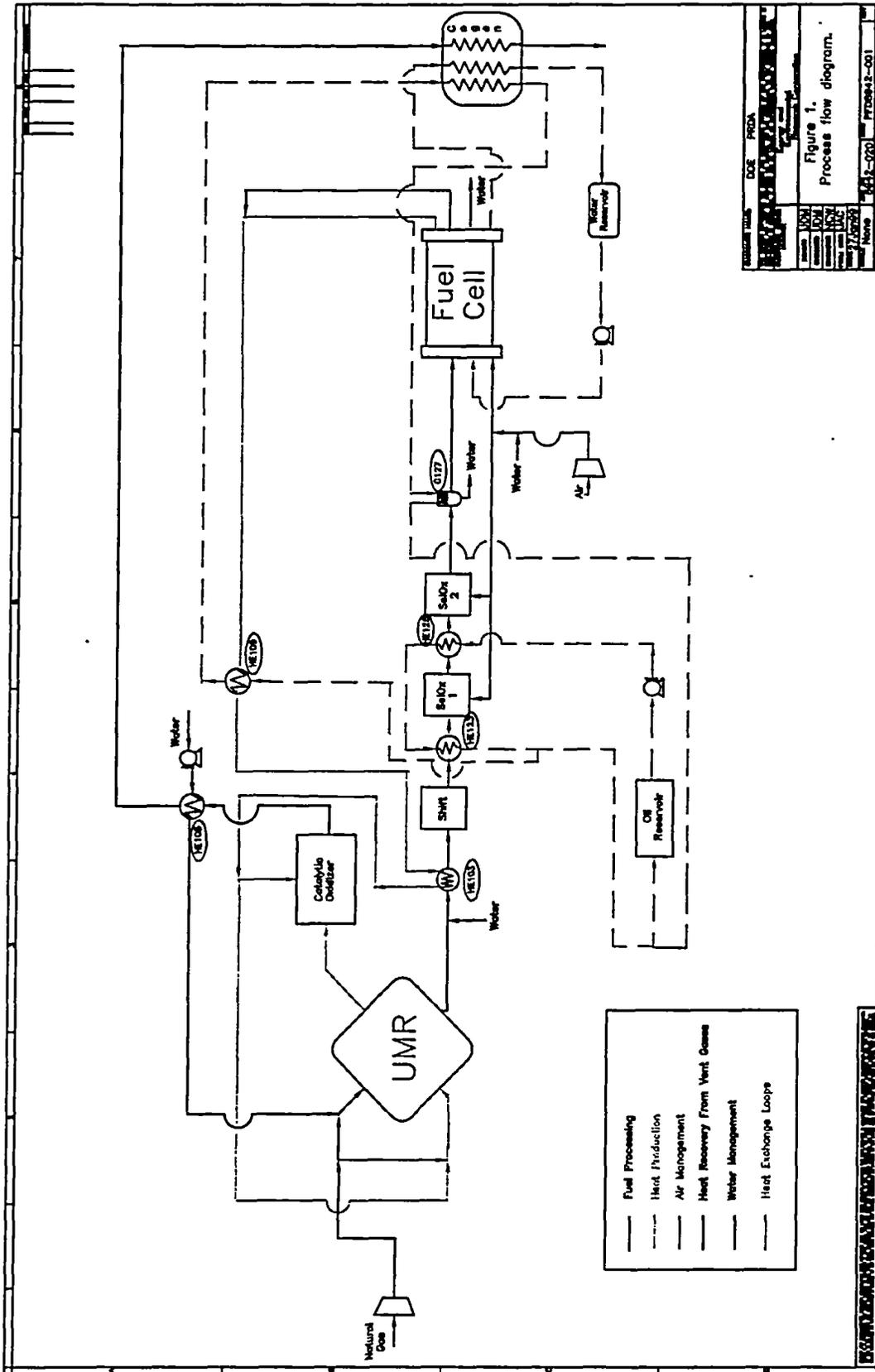
The pilot plant was operated under reduced capacity and with insufficient steam flow and reactant preheat. Despite these restrictions the prototype reactors have demonstrated the capability to meet or exceed many of the performance targets. Table 5 presents the current performance of the pilot facility and projected performance for improved fuel regeneration performance corresponding to performance already demonstrated in the CEC bench-scale tests. The projected performance does not consider process optimization efforts that may increase performance above those demonstrated to date.

TABLE 5. PROTOTYPE REACTOR PERFORMANCE ON THE PILOT TEST FACILITY

Objective	Units	Limited Operation	Projected Operation
Power Output (Electrical Equivalent)	kWe	20	50
Conversion Efficiency	%	42	68
Total Cycle Efficiency (Elec.)	%	19	37
Total Thermal Efficiency	%	42	79
H ₂ Production	ft ³ /day	12,400	30,500
Catalyst Utilization	%	61	61
Absorption Capacity	%	65	65
NO _x Emissions	ppm	NM	NM
CO Untreated Levels	ppm	87	51
CH ₄ Untreated Levels	%	3.8	0.1

NM - not measured

The overall performance shows that improvements in the fuel regeneration chemistry, impacted by steam flow and temperature, are sufficient to raise the conversion efficiency to 68 percent. This is still slightly below the target of 75 percent, however, other process optimization efforts have not been considered. The total cycle efficiency can exceed the 35 percent target and hydrogen production can exceed the 25,000 cubic feet per day level. The current testing has shown that catalyst utilization and the absorber's CO₂ capacity meets the target performance. The CO and CH₄ are reported based on actual measurements of untreated vent gas. The vent gas will be integrated with a catalytic oxidizer that can effectively reduce the emissions to the target levels of 10 ppm CO and 50 ppm CH₄. NO_x levels were not measured. Based upon previous laboratory measurements the reactor NO_x levels are expected to be below the 1 ppm detection limit of the chemiluminescent analyzer.



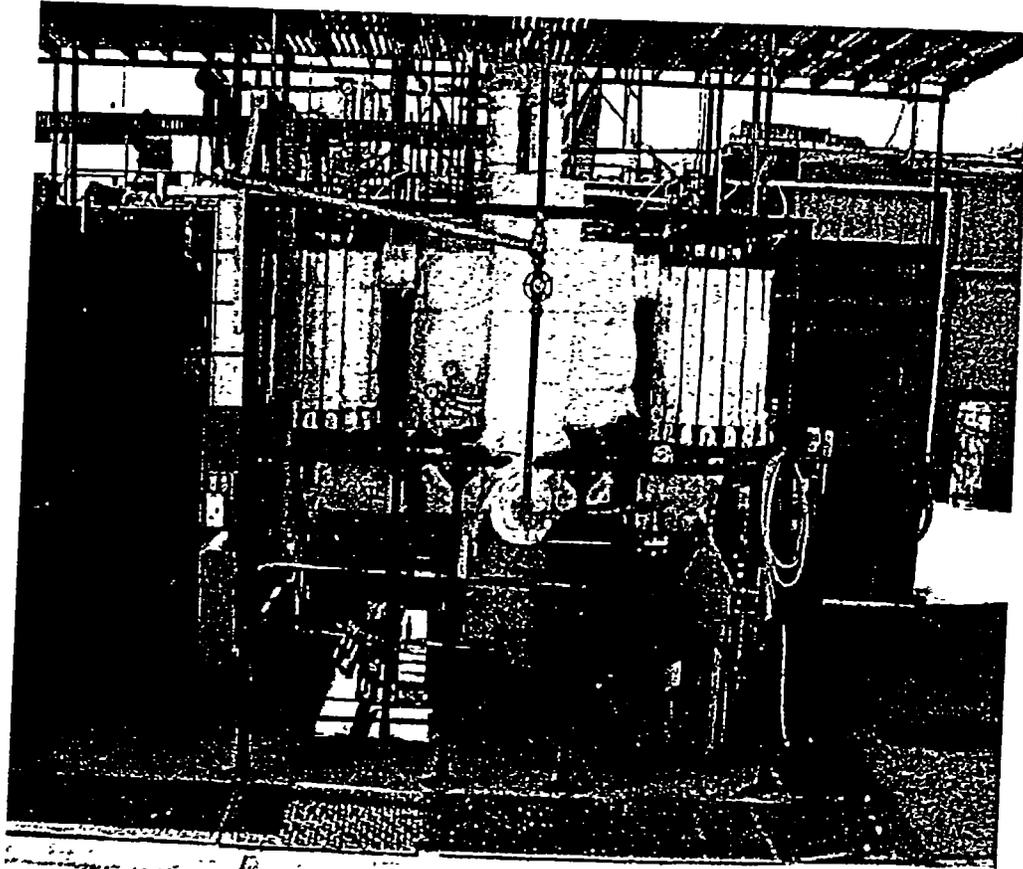


Figure 2. Photograph of the pilot test facility.

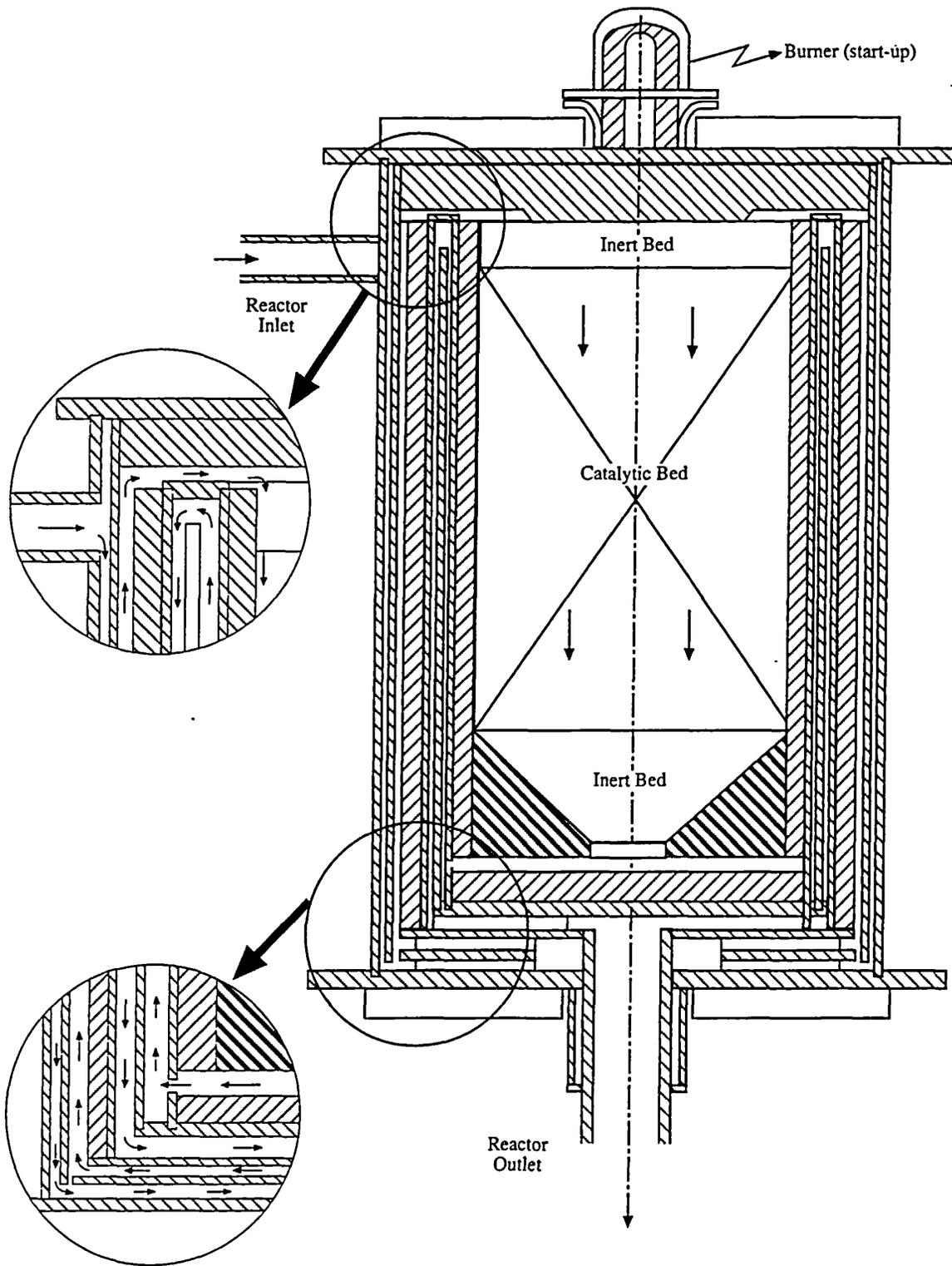


Figure 3. Illustration of the prototype reactor internal multi-channel design.



Figure 4. Prototype reactor housing and internal liners.

GE Energy and Environmental
 Research Corporation
 UMR Close Coupled Heat
 Exchanger
 MAWP 50 PSI@1800°F

Item	Description	Qty.
1	15.125"OD x .1875 wall x 28.375" LG-304SS	1
2	19.125"OD x 1.5" th - 304SS	2
3	3" Flange, 300lb - Weldneck - 304SS	1
4	3" Flange, 300 lb - Slip on - 304SS	1
5	3" SCH 40 Pipe x 10" lg - 304SS	1
6	3" SCH 40 Cap Butt Weld - 304SS	1
7	2" SCH 40 Pipe - 601 Alloy	1
8	1.5" SCH 40 Pipe - 304SS	1

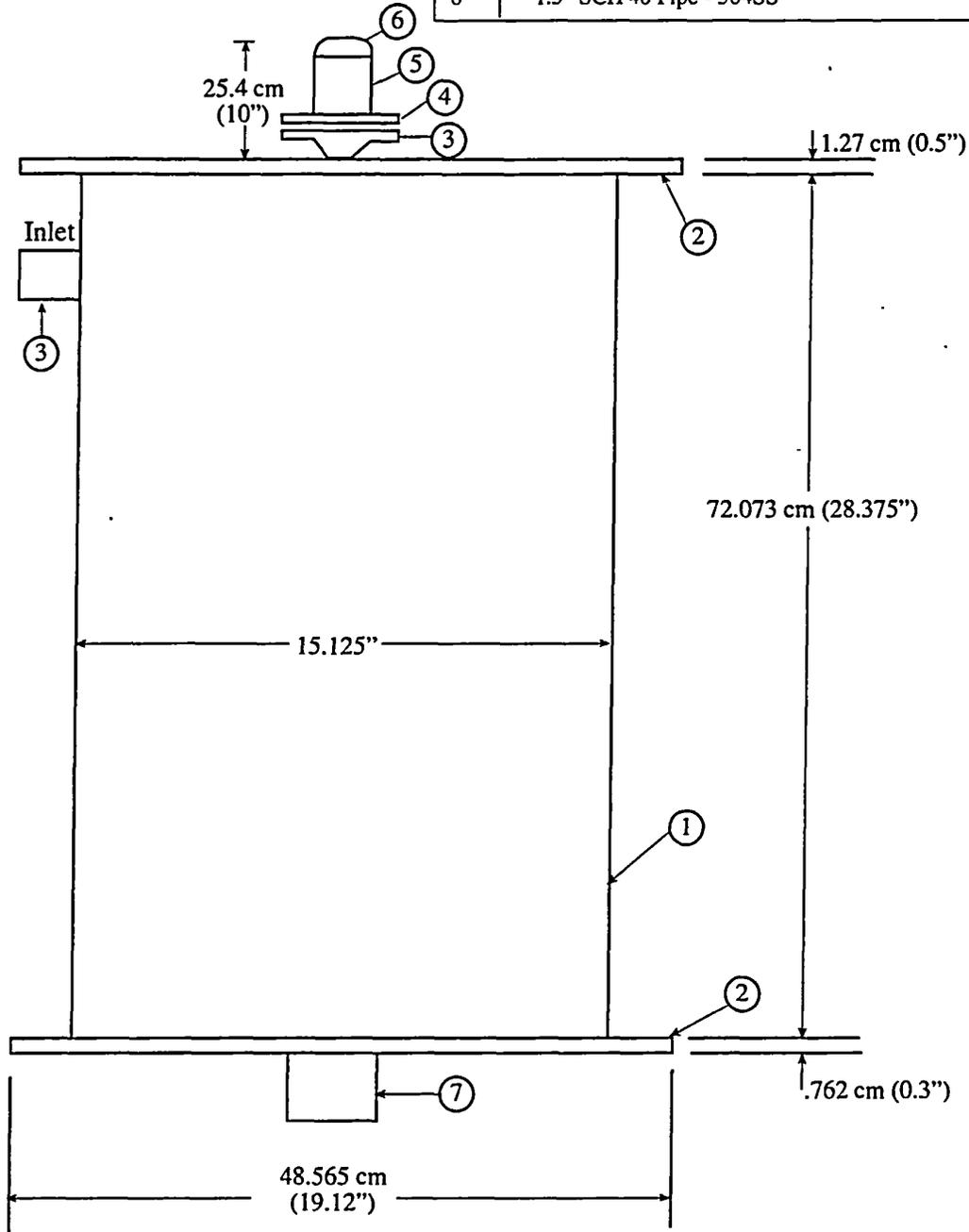


Figure 5. Prototype reactor housing.

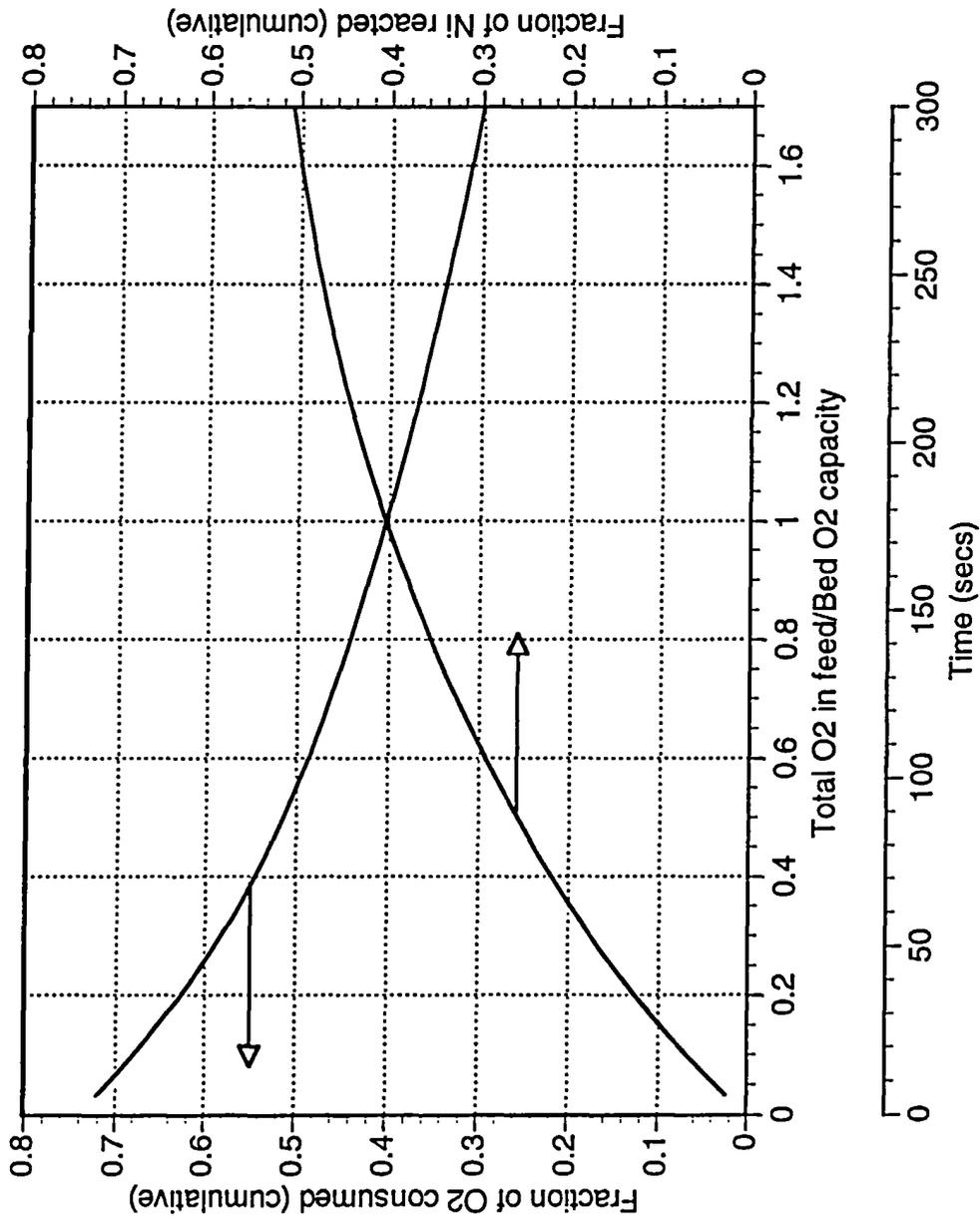


Figure 6. Bench top system data for the fraction of oxygen consumed and nickel reacted during the air regeneration step of the UMR process.

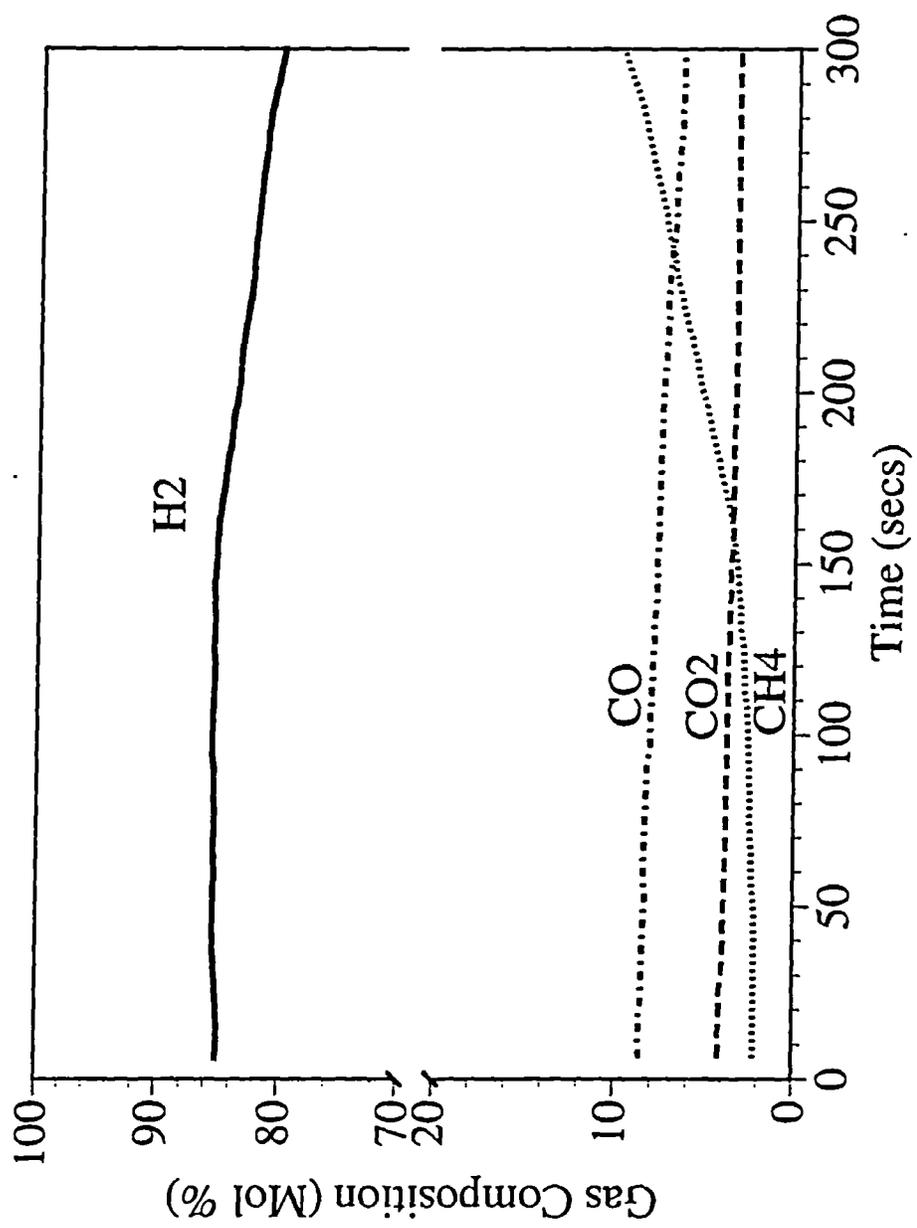


Figure 7. The experimentally measured composition of the syngas from the pilot test facility.

