

Final Technical Report

Project Title: Research, Development and Field Testing of ThermoChemical Recuperation (TCR) for High Temperature Furnaces in the Steel Industry

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Executive Summary

Gas Technology Institute (GTI) evaluated the technical and economic feasibility of utilizing a non-catalytic ThermoChemical Recuperation System (TCRS) to recover a significant amount of energy from the waste gases of natural gas fired steel reheat furnaces. The project was related to DOE-AMO's (formerly known as ITP) one of the technical areas of interest: *Technologies to improve energy efficiency and reduce the carbon footprint of equipment currently used in energy-intensive industries such as iron and steel, and reduce by at least 30% energy consumption and carbon dioxide emission compared to the conventional technologies.*

ThermoChemical Recuperation (TCR) is a technique that recovers sensible heat in the exhaust gas from an industrial process, furnace, engine etc., when a hydrocarbon fuel is used for combustion. TCR enables waste heat recovery by both combustion air preheat and hydrocarbon fuel (natural gas, for example) reforming into a higher calorific fuel. The reforming process uses hot flue gas components (H_2O and CO_2) or steam to convert the fuel into a combustible mixture of hydrogen (H_2), carbon monoxide (CO), and some unreformed hydrocarbons (C_nH_m). Reforming of natural gas with recycled exhaust gas or steam can significantly reduce fuel consumption, CO_2 emissions and cost as well as increase process thermal efficiency. The calorific content of the fuel can be increased by up to ~28% with the TCR process if the original source fuel is natural gas. In addition, the fuel is preheated during the TCR process adding sensible heat to the fuel.

The Research and Development work by GTI was proposed to be carried out in three Phases (Project Objectives).

- Phase I: Develop a feasibility study consisting of a benefits-derived economic evaluation of a ThermoChemical Recuperation (TCR) concept with respect to high temperature reheat furnace applications within the steel industry (and cross-cutting industries). This will establish the design parameters and potential performance of TCR.
- Phase II: Conduct research and development to take the validated technology concept from Phase I to a developmental state for a Phase 3, prototype field test.
- Phase III: Design, fabricate, and prototype field testing of the TCR unit close-coupled to an existing high temperature reheat furnace at a steel company for evaluation under industrial conditions

The project was initiated on September 30, 2008. The report of Phase I results and conclusions was issued on October 30, 2009. The findings were reviewed by the project partners and the collective recommendation was to proceed with Phase II.

Upon the work-conclusion, the Phase II report was issued on March 5, 2012. The scope of work involved the physical testing of a laboratory scale Recuperative Reformer (RR) to validate predicted performances from the feasibility study in Phase I (26% fuel reduction). Although the testing was a successful validation (21% fuel reduction mode), a technical issue

arose, namely a Methane Reforming Rate (MRR) roll off or non-sustaining of the methane reforming rate. GTI's preliminary conclusions were that mechanism(s) producing the methane reforming rate reduction were not entirely known or understood and the chemical kinetics that triggered the roll off mechanism and/or other mechanisms needed to be further evaluated.

GTI developed a plan to uncover the reason(s) for not sustaining a satisfactory Methane Reforming Rate (MRR) of the laboratory scale recuperator reformer (RR). The extended testing program consisted primarily of four tasks based on expected outcomes at that time. The project partners reviewed the proposal and recommended the proposed work extension to proceed and suspension of Phase III pending further review of the results of this work identified as Task 2.5.

Additional Temperature Threshold Testing was undertaken by GTI and simultaneously independent analysis was carried out by the University of California Davis.

Upon completion of the work, the Phase II - Task 2.5 - Extended TCR Testing Report was issued on July 10, 2013. As a result of the work performed in Phase II, Task 2.5, the end-conclusion was that temperature dependency has been affirmed, but with temperatures within the recuperative reformer with higher criticality than the flue gas temperature entering into the recuperative reformer. GTI's further conclusion is that adjustments to the lab recuperative reformer design, given the three-heat exchanger-configuration, remains a valid constraint, and therefore, it would be necessary to scale up to a field experiment capacity level. Design modifications to the recuperative reformer would likely be necessary requiring re-examining space velocity (residence time), heat transfer surface area, plus other considerations, so that a target "temperature profile envelope" within the recuperative reformer would be broad enough to perform satisfactorily in the field with varying flue gas exit temperatures from the majority of the reheat furnace population.

A project review meeting was held with the project partners July 17, 2013. Task 2.5 results were reviewed along with the conclusions and recommendations. GTI proposed three field experiment options for Phase III. On the basis of successful sets of Temperature Threshold Tests (TTT), measured results demonstrated that the current design can capably be scaled up and GTI recommended consideration of these three options for a Phase III field experiment.

Option 1: Production furnace ~250 MMBtu/h

Option 2: Production furnace ~100 - 200 MMBtu/h

Option 3: Production furnace ~50 - 100 MMBtu/h

The project partners' resulting unanimous recommendation was to provisionally proceed with Phase 3 – Option 3.

Subsequently, after further deliberation, review and analysis of their respective field experiment sites, the three steel industry partners determined not to continue to Phase III of the project for both technical reasons and reasons of process economics, i.e., limited applicability of TCR technology due to higher exhaust gas temperature ranges and sensitivity to natural gas prices. As of this report, the current natural gas price is lower than the \$6.03 per

MMBtu projected to return positive NPVs for implementing TCR technology. Accordingly, the project work was terminated effective December 31, 2013.

Background

Although hot charging and hot connecting have increased reheating furnace efficiencies, there is substantial opportunity within the continuous reheat furnace population to reduce fuel consumption even for furnaces equipped with waste heat recovery. One approach for utilizing the energy contained in waste heat is called TCR (ThermoChemical Recuperation), which has been extensively studied by GTI and ECOTERM-Ukraine, who acted as a consultant in this project.

TCR is a technique that recovers sensible heat in the exhaust gas from an industrial process, furnace, or an engine. It uses that heat to transform the fuel source into a reformed fuel with a higher calorific heat content and utilizes this reformed fuel for process heating. Calorific heat in the exhaust can be recovered as well if the exhaust gas can be burned out in the TCR. The reforming process uses hot flue gas components (H_2O and CO_2) or steam to convert the fuel into a combustible mixture of hydrocarbons (C_nH_m), hydrogen (H_2) and carbon monoxide (CO). The calorific content of the fuel can be increased by up to 28% with the TCR process, if the original source fuel is natural gas. In addition, the fuel is preheated during the TCR process, adding sensible heat to the fuel. In the TCR process, steam, CO_2 , or both can be reacted with fuel.

Because both steam and CO_2 can be utilized in the TCR process, it is advantageous for natural gas-fired systems as these gases are major products of combustion and are therefore readily available in a preheated state. Further, they can be used in the same 2:1 ratio as they exist in the combustion products. This enables heat to be 'recouped' both thermally and chemically by creating a hot fuel gas containing C_nH_m , CO , and H_2 .

Project Synopsis – ThermoChemical Recuperation for High Temperature Furnaces in the Steel Industry

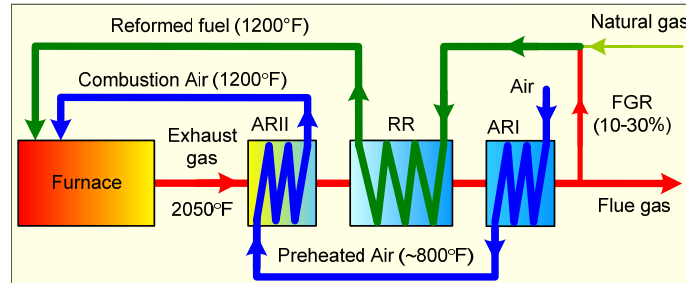
Phase I Validation of the Concept

In this study, the technical and economic feasibility was examined by employing modeling software based on reheat furnace information provided by ArcelorMittal and Republic Engineered Products, who are the steel company partners that have joined this project. Estimates for engineering and capital costs for TCR systems were provided by Thermal Transfer Corporation (TTC), Bloom Engineering, and ArcelorMittal. TTC also recommended applying a factored installation cost based on capital expended.

The Study Approach Taken: Consultation with TTC, and conferring with the project partners periodically were undertaken to evaluate various combinations of recuperative reformer modules and air recuperator modules from the standpoints of achieving relatively minimum surface areas; relatively minimum operating temperatures; optimum flue gas recirculation

flows; optimum pressure drop and ultimately capital expenditures comparing 1) Retrofitting a furnace with an Air Recuperative System (ARS) and; 2) Retrofitting a furnace with a TCRS.

Based on analyses of the calculated results, the three-unit TCRS design (See graphic at the right) was devolved as the optimal design for further economic analysis.



The configuration represents a combination of heat exchangers and reformer that has a surface heat exchange area that is minimized when the first stage air recuperator produces 800°F preheated air. The Energy intensity of this scheme was estimated to be 1.19 MMBtu per ton with 1200°F preheated air and 1200°F reformed fuel temperature resulting in a furnace thermal efficiency of 65% or alternatively an approximately 26% reduction in fuel usage and carbon emissions when compared to the reference recuperated reheat furnace (800°F preheated air).

CAPEX and estimated Return on Investment: The cost estimates were established on the basis of three major categories that would make up retrofitting costs: Estimated Direct Costs, Estimated Indirect Costs and Estimated Contingencies and Fees for 1) The base case of retrofitting a reheat furnace with a recuperative system, and 2) The three-unit TCRS that was optimized.

For retrofitting an ARS on the reference reheat furnace without recuperation, the estimated installed cost was approximately \$3 million, the annual fuel savings were \$9.2 million, the simple payback was 4 months and the ROI was \$33 million (NPV at a 7% discount rate over six years of cash flow).

For retrofitting the optimally designed three-unit TCR System on the reference reheat furnace without recuperation the estimated installed cost was approximately \$9.2 million, the annual fuel savings were \$15.5 million, the simple payback was 7 months and the ROI was \$51 million (NPV at a 7% discount rate over six years of cash flow).

For retrofitting the optimally designed three-unit TCR System on the reference reheat furnace with recuperation the estimated installed cost was approximately \$6.2 million, the annual fuel savings were \$6.3 million, the simple payback was 12 months and the ROI was \$18 million (NPV at a 7% discount rate over six years of cash flow).

The fixed natural gas cost for the above estimates was assumed as a nominal \$9 per million Btu.

It should be noted that no consideration was given for the complete or partial reuse of the existing recuperator of the reference steel reheat furnace which would further improve return

on investment. There may be further reductions in the estimated CAPEX as close inspection of Tables 6 and 7 on page 35 of the Phase I report reveals that estimated Indirect Costs and Contingency and Fees are over 25% of the Installed cost of the optimized three-unit TCRS. We believe that these estimates are conservative and can be managed such that indirect costs and contingencies/fees can be reduced considerably.

Reduced Carbon Footprint and Oxides of Nitrogen: The reference recuperated furnace was estimated as producing 185 pounds of carbon dioxide per ton of steel reheated and 0.8 pounds of oxides of nitrogen per ton of steel reheated. Retrofitting the reference reheat furnace with the three-unit TCRS would reduce the emissions intensities of carbon dioxide and oxides of nitrogen to 142 pounds per reheated ton and 0.63 pounds per reheated ton respectively. On an annualized basis the metric tons of CO₂ and NO_x produced by the three-unit TCRS reheat furnace would be an estimated 107,000 metric tons and 478 metric tons representing reductions of 33,000 metric tons per year of CO₂ and 129 metric tons per year of NO_x respectively.

For details of Phase I work, please refer to Appendix One (Phase I Report).

Phase II - Design and Physical Testing of the Concept Validated in Phase I

The objective of Phase II was to experimentally evaluate the optimal TCRS prototype design. The goal of the experiment was to validate modeled predictions of the performance of the TCRS as applied to a high temperature furnace. A lab-scale TCRS was developed, fabricated, assembled, and tested at GTI's facility. A high temperature furnace with a water cooled load was chosen for the lab-scale TCRS testing. The rated capacity of the furnace was 0.5 MM Btu/hr. The lab-scale non-catalytic recuperative reformer (RR) was developed based on the Phase I results. Thermal Transfer Corporation (TTC) jointly with GTI designed the reformer. TTC fabricated and assembled the unit and shipped it to GTI. Bloom Engineering provided GTI with a high temperature low NO_x burner, recirculation fan and flue gas/natural gas ejector. Combustion air preheating was simulated by electrical heaters instead of a reduced scale two stage recuperator.

In Phase I, the predicted thermal efficiency and fuel savings of a typical reheat furnace were predicted 65% and 26% respectively at combustion air and fuel temperatures of 1200°F. The physical testing in Phase II validated thermal efficiency and fuel savings of 61% and 21% respectively which although lower than initially predicted are in conformance with the modeling results. It should be noted that in the course of testing several issues were discovered and are reported in more detail in the Phase II report contained in Appendix Two. First the above efficiency and fuel savings gains that were validated are associated with a sustained methane reforming rate of a flue gas/natural gas mixture which will be summarized at the end of this section under the heading of Technical Issues/Project Recommendations.

A specific internal flow arrangement in the recuperative reformer was designed based on Phase I results. The flue gas/natural gas mixture was preheated to a temperature of 1200 to 1300°F in the reformer preheater; and reformed in the reformer reactor at approximately the

same temperature. The preheater and reactor consisted of heat exchange tubes which were fully enveloped in the flue gas flow stream. The reactor contained return bends which served to provide an additional flow path for the reforming fuel so that the total volume of the reforming fuel flow in the reactor was substantially higher than the volume in the tubes. The returns were extended to provide the necessary residence time for reforming fuel.

The TCRS lab-scale tests confirmed designed parameters of the reformer preheater and reactor. The pressure drops were in the range of design values. The reforming fuel (flue gas/natural gas mixture) in the preheater was rapidly heated up to the temperature of ~1250°F, the desired temperature for the fuel reforming. The reactor provided sufficient thermal efficiency to transfer heat from the flue gas to the reforming fuel. The residence time in the reactor was high enough to provide partial reforming of the fuel.

During testing, hydrogen and carbon monoxide levels in the reformed fuel were used to preliminarily estimate performance of the recuperative reformer. Comparing measured values of hydrogen and carbon monoxide with theoretical predictions made it possible to determine how well the reformer was performing. Maximum yields of 27% of hydrogen and 11% of carbon monoxide were attained in the experiment. These values were close to theoretical (equilibrium) predictions. Approximately 58% of methane in the natural gas theoretically can be reformed at 1200°F while the measured results confirmed that only ~41% of methane was reformed in the non-catalytic recuperative reformer.

In the judgment of GTI, the technical and economic feasibility of employing a TCRS on a steel reheat furnace with recuperation remains feasible and was demonstrated by lab testing of the recuperative reformer.

With respect to the U.S. reheat furnace population TCR can be viewed as a Return on Investment (ROI) benefit continuum that ranges from a high level of payback of 15 months and \$38 million ROI to a nominal payback level of 33 months and \$6.4 million ROI expressed in current dollars (NPV) at a 7% discount rate over six years of cash flow.

The optimal configuration of two heat exchangers and reformer that has a surface heat exchange area minimized when the first stage air recuperator produces 800°F preheated air is considered to remain valid. The lab testing of the lab-scale TCRS resulting in projecting a furnace thermal efficiency of 61% or alternatively a 21% reduction in fuel usage and carbon emissions when compared to the reference recuperated reheat furnace (800°F preheated air). On an annualized basis the metric tons of CO₂ and NO_x produced by the three-unit TCRS reheat furnace would be an estimated 111,000 metric tons and 406 metric tons representing reductions of 30,000 metric tons per year of CO₂ (21% reduction) and 200 metric tons per year of NO_x (33% reduction) respectively.

Assuming that 80 steel reheat furnaces (approximately 50% of the potential US steel reheat furnace market) employ TCR, the cumulative imputed future fuel usage reductions for both

Flat and Long product plants would be 9.6 trillion Btu. The cumulative CO₂ and NO_x emissions reduction would be 689,000 and 4,700 metric tons per year respectively.

Technical Issues/Project Recommendations

At the end of each test cycle (4 to 6 hours) a slight degradation of the methane reforming rate was observed. It typically required 3-4 hours to preheat and stabilize the TCRS system. Measurements were conducted at these conditions and the system was iteratively adjusted to different conditions in order to collect data for a series of test points. The duration of each test (point) was approximately one hour while measured parameters were stable. For each one hour period, variations in flows, temperatures, and gas compositions were marginal. It was also observed that the methane reforming rate slightly degraded during the period of time from when the specific thermal conditions were attained to a point near the end of a typical test day.

After additional analysis of the test data, it was surmised---and later confirmed---that leakage of the reforming fuel and/or the pre-reformed mixture were short circuiting into the flue gas flowing around and on the outside of the RR thereby “contaminating” the flue gas and the portion of the flue gas used for mixing with the natural gas for reforming.

The leaks were repaired by Thermal Transfer Corporation; and the recuperative reformer was reinstalled. Durability testing was undertaken for approximately 48 continuous hours to determine the asymptoticity of the methane reforming rate. Once the system reached thermal equilibrium, the same gradual reduction in methane reforming rate was observed. An additional phenomenon was observed in that periodically the per cent hydrogen and percent carbon monoxide in the reformed fuel would increase and then decrease over short time intervals (several minutes) without any changes in the process by the staff operating the lab set up. Once it was evident that the methane reforming rate was still decreased and was not asymptotic, several changes to the process variables were intentionally made to attempt to retard or reverse the reduction in methane reforming rate, but without success.

GTI's preliminary conclusions are that the mechanism(s) producing the methane reforming rate decrease are not entirely known or understood. The nature of the chemical kinetics that are triggering the mechanism and/or other mechanisms are still necessary to be evaluated. Other possibilities include: stratification of the natural gas and flue gas downstream of the mixer within the preheater; and/or stratification of a portion of the flue gas/natural gas mixture and the complement of the flue gas/natural gas mixture for part of the residence time within the reformer-reactor.

These technical issues were reviewed with AISI and GTI was requested to prepare a countermeasure-plan to be included in the Phase II report.

For details of Phase II work, please refer to Appendix Two (Phase II Report).

Extended Phase II TCR Testing (proposed)

Since the results of the Durability Test confirmed that the reforming process is gradually retarded over time due to one or more of the above mechanisms, the TCR field experiment as outlined in Phase III was recommended to be postponed and a revised lab test of the TCR system should be carried out with a changed test matrix with a technical objective of identifying the mechanism(s) that are preventing a sustained methane reforming rate and provide a solution.

GTI proposed the following as a reasonable alternative given that (1) proof-of-concept has been verified and; (2) more importantly a well-designed and operational TCR system residing in the GTI combustion laboratory is capable of further testing to evaluate which and how the above mechanisms are retarding the methane reforming rate. Once fully understood, necessary alterations to the reformer design can be made and proceeding to Phase III can be considered.

Accordingly, the team's consensus was to capitalize on the considerable amount of data acquired from modeling and physical testing by proposing a revised scope of work that will focus on identifying the mechanism(s) that are co-opting methane reforming efficiency for long-term operation of TCR as a viable waste heat recovery technique. Below is a brief summary of a preliminary work scope.

Task 1 - Forensic Analysis -- Conduct independent short-duration simulation modeling of the Lab Recuperative Reformer process over a range of operating conditions.

- 1) Develop equations describing chemical reaction kinetics within the Recuperative Reformer
- 2) Conduct Sensitivity Analyses of the process that includes the following independent variables: (Flue gas temperatures supplied; components of flue gas supplied; carbon to steam ratios; physical volume of the RR; and a range of specified space velocities consistent with a range of specified reforming mixtures.).

Task 2 - Conduct iterative testing of current Lab RR under both broader and new test conditions

- 1) Remove both ID fans and reconfigure piping for direct connection of flue gas to mixer.
- 2) Variables to be varied in re Test Matrix
 - a. Flue gas (FG) temperature entering RR---1700°F and 1800°F, capture all data;
 - i. FG: NG (NG is natural gas) ratio for above two FG inlet temperatures above---set at ~10, ~5 and ≤ 2 , capture all data.
 - ii. Reform with steam in lieu of flue gas---use high/mid/low ratio points
 - b. Preheat natural gas with electric heater to achieve FG+NG or STM+NG temperatures into RR of 600°F; 700°F and 800°F

Task 3 - Per test results, devise any necessary changes to the RR design to achieve a sustained methane reforming rate and implement recuperative reformer design changes.

- 1) Confer with TTC on implementation of changes
 - a. Return RR to TTC for changes
 - b. Return RR to GTI and reinstall

Task 4 - Conduct iterative testing of modified/retrofitted Lab RR under varying test conditions to confirm sustained methane reforming rate

Continuing to Phase III work was postponed and approval was given to carrying out ***Extended Phase II TCR Testing*** with the objective of identifying the reason(s) and achieving a solution to the MRR roll off issue.

Phase II – Task 2.5 – Extended TCR Testing

Phase II work involved the physical testing of a laboratory scale Recuperative Reformer (RR) to validate predicted performances from the feasibility study in Phase I (26% fuel reduction). Although the testing was a successful validation (21% fuel reduction mode), a technical issue arose, namely a Methane Reforming Rate (MRR) roll off or non-sustaining of the methane reforming rate. GTI's preliminary conclusions were that mechanism(s) producing the methane reforming rate decrease were not entirely known or understood and the chemical kinetics that are triggering the roll off mechanism and/or other mechanisms needed to be evaluated.

GTI proposed an interim plan (Task 2.5, Extended TCR Testing) as a means to uncovering the reason or reasons for not sustaining satisfactory Methane Reforming Rate (MRR) of the laboratory scale recuperator reformer (RR). The project partners reviewed the proposal and recommended the proposed work extension proceed; and suspension of Phase III pending further review of the results of the Task 2.5 work. AISI formally authorized GTI to proceed with Task 2.5 on July 12, 2012.

The scope of work included Forensic Analysis by the University of California Davis (UCD) to conduct reforming studies using bench scale reactors. In the aggregate, although the study/analyses did produce partial reforming results [and roll offs], the conclusions by UCD as to the possible source(s) of the roll off were insufficient to be utilized as a solution.

In parallel with the UCD analyses, and to augment any useful findings from UCD, GTI carried out internal brainstorming and arrived at an alternative reason for the MRR roll off. After additional review of Phase II test results, GTI theorized that an important aspect of sustained reforming rate to be focused on was the temperature/heat flux profile across the RR (mixture reforming temperature within the reformer) that was governed to a large extent by the temperature of the furnace flue gasses (thermal energy necessary to support satisfactory endothermic reforming) entering into the reactor, i.e., the MRR was temperature/heat flux dependent to a greater extent, in addition to residence time and heat transfer surface areas within the reactor, than previously considered.

Temperature Threshold Tests (TTT) were carried out at several different levels of flue gas temperature. Tests were conducted using 1875°F and 2000°F furnace exhaust gas temperature

over six to eight hour periods each with temperature profiles across the recuperative reformer measured. These tests resulted in sustained MR Rates without roll off. Additional longer-duration testing was done over a broader range of furnace exhaust gas temperatures: From 1650°F, to 1750°F, and up to 1875°F to test repeatability, with and without external preheating of natural gas. These series of tests substantiated that given the design of the laboratory scale recuperative reformer, appropriate temperature profiles across the recuperative reformer sustained MR Rates at furnace exhaust gas temperatures over a range of 1750°F to 2000°F.

The key conclusions reached were that the current design of the laboratory recuperative reformer satisfactorily supports Methane Reforming Rates over a temperature range that matches that of a large number of the steel reheat furnace population during normal production periods that produce exhaust gases within these temperature ranges.

On the basis of these successful sets of TTT measured results that demonstrated a design that can capably be scaled up, GTI recommends consideration of three options for a Phase III field experiment.

- Option 1: Production furnace ~250 MMBtu/h
- Option 2: Production furnace ~100 - 200 MMBtu/h
- Option 3: Production furnace ~50 - 100 MMBtu/h

Specific details of each option are provided in **Appendix Three - Phase II –Task 2.5 – Extended Testing Report** pages C-301to C-307.

The summation below includes several key report restatements.

Accomplishments: Phase I had the objective of establishing the technical efficacy of (non catalytic) ThermoChemical Recuperation through modeling using industry-provided information. Additionally, the economics (ROI at \$9 per MMBtu) of employing TCR were established by developing a preliminary CAPEX. A preliminary three-module design was achieved optimizing heat transfer surface area.

The Phase II had the objective of physically evaluating the optimal TCRS prototype design from Phase I. A lab TCR was designed, built and tested at the combustion laboratory of GTI. The results of the lab tests validated the modeled predictions of the performance of the TCRS as applied to a high temperature furnace. Physical testing yielded a projected fuel reduction of 21% versus the model-predicted 26%. A revised CAPEX and ROI projections were prepared based on new budgetary estimates for the TCR components.

Task 2.5 Extended Testing and evaluation was further carried out to address non-sustainment of the methane reforming rate. The tests revealed temperature level requirements within the recuperative reformer to sustain methane reforming rates within a range of waste gas temperatures of reheat furnaces in the field using TCR for waste heat recovery. Revised ROI calculations were made based on updated cost information.

Three field test options were prepared with preliminary estimated/projected budgets based on new information from the extended testing of Phase II and revised cost information.

A patent application *Non-catalytic Recuperative Reformer US 13/086,433* is pending.

Conclusions: Per work performed in Phase II – Task 2.5 – Extended TCR Testing Task 2.5 the end-conclusion affirmed temperature dependency: temperatures were critical within the recuperative reformer. The key conclusions reached were that the current design of the laboratory recuperative reformer satisfactorily supports Methane Reforming Rates over a temperature range that matches that of a large number of the steel reheat furnace population during normal production periods subject to implementing several design modifications to the recuperative reformer that include re-examining space velocity, heat transfer surface area, and other considerations that would be required.

Appendices List: This final report was organized as shown below according to the work flow from Phase I up to and including the concluding work in Phase II – Task 2.5 – Extended TCR Testing.

Appendix One – Phase I Report (October 30, 2009)

Appendix Two – Phase II Report (March 5, 2012)

Appendix Three – Phase II – Task 2.5 – Extended TCR Testing Report (July 10, 2013) includes:

- **UC Davis Technical Report and Phase III – Field Experiment Options (Proposed)**
- **Details of the three Field Experiment Options – pages C-301 to C-307**

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Executive Summary

GTI was subcontracted by the American Iron and Steel Institute to evaluate the technical and economic feasibility of utilizing a ThermoChemical Recuperation System (TCRS) to recover a significant amount of energy from the waste gases of natural gas fired steel reheat furnaces.

ThermoChemical Recuperation (TCR) is a technique that recovers sensible heat in the exhaust gas from an industrial process, furnace, engine etc. when a hydrocarbon fuel is used for combustion. TCR enables waste heat recovery by both combustion air preheat and hydrocarbon fuel (natural gas, for example) reforming into a higher calorific fuel. The reforming process uses hot flue gas components (H_2O and CO_2) or steam to convert the fuel into a combustible mixture of hydrogen (H_2), carbon monoxide (CO), and some unreformed hydrocarbons (C_nH_m). Reforming of natural gas with recycled exhaust gas or steam can significantly reduce fuel consumption, CO_2 emissions and cost as well as increase process thermal efficiency. The technique has been preliminarily investigated for a number of applications (Nosach, 1995; Maruoka, Mizuochi, Purwanto, & Akiyama, 2004; Sikirica, Kurek, Kozlov, & Khinkis, 2007). The calorific content of the fuel can be increased by up to ~28% with the TCR process if the original source fuel is natural gas. In addition, the fuel is preheated during the TCR process adding sensible heat to the fuel.

Until now, TCR has not been evaluated and developed for commercial adoption because the payback period was unattractive when gas prices were low. With the increases in natural gas prices, TCR is now a viable technology to reduce costs, increase energy efficiency and reduce the industry's CO_2 footprint.

In this study, the technical and economic feasibility was examined by employing modeling software based on reheat furnace information provided by ArcelorMittal and Republic Engineered Products, who are the steel company partners that have joined this project. Estimates for engineering and capital costs for TCR systems were provided by Thermal Transfer Corporation (TTC), Bloom Engineering, and ArcelorMittal. TTC also recommended applying a factored installation cost based on capital expended.

GTI is of the opinion that the technical and economic feasibility of employing a TCRS on a steel reheat furnace with recuperation was demonstrated by this investigation.

With respect to the U.S. reheat furnace population TCR can be viewed as a Return on Investment (ROI) benefit continuum that ranges from a high level of payback of 7 months and \$51 million ROI to a nominal payback level of 12 months and \$18 million ROI expressed in current dollars (NPV) at a 7% discount rate over six years of cash flow.

The specific study-findings and conclusions are summarized below.

Purpose of the project work carried out: This Phase I feasibility study is a report on the evaluation of the technical and economic feasibility of utilizing a TCRS to cost-effectively retrofit a typical reference steel reheat furnace with recuperation; and compare the potential

thermal efficiency gain of the reference steel reheat furnace equipped with a TCRS to the reference reheat furnace with simply an air recuperator. The technical target was to evaluate TCRS designs through modeling to achieve a cost-effective design that increases thermal efficiency and reduces fuel consumption and carbon emissions by at least 30%.

GTI acquired a total of four sets of candidate reference steel reheat furnace specifications from Republic Engineered Products and ArcelorMittal. The steel reheat furnace selected by GTI as representative of the reheat furnace population in the U.S. (see details in Appendix A) was a five zone pusher type furnace with Escher air recuperators operating at a 212 ton per hour rate with 800°F preheated air, an energy intensity of 1.59 MMBtu per ton and a furnace thermal efficiency of 48%.

The GTI approach was to conduct a modeling study that compared several TCRS configurations shown below applied to the reference steel reheat furnace described above having only recuperation.

- 1) A Two-Unit TCRS (Recuperative Reformer (RR) and Air Recuperator (AR) in series)
- 2) A Three-Unit TCRS (Air Recuperator Stage II (ARII), RR and Air Recuperator Stage I (ARI) in series)
- 3) Another Three-Unit TCRS (Two AR in parallel followed by a RR)
- 4) A Four-Unit TCRS (An RR, ARII, Fuel Preheater, and ARI all in series)

Numerical analysis was carried out by utilizing AspenOne software and GTI-developed models. Based on analysis of the calculated results a three-unit TCRS (Configuration 2 above) was shown to be the optimal design and was chosen for further economic analysis.

This optimal configuration represents a combination of heat exchangers and reformer that has a surface heat exchange area that is minimized when the first stage air recuperator produces 800°F preheated air. The final preheated air and reformed fuel temperatures of this optimized TCRS were 1200°F and 1200°F respectively resulting in a furnace thermal efficiency of 65% or alternatively an approximately 26% reduction in fuel usage and carbon emissions when compared to the reference recuperated reheat furnace (800°F preheated air).

an annualized basis the metric tons of CO₂ and NO_x produced by the three-unit TCRS reheat furnace would be an estimated 107,000 metric tons and 478 metric tons representing reductions of 33,000 metric tons per year of CO₂ (24% reduction) and 129 metric tons per year of NO_x (21% reduction).

Assuming that 80 steel reheat furnaces (approximately 50% of the potential US steel reheat furnace market) employ TCR, the cumulative imputed future fuel usage reductions for both Flat and Long product plants would be 12 trillion Btu. The cumulative CO₂ and NO_x emissions reduction would be 800,000 and 3,000 metric tons per year respectively.

The following are key points relative to this study:

1. Steel reheat furnaces were chosen for technical and economic feasibility analysis to be retrofitted by adding a TCRS to recover a significant amount of energy from the furnace exhaust gases.
2. TCR enables waste heat recovery by both combustion air preheat and hydrocarbon fuel (natural gas, for example) reforming into a higher calorific fuel. Therefore TCRS integrates at least one combustion air recuperator (AR) unit and one recuperative reformer (RR) unit.
3. Parameters of various reheat furnaces were analyzed from the point of view of using TCRS. One reheat furnace was chosen for the feasibility analysis. This furnace is representative of a considerable portion of the furnace population in the U.S. steel industry, equipped with a state-of-the-art combustion air recuperator, and has a sufficiently high furnace exhaust gas temperature (~2050°F) at rated operation to implement TCR as a waste heat recovery system.
4. TCRS can be efficiently and effectively used to improve energy efficiency and reduce carbon emissions if the furnace exhaust gas temperature range is 1800°F to 2000°F or higher.
5. Different TCRS configurations were numerically estimated and analyzed in order to optimize the TCRS design. It was found that a three-unit TCRS design (ARII-RR-ARI in series) provides minimum total heat transfer surface area for the heat exchangers and can be considered as an optimal design. This TCRS design provides 26% fuel savings and carbon emissions reduction at acceptable and realistic air and fuel temperatures (1200°F).
6. A level of 31% fuel savings and carbon emissions reduction can be achieved at combustion air and fuel temperatures of approximately 1270°F. Unlike the percent reduction of carbon emissions that corresponds directly to the percent of fuel reduction, TCRS has the potential to reduce NO_x emissions by a greater percentage.
7. There are several other potentials for improved waste heat recovery, namely: a) TCRS with natural gas reforming by adding steam to the flue gas; b) TCRS with natural gas reforming by using steam only and no flue gas utilized; c) TCRS for oxy-fired furnace, and; d) TCRS integrated with a Water Vapor Pump System for both oxy and/or air-fired furnace.

Background

The steel industry is vital to U.S. economic competitiveness and national security. Since energy represents about 15 percent of the total manufacturing cost for steel, steelmakers are highly motivated to reduce energy intensity. Because of the direct relationship between energy use and greenhouse emissions, the industry's aggregate CO₂ emissions per ton of steel shipped would also be reduced by a commensurate amount.

Concept-definition studies in this Phase I work employed a GTI-licensed simulation software that has heat transfer and chemical reaction capability. Key metrics such as fuel flow rates, flue gas flow temperatures, energy intensity, walls losses, product throughput, and product temperatures were provided by ArcelorMittal and Republic Engineered Products

By utilizing a recuperative reformer as the key component of a TCRS, GTI examined the recovery of waste heat contained in the exhaust gases from a reference steel reheat furnace with a production rate of a nominal 212 short tons per hour and the preferential conversion of the flue gases to chemical (fuel) energy and recovering the remaining waste heat for preheating the reformed fuel and the combustion air for increased overall efficiency. The GTI approach was to conduct modeling studies by initially examining two general configurations for the reference steel reheat furnace: 1) With an air recuperator; 2) With a TCRS. The numerical analysis was based on utilizing FurnXpert and AspenOne software and GTI-developed models.

Project Duration and Phases:

The duration of this project is thirty months and involves three phases as explained below.

Phase I: (6 months) Developing a feasibility study consisting of a benefits-derived economic evaluation of a ThermoChemical Recuperation (TCR) concept with respect to high temperature reheat furnace applications within the steel industry (and crosscutting industries). This will establish the design parameters and potential performance of TCR

Phase II: (9 months) Conducting research and development to take the validated technology concept from Phase I to a developmental state for a stage 3, prototype field test.

Phase III: (15 months) Designing, fabricating, and prototype field testing the TCR unit close-coupled to an existing high temperature reheat furnace at a steel company for evaluation under industrial conditions.

Improved Energy Efficiency and reduced Carbon Emissions for Steel Reheat Furnaces:

For most industrial heating processes including furnaces the energy efficiency is defined as the ratio of useful output to gross heat input in percent. The total heat input is provided in the form of fuel chemical energy. The useful output is the heat supplied for heating a material. Other heat

outputs in the furnaces are undesirable heat losses. The major heat or energy losses that occur in the fuel fired furnace are listed below:

- 1) Heat lost through exhaust gases as sensible heat
- 2) Heat loss through furnace walls and doors
- 3) Heat loss through water cooled surfaces

A typical energy balance can be demonstrated by the Sankey diagram in Figure 1 that shows the energy balance for a recuperated reheat furnace. It is clear that exhaust gas losses are a key area for priority attention. Since the furnace operates at high temperature, the exhaust gases leave at high temperatures (1700°F to 2100°F) resulting in poor efficiency. Hence a heat recovery device such as an air recuperator has to be necessarily part of the system. Depending on the furnace exhaust flue gas and air preheat temperatures the furnace energy (thermal) efficiency can vary but ordinarily does not exceed 50%.

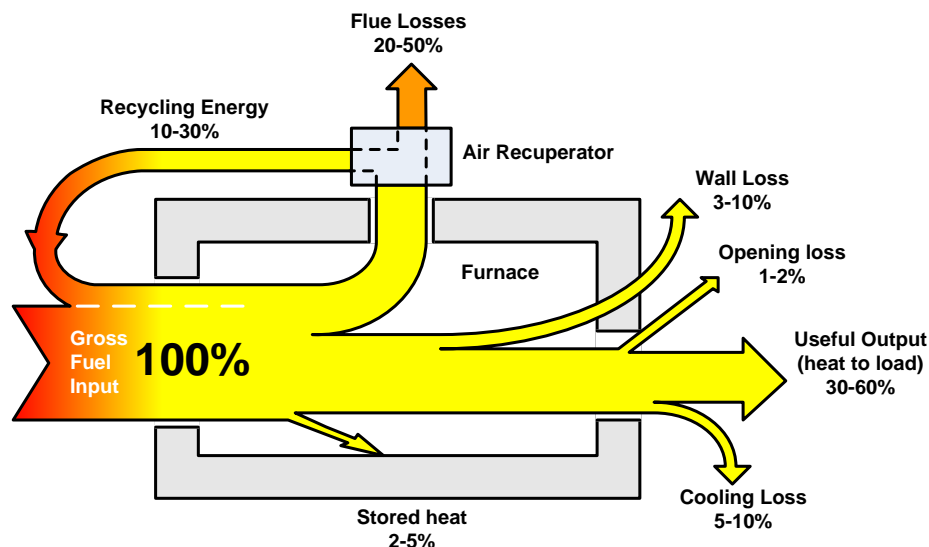


Figure 1. Energy Balance for a Recuperated Reheat Furnace

Major constituents of the furnace flue gas by volume are nitrogen (~72%), water vapor (~17.5%), carbon dioxide (~9%), and oxygen (~1.5%) when natural gas is used as the fuel and air as the oxidizer. On average, each furnace produces ~2.75 pounds of carbon dioxide (carbon emissions) per 1.0 pound of combusted natural gas. Thus, fuel saving lead to a proportionate reduction of carbon emissions.

Energy Conservation and Emissions Reduction by Waste Heat Recovery from Exhaust Gases:

Extracting heat from the furnace flue gases and returning it back to the process is the major action to improve the furnace thermal efficiency and reduce carbon emissions. There are several methods that are generally used in the steel industry for waste heat recovery, that include: preheating cold loads with flue gases (unfired furnace zone); steam generation using waste heat boilers; preheating combustion air by recuperators or regenerators; and oxy-fuel firing (Trinks, Mawhinney, Shannon, Reed, & Garvey, 2004).

TCR for High Temperature Furnaces in the Steel Industry: Phase I Validation of the Concept

Preheating Cold Loads

Preheating cold loads with flue gases can be accomplished in an unfired zone(s) (Figure 2) at the charge end of steel reheat furnaces. In this case energy will be transferred by preheating the load. This reduces the energy that is ultimately lost to the exhaust. In practice, the unfired charging zones of most continuous furnaces serve as preheating zones. Load preheating systems can be difficult to retrofit due to space constraints and are best suited for continuous rather than semi-continuous furnaces.

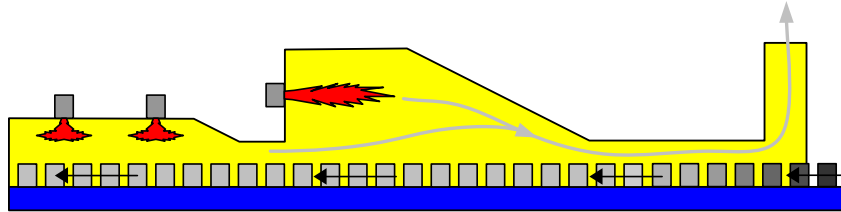


Figure 2. Waste Heat Recovery by Preheating Cold Load in an Unfired Zone

Steam generation using a Waste Heat Boiler

The use of waste heat boilers to recover a portion of the exhaust gas heat is an option for plants that need a source of steam or hot water. The waste heat boiler is similar to conventional boilers with one exception: it is primarily supplied heat by the exhaust gas stream from a process furnace with supplementary firing as necessary. The prime requirement is that the waste gases must contain sufficient usable heat to produce steam or hot water at the condition required. Waste heat boilers may be designed for either radiant or convective heat sources.

The drawbacks to employing this form of waste heat recovery are the following: the necessity for annual boiler inspections, insurance premiums, feed water and condensate pumps, chemical treatment of the feed water and steam service piping and valving, boiler operators, that adds operating expenses and is not needed with air recuperation.

Air recuperation

Air recuperators are heat exchangers that use the energy in hot flue gases to preheat combustion air. Recuperators are the most widely used heat recovery systems in the steel industry. A recuperator (Figure 3) is a gas-to-gas heat exchanger installed between the furnace flue gas exit and the furnace stack. The exhaust gases and air are in adjacent passageways separated by a heat conducting wall. Heat flows steadily through the wall from the hot exhaust gas to the combustion air. Recuperators are available in as many configurations as there are heat exchangers. Common forms are double pipe (pipe in a pipe), shell and tube, and plate types. All may use counter flow, parallel (co-current) flow, and/or cross flow.

Figure 4 shows fuel savings versus the flue (waste) gas and air preheat temperature for 10% excess air (www.hamon-thermaltransfer.com). According to this figure, increasing air preheat temperature from 800°F to 1200°F for example, would reduce the fuel consumption and therefore carbon dioxide emissions by ~13% at a waste gas temperature of 2000°F. It should be

noted that increasing combustion air temperature increases NO_x emissions, typically from 20 to 100 ppmv for a 100°F temperature rise.

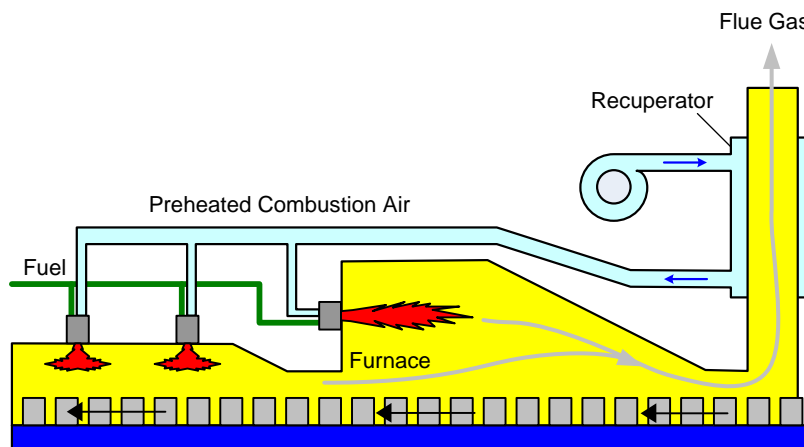


Figure 3. Combustion Air Recuperation System

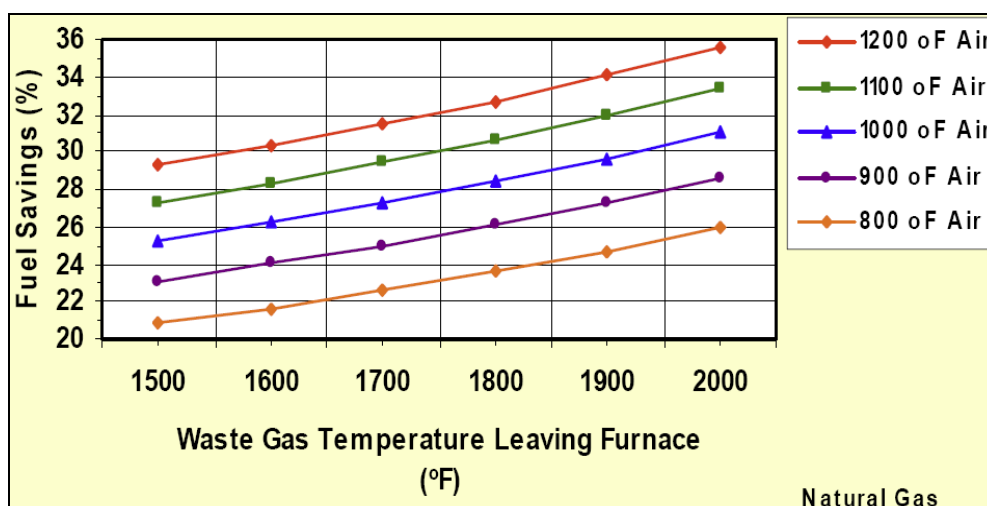


Figure 4. Fuel Savings with Combustion Air Preheat by Recuperation

Recuperators are typically designed with very low pressure drops (0.5 to 1 in. W.C.) on the exhaust gas side. They usually are designed for a greater drop on the air side. Forced draft fans are preferred because of the higher cost of handling hot air or gases with induced draft (ID) fans or blowers for hot gas or hot air. In addition, forced draft fans promote maintaining the interior of the steel reheat furnace under a slightly positive pressure, minimizing ambient air infiltration.

Regenerators

Another alternative to preheat combustion air is with a regenerator, which is an insulated chamber usually filled with metal or ceramic shapes that can absorb and store significant thermal energy. It acts as a rechargeable thermal storage battery for heat and works in an alternating mode. In the first mode, hot flue gas is passed through the chamber thus heating media or refractory in the chamber. In the second mode cold combustion air is passed through the

regenerator chamber thus extracting heat from the media or refractory. At least two regenerators and their associated burners are required for an uninterrupted process: one provides energy to the combustion air while the other recharges (Figure 5). The cycling time can be up to 40 seconds depending upon site conditions and the process. Regenerative burners require the use of a control system to sequentially switch the burners from a regenerative mode to a heat extraction mode. A program of periodic maintenance and measures to minimize the accumulation of media-contamination is required to ensure proper operation of all valve control mechanisms in the burners.

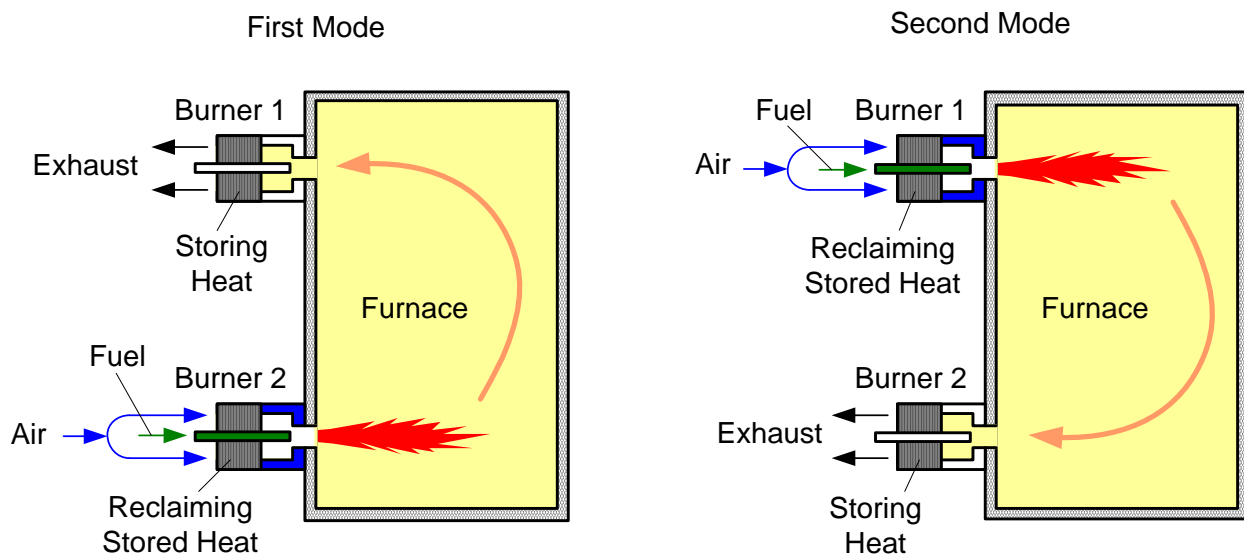


Figure 5. Regeneration Principle for Waste Heat Recovery

The fuel utilization of modern regenerators can be as high as 75% to 85% (Figure 6), with air preheat temperatures within 300°F to 500°F of the products of combustion in the furnace (www.bloomeng.com). Regarding firing systems for industrial furnaces including steel reheat furnaces, fuel utilization efficiency is defined as:

$$\text{Fuel Utilization Efficiency} = 100\% \times \frac{(\text{Gross Fuel Input} - \text{Exhaust Gas Losses} - \text{Other Losses})}{\text{Gross Fuel Input}}$$

Figure 6 shows the efficiency as a function of exhaust gas, or process temperature. For a system without air preheat ($\varepsilon = 0$), it becomes obvious that the efficiency diminishes with rising exhaust gas temperatures. At 2000°F exhaust gas temperature, at least 55% of the fuel input will be lost as hot exhaust gas heat. Corresponding heat losses are less than 20% for regenerative burners with a relative air preheat $\varepsilon = 0.8$ and ~35% for conventional combustion air recuperators with relative air preheat $\varepsilon = 0.4$.

Fuel savings compared to air recuperation are in the range of 10 to 20% and savings of 50% and more, compared to cold air systems, can be achieved with regenerative burners. Low NO_x combustion can be achieved by air staging or in combination with external flue gas recirculation.

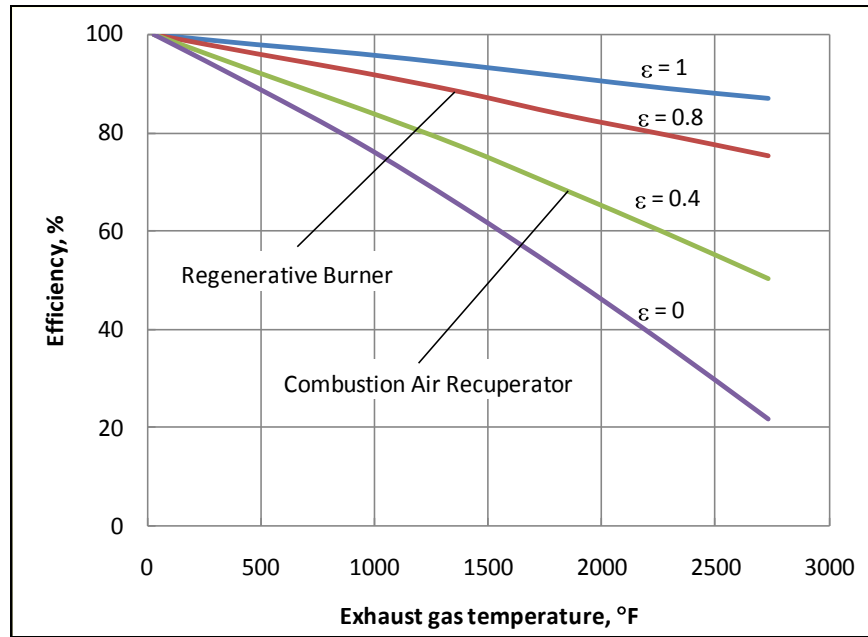
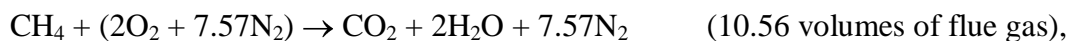


Figure 6. Fuel Utilization Efficiency (ϵ = Relative Air Preheat = Air Preheat Temperature/Exhaust Gas Temperature)

Oxy-Fuel Firing

Although oxy-fuel firing is not considered a method of heat recovery in the strictest sense, it does save energy by reducing the mass of hot waste gases that is lost through the flue. “Oxy-fuel firing” is the substitution oxygen for air in a combustion system. For one volume of methane (the principal constituent of natural gas), the combustion reaction with air is,



is replaced with the reaction for oxy-fuel firing,



Reducing exhaust gases would result in substantial fuel savings. In the case of enriching combustion air with oxygen, the specific amount of energy savings depends on the percentage of oxygen in combustion air and the flue gas temperature. Higher values of oxygen and flue gas temperature offer higher fuel savings. The net economic benefits will primarily be determined by the cost of oxygen compared to the fuel cost reduction savings.

With oxy-fuel firing, the existence of little or no nitrogen in the products of combustion results in keeping NO_x formation to a minimum – provided that there is minimum to none air filtration into the furnace and high purity oxygen is used.

In evaluating oxy-fuel firing, consideration needs to be given to the mass flow reduction of products of combustion, much higher flame temperatures, and extremely higher gas radiation heat transfer in short, longitudinal paths. Processes that depend on high mass flow to provide

uniform product temperatures will be derated from the use of oxy-fuel firing because of its lower mass flow and lower volume for circulation. One solution that could negate these effects would be a combination of oxy-fuel firing with a TCRS which uses a portion of flue gas or flue gas steam condensate for fuel reforming and recirculates the gas through the furnace. In this case the thermal efficiency of the furnace can be substantially increased compared to conventional oxy-fuel firing and the flame temperature will decrease to a beneficial level.

TCRS to Improve Energy Efficiency and Reduce Carbon Emissions

The process of recuperating the energy contained in exhaust gases from high temperature process furnaces, engines, etc., for hydrocarbon fuel reforming is called thermochemical recuperation (TCR). A TCR system (TCRS) can also include oxidant (air or oxygen) preheat thus integrating a combustion air recuperator (AR) and recuperative reformer (RR) into the system. If successfully developed and commercialized in the near/medium term, TCRS will provide increases in furnace thermal efficiency from 15 to 35% and reduce hydrocarbon fuel consumption by 15 to 60% compared with conventional recuperation where only combustion air is preheated. TCRS will also significantly reduce by 30% to 80% air emissions (CO_2 , CO, NO_x , unburned hydrocarbons, etc.).

The major advantage for TCRS is opportunity to cost effectively improve process efficiency beyond what is achievable with conventional air recuperation. TCR has been extensively studied in Ukraine (Nosach, 1995), Japan (Maruoka, Mizuochi, Purwanto, & Akiyama, 2004), the U.S. (Sikirica, Kurek, Kozlov, & Khinkis, 2007), and Russia. For heating processes, efficiency increases of 20% to 50% have been noted, and for processes using thermal cycles (e.g., internal combustion engines, gas turbines) efficiency increases of 8% to 15% have been noted.

Figure 7 depicts a general example of TCRS with natural gas/flue gas reforming to illustrate the concept. AR is the air recuperator and RR is the recuperative reformer. At 1200°F air preheat and reformed fuel temperatures, more than 70% of the total heat in the exhaust is recovered when furnace exhaust gas temperature is 2000°F.

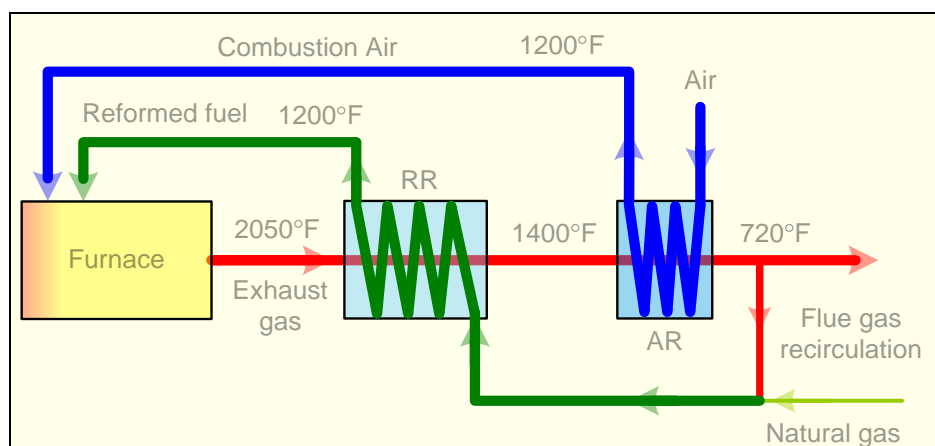
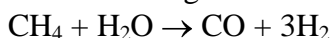


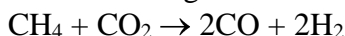
Figure 7. TCRS as Applied to a High-Temperature Steel Reheat Furnace with Natural Gas/Flue Gas Reforming (65% thermal efficiency)

Recuperative reforming is a technique that recovers sensible heat in the exhaust gas, and uses that heat to transform the hydrocarbon fuel source into a reformed fuel having a higher calorific heat content. The reforming process uses the waste heat plus steam (water vapor) and/or carbon dioxide (CO₂) to convert the fuel into a combustible mixture of hydrogen, hydrocarbons, and carbon monoxide (CO). The calorific content of the fuel can be increased by up to ~28% with the TCR process if the original source fuel is natural gas. In the TCR process, steam, CO₂, or both can be reacted with fuel, as shown below (each case is simplified to one reaction).

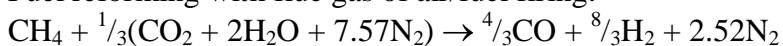
Fuel reforming with steam:



Fuel reforming with carbon dioxide:



Fuel reforming with flue gas of air/fuel firing:



Fuel reforming with flue gas of oxy/fuel firing:



When reformed fuel is combusted in the furnace, fuel economy is improved, system efficiency is increased, and emissions are reduced. In addition, the fuel is preheated during the reforming process, adding sensible heat to the fuel. Because both water vapor and CO₂ can be used in the reforming process, it is advantageous for natural gas-fired systems because both of these gases are major products of combustion and, therefore, are readily available in a preheated state. Further, they can be used in the same ratio as they exist in the combustion products.

TCRS has not been evaluated and developed for commercial adoption because the payback period was unattractive when gas prices were low. Industry now needs this technology as a way to lower costs to remain competitive. Strong interest in TCR has been expressed to GTI by the steel industry, the glass industry, and the aluminum industry during the last several years. GTI has evaluated the TCR approach for direct fired heating applications from a bench-scale test funded by GTI. A feasibility study of TCR for indirect fired heating applications, also funded by GTI, is underway.

A feasibility study of the TCRS with steam for the Japanese steelmaking industry was conducted recently (Maruoka, Mizuochi, Purwanto, & Akiyama, 2004). The study reported the following conclusions. The energy loss in the TCRS was only 15% of the total energy losses in the conventional system. The study also demonstrated the feasibility of treating the waste gases and slags from the steelmaking industry by TCRS and indicated the possibility of solving environmental issues besides offering substantial cost benefits to the steelmaking industry. The reduction in carbon dioxide emissions due to TCRS is as high as 2.05 million tons per year in the Japanese steelmaking industry. The cost benefits that can be aggregated by TCR waste heat recovery systems (based on steam reforming) are \$409 million per year for discharged gases and \$1,945 million per year for slags.

Techno-Economic Validation of the Feasibility of TCR

Reference Steel Reheat Furnace Selection for the Feasibility Study

GTI received the required specifications of existing representative furnaces from the steel industry partners Republic Engineered Products and ArcelorMittal. Based on the data analysis a reference steel reheat furnace was chosen for the feasibility study and optimization for TCR concept development. The following requirements were taken into account to choose the furnace for this feasibility study:

- 1) The furnace should represent a considerable portion of the furnace population in the steel industry
- 2) The furnace should be equipped with a state-of the art recuperative system. This would allow comparing modeling results with existing performance/design data.
- 3) Sufficiently high level of furnace flue gas temperature (at least 1800°F to 2000°F). This would allow the development of a high efficiency TCRS.

GTI reviewed this decision with representatives from ArcelorMittal Research Center for purposes of acquiring a sufficient amount of information to proceed.

Key furnace parameters of the selected reference steel reheat furnace are presented below:

- | | |
|---|--|
| 1) Production rate: 213.2 tons/hr | 8) Excess air: 10% |
| 2) Energy Intensity: 1.58 MMBtu/ton | 9) Waste gas losses: 121.5 MMBtu/hr |
| 3) Fuel: natural gas | 10) Heat to steel: 157 MMBtu/hr |
| 4) Fuel gross heating value: 1018 Btu/scf | 11) Water cooled surface heat loss: 20 MMBtu/hr |
| 5) Fuel heat input: 337 MMBtu/hr | 12) Shell heat losses: 6.9 MMBtu/hr |
| 6) Fuel inlet temperature: 70°F | 13) Furnace waste gas average temp.: 2030°F |
| 7) Air preheat temperature: 800°F | 14) Flue gas temp. after air recuperator: 1150°F |

Furnace Heat Transfer Model Development and Results

GTI conferred with ArcelorMittal Research Center to discuss assistance in modeling of thermal processes within the reference furnace. ArcelorMittal acquired FurnXpert licensed software that allows simulating heat transfer processes within a continuous reheat furnace. GTI requested calculations for the reference furnace at three different conditions (Figure 8): *a*) Without waste heat recovery, *b*) With combustion air recuperation, and *c*) With TCRS. The TCRS includes a recuperative reformer and air recuperator. The recuperative reformer is intended for natural gas reforming with flue gas. As a result of the reforming reaction the reforming fuel (natural gas/flue gas mixture) increases its heating value and decreases temperature of flue gas thus recovering more waste heat compared to the case with air recuperation only.

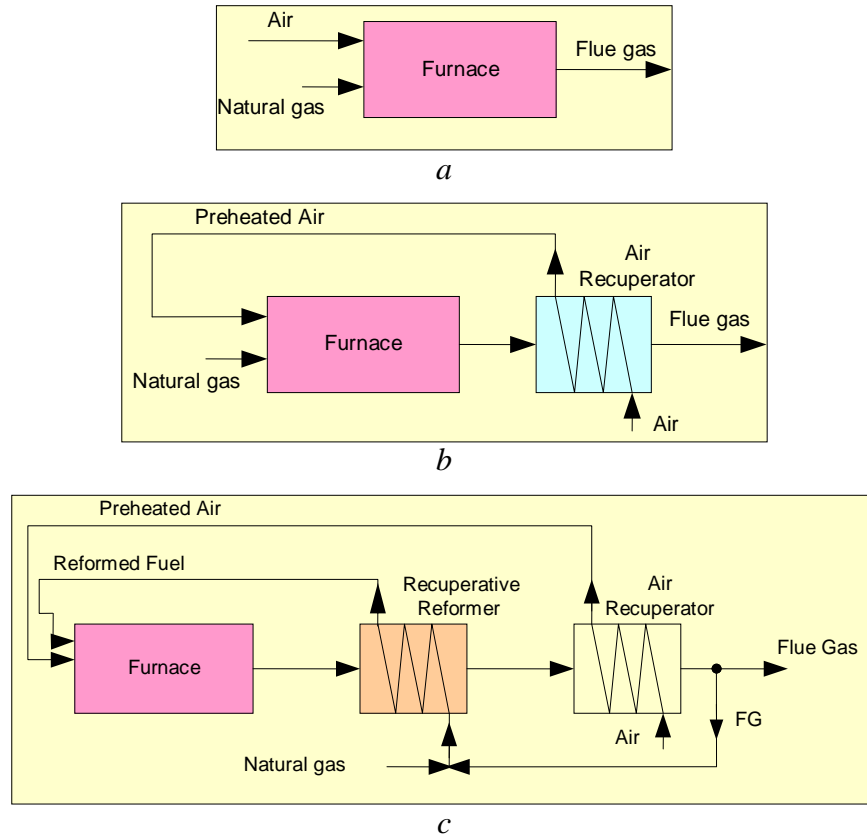


Figure 8. Schematic Diagram of Pusher Furnace Operation at Different Conditions:
a) Without Waste Heat Recovery, b) With Combustion Air Recuperation, c) With TCRS

The initial data for the heat transfer model calculations are summarized in Table 1.

Table 1. Initial Data for Reheat Furnace Thermal Calculations

Furnace Specifics	No Waste Heat Recovery	Combustion Air Recuperation	TCRS
Production rate, tons/hr	212	212	212
Fuel	Natural gas	Natural gas	Reformed fuel
Fuel temperature, °F	100	100	1000
Combustion air temperature, °F	100	800	1000
Excess air, %	10	10	10
Fuel higher heating value HHV, Btu/scf	1018	1018	204

The reformed fuel composition was estimated by GTI using licensed AspenOne software. Using this initial data, ArcelorMittal conducted calculations of the heat transfer within the reference furnace using FurnXpert software. Figure 9 shows the fuel specifications utilized. Natural gas was used for the furnace with no waste heat recovery and with combustion air recuperation. Reformed fuel was used for the furnace with TCRS. The composition of the reformed fuel was estimated by chemical equilibrium at constant pressure (14.7psia) and constant temperature (1200°F). The reformed fuel temperature 1000°F (Table 1) used in the FurnXpert calculation

instead of 1200°F can be explained by the software limitation that the fuel temperature cannot exceed 1000°F.

Fuel Data

Name: **GTI NG spec**

Type of Fuel: ☒ Gaseous ☐ Liquid

Ratio (in Cu.ft / Cu.ft)

Air / Fuel	9.65	Flue / Fuel	10.6779
------------	------	-------------	---------

Heating Value (in Btu / Cu.ft)

HHV	1018	LHV	918.7
-----	------	-----	-------

Product of Combustion (as fraction 0 - 1)

CO ₂ [Dry]	0.11	Calculator	H ₂ O	0.1863	N ₂	0.71
-----------------------	------	------------	------------------	--------	----------------	------

Fuel Composition (%)

N ₂	2.6	O ₂	0	CO ₂	0.6	CO	0
H ₂	0	H	0	O	0	H ₂ O	0
OH	0	NO	0	NO ₂	0		
SO	0	SO ₂	0	SO ₃	0	H ₂ S	0
CH ₄	92.6	C _n H _n	4.2				

Buttons: Reset, New, Ok, Save

a

Fuel Data

Name: **GTI Reformed NG spec**

Type of Fuel: ☒ Gaseous ☐ Liquid

Ratio (in Cu.ft / Cu.ft)

Air / Fuel	1.62	Flue / Fuel	2.3937
------------	------	-------------	--------

Heating Value (in Btu / Cu.ft)

HHV	203.48	LHV	182.39
-----	--------	-----	--------

Product of Combustion (as fraction 0 - 1)

CO ₂ [Dry]	0.11	Calculator	H ₂ O	0.1884	N ₂	0.71
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Fuel Composition (%)

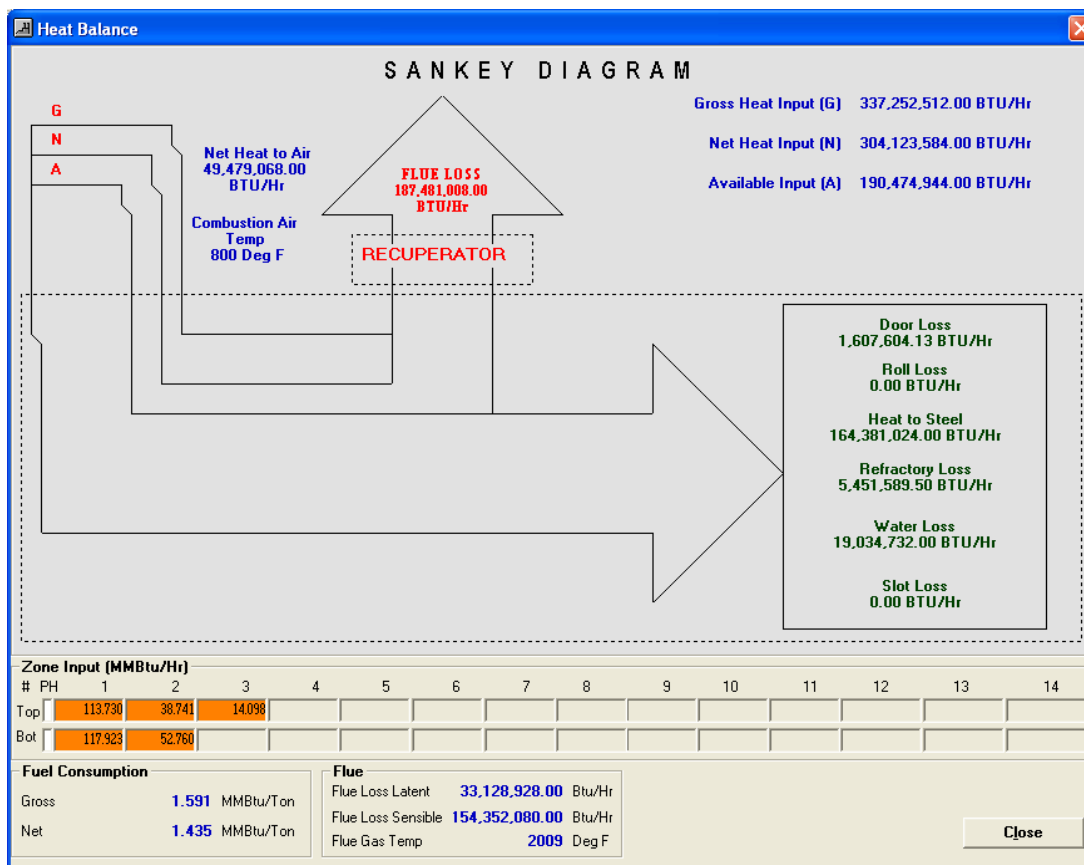
N ₂	43.1	O ₂	0	CO ₂	2.92	CO	14.5
H ₂	30.9	H	0	O	0	H ₂ O	3.04
OH	0	NO	0	NO ₂	0		
SO	0	SO ₂	0	SO ₃	0	H ₂ S	0
CH ₄	5.59	C _n H _n	0				

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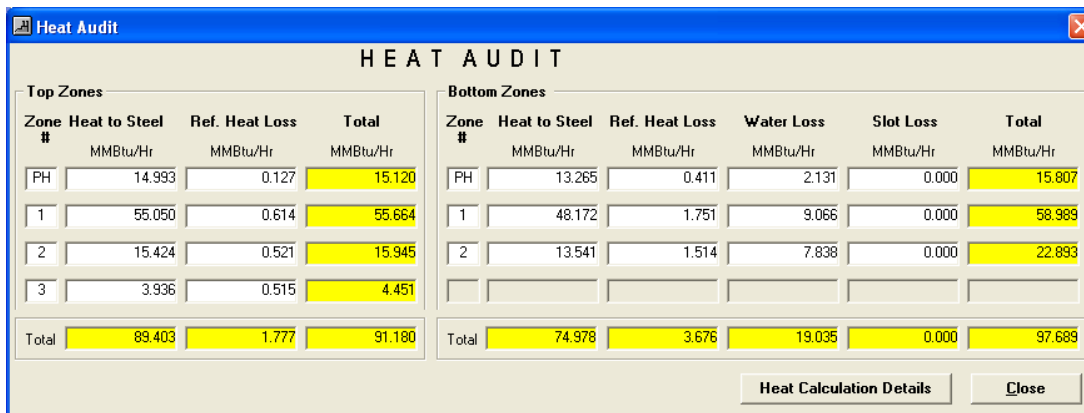
b

Figure 9. Fuel Data used in FurnXpert Calculations:
a) Natural Gas Properties and Composition,
b) Reformed Fuel Properties and Composition

FurnXpert software allows estimating thermal processes within a furnace and fuel saving at given combustion air temperature, fuel temperature, and fuel composition. Output parameters of the calculations are fuel saving, natural gas flow rate, furnace heat losses, exhaust gas temperature, and flue gas (stack) temperature. The estimated heat balance and heat audit output data for the air recuperated furnace is shown in Figure 10 as an example.



a



b

Figure 10. Reference Reheat Furnace with Combustion Air Recuperation:
 a) Sankey Diagram and b) Heat Audit

Additional output data for the air recuperated furnace are presented in Figure 11.

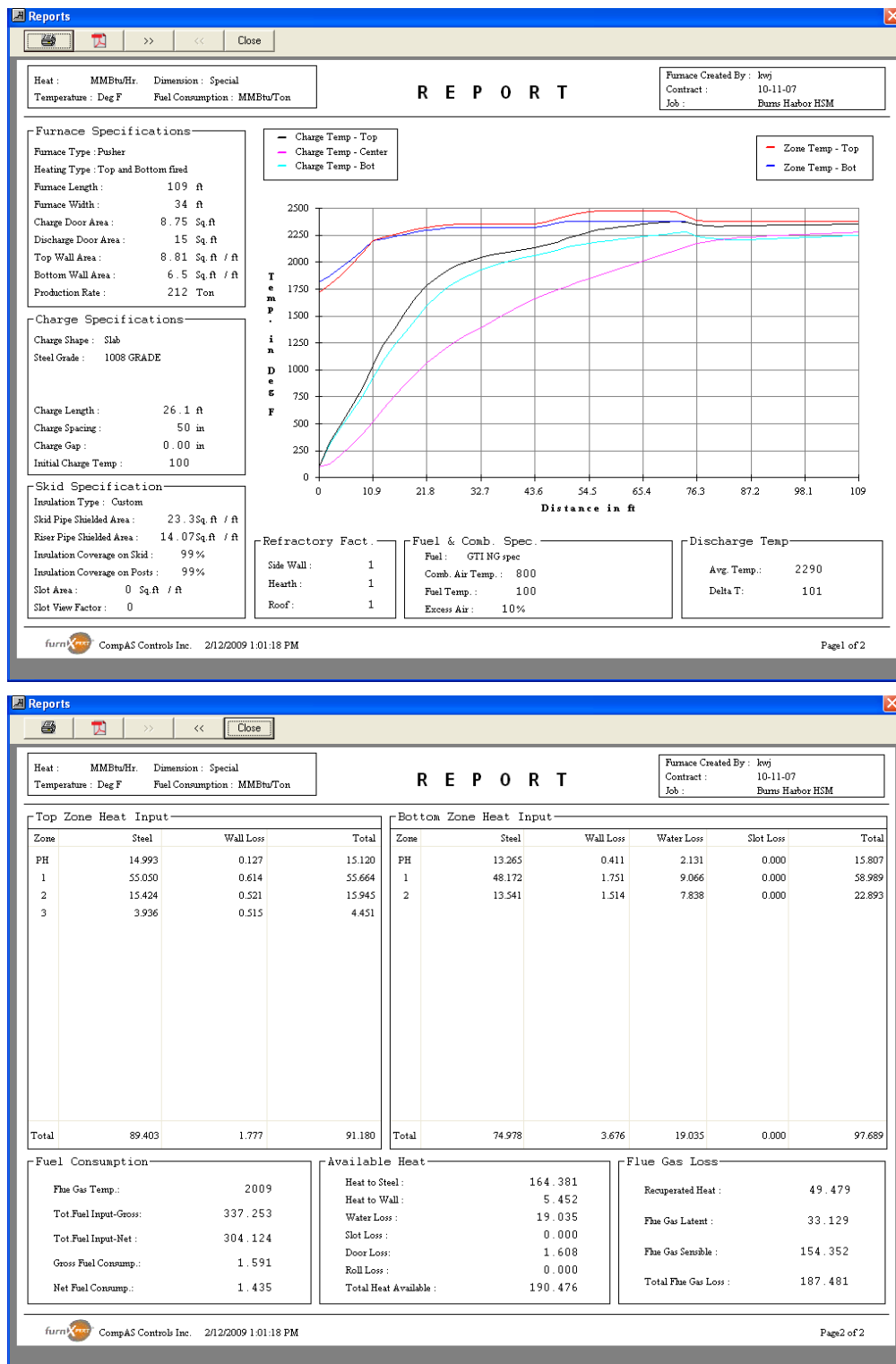


Figure 11. Output Data for the Reference Reheat Furnace with Combustion Air Recuperation

Table 2 summarizes the FurnXpert calculation results. The following conclusions can be made based on the FurnXpert calculations:

- Total heat losses (door, refractory, water) remain the same (~16% of useful heat) for all three cases
- Exhaust gas temperature drops slightly (from 2087°F to 2009°F) in the air recuperation case compared to the furnace without waste heat recovery
- Reforming fuel in the TCRS case does not essentially affect exhaust gas temperature compared to the air recuperation case
- Confirmed significant fuel savings and CO₂ reduction potential when TCRS is used

These calculation results were further used in the AspenOne model to simulate waste heat recovery systems such as combustion air recuperation and TCRS.

Table 2. Results of Reference Steel Reheat Furnace Thermal Evaluation

Furnace Specifics	No waste heat recovery	Combustion air recuperation	TCRS
Production rate, tons/hr	212	212	212
Fuel Type	Natural gas	Natural gas	Reformed fuel
Fuel temperature, °F	100	100	1000
Combustion air temperature, °F	100	800	1000
Natural gas flow rate, SCFH	463,153	331,289	265,473
Energy intensity, MMBtu/ton	2.22	1.59	1.27
Fuel savings and CO₂ reduction, %	-	28.5	42.7
Heat to steel, MMBtu/hr	164.513	164.381	164.39
Total heat losses, MMBtu/hr	26.168	26.095	26.1
Exhaust gas temperature, °F	2087	2009	2014

Waste Heat Recovery System Model Development

GTI used licensed AspenOne V7 software to simulate waste heat recovery systems for the reference furnace. This software includes more than a hundred different packages. For purposes of this study, three packages were used namely, AspenPlus, AspenHYSYS, and Aspen Economic Evaluator. **Aspen Plus** is a process modeling tool for conceptual design, optimization, and performance monitoring for the chemical, polymer, specialty chemical, metals and minerals, and coal power industries. **Aspen HYSYS** is a process modeling tool for conceptual design, optimization, business planning, asset management, and performance monitoring for oil & gas production, gas processing, petroleum refining, and air separation industries. The **Aspen Economic Evaluator** enables rapid evaluation of capital investment projects early in the design process, to understand the economic implications of engineering decisions, for effective project management. Included are built-in engineering and cost content to enable conceptual estimates to be produced.

Aspen HYSYS allows estimating fuel composition and fuel saving at given combustion air and fuel temperatures. Output parameters of the calculations are fuel savings (natural gas flow rate),

TCR for High Temperature Furnaces in the Steel Industry: Phase I Validation of the Concept

furnace waste gas heat losses, and flue gas (stack) temperatures. Combustion air recuperator and recuperative reformer parameters such as pressure drops and heat transfer surface areas can be also estimated for given heat exchangers types and overall heat transfer coefficients. Several different waste heat recovery system configurations were developed to evaluate the systems efficiencies. Among the configurations are: A combustion air recuperation system with one air recuperator; A TCRS with 2 to 4 units (heat exchangers) including a 1 or 2 stage air recuperator and a 1 or 2 stage recuperative reformer. An example of Aspen HYSYS process flow diagram for TCRS with two units (air recuperator plus recuperative reformer) is shown in Figure 12.

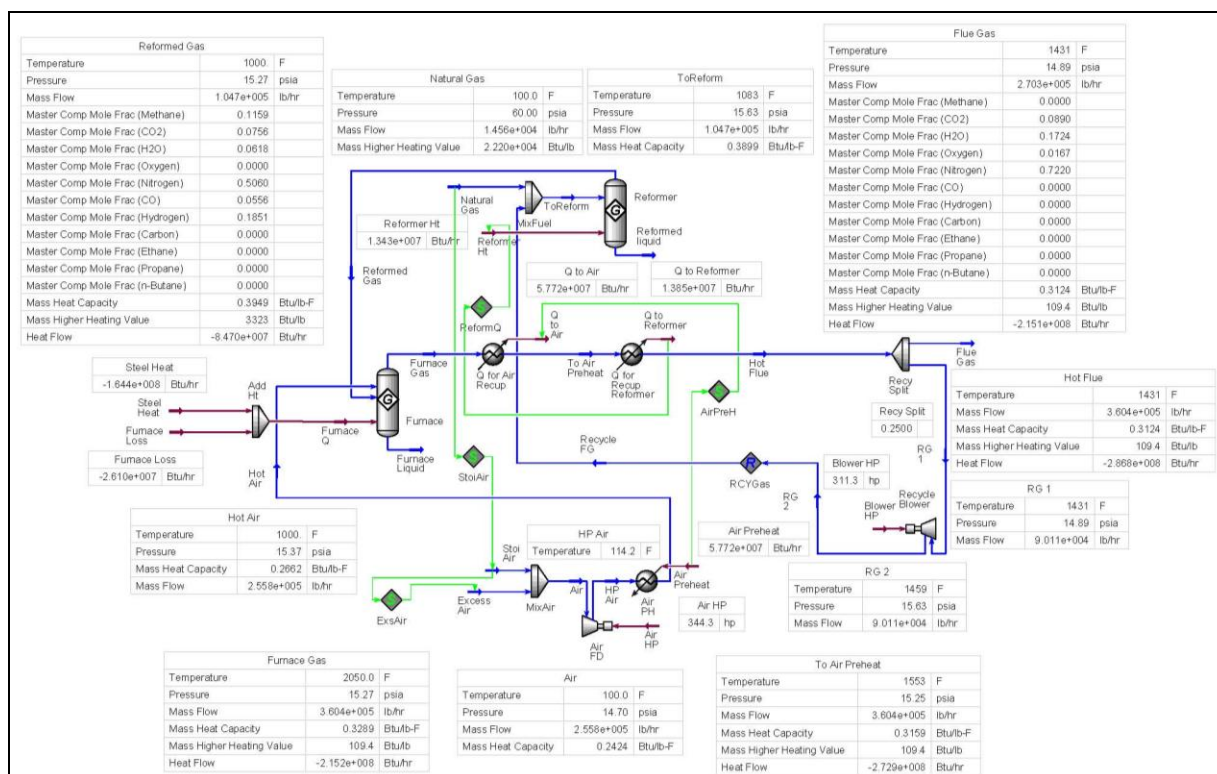


Figure 12. Process Flow Diagram for TCRS in Aspen HYSYS

Results of the Aspen HYSYS calculations for the reference steel rehear furnace with combustion air recuperation and TCRS are presented in Table 3. Furnace exhaust gas temperatures are set to 2050°F for combustion air recuperation and for TCRS. Fuel savings and CO₂ reductions for all the cases are compared to the base case with 800°F combustion air preheat.

Table 3. Results of the Reheat Furnace Waste Heat Recovery Systems Simulation

Waste Heat Recovery Opt	Combustion Air Recuperation					TCRS			
Combustion air temp, °F	800	1000	1200	1400	1800	800	1000	1200	1300
NG /reformed fuel temp, °F	100	100	100	100	100	1200	1200	1200	1300
Fuel/CO ₂ reduction, %	0	6.9	13.1	18.6	27.9	16.7	21.5	26	32.2
Energy intensity, MMBtu/T	1.61	1.5	1.4	1.31	1.16	1.34	1.26	1.19	1.1

Figure 13 shows the furnace thermal efficiency at different combustion air and reformed fuel temperatures. The blue line represents furnace thermal efficiency for a combustion air recuperation system; and the red line portrays the furnace thermal efficiency for a TCR system at a constant combustion air temperature (1200°F) and different reformed fuel temperatures (1000°F to 1400°F). As can be seen, adding fuel reforming to air recuperation can essentially increase the furnace thermal efficiency. The efficiency is increased when the reforming fuel temperature is higher. The limiting factors for temperature increases can be heat exchanger tube materials and cost when the heat exchange surface area is too large.

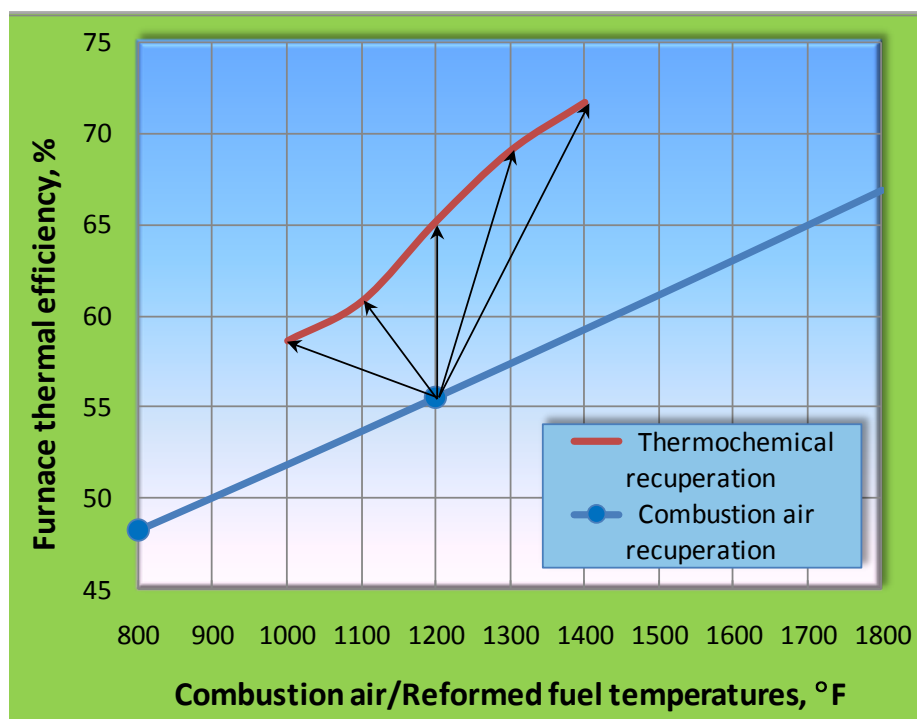


Figure 13. Furnace Thermal Efficiency versus Temperatures of Combustion Air (CA) and Reformed Fuel (RF)

The following conclusions are made from the calculated results shown in Table 3 and Figure 13.

For conventional waste heat recovery (combustion air recuperation):

- Combustion air temperature increases from 800°F to 1400°F provides 18.6% fuel savings and CO₂ reduction
- At 1800°F combustion air temperature, 27.9% fuel saving and CO₂ reduction can be achieved

For TCRS waste heat recovery:

- 32.2% fuel savings and CO₂ reduction can be achieved at much lower temperatures (1300°F) of combustion air and reformed fuel compared to conventional air recuperation.

As seen in Table 3 more than 30% of fuel savings can be achieved by using TCRS compared to the base case (combustion air recuperation at 800°F). The results have been generalized for

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further use in the TCRS optimization. The TCRS model for the pusher reheat furnace was developed based on Aspen HYSYS software.

TCRS Optimization

Four different TCRS configurations were analyzed and compared with high temperature air recuperation. (Figure 14): Case *a*) Two-units in series, Case *b*) Three-units in series, Case *c*) Three in series-parallel, and Case *d*) Four units in series, TCRS designs; RR – Recuperative Reformer, AR – Air Recuperator, I – first stage of air recuperator/reformer, II – second stage of air recuperator/reformer.

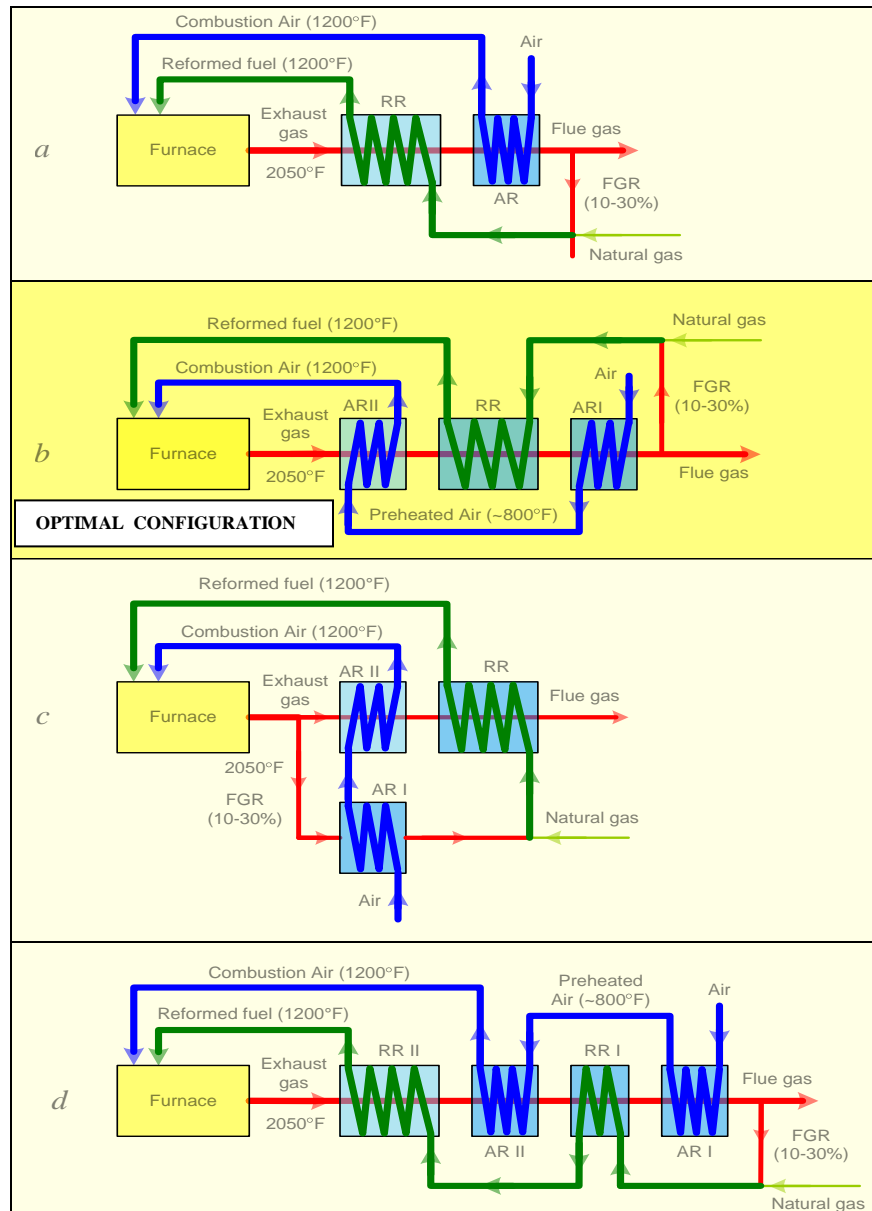


Figure 14. TCR System Schematic Diagrams used for Optimization (Cases *a*, *b*, *c* and *d*)

The following critical design parameters of the TCRS were chosen for further system analysis and evaluation:

- Furnace thermal efficiency (fuel savings)
- Air recuperator (AR) and recuperative reformer (RR) heat transfer surface areas
- AR & RR pressure drops
- Capital Expenditures

Controlled parameters and factors for optimizing the system were:

- Temperature of combustion air (T_A) and reformed fuel (T_{RF})
- Flue gas recirculation (FGR) fraction
- TCRS arrangement
- AR & RR design & configuration
- Overall heat transfer coefficient

A design approach for the heat exchangers (air recuperator, reformer) in the TCRS was jointly developed with TTC. Preliminary calculations have shown that the four unit TCRS design always gives higher total heat transfer surface area compared to the two- or three-unit designs consequently the four-unit design was excluded from further analysis at this time.

Since the furnace thermal efficiency depends on the Flue Gas Recirculation (FGR) fraction optimization can be obtained by selecting the optimum value of FGR. Figure 15 illustrates the relationship between the furnace thermal efficiency versus the FGR fraction at different temperatures. As can be seen the optimal value of the FGR fraction (dotted line) is increased

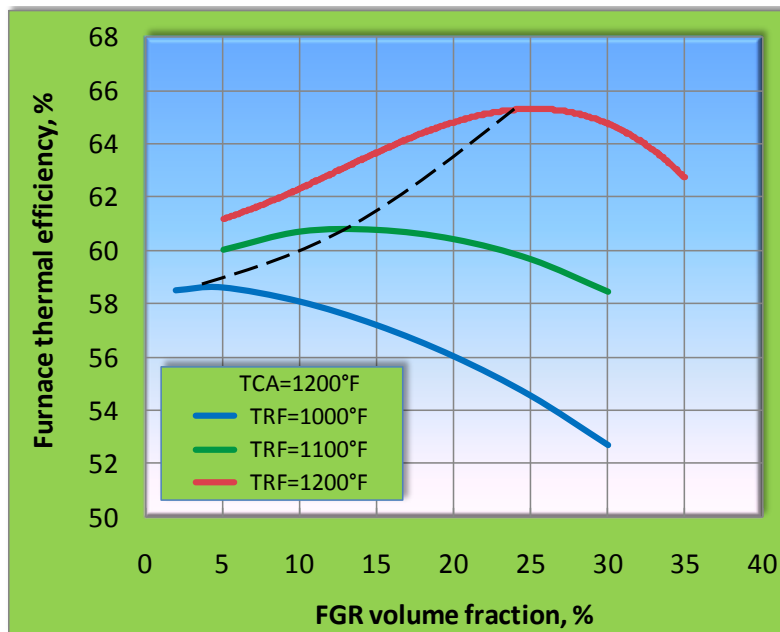


Figure 15. Furnace Thermal Efficiency versus FGR Fraction at various Reforming Fuel Temperatures $T_{RF} = 1000^{\circ}\text{F}$ to 1200°F

with increases in reformed fuel temperature T_{RF} . At the intersection of the $T_{RF} = 1200^{\circ}\text{F}$ for a fixed 1200°F air preheat the optimum FGR range is found to be 20% to 29%. In this case the furnace thermal efficiency is at maximum for these conditions.

Figure 16 shows heat exchange surface areas for the three-unit TCRS at various combustion air temperatures after the first stage air recuperator. As we can see from the figure the heat exchange total surface area (**Case b**) is minimal when the air temperature after the first stage air recuperator (ARI) is at $T_{ARI} \approx 800^{\circ}\text{F}$.

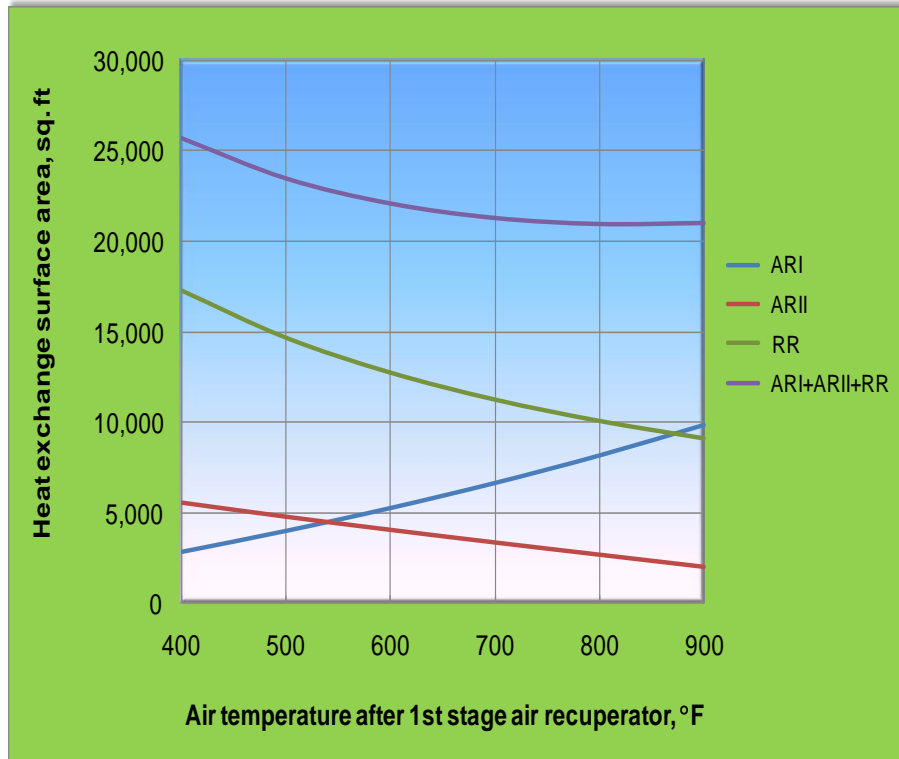


Figure 16. Heat Exchange Surface Areas at $T_{CA}=T_{RF}=1200^{\circ}\text{F}$

All the calculations were conducted at an excess air level of 10%. This parameter was not optimized as it is considered to be a realistic operating point for the reference furnace use in this study. Figure 17 shows that maximum furnace efficiency can be achieved at stoichiometric operation or 0% excess air.

Preliminary results of the TCRS optimization showed that for 1200°F combustion air preheat temperature and 1200°F reformed fuel temperature were, for all intents and purposes, at optimal temperature levels to achieve high furnace efficiency at low payback. For the optimization study, the percentage of FGR, the temperature of preheated combustion air after the first stage of air preheat, and reforming temperature were the main parameters to be focused on.

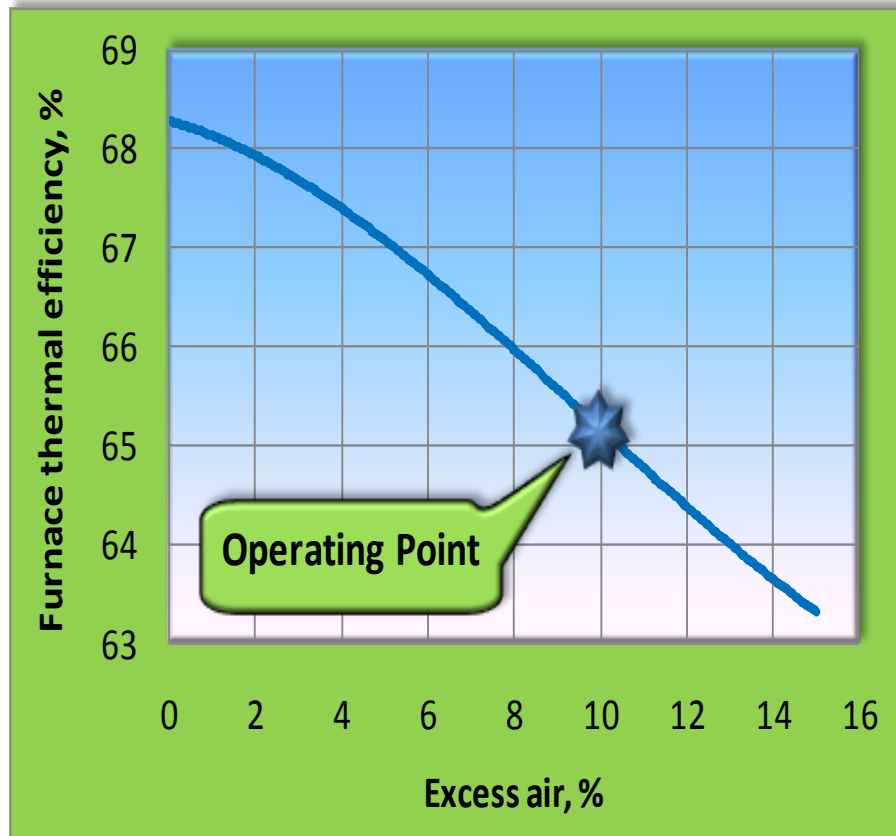


Figure 17. Furnace Thermal Efficiency versus Excess Air at $T_{CA}=T_{RF}=1200^{\circ}\text{F}$

Table 4 summarizes the furnace operating conditions and outputs with and without TCRS for 1200°F combustion air temperature and 1200°F reformed fuel temperature. The total surface areas are calculated base on the overall heat transfer coefficient $U = 8.86 \text{ Btu}/(\text{ft}^2 \times \text{hr} \times ^{\circ}\text{F})$ provided by TTC. Comparing natural gas (N.G.) fuel savings and total heat transfer surface area for both the air recuperator and the recuperative reformer the optimal TCRS parameters were determined. The results of optimization showed that less surface area is required when the temperature of the first stage air recuperator (ARI) is at $T_{ARI} \approx 800^{\circ}\text{F}$ (highlighted pink rows).

Based on analysis of the calculated results as summarized in Table 4 below, The TCRS configuration with three units (**Case b**) performs the best among all the cases based on: The total heat exchangers surface areas needed; Thermal Efficiency and Energy Intensity and therefore is considered as an optimal design and chosen for further economic analysis. The highest thermal efficiency and lowest energy intensity are achieved at a 23% FGR fraction.

Table 4. Reheat Furnace Waste Heat Recovery Systems Data for Optimization

HX Units	FGR Fraction	Combustion Air Recuperator Temp, °F		Reformed Temp, °F		Exhaust Gas Temp, °F		N.G. Flow	N.G. Savings	Heat Transfer Surface Area, ft ²			
		T _{ARI}	T _{ARII}	In	Out	Exhaust	Stack	lb/hr	%	AR/ARII	RR	ARI	Total
1	0.00	-	800	-	-	2050	1542	15351	0	5056	-	-	5056
2	10.00	-	1200	488.5	1200	2050	860	11751	42.6	6175	17041	-	23217
3	10.00	500	1200	479	1200	2050	833	11751	42.6	4550	7511	3373	15433
3	10.00	600	1200	479	1200	2050	833	11751	42.6	3976	6509	4364	14849
3	10.00	700	1200	479	1200	2050	833	11751	42.6	3379	5743	5406	14528
3	10.00	800	1200	479	1200	2050	833	11751	42.6	2757	5140	6509	14406
3	10.00	900	1200	479	1200	2050	833	11751	42.6	2110	4652	7675	14438
3	10.00	1000	1200	479	1200	2050	833	11751	42.6	1435	4245	8904	14584
3	10.00	1100	1200	479	1200	2050	833	11751	42.6	745	3906	10217	14868
2	20.00	-	1200	560.6	1200	2050	754	11374	44.4	6047	29045	-	35092
3	20.00	500	1200	547.5	1200	2050	727	11374	44.4	4284	13326	3989	21599
3	20.00	600	1200	547.7	1200	2050	727.1	11374	44.4	3757	11563	5227	20547
3	20.00	700	1200	547.7	1200	2050	727.1	11374	44.4	3204	10195	6570	19970
3	20.00	800	1200	547.7	1200	2050	727.1	11374	44.4	2624	9124	8044	19792
3	20.00	900	1200	547.7	1200	2050	727.1	11374	44.4	2016	8251	9658	19925
3	20.00	1000	1200	547.7	1200	2050	727.1	11374	44.4	1376	7520	11428	20324
3	20.00	1100	1200	548	1200	2050	727	11374	44.4	705	6914	13418	21037
3	22.89	800	1200	566.2	1200	2050	721.4	11357	44.5	2608	10167	8286	21061
2	25.00	-	1200	597.1	1200	2050	752	11373	44.4	5684	33438	-	39122
3	25.00	500	1200	583	1200	2050	725	11373	44.4	4228	15740	4067	24036
3	25.00	700	1200	584	1200	2050	725	11373	44.4	3173	12140	6783	22096
3	25.00	800	1200	583.2	1200	2050	725.2	11373	44.4	2602	10873	8355	21831
3	25.00	900	1200	584	1200	2050	725	11373	44.4	2003	9859	10119	21981
3	25.00	1100	1200	584	1200	2050	725	11373	44.4	704	8285	14377	23365
2	30.00	-	1200	655.7	1200	2050	789	11514	43.7	5662	35759	-	41421
3	30.00	500	1200	642	1200	2050	764	11514	43.7	4227	17569	3900	25695
3	30.00	700	1200	642	1200	2050	764	11514	43.7	3180	13678	6534	23392
3	30.00	900	1200	642	1200	2050	764	11514	43.7	2014	11196	9828	23038
3	30.00	1100	1200	642	1200	2050	764	11514	43.7	711	9460	14143	24313

Emissions reductions - Carbon Dioxide Reduction Potential

Figure 18 shows CO₂ emissions for both air recuperation and TCRS for comparison. The flue gas constituents (CO₂, H₂O, and N₂) are not changed when TCRS is used. CO₂ reduction in the case of TCRS directly related to the lower natural gas flow rate(s).

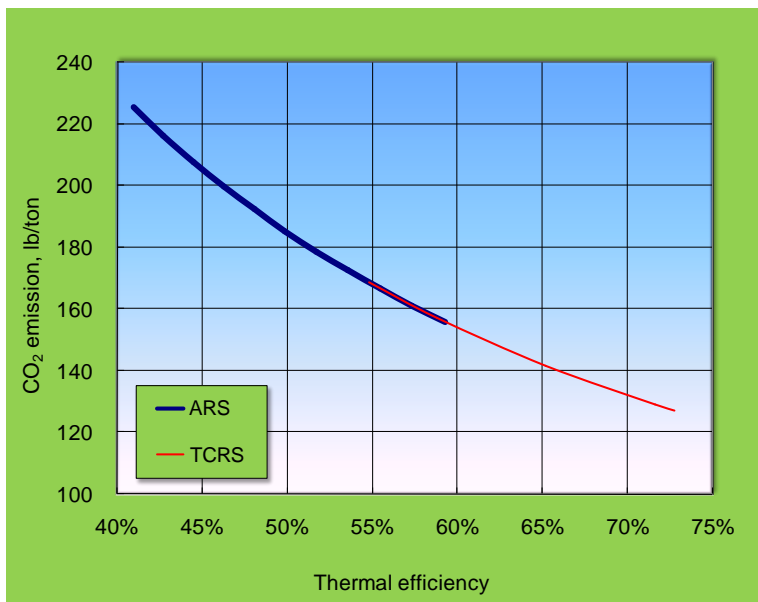


Figure 18. CO₂ Reduction ARS and TRC

Emissions reductions Oxides of Nitrogen Reduction Potential

The lower combustion temperature in the case of TCR system compared to air recuperation leads to an even greater relative reduction in NO_x emission compared to that of CO₂ (Figure 19).

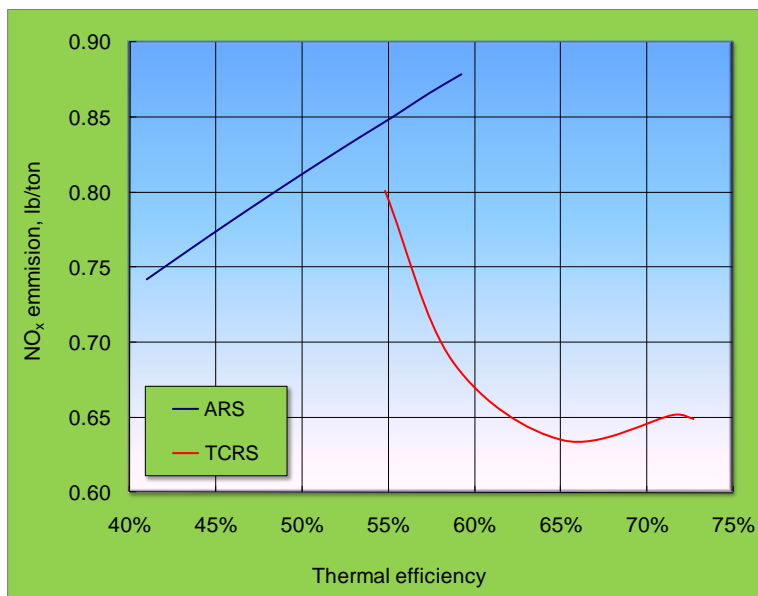


Figure 19. NO_x Emissions for ARS and TCRS

Heat Exchanger Designs and Arrangements

The optimal parameters from this study for the TCRS have been used for further feasibility analysis. Potential heat exchangers (air recuperator and recuperative reformer) designs have been evaluated jointly by GTI and TTC. Figure 20 and Figure 21 show preliminary air recuperator study-drawings for the first and second stages of a combustion air recuperator.

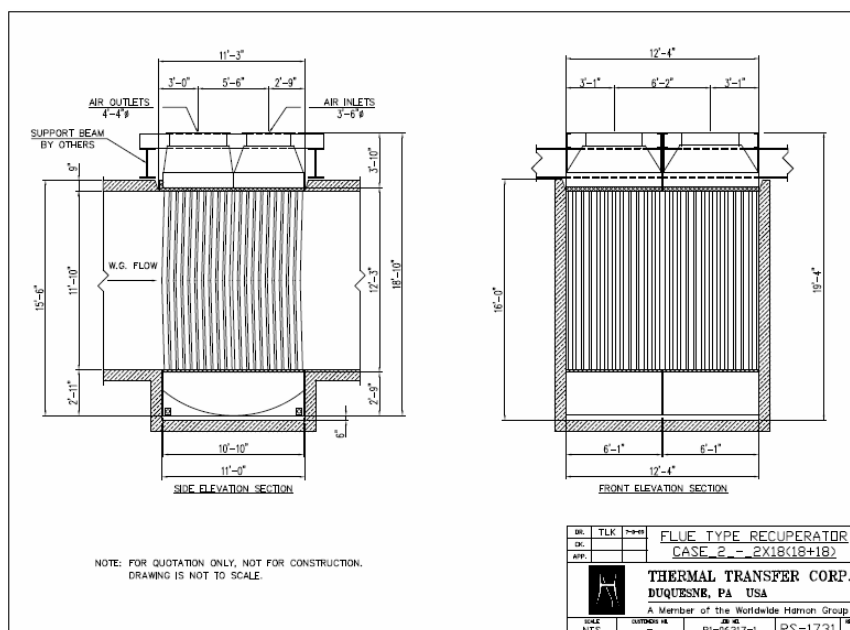


Figure 20. Air Recuperator – First Stage for Case *b*
(Waste Gas Inlet Temperature = 1182°F and Air Outlet Temperature = 800°F)

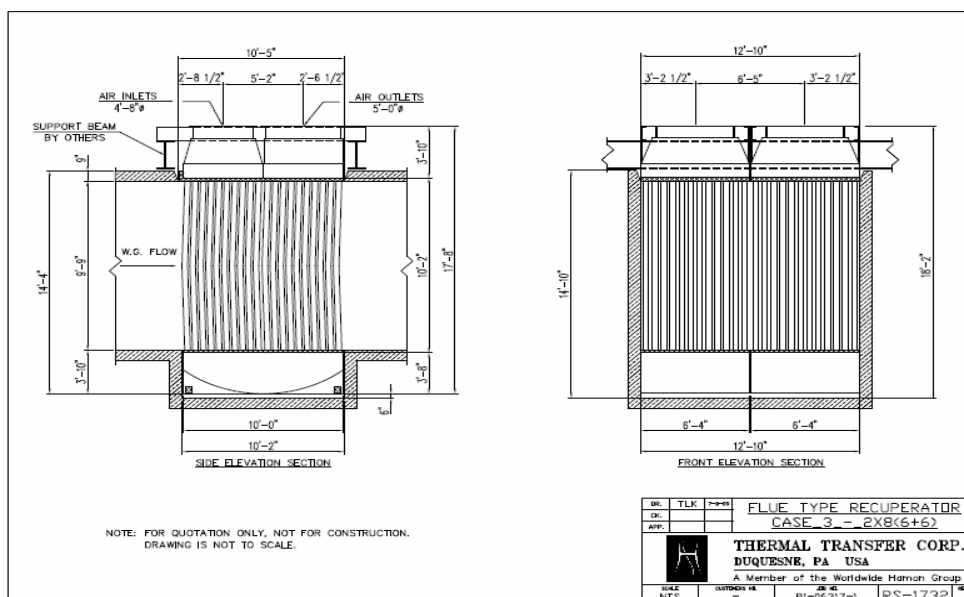


Figure 21. Air Recuperator – Second Stage for Case *b*
(Waste Gas Inlet Temperature= 2050°F and Air Outlet Temperature = 1200°F)

Figure 22 illustrates the preliminary recuperative reformer study-drawing.

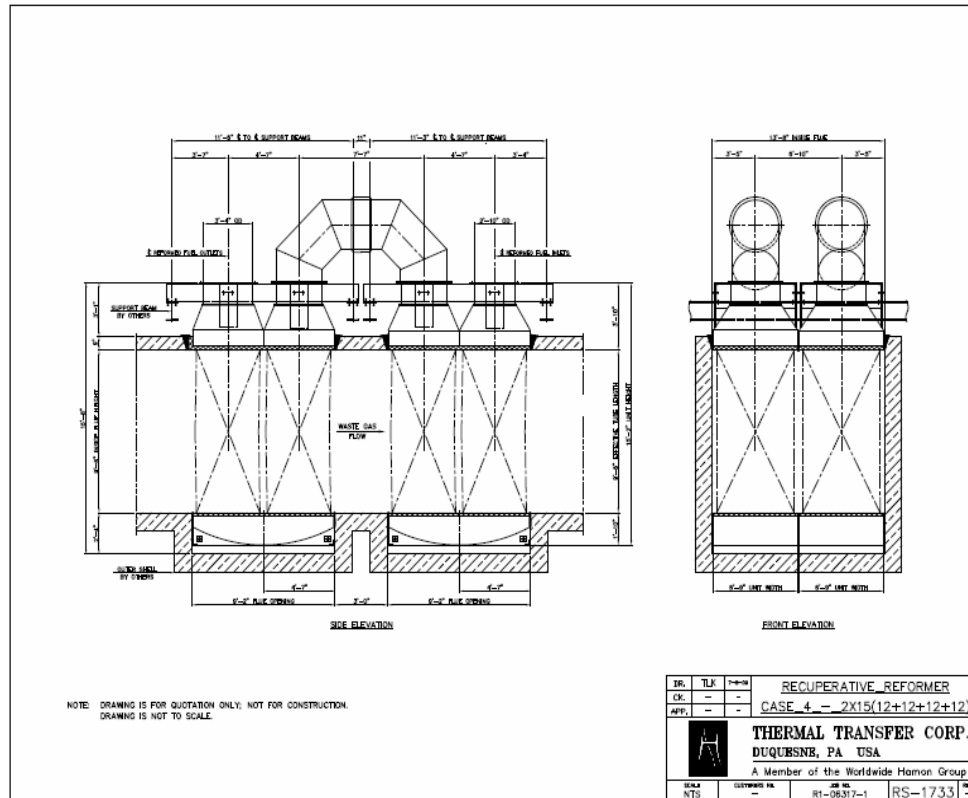


Figure 22. Recuperative Reformer for Case *b*
(Waste Gas Inlet Temperature = 1810°F and
Reformed Fuel Outlet Temperature = 1200°F)

AR & TCRS (Case *b*) Footprints

The footprints (dimensional envelopes) for the heat exchangers for both the reference steel reheat furnace recuperator and the three heat exchange units of the optimized TCRS have been preliminarily established including the inlet and outlet dimensions for attachment to the furnace exhaust gas outlet ductwork for the given temperature and flow conditions.

For the AR --

The length, width and height were established as 9.7 feet long \times 17.8 feet wide \times 10.8 feet in height given the parameters of this study:

- Combustion air preheat temperature \approx 800°F
- Nominal furnace firing rate \approx 341 MMBtu per hour
- Nominal waste gas flow \approx 293,000 pounds per hour
- Furnace thermal efficiency \approx 48%

For the TCRS --

The length, width and height were established as 27.4 feet long \times 17.8 feet wide \times 10.8 feet in height given the parameters of this study:

- Combustion air preheat temperature $\approx 1200^{\circ}\text{F}$
- Reformed fuel temperature $\approx 1200^{\circ}\text{F}$
- Nominal furnace firing rate ≈ 252 MMBtu per hour
- Nominal waste gas flow $\approx 216,000$ pounds per hour
- Furnace thermal efficiency $\approx 65\%$

Figure 23 illustrates depicts the conventional air recuperator and the three-unit TCRS overall dimensions to visual scale for comparison.

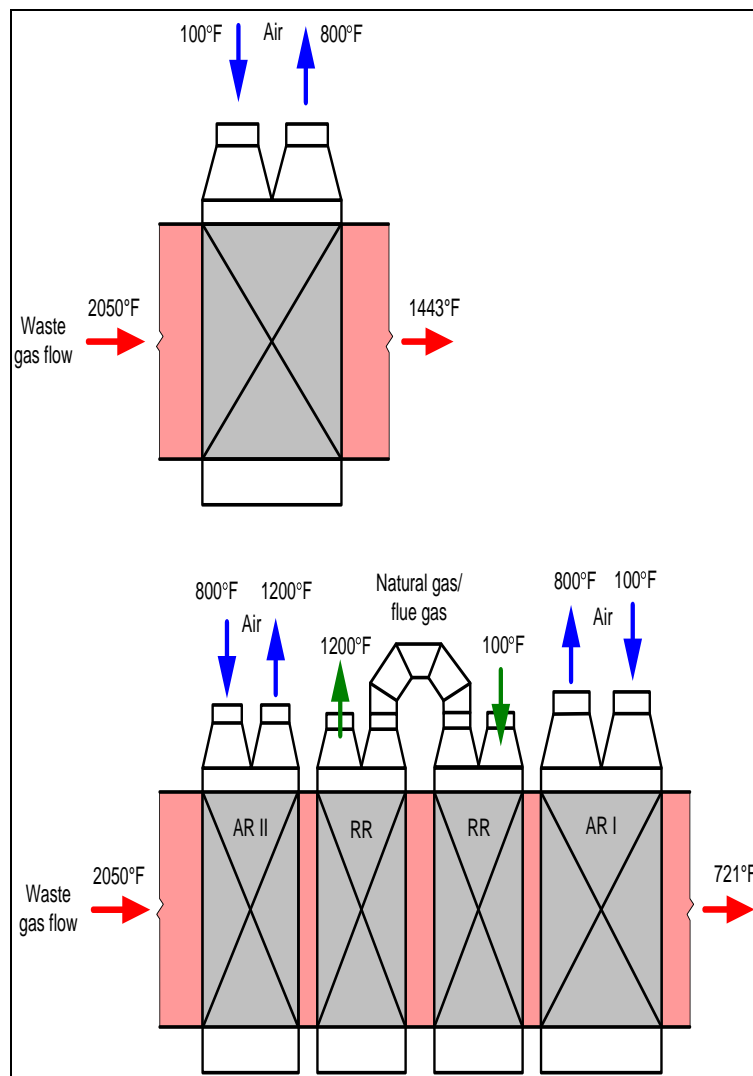


Figure 23. Conventional Air Recuperator and Case *b* Size Comparison

Economic Analyses

The AspenOne economic analyzer was used for analyzing the economics. The following elements made up the analyses-

- Capital Expenditures (CAPEX)
 - Direct cost estimates for equipment and labor (heat exchangers, fans, piping, insulation, burners, instrumentation, electrical, engineering, etc.)
 - Indirect cost estimates
 - Contingency cost estimates
- Simple payback calculations

The major equipment components were identified that will be necessary for retrofitting and installing the TCRS. These components are shown in the simplified process flow diagram in Figure 24.

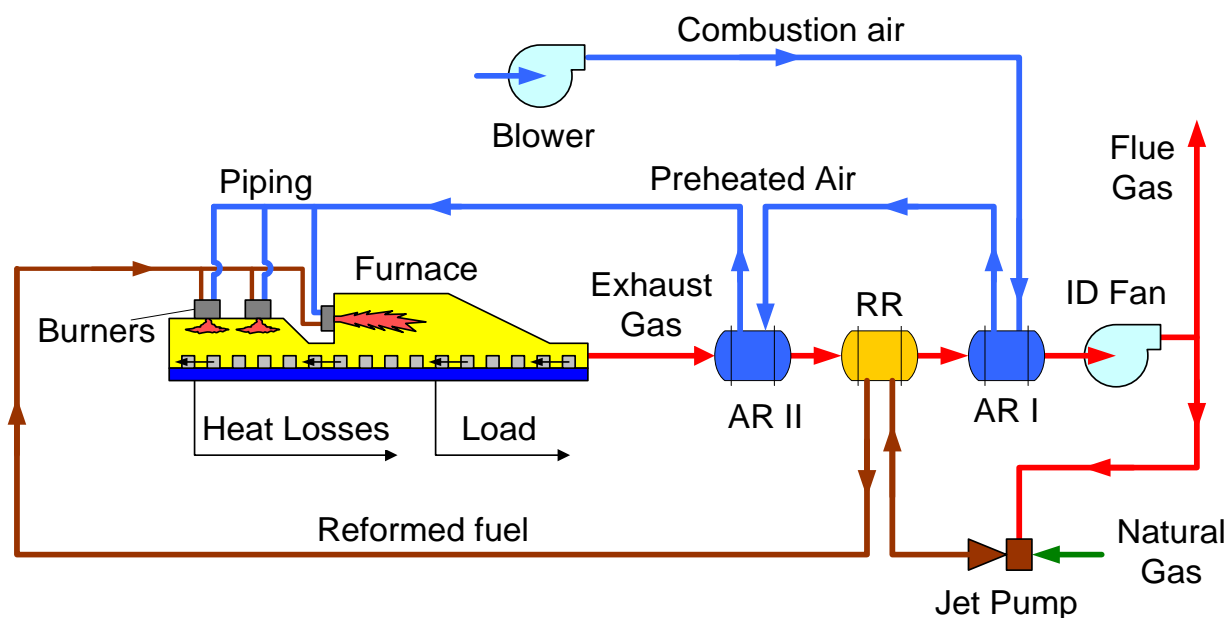


Figure 24. Process Flow Diagram of Steel Reheat Furnace with Case *b*

The methodology employed in establishing the equipment prices was as per the approaches described in (Guthrie, 1974, Perry, Green, & Maloney, 1997, and Gael, D. & Vasudevan); where the purchase price of each piece of equipment is multiplied by a 'module factor' to obtain the total expenditure required to procure and install the equipment and to make it ready for operation. Guthrie and Gael, D. & Vasudevan provided coefficients, unique to each equipment type, while Perry, Green, & Maloney provided coefficients for various types of plants.

Major units to be installed that make up the typical TCRS (Case b)

A sequence of heat exchangers, starting from the waste gas outlet of the reheat furnace as follows:

- The 'HOT' air recuperator (ARII) – provides preheated combustion air from the hot waste gases exiting the furnace (2050°F) from 100°F to 800°F (which is further increased to 1200°F out of 'COLD' air recuperator (ARI), the second air recuperator). Per review by TTC, this heat exchanger will likely be designed to use a co-current flow scheme to avoid overheating of the heat transfer piping at the hot inlet end.

The Recuperative Reformer (RR), that is essentially a reactor with a heat exchanger – converts the thermal energy of flue gases exiting ARII into chemical and thermal energy contained in the reformed fuel. Since the specific design of the RR will not be finalized until physical lab-testing is completed, it was modeled as the aggregate of a heat exchanger and jacketed non-agitated reactor. The heat duty of the heat exchanger component is equal to the heat consumed in the reactor to produce partially reformed fuel at a specified temperature. The heat exchange surface was calculated assuming counter-current flow scheme with the cold stream of gas having a pseudo specific heat that provided the specified temperature at the cold stream outlet.

- The 'COLD' air recuperator (ARI) – transfers the sensible heat from flue gases exiting RR to ambient temperature combustion air delivered by the combustion air fan(s). Due to lower temperatures than that in ARII, it is possible to use counter-current flow scheme for this unit.
- Induced Draft Fan – compensates for the pressure losses of the hot waste gases across the three heat exchange units by augmenting the natural draft of the furnace stack.
- Combustion air fan – provides the necessary volume of ambient combustion at a delivery or inlet pressure to compensate for pressure losses of the relatively cold streams of air across ARI and ARII. Whether an upgrade to the existing fan motor and or impeller or both will need to be determined on a case by case basis.
- Venturi-type mixer – utilizes the pressure of the natural gas fuel as the motive force to inspirate the required flue gas thereby mixing the natural gas and the flue gas in direct proportion to the volume of gas passing into/through the mixer allowing the natural gas/flue gas ratio to remain constant thought the mixer capability range.
- New burners – required due to higher temperature of fuel and air as well higher fuel volumetric flow.

Estimated equipment costs were obtained from vendor quotes and estimates based on unit capacities (see Table 5). According to (Gael, D. & Vasudevan, 2009) unit purchase price is scalable as a function of a specific unit's capacity:

$$C_p^v = C_p^u \left(\frac{v}{u} \right)^\alpha$$

Where C_p^v – purchase price of the unit, which has a size or capacity v , C_p^u – purchase price of the unit, which has a size or capacity u , α - exponent specific for every equipment type.

Table 5. Summary of Estimated Equipment Costs

Equipment	Size/Capacity	Base Pricing	α
'HOT' Air Recuperator	2,727 ft ²	\$378,990	0.6
Recup Reformer Heat Exchanger	8,507 ft ²	\$512,500	0.6
Recup Reformer Reactor	2474 ft ³	\$246,855	0.73
'COLD' Air Recuperator	9,536 ft ²	\$329,850	0.6
ID fan	82.2 bhp	\$32,255	0.9
Combustion Air Fan	391 bhp	\$49,749	0.9
Ejector-type mixer	555 lbs/hr	\$12,700	0.6
New Nozzle Mix Burners	40	\$21,700	1.0

The base case (reference steel reheating furnace) for making a modeling-comparison with respect to the TCRS was a recuperated pusher reheat furnace with Escher air recuperators. The main set of specifications of this reference steel reheating furnace is presented below:

- Production rate \approx 212 tons per hour
- Energy Intensity \approx 1.59 MMBtu per ton reheated steel
- Fuel is natural gas
- Fuel gross heating value \approx 1018 Btu per standard cubic foot
- Fuel heat input \approx 337 MMBtu per hour
- Fuel delivery temperature \approx 100°F*
- Air preheat temperature \approx 800°F
- Excess air \approx 10%*
- Heat to steel \approx 157 MMBtu per hour*
- Water cooled surface area heat losses \approx 20 MMBtu per hour*
- Shell heat losses \approx 6.9 MMBtu per hour*
- Furnace waste gas average temperature \approx 2030°F
- Flue gas temperature after air recuperator \approx 1150°F

*The system shown in Figure 24 was modeled using ASPEN PLUS software with a base set of the specifications retained in the ASPEN database. The system shown in Figure 25 was also modeled to establish a comparison of TCRS with a typical ARS.

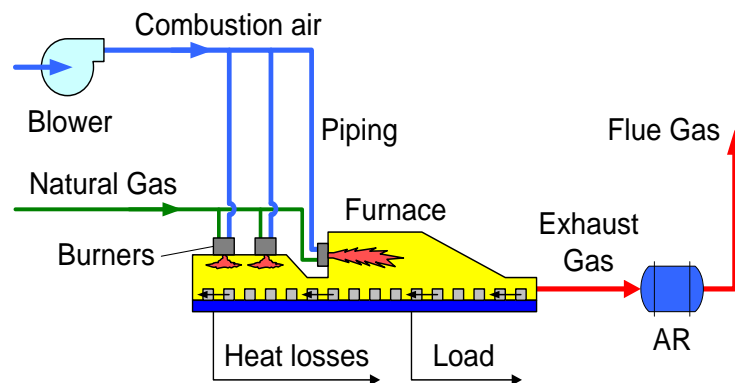
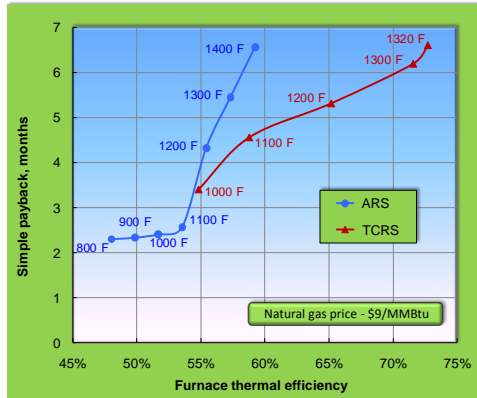


Figure 25. Process Flow Diagram of Reference Steel Furnace with ARS

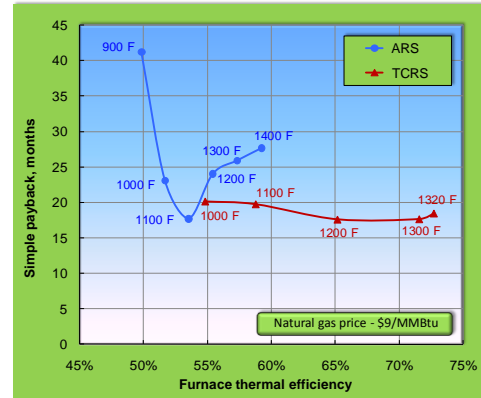
The ARS for the reference steel furnace (base case) was modeled for air preheat temperatures that ranged from 800°F to 1400°F. The base case for comparison purposes was chosen for delivering 800°F combustion air preheat. Fuel reduction savings of the three-unit TCRS were calculated with respect to this base case.

For the three-unit TCRS, an optimum temperature for the ‘Cold’ air recuperator (ARI) was found at the 700°F level. Consequently, an economic analysis was carried out for both the three-unit TCRS with temperatures ranging from 1000°F to 1320°F (with combustion air and reformed fuel temperatures equal in magnitude) and the air preheating system. An optimum flue gas recirculation rate was found for each three-unit TCR system temperature. An annual capacity utilization of 90% (~7,890 hours per year) was assumed for the simple payback calculations.

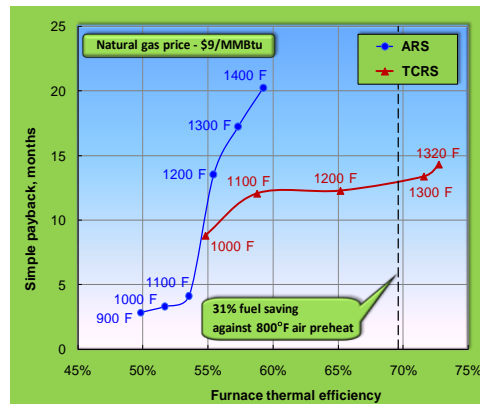
The results obtained are shown graphically in Figure 26 through Figure 28. As can be seen, the three-unit TCRS has a much lower capital expenditure level and lower simple payback compared to conventional air recuperation at the same furnace thermal efficiency. Additionally, the feasibility of fuel savings and CO₂ reductions to exceed 30% are achievable with TCRS compared to the air recuperation-only option (The 31% of fuel savings alluded to in Figure 27 relates to approximately 1270°F combustion air and reformed fuel temperatures.).



a



b

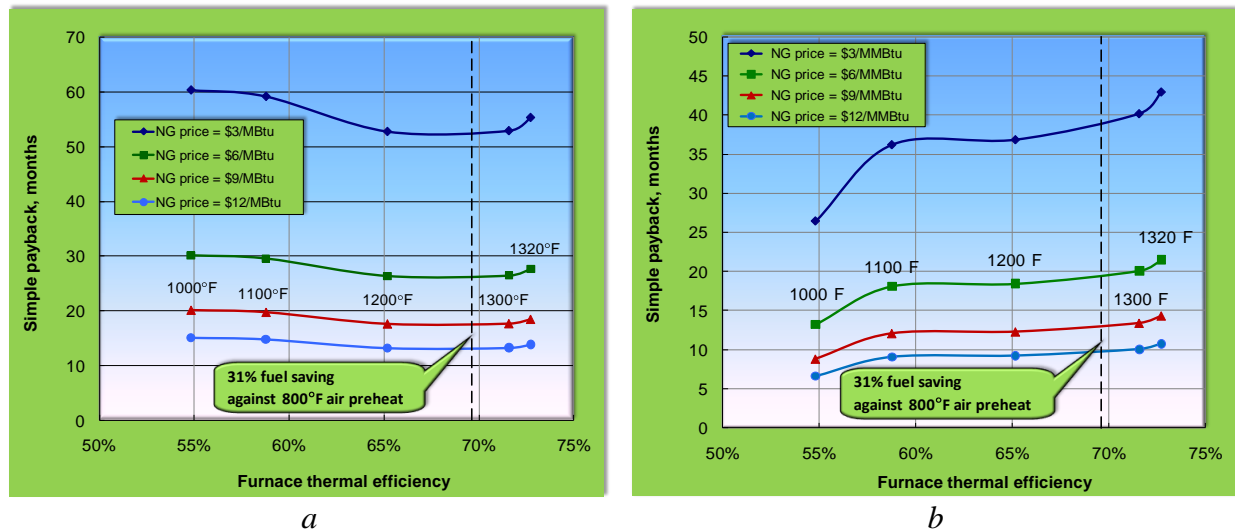


c

Figure 26. Simple Paybacks Comparisons - ARS and Three-Unit TCRS (Case *b*):
a) Unrecuperated Furnace, *b*) New Furnace, Fuel Savings Compared with 800°F Air Preheat, and *c*) Retrofitted Furnace, Fuel Savings Compared with 800°F Air Preheat



Figure 27. CAPEX for ARS and Case *b* for Waste Heat Recovery



**Figure 28. Simple Paybacks at Various Natural Gas Prices for Case *b*
Compared to a Recuperated Furnace with 800°F Air Preheat:
a) New Furnace and b) Retrofitted Furnace**

The results of the Economic Analysis calculations and cost estimates comparing the ARS and Case *b* are summarized below in Table 6 and Table 7 respectively. Note that the base case being compared to is the reference steel reheat furnace with recuperation supplying preheated air at 800°F with the column highlighted in blue (Table 6). The calculations and cost estimates for the optimized Case *b* is highlighted in blue (Table 7).

Table 6. Estimated CAPEX for a range of Air Recuperation Systems

Combustion air temperature, °F	800	900	1000	1100	1200
Heat exchanger estimates	\$335,077	\$381,775	\$439,449	\$522,880	\$1,102,648
Direct Cost estimates					
Equipment f.o.b. price	\$1,369,483	\$1,408,395	\$1,458,890	\$1,535,684	\$2,109,302
Materials used for installation	\$282,834	\$313,888	\$352,898	\$410,342	\$820,317
Direct labor	\$260,188	\$287,311	\$321,528	\$372,132	\$735,571
Total direct materials and labor	\$1,912,506	\$2,009,594	\$2,133,316	\$2,318,157	\$3,665,190
Indirect Cost estimates					
Freight, insurance, taxes	\$70,208	\$75,655	\$82,725	\$93,476	\$173,782
Construction overhead	\$180,520	\$199,519	\$223,469	\$258,859	\$512,734
Contractor engineering expenses	\$113,163	\$124,086	\$137,957	\$158,611	\$308,388
Total indirect project costs	\$363,891	\$399,260	\$444,151	\$510,945	\$994,904
Bare module capital	\$1,408,396	\$1,540,854	\$1,709,467	\$1,961,102	\$3,792,094
Contingency/Fee estimates					
Contingency	\$212,265	\$232,273	\$257,738	\$295,734	\$572,122
Fee	\$43,793	\$47,982	\$53,305	\$61,238	\$118,835
Total contingency and fee	\$256,058	\$280,255	\$311,044	\$356,972	\$690,957
Total module capital	\$1,664,454	\$1,821,109	\$2,020,511	\$2,318,074	\$4,483,052
Auxiliary facilities	\$499,336	\$546,333	\$606,153	\$695,422	\$1,344,915
Total Estimated Costs	\$3,031,791	\$3,235,442	\$3,494,664	\$3,881,497	\$6,695,967

Table 7. Estimated CAPEX for a range of TCR Systems

Air/Reformed fuel temperature, °F	1000	1100	1200	1300	1320
Heat exchanger estimates	\$617,585	\$869,357	\$1,219,705	\$1,749,407	\$1,939,835
Direct Cost estimates					
Equipment f.o.b. price	\$1,839,469	\$2,303,904	\$2,723,137	\$3,205,136	\$3,395,249
Materials used for installation	\$555,482	\$837,489	\$1,124,450	\$1,481,851	\$1,617,472
Direct labor	\$510,901	\$769,489	\$1,026,467	\$1,341,388	\$1,461,673
Total direct materials and labor	\$2,905,852	\$3,910,882	\$4,874,054	\$6,028,376	\$6,474,394
Indirect Cost estimates					
Freight, insurance, taxes	\$136,006	\$201,027	\$259,719	\$327,199	\$353,815
Construction overhead	\$353,846	\$532,007	\$710,598	\$931,002	\$1,015,002
Contractor engineering expenses	\$219,842	\$326,892	\$432,318	\$561,522	\$611,075
Total indirect project costs	\$709,694	\$1,059,925	\$1,402,635	\$1,819,723	\$1,979,892
Bare module capital	\$2,747,546	\$4,102,807	\$5,408,689	\$6,980,099	\$7,586,286
Contingency/Fee estimates					
Contingency	\$413,985	\$618,029	\$814,962	\$1,052,263	\$1,143,762
Fee	\$85,267	\$127,083	\$167,871	\$217,450	\$236,512
Total contingency and fee	\$499,252	\$745,112	\$982,834	\$1,269,713	\$1,380,274
Total module capital	\$3,246,798	\$4,847,919	\$6,391,523	\$8,249,812	\$8,966,561
Auxiliary facilities	\$974,039	\$1,454,376	\$1,917,457	\$2,474,944	\$2,689,968
Total estimated costs	\$5,088,838	\$7,170,295	\$9,176,980	\$11,592,756	\$12,524,529

Potentials for further incremental gains for Next Generation TCRS

There are some potentials for improved waste heat recovery beyond that reported on above, namely: 1) TCRS with natural gas reforming by adding steam to the flue gas; 2) TCRS with natural gas reforming by using steam only and no flue gas utilized (see Figure 29); 3) TCRS for oxy-fired furnaces; 4) TCRS integrated with a Water Vapor Pump System (WVPS) for both oxy and/or air-fired furnaces.

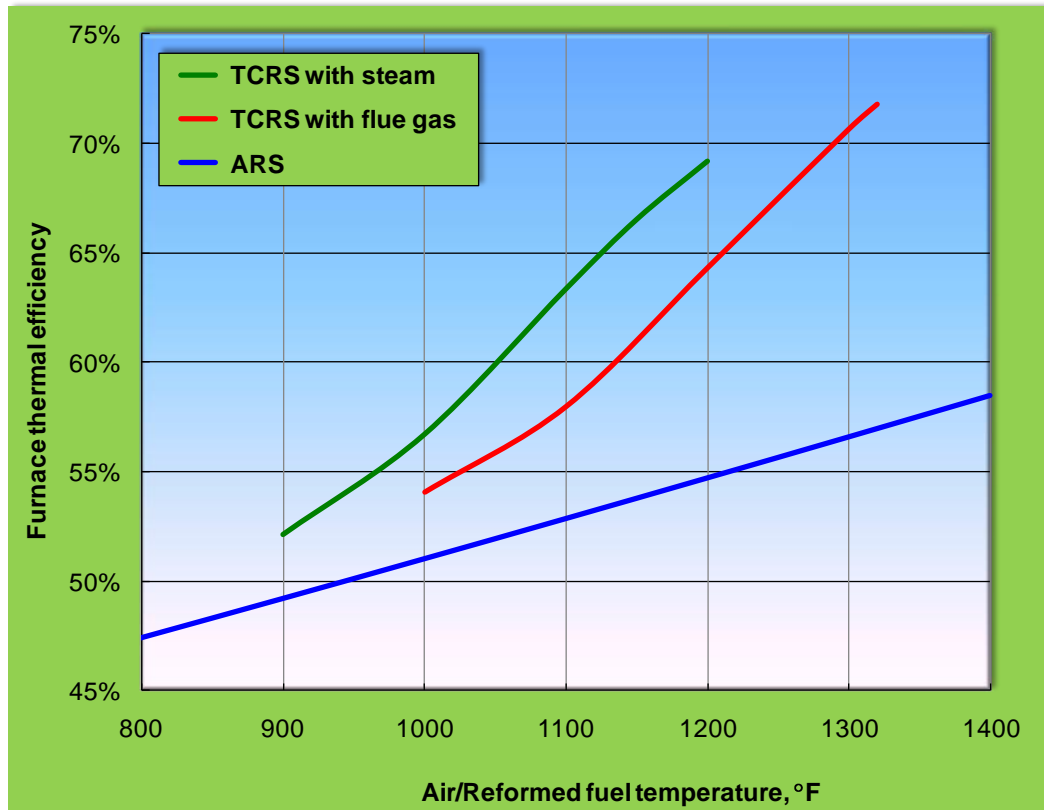


Figure 29. Furnace Thermal Efficiencies vs. Air and Reformed Fuel Temperatures for Reference Steel Reheat Furnace with: ARS (Blue) exclusively, TCRS with Flue Gas exclusively (Red), and Steam (Green) exclusively

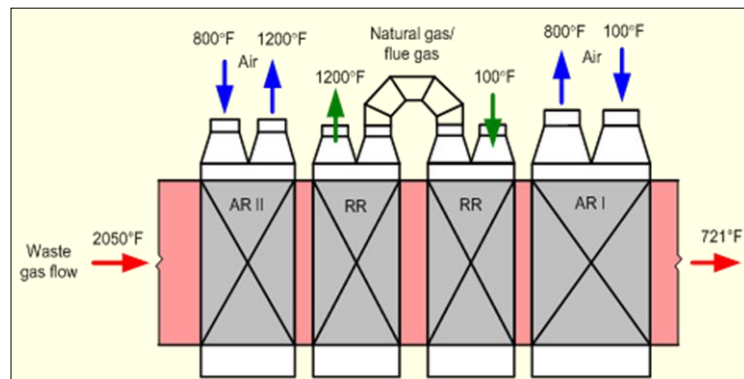
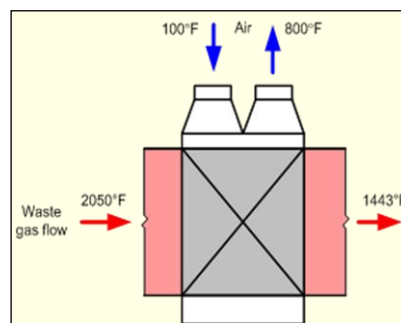
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List of Acronyms

Acronym	Description
AISI	American Iron and Steel Institute
GTI	Gas Technology Institute
TCR	ThermoChemical Recuperation
CAPEX	Capital Expenditures
ROI	Return on Investment
NPV	Net Present Value
MMBtu	Million British Thermal Units
TTC	Thermal Transfer Corporation
ARS	Air Recuperator System
TCRS	ThermoChemical System
WVPS	Water Vapor Pump System
T_{RF}	Reformed Fuel Temperature
FGR	Flue Gas Recirculation
CO_2	Carbon Dioxide
NO_x	Oxides of Nitrogen
CH_4	Methane
RR	Recuperative Reformer,
T_A	Temperature of Combustion Air
RF	Reformed Fuel
U	Heat Transfer Coefficient
α	Exponential scaling factor for pricing estimates
ε	Relative Air Preheat
T_{ARI}	Temperature of Combustion Air – First Stage Air Recuperator
T_{ARI}	Temperature of Combustion Air – Second Stage Air Recuperator

Dimensional-comparisons of the heat exchanger units or modules are depicted at the right and below. The graphic at the right is a typical air recuperator that was sized by (TTC) for the reference steel rehear furnace that was used as the basis for comparison in this study. The length, width and height were established as 9.7 feet \times 17.8 feet \times 10.8 feet.



The graphic at the left represents the scheme and estimated dimensions of the three-unit TCRS resulting from GTI modeling, calculations and information provided by TTC. The length width and height was established as 27.4 feet \times 17.8 feet \times 10.8 feet. It should be noted that no effort was made to evaluate whether there was the potential to utilize a

portion of or the entire heat transfer surface of an existing air recuperator. GTI believes that the potential for utilizing existing heat transfer surface area certainly exists in the majority of cases but deemed that each installation will be unique from this standpoint and that engineering would need to be conducted to establish this feasibility-of-utilization.

It should be noted that the efficiency step change reported on in this Phase I work of increasing the reference rehear furnace (recuperated) thermal efficiency to 65% from 48% would require an air recuperator capable of producing preheated air at a temperature of 1700°F. The implications of the metallurgical requirements of the heat transfer tubes; the additional engineering considerations with respect to piping, valving, etc. due to 1700°F preheat temperature would, in GTI's opinion preclude this option being selected over that of a TCRS due to the increased cost of higher grade tube materials and reduce longevity of the heat exchanger due to higher tube wall temperatures.

CAPEX and estimated Return on Investment: The cost estimates were established on the basis of three major categories that would make up retrofitting costs. Estimated Direct Costs, Estimated Indirect Costs and Estimated Contingencies and Fees for 1) The base case of retrofitting a rehear furnace with a recuperative system, and; 2) The three-unit TCRS that was optimized.

For retrofitting an ARS on the reference rehear furnace without recuperation, the estimated installed cost was approximately \$3 million, the annual fuel savings were \$9.2 million, the simple payback was 4 months and the ROI was \$33 million (NPV at a 7% discount rate over six years of cash flow).

For retrofitting the optimally designed three-unit TCR System on the reference rehear furnace without recuperation the estimated installed cost was approximately \$9.2 million,

the annual fuel savings were \$15.5 million, the simple payback was 7 months and the ROI was \$51 million (NPV at a 7% discount rate over six years of cash flow).

For retrofitting the optimally designed three-unit TCR System on the reference reheat furnace with recuperation the estimated installed cost was approximately \$6.2 million, the annual fuel savings were \$6.3 million, the simple payback was 12 months and the ROI was \$18 million (NPV at a 7% discount rate over six years of cash flow).

The fixed natural gas cost for the above estimates was assumed as a nominal \$9 per million Btu.

It should be noted that no consideration was given for the complete or partial reuse of the existing recuperator of the reference steel reheat furnace which would further improve return on investment. There may be further reductions in the CAPEX as close inspection of Table 7 reveals that estimated Indirect Costs and Contingency and Fees are over 25% of the Installed cost of the optimized three-unit TCRS. We believe that these estimates are conservative and can be managed such that indirect costs and contingencies/fees can be reduced considerably.

Reduced Carbon Footprint and Oxides of Nitrogen: The reference recuperated furnace was estimated as producing 185 pounds of carbon dioxide per ton of steel reheated and 0.8 pounds of oxides of nitrogen per ton of steel reheated. Retrofitting the reference reheat furnace with the three-unit TCRS would reduce the emissions intensities of carbon dioxide and oxides of nitrogen to 142 pounds per reheated ton and 0.63 pounds per reheated ton respectively. On an annualized basis the metric tons of CO₂ and NO_x produced by the three-unit TCRS reheat furnace would be an estimated 107,000 metric tons and 478 metric tons representing reductions of 33,000 metric tons per year of CO₂ and 129 metric tons per year of NO_x.

*Imputing results to 50% of the U.S. steel reheat furnace population:*¹ In order to add perspective as to the potential to the retrofitting of steel reheat furnaces, an estimated projection for frame-of-reference purposes only is included as summarized below. To remain conservative, 50% of the recuperated furnace population (approximately 80 steel reheat furnaces) was assumed as the steel reheat furnace market in the U.S.

The energy intensities (EIs) of each of the three steel segments (See table at the right), Integrated, Minimills and Converter/Specialty that making up the Flat and Long product plants representative a

Imputed Future Fuel Usage Reductions – TBtu per Year

Flat/Long Plants		Recuperated Furnaces-MMBtu per Ton	
<i>Recuperated</i>	<i>TCR</i>	<i>Current</i>	<i>Future</i>
Integrated		1.18	0.87
Minimills		1.11	0.82
Converter/Specialty		1.40	1.03

composite or aggregate of EIs of the furnace populations within each segment. The approach employed was to scale back the energy intensities (composite energy intensities) of recuperated furnaces in three steel segments (see) on a prorated basis using the percent improvement in

¹ 2003 North American Hot Strip & Plate Mill Market Study (*Customized Final Report*), prepared for Gas Technology Institute by AIM MARKET RESEARCH

thermal furnace efficiency of the base case recuperated furnace in this study when equipped with a three-unit TCRS recognizing that the level of precision in making these projections will not be as high as in this report for the reference furnace studied since the furnaces making up 50% of the U.S. population were not studied in detail as the reference steel reheat furnace was for this study.

Finally, below are two tables summarizing the imputed reductions in energy consumption and emissions reductions for the ultimate equipping/retrofitting of 50% of the recuperated furnace population with TCRS. The reductions were projected by the imputed future energy intensities shown in the table above.

Imputed Future Fuel Usage Reductions – TBtu per Year

Plants	Current	Future	Reductions		Savings
			TBtu	%	
Flat and Long	TBtu	TBtu	TBtu	%	\$-mill
Integrated	26.6	19.7	7.0	26.3	63.0
Minimills	16.0	11.8	4.2	26.3	37.6
Converters/Specialty	2.9	2.2	0.77	26.6	6.9
Totals-cum	45.6	33.7	11.9	26.1	107.0

Imputed Emissions Reductions – Tons (metric) per Year

Emissions	Current	Future	Reductions	%
CO ₂	3,300,000	2,500,000	800,000	24.2
NO _x	14,000	11,000	3,000	21.4

Appendix B

SUMMARY

TCR Evaluation by ECOTERM per Subcontract No. S00000061

A significant part of natural gas is spent in different countries for the firing of high-temperature industrial furnaces in metallurgy, machine building, chemical industry, production of building materials, etc. The coefficient of fuel utilization (CFU) in such furnaces is usually quite low, and, therefore, the search for ways of its substantial increase represents an urgent problem. The most promising way of solution of this problem consists of using thermochemical recuperation (TCR), i.e., natural gas reforming with combustion products, together with air heating at the expense of sensible heat of exhaust gases (such a scheme is called “*TCR system*”).

The aim of the present work is to develop an optimal TCR system for high-temperature industrial furnaces. The work consists of three parts:

- (1) thermodynamic analysis of different TCR systems in order to find the optimal conditions of their realization;
- (2) development of a concept of the design of a thermochemical reformer for TCR system and a method for computation of the parameters of its working process;
- (3) analysis of the mechanism and features of non-catalytic reforming.

1. Thermodynamic analysis of TCR systems was carried out with using the following assumptions:

- the initial fuel represents pure methane;
- at a given final temperature of the reacting mixture (methane + combustion products), the composition of reformed fuel is equilibrium;
- the excess-air coefficient in the furnace is $\alpha = 1.1$;
- in each apparatus of the TCR system, there are heat losses constituting 3 – 5 % of the heat transferred from combustion products to reacting mixture or air;
- the temperature of combustion products after the furnace is $2050^\circ\text{F} = 1394^\circ\text{K}$;
- the final temperature of reformed fuel and air has to be not higher than $1200^\circ\text{F} = 21.9^\circ\text{K}$.

In the first part of these investigations, we considered four variants of TCR system: (a) with upstream recuperative reformer; (b) with upstream air heater; (c) with two apparatus for air heating and reformer between them; (d) with two apparatus for air heating, placed in parallel by the flow of combustion products, and downstream reformer. In order to characterize the efficiency of TCR system, we used two parameters: CFU and the coefficient of heat transfer efficiency (CHTE), which is equal to a sum of the ratios of the quantity of heat transferred in a certain apparatus to the mean temperature difference in it over all apparatus of the system under consideration. These studies enabled us to establish that variant (c) gives the best results.

In the second part of these investigations, we studied the effect of excess-reagent coefficient in fuel reforming β on the parameters of TCR system (c). The range $0.7 \leq \beta \leq 1.0$ was considered (for lower β values, the quantity of heat stored in the nonreacting part of combustion

products can be insufficient for reforming). The results obtained show that, with decrease in β , the completeness of reforming becomes significantly lower, the quantity of heat transferred in the reformer decreases as well, but low β have also a substantial advantage: the CHTE is reduced appreciably, and, hence, the necessary area of hear transfer surface becomes lower. Since the CFU changes insignificantly with β , it is recommended to use lower β values.

2. The results of experiments, carried out at ECOTERM, show that, in the presence of a nickel catalyst, more than 80 % of methane react at 850 – 900 K during several fractions of a second (i.e., reforming is realized practically instantly). On the other hand, reforming is practically absent at ~ 900 K without catalysts if the residence time of reacting mixture in the reformer is not great. Hence, we decided to divide the process of reforming into two stages: heat supply to reacting mixture and chemical reaction itself. Further, we chose the design of recuperative reformer consisting of several sections, each of which includes two blocks: non-catalytic and catalytic. In the first block, heat is transferred from flue gases to reacting mixture, and, in the second, the heat stored in the mixture, is spent for realizing the chemical reaction. Finally, we chose the design of non-catalytic block as a shell-and-tube heat exchanger, which is convenient in manufacture and operation and provides a high intensity of heat transfer. The apparatus contains a staggered tube bank, where combustion products move inside the tubes 63/59 mm in diameter (for decreasing the pressure losses of this flow), and reacting mixture between the tubes. The general scheme of motion of the working media in the reformer is counterflow.

The aim of computation of the parameters of working process in the reformer is to find the intensity of heat transfer, the necessary area of hear transfer surface, and the length of non-catalytic block of each section. For each variant of computations, the temperatures and enthalpies of both working media before and after the reformer are known from thermodynamic analysis (item 1). Computations are carried out by sections, beginning from the cold end of apparatus: first the non-catalytic block and then catalytic. For each section, the temperatures of working media are known at its cold end from the results of computation of the previous section (or, for the first, from thermodynamic analysis). Since the temperatures of working media at the hot end of each section are unknown beforehand, we assign their values (satisfying the heat balance equation), calculate all parameters of heat transfer, and construct the corresponding iteration process. The catalytic block of each section is calculated with the help of code developed at ECOTERM earlier.

The computational methods mentioned above and the corresponding codes make it possible to find all parameters of the reformer, to study the dependence of characteristics of TCR system on determining parameters, and to optimize its operation. In particular, the results of computations confirm the conclusion (item 1) that the necessary area of hear transfer surface becomes lower with decrease in β .

3. Since experimental data show that a not great amount of hydrogen exerts an appreciable catalytic action on the reaction of natural gas reforming, we propose to carry out the process of non-catalytic reforming with $\beta < 1$. In this case, with heating of the reacting mixture to 700 – 800 K, a certain amount of methane will be subjected to pyrolysis with the formation of hydrogen. This idea was completely confirmed in our experiments at a metal-heating furnace for

$\beta = 0.75 - 0.85$: the application of non-catalytic reforming made it possible to shorten the consumption of natural gas by $\sim 30\%$. In addition, we propose a new procedure of lighting up of the TCR system for an industrial furnace: step-by-step increase in the flow rates of natural gas and reagent-combustion products.

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Thermochemical Recuperation for High Temperature Furnaces in the Steel Industry: Phase II - Design and Physical Testing of the Concept Validated in Phase I

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Executive Summary

GTI was subcontracted by the American Iron and Steel Institute to evaluate the technical and economic feasibility of utilizing a ThermoChemical Recuperation System (TCRS) to recover a significant amount of energy from the waste gases of natural gas fired steel reheat furnaces.

ThermoChemical Recuperation (TCR) is a technique that recovers sensible heat in the exhaust gas from an industrial process, furnace, engine, etc. when a hydrocarbon fuel is used for combustion. TCR enables waste heat recovery by both combustion air preheat and hydrocarbon fuel (natural gas, for example) reforming into a higher calorific fuel. The reforming process uses hot flue gas components (H_2O and CO_2) or steam to convert the fuel into a combustible mixture of hydrogen (H_2), carbon monoxide (CO), and some unreformed hydrocarbons (C_nH_m). Reforming of natural gas with recycled exhaust gas or steam can significantly reduce fuel consumption, CO_2 emissions and cost as well as increase process thermal efficiency. The technique has been preliminarily investigated for a number of applications (Nosach, 1995; Maruoka, Mizuochi, Purwanto, & Akiyama, 2004; Sikirica, Kurek, Kozlov, & Khinkis, 2007). The calorific content of the fuel can be increased by up to ~28% with the TCR process if the original source fuel is natural gas. In addition, the fuel is preheated during the TCR process adding sensible heat to the fuel.

Until recently, TCR has not been evaluated and developed for commercial adoption because the payback period was unattractive when gas prices were low. With future increases in natural gas prices, TCR is now a viable technology to reduce costs, increase energy efficiency and reduce the industry's CO_2 footprint.

The technical and economic feasibility of TCRS was examined in Phase I of the project. The technical target was to evaluate TCRS designs through modeling to achieve a cost-effective design that increases thermal efficiency and reduces fuel consumption and carbon emissions by at least 30%. Efficiency of the system was evaluated by employing modeling software based on reheat furnace information provided by steel company partners. Several TCRS configurations were evaluated. A three-unit TCRS was shown to be the optimal design and was chosen for further economic analysis. This optimal configuration represented a combination of two stage combustion air recuperator and fuel reformer resulting in a furnace thermal efficiency at least 65% or alternatively at least 26% reduction in fuel usage and carbon emissions when compared to the reference recuperated reheat furnace (800°F preheated air). A level of 31% fuel savings and carbon emissions reduction can be achieved at combustion air and fuel temperatures of approximately 1270°F at equilibrium fuel conversion.

The objective of Phase II was to experimentally evaluate the optimal TCRS prototype design. The goal of the experiment was to validate modeled predictions of the performance of the TCRS as applied to a high temperature furnace. A lab-scale TCRS was developed, fabricated, assembled, and tested at GTI's facility. A high temperature furnace with a water cooled load was chosen for the lab-scale TCRS testing. The rated capacity of the furnace was 0.5 MM Btu/hr. The lab-scale non-catalytic recuperative reformer (RR) was developed based on the Phase I results. Thermal Transfer Corporation (TTC) jointly with GTI designed the reformer. TTC fabricated and assembled the unit and shipped it to GTI. Bloom Engineering provided GTI with a high temperature low NO_x burner, recirculation fan and flue gas/natural gas ejector. Combustion air preheating was simulated by electrical heaters instead of a reduced scale two stage recuperator.

In Phase I, the predicted thermal efficiency and fuel savings of a typical reheat furnace were predicted 65% and 26% respectively at combustion air and fuel temperatures of 1200°F. The physical testing in Phase II validated thermal efficiency and fuel savings of 61% and 21% respectively which although lower than initially predicted are in conformance with the modeling results. It should be noted that in the course of testing several issues were discovered and are reported in more detail in the body of this report. First the above efficiency and fuel savings gains that were validated are associated with a sustained methane reforming rate of a flue gas/natural gas mixture which will be summarized at the end of this section under the heading of Technical Issues/Project Recommendations.

A specific internal flow arrangement in the recuperative reformer was designed based on Phase I results. The flue gas/natural gas mixture was preheated to a temperature of (1200 to 1300°F) in the reformer preheater; and reformed in the reformer reactor at approximately the same temperature. The preheater and reactor consisted of heat exchange tubes which were fully enveloped in the flue gas flow stream. The reactor contained return bends which served to provide an additional flow path for the reforming fuel so that the total volume of the reforming fuel flow in the reactor was substantially higher than the volume in the tubes. The returns were extended to provide the necessary residence time for reforming fuel.

The TCRS lab-scale tests confirmed designed parameters of the reformer preheater and reactor. The pressure drops were in the range of design values. The reforming fuel (flue gas/natural gas mixture) in the preheater was rapidly heated up to the temperature of ~1250°F, the desired temperature for the fuel reforming. The reactor provided sufficient thermal efficiency to transfer heat from the flue gas to the reforming fuel. The residence time in the reactor was high enough to provide partial reforming of the fuel.

During testing, hydrogen and carbon monoxide levels in the reformed fuel were used to preliminarily estimate performance of the recuperative reformer. Comparing measured values of hydrogen and carbon monoxide with theoretical predictions made it possible to determine how well the reformer was performing. Maximum yields of 27% of hydrogen and 11% of carbon monoxide were attained in the experiment. These values were close to theoretical (equilibrium) predictions. Approximately 58% of methane in the natural gas theoretically can be reformed at 1200°F while the measured results confirmed that only ~41% of methane was reformed in the non-catalytic recuperative reformer.

In the judgment of GTI, the technical and economic feasibility of employing a TCRS on a steel reheat furnace with recuperation remains feasible and was demonstrated by lab testing of the recuperative reformer.

With respect to the U.S. reheat furnace population TCR can be viewed as a Return on Investment (ROI) benefit continuum that ranges from a high level of payback of 15 months and \$38 million ROI to a nominal payback level of 33 months and \$6.4 million ROI expressed in current dollars (NPV) at a 7% discount rate over six years of cash flow.

The optimal configuration of two heat exchangers and reformer that has a surface heat exchange area minimized when the first stage air recuperator produces 800°F preheated air is considered to remain valid. The lab testing of the lab-scale TCRS resulting in projecting a furnace thermal efficiency of 61% or alternatively a 21% reduction in fuel usage and carbon emissions when compared to the reference recuperated reheat furnace (800°F preheated air). On an annualized basis the metric tons of CO₂ and NO_x produced by the three-unit TCRS reheat furnace would be an estimated 111,000 metric tons and 406 metric tons representing reductions of 30,000 metric tons per year of CO₂ (21% reduction) and 200 metric tons per year of NO_x (33% reduction).

Assuming that 80 steel reheat furnaces (approximately 50% of the potential US steel reheat furnace market) employ TCR, the cumulative imputed future fuel usage reductions for both Flat and Long product plants would be 9.6 trillion Btu. The cumulative CO₂ and NO_x emissions reduction would be 689,000 and 4,700 metric tons per year respectively.

Technical Issues/Project Recommendations

The reason for the earlier emphasis on a sustained methane reforming rate is that at the end of each test cycle (4 to 6 hours) a slight degradation of the methane reforming rate was observed. It typically required 3-4 hours to preheat and stabilize the TCRS system. Measurements were conducted at these conditions and the system was iteratively adjusted to different conditions in order to collect data for a series of test points. The duration of each test (point) was approximately one hour while measured parameters were stable. For each one hour period, variations in flows, temperatures, and gas compositions were marginal. It was also observed that

TCR for High Temperature Furnaces in the Steel Industry:
Phase II - Design and Physical Testing of the Concept

the methane reforming rate slightly degraded during the period of time from when the specific thermal conditions were attained to a point near the end of a typical test day.

After each daily test, the TCR system was shut down and cooled for renewed testing usually the next day. Upon restarting the system and when thermal stable conditions were again reached the methane reforming rate returned to the peak rate of the previous test but the same degradation of methane reforming rate would occur. Several reasons or mechanisms for this phenomenon were considered: (1) Amorphous carbon was being generated within the RR that in turn affected the methane reforming rate; and upon restarting from cold conditions, the carbon deposits were burned off the heat transfer surfaces thereby the RR was essentially “regenerated.” It was further conjectured that carbon would again be gradually redeposited as the next lab test progressed with the methane reforming rate declining again. A bore scope was employed to inspect the interior of the RR, through the flue gas/natural gas mixture port, to the extent capable. No carbon deposition was visually observed. When GTI partially disassembled the RR plenums to inspect the leaks, no carbon deposition was visually observed in those internal areas.

After additional analysis of the test data, it was surmised---and later confirmed---that leakage of the reforming fuel and/or the pre-reformed mixture were short circuiting into the flue gas flowing around and on the outside of the RR thereby “contaminating” the flue gas and the portion of the flue gas used for mixing with the natural gas for reforming.

The leaks were repaired by Thermal Transfer Corporation; and the recuperative reformer was reinstalled. Durability testing was undertaken for approximately 48 continuous hours to determine the asymptoticity of the methane reforming rate. Once the system reached thermal equilibrium, the same gradual reduction in methane reforming rate was observed. An additional phenomenon was observed in that periodically the per cent hydrogen and percent carbon monoxide in the reformed fuel would increase and then decrease over short time intervals (several minutes) without any changes in the process by the staff operating the lab set up. Once it was evident that the methane reforming rate was still decreased and was not asymptotic, several changes to the process variables were intentionally made to attempt to retard or reverse the reduction in methane reforming rate, but without success.

GTI’s preliminary conclusions are that the mechanism(s) producing the methane reforming rate decrease (are) not entirely known or understood. The nature of the chemical kinetics that are triggering the mechanism and/or other mechanisms are still necessary to be evaluated. Other possibilities include: stratification of the natural gas and flue gas downstream of the mixer within the preheater; and/or stratification of a portion of the flue gas/natural gas mixture and the complement of the flue gas/natural gas mixture for part of the residence time within the reformer-reactor.

These technical issues were reviewed with AISI and GTI was requested to prepare a countermeasure-plan to be included in the Phase II report.

Extended Phase II TCR Testing (proposed)

Since the results of the Durability Test confirmed that the reforming process is gradually retarded over time due to one or more of the above mechanisms, the TCR field experiment as outlined in Phase III is recommended to be postponed and a revised lab test of the TCR system should be carried out with a changed test matrix with a technical objective of identifying the mechanism(s) that are preventing a sustained methane reforming rate and provide a solution.

GTI proposes that the following is a reasonable alternative given that (1) Proof-of-concept has been verified and; (2) More importantly a well-designed and operational TCR system residing in the GTI combustion laboratory is capable of further testing to evaluate which and how the above mechanisms are retarding the methane reforming rate. Once fully understood, necessary alterations to the reformer design can be made and proceeding to Phase III can be considered.

Accordingly, the teams' consensus is to capitalize on the considerable amount of data acquired from modeling and physical testing by proposing a revised scope of work that will focus on identifying the mechanism(s) that are co-opting methane reforming efficiency for long-term operation of TCR as a viable waste heat recovery technique. Below is a brief summary of a preliminary work scope.

Task 1 - Forensic Analysis -- Conduct independent short-duration simulation modeling of the Lab Recuperative Reformer process over a range of operating conditions.

- 1) Develop equations describing chemical reaction kinetics within the Recuperative Reformer
- 2) Conduct Sensitivity Analyses of the process that includes the following independent variables: (Flue gas temperatures supplied; components of flue gas supplied; carbon to steam ratios; physical volume of the RR; and a range of specified space velocities consistent with a range of specified reforming mixtures.).

Task 2 - Conduct iterative testing of current Lab RR under both broader and new test conditions

- 1) Remove both ID fans and reconfigure piping for direct connection of flue gas to mixer.
- 2) Variables to be varied in re Test Matrix
 - a. Flue gas (FG) temperature entering RR---1700°F and 1800°F, capture all data;
 - i. FG:NG ratio for above two FG inlet temperatures above---set at ~10, ~5 and ≤ 2 , capture all data.
 - ii. Reform with steam in lieu of flue gas----use high/mid/low ratio points
 - b. Preheat natural gas with electric heater to achieve FG+NG or STM+NG temperatures into RR of 600°F; 700°F and 800°F

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Task 3 - Per test results, devise any necessary changes to the RR design to achieve a sustained methane reforming rate and implement recuperative reformer design changes.

- 1) Confer with TTC on implementation of changes
 - a. Return RR to TTC for changes
 - b. Return RR to GTI and reinstall

Task 4 - Conduct iterative testing of modified/retrofitted Lab RR under varying test conditions to confirm sustained methane reforming rate

Subject to approval to postpone the original Phase III work and to carry out a revised scope of work, a detailed Scope of Work will be prepared and a budget estimated.

Background

Concept-definition studies in Phase I work employed a GTI-licensed simulation software that has heat transfer and chemical reaction capability. Key metrics such as fuel flow rates, flue gas flow temperatures, energy intensity, walls losses, product throughput, and product temperatures were provided by ArcelorMittal and Republic Engineered Products.

The GTI approach was to conduct modeling studies by initially examining two general configurations for the reference steel reheat furnace: 1) With an air recuperator; 2) With a TCRS. The numerical analysis was based on utilizing FurnXpert and AspenOne software and GTI-developed models.

Project Duration and Phases

The duration of this project as proposed was thirty months and involved three phases:

Phase I: (13 Months) September 30, 2008 to October 30, 2009 Developing a feasibility study consisting of a benefits-derived economic evaluation of a ThermoChemical Recuperation (TCR) concept with respect to high temperature reheat furnace applications. This established the design parameters and potential performance of the TCR.

Phase II: (27 Months) October 30, 2009 to January 31, 2012 Conducting research and development to take the validated technology concept from Phase I to a developmental state for a stage 3, prototype field test.

Phase III: (15 Months) TBD Designing, fabricating, and prototype field testing the TCR unit close-coupled to an existing high temperature reheat furnace at a steel company for evaluation under industrial conditions.

Improved Energy Efficiency and reduced Carbon Emissions for Steel Reheat Furnaces

For most industrial heating processes including furnaces the energy efficiency is defined as the ratio of useful output to gross heat input in percent. The total heat input is provided in the form of fuel chemical energy. The useful output is the heat supplied for heating a material. Other heat outputs in the furnaces are undesirable heat losses. The major heat or energy losses that occur in the fuel fired furnace are listed below:

- Heat lost through exhaust gases as sensible heat
- Heat loss through furnace walls and doors
- Heat loss through water cooled surfaces

A typical energy balance can be demonstrated by the Sankey diagram in Figure 1 that shows the energy balance for a recuperated reheat furnace. It is clear that exhaust gas losses are a key area for priority attention. Since the furnace operates at high temperature, the exhaust gases leave at high temperatures (1700°F to 2100°F) resulting in poor efficiency. Hence a heat recovery device such as an air recuperator has to be necessarily part of the system. Depending on the furnace exhaust flue gas and air preheat temperatures the furnace energy (thermal) efficiency can vary but ordinarily does not exceed 50%.

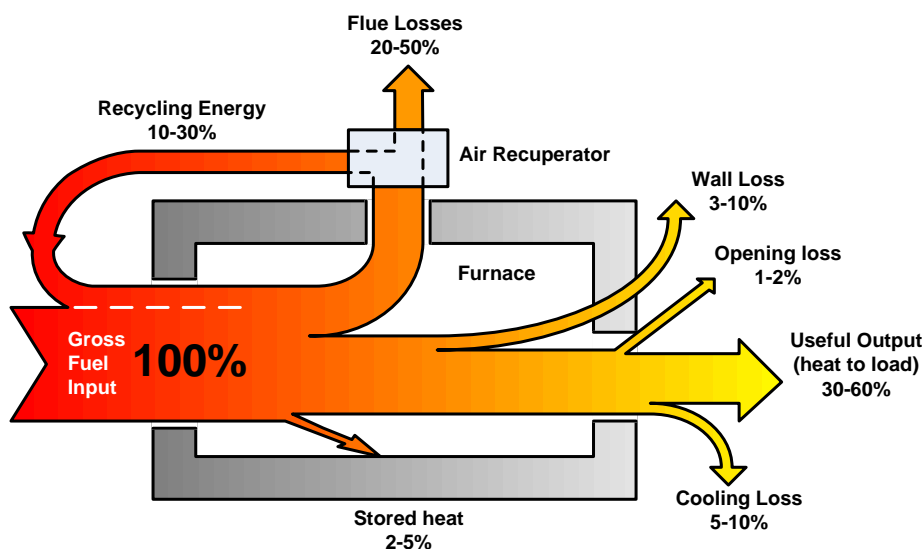


Figure 1. Energy Balance for a Recuperated Reheat Furnace

Major constituents of the furnace flue gas by volume are nitrogen (~72%), water vapor (~17.5%), carbon dioxide (~9%), and oxygen (~1.5%) when natural gas is used as the fuel and air as the oxidizer. On average, each furnace produces ~2.75 pounds of carbon dioxide (carbon emissions) per 1.0 pound of combusted natural gas. Fuel savings lead to a proportionate reduction of carbon emissions.

Energy Conservation and Emissions Reduction by Waste Heat Recovery from Exhaust Gases

Extracting heat from the furnace flue gases and returning it back to the process is the major technique to improve the furnace thermal efficiency and reduce carbon emissions. There are several methods that are generally used in the steel industry for waste heat recovery, that include: preheating cold loads with flue gases (unfired furnace zone); steam generation using waste heat boilers; preheating combustion air by recuperators or regenerators; and oxy-fuel firing.

Preheating cold loads with flue gases can be accomplished in an unfired zone(s) at the charge end of steel reheat furnaces. In this case energy will be transferred by preheating the load. This reduces the energy that is ultimately lost to the exhaust.

In practice, the unfired charging zones of most continuous furnaces serve as preheating zones. Load preheating systems can be difficult to retrofit due to space constraints and are best suited for continuous rather than semi-continuous furnaces.

The use of waste heat boilers to recover a portion of the exhaust gas heat is an option for plants that need a source of steam or hot water. The waste heat boiler is similar to conventional boilers with one exception: it is primarily supplied heat by the exhaust gas stream from a process furnace with supplementary firing as necessary. The prime requirement is that the waste gases must contain sufficient usable heat to produce steam or hot water at the condition required. Waste heat boilers may be designed for either radiant or convective heat sources.

Air recuperators are heat exchangers that use the energy in hot flue gases to preheat combustion air. Recuperators are the most widely used heat recovery systems in the steel industry. A recuperator is a gas-to-gas heat exchanger installed between the furnace flue gas exit and the furnace stack. The exhaust gases and air are in adjacent passageways separated by a heat conducting wall. Heat flows steadily through the wall from the hot exhaust gas to the combustion air. Recuperators are available in as many configurations as there are heat exchangers. Common forms are double pipe (pipe in a pipe), shell and tube, and plate types. All may use counter flow, parallel (co-current) flow, and/or cross flow.

Increasing air preheat temperature from 800°F to 1200°F for example, reduces the fuel consumption and therefore carbon dioxide emissions by ~13% at a waste gas temperature of 2000°F. It should be noted that increasing combustion air temperature increases NOX emissions, typically from 20 to 100 ppmv for a 100°F temperature rise.

Recuperators are typically designed with very low pressure drops (0.5 to 1 in. W.C.) on the exhaust gas side. They usually are designed for a greater drop on the air side. Forced draft fans are preferred because of the higher cost of handling hot air or gases with induced draft (ID) fans or blowers for hot gas or hot air. In addition, forced draft fans promote maintaining the interior of the steel reheat furnace under a slightly positive pressure, minimizing ambient air infiltration.

Another alternative to preheat combustion air is with a regenerator, which is an insulated chamber usually filled with metal or ceramic shapes that can absorb and store significant thermal energy. It acts as a rechargeable thermal storage battery for heat and works in an alternating mode. In the first mode, hot flue gas is passed through the chamber thus heating media or refractory in the chamber. In the second mode cold combustion air is passed through the

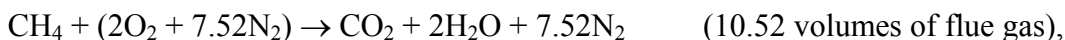
regenerator chamber thus extracting heat from the media or refractory. At least two regenerators and their associated burners are required for an uninterrupted process: one provides energy to the combustion air while the other recharges. The cycling time can be up to 40 seconds depending upon site conditions and the process. Regenerative burners require the use of a control system to sequentially switch the burners from a regenerative mode to a heat extraction mode. A program of periodic maintenance and measures to minimize the accumulation of media-contamination is required to ensure proper operation of all valve control mechanisms in the burners.

The fuel utilization of modern regenerators can be as high as 75% to 85%, with air preheat temperatures within 300°F to 500°F of the products of combustion in the furnace. Regarding firing systems for industrial furnaces including steel reheat furnaces, fuel utilization efficiency E_f is defined as:

$$E_f = 100\% \times (\text{Gross Fuel Input} - \text{Exhaust Gas Losses} - \text{Other Losses}) / \text{Gross Fuel Input}$$

For a system without air preheat ($\epsilon = 0$), it becomes obvious that the efficiency diminishes with rising exhaust gas temperatures. At 2000°F exhaust gas temperature, at least 55% of the fuel input will be lost as hot exhaust gas heat. Corresponding heat losses are less than 20% for regenerative burners with a relative air preheat $\epsilon = 0.8$ and ~35% for conventional combustion air recuperators with relative air preheat $\epsilon = 0.4$. Fuel savings compared to air recuperation are in the range of 10 to 20% and savings of 50% and more, compared to cold air systems, can be achieved with regenerative burners. Low NOX combustion can be achieved by air staging or in combination with external flue gas recirculation.

Although oxy-fuel firing is not considered a method of heat recovery in the strictest sense, energy is saved by reducing the mass of hot waste gases that is lost through the flue. “Oxy-fuel firing” is the substitution oxygen for air in a combustion system. For one volume of methane (the principal constituent of natural gas), the combustion reaction with air is,



is replaced with the reaction for oxy-fuel firing,



Reducing exhaust gases results in substantial fuel savings. In the case of enriching combustion air with oxygen, the specific amount of energy savings depends on the percentage of oxygen in combustion air and the flue gas temperature. Higher values of oxygen and flue gas temperature

offer higher fuel savings. The net economic benefits will primarily be determined by the cost of oxygen compared to the fuel cost reduction savings.

In evaluating oxy-fuel firing, consideration needs to be given to the mass flow reduction of products of combustion, much higher flame temperatures, and extremely higher gas radiation heat transfer in short, longitudinal paths. Processes that depend on high mass flow to provide uniform product temperatures will be derated from the use of oxy-fuel firing because of its lower mass flow and lower volume for circulation. One solution that could negate these effects would be a combination of oxy-fuel firing with a TCRS which uses a portion of flue gas or flue gas steam condensate for fuel reforming and recirculates the gas through the furnace. In this case the thermal efficiency of the furnace can be substantially increased compared to conventional oxy-fuel firing and the flame temperature will decrease to a beneficial level.

The process of recuperating the energy contained in exhaust gases from high temperature process furnaces, engines, etc., for hydrocarbon fuel reforming is called thermochemical recuperation (TCR). A TCR system (TCRS) can also include oxidant (air or oxygen) preheat thus integrating a combustion air recuperator (AR) and recuperative reformer (RR) into the system. When successfully developed and commercialized, TCRS will provide increases in furnace thermal efficiency from 15 to 35% and reduce hydrocarbon fuel consumption by 15 to 60% compared with conventional recuperation where only combustion air is preheated. TCRS will also significantly reduce air emissions by 30% to 80%. The major advantage for TCRS is the opportunity to cost effectively improve process efficiency beyond what is achievable with conventional air recuperation. TCR has been extensively studied in Ukraine (Nosach, 1995), Japan (Maruoka, Mizuochi, Purwanto, & Akiyama, 2004), the U.S. (Sikirica, Kurek, Kozlov, & Khinkis, 2007), and Russia. For heating processes, efficiency increases of 20% to 50% have been noted, and for processes using thermal cycles (e.g., internal combustion engines, gas turbines) efficiency increases of 8% to 15% have been noted.

Figure 2 depicts a general example of TCRS with natural gas/flue gas reforming to illustrate the concept. AR is the air recuperator and RR is the recuperative reformer. At 1200°F air preheat and reformed fuel temperatures, more than 70% of the total heat in the exhaust is recovered when furnace exhaust gas temperature is 2000°F.

The technique of recuperative reforming recovers sensible heat in the exhaust gas, and uses that heat to transform the hydrocarbon fuel source into a partially reformed fuel having a higher calorific heat content. The reforming process uses the waste heat plus steam (water vapor) and/or carbon dioxide (CO₂) to convert the fuel into a combustible mixture of hydrogen, hydrocarbons,

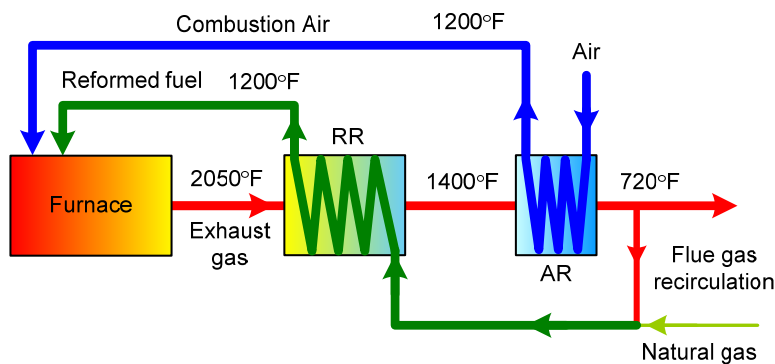
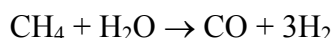


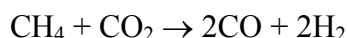
Figure 2. TCRS as Applied to a High-Temperature Steel Reheat Furnace with Natural Gas/Flue Gas Reforming (65% thermal efficiency)

and carbon monoxide (CO). The calorific content of the fuel can be increased by up to ~28% with the TCR process if the original source fuel is natural gas. In the TCR process, steam, CO₂, or both can be reacted with fuel, as shown below (each case is simplified to one reaction).

Fuel reforming with steam:



Fuel reforming with carbon dioxide:



Fuel reforming with flue gas of air/fuel firing:

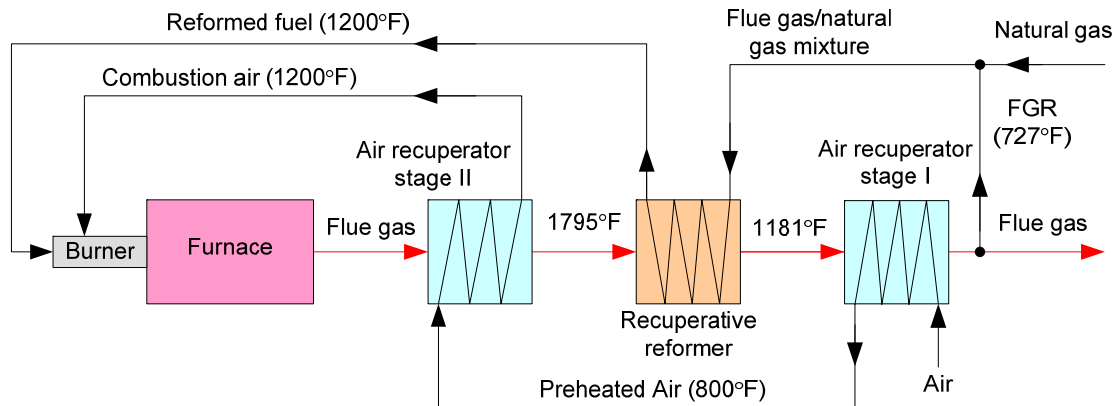


When reformed fuel is combusted in the furnace, fuel economy is improved, system efficiency is increased, and emissions are reduced. In addition, the fuel is preheated during the reforming process, adding sensible heat to the fuel. Because both water vapor and CO₂ can be used in the reforming process, it is advantageous for natural gas-fired systems because both of these gases are major products of combustion and, therefore, are readily available in a preheated state. Further, they can be used in the same ratio as they exist in the combustion products.

TCRS was not evaluated and developed for commercial adoption because the payback period was unattractive when gas prices were low. Strong interest in TCR has been expressed to GTI by the steel industry, the glass industry, and the aluminum industry during the last several years. GTI has evaluated the TCR approach for direct fired heating applications from a bench-scale test

funded by GTI. A feasibility study of TCR for indirect fired heating applications, also funded by GTI, was carried out.

Summary of the TCRS Concept Validated in Phase I



The Energy intensity of this scheme was estimated to be 1.19 MMBtu per ton with 1200°F preheated combustion air and 1200°F reformed fuel temperature resulting in a furnace thermal efficiency of 65% or alternatively a 26% reduction in fuel usage and carbon emissions when compared to the reference recuperated reheat furnace (800°F preheated combustion air).

Phase II – Recuperative Reformer Design and Testing of the TCRS Concept Validated in Phase I

Selection of GTI Lab-scale Furnace for TCRS Testing

Several furnaces in the GTI combustion laboratory were candidates for lab-scale TCRS testing. The following parameters and features of the lab-scale furnace and TCRS were considered (based on Phase I results) to select the furnace:

- Flue gas temperature exiting the furnace capability to 2050°F
- Combustion air temperature capability to 1200°F
- Reformed fuel temperature capability to 1200°F
- Variable water cooled load
- Existing natural gas and combustion air piping train
- Variable speed drive combustion air fan
- Flue Gas Recirculation

A high temperature furnace (Figure 4) with a water cooled load was chosen for the lab-scale TCRS testing. This furnace has the capability of controlling flue gas temperature by adjusting the water cooled load (probes) inserted into the furnace from the furnace roof. The furnace also has an electrical air heater that was used to simulate combustion air recuperation with air preheat up to 800°F. The rated capacity of the furnace is 0.5 MM Btu/hr and the flue gas temperature at the furnace exhaust can be as high as 2400°F.

For cost-containment purposes combustion air preheating was simulated by electrical heaters instead in place of a scaled down two stage recuperators. It was concluded that preheating combustion air with electrical heaters would not affect the results of the TCRS study and additionally would increase flexibility of the lab-scale TCRS experimental setup.

An additional combustion air heater was installed to provide preheated combustion air from 800°F to 1200°F is shown in Figure 5.



Figure 4. GTI High-Temperature Furnace with Water Cooled Load



Figure 5. Second Stage Combustion Air Heater

Lab-Scale TCRS

The lab-scale TCRS was evaluated based on predetermined furnace operating parameters. Figure 6 illustrates the TCRS flow diagram with ranges of the predetermined parameters. The flue gas temperature exiting the furnace was selected to correspond to the temperature ($\sim 1795^{\circ}\text{F}$) of the flue gas at the exit of a stage II air recuperator. This temperature was controlled by adjusting the water cooled load in the furnace. Flue gas recirculation (FGR) temperature was selected to correspond to the temperature ($\sim 727^{\circ}\text{F}$) of the flue gas at the exit of the stage I air recuperator. A water cooled heat exchanger was installed in the flue gas recirculation line to maintain the desired FGR temperature.

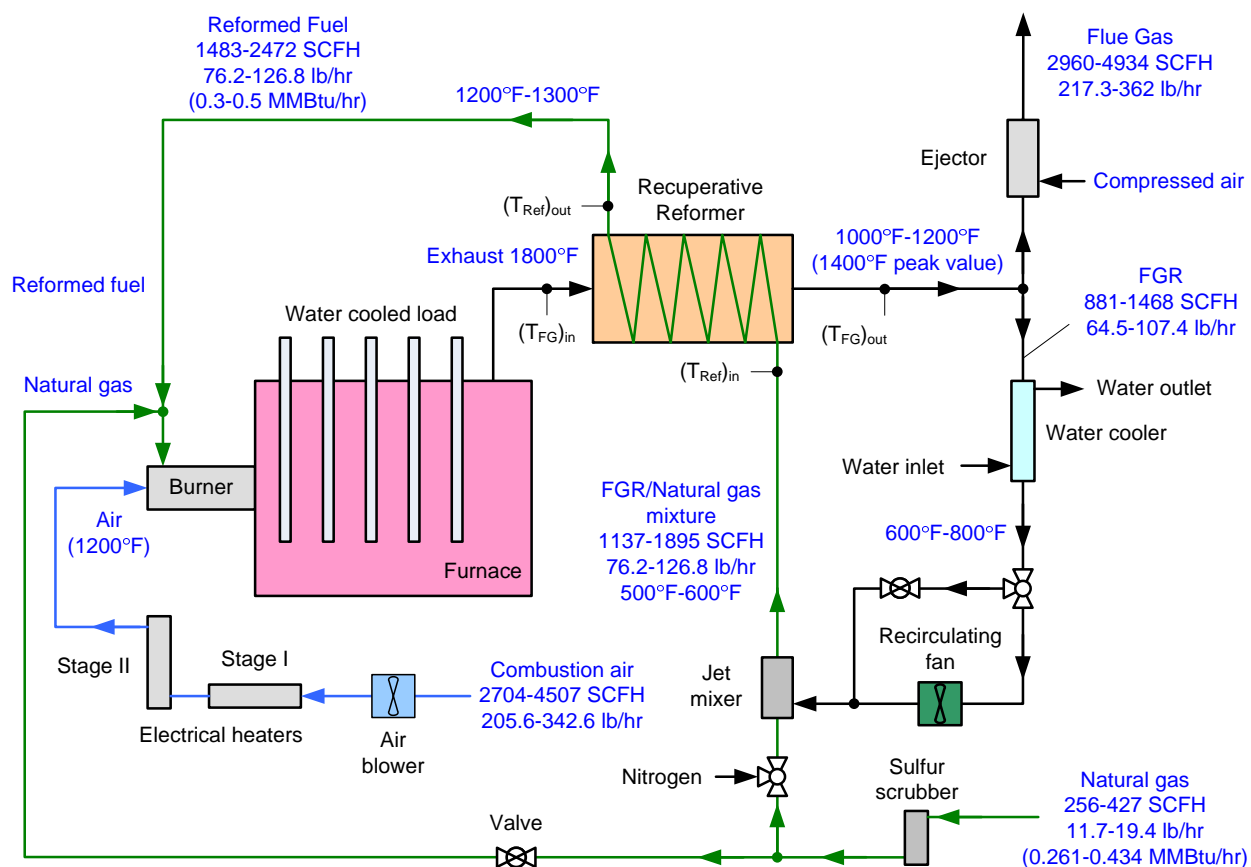


Figure 6. Lab-scale TCRS Flow Diagram

There are several other key components in the lab-scale TCRS experimental setup: a flue gas ejector or venturi nozzle was installed within the stack entrance. The purpose of this ejector was to control the pressure within the test furnace by varying flue gas flow to the stack. Controlling furnace pressure (usually slightly negative or zero) in the furnace was necessary to minimize drawing in ambient air into the flue gas from finding its way into the flue gas that mixes with the natural gas.

Another component of the lab-scale TCRS experimental setup was a sulfur scrubber which was installed at the natural gas supply line. The function of the sulfur scrubber was to desulfurize natural gas which contains naturally occurring H₂S and mercaptan sulfur. Although the sulfur scrubber not needed for non-catalytic reforming this feature was included in the test set up to virtually eliminate any unforeseen issues connected with possible affects of sulfur contamination.

Hot Air and Reformed Fuel, Ultra Low NO_x Burner

A high temperature (1200°F combustion air and 1200°F reformed fuel) burner was required to be used in the TCRS. This burner needed to be capable of handling a high fuel flow rate as the fuel is a partially reformed mixture of natural gas and flue gas. Bloom Engineering was provided the furnace test parameters that included the specific firing rate, temperature and flows (air and fuel), and pressures. Bloom Engineering Company supplied the hot air ultra low NO_x burner (See Figure 7), including a gas mixer for mixing flue gas and natural gas (which provided a boost to the mixture pressure) and other ancillary control equipment.



Figure 7. Hot Air Ultra Low NO_x Burner by Bloom Engineering Co.

The burner was supplied with a lab and UV flame detector. The lab was installed into the coupling located on top of the burner body. The UV detector was installed through the coupling that is located near the horizontal centerline of the burner body. The UV detector port was modified for use as a natural gas supply port for burner start up and furnace heat up operation.

Flue Gas Recirculation Fans

The flue gas and natural gas mixer pressure was boosted by the FGR fans allowing flue gas to be recirculated; the FGR fans were installed in series to provide a wide range of FGR flows over the test operating range. The fans were specified to operate at a moderately high temperature (up to 600°F) and provide flue gas pressure (up to 24" W.C.) to overcome pressure drops across the reformer, piping and burner. Additional sealing to the extent possible between the shafts and the housing was necessary to eliminate flue gas leakage out or ambient air infiltration into the flowing flue gas. It was determined that two fans in series would allow the attainment of performance at a least cost. The two FGR fans were assembled on a frame and supplied by The Canada Blower Company (Figure 8).



Figure 8. Flue Gas Recirculation Fans in Series

Variable speed drives were used to control the blower speeds thereby adjusting FGR flows. This level of FGR flow control was considered critical for purposes of adjusting the FGR/natural gas ratio.

Development and Design of the Non-Catalytic Recuperative Reformer

GTI proposed a non-catalytic recuperative reformer for TCRS (patent pending). Operation of the reformer without catalyst essentially reduces the reformer cost and maintenance.

A different approach needed be taken to design the recuperative reformer when compared, for example, with typical methane reformers that are widely used for hydrogen production. The following conditions required to be taken into consideration for developing and designing the recuperative reformer. First, the recuperative reformer is a heat exchanger apparatus which has hot flue gas flowing over one side of a heat exchange surface and colder flow of flue gas/natural gas mixture (reforming fuel) flowing over the opposite side of the surface. The heat exchanger design needed to provide conditions for fast preheating of the relatively cold flue gas/natural gas mixture up to the temperature approximately equal to the desired temperature of the reformed fuel (1200-1300°F in our case) and reforming at this temperature while preventing temperatures higher than 1200-1300°F of reforming fuel in the reformer.

Structurally the recuperative reformer needed to contain a preheater where the reforming fuel is primarily preheated with little or no reforming followed by a non-catalytic reactor where the reforming fuel is being reformed at an approximately constant temperature. It should be obvious that the reforming reaction rates in a non-catalytic reactor are much lower compared to the rates in a catalytic reactor. As a result of the reduced reaction rates, the residence time of the reforming mixture in the reactor was much higher compared to the residence time in a catalytic reformer consequently it is reasonable to expect that the non-catalytic reactor would be larger compared to the catalytic reactor. On the other hand, the heat exchange surface area in a non-catalytic reactor should be limited to the area just sufficient enough to provide enough heat to support the endothermic reforming reaction. This means that a non-catalytic reactor should contain certain heat exchange surface area and volume to provide residence time for reforming fuel. The residence time then, dictates how large this space should be.

GTI conducted a bench scale laboratory test to evaluate the residence time necessary to accomplish this requirement. An existing small-scale recuperative reformer was utilized for this purpose. The laboratory test was conducted using a GTI natural gas-fired modified heat treat furnace. Based on the obtained results it was concluded that the residence time in the recuperative reformer to be designed and built for the Phase II tests required to be at least seven seconds or higher depending on the reformer surface area which is in contact with reforming fuel. This additionally acquired knowledge about the residence time for non-catalytic reforming allowed reducing the number of experiments in the lab laboratory test by eliminating conditions (levels) with too low or too high values of residence time. A more detailed description of this experiment and test results are presented in Appendix A of the report.

Based on the above described approach of the recuperative reformer design the following internal flow arrangement in the reformer was proposed (Figure 9). The FGR/natural gas mixture is preheated to a reforming temperature of (1200 to 1300°F) in the reformer preheater and then reformed in the reformer reactor at approximately the same temperature (1200 to 1300°F). The

preheater and reactor consist of tubes or plates which are completely enveloped in the flue gas flow stream. The reactor return bends (Figure 9) needed to be placed outside of the central flue gas duct within two plenums as shown. These return bends serve to provide an additional flow path for the reforming fuel so that the total volume of the reforming fuel flow in the reactor is substantially higher than the volume in the tubes or plates. For this particular design of the lab-scale reformer the total volume of the return bends was set to 5.205 ft³ by calculations.

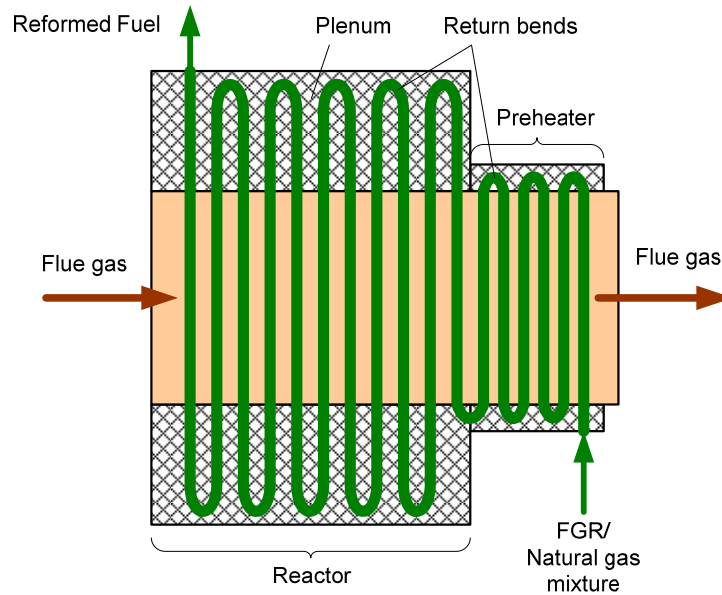


Figure 9. Flow Paths in Recuperative Reformer

Another key factor in the resultant recuperative reformer design is the effect of chemical reactions on the heat transfer in the reformer. In this connection, there was a consideration as to how to calculate the heat exchange surface area of tubes or plates in the reactor. As a first approximation, the effect of the reforming reactions was taken into account by using a pseudo specific heat of the reformed fuel at the reactor outlet. This pseudo specific heat $(c_p)_{\text{pseudo}}$ can be found from the following equations:

$$(c_p)_{\text{pseudo}} = (Q_t - m \times c_{p1} \times t_1) / (m \times t_2), \quad (1)$$

$$Q_t = Q_c + Q_r, \text{ Btu/hr} \quad (2)$$

$$Q_c = m \times (c_{p2} \times t_2 - c_{p1} \times t_1), \quad (3)$$

$$Q_r = m \times (\text{HHV}_2 - \text{HHV}_1), \quad (4)$$

Here

c_{p1} – specific heat of the reforming fuel at the reactor inlet, Btu/(lb×°F)

c_{p2} – specific heat of the reforming fuel at the reactor outlet, Btu/(lb×°F)

HHV_1 – higher heating value of the reforming fuel at the reactor inlet, Btu/lb
 HHV_2 – higher heating value of the reforming fuel at the reactor outlet, Btu/lb
 m – reforming fuel mass flow rate, lb/hr
 Q_c – convective heat flow in the reactor, Btu/hr
 Q_r – heat flow due to the reforming fuel heating value change in the reactor, Btu/hr
 t_1 – temperature of the reforming fuel at the reactor inlet, °F
 t_2 – temperature of the reforming fuel at the reactor outlet, °F

To intensify heat transfer and reforming reaction rates in the reformer it was determined that to use inserts with extended surfaces in heat exchange tubes (or between plates) and return bends of the reactor would serve this purpose.

This conceptual design of the recuperative reformer was shared with Thermal Transfer Corporation (TTC) which agreed to co-develop the lab-scale recuperative reformer design, fabricate and assemble it. GTI also provided TTC with the initial parameters of the process:

Flue gas temperature at the reformer inlet: 1800°F
 Flue gas flow rate including FGR: 3,841...6,402 SCFH (281.8...469.4 lb/hr)
 Natural gas flow rate: 256...427 SCFH (11.7...19.4 lb/hr)
 Combustion air flow rate: 2,704...4,507 SCFH (205.6...342.6 lb/hr)
 FGR flow rate: 881...1,468 SCFH (64.5...107.4 lb/hr)
 FGR/natural gas mixture temperature at the reformer inlet: up to 600°F
 FGR/natural gas mixture flow rate at the reformer inlet: 1,137...1,895 SCFH (76.2...126.8 lb/hr)
 Reformed fuel temperature at the reformer outlet: 1200...1300°F
 Flue gas/FGR composition (% volume): $N_2=72.1\%$, $H_2O=17.3\%$, $CO_2=8.9\%$, $O_2=1.7\%$
 Composition of the flue gas/Natural gas mixture in the preheater and at the reactor inlet (% volume): $N_2=55.843\%$, $CH_4=21.755\%$, $H_2O=13.326\%$, $CO_2=7.092\%$, $H_2=0.023\%$, $O_2=1.343\%$, $C_2H_6=0.526\%$, $C_3H_8=0.069\%$, $C_4H_{10}=0.023\%$
 Composition of reformed fuel at the reactor outlet (% volume): $N_2=42.94\%$, $CH_4=5.697\%$, $H_2O=2.877\%$, $CO=14.704\%$, $CO_2=2.819\%$, $H_2=30.963\%$

Upon finalizing the design, fabrication drawings were prepared by TTC. A general view of the recuperative reformer design is shown in Figure 10. As previously discussed, there are two sections in the recuperative reformer unit: a preheater and a reactor. The preheater is a tubular heat exchanger which consists of three parallel rows of tubes in the transversal direction and twelve rows of tubes in the longitudinal direction. The reactor is a tubular heat exchanger which consists of three parallel rows of tubes in the transversal direction and fifteen rows of tubes in the longitudinal direction.

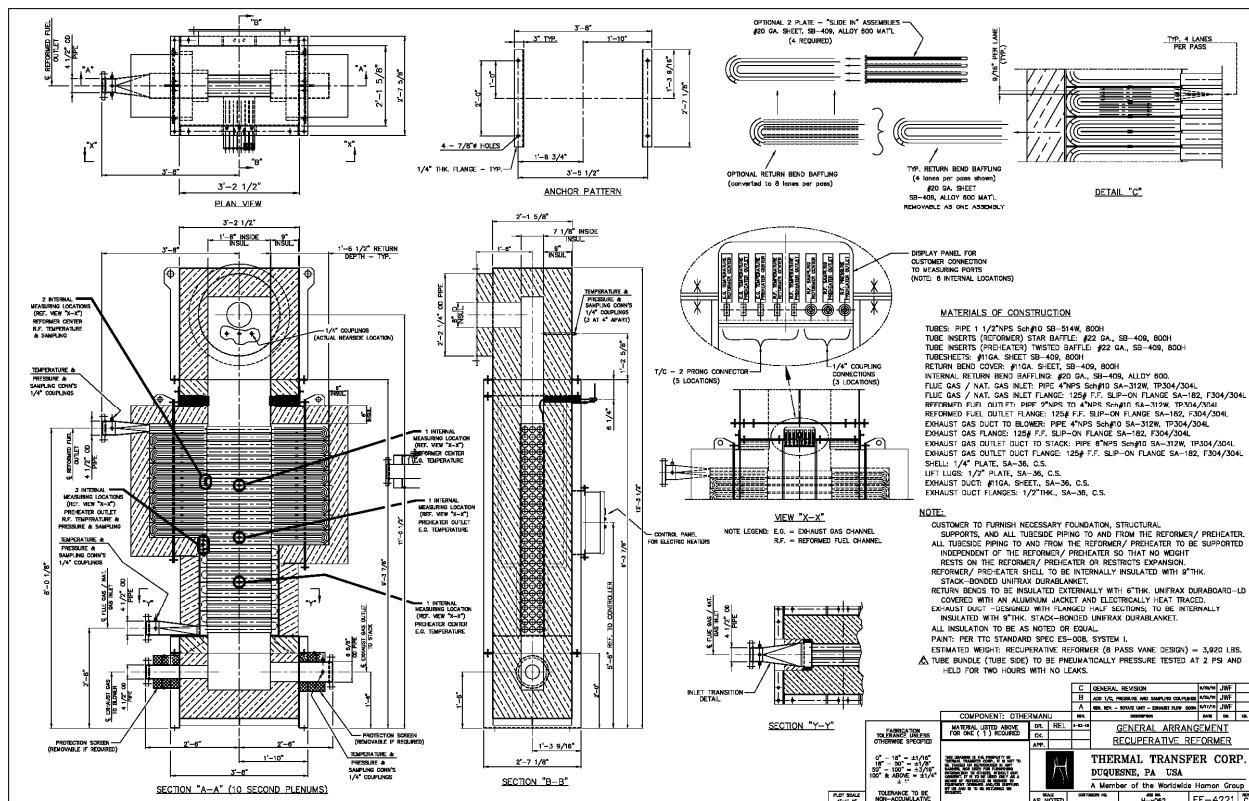


Figure 10. General View of the Recuperative Reformer Design

The reactor returns are extended to provide the necessary residence time for reforming fuel. Return bend baffling provides a uniform flow of the reforming mixture and extends surface area which is in contact with the reforming fuel. There are two options of the return bend baffling in the reactor: four and eight vanes per pass. The baffling was designed as capable of being removed to test without extended surfaces.

It was also decided to install heat tracing on the reformer plenums walls. This would allow for faster preheating the reformer at start up and better control of heat losses. A field scale reformer for steel rehear furnaces would not be equipped with heat tracing.

Recuperative Reformer Fabrication and Assembling At TTC Located in Duquesne, PA

Figure 11 shows several components of the recuperative reformer during fabrication and assembling. The return bends (c) are removable/replaceable so that total volume of the return bends as well as residence time of the reforming fuel in the reactor can be varied. The inserts (d) were designed by TTC to provide higher heat transfer and fuel reforming rates in the tubes.



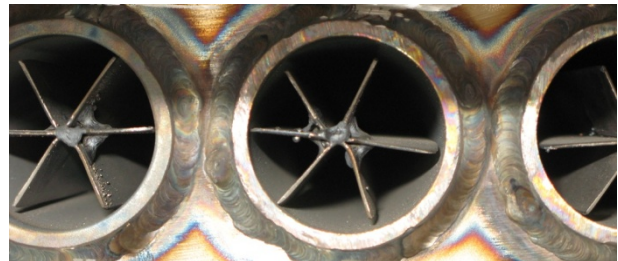
a) Reformer Tube Bank



b) Reformer Tube Bank with Plenums



c) Return Bends



d) Inserts



e) Insulated Reformer Shell



f) Exhaust Connection from Furnace to Reformer

Figure 11. Key Elements of the Recuperative Reformer During Fabrication and Assembly

The recuperative reformer was partially assembled at TTC, leak checked, and then shipped to GTI. After the reformer was assembled the tube bundle (tube side) was pneumatically pressure tested at 2 PSIG and hold for two hours with no leaks.

Figure 12 shows general arrangement of the recuperative reformer in the GTI combustion laboratory. TTC was provided with this drawing and all dimensions required for the reformer design and fabrication.



Shake-down test showed that there was a leak of ambient air to the flue gas flow in the reformer causing increased oxygen content in the flue gas recirculation flow. This leak of ambient air to the flue gas flow would be acceptable in an air recuperator but it is critical for the recuperative reformer. TTC was informed about the leak, and they advised a solution. To minimize the leak, all gaps in the reformer shell were sealed from outside using high temperature sealer.





Figure 13. TCRS Setup in GTI Laboratory

Test Plan, Data Acquisition System, and Data Processing

A. Description of the Process to be Tested

The goal of the laboratory evaluation was to validate modeled predictions of the performance of a TCRS as applied to a high temperature furnace. Testing was conducted for conditions simulating the steel reheat furnace evaluated in phase I of the project. In Phase I the reference steel reheat furnace equipped with a TCRS contained three units: an Air Recuperator Stage II (ARII), a Recuperative Reformer (RR) and an Air Recuperator Stage I (ARI) in series (Figure 14). The three-unit TCRS design was devolved to as the optimal design for further evaluation by physical testing in Phase II. The configuration represents a combination of heat exchangers and reformer that has a surface heat exchange area that is minimized when the first stage air recuperator produces 800°F preheated air. The energy intensity of this scheme was estimated to be 1.19 MMBtu per ton with 1200°F preheated air and 1200°F reformed fuel temperature resulting in a furnace thermal efficiency of 65% or alternatively a 26% reduction in fuel usage and carbon emissions when compared to a recuperated reheat furnace (800°F preheated air).

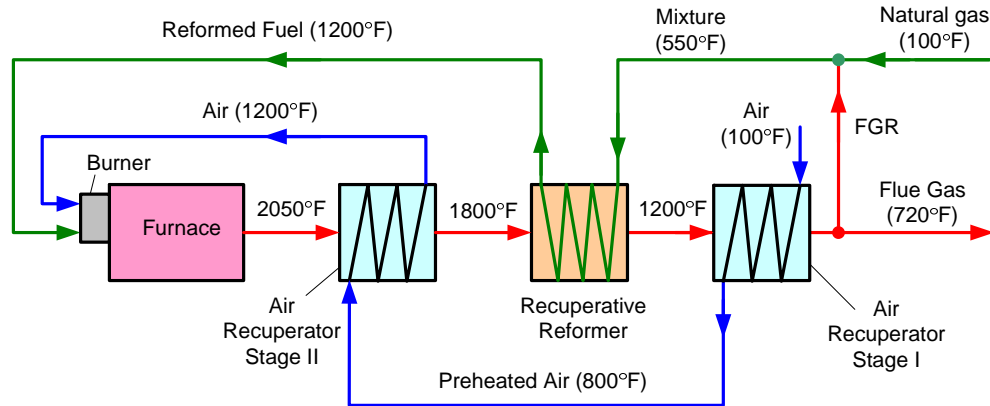


Figure 14. Flow Diagram of the Reference Steel Reheat Furnace with TCRS

For the laboratory test, the TCRS was simplified by eliminating both stages of the combustion air recuperator from the study. In this case, combustion air was heated using an electrical heater (Figure 5), avoiding the expense connected with lab-scale air recuperators design and fabrication. A furnace water cooled load was used to control flue gas temperature entering the recuperative reformer and a water cooled heat exchanger was installed in the flue gas recirculation (FGR) line to maintain the desired FGR/natural gas mixture temperature before the recuperative reformer.

The TCRS experimental rig was used to test recuperative reforming using a fraction of the high temperature furnace flue gas mixed with natural gas. Test results were used to estimate system efficiency and confirm the practicality of this approach for expected operating conditions. The reformed fuel produced in the experimental rig was combusted in the furnace. Flue gas flow rate, composition and temperature were controlled in order to provide comparable conditions specified in Phase I of the project.

Preliminary estimated values of the simulated furnace flue gas conditions and FGR/natural gas mixture were as follows:

Flue gas composition (% volume): $\text{CO}_2 = 8.9\%$; $\text{H}_2\text{O} = 17.3\%$; $\text{N}_2 = 72.1\%$; $\text{O}_2 = 1.7\%$

Temperature of the furnace flue gas before the reformer: $(T_{\text{FG}})_{\text{in}} = 1800^\circ\text{F}$

Temperature of the FGR/natural gas mixture entering the reformer: $(T_{\text{Ref}})_{\text{in}} = 500^\circ\text{F} - 600^\circ\text{F}$

Flue gas and natural gas flow rates for reforming were in the range that would allow having sufficient residence time for chemical equilibrium reforming. A maximum natural gas flow rate of up to approximately 19.4 lb/hr with the flue gas flow rate for reforming expected to be up to 107.4 lb/hr. The maximum amount of FGR was estimated as $V_{\text{FGR}} / (V_{\text{Natural gas}} + V_{\text{air}}) * 100\%$ and

projected to be about 50%. Here, V_{FGR} , $V_{\text{Natural gas}}$ and V_{air} are flue gas recirculation, natural gas and combustion air respectively in STP volume flow rates.

B. Rationale for the Tests

GTI has previously carried out HYSYS model simulations using thermochemical recuperation to recover waste heat from a high temperature furnace and thereby increasing the furnace thermal efficiency. Commercial steam catalytic reforming of natural gas for hydrogen production is done at high temperatures (1500 - 2000°F). Experimental data on the performance of non-catalytic flue gas reforming at lower temperatures (~1200°F) representative of high temperature furnaces was needed. With the experimental data from Phase II work, GTI expected to have a high degree of confidence in predictions of improvements in system efficiency using recuperative flue gas reforming. Testing would also provide data to quantify the conversion efficiency as a function of reforming temperature and fraction(s) of FGR.

C. Performance Targets

The key indicator of the effectiveness of TCR is the conversion efficiency of the recuperative reformer. Specifically, how much of the hydrocarbon fuel is converted to hydrogen is an easy-to-measure indicator of how much waste heat energy from the furnace exhaust has been converted to chemical fuel energy. The measured inlet and outlet flows and reformed fuel compositions from the recuperative reformer were used to calculate conversion efficiencies. These values were compared to predicted reformed fuel compositions for chemical equilibrium conditions.

D. Test Objectives and Technical Approach

The laboratory test objectives included evaluating:

- The effect of residence time on reforming fuel conversion rate
- The effect of FGR fraction for the flue gas reforming of natural gas on methane conversion rate
- If carbon deposition on the reformer surfaces occurred and if so possible ways to control depositions

The technical approach was based on the use of an existing bench-scale TCR experimental rig. This rig has been used extensively to evaluate flue gas reforming at furnace conditions and flue gas reforming at temperatures representative of steel reheat furnaces.

The following activities were planned:

- Design and build a non-catalytic flue gas recuperative reformer for reforming of natural gas
- Select/acquire and assemble ancillary equipment for the experimental set-up including the furnace, burner, recuperative reformer, combustion air heater and a data acquisition system
- Conduct laboratory tests to demonstrate recuperative reformer performance and to determine any technical issues

E. Facilities, equipment, and instrumentation

Measuring port locations are shown in Figure 10. An Instrument Index is presented in Table 1 below. A Horiba Gas analyzer was used to measure flue gas composition: NO_x (ppm), CO (ppm), CO₂ (%), and O₂ (%). A Varian Micro gas chromatograph was used to measure the reformed fuel composition (% volume): H₂, O₂, N₂, CH₄, CO, CO₂, C₂H₄, C₂H₆, C₃H₈, i-C₄H₁₀, n-C₄H₁₀, and C₂H₂. The flowing FGR fraction and the reformed fuel to the burner were estimated by measuring differential pressures across individual orifice plates.

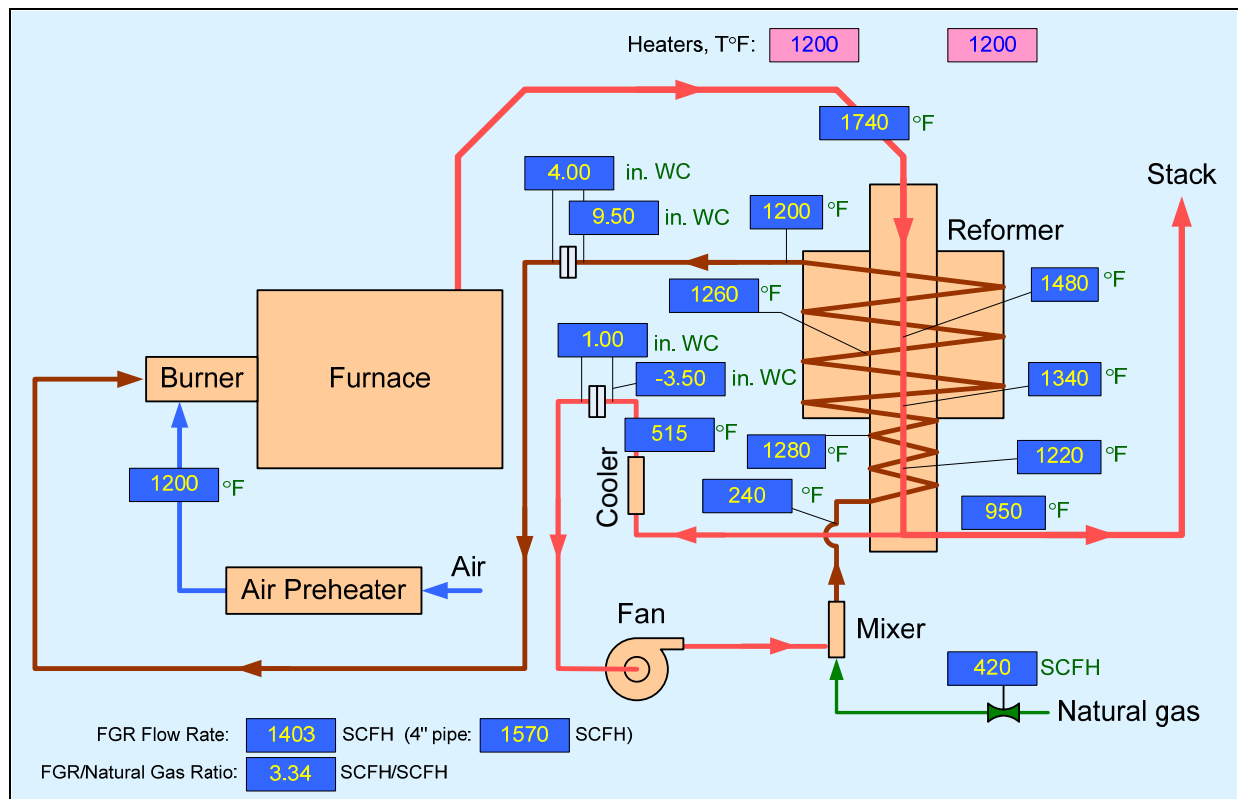


Figure 15. Real Time Monitoring Scheme of the TCRS (numbers are shown as an example)

Table 1. Instrument Index

Item #	Service	Instrument location	Instrument type	Mfg	Range	Signal type	Comment
1.	Inlet air flow rate	Δp transmitter	1 st heater inlet (existing)	Bailey (available in the lab)	0-30 "WC	4-20 mA + local reading	Required orifice size: 1.01"
		Mass flow meter	1 st heater inlet	SIERRA (available in the lab)	0-20,000 scfh	4-20 mA + local reading	Measuring section to be inserted into existing pipe.
2.	Inlet air static pressure	Pressure Transmitter	1 st heater inlet (existing)	Bailey (installed)	0-200 "WC	4-20 mA + local reading	HP pressure port
3.	1 st heater air temp	T/C	1 st heater outlet (existing)		50-2000 °F	0-45 mV	
4.	Combustion air temp	T/C	2 nd heater outlet (existing)		50-2000 °F	0-45 mV	
5.	Reformer FG inlet temp	T/C	Reformer FG (hot) inlet		50-2000 °F	0-45 mV	K-type
6.	Reformer FG outlet temp	T/C	Reformer FG (hot) outlet		50-2000 °F	0-45 mV	K-type
7.	Furnace static pressure	Pressure Transmitter	Furnace Shell				
8.	FG temp after water cooler	T/C	Water cooler outlet		50-2000 °F	0-45 mV	K-type
9.	FG temp	T/C-std	Mixer inlet	K-type T/C with std calibration – FG/NG ratio deviation $\pm 6\%$			
		T/C-spec		K-type T/C with special calibration – FG/NG deviation ratio $\pm 3\%$			
		RTD		RTD – FG/NG ratio deviation $\pm 2\%$			
10.	FG/NG mix temperature	T/C-std	Mixer outlet	Standard TC (available)			
		T/C-spec		Special T/C to be ordered			
		RTD		RTD + 2-point process meter/recorder to be ordered			
11.	NG temp	T/C	Mixer inlet		50-2000 °F	0-45 mV	K-type gives adequate tolerance
12.	FG/NG mix composition	Gas Chromatograph	Reformer RF (cold) inlet				
13.	RF composition	Gas Chromatograph	Reformer RF (cold) outlet				
14.	FG composition	Analyzer	Water cooler outlet	Horiba			Sampling pump required
15.	Water content	Condenser	Reformer RF (cold) outlet				Dry gas totalizer + 3-way switch
16.	Water content	Condenser	Reformer RF (cold) inlet				+sampling pump required.

F. Test Procedure

The experimental set-up allowed controlling the furnace exhaust gas temperature by adjusting the water cooled load in the furnace. Exhaust gas from the furnace was used as a heat source for endothermic reforming and a reagent to reform natural gas. The reformed fuel was combusted in

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Phase II - Design and Physical Testing of the Concept

the furnace using a Bloom baffle burner designed for high temperature gas fuels. During the tests the various reformed fuel compositions were analyzed and recorded.

G. Data Analysis and Quality Assurance Procedures

After data collection the following parameters were determined based on the measured parameters:

Reforming process completeness and methane conversion rate

The key result from the tests is process completeness: the magnitude of how much fuel was capable of being reformed. Process completeness is related to how much energy was recovered compared to the theoretical equilibrium prediction. This key parameter, process completeness, was defined in terms of measured data as

$$\text{Reforming process completeness} = \frac{(\text{measured methane conversion rate})}{(\text{calculated equilibrium methane conversion rate})}$$

where the methane conversion rate is defined as

$$\text{Methane conversion rate} = 1 - \frac{(\text{outlet mass concentration of methane})}{(\text{inlet mass concentration of methane})}$$

Equilibrium gas compositions were estimated using GTI licensed Aspen HYSYS software.

Reformer residence time

Reformer residence time was estimated as:

$$\text{Reformer residence time} = \frac{(\text{reformer volume})}{(\text{measured standard flow rate of reforming fuel})}$$

Essentially the residence time is a function of the capacity of the reformer and natural gas/flue gas mixture flow rate for the reformer. The larger the reformer volume, the higher the residence time will be, assuming the inflow and outflow rates are held constant. Higher residence time would provide more amount of time for the reforming fuel to be spent in the reformer thus having more time for chemical reactions in the reformer to complete the reforming process.

Volumetric flow rate of the dry flue gas

Flue gas flow rate into the reformer was controlled by adjusting the speed of both recirculation fans or a damper in the FGR by-pass line. The flue gas and natural gas were mixed in the jet

mixer and fed into the reformer. The volumetric flow rate of the flue gas was measured by an orifice plate. This flow rate can also be estimated based on nitrogen volumes measurement at the reformer inlet and outlet. The volume fraction of nitrogen in each of the streams was known, and the flow rate of natural gas was metered; this was enough information to calculate the volumetric flow rate of the dry flue gas:

$$V_{fg}^d = V_{ng} \frac{N_2^{mix} - N_2^{ng}}{N_2^{dfg} - N_2^{mix}}$$

Here V_{fg}^d is volumetric flow of dry flue gas, scfh; V_{ng} is volumetric flow of natural gas, scfh; N_2^{mix} is nitrogen volume fraction at reformer inlet, N_2^{ng} is nitrogen volume fraction in natural gas, N_2^{dfg} is nitrogen volume fraction in exhaust. The relative error of the flow rate measurement approximates that of the flow meter, $\pm 2.5\%$.

Flue gas water content

The water content of exhaust gas (and hence, of reformer inlet gas) is determined by material balance calculations:

$$H_2O_{fg} = \frac{\frac{H_{ng}^w \cdot d_{ng} \cdot MW_{H_2O}}{MW_{H_2} \cdot d_{H_2}} + \alpha V_0^{air} H_2O^{air}}{V_0^{fg} + (\alpha - 1)V_0^{air}}$$

Here H_2O_{fg} is volume fraction of water in flue gas, H_{ng}^w is mass fraction of hydrogen in natural gas, MW_{H_2} is molecular weight of hydrogen, g/mol; MW_{H_2O} is the molecular weight of water, g/mol; d_{ng} and d_{H_2} are the density of natural gas and hydrogen respectively, lb/scf; α is the air ratio; V_0^{air} is stoichiometric wet air for natural gas combustion, cf/cf; H_2O^{air} is the water volume fraction in wet air, cf/cf; V_0^{fg} is the stoichiometric natural gas combustion products, cf/cf. Relative error, presuming some deviation in composition, is approximately $\pm 4\%$.

Water vapor flow rates

Water vapor flow rate at the recuperative reformer outlet was determined by reformer material balance calculations (oxygen-based):

$$V_{H_2O}^{out} = \frac{V_d^{in} (O_2^{in} d_{O_2} + v_{CO}^O CO^{in} d_{CO} + v_{CO_2}^O CO_2^{in} d_{CO_2}) + v_{H_2O}^O V_{H_2O}^{in} d_{H_2O} - V_d^{out} (O_2^{out} d_{O_2} + v_{CO}^O CO^{out} d_{CO} + v_{CO_2}^O CO_2^{out} d_{CO_2})}{v_{H_2O}^O d_{H_2O}}$$

here $V_{H_2O}^{out}$ and $V_{H_2O}^{in}$ are the water vapor flow rates at the reformer outlet and inlet respectively, scfh; V_d^{in} and V_d^{out} are the dry gas flow rates at the recuperative reformer inlet and outlet respectively, scfh; O_2^{in} , CO^{in} and CO_2^{in} are the volume fractions of O_2 , CO and CO_2 respectively, in dry gas at reformer inlet; O_2^{out} , CO^{out} and CO_2^{out} are the volume fractions of O_2 , CO and CO_2 , respectively, in dry gas at the recuperative reformer outlet; d_{O_2} , d_{CO} , d_{H_2O} and d_{CO_2} are densities of O_2 , CO , H_2O (g) and CO_2 , respectively, lb/scf; $v_{H_2O}^O$, v_{CO}^O and $v_{CO_2}^O$ are mass fractions of oxygen in H_2O , CO and CO_2 , respectively. The relative error in these calculations is about $\pm 10 - 15\%$ at typical test conditions.

Lab-scale TCRS Start-up, Preheating, and Shutdown

The start-up, preheating, and shutdown procedures of the TCRS was an important part of the study to guarantee safe and controlled operation of the industrial furnace equipped with a recuperative reformer. Before TCRS operation the reformer tubes and piping are cold and air filled. Introducing natural gas directly into the reformer at the furnace start-up can create an explosive mixture of natural gas and air in the reformer and lead to unsafe operation of the TCRS. To prevent this condition the following generalized start-up procedure of the TCRS was established:

1. Initiate low FGR flow through the recuperative reformer by activating recirculation fan or use pressurized nitrogen (instead of natural gas) to create suction in the natural gas/flue gas mixer (Figure 15) at the reformer inlet;
2. Introduce natural gas directly to the burners and start the burners in same way as a normal (without TCRS) startup with air/natural gas;
3. Adjust FGR flow so that the flow equals the nominal value as with reforming, for example (FGR volume flow, SCFH) = $3.3 \times$ (Natural gas volume flow rate, SCFH).

After start-up, the reformer tubes and FGR flow in the reformer should be preheated to temperatures which are slightly lower ($100^\circ\text{F} - 200^\circ\text{F}$) than the temperatures at normal operating conditions with the fuel reforming. These temperatures are to be measured during the start-up and preheating and based on the measurements a decision can be made whether to switch the natural gas from the burners to reformer for TCRS operation. To minimize the number of measuring points for control purposes it is recommended to measure the FGR temperature at the reformer outlet only during reformer preheating. If the operating temperature of the reformed fuel is to be 1200°F the natural gas can be switched from the burners to the reformer inlet when this temperature is $\sim 1000^\circ\text{F}$ or higher.

Natural gas switching from the burners to the reformer should be also conducted by a specific procedure to eliminate any safety issues. The natural gas flow to the burners can be gradually decreased and simultaneously the natural gas flow to the mixer at the reformer inlet can be supplied and gradually increased to where the natural gas flow to the burners is zero and there is a full flow of natural gas to the mixer.

A procedure is also required at furnace shutdown. The natural gas supplied to the reformer can be shut off while combustion air continues to be supplied to the burner. For a short period of time, after the natural gas is shut off, flame will still be visible from the burner until the remaining reforming mixture in the reformer is completely combusted.

Recuperative Reformer Design Validation

The first step of the TCRS lab-scale testing was to validate design parameters of the recuperative reformer, particularly to confirm that the reformer hydrodynamic characteristics (such as pressure drop), thermal parameters (temperature, heat flux, etc.), heat transfer efficiency, and chemical reaction rates met the design requirements. The following metrics were measured and compared with the designed parameters:

- Pressure drop in the reformer and burner
- Flue gas and reforming fuel temperatures at the reformer inlet and outlet as well as in the middle of the reformer
- Reforming fuel composition at the reforming inlet and outlet

Maximum pressure drop across the flue gas side of recuperative reformer was measured as 0.7" W.C. at maximum firing rate (0.434 MMBtu/hr), flue gas/natural gas ratio 3.34, and combustion air temperature of 1200°F. Maximum pressure drop through the burner was measured as 5.1" W.C. at the same conditions. These results confirmed predictions showing that the pressure drops are in the range of design values.

Reforming fuel inlet and outlet temperatures in the reformer preheater were measured to confirm design parameters of the preheater. The preheater serves to rapidly preheat flue gas/natural gas mixture (reforming fuel) to the temperatures that are close to the design value of the reformed fuel temperature. The design was developed such that the reforming fuel temperature at the preheater outlet would be approximately equal to the reformed fuel temperature at the reactor outlet.

After the preheater, the preheated natural gas/flue gas mixture enters the reactor where the mixture is reformed. An appropriate design of the reactor should provide approximately constant temperature of the reforming fuel along the reactor length. Essentially higher or lower temperatures of the fuel at the reactor outlet compared to the reactor inlet would indicate an

unsuitable reactor design. A lower temperature of the reforming fuel at the reactor outlet compared to the reactor inlet can be a result of the following: less heat compared to the design value is supplied to the reactor from the flue gas so that the fuel is reformed at a lower temperature. In this case the reforming rate of the fuel is lower than the design value and as a result of that a lower hydrogen content will be measured in the reformed fuel. Higher temperatures of the reforming fuel at the reactor outlet compared to the reactor inlet can result from one of the following one or both reasons. There is not enough residence time in the reactor consequently the fuel is not reforming efficiently. In this case the reforming rate of the fuel is lower than the design value and as a consequence a lower hydrogen content will be measured in the reformed fuel. The other reason is that more heat compared to the design value is supplied to the reactor from the flue gas so that the fuel is reformed at a higher temperature. In this case the reforming rate of the fuel will be higher (if appropriate residence time) than the design value and as a result a higher hydrogen content will be measured in the reformed fuel.

Summarization of Phase II Test Results

A Typical distribution of the reforming fuel temperature in the reformer preheater and reactor is shown in Figure 16. The reforming temperature was controlled by adjusting temperatures of the furnace exhaust gas and flue gas recirculation flows. The furnace exhaust gas flow temperature was controlled by adjusting water cooled probes in the furnace. The flue gas recirculation (FGR) flow temperature was controlled by adjusting water cooler installed at FGR line. As can be seen from the figure, the reforming fuel (flue gas/natural gas mixture) in the preheater is rapidly heated up from a low temperature ($\sim 160^{\circ}\text{F}$) to the temperature of $\sim 1250^{\circ}\text{F}$ the desired temperature for the fuel reforming. These measured results confirmed that the heat transfer area and heat transfer rate in the reformer preheater are sufficient to provide desired parameters of the reforming fuel at the reactor inlet.

The measured results of the reforming fuel temperatures at the reactor inlet (thermocouple location 2), middle (thermocouple location 3), and outlet (thermocouple location 4) demonstrated that the temperature distribution along the reactor is uniform and all the temperatures approximate the design values (Figure 16). This confirmed that the reformer was properly designed and contained sufficient heat transfer area and heat transfer efficiency to provide heat from the flue gas to the reforming fuel. The residence time in the reactor was high enough to provide partial reforming of the fuel. It is surmised that the residence time can even be slightly lower. Some temperature reduction of the reforming fuel in the reactor (thermocouple locations 2 through 4) is a result of endothermic reactions. The temperature distribution can be further improved upon (constant temperature between points 2 and 4) by adjusting heat transfer areas or flow rates within the reactor (by modifying reactor design).

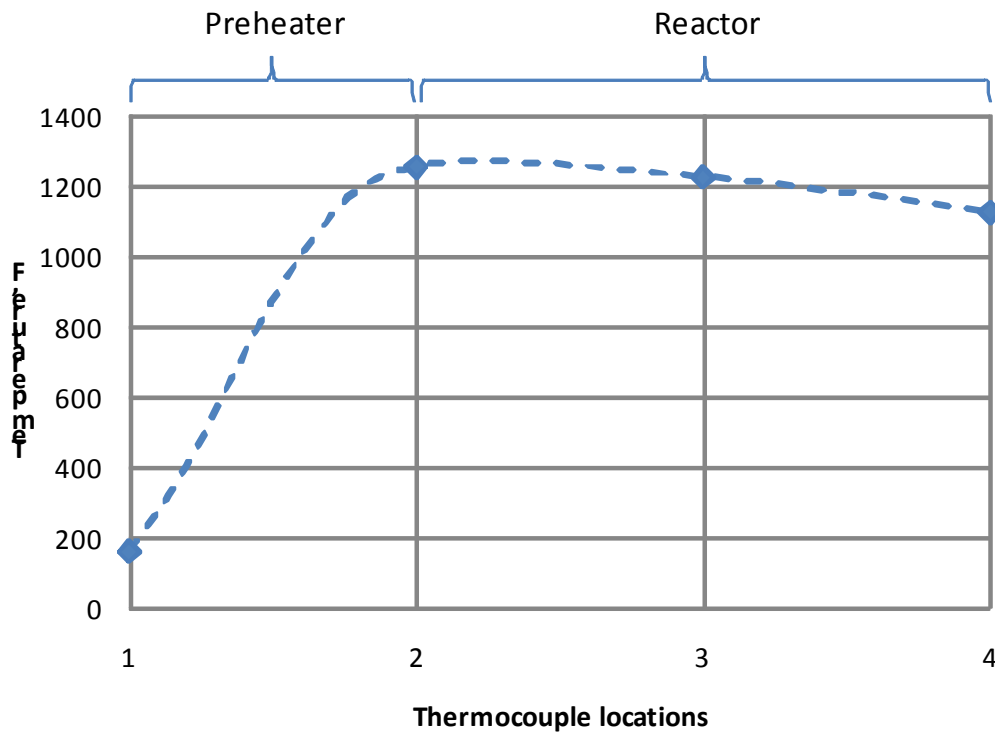


Figure 16. Typical Distribution of Reforming Fuel Temperature in the Reformer Preheater and the Reactor
(Thermocouple Locations: 1 and 2 – Preheater Inlet and Outlet, 3 and 4 – Middle Out and Outlet of the Reactor)

Burner Performance Validation

A Bloom burner that was used in the TCRS testing demonstrated good performance at start up and firing in wide ranges of the natural gas flow rate (100 SCFH – 450 SCFH), FGR flow rate (0 - 3,000 SCFH), excess air (0 - 10%), temperatures of combustion air (100°F - 1200°F) and reformed fuel (800°F - 1300°F). No burner overheating occurred, nor was unstable operation observed during the tests.

Recuperative Reformer Performance Validation

The performance of the recuperative reformer depends on many factors, parameters, and operating conditions. There are several design parameters that may affect performance of the recuperative reformer. Some of them are *efficiency of heat transfer* in the reformer, *residence time*, *tube and wall material* used in the reformer and *surface area* which is in contact with the reforming fuel. As previously noted, preliminary tests showed that the reformer provided sufficient heat transfer and provided enough heat to the reforming fuel to compensate for energy

outflow due to endothermic reactions. The reformer heat load (natural gas flow rate), reforming fuel temperature, flue gas/natural gas flow ratios, and excess air to natural gas ratios were varied in the experiments to analyze the reformer performance.

The reformer performance was characterized by such parameters as *process completeness* and *methane conversion rate* (see Data Analysis and Quality Assurance Procedures – Section G, page 32). During testing, hydrogen and carbon monoxide contents in the reformed fuel were also used to preliminarily estimate performance of the recuperative reformer. Comparing measured values of hydrogen and carbon monoxide with their theoretical predictions made it possible to determine how well the reformer was performing. For example, the theoretical reformed fuel composition at design conditions (1200°F reforming temperature, flue gas/natural gas volume ratio ~ 3.3:1) should result in the following (% volume): CH₄=5.7%, CO₂=2.82%, H₂O=2.88%, N₂=42.94%, CO=14.7%, H₂=30.96%. Matching this composition with measuring values would provide 100% process completeness. In actual practice process completeness is lower than 100%. GTI expected that process completeness for a non-catalytic reformer would not be higher than 80% - 90%. With this target (for example, 85% process completeness) for the experiments the expected reformed fuel composition should be: CH₄=7.6%, CO₂=3.95%, H₂O=3.65%, N₂=44.41%, CO=12.47%, H₂=27.92%. Since the measurements are based on dry values, the dry composition of the reforming fuel is: CH₄=7.89%, CO₂=4.1%, N₂=46.09%, CO=12.94%, H₂=28.98%. Consequently, comparing measured values of hydrogen and carbon monoxide with theoretical predictions a qualitative determination can be made as to how well the reformer was performing and adjusting the experimental plan as necessary.

Technical/Performance Issue

Observations of hydrogen and carbon monoxide values over time showed that the recuperative reformer performed less efficiently at the beginning of the each experiment compared to the later results prior to shutting down the test set up. Hydrogen and carbon monoxide contents in the reformed fuel were in the ranges of 16% - 23% and 6% - 9% (dry basis) respectively while the theoretical predictions were approximately 29% H₂ and 13.5% CO. During the experiments, these values were gradually increasing and reached their maximums, which were nearer the theoretical predictions. One explanation for such an increase in the reformer performance can be explained by the catalytic effect of metal surfaces inside the reformer on the reforming reaction rates. The metal surfaces have some catalytic activity that promotes the reforming reactions.

Being in sustained contact with the high temperature gas mixture, the metal heat transfer surfaces could increase their catalytic activity because of the naturally occurring surface oxidation/reduction activity. Another explanation could also be another mechanism of increased reforming rate called carbonization, which causes increased catalytic activity of the metal surface when carbon is formed on the surface (Moayeri and Trimm 2007). The main series of the experiments were done after the reformer performance was stabilized.

Figure 17 shows the dry reforming product compositions (H_2 and CO) measured by the gas chromatograph at different reforming temperatures. The reforming temperature was taken as averaged temperature between middle of the reactor (thermocouple location 3, Figure 17) and reactor outlet (thermocouple location 4). H_2 and CO contents increased as the temperature increased. Maximum yields of 27% of hydrogen and 11% of carbon monoxide were observed in the experiment at chosen conditions.

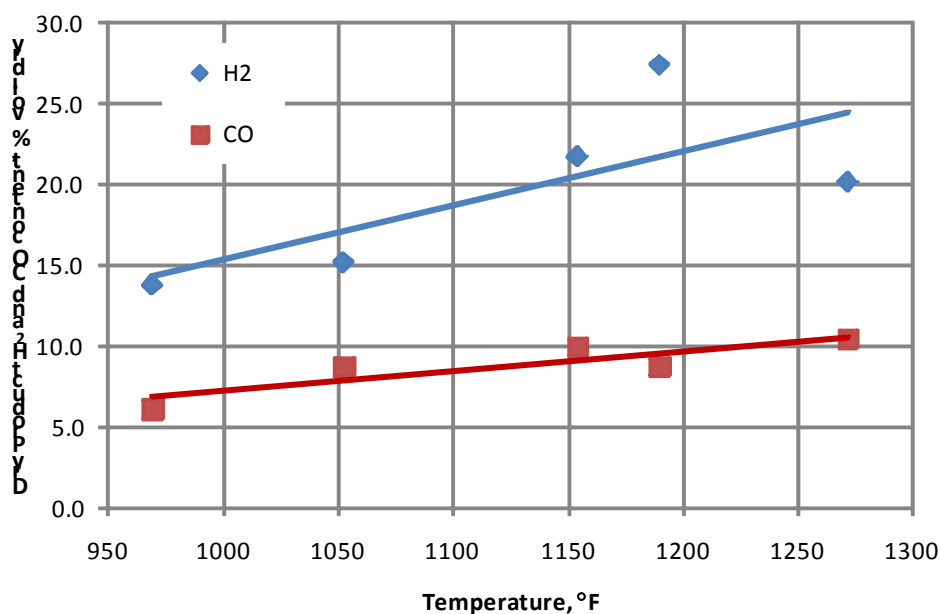


Figure 17. Dry Reformed Fuel H_2 and CO Components versus Reforming Temperature (FGR/NG=3.34, Residence time 10 sec)

The methane conversion rate is shown in Figure 18. As can be seen, methane conversion started at temperatures lower than $\sim 1000^\circ\text{F}$ and increased as the temperature increased. Approximately 58% of methane in natural gas can theoretically be reformed at 1200°F while the measured results confirmed that only $\sim 41\%$ of methane was reformed in the non-catalytic recuperative reformer. This corresponds to $\sim 70\%$ reforming process completeness (Figure 19).

Figure 19 shows the effect of reforming temperature on the reforming process completeness. The process completeness is decreased from $\sim 72\%$ at a 980°F reforming temperature to $\sim 65\%$ at a 1315°F reforming temperature.

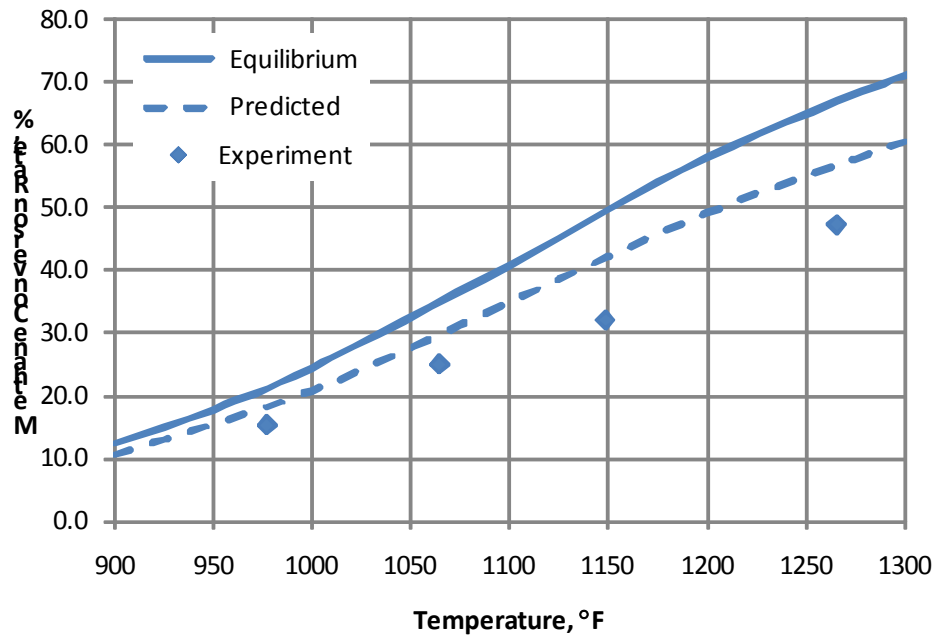


Figure 18. Methane Conversion Rate versus Reforming Temperature
(FGR/NG=3.34, Residence time 10 sec)

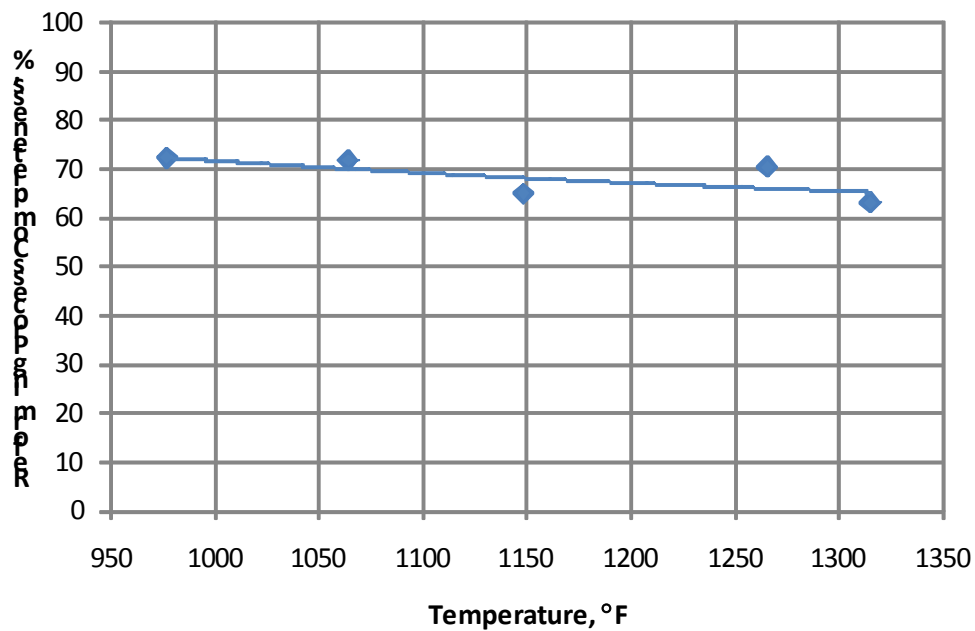


Figure 19. Reforming Process Completeness Versus Reforming Temperature
(FGR/NG=3.34, Residence time 10 sec)

During testing it was determined that the efficiency (methane conversion rate) of the recuperative reformer would slightly degrade with time and appeared to plateau at the end of the test cycle (Figure 20). The degradation test was conducted for a test cycle of more than six hours and with the methane conversion rate consistently reducing from 42.4% to ~31% at the end of this time period. Estimated equilibrium conversion rate was 53-57% during the test. Additional continuous running test (Durability Testing)) was determined to be required to evaluate whether the degradation is asymptotic at the six hour mark and if not when and at what level does efficiency degradation become asymptotic. It should be noted that upon restarting the test furnace for another test cycle from a cold start and once operating equilibrium was reached, recuperative reformer efficiency returned to the original level only to degrade again as described above.

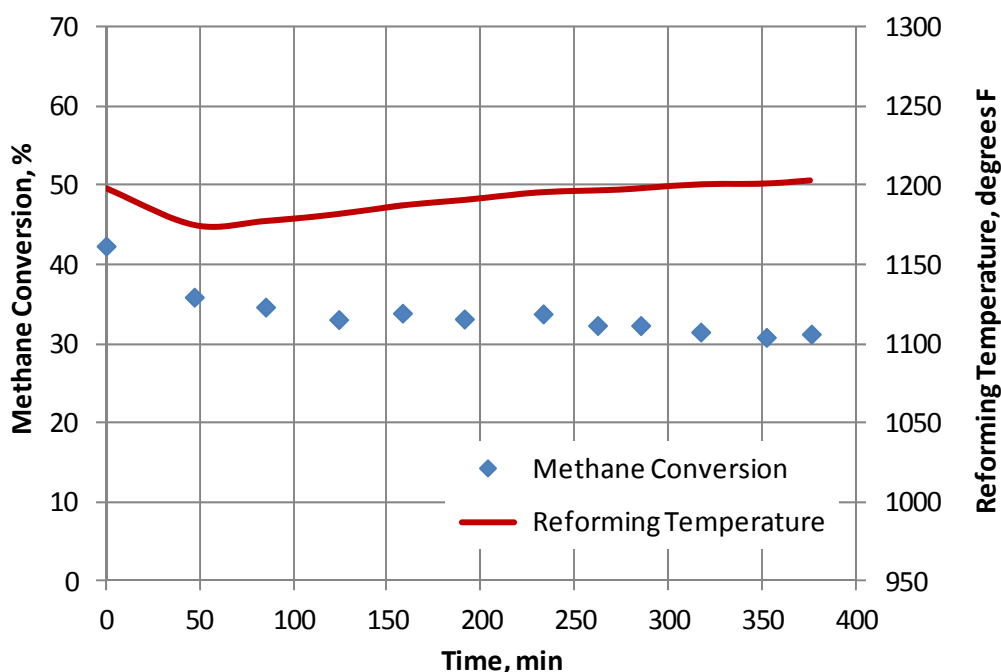


Figure 20. Methane Conversion Rate and Reforming Temperature Versus Time (FGR/NG=3.34, Residence time 10 sec)

Emissions Reductions

Oxides of Nitrogen (NO_x)---The lab tests confirmed that the Oxides of Nitrogen are reduced by approximately 33% (Figure 21) as measured against the standard operation of the Bloom low NO_x burner used in these lab tests. Accordingly, the nominal projected pounds of NO_x per ton of reheated steel is reduced from ~0.8 to ~0.54lbs per ton of reheated steel.

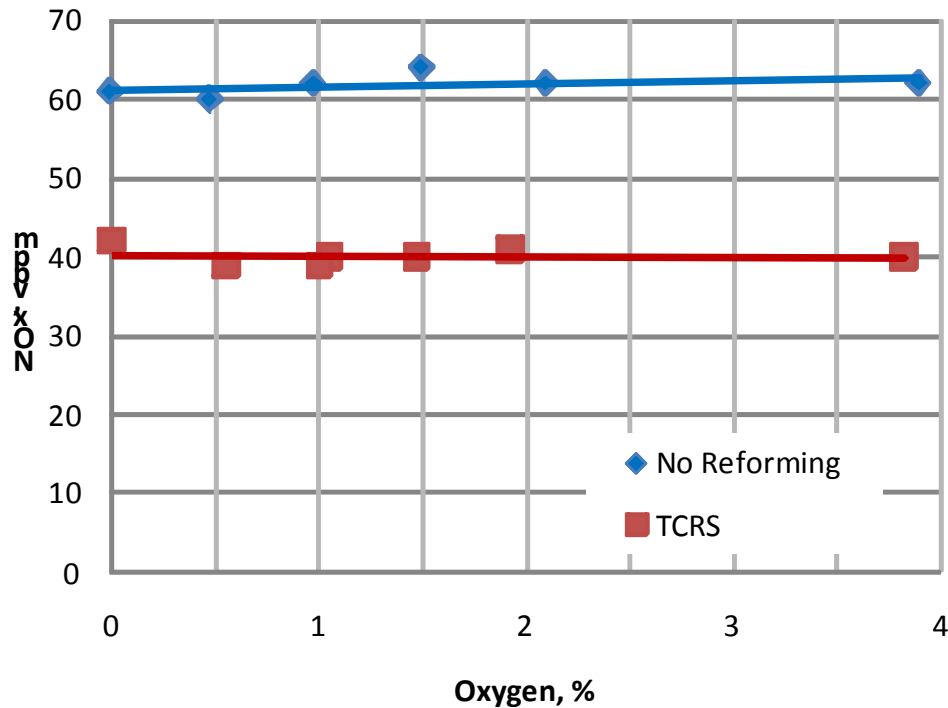


Figure 21. NO_x Emissions (dry)
(FGR/NG=3.34, Residence time 10 sec)

Carbon Dioxide (CO₂)---Since carbon dioxide is a direct function of the fuel combusted, the reduction in fuel usage of 21% translates to a nominal projected pounds of CO₂ per ton of reheated steel reduced from 185 lbs of carbon dioxide per ton of steel reheated to 146 lbs of carbon dioxide per ton of steel reheated.

Carbon Monoxide (CO)---One additional finding shown in Figure 22 is that for those operating periods where excess oxygen in the flue gas from the reheat furnace is 1% and lower there is a substantial reduction in carbon monoxide emissions.

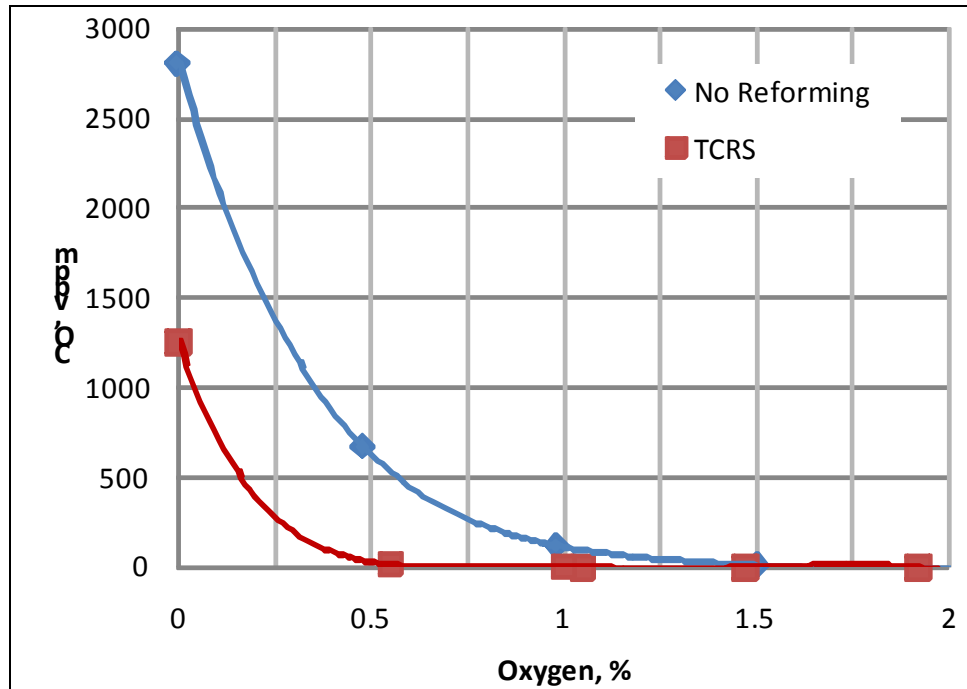


Figure 22. CO Emissions (dry) versus oxygen content in the furnace exhaust gas (FGR/NG=3.34, Residence time 10 sec)

Recuperative Reformer Leakage Issue

The lab-scale TCR system test results indicated that internal leakage developed in the recuperative reformer. Notwithstanding that the test results were not compromised it was determined to be necessary to repair the reformer before further Durability Testing was undertaken. The recuperative reformer was partially disassembled (Figure 23) by GTI staff and pressure tested to locate the leak(s). Leakage was confirmed but not located since further disassembling of the reformer unit by GTI would not be cost effective. A discussion was held with Thermal Transfer Corp. (TTC) on the cost and schedule for returning the reformer to TTC (leveraging their staff and equipment for cost effectiveness purposes). Approval by AISI was secured for GTI to proceed with this plan. The recuperative reformer was disconnected from the GTI experimental rig (Figure 24) and shipped to TTC for repair(s). TTC disassembled and pressure tested the unit, and discovered several points of leakage (Figure 25). TTC repaired the sources of leakage and shipped the unit back to GTI on 30 December 2011.



Figure 23. Partially Disassembled Recuperative Reformer at GTI Laboratory



Figure 24. Recuperative Reformer Prepared for Shipment to TTC

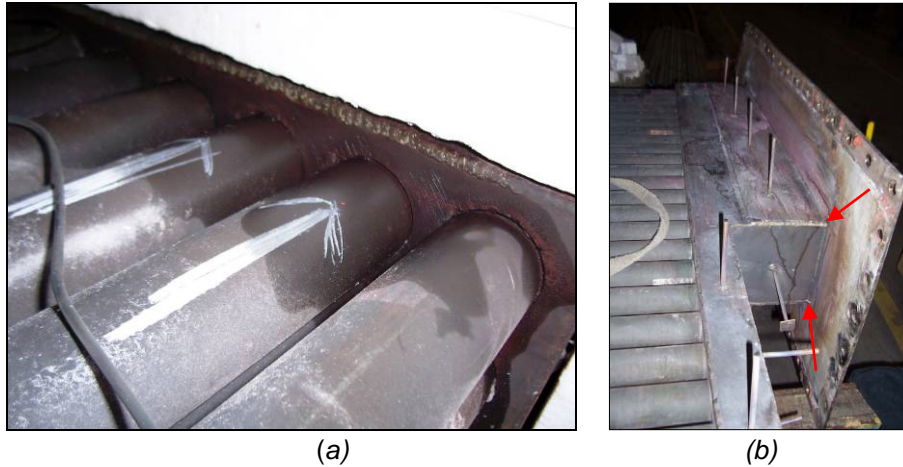


Figure 25. Leakage Locations at the Tube Sheet (a) and Plenum (b)

Durability Test Summary

Subsequent to the leaks being repaired by TTC and the return of the Recuperative Reformer, a Durability Test was undertaken to determine whether the methane reforming rate degradation that was observed during the planned Phase II tests was already asymptotic or leveled out at a lower level of methane reforming.

The Recuperative Reformer was reconnected and the TCRS was retested for approximately 48 continuous hours. Once the system reached thermal equilibrium, the same gradual reduction in methane reforming rate was observed. An additional phenomenon was observed in that periodically the percent H₂ would increase and then decrease over a short time interval (several minutes) without any changes in the process by the staff operating the lab set up. Once it was evident that the methane reforming rate was still decreased and was not asymptotic, several changes to the process variables were intentionally made to attempt to retard or reverse this effect. See Appendix B for several graphical representations of the durability test results.

- Decreased Flue Gas to Natural Gas (FGR/NG) Ratio in several steps down to FGR/NG~3.3
- Drove the static pressure of the flue gas within the RR from negative to positive to avoid air infiltration into the flue gas.
- Increased the flue gas temperature entering the RR from an average of 1625°F to 1700°F. Insufficient time was available to increase the temperature to 1800°F and 1900°F
- Operated the test furnace at near stoichiometric such that the flue gases supplied to the RR contained < 1% oxygen.

None of the above process changes had a material effect on retarding the decrease in the methane reforming rate. During these changes it was also found that at certain conditions (at a low

FGR/NG ratio ~3.3, etc.) the methane reforming rate became unstable and had began changing from low to very high values. The hydrogen content in the reformed fuel was changing from 2% to 18% (Figure 26) which is indicative of large changes in the methane reforming rate.

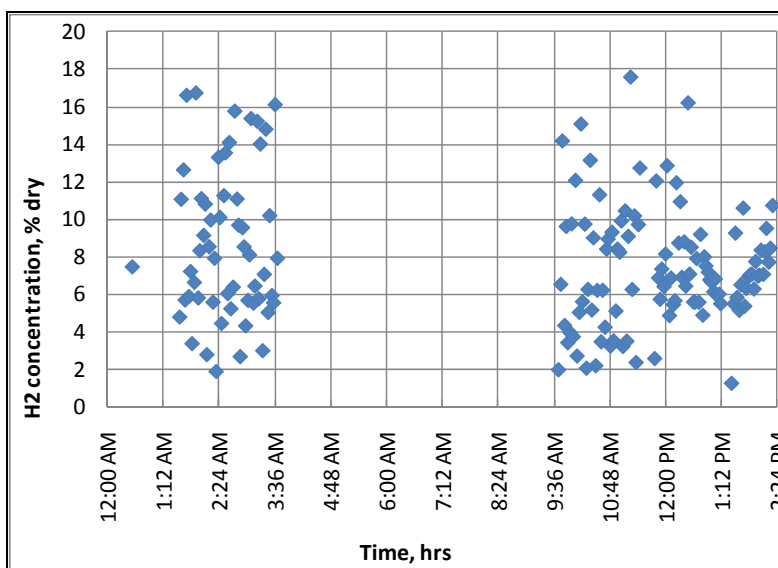


Figure 26. Hydrogen Content in the Reformed Fuel versus Time

Conclusions

GTI's preliminary conclusions are that the mechanism(s) producing the MRR decrease is (are) not entirely known or understood. The nature of the chemical kinetics that is triggering the mechanism and/or the other mechanisms described above is still necessary to be evaluated. Other possibilities include: stratification of the natural gas and flue gas downstream of the mixer within the preheater; and/or stratification of a portion of the flue gas/natural gas mixture and the complement of the flue gas/natural gas mixture for part of the residence time within the reformer-reactor.

Recommendations

Since the results of the endurance tests confirmed that the reforming process is gradually retarded over time due to one or more of the above mechanisms the TCR field experiment as outlined in Phase III is recommended to be postponed and a broader series of lab testing the TCR system to be approved with a revised test matrix based on a General Scope of Work for Extended Phase II TCR Testing that was prepared (see Appendix C) with the technical objectives being to identify the mechanism(s) that are preventing a sustained methane reforming rate; devise and implement a solution to sustain the methane reforming rate.

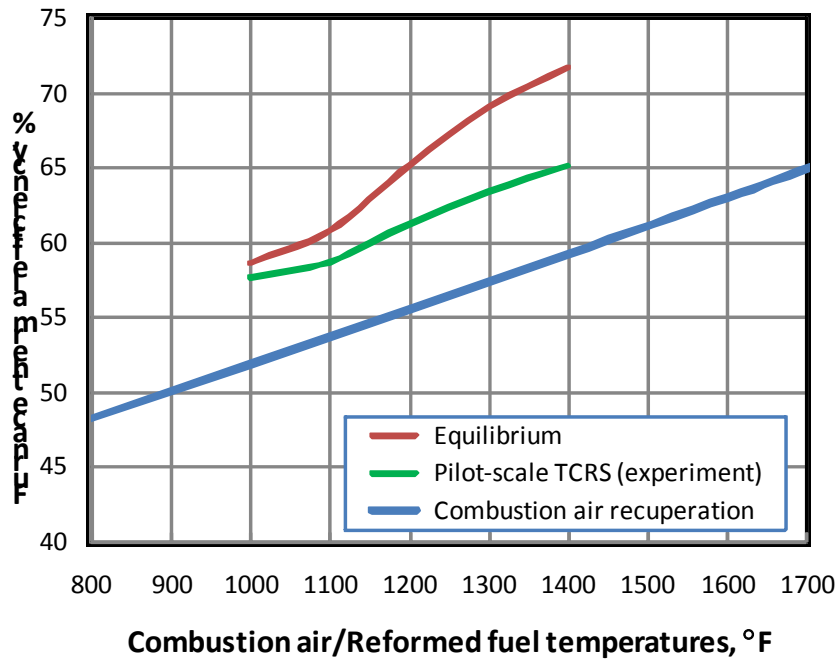
GTI staff have discussed the above internally and believe that the following is a reasonable alternative given that (1) Proof-of-concept has been verified and; (2) More importantly a well-designed and operational TCR system residing in the GTI combustion laboratory is capable of further testing to evaluate which and how the above mechanisms are retarding the methane reforming rate. Once fully understood, necessary alterations to the reformer design can be made.

Accordingly, the teams' consensus is to capitalize on the considerable amount of data acquired from modeling and physical testing by proposing a revised scope of work that will focus on identifying the mechanism(s) that are co-opting methane reforming efficiency for long-term operation of TCR as a viable waste heat recovery technique. The revised scope of work will consist of kinetic modeling; adding instrumentation to more fully extract additional operating information (For example, sampling the flue gas/natural gas mixture at several points within the recuperative reformer. Currently the flue gas/natural gas mixture is sampled before entry into the recuperative reformer and the reformed fuel is sampled after exiting the recuperative reformer.) from the existing system that will enable the team to identify the mechanism(s) of MRR retardation; to conceive of the necessary modifications to the design; to build and to retrofit one or more modifications to the RR; iteratively retest the retrofitted RR until the RR achieves and sustains the predicted methane reforming rate for extended hours of operation. The revised schedule for the above revised Scope of Work is currently estimated as six months.

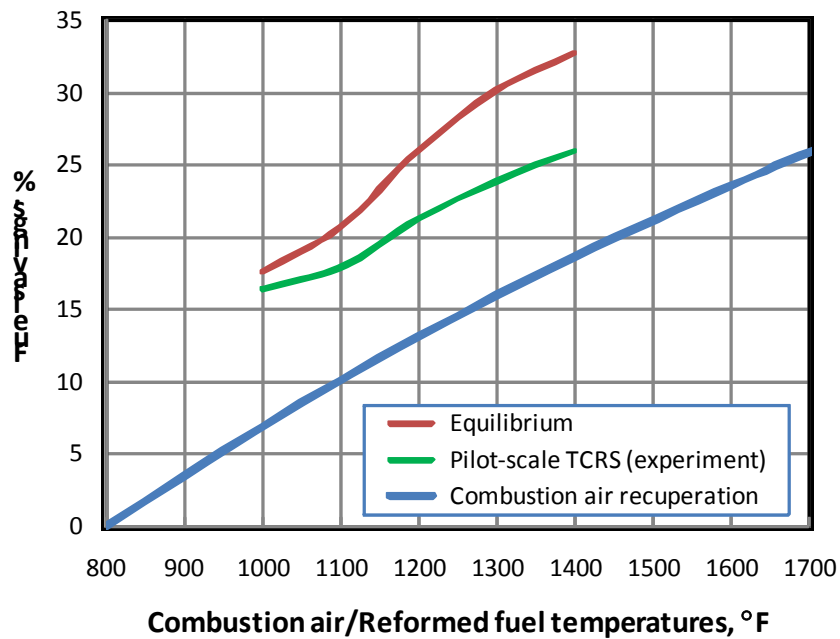
TCRS Performance Validation

Based on the physical test data obtained from the lab-scale experiments, the TCRS performance potential evaluated in Phase I was revised accordingly. Figure 27 shows the furnace thermal efficiency with combustion air recuperation and TCR system. The blue line represents furnace thermal efficiency for an air recuperated furnace. The red line, which is the ideal, shows TCR system evaluated in Phase I based on chemical equilibrium calculations; green line portrays the furnace thermal efficiency for the TCR system evaluated in Phase II based on the experimental results for the lab-scale test furnace at the achieved methane reforming rate with no degradation. As one can see from the figure the revised thermal efficiencies of the furnace are lower compared to the equilibrium predictions, i.e. approximately 61%. This should be taken into account when fuel savings and capital expenditures are estimated.

Figure 28 shows fuel savings with combustion air recuperation and TCRS. As one can see from the figure, actual fuel savings using the non-catalytic reformer at 1200°F would be approximately 21% compared to the fuel consumption in the furnace with combustion air recuperation at 800°F. It would require approximately 1500°F combustion air preheat to achieve the same fuel savings as for the TCRS at 1200°F.



**Figure 27. Furnace Thermal Efficiency
Versus Combustion Air/Reformed Fuel Temperatures**



**Figure 28. TCRS Fuel Savings
Compared to Fuel Consumption at 800°F Air Recuperation**

Revised TCR System Information Based on Phase II Test Results

The optimum three-stage TCR System configuration resulting from Phase I analysis was re-evaluated as a result of the physical lab testing carried out in Phase II. On this basis, additional technical information was provided to Thermal Transfer Corporation for obtaining a revised budgetary estimate and new physical dimensions and heat transfer module arrangement.

Figure 29 is a drawing showing the revised recuperative reformer based on Thermal Transfer Corporation's revisions per the Phase II results. Once major difference from the previous preliminary design is the preheater for the flue gas/natural gas mixture is not integrated into the recuperative reformer is now a separate module.

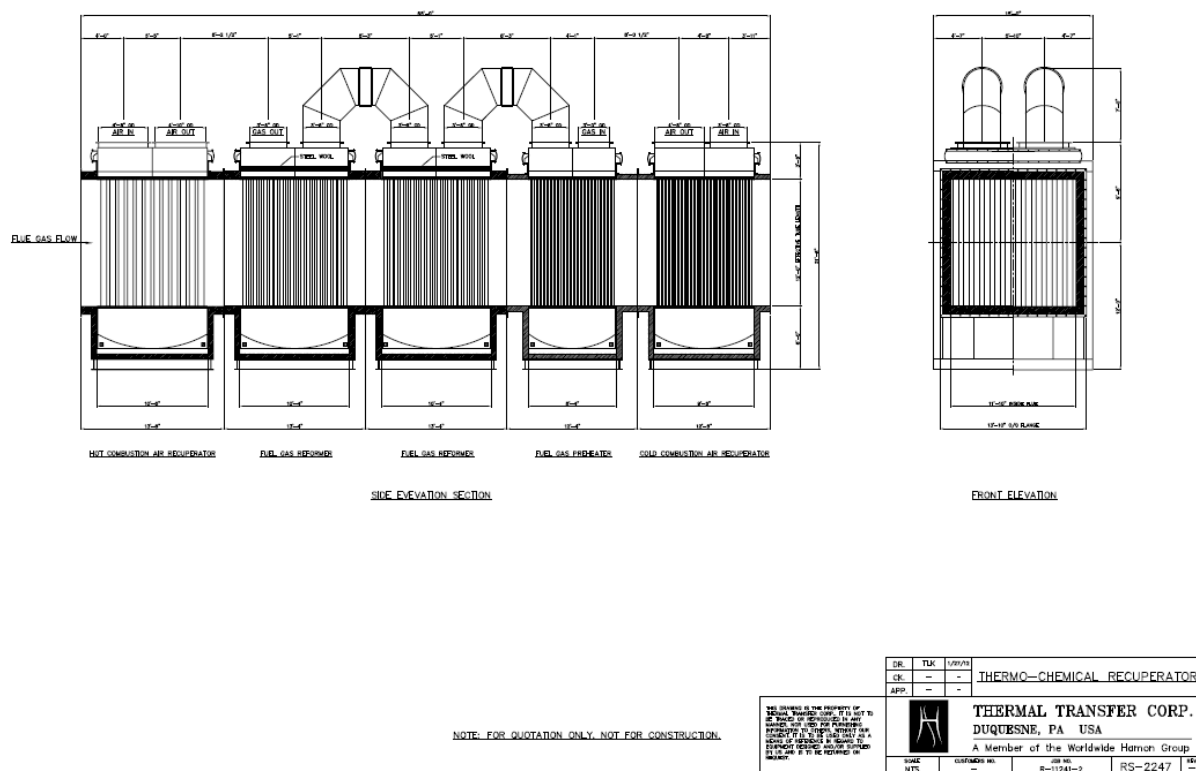


Figure 29. Full Scale TCRS -Air Recuperation (AR) and Thermochemical Recuperation (TCR)

AR & TCR Footprints

For the AR

The length, width and height were established as 14.2 feet long × 15 feet wide × 21.5 feet in height given revised parameters from lab testing:

TCR for High Temperature Furnaces in the Steel Industry:
Phase II - Design and Physical Testing of the Concept

Combustion air preheat temperature $\approx 800^{\circ}\text{F}$
Nominal furnace firing rate ≈ 335 MMBtu per hour
Nominal waste gas flow $\approx 285,100$ pounds per hour
Furnace thermal efficiency $\approx 48\%$

Note: the dimensions include the tube bundle and the outer shell.

For the TCRS

The length, width and height were established as 65 feet long x 15 feet wide \times 21.5 feet in height given the revised parameters from lab testing:

Combustion air preheat temperature $\approx 1200^{\circ}\text{F}$
Reformed fuel temperature $\approx 1200^{\circ}\text{F}$
Nominal furnace firing rate ≈ 245 MMBtu per hour
Nominal waste gas flow $\approx 261,324$ pounds per hour
Furnace thermal efficiency $\approx 61\%$

Note: the dimensions include the tube bundle and the outer shell.

CAPEX and Simple Payback Based on Phase II Results

For purposes of comparison, the CAPEX values in Table 2 and Table 3 were established based on the Phase II results and revised budgetary estimates from Thermal Transfer Corporation.

It should be noted that the estimated cost of the TCRS increased by 100% whereas the estimated cost of an ARS increased by 42%. Although both utilize 304SS and 310 SS, the TCRS contains additional heat transfer surface areas consisting of these stainless steel grades. We believe additional opportunities to reduce and minimize reliance on this metallurgy may become evident when Extended Phase II TCR Testing is carried out, subject to approval.

Figure 30 and Figure 31 illustrate the revised capital expenditures (CAPEX) and simple paybacks for TCRS compared to a recuperated furnace with 800°F Air Preheat (Retrofitted Furnace). As can be seen, the TCRS option has a much lower capital expenditure level and lower simple paybacks compared to conventional air recuperation at matching furnace thermal efficiencies.

Table 2. Estimated CAPEX for the reference Air Recuperation System

Combustion air temperature, °F	800
Heat exchanger estimate	\$593,100
Direct Cost estimates	
Equipment f.o.b. price	\$ 1,627,507
Materials used for installation	\$ 466,031
Direct labor	\$ 422,743
Total direct materials and labor	\$ 2,516,280
Indirect Cost estimates	
Freight, insurance, taxes	\$ 106,331
Construction overhead	\$ 294,051
Contractor engineering expenses	\$ 180,249
Total indirect project costs	\$ 580,630
Bare module capital	\$ 2,228,911
Contingency/Fee estimates	
Contingency	\$ 336,116
Fee	\$ 69,596
Total contingency and fee	\$ 405,711
Total module capital	\$ 2,634,622
Auxiliary facilities	\$ 790,387
Total Estimated Costs	\$ 4,293,009

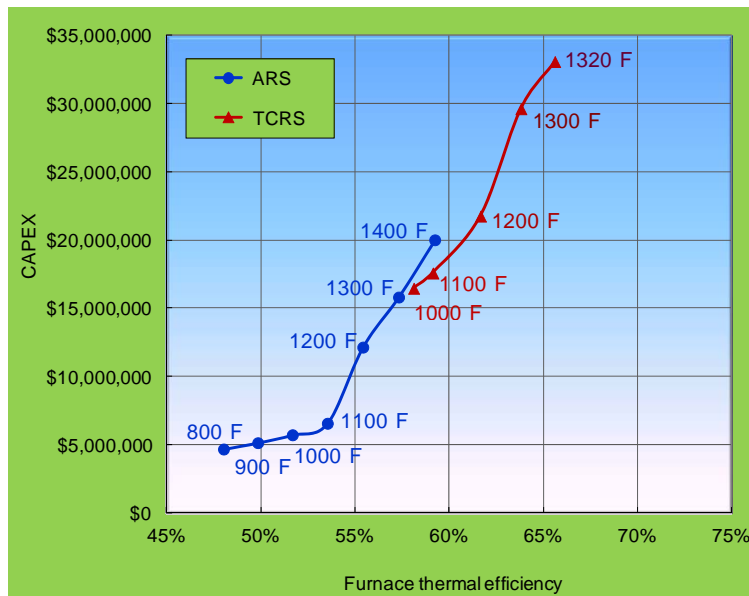


Figure 30. CAPEX for Air Recuperated System (ARS) and TCRS

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Table 3. Estimated CAPEX for the current TCRS configuration

Air/Reformed fuel temperature, °F	1200
Heat exchanger estimate	\$3,077,700
Direct Cost estimates	
Equipment f.o.b. price	\$ 4,581,132
Materials used for installation	\$ 2,443,627
Direct labor	\$ 2,197,004
Total direct materials and labor	\$ 9,221,763
Indirect Cost estimates	
Freight, insurance, taxes	\$ 519,839
Construction overhead	\$ 1,528,116
Contractor engineering expenses	\$ 915,396
Total indirect project costs	\$ 2,963,351
Bare module capital	\$ 11,317,113
Contingency/Fee estimates	
Contingency	\$ 1,706,800
Fee	\$ 353,671
Total contingency and fee	\$ 2,060,471
Total module capital	\$ 13,377,584
Auxiliary facilities	\$ 4,013,275
Total Estimated Costs	\$ 18,258,860

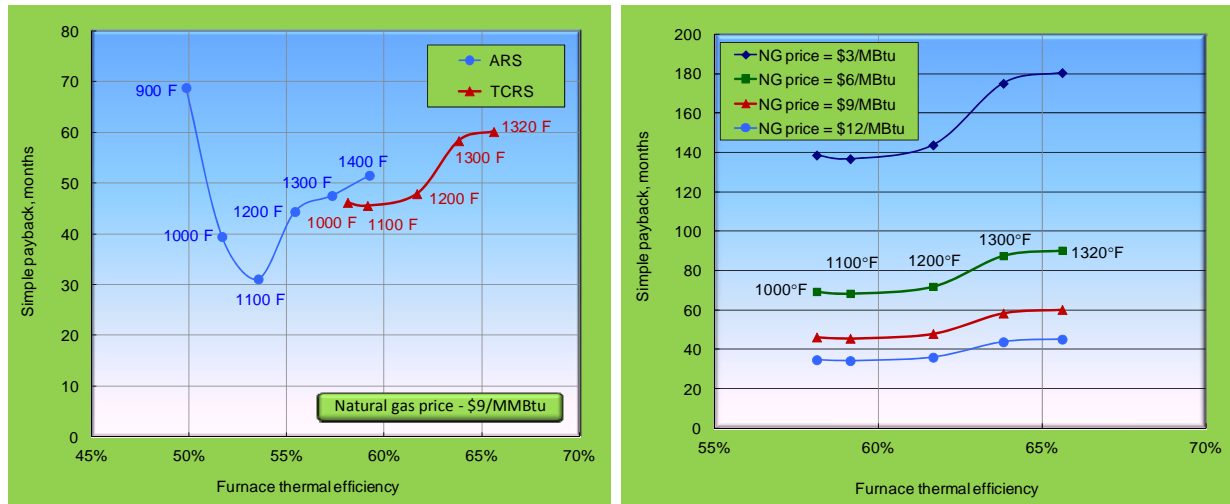


Figure 31. Simple Paybacks for TCRS Compared to a Recuperated Furnace with 800°F Air Preheat

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List of Acronyms

Acronym	Description
AISI	American Iron and Steel Institute
GTI	Gas Technology Institute
TCR	ThermoChemical Recuperation
CAPEX	Capital Expenditures
MMBtu	Million British Thermal Units
NPV	Net Present Value
TTC	Thermal Transfer Corporation
ARS	Air Recuperator System
TCRS	ThermoChemical System
WVPS	Water Vapor Pump System
T_{RF}	Reformed Fuel Temperature
FGR	Flue Gas Recirculation
CO ₂	Carbon Dioxide
NO _x	Oxides of Nitrogen
CH ₄	Methane
RR	Recuperative Reformer,
T_A	Temperature of Combustion Air
RF	Reformed Fuel
U	Heat Transfer Coefficient
ε	Relative Air Preheat
T_{ARI}	Temperature of Combustion Air – First Stage Air Recuperator
T_{ARII}	Temperature of Combustion Air – Second Stage Air Recuperator

Appendices

Appendix A

Experimental Evaluation of Residence Time for Non-Catalytic Reformer

Testing Objectives

The numerous variables in the lab-scale TCRS testing require a multifactor design of the test matrix and large number of experiments with different initial conditions (levels) to augment/optimize the main body of testing and reduce the number of experiments in the lab-scale TCRS tests.

Optimized the number of experimental conditions was initiated by a short preliminary test that was conducted using another existing TCRS (experimental rig) at GTI combustion laboratory. The existing experimental rig installed on a GTI heat treat furnace contains a preheater and a recuperative reformer. The recuperative reformer design allows testing the reformer with and without a catalyst. The experimental rig is very flexible, allows changing reforming temperature, reforming fuel flow rate, and other parameters of the TCRS.

The existing recuperative reformer was used to confirm residence times required to reform natural gas with flue gas. The additional knowledge about the residence time for non-catalytic reforming allows reducing the number of experiments in the lab-scale test by eliminating conditions (levels) with too low or too high values of residence time. For example, the residence time low level can characterize experimental conditions when the reforming reaction rate is lower than 10% of theoretical prediction by equilibrium. The residence time high level can be limited by 90% of theoretical prediction by equilibrium or limited by the reformer dimensions. The higher residence time requires a larger reformer.

Experimental Setup and Measuring Equipment

Laboratory tests were conducted using the GTI natural gas-fired heat treat furnace which is equipped with several burners. One of the burners (Figure A1) was used both as a high temperature flue gas source and heat source for the reformer; the other burners were not used. Produced reformed fuel was flared.

Flue gas from the burner simulated the lab-scale furnace exhaust and was controlled by natural gas/combustion air flow ratio. Flue gas composition was specified to provide comparable conditions with the lab-scale furnace and maintained close to the following values (by volume): $\text{CO}_2=8.1\%$; $\text{H}_2\text{O}=16.1\%$; $\text{O}_2=4\%$; $\text{N}_2=71.8\%$. The flue gas temperature was in the range of

1230°F-1670°F. Desulfurized, line natural gas was used for reforming. Its composition was approximately the same during all tests. Typical values of the natural gas major components were (mole fraction, %): CO₂=1.0%, N₂=1.2%, CH₄ (methane) = 95%, C₂H₆ (ethane) = 2.4%, C₃H₈ (propane) = 0.3%, i-C₄H₁₀ (i-butane) = 0.05%, n-C₄H₁₀ (n-butane) = 0.05%. The lower heating value of the natural gas was approximately 20,320 Btu/lb.

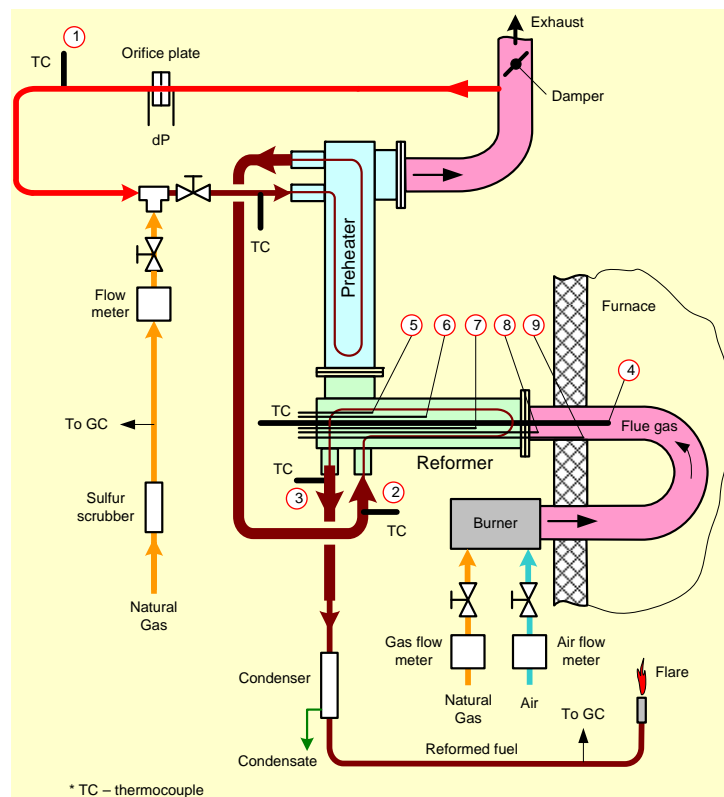


Figure A1. Laboratory Setup for Flue Gas/Natural Gas Reforming

The Eclipse 4" Therm-Thief Bayonet-Ultra Recuperator (Figure A2) was used as the recuperative reformer. It is a tubular type heat exchanger with five heat exchange double tubes. Removable inserts (metal or catalytic) can be placed inside inner tubes (Figure A3) and inspected after each test in order to observe if carbon deposited on the metal or catalytic surface.

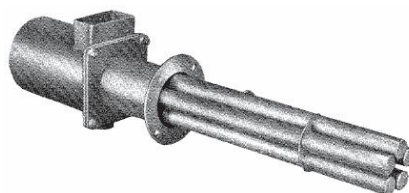


Figure A2. Eclipse ThermThief Bayonet-Style Recuperator Used as a Reformer

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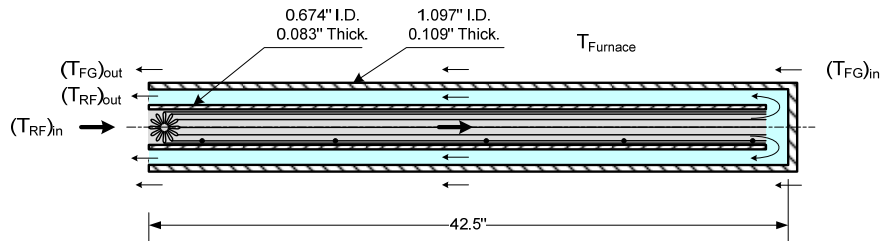


Figure A3. Tube Exchange Tube with Metal Mesh inside Inner Tube

A metal mesh (Figure A4) as extended surface for the reforming reaction was used in some of the tests. The mesh material is Monel.



Figure A4. Metal Mesh inside Reformer Tubes

Thermocouples were installed inside inner tubes of the reformer between the tube wall and catalyst at different locations (Figure A5) in order to measure temperature profile of the reforming gas.

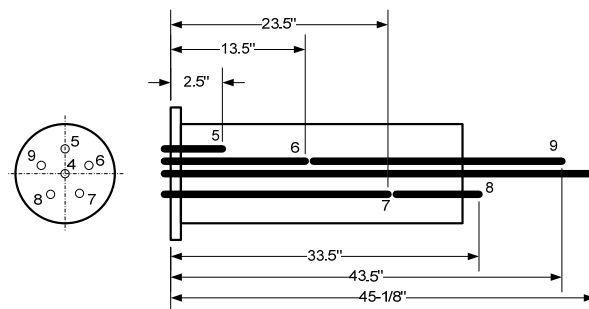


Figure A5. Thermocouple Position in Heat Exchange Tubes

A photograph of the test setup is shown in Figure A6. The burner on the left and burner in the middle were not used. Burner No. 1 is partially obscured behind the insulated pipe exiting one of the recuperators. Both recuperators are bayonet-style Eclipse ThermThiefs, model BU, shown in

Figure A2. Each of the five cylinders contains interior parts for heat exchange. Two recuperators were needed to raise the temperature of the natural gas plus flue gas mixture enough to allow reforming. The schematic in Figure A1 indicates the direction of flows in the setup. Burner No. 1 burns natural gas to simulate hot flue gas exiting a real furnace; the flue gas then exits the U-tube and transfers heat through two recuperators to reform the fuel. Downstream of the recuperators, part of the flue gas is added to the natural gas for reforming.

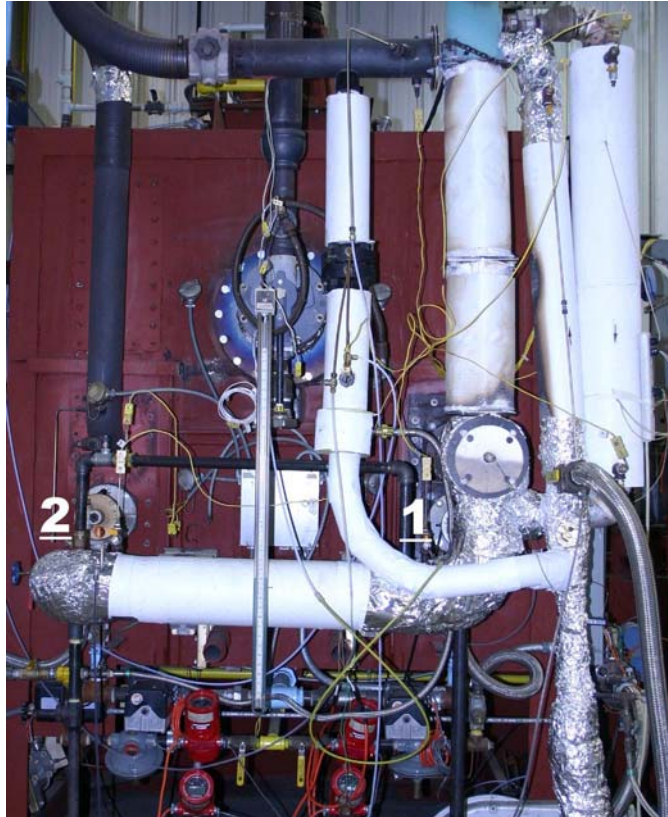


Figure A6. Laboratory Setup with Burner No. 1 Firing Natural Gas

The following parameters were estimated during the test:

- temperature of the exhaust gas
- inlet and outlet temperatures of the reforming mixture
- composition of exhaust gas
- composition of natural gas
- composition of the reformed fuel
- natural gas flow rate for reforming
- exhaust gas flow rate for reforming

Instruments used in the laboratory tests are listed in Table A1. A Horiba portable gas analyzer was used to measure flue gas composition, with house gas composition presumed constant. The house gas composition was sampled once on three different days, analyzed in GTI's chemical laboratory by ASTM D1945-96(01), and the sample average was used for calculations. The Varian micro gas chromatograph was used to measure the composition of reformed fuel at the reformer outlet. Temperature data was collected periodically by the data acquisition system attached to the furnace.

Table A1. Instruments Used

Measurement Device	Measured parameter
Horiba PG-250 portable gas analyzer	Flue gas composition just before exhausting
Varian CP 4900 gas chromatograph	Reformed fuel composition at the reformer outlet
Laboratory gas chromatograph	Natural gas composition over three days
K-type thermocouples	Temperature at various locations in the process
Sierra mass flow meters	Natural gas flow rate and air flow rate
U-tube manometer and orifice plates	Flow rate of process flue gas

Key TCRS process parameters are temperature and residence time of mixture inside reformer. The process temperature was measured by 2 thermocouples installed at the reformer inlet and reformer outlet. Other thermocouples (5) were installed inside each of recuperator's heat exchange tubes (with installation depth varied from 2.5" to 45.125"). Installation depth was measured from the outer surface of recuperator's flange (Figure A5)

Residence time was evaluated from reaction mixture flowrate, process temperature and recuperator's geometry (Figure A7).

The volume used for residence time estimation consisted of (1) recuperator's inlet plenum, (2) volumes of heat exchanging tubes and annuluses, (3) recuperator's outlet plenum and (4) outlet pipe from recuperator to flare (straight horizontal insulated pipe in Figure A6).

Volumes of reformer's components were estimated as follows:

Reformer's inlet plenum: 94.7 in³
 HX tubes and annuluses: 202.0 in³
 Reformer's outlet plenum: 38.6 in³
 Outlet pipe from reformer to flare: 325.3 in³

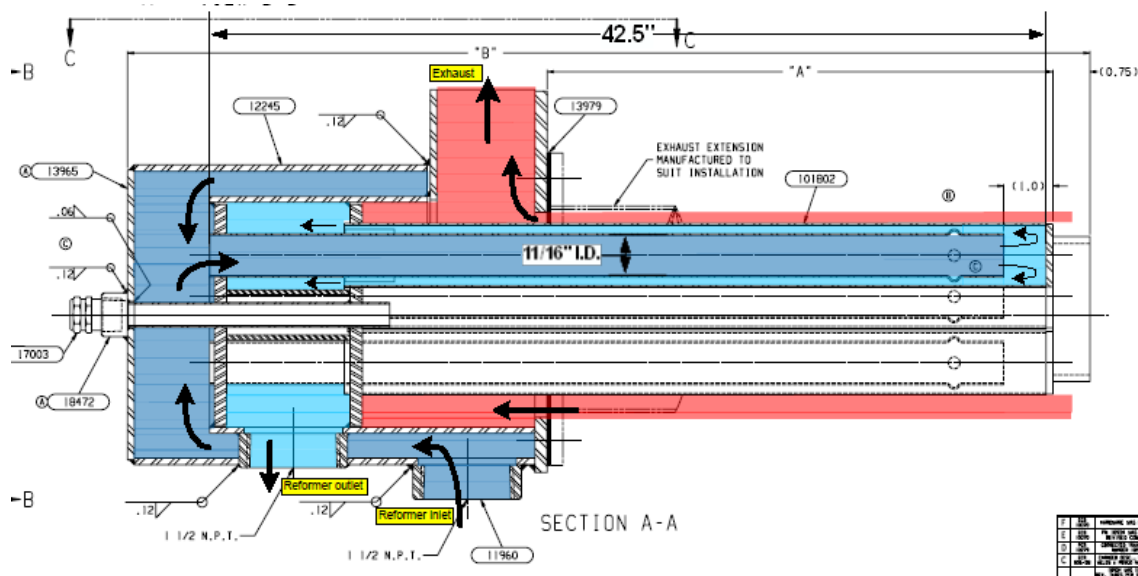


Figure A7. Recuperator/Reformer Geometry

Based on total volume and process temperature 1200°F, reaction mixture flowrate through reformer should be 136 acfh (43.4 scfh) to achieve a residence time of 10 s. Assuming flue gas (FG) to natural gas (NG) ratio of 3.5, flowrates of FG and NG should be 33.7 scfh and 9.6 scfh correspondingly.

From the shakedown tests, it was found that, due to low gas flowrate in the reformer, temperature distribution in the reformer is very uneven, except temperature inside HX tubes and annuluses. Typical values are shown in Table A2. Thermocouple in tube 1 is inserted at 3" from outer reformer flange, so it actually measures temperature in the inlet plenum (see Figure A4). Based on the measured results, due to low temperature in reformer plenums and outlet pipe, only the volume inside HX tubes should be considered to calculate the residence time.

Tests 1 through 7 shown in the table were conducted without any inserts in the reformer tubes. Tests 8 and 9 (two last columns in Table A2) were conducted with the metal mesh inserted into heat exchange tubes (Figure A4) of the recuperative reformer. In all the tests except test No.6 the average reforming temperature in reformer tubes was maintained approximately the same in the range of 1205°F-1228°F. The average reforming temperature in the test No.6 was 1504°F.

Results and Discussion

Hydrogen content in the reformed fuel can be used for qualitative analysis of the TCRS efficiency and reforming reactions rates. As we can see from Table A2 there is low hydrogen content in the reformed fuel when the residence time is lower than seven seconds (tests No.1 and No.3). Increasing the residence time to thirteen seconds allows achieving more hydrogen content

in the reformed fuel (tests Nos. 2, 3, 4, 5, and 7) which is evidence of higher fuel reforming rate and higher TCRS efficiency. It is obvious that the reforming rate is higher at higher reforming temperature (test No. 6).

Metal mesh in the heat exchange tubes of the reformer promotes the reforming reactions and leads to higher hydrogen content in the reformed fuel (test Nos. 8 and 9). Thus, hydrogen content in the reformed fuel is increased from ~3.8% (test No. 4) to ~9% (tests Nos. 8 and 9) when the mesh was inserted into the tubes.

Based on the obtained results we can conclude that the residence time in the reformer should be at least seven seconds or higher. Extended metal surface should be used in the reformer to promote the reforming reactions. This can be done by increasing the heat transfer surface area of the reformer or putting inserts in the reforming fuel flow.

Table A2. Test Results

Test #			1	2	3	4	5	6	7	8	9
Test date			11/11/2010	11/11/2010	11/11/2010	11/11/2010	11/23/2010	12/3/2010	12/3/2010	12/20/2010	12/20/2010
Temperatures	Hot flue gas (pos.4, Figure 1)	F	1313	1345	1354	1361	1327	1668	1397	1231	1237
	Preheater inlet mixture	F	548	512	522	518	623	738	710	587	583
	Tube 1, pos.5	F	813	765	766	700	823	965	834	711	716
	Tube 2, pos.6	F	1223	1224	1219	1227	1230	1519	1235	1229	1233
	Tube 3, pos.7	F	1237	1240	1236	1240	1231	1536	1232	1247	1249
	Tube 4, pos.8	F	1142	1153	1150	1154	1131	1403	1127	1153	1154
	Tube 5, pos.9	F	1218	1237	1240	1245	1231	1558	1316	1271	1274
	Outlet mixture (pos.3, Figure 1)	F	589	496	434	406	617	756	588	495	464
	HX average	F	1205	1214	1211	1217	1206	1504	1228	1225	1228
Flue gas composition	CO ₂	%	9.57	9.75	9.7	9.77	9.61	9.91	10.33	11.62	11.58
	O ₂	%	5.1	4.8	4.86	4.78	5.07	3.03	2.22	0.62	0.72
	NO	ppm	57.3	52	53	53.2	66	92	50	60.8	61.1
FG flowrate		scfh	34	16	16	12	12	12	12	12	12
NG flowrate		scfh	9.6	3.2	6	3.2	3.3	3.3	3.3	3.3	3.3
residence time in reformer		s	5.6	12.9	11.3	16.5	15.9	13.7	15.6	16.3	16.3
Residence time in HX tubes		s	3.5	8.0	7.0	10.2	9.8	8.4	9.6	10.0	10.1
Reformed fuel composition	H ₂	%	0.20	0.61	1.22	3.76	4.8	25.4	18.09	8.91	9.07
	O ₂	%	0	0	0	0	0	0	0	0	0
	N ₂	%	58.33	59.74	44.89	45.00	47.58	41.21	50.54	52.21	50.24
	CH ₄	%	34.09	32.07	47.95	44.25	42.49	17.87	19.83	31.31	33.38
	CO	%	0.00	0.00	0.00	1.04	0.8	7.05	6.38	2.04	2.18
	CO ₂	%	7.36	7.55	5.90	5.93	6.33	8.08	5.25	6.76	6.51
	C ₂ H ₆	%	0.02	0.04	0.03	0.03	0.33	0	0.14	0.38	0.39

Appendix B

48-Hour Durability Test – Graphical Results

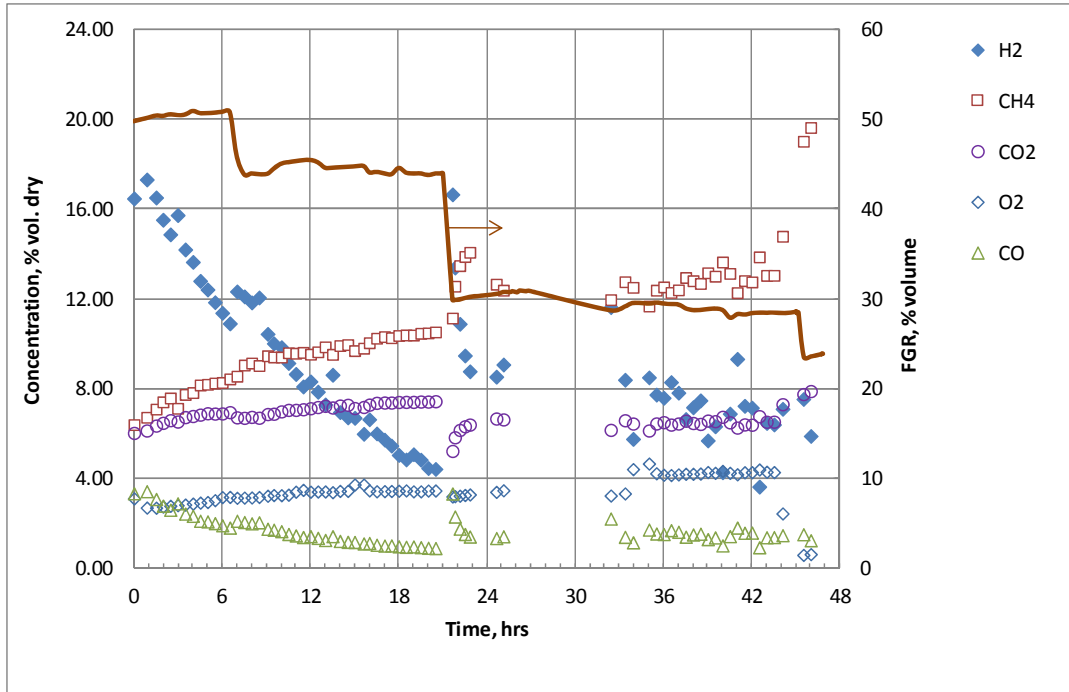


Figure B1. Reformed Fuel Components (dry) – 48 Hours

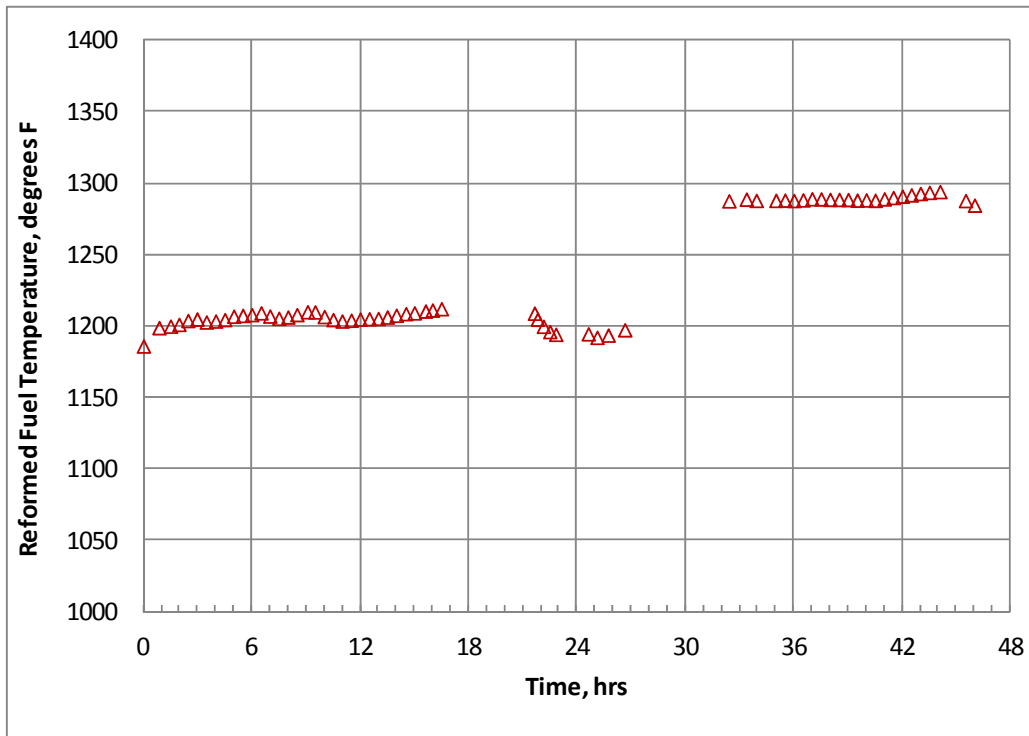


Figure B2. Reformed Fuel Temperature – 48 Hours

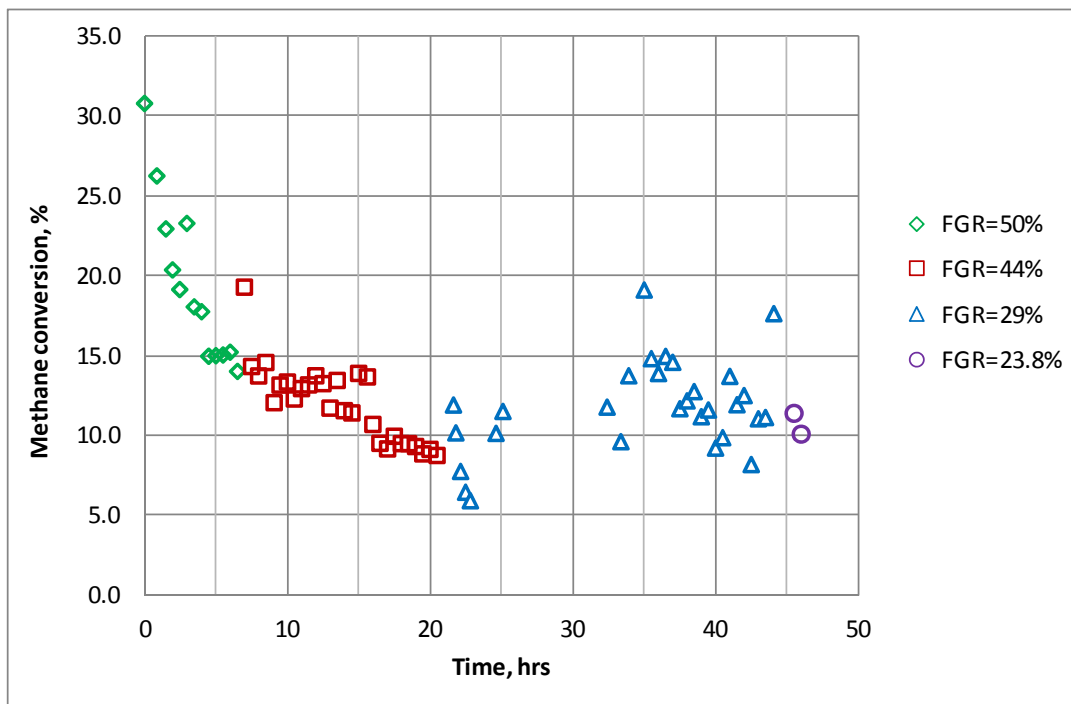


Figure B3. Methane Conversion Rate -48 Hours

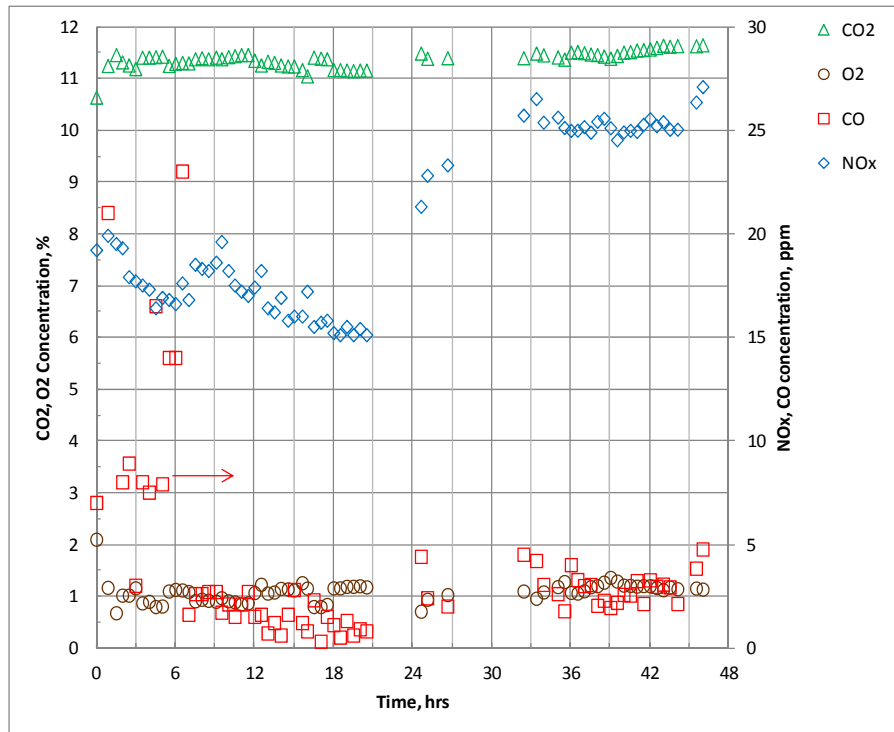
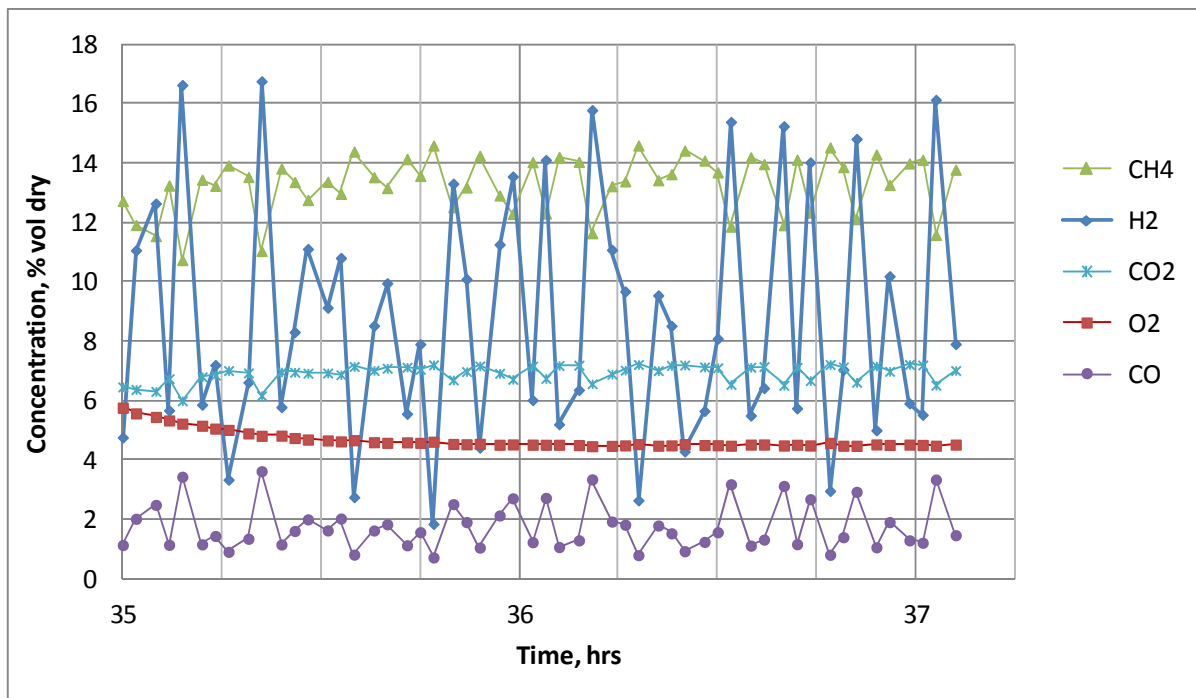


Figure B4. Furnace Exhaust Gas Composition (dry) – 48 Hours



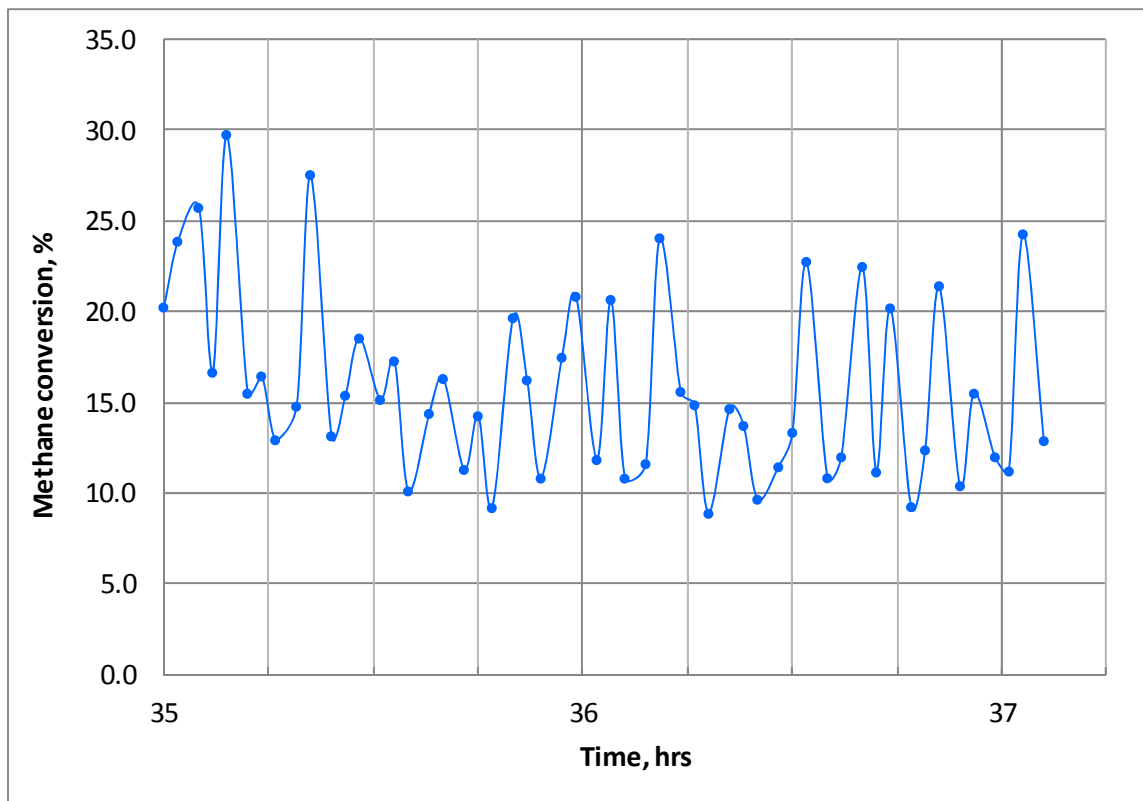
**Figure B5. Instability of Reformed Fuel Composition
(dry, FGR = 29% of Total Furnace Flue Gas)
During a Portion of the 48 Hour Test**

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Note in Figure B5 that CO directly tracks H₂; and CH₄ inversely tracks both CO and H₂ which is indicative that the existing instrumentation was accurately detecting and measuring the varying levels of reforming that were occurring. Instrumentation/internal sampling was lacking to detect and measure the extent of the reactions/kinetics that were occurring within the recuperative reformer.

Figure B6 is complementary to that of the data shown in Figure B5 in that the methane reforming with increases and decreases in hydrogen, carbon monoxide and methane. The methane reforming rate was previously defined in this report and is restated here.

$$\text{Reforming process completeness} = \frac{(\text{measured methane conversion rate})}{(\text{calculated equilibrium methane conversion rate})}$$



**Figure B6. Instability of Methane Conversion Rate
(FGR=29% of Total Furnace Flue Gas)
During a Portion of the 48 Hour Test**

Appendix C

Extended Phase II TCR Testing----Proposed Scope of Work, Schedule and Budget

Proposed Scope of Work

Task 1 - Forensic Analysis -- Conduct independent short-duration simulation modeling of the Lab Recuperative Reformer process over a range of operating conditions.

- 1) Develop a system of equations describing chemical reaction kinetics within the Lab Recuperative Reformer
- 2) Conduct Sensitivity Analyses of the process that includes the following independent variables: (Flue gas temperatures supplied; components of flue gas supplied; carbon to steam ratios; physical volume of the RR; and a range of specified space velocities consistent with a range of specified reforming mixtures.).

Task 2 - Conduct iterative testing of current Lab RR under both broader and new test conditions.

- 1) Maintain <1% xs oxygen in furnace flue gasses to RR.
- 2) Eliminate potential ambient air leakage into flue gas for mixing--Remove ID fans and reconfigure piping for direct connection of flue gas to mixer. Retain/ revise RFG cooler.
- 3) Prepare two FG sampling ports---1) Inlet of water cooler; 2) and inlet of gas mixer.
- 4) Maintain positive pressure on flue gas side of Lab TCR during operation of TCRS.
- 5) Use two Horiba analyzers: one to measure flue gas components at exit of furnace; and one to sample oxygen readings at various points in the system and for back up.
- 6) Use two GCs; one to simultaneously sample 1 – 3 intermediate points from within the RR; and one to sample reformed fuel supplied to burner. Both units to be set for minimum dwell times, i.e., 1- 2 minutes sampling.
- 7) Arrange for 4 – 6 grab samples of reformed fuel to be taken each morning of operation, until GC calibrations are confirmed, for GTI analytical lab to provide same-day results.
- 8) Variables to be varied in re Test Matrix
 - a. Flue gas temperature entering RR---- set at 1700°F, hold and capture all data; set at 1800°F, hold and capture all data;
 - i. FG:NG ratio for each of the four FG inlet temperatures above----set at ~10, hold and capture all data; set at ~5, hold and capture all data; and set at ≤ 2 , hold and capture all data.
 - ii. Reform with steam in lieu of flue gas----use high/mid/low ratio points
 - b. Preheat natural gas with electric heater to achieve FG+NG or STM+NG temperatures into RR of 600°F; 700°F and 800°F.

Task 3 - Depending on test results, devise any necessary changes to the RR design to sustain CH₄ Reforming Rate (MRR) and implement changes.

- 1) Confer with TTC on implementation of changes
 - a. Return RR to TTC for changes
 - b. Return RR to GTI and reinstall

Task 4 - Conduct iterative testing of modified/retrofitted Lab RR under varying test conditions to confirm sustained CH₄ Reforming Rate (MRR).

Proposed Schedule and Budget

Tasks	2012 - Months						Budget (\$) by Task
	1	2	3	4	5	6	
1 Modeling Simulation	■						\$ 41,058
2 Iterative testing of Lab RR	■	■	■				155,090
3 Implement changes to RR design			■	■			94,409
4 Re-conduct iterative testing / Prepare Report					■	■	89,308
Total							\$379,864

Appendix D

Energy and Emissions Reductions and Cost-Benefit Effects on Steel Industry Reheat Furnace Population in Using TCRS

The efficiency step change validated in this Phase I work of increasing the reference reheat furnace (recuperated) thermal efficiency to 61% from 48% requires an air recuperator capable of producing preheated air at a temperature of 1700°F. The implications of the metallurgical requirements of the heat transfer tubes; the additional engineering considerations with respect to piping, valving, etc. due to 1700°F preheat temperature would, in GTI's opinion preclude this option being selected over that of a TCRS due to the increased cost of even higher grade tube materials and reduce longevity of the heat exchanger due to higher tube wall temperatures.

CAPEX and estimated Return on Investment: The cost estimates were established on the basis of three major categories that would make up retrofitting costs. Estimated Direct Costs, Estimated Indirect Costs and Estimated Contingencies and Fees for 1) The base case of retrofitting a reheat furnace with a recuperative system, and; 2) The three-unit TCRS that was optimized and validated in Phase II.

For retrofitting an ARS on the reference reheat furnace without recuperation, the estimated installed cost was approximately \$4.3 million, the annual fuel savings were \$9.2 million, the simple payback was 4 months and the ROI was \$31 million (NPV at a 7% discount rate over six years of cash flow).

In summary, for retrofitting the optimally designed three-unit TCR System on the reference reheat furnace without recuperation the estimated installed cost was approximately \$18.3 million, the annual fuel savings were \$14.3 million, the simple payback was 15 months and the ROI was \$38 million (NPV at a 7% discount rate over six years of cash flow).

For retrofitting the optimally designed three-unit TCR System on the reference reheat furnace with recuperation the estimated installed cost was approximately \$14 million, the annual fuel savings were \$14.3 million, the simple payback was 12 months and the ROI was \$6.4 million (NPV at a 7% discount rate over six years of cash flow).

The fixed natural gas cost for the above estimates was assumed as a nominal \$9 per million Btu.

It should be noted that no consideration was given for the complete or partial reuse of the existing recuperator of the reference steel reheat furnace which would further improve return on investment. There may be further reductions in the CAPEX as close inspection of **Error!**

Reference source not found. reveals that estimated Indirect Costs and Contingency and Fees are over 50% of the Installed cost of the optimized three-unit TCRS. We believe that these estimates are conservative and can be managed such that indirect costs and contingencies/fees can be reduced considerably.

Reduced Carbon Footprint and Oxides of Nitrogen: The reference recuperated furnace was estimated as producing 185 pounds of carbon dioxide per ton of steel reheated and 0.8 pounds of oxides of nitrogen per ton of steel reheated. Retrofitting the reference reheat furnace with the three-unit TCRS would reduce the emissions intensities of carbon dioxide and oxides of nitrogen to 146 pounds per reheated ton and 0.54 pounds per reheated ton respectively. On an annualized basis the metric tons of CO₂ and NO_x produced by the three-unit TCRS reheat furnace would be an estimated 111,000 metric tons and 406 metric tons representing reductions of 30,000 metric tons per year of CO₂ and 200 metric tons per year of NO_x.

*Imputing results to 50% of the U.S. steel reheat furnace population:*¹ In order to benchmark the potential to the retrofitting of steel reheat furnaces, an estimated projection for frame-of-reference purposes only is included as summarized below. To remain conservative, 50% of the recuperated furnace population (approximately 80 steel reheat furnaces) was assumed as the steel reheat furnace market in the U.S.

The energy intensities (EIs) of each of the three steel segments (See table at the right), Integrated, Minimills and Converter/Specialty that making up the Flat and Long product plants

Imputed Future Fuel Usage Reductions – TBtu per Year

Flat/Long Plants		Recuperated Furnaces-MMBtu per Ton	
<i>Recuperated</i>	<i>TCR</i>	<i>Current</i>	<i>Future</i>
Integrated		1.18	0.93
Minimills		1.11	0.88
Converter/Specialty		1.40	1.11

representative composite or aggregate of EIs of the furnace populations within each segment. The approach employed was to scale back the energy intensities (composite energy intensities) of recuperated furnaces in three steel segments (see) on a prorate basis using the percent improvement in thermal furnace efficiency of the base case recuperated furnace in this study when equipped with a three-unit TCRS recognizing that the level of precision in making these projections will not be as high as in this report for the reference furnace studied since the furnaces making up 50% of the U.S. population were not studied in detail as the reference steel reheat furnace was for this study.

¹ 2003 North American Hot Strip & Plate Mill Market Study (*Customized Final Report*), prepared for Gas Technology Institute by AIM MARKET RESEARCH

Finally, below are two tables summarizing the imputed reductions in energy consumption and emissions reductions for the ultimate equipping/retrofitting of 50% of the recuperated furnace population with TCRS. The reductions were projected by the imputed future energy intensities shown in the table above.

Imputed Future Fuel Usage Reductions – TBtu per Year

Plants	Current	Future	Savings
Flat and Long	TBtu	TBtu	\$-mill
Integrated	26.6	21	50.4
Minimills	16.0	12.6	30.6
Converters/Specialty	2.9	2.3	5.4
Totals-cum	45.6	36	86.4

Imputed Emissions Reductions – Tons (metric) per Year

Emissions	Current	Future	Reductions
CO ₂	3,300,000	2,500,000	700,000
NO _x	14,000	9,500	4,700

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Executive Summary

Phase II work (See **Appendix A**) involved the physical testing of a laboratory scale Recuperative Reformer (RR) to validate predicted performances from the feasibility study in Phase I (26% fuel reduction). Although the testing was a successful validation (21% fuel reduction mode), a technical issue arose, namely a Methane Reforming Rate (MRR) roll off or non-sustaining of the methane reforming rate. GTI's preliminary conclusions were that mechanism(s) producing the methane reforming rate decrease were not entirely known or understood and the chemical kinetics that are triggering the roll off mechanism and/or other mechanisms needed to be evaluated.

GTI proposed an interim plan (Task 2.5, Extended TCR Testing) as a means to uncovering the reason or reasons for not sustaining satisfactory Methane Reforming Rate (MRR) of the laboratory scale recuperator reformer (RR). The project partners reviewed the proposal and recommended the proposed work extension proceed and suspension of Phase III pending further review of the results of the Task 2.5 work. AISI formally authorized GTI to proceed with Task 2.5 on July 12, 2012.

The scope of work included Forensic Analysis by the University of California Davis (UCD) to conduct reforming studies using bench scale reactors (See **Appendix B**). In the aggregate, although the study/analyses did produce partial reforming results [and roll offs], the conclusions by UCD as to the possible source(s) of the roll off were insufficient to be utilized as a solution.

In parallel with the UCD analyses, and to augment any useful findings from UCD, GTI carried out internal brainstorming and arrived at an alternative reason for the MRR roll off. After additional review of Phase II test results, GTI theorized that an important aspect of sustained reforming rate to be focused on was the temperature/heat flux profile across the RR (mixture reforming temperature within the reformer) that was governed to a large extent by the temperature of the furnace flue gasses (thermal energy necessary to support satisfactory endothermic reforming) entering into the reactor, i.e., the MRR was temperature/heat flux dependent to a greater extent, in addition to residence time and heat transfer surface areas within the reactor, than previously considered.

Temperature Threshold Tests (TTT) were carried out at several different levels of flue gas temperature. Tests using 1875°F and 2000°F furnace exhaust gas temperature over six to eight hour periods each with temperature profiles across the recuperative reformer measured. These tests resulted in sustained MR Rates without roll off. Additional longer-duration testing was done over a broader range of furnace exhaust gas temperatures: From 1650°F, to 1750°F, and up to 1875°F to test repeatability, with and without external preheating of natural gas. These series of tests substantiated that given the design of the laboratory scale recuperative reformer, appropriate temperature profiles across the recuperative reformer sustained MR Rates at furnace exhaust gas temperatures over a range of 1750°F to 2000°F.

The key conclusions reached were that the current design of the laboratory recuperative reformer satisfactorily supports Methane Reforming Rates over a temperature range that matches that of a

large number of the steel reheat furnace population during normal production periods that produce exhaust gases within these temperature ranges.

On the basis of these successful sets of TTT measured results that demonstrated a design that can capably be scaled up, GTI recommends consideration of three options for a Phase III field experiment.

Option 1: Production furnace ~250 MMBtu/h

Option 2: Production furnace ~100 - 200 MMBtu/h

Option 3: Production furnace ~50 - 100 MMBtu/h

Specific details of each option are provided in **Appendix C**.

Phase II – Task 2.5 – Extended TCR Testing Program

Work Scope

The extended program consisted of primarily four tasks based on expected outcomes at that time.

Task 1 - Forensic Analysis (GTI Noncatalytic Reforming Parametric Study)—Conduct a parametric study (bench-scale testing) to simulate/evaluate the GTI pilot-scale Lab Recuperative Reformer performance for a range of operating conditions.

Task 2 - Conduct iterative testing of current Laboratory recuperative reformer (RR) under both broader and new test conditions.

Task 3 - Depending on test results, devise any necessary changes to the RR design to sustain Methane Reforming Rate (MRR) and implement changes.

- Confer with Thermal Transfer Corp. (TTC) on implementation of changes
- Return RR to TTC for changes
- Return RR to GTI and reinstall

Task 4 - Iterative testing of modified Lab RR under varying test conditions to confirm sustained MRR.

During subcontract negotiations with UCD, GTI carried out two supplementary tests of the current lab pilot scale reformer as described below.

GTI Supplementary Base Line Tests

While subcontract negotiations were carried out between GTI and UC Davis, it was decided to carry out supplementary Base Line tests of the laboratory reformer by reconfiguring the piping network as explained below to augment the previously measured results. The diagram below represents the test set up during last tests during Phase II (Durability Testing) (See **Appendix A**) prior to this reconfiguring.

As can be seen in the schematics [see Figure 1 and Figure 2] below GTI reconfigured the pipework of the lab TCR set up to minimize infiltration/exfiltration of ambient air and reconducted tests to further evaluate any changes in the Methane Reforming Rate (MRR).

The first series of tests involved Steam/Natural Gas reforming which consisted of three separate tests conducted on August 15, 16, and 17 2012—MRR roll off was again observed.

A second series of tests involved Flue Gas/Natural Gas reforming which consisted of three separate tests conducted on September 11 and 12, 2012—MRR roll off was also observed.

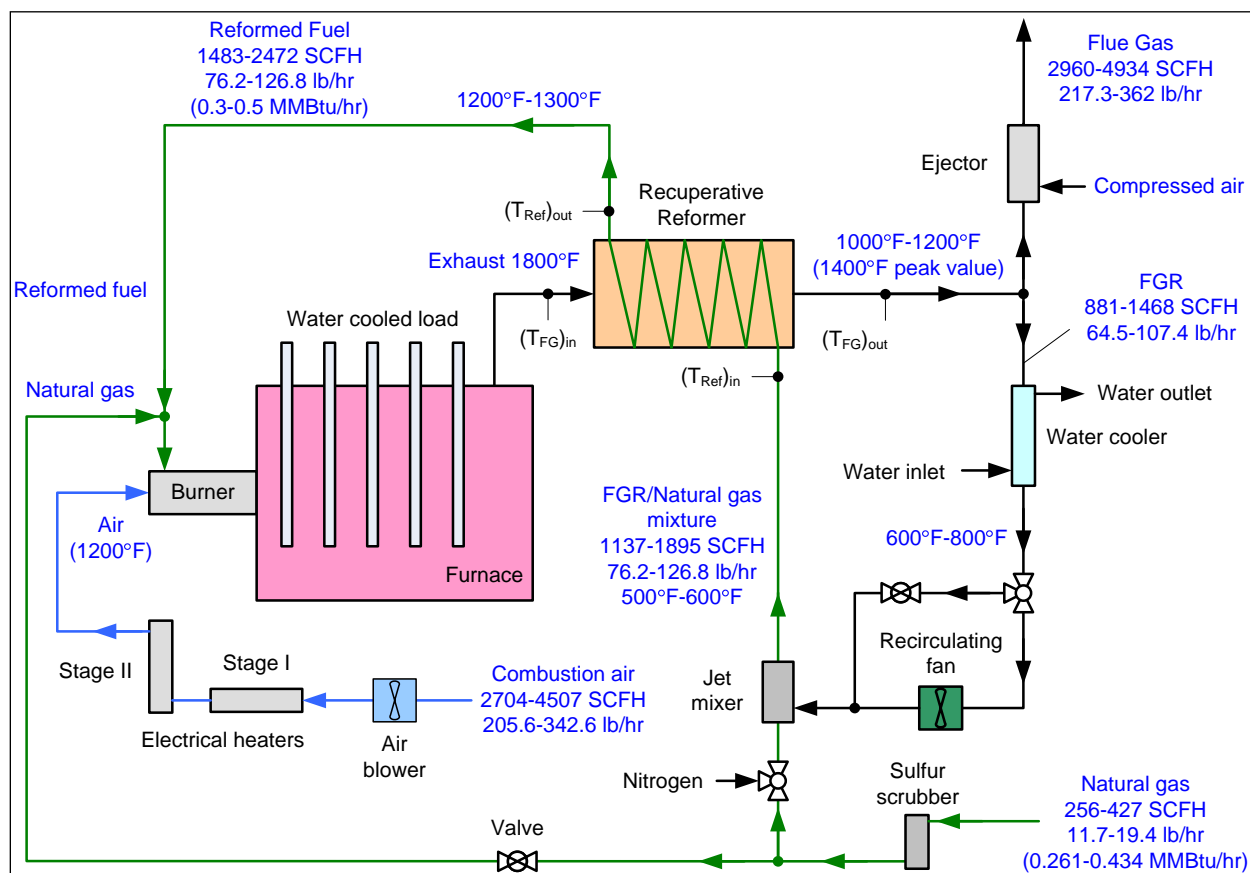


Figure 1. Diagram of TCR Lab Unit Prior to Task 2.5

Steam – Natural Gas Reforming Supplementary Test

GTI conducted tests using the Lab Scale TCR system with steam/natural gas reforming to obtain additional information for determining a solution to the reforming rate degradation issue. Analysis of the results indicated a stable reforming rate during 1-2 hours in the beginning of each test then slow retarding of the reforming rate. In the middle of the reformer section and at the exit of the reformer there were periodical fluctuations of the reforming rate. See Figure 2 for a schematic of the test setup, and Figure 3 for photos of the test setup. A summarization of key observations and conclusions follows.

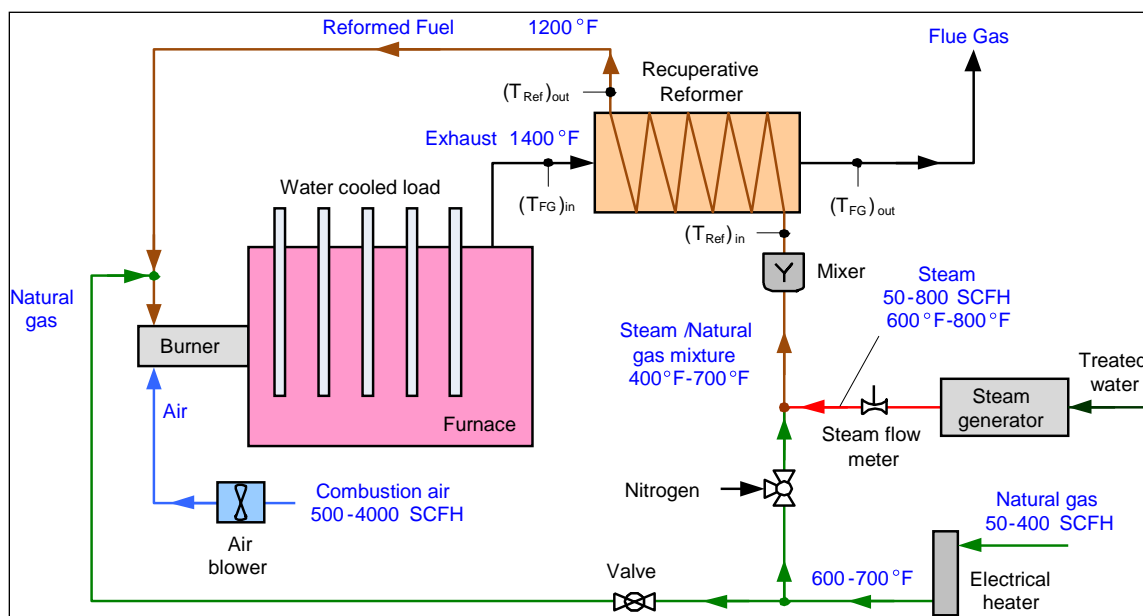


Figure 2. Diagram of Reconfigured TCR Lab Unit for Steam/Methane Reforming Test



Figure 3. Physical Arrangement of the Equipment Components

Description of the Process

The goal of the laboratory evaluation was to conduct a baseline test for steam/natural gas reforming to augment the previous and last durability tests and to ascertain whether steam instead of flue gas had any effects that would change the measured test results. Three successive days of testing were conducted with test conditions as described below. During day one and day two the steam natural gas ratios were 3:1 and on day three the ratio was changed to 1:1.

Experimental Conditions

- Natural gas composition (volume, dry): H₂=1%, CO₂=0.89%, O₂=0.04%, N₂=1.15%, CH₄=95.4%, C₂H₆=2.09%, other minor hydrocarbons totaled ~1%; S (total) =5.11 ppm.
- Flue gas composition (% volume): CO₂ = 8.9%; H₂O = 17.3%; N₂ =72.1%; O₂ = 1.7%.

Test Matrix

The test matrix for the steam/natural gas reforming supplementary base line test is shown in Table 1.

Table 1. Test Matrix for Steam/Natural Gas Reforming Tests in August 2012

Dates of Tests - 2012	8-15	8-16	8-17
Total time on reforming, hours	2	5.3	6.3
Natural gas temperature, °F	600	600	650
Natural gas flow rate to reformer, SCFH	75	67	178
Furnace exhaust temperature, °F	1710	1604	1596
Flue gas exit temperature, °F	862	970	949
Steam temperature, °F	600	800	800
Steam flow rate, SCFH	225	201	175
Steam/Carbon mole ratio	3:1	3:1	1:1
Reforming fuel temperature at preheater inlet, °F	365	386	457
Reforming fuel average temperature, °F	1106	1243	1240

Results, Discussions, and Conclusions

The natural gas sulfur scrubber was not used during these tests. Thermodynamically, the test conditions with a steam/carbon mole ratios >1.5 and average reforming temperatures ~1200°F are characterized by non carbon formation in the reforming reactions. Thermodynamics predicts that carbon deposition should occur at steam/carbon ratios <1.5.

The reforming rate was stable for 1-2 hours at the beginning of each test and slowly degraded for the remainder of the test. It was suspected that had testing continued the reforming rate would have degraded as per previous test results in Phase II durability testing.

The following reformed fuel compositions (dry basis) were measured in the tests:

- *Steam/carbon=3:1* (August 15 -16):

- At the outset, the reformed fuel constituents were measured as:
H₂=46.67%, O₂=0%, N₂=0%, CH₄=37.23%, CO=4.45%, CO₂=10.31%,
C₂H₄=0.07%, C₂H₆=1.22%, C₃H₈=0.07%.
- In 5 hours, the reformed fuel constituents were measured as:
H₂=43.47%, O₂=0%, N₂=0%, CH₄=42.45%, CO=3.66%, CO₂=8.76%,
C₂H₄=0.11%, C₂H₆=1.48%, C₃H₈=0.08%.
- *Steam/carbon=1:1* (August 17):
 - At the outset the reformed fuel constituents were measured as
H₂=36.32%, O₂=0%, N₂=0%, CH₄=50.71%, CO=6.11%, CO₂=5.17%,
C₂H₄=0.05%, C₂H₆=1.56%, C₃H₈=0.09%.
 - In 5 hours, the reformed fuel constituents were measured as:
H₂=33.09%, O₂=0%, N₂=0%, CH₄=56.53%, CO=5.42%, CO₂=2.48%,
C₂H₄=0.21%, C₂H₆=2.14%, C₃H₈=0.14%.

Figure 4 below shows H₂ and CH₄ levels in the reformed fuel (dry basis) together with the furnace exhaust gas temperature (T_{exh}) and reforming fuel average temperature (T_{ref}) during the test of August 17, 2012 with steam/natural gas reforming.

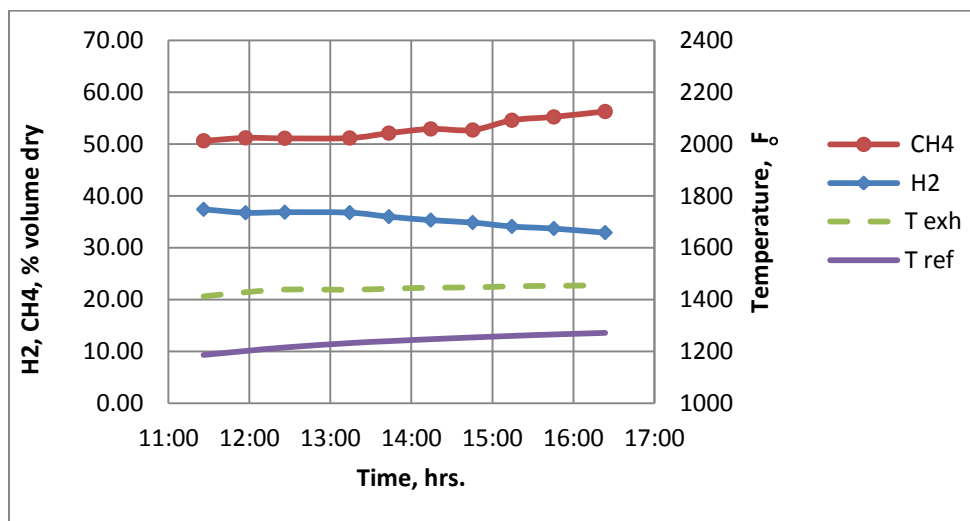


Figure 4. Reformed Fuel Compositions at Reformer Outlet; T_{exh} – Furnace Exhaust Gas Temperature; T_{ref} – Reformed Fuel Average Temperature; and Steam/Methane Volume Ratio = 1:1, 17 August 2012

This experiment for natural gas reforming with steam was conducted as a baseline test for further experimental study. Test results indicated initial stable reforming with a high methane reforming rate (~47% and ~37% hydrogen yield) during the first 2 hours of the test before roll off began to occur.

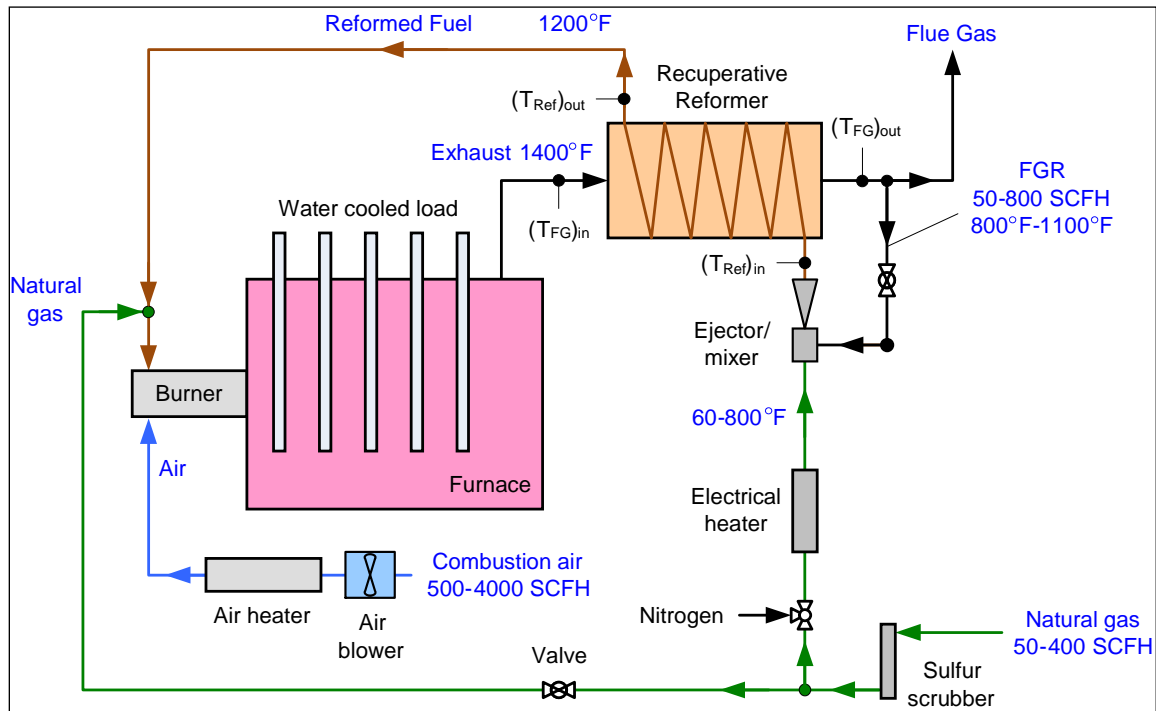
Flue Gas – Natural Gas Reforming Supplementary Test

Similar to the steam/natural gas reforming tests, GTI conducted a testing program, using the Lab Scale TCR system with flue gas/natural gas reforming to obtain further additional information for determining a solution to the reforming rate degradation issue. Analysis of these results

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indicated a stable reforming rate during 1-2 hours in the beginning of each test then slow retarding of the reforming rate. In the middle section and the exit of the reformer there were periodical fluctuations of the reforming rate. See Figure 5 for a schematic of the test setup, and Figure 6 for photos of the test setup. A summarization of key observations and conclusions follows.



**Figure 5. Lab-Scale Thermochemical Recuperation System (TCRS)
Simplified Flow Diagram for Flue Gas/Natural Gas Reforming**

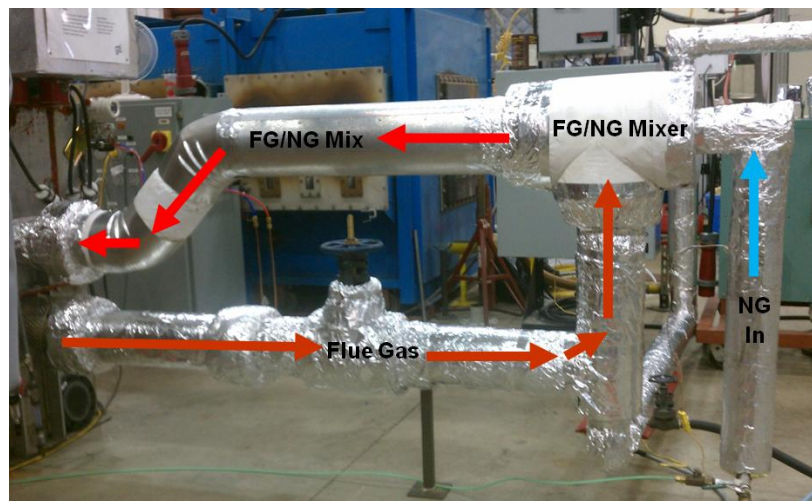


Figure 6. Reconfigured TCR Lab Unit Piping for Flue Gas/Natural Gas Reforming Tests

Description of the Process

The goal of the laboratory evaluation was to conduct a baseline test for flue gas/natural gas reforming to augment the previous and last durability tests and to ascertain whether reduced air infiltration had any effects that would change the measured test results. The primary differences between previous test setups and this test set up was that the FGR fan and the flue gas cooler was removed from the flue gas piping system. Two successive days of testing were conducted with test conditions as described below. During day one the natural gas was not preheated; during day two the natural gas was preheated to 750°F.

Experimental Conditions

- Natural gas composition (typical, % volume, dry): At the outset, the reformed fuel constituents were measured as: $\text{CO}_2=0.9\%$, $\text{O}_2=0.04\%$, $\text{N}_2=1.15\%$, $\text{CH}_4=95.4\%$, $\text{C}_2\text{H}_6=2.09\%$, other minor hydrocarbons totaled $\sim 1\%$; S (total) = 5.11 ppm.
- Flue gas composition was measured as: (typical, % volume): $\text{CO}_2 = 9.19\%$; $\text{H}_2\text{O} = 17.95\%$; $\text{N}_2=71.96\%$; $\text{O}_2 = 0.9\%$ (wet); $\text{CO}_2 = 11.2\%$; $\text{N}_2=87.7\%$; $\text{O}_2 = 1.1\%$ (dry).
- Flue gas only (no steam) was used to reform natural gas.
- The natural gas was desulfurized for this supplemental test. The reason for opting to use the sulfur scrubber was to eliminate a possible (negative or positive) influence of sulfur on the test results.

Test Matrix

The test matrix for the flue gas/natural gas reforming supplementary base line test is shown in Table 2.

Table 2. Test Matrix for Flue Gas/Natural Gas Reforming Test, September 2012

Dates of Tests - 2012	9-11	9-12	9-12
Total time on reforming, hours	6	2	4
Natural gas temperature, °F	68	68	750
Natural gas flow rate to reformer, SCFH	182	187	185
Furnace exhaust temperature, °F	1500	1510	1530
Flue gas exit temperature, °F	780	770	815
Flue gas flow rate, SCFH	600	615	610
Flue gas/Natural gas ratio, SCFH/SCFH	3.3:1	3.3:1	3.3:1
Reforming fuel temperature at preheater inlet, °F	265	230	500
Reforming fuel average temperature, °F	1250	1250	1270

Results, Discussions, and Conclusions

Thermodynamically the test condition with a flue gas/natural gas volume ratio $\sim 3.3:1$ corresponds to the ratio of (steam plus carbon dioxide)/methane $\sim 1:1$. At this ratio and reforming temperature $\sim 1200 - 1300^\circ\text{F}$ the reforming process is characterized by an inclination for carbon formation in the reforming reactions. This may or may not be critical for the reforming process in a non-catalytic reformer since formed carbon primarily affects catalysts.

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The reforming rate (or hydrogen yield) was stable during 1-2 hours at the beginning of each test and slowly degraded and started fluctuating (Figure 7 through Figure 9 below) for the remainder of the test.

Reforming fuel compositions were measured at the inlet, midpoint, and outlet of the reformer. Test results showed that the fuel compositions at the middle point of the reformer were very close or equivalent to the compositions at the reformer outlet (Figure 8 and Figure 9) for both cases (preheated and non-preheated natural gas).

As an example, the following reformed fuel compositions (dry basis) were measured in the tests:

- Reformer inlet: $H_2=0\%$, $O_2=1.85\%$, $N_2=64.18\%$, $CH_4=24.64\%$, $CO=0\%$, $CO_2=7.38\%$, $C_2H_4=0\%$, $C_2H_6=1.17\%$, $C_3H_8=0.09\%$, $C_4H_{10}=0.67\%$.
- Reformer outlet: $H_2=21.37\%$, $O_2=0.04\%$, $N_2=51.22\%$, $CH_4=15.72\%$, $CO=5.86\%$, $CO_2=5.44\%$, $C_2H_4=0.01\%$, $C_2H_6=0.33\%$, $C_3H_8=0.02\%$, $C_4H_{10}=0$.

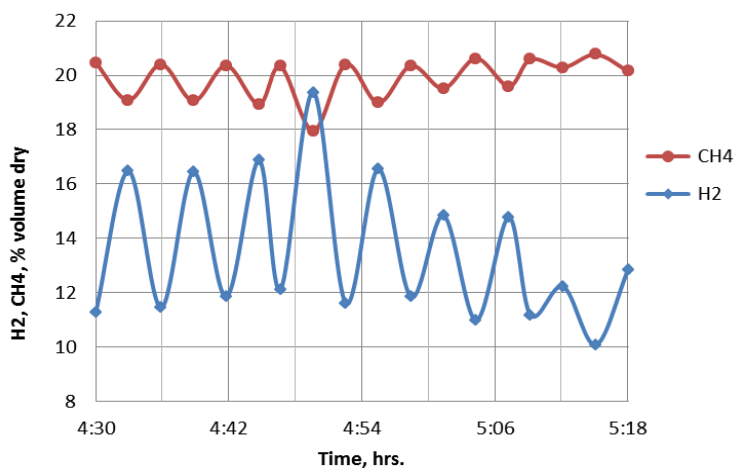


Figure 7. Reformed Fuel Composition at the Reformer Outlet for Baseline Test (Non-Preheated Natural Gas), 11 September 2012

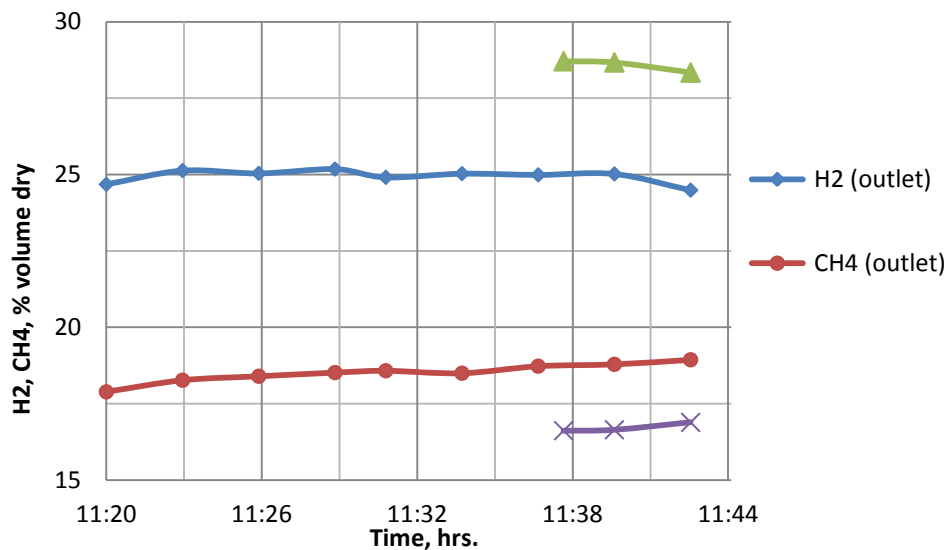


Figure 8. Reformed Fuel Composition at Outlet and Mid Point of the Reformer for Baseline Test (Non-Preheated Natural Gas), 12 September 2012

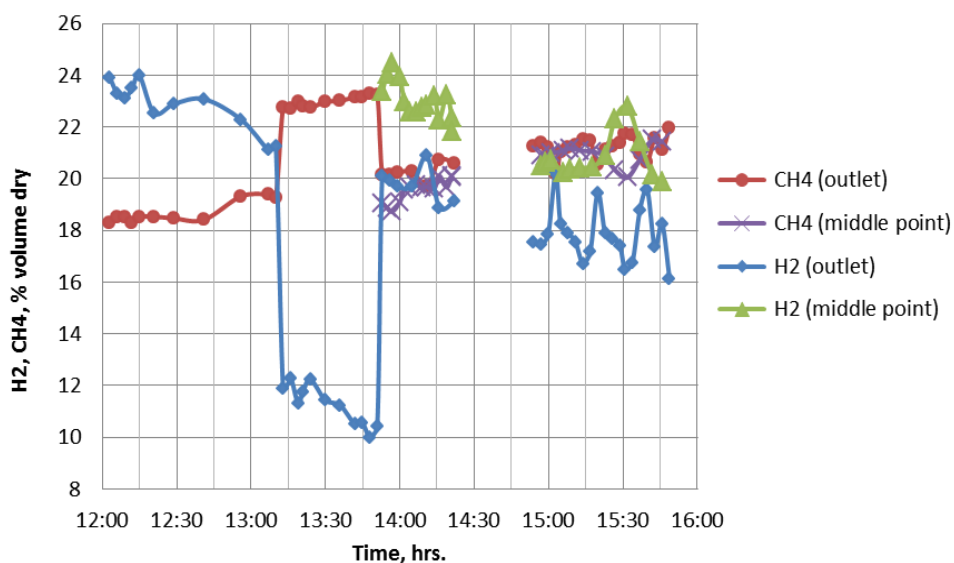


Figure 9. Reformed Fuel Composition at Outlet and Mid Point of the Reformer for Baseline Test (Preheated Natural Gas), 12 September 2012

Additional Comments in re Graphical Events

In the preheat tests of 12 September 2012 shown in Figure 9 there are four distinct time periods (totaling four hours) where step changes occurred. Reforming was started at 10:15 with ambient natural gas and continued to 11:40 when natural gas preheating was initiated.

Time period one

Between 12:00 and 13:14 the %CH₄ increases by about 2% and the %H₂ decreases by about 2%. Indicates that the methane reforming rate is starting to be retarded under these test conditions.

Time period two

At 13:15 there was a large step change in %CH₄ and %H₂ levels. It was not immediately evident as to what transpired. At 13:10 the natural gas temperature set point was set at 700°F. It was subsequently determined that prior to this reset the natural gas heater was not functioning properly.

Time period three

The gap between 14:22 and 14:52 was due to GC sample line issues.

Time period four

As can be seen the level or rate %H₂ (proportional to MRR) was periodically unstable and was slowly beginning to reduce.

University Of California Davis Hydrogen Production and Utilization Lab - Forensic Analysis

UC Davis' subcontract negotiations were completed on 21 Dec 2012 necessitating a No Cost Time Extension by GTI that was subsequently approved by AISI. The Forensic Analysis began shortly after 1 January 2013.

The following is a brief summarization of the testing and analysis performed by UCD as reported by Professor Dr. Erickson and his lab team leader Kevin Uy - Graduate Student Researcher. The UC Davis report in its entirety is attached in **Appendix B**.

For example-purposes, UCD was provided test parameters and with an initial Test Matrix by GTI as shown in Table 3:

- Steam to carbon ratio (including CH₄ and CO₂) at 0.4, 0.46 and 0.62 in the flue gas/natural gas mixture.
- GHSV at 360 hr⁻¹, to 720 hr⁻¹ (Corresponds to residence time of 10 sec. and 5 sec. respectively)
- Reforming gas mixture at 1200°F (To be varied from 1200°F to 1300°F average bed temperature.)

Table 3. Test Settings

Setting No.	Specialty Mixture	Water	Natural Gas
	SLPM	ml/min	SLPM
1, 2	7.84	1.39	3.4
3, 4	15.69	2.79	6.79
5, 6	8.17	1.45	3.00
7, 8	16.33	2.9	6.01
9, 10	8.85	1.57	2.17
11, 12	17.7	3.14	4.34

The UCD reactor study operating conditions are represented in Figure 10.

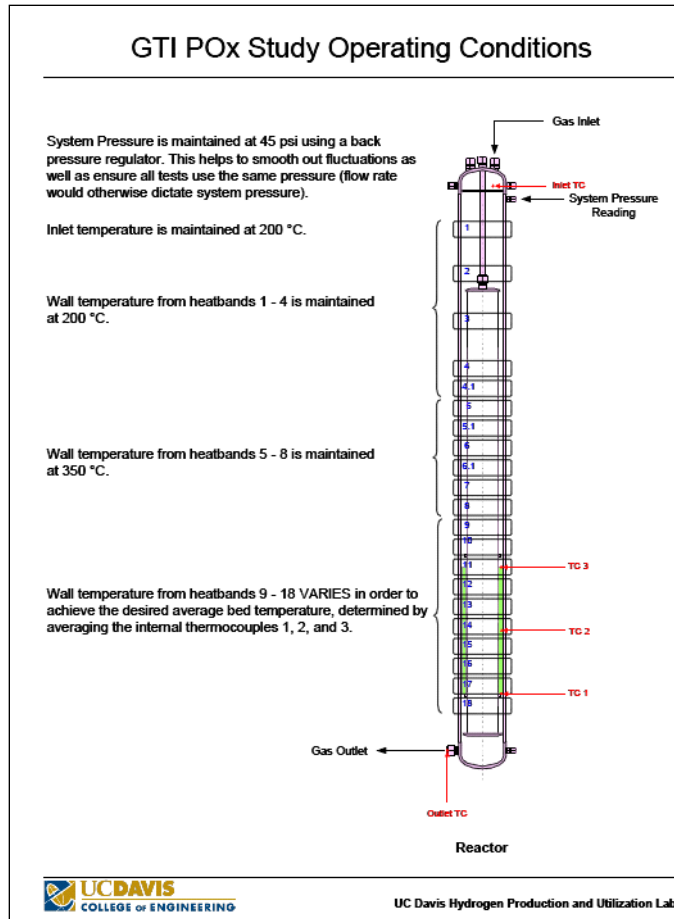


Figure 10. General Operating Conditions

Equipment

UCD fabricated two bench scale reactors for their analysis. One reactor was specified as the Baseline Reactor (see Figure 11 below).

The second reactor (Inserts Reactor) was identical to the Baseline Reactor but contained inserts made from the same alloy (800H) that made up the heat transfer/reaction surfaces of the GTI pilot scale Lab Reformer (see Figure 12 below). The reasoning behind equipping the reactor with the 800H alloy was to evaluate what effect, if any, this metallurgy had in re surface reactions that could be deleterious to sustaining MRR.

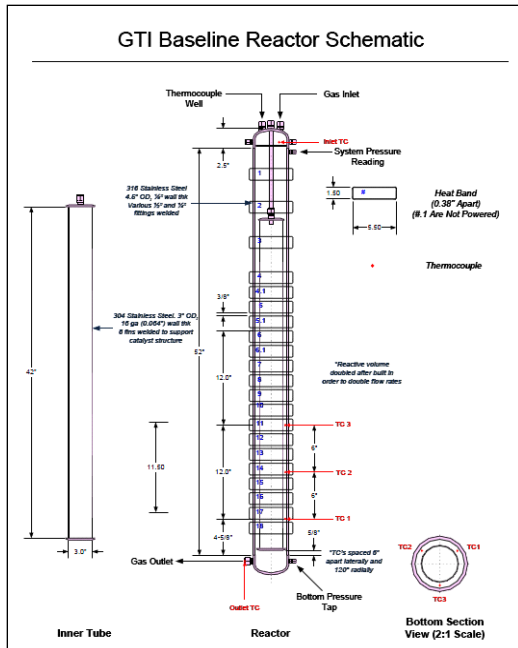


Figure 11. First of Two Forensic Test Reactors at UC-Davis to Examine the Cause of the Methane Reforming Rate (MRR) Fall Off
(Unit shown fully instrumented without insulation.)

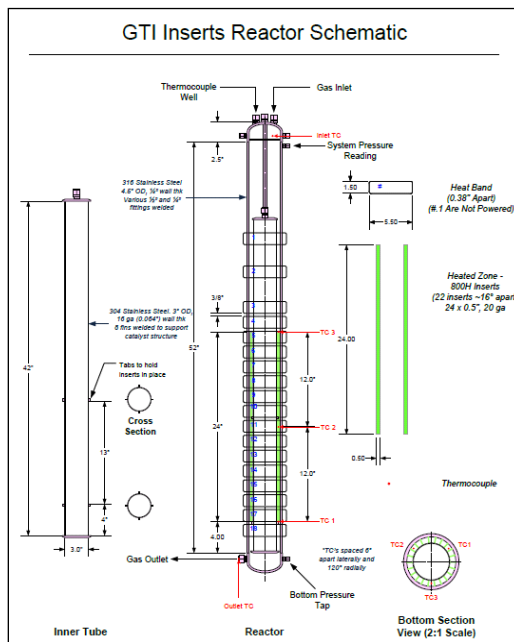


Figure 12. Second of Two Forensic Test Reactors at UC-Davis with High Nickel Alloy Inserts (800H) Installed to Examine the Cause of the Methane Reforming Rate (MRR) Fall Off
(Shown in Construction with only Lower Inserts Installed.)

Summarization of UCD Tests

Below is a condensed chronology of tests that UCD carried out with both reactors. Each test is summarized based on test; results including numerous conference calls between GTI and UCD testing staff in an attempt to adjust the testing protocols as was necessary. The full details are included in the UCD report in **Appendix B**.

Baseline Reactor Tests No. 1 (3-4-13) and No. 2 (3-6-13) – No Hydrogen Yielded

Baseline Test 1 Results

The first test wave did not yield data indicating reforming occurred. Average reactor temperatures ranged from 648°C - 705°C; at two space velocity levels of 360h⁻¹ and 720h⁻¹. For the second wave of tests, per GTI advisements, the average reforming temperature was increased (ranged from 705°C - 764°C) and test data was collected for two space velocity levels 360h⁻¹ and 180h⁻¹. For this wave, preliminary-raw test data indicated some reforming including some phenomena to be analyzed. This test was inconclusive.

Baseline Test 2 Results

UCD achieved 760 °C bed temperature at 180h⁻¹ and were producing small amounts of hydrogen. All points were maintained 3:1 S:C ratio. The introduction of air did not have an effect on hydrogen production. This test was inconclusive.

Inserts Reactor Tests No. 1 (3-12-13) – No Hydrogen Yield – and No. 2 (3-14-13) Part 1 – No Apparent Hydrogen Yield – and Part 2 – Apparent Hydrogen Yield

Inserts Test No. 1

All points performed were at 3:1 Steam:Carbon (S:C) ratio and used only steam and methane. A slight increase in hydrogen production was observed over the baseline reactor, however this increase was very small and negligible. This test was inclusive.

Inserts Test No. 2.1

The points from previous Baseline Test were repeated (high S:C ratio with varying amounts of O₂%). Points 2 and 3 exhibited a “swinging” effect. The dipping H₂ values match the baseline test results (no H₂ produced). Each time the air flow rate was increased, the H₂ values would drop, stay flat and swinging would occur.

Inserts Test No. 2.2

For Test No. 2.2, UCD returned back to the final point from the 3-4-13 test. A large increase in hydrogen was observed, followed by a prolonged tailing off. It settled around 3%, whereas previous test settled at 3.4%. This was the first indication that Hydrogen was capable of being yielded. From that standpoint the test was somewhat conclusive.

Inserts Reactor Tests No. 3 (3-15-13) – Apparent Hydrogen Yield – and No. 4 (3-19-13) – Apparent Hydrogen Yield

Inserts Test No. 3

UCD performed what they termed a “reduction procedure” on the inserts reactor. Initially it was reported no reduction was taking place, as H₂ entered the reactor at 2.2% and exited at 2%. Upon reducing the nitrogen flowrates, however the reactor appeared to consume hydrogen. This condition was allowed to continue for a period of time. This led UCD to preliminarily conclude that reduction did in fact make a difference, and that the 800H inserts may be acting as a catalyst.

Inserts Test No. 4

UCD repeated Inserts Test No. 3, both with and without added hydrogen. A “reduction procedure” was conducted for four hours, next steam and methane were introduced. The hydrogen spike was replicated to nearly the same value. UCD preliminarily concluded that hydrogen does not contribute to propagating further reformation reactions.

Inserts Reactor Test No. 5 (3-20-13) – Apparent Hydrogen Yield (CH₄ on/off)

Inserts Test No. 5

GTI preliminarily conjectured that either CH₄ or CO could be deactivating the reactor surfaces and requested that UCD carry out a test where CH₄ was shut off for about 30 minutes. There was no rebound in H₂ yield indicating the CH₄ was not promoting deactivation.

Baseline Reactor Test No. 3 (3-20-13) – Apparent Hydrogen Yield (CH₄ On/Off)

UCD was directed to replicate the Inserts Test No. 5, using identical test conditions, with the Baseline reactor to rule out any 800H alloy effects.

A spike was seen very similar in magnitude and profile to that seen in the inserts reactor tests. These results suggested that previously seen spikes in hydrogen for the inserts reactor were not due to the presence of 800H inserts (Possibly gas-phase reactions and not surface based).

Baseline Reactor Test No. 4 (5-3-13) – Apparent Hydrogen Yield (CO On/Off)

The procedure followed was: For Test 1, the surface was activated with H₂ for one hour. The same percentage of CO was introduced for 30 minutes. Subsequently, steam and methane were added for one hour to observe hydrogen produced. For Test 2, was identical except CO was introduced at half the amount (with the other half as H₂).

Based on these results, it did not appear that CO had an effect on the reaction surfaces and the hydrogen produced as the spikes observed were very similar in magnitude and roll off to results previously observed.

Baseline Reactor Test No. 5 (5-17-13) – Apparent Hydrogen Yield (CO On/Off)

The purpose of this test was to mimic the reduction procedure, but replace hydrogen with methane and observe the results.

Reforming followed and a hydrogen spike very similar in magnitude and behavior to those previous was observed. It was noted, though, that a spike in carbon monoxide was also seen.

Summary of UCD Forensic Analysis

UCD was able to momentarily produce some semblance of reforming by virtue of hydrogen being yielded with and without the 800H inserts. Similar to the eventual roll off with the GTI lab unit, there was a roll off of MRR for each reactor. The UCD reactors rolled off within minutes of hydrogen being yielded whereas it was several hours before roll off occurred at GTI.

UCD determined it necessary to “activate” or “condition” the reaction surfaces during the course of testing by running hydrogen through the reactor for about 30 minutes prior to attempting reforming, and conjectured that either CH₄ or CO could be deactivating the reactor surfaces. The baseline line reactor outer shell is 316SS; and the inner tube is 304SS. 316SS contains 11-14% Ni; 304SS contains ~8% Ni. 800H alloy contains 30 - 35% Ni.

It is known that nickel and iron both can form carbonyls given suitable conditions. In the case of nickel a reaction with CO can produce Ni(CO)₄. It was decided to follow this reasoning because of the preliminary results by UCD.

Further tests with shutting off the CH₄ flow and turning on a CO flow in the middle of the test runs indicated that CH₄ and CO were not sources of deactivation.

UC Davis concluded that there was likely insufficient reforming temperature to promote and sustain methane reforming. Unfortunately, it was determined that the electrical heating system used to provide heat to the reforming mixture and subsequent gas mixtures would require replacement with another upgraded heat source which was not capable of being implemented within the time frame of the GTI project and further would have required securing additional funding.

GTI Temperature Threshold Tests

Background

In parallel with the work carried out by UC Davis, and to augment their work, GTI brainstorming produced an alternative reason for the methane reforming rate (MRR) roll off. GTI theorized that the highest furnace exhaust gas temperature (flue gas inlet to the GTI lab Recuperative Reformer) of 1740°F during Phase II testing produced a lower average reforming temperature below the temperature threshold for sustained MRR. Accordingly, GTI prepared to conduct Temperature Threshold Tests (TTT) at flue gas temperatures of 1875°F and 2000°F for a minimum of six hours each.

The consensus was that the thermal temperature profile across the reformer section of the GTI lab unit recuperative reformer was at a sufficient level to initiate a satisfactory MRR but not sufficiently high enough to maintain a sustained MRR over time causing the endothermic reforming to momentarily stop/diminish; which in turn causes the temperature to momentarily rise and fall; which in turn causes the endothermic reforming to stop/restart repeatedly which could be a part of or the explanation for why the tests were not sustaining MRR and the process becoming erratic as occurred during durability testing that concluded scheduled Phase II work.

It was reasoned that some combination of changes in the internal design such as a slight increase in surface area; reduction in space velocity; turbulent flow devices and possibly configuration changes would be necessary and should be revisited in the scale up design for a Phase III field experiment. Since the Task 2.5 schedule was constrained it was obvious that these design-steps would not be able to be carried out for the lab recuperative reformer design. The alternative was to consider elevating the temperature of the flue gas exiting the test furnace entering the lab recuperative reformer achieving the necessary temperature profile as an expedient alternative.

Description of the Temperature Threshold Test Procedure

Preceding results of laboratory testing of the lab Recuperative Reformer showed that reforming of natural gas with flue gas non-catalytically was accompanied by a gradual roll off in reforming rate which led to a reduction of the TCR system efficiency which was unacceptable. Additional tests were required to reveal causes of the deterioration process.

The goals of these temperature threshold tests would be to determine if a higher reforming temperature profile across the reformer would mitigate MRR roll off; and also to determine if there is a temperature threshold range whereby the reforming process is stable. The test setup (see Figure 13) was the same as that used in the September 2012 supplementary flue gas/natural gas baseline test. Three days of temperature threshold tests were conducted. The natural gas was preheated to 750°F on each test day.



- Natural gas composition (typical, % volume, dry): $\text{CO}_2=0.9\%$, $\text{O}_2=0.04\%$, $\text{N}_2=1.15\%$, $\text{CH}_4=95.4\%$, $\text{C}_2\text{H}_6=2.09\%$, $\text{C}_2\text{H}_4=0.002\%$, $\text{C}_3\text{H}_8=0.225\%$, $\text{i-C}_4\text{H}_{10}=0.025\%$, $\text{n-C}_4\text{H}_{10}=0.032\%$, $\text{i-C}_5\text{H}_{12}=0.009\%$, $\text{n-C}_5\text{H}_{12}=0.007\%$, $\text{C}_6\text{H}_{14}=0.016\%$, $\text{S}(\text{total})=5.11 \text{ ppm}$
- Flue gas composition (typical, % volume): $\text{CO}_2 = 9.19\%$; $\text{H}_2\text{O} = 17.95\%$; $\text{N}_2=71.96\%$; $\text{O}_2 = 0.9\%$ (wet); $\text{CO}_2 = 11.2\%$; $\text{N}_2=87.7\%$; $\text{O}_2 = 1.1\%$ (dry)
- Firing rate: 100,000 – 400,000 Btu/hr
- Flue gas/natural gas ratio: 0.75 – 5.0 (by volume)
- Furnace exhaust temperature: $1500^\circ\text{F} - 2000^\circ\text{F}$
- Preheated combustion air temperature: $800^\circ\text{F} - 1200^\circ\text{F}$
- Preheated natural gas temperature: $400^\circ\text{F} - 800^\circ\text{F}$
- Reforming fuel temperature (reformer outlet): $1200^\circ\text{F} - 1500^\circ\text{F}$
- Reformer space velocity: $180 \text{ h}^{-1} - 720 \text{ h}^{-1}$
- Flue gas only (no steam) was used to reform natural gas.
- Sulfur scrubber was used to desulfurize the natural gas

The test matrix for the flue gas/natural gas reforming temperature threshold test is shown in Table 4. Since the major goal of this laboratory evaluation was to determine if there is an average

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reforming temperature threshold whereby the reforming process is stable over time, the test matrix was intended for providing guidelines for testing subject to modification during the experiment.

Table 4. Test Matrix for Temperature Threshold Tests – May 2013

Dates of Tests - 2013	5-8	5-9	5-16
Total time on reforming, hours	6	6	6
Natural gas temperature, °F	750	750	750
Natural gas flow rate to reformer, SCFH	180	180	180
Firing rate *, MMBtu/hr	0.3-0.5	0.3-0.5	0.3-0.5
Combustion air temperature *, °F	800	800	800
Furnace exhaust temperature **, °F	1875	2000	1750
Flue gas exit temperature, °F	780	770	815
Flue gas flow rate, SCFH	600	615	610
Flue gas/Natural gas ratio, SCFH/SCFH	3.3:1	3.3:1	3.3:1
Reforming fuel temperature at preheater inlet, °F	265	230	500
Reforming fuel average temperature, °F	1300	1400	1500

*) Firing rate and combustion air temperature are variable w/r/t adjusted furnace exhaust temperature

**) Thermal Transfer Corp. confirmed metal temperature limits for the reformer as 2100°F for continuous service

Measurement parameters

- Combustion air, natural gas, flue gas recirculation flow rates and temperatures
- Furnace exhaust gas composition
- Flue gas composition at the exit of the reformer
- Flue gas/natural gas mixture composition at the reformer inlet
- Reforming fuel composition at the reformer middle
- Reformed fuel composition at the reformer outlet
- Reforming fuel characteristic temperature (Averaged temperature between middle and outlet of reformer)

Results, Discussions, and Conclusions

Temperature Threshold Test No. 1 — 8 May 2013

The flue gas produced by the test furnace and supplied to the recuperative reformer was held constant in terms of volumetric flow and temperature at 1875°F and was carried out for approximately 6.5 hours. Additionally, the flue gas to natural gas ratio was held constant, and therefore the residence time was constant, at a value of ~3.3 cubic feet of flue gas to 1 cubic foot of externally preheated natural gas. The methane reforming rate reached a sustained and steady value.

Temperature Threshold Test No. 2 — 9 May 2013

The flue gas produced by the test furnace and supplied to the recuperative reformer was held constant at 2000°F and was carried out for approximately 8 hours. The same flue gas to externally preheated natural gas ratio as in the first test was maintained. The methane reforming rate again reached a sustained and steady value.

Figure 14 below contains two sets of measured values from tests No. 1 and No. 2. For each set of flue gas temperature level entering the reformer section there are four associated components of the reformed fuel (hydrogen; carbon monoxide; methane and carbon dioxide). As can be seen, after an initial period of approximately two hours stable and sustained methane reforming rate was accomplished and roll off did not occur. The stable operation of the MRR essentially confirmed the supposition that a stable thermochemical reforming process is dependent on a satisfactory thermal temperature profile across the reformer section within the GTI lab recuperative reformer.

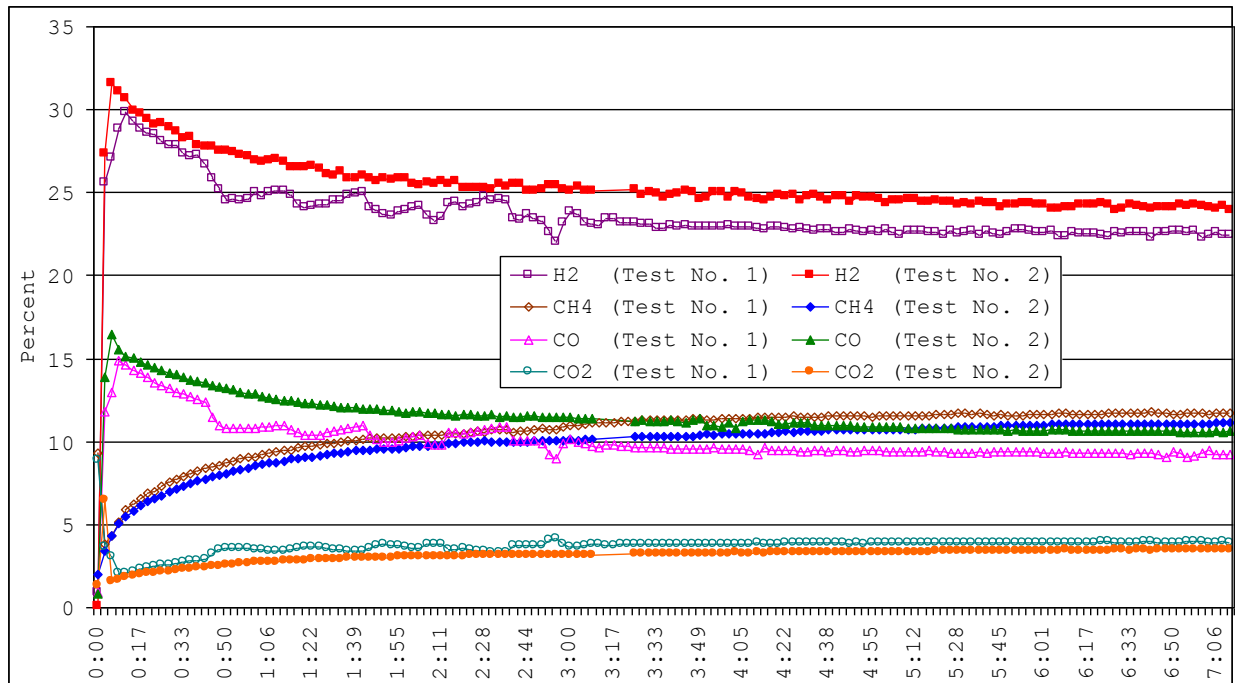


Figure 14. Composition of the Reformed Fuel at the Outlet of the Recuperative Reformer for Tests No. 1 and No. 2 (first 7 hours)

Figure 15 shows the average methane reforming rate for the last hour of testing from tests No. 1 and No. 2 along with the average species concentrations of the reformed fuel at the outlet of the recuperative reformer, average reforming mixture temperature, and the average flue gas temperature.

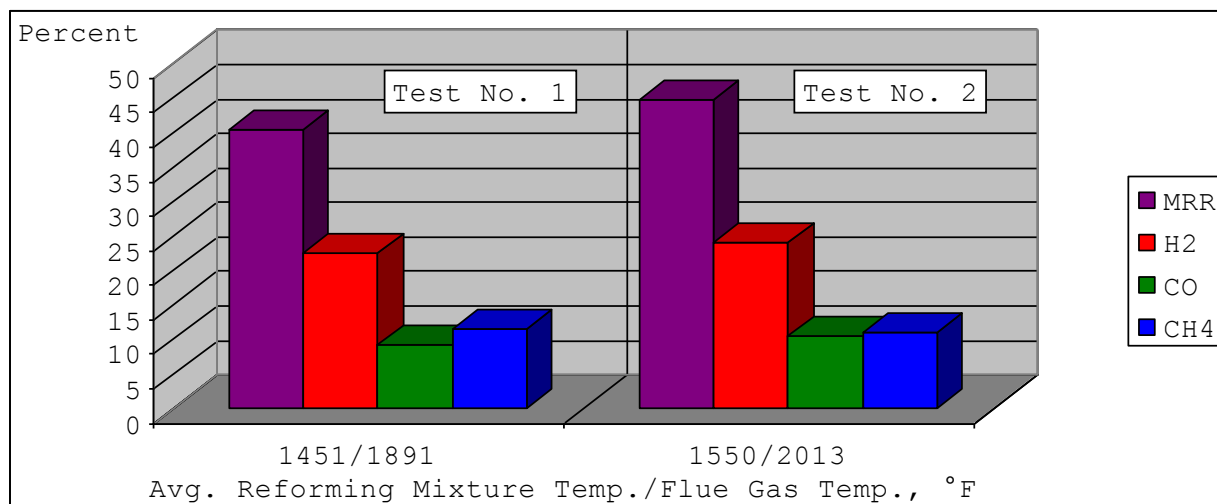


Figure 15. Average Methane Reforming Rate and Species Concentrations from the Recuperative Reformer for Tests No. 1 and No. 2 (last hour)

Figure 14 and Figure 15 show that the higher flue gas inlet temperature improved the reforming rate by maintaining a sufficient temperature profile across the reformer. Upon reporting these results to the AISI, it was recommended that in order to sufficiently prove the Methane Reforming Rate (MRR) fall off has been resolved, additional testing or another data point was required using the same conditions and procedures as the May 8th and 9th TTTs, to prove repeatability of the process, and specifically a TTT be performed at a lower flue gas inlet temperature level where the MRR roll off occurs to buttress that the internal reforming process is temperature sensitive.

Accordingly, four additional Temperature Threshold Tests were carried out, in the order shown below, to confirm repeatability and also to establish an approximate temperature profile that establishes a lower temperature threshold boundary for sustained MRR for this lab recuperative reformer.

Temperature Threshold Test No. 3 — 16 May 2013

The flue gas produced by the test furnace and supplied to the recuperative reformer was held constant in terms of volumetric flow and temperature at 1750°F and was carried out for approximately 6 hours. As was done previously, the flue gas to natural gas ratio was held constant, and therefore the residence time was constant, at a value of ~3.3 cubic feet of flue gas to 1 cubic foot of externally preheated natural gas. No roll off was measured.

Temperature Threshold Test No. 4 — 16 May 2013

The flue gas produced by the test furnace and supplied to the recuperative reformer was held constant in terms of volumetric flow and temperature at 1750°F and was carried out for approximately 1 hour subsequent to Test No. 3. As was done previously, the flue gas to natural gas ratio was held constant, and therefore the residence time was constant, at a value of ~3.3 cubic feet of flue gas to 1 cubic foot of ambient temperature natural gas. No roll off was measured.

Temperature Threshold Test No. 5 — 16 May 2013

The flue gas produced by the test furnace and supplied to the recuperative reformer was held constant in terms of volumetric flow and the temperature was ramped down to 1650°F subsequent to Test No. 4 and was carried out for approximately 1 hour. As was done previously, the flue gas to natural gas ratio was held constant, and therefore the residence time was constant, at a value of ~3.3 cubic feet of flue gas to 1 cubic foot of ambient temperature natural gas. Roll off occurred relatively immediately.

Temperature Threshold Test No. 6 — 16 May 2013

The flue gas produced by the test furnace and supplied to the recuperative reformer was held constant in terms of volumetric flow and the temperature was ramped up to 1875°F subsequent to Test No. 5 and was carried out for approximately 1 hour. As was done previously, the flue gas to natural gas ratio was held constant, and therefore the residence time was constant, at a value of ~3.3 cubic feet of flue gas to 1 cubic foot of externally preheated natural gas. The roll off was reversed and MRR was resustained.

The graph in Figure 16 contains four sets of information from tests No. 3 through No. 6. For each set of flue gas temperature level entering the reformer section there are four associated components of the reformed fuel (hydrogen; carbon monoxide; methane and carbon dioxide). As can be seen, after an initial period of approximately two hours, stable and sustained methane reforming was accomplished over the durations of tests No. 3 and No. 4. For Test No. 5 after ramp down to 1650°F there was a clear indication that MRR roll off was occurring and continuing; after ramp up to 1875°F in test No. 6 it was evident that MRR recovered and was stable.

Figure 17 shows the average methane reforming rate for the last hour of testing for tests No. 3, No. 4, No. 5, and No. 6 along with the average species concentrations of the reformed fuel at the outlet of the recuperative reformer, average reforming mixture temperature, and the average flue gas temperature.

Figure 16 and Figure 17 again illustrate that the higher flue gas inlet temperature improves the reforming rate by maintaining a sufficient temperature profile across the reformer.

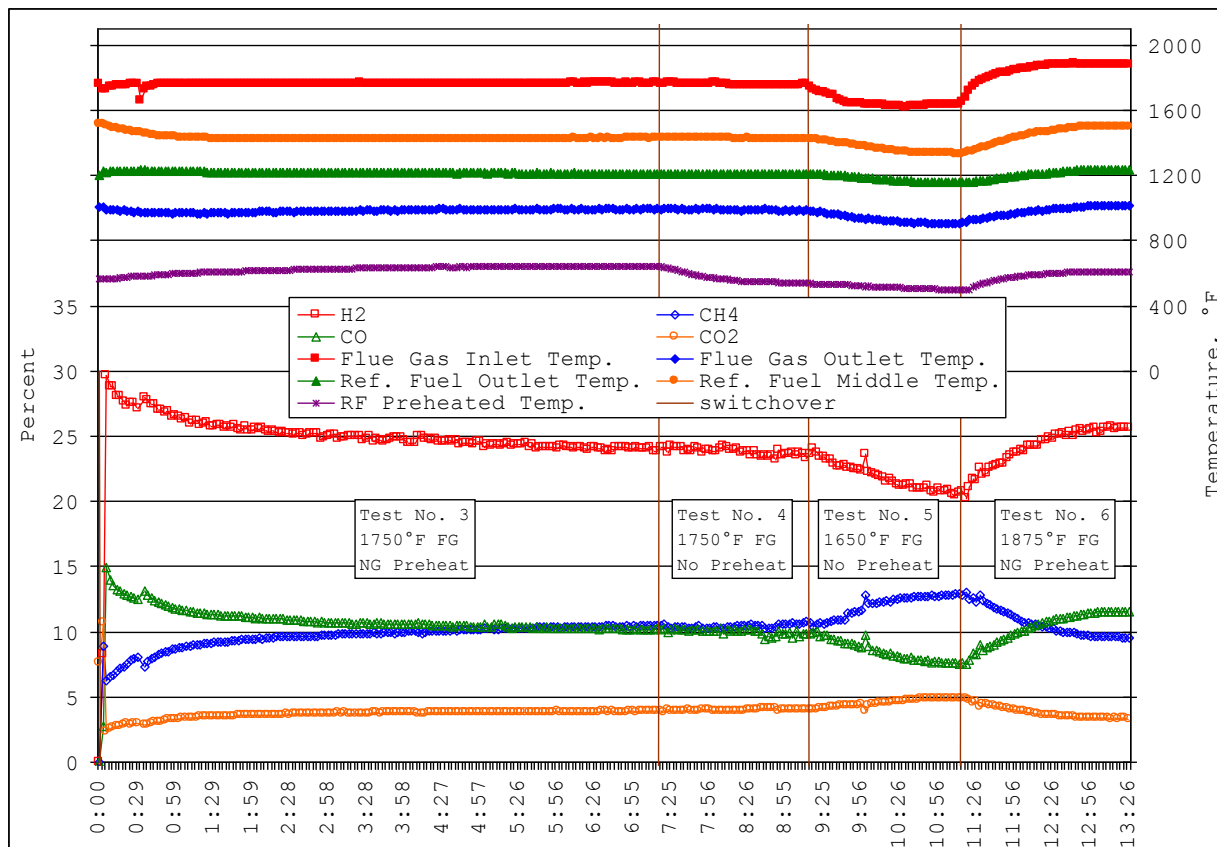


Figure 16. Composition of the Reformed Fuel at the Outlet of the Recuperative Reformer and Selected Temperatures for Tests No. 3, No. 4, No. 5, and No. 6

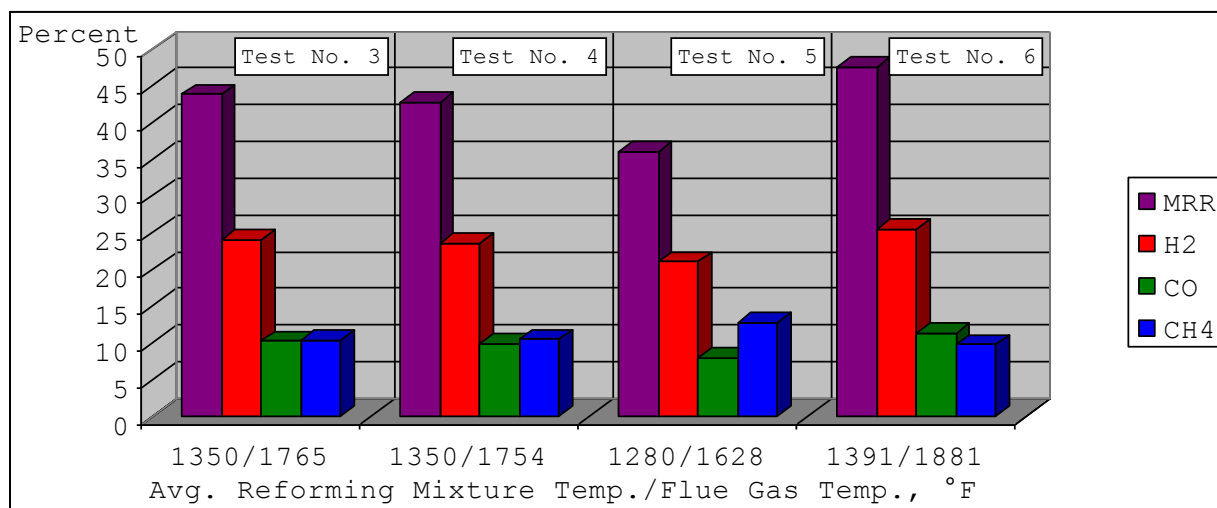


Figure 17. Average Methane Reforming Rate and Species Concentrations from the Recuperative Reformer for Tests No. 1 and No. 2 (last hour)

Comparison of Temperature Threshold Tests with 48 hour Durability Test – Measured Results

When the data from the Temperature Threshold Tests, which achieved a sustained methane reforming rate, is compared with that from the 48 hour Durability Test held in January 2012, which had declining or unstable methane reforming rates (see Figure 18), one can see in the first 21 hours of the latter that a high ratio of flue gas to natural gas in the reforming mixture, and lower flue gas and reforming mixture temperatures were not conducive to maintaining the hydrogen production and methane reforming rate. At 21 hours, when the ratio of flue gas to natural gas in the reforming mixture was reduced to near its theoretical ideal for partial reforming, but with the lower temperatures, the methane reforming rate during the Durability Test recovered initially, but then declined again before becoming erratic. At 29-33 hours, with an increase in the temperatures, there is an increase in the average hydrogen production, followed by a more steady average of hydrogen. During the last hour, with a further increase in temperatures, there is an increasing and less erratic level of hydrogen production.

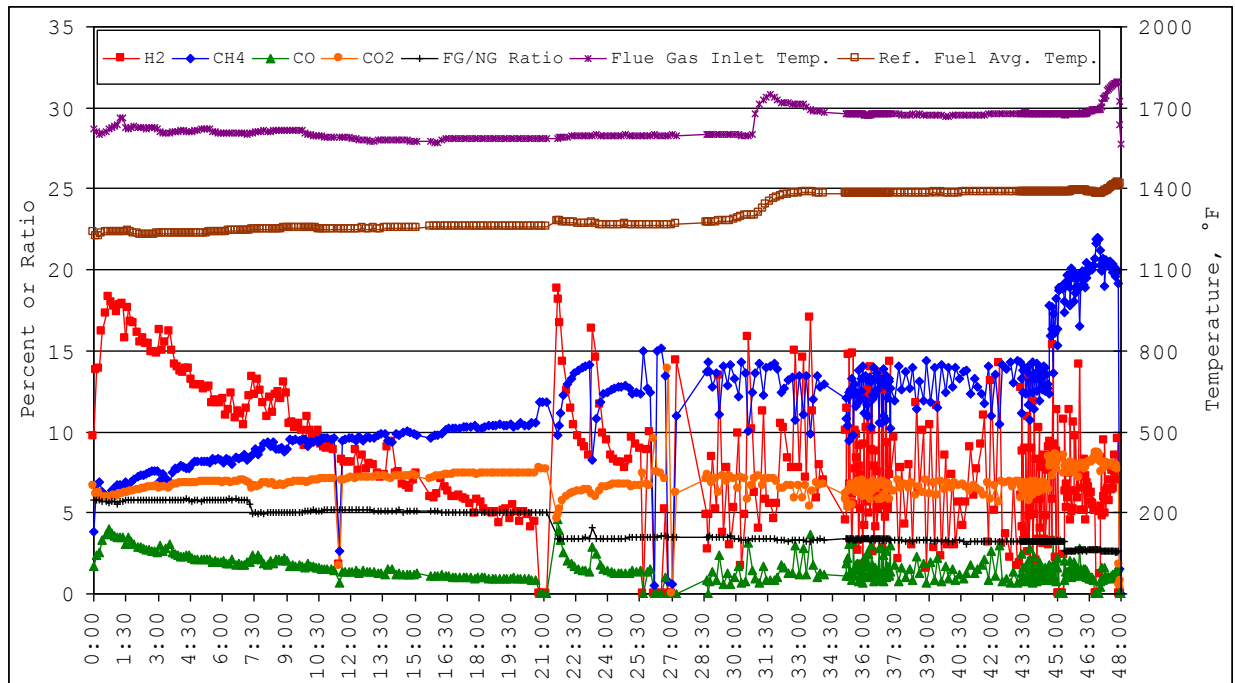


Figure 18. Average Methane Reforming Rate and Species Concentrations from the Recuperative Reformer for the Durability Test

Figure 19 shows the average methane reforming rate for the last hour or so of testing from the various test regimes of the 48 hour Durability Test along with average species concentrations of the reformed fuel at the outlet of the recuperative reformer, average reforming mixture temperature, and the average flue gas temperature. Only the data from the third regime, with the flue gas to natural gas ratio of 3.3, was steady (though erratic). The data from the first and second regimes were still declining, while the data from the fourth regime was still climbing.

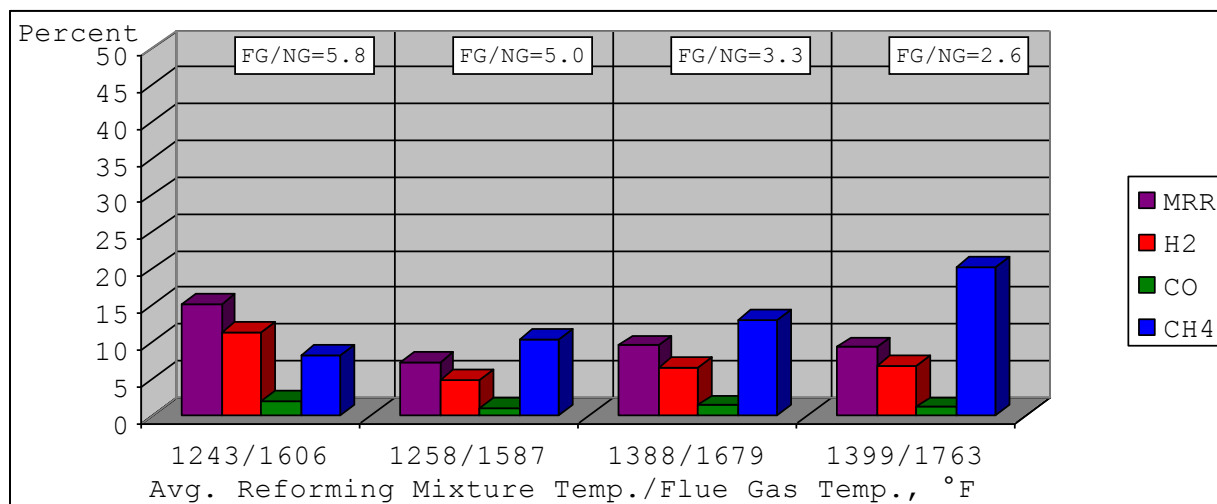


Figure 19. Average Methane Reforming Rate and Species Concentrations from the Recuperative Reformer for the Durability Test

Conclusions

The purpose of the above comparisons is intended to demonstrate that although the 48 hour Durability Test seemingly failed at that time to produce measured results that provided insight into the reason(s) for the MRR roll off and at times unstable operation, it is clear that had the understanding been formed at that time that the lab recuperative reformer was reforming-temperature-sensitive to a greater degree than appreciated, a simple elevation of flue gas temperatures would have yielded a sustained MRR as was shown in the TT Tests.

Consequently the end-conclusion is that temperature dependency has been affirmed but with temperatures within the recuperative reformer with higher criticality than the flue gas temperature entering into the recuperative reformer. GTI's further conclusion is that adjustments to the lab recuperative reformer design, given the three-heat exchanger-configuration remains a valid constraint, will be necessary to scale up to a field experiment capacity level. Design adjustment to the recuperative reformer meaning re-examining space velocity (residence time); heat transfer surface area plus other considerations so that a target "temperature profile envelope" within the recuperative reformer will be broad enough to perform satisfactorily in the field with varying flue gas exit temperatures from the majority of the reheat furnace population.

Based on the TT Tests confirming that MRR roll off has been mitigated, GTI anticipates that the three-module TCRS design will require design revisions(s) to the recuperative reformer. GTI believes that the core lab recuperative reformer design remains as the basis for scale up purposes.

The key conclusions reached were that the current design of the laboratory recuperative reformer satisfactorily supports Methane Reforming Rates over a temperature range that matches that of a large number of the steel reheat furnace population during normal production periods that produce exhaust gases within these temperature ranges.

On the basis of these successful sets of TTT measured results that demonstrated a design that can capably be scaled up, GTI recommends consideration of three options for a Phase III field experiment.

Option 1: Production furnace ~250 MMBtu/h

Option 2: Production furnace ~100 - 200 MMBtu/h

Option 3: Production furnace ~50 - 100 MMBtu/h

Specific details of each option are provided in **Appendix C**.

Appendix A – Phase II Report

GTI was subcontracted by the American Iron and Steel Institute to evaluate the technical and economic feasibility of utilizing a ThermoChemical Recuperation System (TCRS) to recover a significant amount of energy from the waste gases of natural gas fired steel reheat furnaces. ThermoChemical Recuperation (TCR) is a technique that recovers sensible heat in the exhaust gas from an industrial process, furnace, engine, etc. when a hydrocarbon fuel is used for combustion. TCR enables waste heat recovery by both combustion air preheat and hydrocarbon fuel (natural gas, for example) reforming into a higher calorific fuel. The reforming process uses hot flue gas components (H_2O and CO_2) or steam to convert the fuel into a combustible mixture of hydrogen (H_2), carbon monoxide (CO), and some unreformed hydrocarbons (C_nH_m). Reforming of natural gas with recycled exhaust gas or steam can significantly reduce fuel consumption, CO_2 emissions and cost as well as increase process thermal efficiency. The technique has been preliminarily investigated for a number of applications (Nosach, 1995; Maruoka, Mizuochi, Purwanto, & Akiyama, 2004; Sikirica, Kurek, Kozlov, & Khinkis, 2007). The calorific content of the fuel can be increased by up to ~28% with the TCR process if the original source fuel is natural gas. In addition, the fuel is preheated during the TCR process adding sensible heat to the fuel.

Until recently, TCR has not been evaluated and developed for commercial adoption because the payback period was unattractive when gas prices were low. With future increases in natural gas prices, TCR is now a viable technology to reduce costs, increase energy efficiency and reduce the industry's CO_2 footprint.

The technical and economic feasibility of TCRS was examined in Phase I of the project. The technical target was to evaluate TCRS designs through modeling to achieve a cost-effective design that increases thermal efficiency and reduces fuel consumption and carbon emissions by at least 30%. Efficiency of the system was evaluated by employing modeling software based on reheat furnace information provided by steel company partners. Several TCRS configurations were evaluated. A three-unit TCRS was shown to be the optimal design and was chosen for further economic analysis (see Appendix A1). This optimal configuration represented a combination of two stage combustion air recuperator and fuel reformer resulting in a furnace thermal efficiency at least 65% or alternatively at least 26% reduction in fuel usage and carbon emissions when compared to the reference recuperated reheat furnace (800°F preheated air). A level of 31% fuel savings and carbon emissions reduction can be achieved at combustion air and fuel temperatures of approximately 1270°F at equilibrium fuel conversion.

The objective of Phase II was to experimentally evaluate the optimal TCRS prototype design. The goal of the experiment was to validate modeled predictions of the performance of the TCRS as applied to a high temperature furnace. A lab-scale TCRS was developed, fabricated, assembled, and tested at GTI's facility. A high temperature furnace with a water cooled load was chosen for the lab-scale TCRS testing. The rated capacity of the furnace was 0.5 MM Btu/hr. The lab-scale non-catalytic recuperative reformer (RR) was developed based on the Phase I results. Thermal Transfer Corporation (TTC) jointly with GTI designed the reformer. TTC fabricated and assembled the unit and shipped it to GTI. Bloom Engineering provided GTI with a

high temperature low NO_x burner, recirculation fan and flue gas/natural gas ejector. Combustion air preheating was simulated by electrical heaters instead of a reduced scale two stage recuperator.

In Phase I, the predicted thermal efficiency and fuel savings of a typical reheat furnace were predicted 65% and 26% respectively at combustion air and fuel temperatures of 1200°F. The physical testing in Phase II validated thermal efficiency and fuel savings of 61% and 21% respectively which although lower than initially predicted are in conformance with the modeling results. It should be noted that in the course of testing several issues were discovered and are reported in more detail in the body of this report. First the above efficiency and fuel savings gains that were validated are associated with a sustained methane reforming rate of a flue gas/natural gas mixture which will be summarized at the end of this section under the heading of Technical Issues/Project Recommendations.

A specific internal flow arrangement in the recuperative reformer was designed based on Phase I results. The flue gas/natural gas mixture was preheated to a temperature of (1200 to 1300°F) in the reformer preheater; and reformed in the reformer reactor at approximately the same temperature. The preheater and reactor consisted of heat exchange tubes which were fully enveloped in the flue gas flow stream. The reactor contained return bends which served to provide an additional flow path for the reforming fuel so that the total volume of the reforming fuel flow in the reactor was substantially higher than the volume in the tubes. The returns were extended to provide the necessary residence time for reforming fuel.

The TCRS lab-scale tests confirmed designed parameters of the reformer preheater and reactor. The pressure drops were in the range of design values. The reforming fuel (flue gas/natural gas mixture) in the preheater was rapidly heated up to the temperature of ~1250°F, the desired temperature for the fuel reforming. The reactor provided sufficient thermal efficiency to transfer heat from the flue gas to the reforming fuel. The residence time in the reactor was high enough to provide partial reforming of the fuel.

During testing, hydrogen and carbon monoxide levels in the reformed fuel were used to preliminarily estimate performance of the recuperative reformer. Comparing measured values of hydrogen and carbon monoxide with theoretical predictions made it possible to determine how well the reformer was performing. Maximum yields of 27% of hydrogen and 11% of carbon monoxide were attained in the experiment. These values were close to theoretical (equilibrium) predictions. Approximately 58% of methane in the natural gas theoretically can be reformed at 1200°F while the measured results confirmed that only ~41% of methane was reformed in the non-catalytic recuperative reformer.

In the judgment of GTI, the technical and economic feasibility of employing a TCRS on a steel reheat furnace with recuperation remains feasible and was demonstrated by lab testing of the recuperative reformer.

With respect to the U.S. reheat furnace population TCR can be viewed as a Return on Investment (ROI) benefit continuum that ranges from a high level of payback of 15 months and \$38 million

ROI to a nominal payback level of 33 months and \$6.4 million ROI expressed in current dollars (NPV) at a 7% discount rate over six years of cash flow.

The optimal configuration of two heat exchangers and reformer that has a surface heat exchange area minimized when the first stage air recuperator produces 800°F preheated air is considered to remain valid. The lab testing of the lab-scale TCRS resulting in projecting a furnace thermal efficiency of 61% or alternatively a 21% reduction in fuel usage and carbon emissions when compared to the reference recuperated reheat furnace (800°F preheated air). On an annualized basis the metric tons of CO₂ and NO_x produced by the three-unit TCRS reheat furnace would be an estimated 111,000 metric tons and 406 metric tons representing reductions of 30,000 metric tons per year of CO₂ (21% reduction) and 200 metric tons per year of NO_x (33% reduction).

Assuming that 80 steel reheat furnaces (approximately 50% of the potential US steel reheat furnace market) employ TCR, the cumulative imputed future fuel usage reductions for both Flat and Long product plants would be 9.6 trillion Btu. The cumulative CO₂ and NO_x emissions reduction would be 689,000 and 4,700 metric tons per year respectively.

Technical Issues/Project Recommendations

The reason for the earlier emphasis on a sustained methane reforming rate is that at the end of each test cycle (4 to 6 hours) a slight degradation of the methane reforming rate was observed. It typically required 3-4 hours to preheat and stabilize the TCRS system. Measurements were conducted at these conditions and the system was iteratively adjusted to different conditions in order to collect data for a series of test points. The duration of each test (point) was approximately one hour while measured parameters were stable. For each one hour period, variations in flows, temperatures, and gas compositions were marginal. It was also observed that the methane reforming rate slightly degraded during the period of time from when the specific thermal conditions were attained to a point near the end of a typical test day.

After each daily test, the TCR system was shut down and cooled for renewed testing usually the next day. Upon restarting the system and when thermal stable conditions were again reached the methane reforming rate returned to the peak rate of the previous test but the same degradation of methane reforming rate would occur. Several reasons or mechanisms for this phenomenon were considered: (1) Amorphous carbon was being generated within the RR that in turn affected the methane reforming rate; and upon restarting from cold conditions, the carbon deposits were burned off the heat transfer surfaces thereby the RR was essentially “regenerated.” It was further conjectured that carbon would again be gradually redeposited as the next lab test progressed with the methane reforming rate declining again. A bore scope was employed to inspect the interior of the RR, through the flue gas/natural gas mixture port, to the extent capable. No carbon deposition was visually observed. When GTI partially disassembled the RR plenums to inspect the leaks, no carbon deposition was visually observed in those internal areas. After additional analysis of the test data, it was surmised—and later confirmed—that leakage of the reforming fuel and/or the pre-reformed mixture were short circuiting into the flue gas flowing around and on the outside of the RR thereby “contaminating” the flue gas and the portion of the flue gas used for mixing with the natural gas for reforming.

The leaks were repaired by Thermal Transfer Corporation; and the recuperative reformer was reinstalled. Durability testing was undertaken for approximately 48 continuous hours to determine the asymptoticity of the methane reforming rate. Once the system reached thermal equilibrium, the same gradual reduction in methane reforming rate was observed. An additional phenomenon was observed in that periodically the per cent hydrogen and percent carbon monoxide in the reformed fuel would increase and then decrease over short time intervals (several minutes) without any changes in the process by the staff operating the lab set up. Once it was evident that the methane reforming rate was still decreased and was not asymptotic, several changes to the process variables were intentionally made to attempt to retard or reverse the reduction in methane reforming rate, but without success.

GTI's preliminary conclusions are that the mechanism(s) producing the methane reforming rate decrease (are) not entirely known or understood. The nature of the chemical kinetics that are triggering the mechanism and/or other mechanisms are still necessary to be evaluated. Other possibilities include: stratification of the natural gas and flue gas downstream of the mixer within the preheater; and/or stratification of a portion of the flue gas/natural gas mixture and the complement of the flue gas/natural gas mixture for part of the residence time within the reformer-reactor.

These technical issues were reviewed with AISI and GTI was requested to prepare a countermeasure-plan to be included in the Phase II report.

Extended Phase II TCR Testing (proposed)

Since the results of the Durability Test confirmed that the reforming process is gradually retarded over time due to one or more of the above mechanisms, the TCR field experiment as outlined in Phase III is recommended to be postponed and a revised lab test of the TCR system should be carried out with a changed test matrix with a technical objective of identifying the mechanism(s) that are preventing a sustained methane reforming rate and provide a solution.

GTI proposes that the following is a reasonable alternative given that (1) Proof-of-concept has been verified and; (2) More importantly a well-designed and operational TCR system residing in the GTI combustion laboratory is capable of further testing to evaluate which and how the above mechanisms are retarding the methane reforming rate. Once fully understood, necessary alterations to the reformer design can be made and proceeding to Phase III can be considered.

Accordingly, the teams' consensus is to capitalize on the considerable amount of data acquired from modeling and physical testing by proposing a revised scope of work that will focus on identifying the mechanism(s) that are co-opting methane reforming efficiency for long-term operation of TCR as a viable waste heat recovery technique. Below is a brief summary of a preliminary work scope.

Task 1 - Forensic Analysis—Conduct independent short-duration simulation modeling of the Lab Recuperative Reformer process over a range of operating conditions.

- Develop equations describing chemical reaction kinetics within the Recuperative Reformer

- Conduct Sensitivity Analyses of the process that includes the following independent variables: (Flue gas temperatures supplied; components of flue gas supplied; carbon to steam ratios; physical volume of the RR; and a range of specified space velocities consistent with a range of specified reforming mixtures.).

Task 2 - Conduct iterative testing of current Lab RR under both broader and new test conditions

- Remove both ID fans and reconfigure piping for direct connection of flue gas to mixer.
- Variables to be varied in re Test Matrix
- Flue gas (FG) temperature entering RR—1700°F and 1800°F, capture all data;
- FG:NG ratio for above two FG inlet temperatures above—set at ~10, ~5 and ≤ 2 , capture all data.
- Reform with steam in lieu of flue gas—use high/mid/low ratio points
- Preheat natural gas with electric heater to achieve FG+NG or STM+NG temperatures into RR of 600°F; 700°F and 800°F

Task 3 - Per test results, devise any necessary changes to the RR design to achieve a sustained methane reforming rate and implement recuperative reformer design changes.

- Confer with TTC on implementation of changes
- Return RR to TTC for changes
- Return RR to GTI and reinstall

Task 4 - Conduct iterative testing of modified/retrofitted Lab RR under varying test conditions to confirm sustained methane reforming rate

Subject to approval to postpone the original Phase III work and to carry out a revised scope of work, a detailed Scope of Work will be prepared and a budget estimated.

Background

Concept-definition studies in Phase I work employed a GTI-licensed simulation software that has heat transfer and chemical reaction capability, Key metrics such as fuel flow rates, flue gas flow temperatures, energy intensity, walls losses, product throughput, and product temperatures were provided by ArcelorMittal and Republic Engineered Products.

The GTI approach was to conduct modeling studies by initially examining two general configurations for the reference steel reheat furnace: 1) With an air recuperator; 2) With a TCRS. The numerical analysis was based on utilizing FurnXpert and AspenOne software and GTI-developed models.

Project Duration and Phases

The duration of this project as proposed was thirty months and involved three phases:

- Phase I: (13 Months) September 30, 2008 to October 30, 2009 Developing a feasibility study consisting of a benefits-derived economic evaluation of a ThermoChemical Recuperation (TCR) concept with respect to high temperature reheat furnace applications. This established the design parameters and potential performance of the TCR.
- Phase II: (27 Months) October 30, 2009 to January 31, 2012 Conducting research and development to take the validated technology concept from Phase I to a developmental state for a stage 3, prototype field test.
- Phase III: (24 Months) TBD Designing, fabricating, and prototype field testing the TCR unit close-coupled to an existing high temperature reheat furnace at a steel company for evaluation under industrial conditions.

Improved Energy Efficiency and reduced Carbon Emissions for Steel Reheat Furnaces

For most industrial heating processes including furnaces the energy efficiency is defined as the ratio of useful output to gross heat input in percent. The total heat input is provided in the form of fuel chemical energy. The useful output is the heat supplied for heating a material. Other heat outputs in the furnaces are undesirable heat losses. The major heat or energy losses that occur in the fuel fired furnace are listed below:

- Heat lost through exhaust gases as sensible heat
- Heat loss through furnace walls and doors
- Heat loss through water cooled surfaces

A typical energy balance can be demonstrated by the Sankey diagram in Figure A1 that shows the energy balance for a recuperated reheat furnace. It is clear that exhaust gas losses are a key area for priority attention. Since the furnace operates at high temperature, the exhaust gases leave at high temperatures (1700°F to 2100°F) resulting in poor efficiency. Hence a heat recovery device such as an air recuperator has to be necessarily part of the system. Depending on the furnace exhaust flue gas and air preheat temperatures the furnace energy (thermal) efficiency can vary but ordinarily does not exceed 50%.

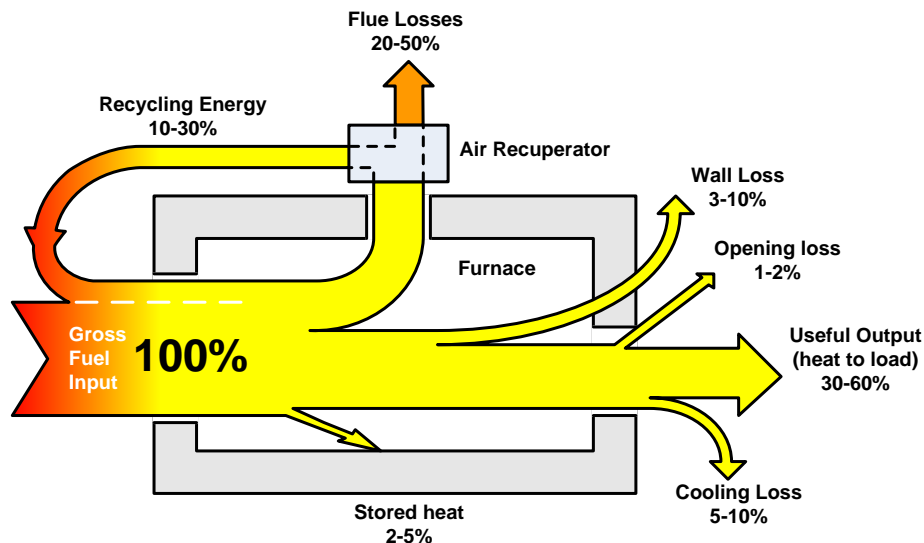


Figure A1. Energy Balance for a Recuperated Reheat Furnace

Major constituents of the furnace flue gas by volume are nitrogen (~72%), water vapor (~17.5%), carbon dioxide (~9%), and oxygen (~1.5%) when natural gas is used as the fuel and air as the oxidizer. On average, each furnace produces ~2.75 pounds of carbon dioxide (carbon emissions) per 1.0 pound of combusted natural gas. Fuel savings lead to a proportionate reduction of carbon emissions.

Energy Conservation and Emissions Reduction by Waste Heat Recovery from Exhaust Gases

Extracting heat from the furnace flue gases and returning it back to the process is the major technique to improve the furnace thermal efficiency and reduce carbon emissions. There are several methods that are generally used in the steel industry for waste heat recovery, that include: preheating cold loads with flue gases (unfired furnace zone); steam generation using waste heat boilers; preheating combustion air by recuperators or regenerators; and oxy-fuel firing.

Preheating cold loads with flue gases can be accomplished in an unfired zone(s) at the charge end of steel reheat furnaces. In this case energy will be transferred by preheating the load. This reduces the energy that is ultimately lost to the exhaust.

In practice, the unfired charging zones of most continuous furnaces serve as preheating zones. Load preheating systems can be difficult to retrofit due to space constraints and are best suited for continuous rather than semi-continuous furnaces.

The use of waste heat boilers to recover a portion of the exhaust gas heat is an option for plants that need a source of steam or hot water. The waste heat boiler is similar to conventional boilers with one exception: it is primarily supplied heat by the exhaust gas stream from a process furnace with supplementary firing as necessary. The prime requirement is that the waste gases must contain sufficient usable heat to produce steam or hot water at the condition required. Waste heat boilers may be designed for either radiant or convective heat sources.

Air recuperators are heat exchangers that use the energy in hot flue gases to preheat combustion air. Recuperators are the most widely used heat recovery systems in the steel industry. A recuperator is a gas-to-gas heat exchanger installed between the furnace flue gas exit and the furnace stack. The exhaust gases and air are in adjacent passageways separated by a heat conducting wall. Heat flows steadily through the wall from the hot exhaust gas to the combustion air. Recuperators are available in as many configurations as there are heat exchangers. Common forms are double pipe (pipe in a pipe), shell and tube, and plate types. All may use counter flow, parallel (co-current) flow, and/or cross flow.

Increasing air preheat temperature from 800°F to 1200°F for example, reduces the fuel consumption and therefore carbon dioxide emissions by ~13% at a waste gas temperature of 2000°F. It should be noted that increasing combustion air temperature increases NO_x emissions, typically from 20 to 100 ppmv for a 100°F temperature rise.

Recuperators are typically designed with very low pressure drops (0.5 to 1 in. W.C.) on the exhaust gas side. They usually are designed for a greater drop on the air side. Forced draft fans are preferred because of the higher cost of handling hot air or gases with induced draft (ID) fans or blowers for hot gas or hot air. In addition, forced draft fans promote maintaining the interior of the steel reheat furnace under a slightly positive pressure, minimizing ambient air infiltration.

Another alternative to preheat combustion air is with a regenerator, which is an insulated chamber usually filled with metal or ceramic shapes that can absorb and store significant thermal energy. It acts as a rechargeable thermal storage battery for heat and works in an alternating mode. In the first mode, hot flue gas is passed through the chamber thus heating media or refractory in the chamber. In the second mode cold combustion air is passed through the regenerator chamber thus extracting heat from the media or refractory. At least two regenerators and their associated burners are required for an uninterrupted process: one provides energy to the combustion air while the other recharges. The cycling time can be up to 40 seconds depending upon site conditions and the process. Regenerative burners require the use of a control system to sequentially switch the burners from a regenerative mode to a heat extraction mode. A program of periodic maintenance and measures to minimize the accumulation of media-contamination is required to ensure proper operation of all valve control mechanisms in the burners.

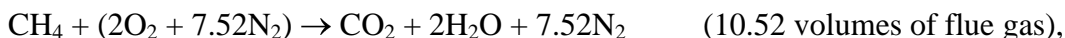
The fuel utilization of modern regenerators can be as high as 75% to 85%, with air preheat temperatures within 300°F to 500°F of the products of combustion in the furnace. Regarding firing systems for industrial furnaces including steel reheat furnaces, fuel utilization efficiency E_f is defined as:

$$E_f = 100\% \times (\text{Gross Fuel Input} - \text{Exhaust Gas Losses} - \text{Other Losses}) / \text{Gross Fuel Input}$$

For a system without air preheat ($\epsilon = 0$), it becomes obvious that the efficiency diminishes with rising exhaust gas temperatures. At 2000°F exhaust gas temperature, at least 55% of the fuel input will be lost as hot exhaust gas heat. Corresponding heat losses are less than 20% for regenerative burners with a relative air preheat $\epsilon = 0.8$ and ~35% for conventional combustion air recuperators with relative air preheat $\epsilon = 0.4$. Fuel savings compared to air recuperation are in

the range of 10 to 20% and savings of 50% and more, compared to cold air systems, can be achieved with regenerative burners. Low NO_x combustion can be achieved by air staging or in combination with external flue gas recirculation.

Although oxy-fuel firing is not considered a method of heat recovery in the strictest sense, energy is saved by reducing the mass of hot waste gases that is lost through the flue. “Oxy-fuel firing” is the substitution oxygen for air in a combustion system. For one volume of methane (the principal constituent of natural gas), the combustion reaction with air is,



is replaced with the reaction for oxy-fuel firing,



Reducing exhaust gases results in substantial fuel savings. In the case of enriching combustion air with oxygen, the specific amount of energy savings depends on the percentage of oxygen in combustion air and the flue gas temperature. Higher values of oxygen and flue gas temperature offer higher fuel savings. The net economic benefits will primarily be determined by the cost of oxygen compared to the fuel cost reduction savings.

In evaluating oxy-fuel firing, consideration needs to be given to the mass flow reduction of products of combustion, much higher flame temperatures, and extremely higher gas radiation heat transfer in short, longitudinal paths. Processes that depend on high mass flow to provide uniform product temperatures will be derated from the use of oxy-fuel firing because of its lower mass flow and lower volume for circulation. One solution that could negate these effects would be a combination of oxy-fuel firing with a TCRS which uses a portion of flue gas or flue gas steam condensate for fuel reforming and recirculates the gas through the furnace. In this case the thermal efficiency of the furnace can be substantially increased compared to conventional oxy-fuel firing and the flame temperature will decrease to a beneficial level.

The process of recuperating the energy contained in exhaust gases from high temperature process furnaces, engines, etc., for hydrocarbon fuel reforming is called thermochemical recuperation (TCR). A TCR system (TCRS) can also include oxidant (air or oxygen) preheat thus integrating a combustion air recuperator (AR) and recuperative reformer (RR) into the system. When successfully developed and commercialized, TCRS will provide increases in furnace thermal efficiency from 15 to 35% and reduce hydrocarbon fuel consumption by 15 to 60% compared with conventional recuperation where only combustion air is preheated. TCRS will also significantly reduce air emissions by 30% to 80%. The major advantage for TCRS is the opportunity to cost effectively improve process efficiency beyond what is achievable with conventional air recuperation. TCR has been extensively studied in Ukraine (Nosach, 1995), Japan (Maruoka, Mizuochi, Purwanto, & Akiyama, 2004), the U.S. (Sikirica, Kurek, Kozlov, & Khinkis, 2007), and Russia. For heating processes, efficiency increases of 20% to 50% have been noted, and for processes using thermal cycles (e.g., internal combustion engines, gas turbines) efficiency increases of 8% to 15% have been noted.

Figure A2 depicts a general example of TCRS with natural gas/flue gas reforming to illustrate the concept. AR is the air recuperator and RR is the recuperative reformer. At 1200°F air preheat and reformed fuel temperatures, more than 70% of the total heat in the exhaust is recovered when furnace exhaust gas temperature is 2000°F.

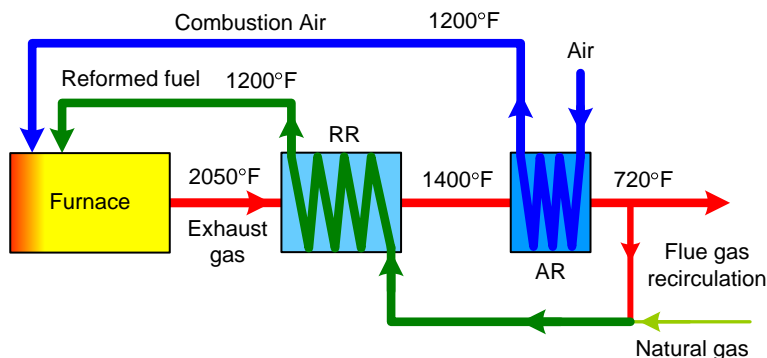
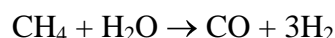


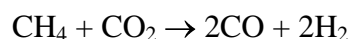
Figure A2. TCRS as Applied to a High-Temperature Steel Reheat Furnace with Natural Gas/Flue Gas Reforming (65% thermal efficiency)

The technique of recuperative reforming recovers sensible heat in the exhaust gas, and uses that heat to transform the hydrocarbon fuel source into a partially reformed fuel having a higher calorific heat content. The reforming process uses the waste heat plus steam (water vapor) and/or carbon dioxide (CO₂) to convert the fuel into a combustible mixture of hydrogen, hydrocarbons, and carbon monoxide (CO). The calorific content of the fuel can be increased by up to ~28% with the TCR process if the original source fuel is natural gas. In the TCR process, steam, CO₂, or both can be reacted with fuel, as shown below (each case is simplified to one reaction).

- Fuel reforming with steam:



- Fuel reforming with carbon dioxide:



- Fuel reforming with flue gas of air/fuel firing:



When reformed fuel is combusted in the furnace, fuel economy is improved, system efficiency is increased, and emissions are reduced. In addition, the fuel is preheated during the reforming process, adding sensible heat to the fuel. Because both water vapor and CO₂ can be used in the reforming process, it is advantageous for natural gas-fired systems because both of these gases are major products of combustion and, therefore, are readily available in a preheated state. Further, they can be used in the same ratio as they exist in the combustion products.

TCRS was not evaluated and developed for commercial adoption because the payback period was unattractive when gas prices were low. Strong interest in TCR has been expressed to GTI by the steel industry, the glass industry, and the aluminum industry during the last several years. GTI has evaluated the TCR approach for direct fired heating applications from a bench-scale test

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funded by GTI. A feasibility study of TCR for indirect fired heating applications, also funded by GTI, was carried out.

A feasibility study of the TCRS with steam for the Japanese steelmaking industry was conducted several years ago (Maruoka, Mizuochi, Purwanto, & Akiyama, 2004). The study reported the following conclusions. The energy loss in the TCRS was only 15% of the total energy losses in the conventional system. The study also demonstrated the feasibility of treating the waste gases and slags from the steelmaking industry by TCRS and indicated the possibility of solving environmental issues besides offering substantial cost benefits to the steelmaking industry. The reduction in carbon dioxide emissions due to TCRS is as high as 2.05 million tons per year in the Japanese steelmaking industry. The feasibility study stated that the cost benefits that can be aggregated by TCR waste heat recovery systems (based on steam reforming) are \$409 million per year for discharged gases and \$1,945 million per year for slags.

Summary of the TCRS Concept Validated in Phase I

Based on Phase I results, the three-unit TCRS design (Figure A3) emerged as the least cost optimal design. The configuration represents a combination of a two-stage air recuperator and recuperative reformer that has a heat exchange surface area minimized when the first stage air recuperator produces 800°F preheated air.

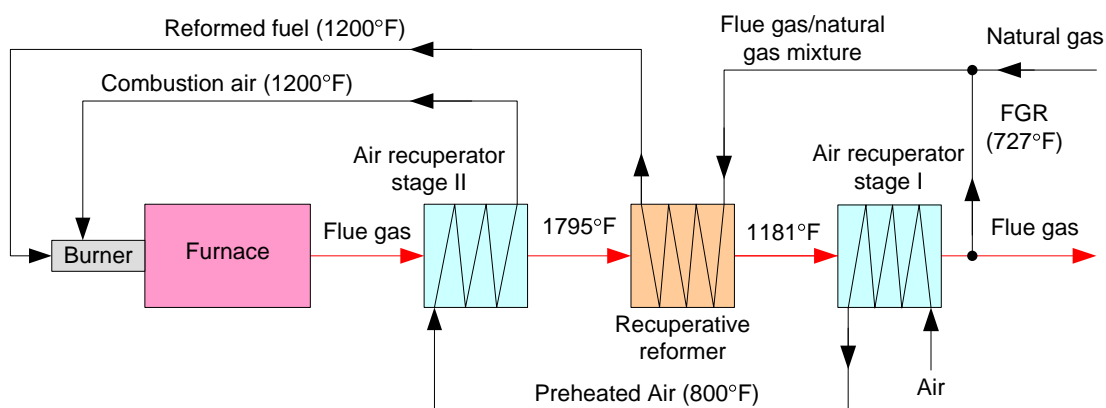


Figure A3. Optimal TCRS Concept Validated in Phase I

The Energy intensity of this scheme was estimated to be 1.19 MMBtu per ton with 1200°F preheated combustion air and 1200°F reformed fuel temperature resulting in a furnace thermal efficiency of 65% or alternatively a 26% reduction in fuel usage and carbon emissions when compared to the reference recuperated reheat furnace (800°F preheated combustion air).

Phase II – Recuperative Reformer Design and Testing of the TCRS Concept Validated in Phase I

Selection of GTI Lab-scale Furnace for TCRS Testing

Several furnaces in the GTI combustion laboratory were candidates for lab-scale TCRS testing. The following parameters and features of the lab-scale furnace and TCRS were considered (based on Phase I results) to select the furnace:

- Flue gas temperature exiting the furnace capability to 2050°F
- Combustion air temperature capability to 1200°F
- Reformed fuel temperature capability to 1200°F
- Variable water cooled load
- Existing natural gas and combustion air piping train
- Variable speed drive combustion air fan
- Flue Gas Recirculation

A high temperature furnace (Figure A4) with a water cooled load was chosen for the lab-scale TCRS testing. This furnace has the capability of controlling flue gas temperature by adjusting the water cooled load (probes) inserted into the furnace from the furnace roof. The furnace also has an electrical air heater that was used to simulate combustion air recuperation with air preheat up to 800°F. The rated capacity of the furnace is 0.5 MM Btu/hr and the flue gas temperature at the furnace exhaust can be as high as 2400°F.

For cost-containment purposes combustion air preheating was simulated by electrical heaters instead in place of a scaled down two stage recuperators. It was concluded that preheating combustion air with electrical heaters would not affect the results of the TCRS study and additionally would increase flexibility of the lab-scale TCRS experimental setup.

An additional combustion air heater was installed to provide preheated combustion air from 800°F to 1200°F is shown in Figure A5.



Figure A4. GTI High-Temperature Furnace with Water Cooled Load



Figure A5. Second Stage Combustion Air Heater

Lab-Scale TCRS

The lab-scale TCRS was evaluated based on predetermined furnace operating parameters. Figure A6 illustrates the TCRS flow diagram with ranges of the predetermined parameters. The flue gas temperature exiting the furnace was selected to correspond to the temperature ($\sim 1795^{\circ}\text{F}$) of the flue gas at the exit of a stage II air recuperator. This temperature was controlled by adjusting the water cooled load in the furnace. Flue gas recirculation (FGR) temperature was selected to correspond to the temperature ($\sim 727^{\circ}\text{F}$) of the flue gas at the exit of the stage I air recuperator. A water cooled heat exchanger was installed in the flue gas recirculation line to maintain the desired FGR temperature.

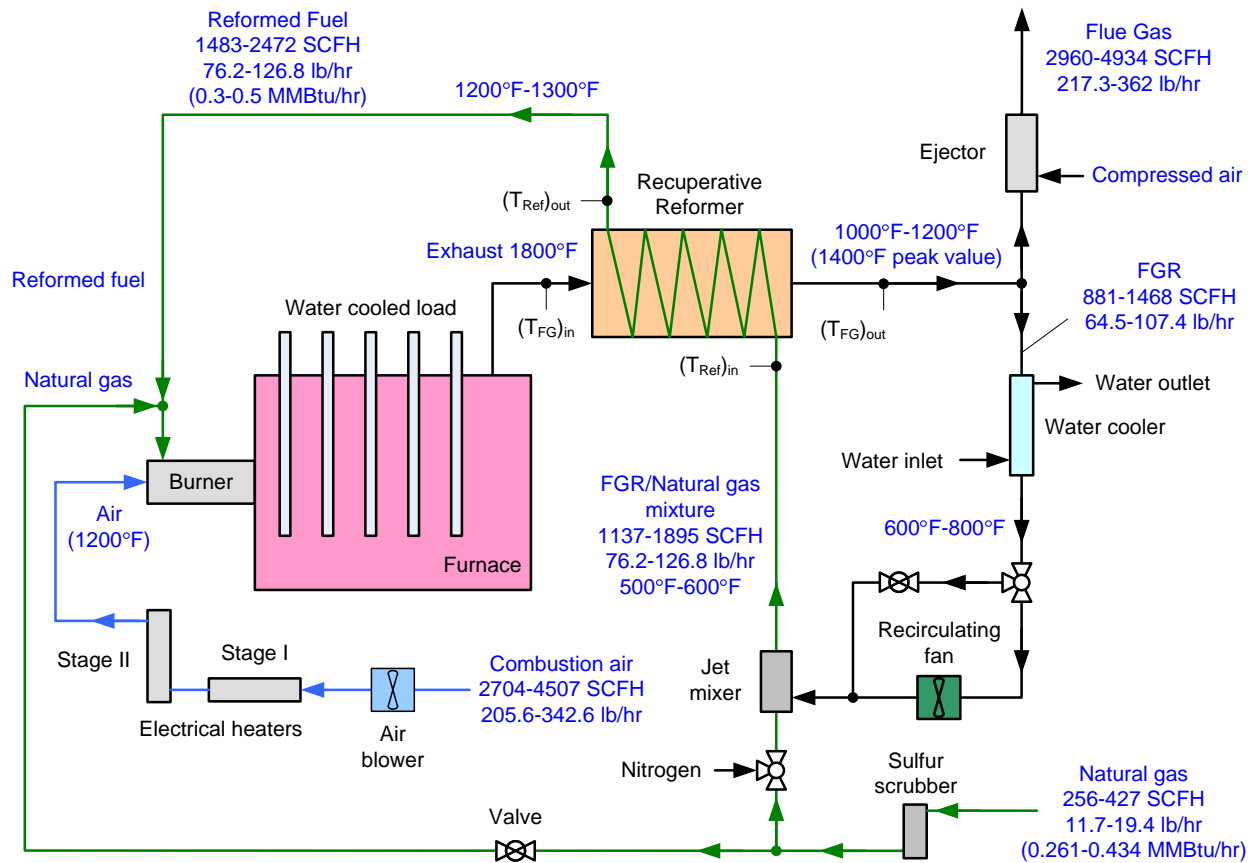


Figure A6. Lab-scale TCRS Flow Diagram

There are several other key components in the lab-scale TCRS experimental setup: a flue gas ejector or venturi nozzle was installed within the stack entrance. The purpose of this ejector was to control the pressure within the test furnace by varying flue gas flow to the stack. Controlling furnace pressure (usually slightly negative or zero) in the furnace was necessary to minimize drawing in ambient air into the flue gas from finding its way into the flue gas that mixes with the natural gas.

Another component of the lab-scale TCRS experimental setup was a sulfur scrubber which was installed at the natural gas supply line. The function of the sulfur scrubber was to desulfurize natural gas which contains naturally occurring H_2S and mercaptan sulfur. Although the sulfur

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scrubber not needed for non-catalytic reforming this feature was included in the test set up to virtually eliminate any unforeseen issues connected with possible effects of sulfur contamination.

Hot Air and Reformed Fuel, Ultra Low NO_x Burner

A high temperature (1200°F combustion air and 1200°F reformed fuel) burner was required to be used in the TCRS. This burner needed to be capable of handling a high fuel flow rate as the fuel is a partially reformed mixture of natural gas and flue gas. Bloom Engineering was provided the furnace test parameters that included the specific firing rate, temperature and flows (air and fuel), and pressures. Bloom Engineering Company supplied the hot air ultra low NO_x burner (See Figure A7), including a gas mixer for mixing flue gas and natural gas (which provided a boost to the mixture pressure) and other ancillary control equipment.



Figure A7. Hot Air Ultra Low NO_x Burner by Bloom Engineering Co.

The burner was supplied with a lab and UV flame detector. The lab was installed into the coupling located on top of the burner body. The UV detector was installed through the coupling that is located near the horizontal centerline of the burner body. The UV detector port was modified for use as a natural gas supply port for burner start up and furnace heat up operation.

Flue Gas Recirculation Fans

The flue gas and natural gas mixer pressure was boosted by the FGR fans allowing flue gas to be recirculated; the FGR fans were installed in series to provide a wide range of FGR flows over the test operating range. The fans were specified to operate at a moderately high temperature (up to 600°F) and provide flue gas pressure (up to 24" W.C.) to overcome pressure drops across the reformer, piping and burner. Additional sealing to the extent possible between the shafts and the housing was necessary to eliminate flue gas leakage out or ambient air infiltration into the

flowing flue gas. It was determined that two fans in series would allow the attainment of performance at a least cost. The two FGR fans were assembled on a frame and supplied by The Canada Blower Company (Figure A8).



Figure A8. Flue Gas Recirculation Fans in Series

Variable speed drives were used to control the blower speeds thereby adjusting FGR flows. This level of FGR flow control was considered critical for purposes of adjusting the FGR/natural gas ratio.

Development and Design of the Non-Catalytic Recuperative Reformer

GTI proposed a non-catalytic recuperative reformer for TCRS (patent pending). Operation of the reformer without catalyst essentially reduces the reformer cost and maintenance.

A different approach needed be taken to design the recuperative reformer when compared, for example, with typical methane reformers that are widely used for hydrogen production. The following conditions required to be taken into consideration for developing and designing the recuperative reformer. First, the recuperative reformer is a heat exchanger apparatus which has hot flue gas flowing over one side of a heat exchange surface and colder flow of flue gas/natural gas mixture (reforming fuel) flowing over the opposite side of the surface. The heat exchanger design needed to provide conditions for fast preheating of the relatively cold flue gas/natural gas mixture up to the temperature approximately equal to the desired temperature of the reformed fuel (1200-1300°F in our case) and reforming at this temperature while preventing temperatures higher than 1200-1300°F of reforming fuel in the reformer.

Structurally the recuperative reformer needed to contain a preheater where the reforming fuel is primarily preheated with little or no reforming followed by a non-catalytic reactor where the reforming fuel is being reformed at an approximately constant temperature. It should be obvious

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that the reforming reaction rates in a non-catalytic reactor are much lower compared to the rates in a catalytic reactor. As a result of the reduced reaction rates, the residence time of the reforming mixture in the reactor was much higher compared to the residence time in a catalytic reformer consequently it is reasonable to expect that the non-catalytic reactor would be larger compared to the catalytic reactor. On the other hand, the heat exchange surface area in a non-catalytic reactor should be limited to the area just sufficient enough to provide enough heat to support the endothermic reforming reaction. This means that a non-catalytic reactor should contain certain heat exchange surface area and volume to provide residence time for reforming fuel. The residence time then, dictates how large this space should be.

GTI conducted a bench scale laboratory test to evaluate the residence time necessary to accomplish this requirement. An existing small-scale recuperative reformer was utilized for this purpose. The laboratory test was conducted using a GTI natural gas-fired modified heat treat furnace. Based on the obtained results it was concluded that the residence time in the recuperative reformer to be designed and built for the Phase II tests required to be at least seven seconds or higher depending on the reformer surface area which is in contact with reforming fuel. This additionally acquired knowledge about the residence time for non-catalytic reforming allowed reducing the number of experiments in the lab laboratory test by eliminating conditions (levels) with too low or too high values of residence time. A more detailed description of this experiment and test results are presented later in Appendix A2 of the report.

Based on the above described approach of the recuperative reformer design the following internal flow arrangement in the reformer was proposed (see Figure A8). The FGR/natural gas mixture is preheated to a reforming temperature of (1200 to 1300°F) in the reformer preheater and then reformed in the reformer reactor at approximately the same temperature (1200 to 1300°F). The preheater and reactor consist of tubes or plates which are completely enveloped in the flue gas flow stream. The reactor return bends (see Figure A9) needed to be placed outside of the central flue gas duct within two plenums as shown. These return bends serve to provide an additional flow path for the reforming fuel so that the total volume of the reforming fuel flow in the reactor is substantially higher than the volume in the tubes or plates. For this particular design of the lab-scale reformer the total volume of the return bends was set to 5.205 ft³ by calculations.

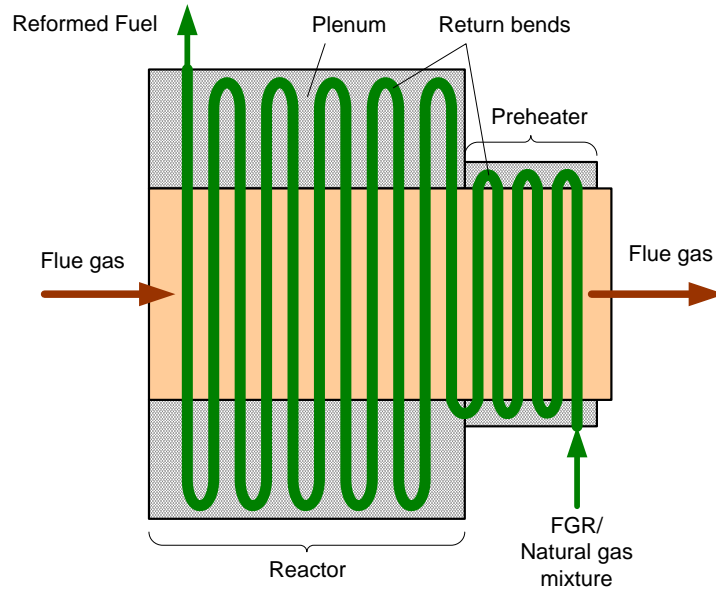


Figure A9. Flow Paths in Recuperative Reformer

Another key factor in the resultant recuperative reformer design is the effect of chemical reactions on the heat transfer in the reformer. In this connection, there was a consideration as to how to calculate the heat exchange surface area of tubes or plates in the reactor. As a first approximation, the effect of the reforming reactions was taken into account by using a pseudo specific heat of the reformed fuel at the reactor outlet. This pseudo specific heat $(c_p)_{\text{pseudo}}$ can be found from the following equations:

$$(c_p)_{\text{pseudo}} = (Q_t - m \times c_{p1} \times t_1) / (m \times t_2), \quad (1)$$

$$Q_t = Q_c + Q_r, \text{ Btu/hr} \quad (2)$$

$$Q_c = m \times (c_{p2} \times t_2 - c_{p1} \times t_1), \quad (3)$$

$$Q_r = m \times (\text{HHV}_2 - \text{HHV}_1), \quad (4)$$

Here

c_{p1} = specific heat of the reforming fuel at the reactor inlet, Btu/(lb×°F)

c_{p2} = specific heat of the reforming fuel at the reactor outlet, Btu/(lb×°F)

HHV_1 = higher heating value of the reforming fuel at the reactor inlet, Btu/lb

HHV_2 = higher heating value of the reforming fuel at the reactor outlet, Btu/lb

m = reforming fuel mass flow rate, lb/hr

Q_c = convective heat flow in the reactor, Btu/hr

Q_r = heat flow due to the reforming fuel heating value change in the reactor, Btu/hr

t_1 = temperature of the reforming fuel at the reactor inlet, °F

t_2 = temperature of the reforming fuel at the reactor outlet, °F

To intensify heat transfer and reforming reaction rates in the reformer it was determined that to use inserts with extended surfaces in heat exchange tubes (or between plates) and return bends of the reactor would serve this purpose.

This conceptual design of the recuperative reformer was shared with Thermal Transfer Corporation (TTC) which agreed to co-develop the lab-scale recuperative reformer design, fabricate and assemble it. GTI also provided TTC with the initial parameters of the process:

- Flue gas temperature at the reformer inlet: 1800°F
- Flue gas flow rate including FGR: 3,841...6,402 SCFH (281.8...469.4 lb/hr)
- Natural gas flow rate: 256...427 SCFH (11.7...19.4 lb/hr)
- Combustion air flow rate: 2,704...4,507 SCFH (205.6...342.6 lb/hr)
- FGR flow rate: 881...1,468 SCFH (64.5...107.4 lb/hr)
- FGR/natural gas mixture temperature at the reformer inlet: up to 600°F
- FGR/natural gas mixture flow rate at the reformer inlet: 1,137...1,895 SCFH (76.2...126.8 lb/hr)
- Reformed fuel temperature at the reformer outlet: 1200...1300°F
- Flue gas/FGR composition (% volume): $N_2=72.1\%$, $H_2O=17.3\%$, $CO_2=8.9\%$, $O_2=1.7\%$
- Composition of the flue gas/Natural gas mixture in the preheater and at the reactor inlet (% volume): $N_2=55.843\%$, $CH_4=21.755\%$, $H_2O=13.326\%$, $CO_2=7.092\%$, $H_2=0.023\%$, $O_2=1.343\%$, $C_2H_6=0.526\%$, $C_3H_8=0.069\%$, $C_4H_{10}=0.023\%$
- Composition of reformed fuel at the reactor outlet (% volume): $N_2=42.94\%$, $CH_4=5.697\%$, $H_2O=2.877\%$, $CO=14.704\%$, $CO_2=2.819\%$, $H_2=30.963\%$

Upon finalizing the design, fabrication drawings were prepared by TTC. A general view of the recuperative reformer design is shown in Figure A11. As previously discussed, there are two sections in the recuperative reformer unit: a preheater and a reactor. The preheater is a tubular heat exchanger which consists of three parallel rows of tubes in the transversal direction and twelve rows of tubes in the longitudinal direction. The reactor is a tubular heat exchanger which consists of three parallel rows of tubes in the transversal direction and fifteen rows of tubes in the longitudinal direction.



Reformer Tube Bank



Reformer Tube Bank with Plenums



Return Bends



Inserts



Insulated Reformer Shell



Exhaust Connection from Furnace to Reformer

Figure A11. Key Elements of the Recuperative Reformer During Fabrication and Assembly

The recuperative reformer was partially assembled at TTC, leak checked, and then shipped to GTI. After the reformer was assembled the tube bundle (tube side) was pneumatically pressure tested at 2 PSIG and hold for two hours with no leaks.

Arrangement and Installation of the Recuperative Reformer in GTI Laboratory

Figure A12 shows general arrangement of the recuperative reformer in the GTI combustion laboratory. TTC was provided with this drawing and all dimensions required for the reformer design and fabrication.

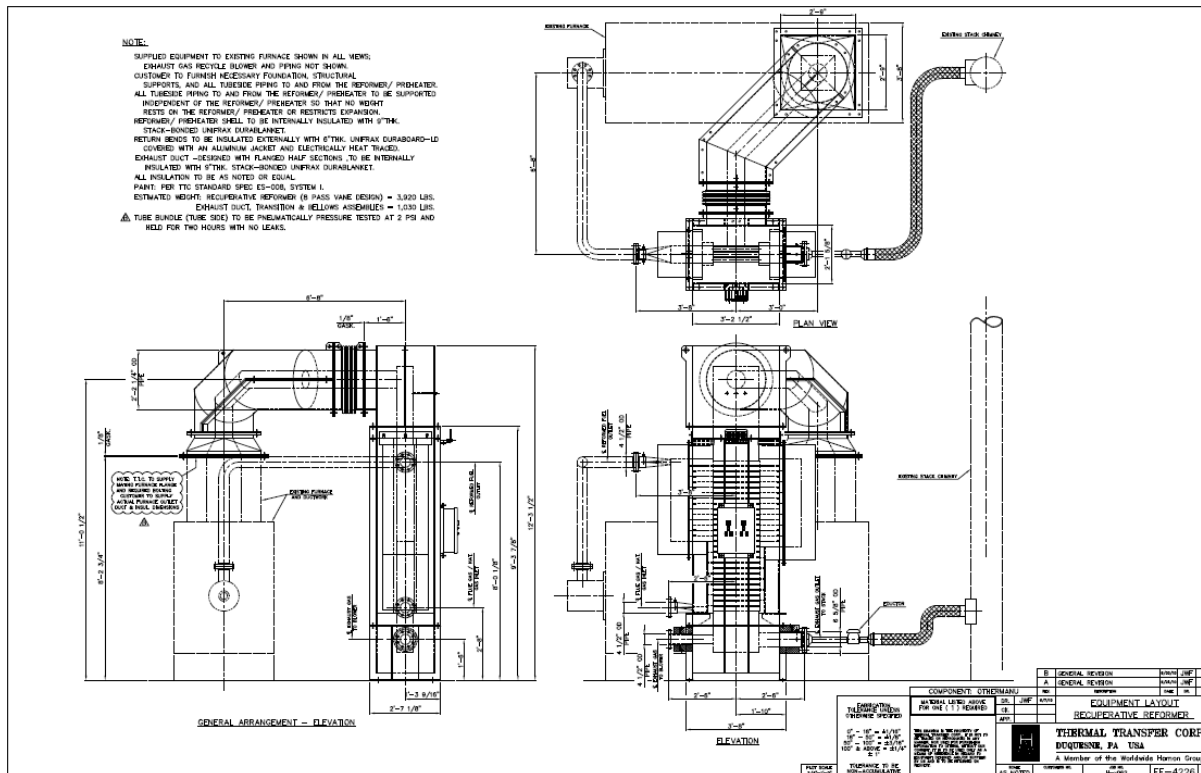


Figure A12. General Arrangement of Recuperative Reformer at GTI Combustion Laboratory

The recuperative reformer was finally assembled including all connections and installed in GTI combustion laboratory. The photo in Figure A13 is of the installed TCRS with the recuperative reformer. All the piping and recirculation fans were externally insulated to reduce heat losses.

Shake-down test showed that there was a leak of ambient air to the flue gas flow in the reformer causing increased oxygen content in the flue gas recirculation flow. This leak of ambient air to the flue gas flow would be acceptable in an air recuperator but it is critical for the recuperative reformer. TTC was informed about the leak, and they advised a solution. To minimize the leak, all gaps in the reformer shell were sealed from outside using high temperature sealer.



Figure A13. TCRS Setup in GTI Laboratory

Test Plan, Data Acquisition System, and Data Processing

Description of the Process to be Tested

The goal of the laboratory evaluation was to validate modeled predictions of the performance of a TCRS as applied to a high temperature furnace. Testing was conducted for conditions simulating the steel reheat furnace evaluated in phase I of the project. In Phase I the reference steel reheat furnace equipped with a TCRS contained three units: an Air Recuperator Stage II (ARII), a Recuperative Reformer (RR) and an Air Recuperator Stage I (ARI) in series (see Figure A14). The three-unit TCRS design was devolved to as the optimal design for further evaluation by physical testing in Phase II. The configuration represents a combination of heat exchangers and reformer that has a surface heat exchange area that is minimized when the first stage air recuperator produces 800°F preheated air. The energy intensity of this scheme was estimated to be 1.19 MMBtu per ton with 1200°F preheated air and 1200°F reformed fuel temperature resulting in a furnace thermal efficiency of 65% or alternatively a 26% reduction in fuel usage and carbon emissions when compared to a recuperated reheat furnace (800°F preheated air).



The TCRS experimental rig was used to test recuperative reforming using a fraction of the high temperature furnace flue gas mixed with natural gas. Test results were used to estimate system efficiency and confirm the practicality of this approach for expected operating conditions. The reformed fuel produced in the experimental rig was combusted in the furnace. Flue gas flow rate, composition and temperature were controlled in order to provide comparable conditions specified in Phase I of the project.

- Flue gas composition (% volume): $\text{CO}_2 = 8.9\%$; $\text{H}_2\text{O} = 17.3\%$; $\text{N}_2 = 72.1\%$; $\text{O}_2 = 1.7\%$
- Temperature of the furnace flue gas before the reformer: $(T_{\text{FG}})_{\text{in}} = 1800^\circ\text{F}$
- Temperature of the FGR/natural gas mixture entering the reformer: $(T_{\text{Ref}})_{\text{in}} = 500^\circ\text{F} - 600^\circ\text{F}$



Rationale for the Tests

GTI has previously carried out HYSYS model simulations using thermochemical recuperation to recover waste heat from a high temperature furnace and thereby increasing the furnace thermal efficiency. Commercial steam catalytic reforming of natural gas for hydrogen production is done at high temperatures (1500 - 2000°F). Experimental data on the performance of non-catalytic flue gas reforming at lower temperatures (~1200°F) representative of high temperature furnaces was needed. With the experimental data from Phase II work, GTI expected to have a high degree of confidence in predictions of improvements in system efficiency using recuperative flue gas reforming. Testing would also provide data to quantify the conversion efficiency as a function of reforming temperature and fraction(s) of FGR.

Performance Targets

The key indicator of the effectiveness of TCR is the conversion efficiency of the recuperative reformer. Specifically, how much of the hydrocarbon fuel is converted to hydrogen is an easy-to-measure indicator of how much waste heat energy from the furnace exhaust has been converted to chemical fuel energy. The measured inlet and outlet flows and reformed fuel compositions from the recuperative reformer were used to calculate conversion efficiencies. These values were compared to predicted reformed fuel compositions for chemical equilibrium conditions.

Test Objectives and Technical Approach

The laboratory test objectives included evaluating:

- The effect of residence time on reforming fuel conversion rate
- The effect of FGR fraction for the flue gas reforming of natural gas on methane conversion rate
- If carbon deposition on the reformer surfaces occurred and if so possible ways to control depositions

The technical approach was based on the use of an existing bench-scale TCR experimental rig. This rig has been used extensively to evaluate flue gas reforming at furnace conditions and flue gas reforming at temperatures representative of steel reheat furnaces.

The following activities were planned:

- Design and build a non-catalytic flue gas recuperative reformer for reforming of natural gas
- Select/acquire and assemble ancillary equipment for the experimental set-up including the furnace, burner, recuperative reformer, combustion air heater and a data acquisition system
- Conduct laboratory tests to demonstrate recuperative reformer performance and to determine any technical issues

Facilities, equipment, and instrumentation

Measuring port locations are shown in Figure A16. An Instrument Index is presented in Table A1 below. A Horiba Gas analyzer was used to measure flue gas composition: NO_x (ppm), CO (ppm), CO₂ (%), and O₂ (%). A Varian Micro gas chromatograph was used to measure the reformed fuel composition (% volume): H₂, O₂, N₂, CH₄, CO, CO₂, C₂H₄, C₂H₆, C₃H₈, i-C₄H₁₀, n-C₄H₁₀, and C₂H₂. The flowing FGR fraction and the reformed fuel to the burner were estimated by measuring differential pressures across individual orifice plates.

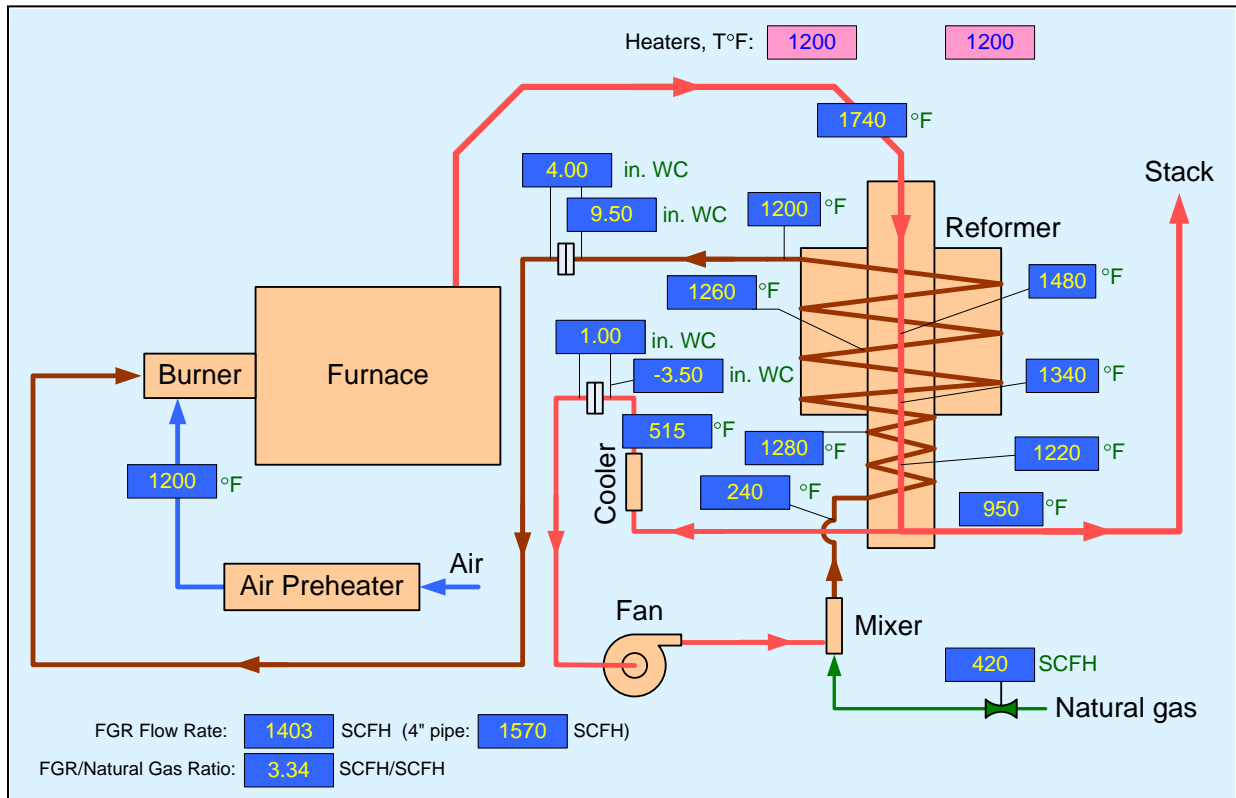


Figure A15. Real Time Monitoring Scheme of the TCRS (numbers are shown as an example)

Table A1. Instrument Index

Item #	Service	Instrument location	Instrument type	Mfg	Range	Signal type	Comment
	Inlet air flow rate	Δp transmitter	1 st heater inlet (existing)	Bailey (available in the lab)	0-30 "wc	4-20 mA + local reading	Required orifice size: 1.01"
		Mass flow meter	1 st heater inlet	SIERRA (available in the lab)	0-20,000 SCFH	4-20 mA + local reading	Measuring section to be inserted into existing pipe.

	Inlet air static pressure	Pressure Transmitter	1 st heater inlet (existing)	Bailey (installed)	0-200 "wc	4-20 mA + local reading	HP pressure port
	1 st heater air temp	T/C	1 st heater outlet (existing)		50-2000°F	0-45 mV	
	Combustion air temp	T/C	2 nd heater outlet (existing)		50-2000°F	0-45 mV	
	Reformer FG inlet temp	T/C	Reformer FG (hot) inlet		50-2000°F	0-45 mV	K-type
	Reformer FG outlet temp	T/C	Reformer FG (hot) outlet		50-2000°F	0-45 mV	K-type
	Furnace static pressure	Pressure Transmitter	Furnace Shell				
	FG temp after water cooler	T/C	Water cooler outlet		50-2000°F	0-45 mV	K-type
	FG temp	T/C-std	Mixer inlet	K-type T/C with std calibration – FG/NG ratio deviation $\pm 6\%$			
		T/C-spec		K-type T/C with special calibration – FG/NG deviation ratio $\pm 3\%$			
		RTD		RTD – FG/NG ratio deviation $\pm 2\%$			
	FG/NG mix temperature	T/C-std	Mixer outlet	Standard TC (available)			
		T/C-spec		Special T/C to be ordered			
		RTD		RTD + 2-point process meter/recorder to be ordered			
	NG temp	T/C	Mixer inlet		50-2000°F	0-45 mV	K-type gives adequate tolerance
	FG/NG mix composition	Gas Chromatograph	Reformer RF (cold) inlet				
	RF composition	Gas Chromatograph	Reformer RF (cold) outlet				
	FG composition	Analyzer	Water cooler outlet	Horiba			Sampling pump required

	Water content	Condenser	Reformer RF (cold) outlet				Dry gas totalizer + 3-way switch
	Water content	Condenser	Reformer RF (cold) inlet				+sampling pump required.

Test Procedure

The experimental set-up allowed controlling the furnace exhaust gas temperature by adjusting the water cooled load in the furnace. Exhaust gas from the furnace was used as a heat source for endothermic reforming and a reagent to reform natural gas. The reformed fuel was combusted in the furnace using a Bloom baffle burner designed for high temperature gas fuels. During the tests the various reformed fuel compositions were analyzed and recorded.

Data Analysis and Quality Assurance Procedures

After data collection the following parameters were determined based on the measured parameters:

Reforming process completeness and methane conversion rate

The key result from the tests is process completeness: the magnitude of how much fuel was capable of being reformed. Process completeness is related to how much energy was recovered compared to the theoretical equilibrium prediction. This key parameter, process completeness, was defined in terms of measured data as

$$\text{Reforming process completeness} = \frac{(\text{measured methane conversion rate})}{(\text{calculated equilibrium methane conversion rate})}$$

where the methane conversion rate is defined as

$$\text{Methane conversion rate} = 1 - \frac{(\text{outlet mass concentration of methane})}{(\text{inlet mass concentration of methane})}$$

Equilibrium gas compositions were estimated using GTI licensed Aspen HYSYS software.

Reformer residence time

Reformer residence time was estimated as:

$$\text{Reformer residence time} = \frac{(\text{reformer volume})}{(\text{measured standard flow rate of reforming fuel})}$$

Essentially the residence time is a function of the capacity of the reformer and natural gas/flue gas mixture flow rate for the reformer. The larger the reformer volume, the higher the residence time will be, assuming the inflow and outflow rates are held constant. Higher residence time would provide more amount of time for the reforming fuel to be spent in the reformer thus having more time for chemical reactions in the reformer to complete the reforming process.

Volumetric flow rate of the dry flue gas

Flue gas flow rate into the reformer was controlled by adjusting the speed of both recirculation fans or a damper in the FGR by-pass line. The flue gas and natural gas were mixed in the jet mixer and fed into the reformer. The volumetric flow rate of the flue gas was measured by an orifice plate. This flow rate can also be estimated based on nitrogen volumes measurement at the reformer inlet and outlet. The volume fraction of nitrogen in each of the streams was known, and the flow rate of natural gas was metered; this was enough information to calculate the volumetric flow rate of the dry flue gas:

$$V_{fg}^d = V_{ng} \frac{N_2^{mix} - N_2^{ng}}{N_2^{dfg} - N_2^{mix}}$$

Here V_{fg}^d is volumetric flow of dry flue gas, SCFH; V_{ng} is volumetric flow of natural gas, SCFH; N_2^{mix} is nitrogen volume fraction at reformer inlet, N_2^{ng} is nitrogen volume fraction in natural gas, N_2^{dfg} is nitrogen volume fraction in exhaust. The relative error of the flow rate measurement approximates that of the flow meter, $\pm 2.5\%$.

Flue gas water content

The water content of exhaust gas (and hence, of reformer inlet gas) is determined by material balance calculations:

$$H_2O_{fg} = \frac{\frac{H_{ng}^w \cdot d_{ng} \cdot MW_{H_2O}}{MW_{H_2} \cdot d_{H_2}} + \alpha V_0^{air} H_2O^{air}}{V_0^{fg} + (\alpha - 1)V_0^{air}}$$

Here H_2O_{fg} is volume fraction of water in flue gas, H_{ng}^w is mass fraction of hydrogen in natural gas, MW_{H_2} is molecular weight of hydrogen, g/mol; MW_{H_2O} is the molecular weight of water, g/mol; d_{ng} and d_{H_2} are the density of natural gas and hydrogen respectively, lb/SCF; α is the air ratio; V_0^{air} is stoichiometric wet air for natural gas combustion, cf/cf; H_2O^{air} is the water volume fraction in wet air, cf/cf; V_0^{fg} is the stoichiometric natural gas combustion products, cf/cf. Relative error, presuming some deviation in composition, is approximately $\pm 4\%$.

Water vapor flow rates

Water vapor flow rate at the recuperative reformer outlet was determined by reformer material balance calculations (oxygen-based):

$$V_{H_2O}^{out} = \frac{v_d^{in}(O_2^{in}d_{O_2} + v_{CO}^O CO^{in}d_{CO} + v_{CO_2}^O CO_2^{in}d_{CO_2}) + v_{H_2O}^O V_{H_2O}^{in}d_{H_2O} - V_d^{out}(O_2^{out}d_{O_2} + v_{CO}^O CO^{out}d_{CO} + v_{CO_2}^O CO_2^{out}d_{CO_2})}{v_{H_2O}^O d_{H_2O}}$$

here $V_{H_2O}^{out}$ and $V_{H_2O}^{in}$ are the water vapor flow rates at the reformer outlet and inlet respectively, SCFH; V_d^{in} and V_d^{out} are the dry gas flow rates at the recuperative reformer inlet and outlet respectively, SCFH; O_2^{in} , CO^{in} , and CO_2^{in} are the volume fractions of O_2 , CO and CO_2 respectively, in dry gas at reformer inlet; O_2^{out} , CO^{out} , and CO_2^{out} are the volume fractions of O_2 , CO and CO_2 , respectively, in dry gas at the recuperative reformer outlet; d_{O_2} , d_{CO} , d_{H_2O} and d_{CO_2} are densities of O_2 , CO , H_2O (g), and CO_2 , respectively, lb/SCFH; $\nu_{H_2O}^O$, ν_{CO}^O , and $\nu_{CO_2}^O$ are mass fractions of oxygen in H_2O , CO , and CO_2 , respectively. The relative error in these calculations is about $\pm 10 - 15\%$ at typical test conditions.

Lab-scale TCRS Start-up, Preheating, and Shutdown

The start-up, preheating, and shutdown procedures of the TCRS was an important part of the study to guarantee safe and controlled operation of the industrial furnace equipped with a recuperative reformer. Before TCRS operation the reformer tubes and piping are cold and air filled. Introducing natural gas directly into the reformer at the furnace start-up can create an explosive mixture of natural gas and air in the reformer and lead to unsafe operation of the TCRS. To prevent this condition the following generalized start-up procedure of the TCRS was established:

1. Initiate low FGR flow through the recuperative reformer by activating recirculation fan or use pressurized nitrogen (instead of natural gas) to create suction in the natural gas/flue gas mixer (see Figure A15) at the reformer inlet;
2. Introduce natural gas directly to the burners and start the burners in same way as a normal (without TCRS) startup with air/natural gas;
3. Adjust FGR flow so that the flow equals the nominal value as with reforming, for example (FGR volume flow, SCFH) = $3.3 \times (\text{Natural gas volume flow rate, SCFH})$.

After start-up, the reformer tubes and FGR flow in the reformer should be preheated to temperatures which are slightly lower ($100^\circ\text{F} - 200^\circ\text{F}$) than the temperatures at normal operating conditions with the fuel reforming. These temperatures are to be measured during the start-up and preheating and based on the measurements a decision can be made whether to switch the natural gas from the burners to reformer for TCRS operation. To minimize the number of measuring points for control purposes it is recommended to measure the FGR temperature at the reformer outlet only during reformer preheating. If the operating temperature of the reformed fuel is to be 1200°F the natural gas can be switched from the burners to the reformer inlet when this temperature is $\sim 1000^\circ\text{F}$ or higher.

Natural gas switching from the burners to the reformer should be also conducted by a specific procedure to eliminate any safety issues. The natural gas flow to the burners can be gradually decreased and simultaneously the natural gas flow to the mixer at the reformer inlet can be supplied and gradually increased to where the natural gas flow to the burners is zero and there is a full flow of natural gas to the mixer.

A procedure is also required at furnace shutdown. The natural gas supplied to the reformer can be shut off while combustion air continues to be supplied to the burner. For a short period of time, after the natural gas is shut off, flame will still be visible from the burner until the remaining reforming mixture in the reformer is completely combusted.

Recuperative Reformer Design Validation

The first step of the TCRS lab-scale testing was to validate design parameters of the recuperative reformer, particularly to confirm that the reformer hydrodynamic characteristics (such as pressure drop), thermal parameters (temperature, heat flux, etc.), heat transfer efficiency, and chemical reaction rates met the design requirements. The following metrics were measured and compared with the designed parameters:

Pressure drop in the reformer and burner

Flue gas and reforming fuel temperatures at the reformer inlet and outlet as well as in the middle of the reformer

Reforming fuel composition at the reforming inlet and outlet

Maximum pressure drop across the flue gas side of recuperative reformer was measured as 0.7" W.C. at maximum firing rate (0.434 MMBtu/hr), flue gas/natural gas ratio 3.34, and combustion air temperature of 1200°F. Maximum pressure drop through the burner was measured as 5.1" W.C. at the same conditions. These results confirmed predictions showing that the pressure drops are in the range of design values.

Reforming fuel inlet and outlet temperatures in the reformer preheater were measured to confirm design parameters of the preheater. The preheater serves to rapidly preheat flue gas/natural gas mixture (reforming fuel) to the temperatures that are close to the design value of the reformed fuel temperature. The design was developed such that the reforming fuel temperature at the preheater outlet would be approximately equal to the reformed fuel temperature at the reactor outlet.

After the preheater, the preheated natural gas/flue gas mixture enters the reactor where the mixture is reformed. An appropriate design of the reactor should provide approximately constant temperature of the reforming fuel along the reactor length. Essentially higher or lower temperatures of the fuel at the reactor outlet compared to the reactor inlet would indicate an unsuitable reactor design. A lower temperature of the reforming fuel at the reactor outlet compared to the reactor inlet can be a result of the following: less heat compared to the design value is supplied to the reactor from the flue gas so that the fuel is reformed at a lower temperature. In this case the reforming rate of the fuel is lower than the design value and as a result of that a lower hydrogen content will be measured in the reformed fuel. Higher temperatures of the reforming fuel at the reactor outlet compared to the reactor inlet can result from one of the following one or both reasons. There is not enough residence time in the reactor consequently the fuel is not reforming efficiently. In this case the reforming rate of the fuel is lower than the design value and as a consequence a lower hydrogen content will be measured in the reformed fuel. The other reason is that more heat compared to the design value is supplied to the reactor from the flue gas so that the fuel is reformed at a higher temperature. In this case the

reforming rate of the fuel will be higher (if appropriate residence time) than the design value and as a result a higher hydrogen content will be measured in the reformed fuel.

Summarization of Phase II Test Results

A Typical distribution of the reforming fuel temperature in the reformer preheater and reactor is shown in Figure A16. The reforming temperature was controlled by adjusting temperatures of the furnace exhaust gas and flue gas recirculation flows. The furnace exhaust gas flow temperature was controlled by adjusting water cooled probes in the furnace. The flue gas recirculation (FGR) flow temperature was controlled by adjusting water cooler installed at FGR line. As can be seen from the figure, the reforming fuel (flue gas/natural gas mixture) in the preheater is rapidly heated up from a low temperature ($\sim 160^{\circ}\text{F}$) to the temperature of $\sim 1250^{\circ}\text{F}$ the desired temperature for the fuel reforming. These measured results confirmed that the heat transfer area and heat transfer rate in the reformer preheater are sufficient to provide desired parameters of the reforming fuel at the reactor inlet.

The measured results of the reforming fuel temperatures at the reactor inlet (thermocouple location 2), middle (thermocouple location 3), and outlet (thermocouple location 4) demonstrated that the temperature distribution along the reactor is uniform and all the temperatures approximate the design values (see Figure A16). This confirmed that the reformer was properly designed and contained sufficient heat transfer area and heat transfer efficiency to provide heat from the flue gas to the reforming fuel. The residence time in the reactor was high enough to provide partial reforming of the fuel. It is surmised that the residence time can even be slightly lower. Some temperature reduction of the reforming fuel in the reactor (thermocouple locations 2 through 4) is a result of endothermic reactions. The temperature distribution can be further improved upon (constant temperature between points 2 and 4) by adjusting heat transfer areas or flow rates within the reactor (by modifying reactor design).

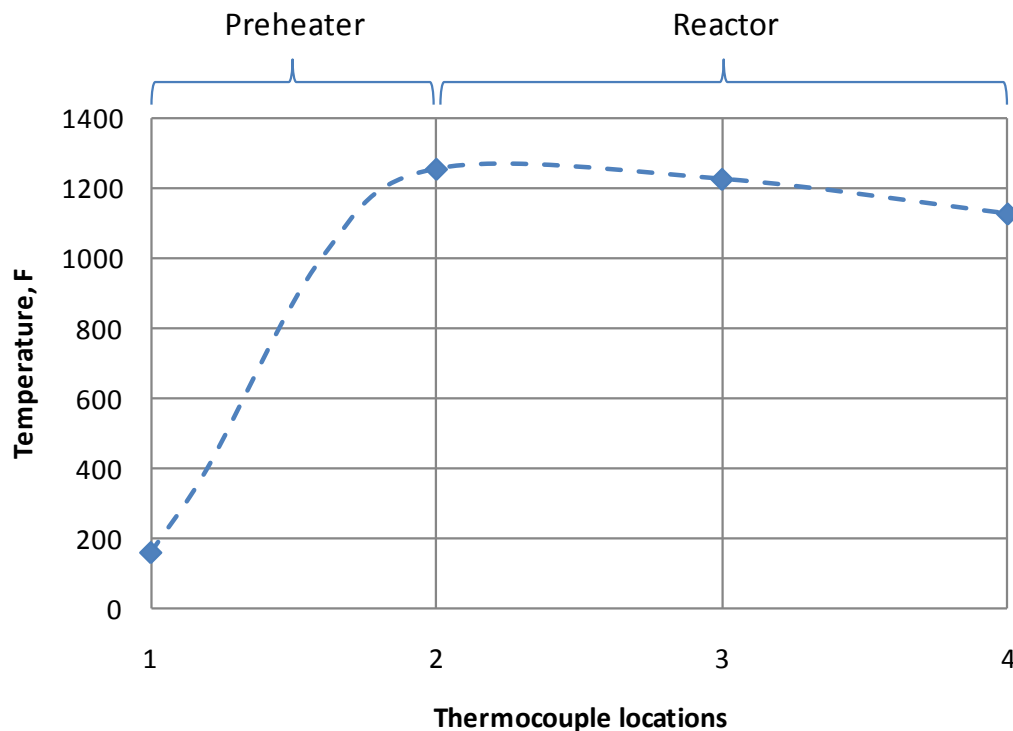


Figure A16. Typical Distribution of Reforming Fuel Temperature in the Reformer Preheater and the Reactor
(Thermocouple Locations: 1 and 2 – Preheater Inlet and Outlet, 3 and 4 – Middle Out and Outlet of the Reactor)

Burner Performance Validation

A Bloom burner that was used in the TCRS testing demonstrated good performance at start up and firing in wide ranges of the natural gas flow rate (100 SCFH – 450 SCFH), FGR flow rate (0 - 3,000 SCFH), excess air (0 - 10%), temperatures of combustion air (100°F - 1200°F) and reformed fuel (800°F - 1300°F). No burner overheating occurred, nor was unstable operation observed during the tests.

Recuperative Reformer Performance Validation

The performance of the recuperative reformer depends on many factors, parameters, and operating conditions. There are several design parameters that may affect performance of the recuperative reformer. Some of them are *efficiency of heat transfer* in the reformer, *residence time*, *tube and wall material* used in the reformer and *surface area* which is in contact with the reforming fuel. As previously noted, preliminary tests showed that the reformer provided sufficient heat transfer and provided enough heat to the reforming fuel to compensate for energy outflow due to endothermic reactions. The reformer heat load (natural gas flow rate), reforming fuel temperature, flue gas/natural gas flow ratios, and excess air to natural gas ratios were varied in the experiments to analyze the reformer performance.

The reformer performance was characterized by such parameters as *process completeness* and *methane conversion rate* (see Data Analysis and Quality Assurance Procedures – Section G, page 32). During testing, hydrogen and carbon monoxide contents in the reformed fuel were also used to preliminarily estimate performance of the recuperative reformer. Comparing measured values of hydrogen and carbon monoxide with their theoretical predictions made it possible to determine how well the reformer was performing. For example, the theoretical reformed fuel composition at design conditions (1200°F reforming temperature, flue gas/natural gas volume ratio ~ 3.3:1) should result in the following (% volume): CH₄=5.7%, CO₂=2.82%, H₂O=2.88%, N₂=42.94%, CO=14.7%, H₂=30.96%. Matching this composition with measuring values would provide 100% process completeness. In actual practice process completeness is lower than 100%. GTI expected that process completeness for a non-catalytic reformer would not be higher than 80% - 90%. With this target (for example, 85% process completeness) for the experiments the expected reformed fuel composition should be: CH₄=7.6%, CO₂=3.95%, H₂O=3.65%, N₂=44.41%, CO=12.47%, H₂=27.92%. Since the measurements are based on dry values, the dry composition of the reforming fuel is: CH₄=7.89%, CO₂=4.1%, N₂=46.09%, CO=12.94%, H₂=28.98%. Consequently, comparing measured values of hydrogen and carbon monoxide with theoretical predictions a qualitative determination can be made as to how well the reformer was performing and adjusting the experimental plan as necessary.

Technical/Performance Issue

Observations of hydrogen and carbon monoxide values over time showed that the recuperative reformer performed less efficiently at the beginning of the each experiment compared to the later results prior to shutting down the test set up. Hydrogen and carbon monoxide contents in the reformed fuel were in the ranges of 16% - 23% and 6% - 9% (dry basis) respectively while the theoretical predictions were approximately 29% H₂ and 13.5% CO. During the experiments, these values were gradually increasing and reached their maximums, which were nearer the theoretical predictions. One explanation for such an increase in the reformer performance can be explained by the catalytic effect of metal surfaces inside the reformer on the reforming reaction rates. The metal surfaces have some catalytic activity that promotes the reforming reactions. Being in sustained contact with the high temperature gas mixture, the metal heat transfer surfaces could increase their catalytic activity because of the naturally occurring surface oxidation/reduction activity. Another explanation could also be another mechanism of increased reforming rate called carbonization, which causes increased catalytic activity of the metal surface when carbon is formed on the surface (Moayeri and Trimm 2007). The main series of the experiments were done after the reformer performance was stabilized.

Figure A17 shows the dry reforming product compositions (H₂ and CO) measured by the gas chromatograph at different reforming temperatures. The reforming temperature was taken as averaged temperature between middle of the reactor (thermocouple location 3, Figure A17) and reactor outlet (thermocouple location 4). H₂ and CO contents increased as the temperature increased. Maximum yields of 27% of hydrogen and 11% of carbon monoxide were observed in the experiment at chosen conditions.

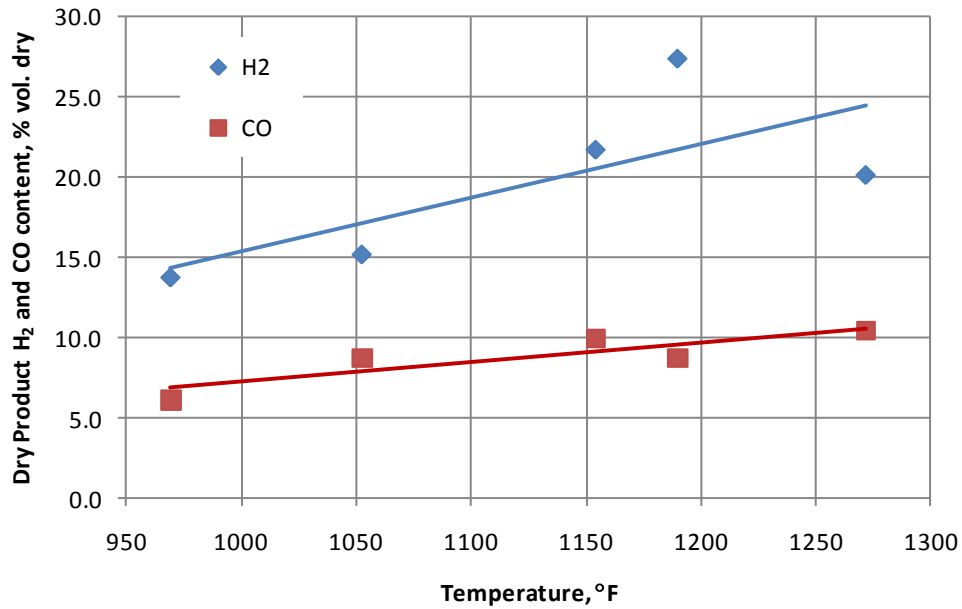


Figure A17. Dry Reformed Fuel H₂ and CO Components versus Reforming Temperature
(FGR/NG=3.34, Residence time 10 sec)

The methane conversion rate is shown in Figure A18. As can be seen, methane conversion started at temperatures lower than ~1000°F and increased as the temperature increased. Approximately 58% of methane in natural gas can theoretically be reformed at 1200°F while the measured results confirmed that only ~41% of methane was reformed in the non-catalytic recuperative reformer. This corresponds to ~70% reforming process completeness (see Figure A19).

Figure A19 shows the effect of reforming temperature on the reforming process completeness. The process completeness is decreased from ~72% at a 980°F reforming temperature to ~65% at a 1315°F reforming temperature.

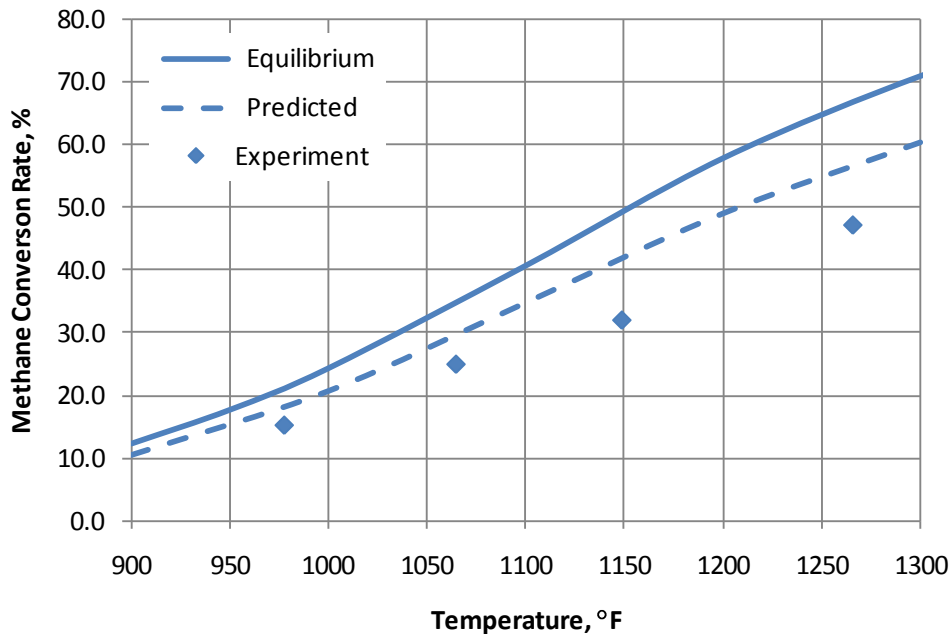


Figure A18. Methane Conversion Rate versus Reforming Temperature
(FGR/NG=3.34, Residence time 10 sec)

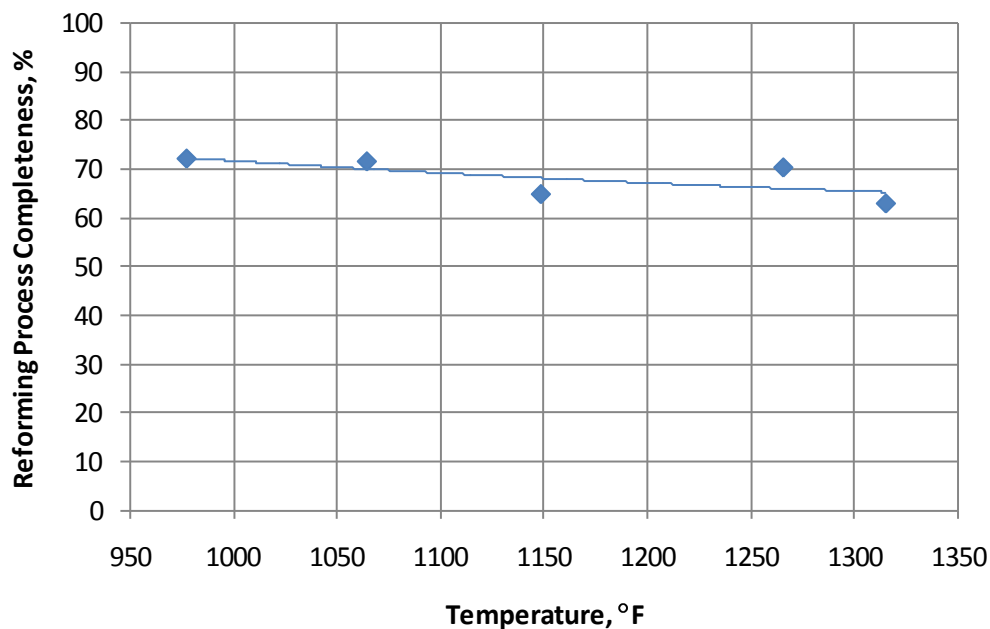


Figure A19. Reforming Process Completeness Versus Reforming Temperature
(FGR/NG=3.34, Residence time 10 sec)

During testing it was determined that the efficiency (methane conversion rate) of the recuperative reformer would slightly degrade with time and appeared to plateau at the end of the

test cycle (see Figure A20). The degradation test was conducted for a test cycle of more than six hours and with the methane conversion rate consistently reducing from 42.4% to ~31% at the end of this time period. Estimated equilibrium conversion rate was 53-57% during the test. Additional continuous running test (Durability Testing) was determined to be required to evaluate whether the degradation is asymptotic at the six hour mark and if not when and at what level does efficiency degradation become asymptotic. It should be noted that upon restarting the test furnace for another test cycle from a cold start and once operating equilibrium was reached, recuperative reformer efficiency returned to the original level only to degrade again as described above.

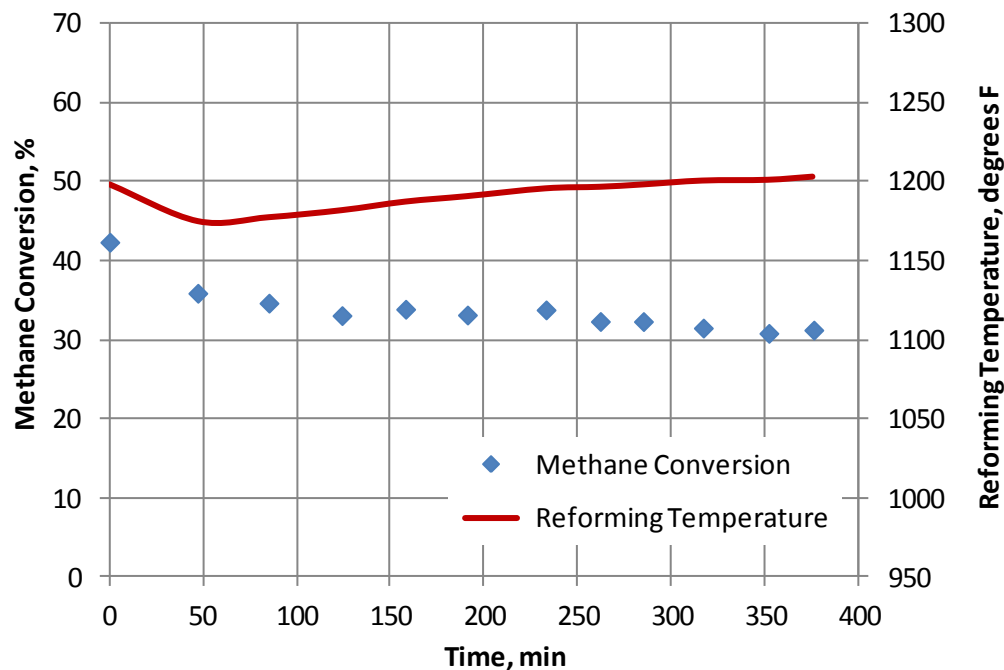


Figure A20. Methane Conversion Rate and Reforming Temperature Versus Time
(FGR/NG=3.34, Residence time 10 sec)

Emissions Reductions

Oxides of Nitrogen (NO_x)—The lab tests confirmed that the Oxides of Nitrogen are reduced by approximately 33% (see Figure A21) as measured against the standard operation of the Bloom low NO_x burner used in these lab tests. Accordingly, the nominal projected pounds of NO_x per ton of reheated steel is reduced from ~0.8 to ~0.54 lb per ton of reheated steel.

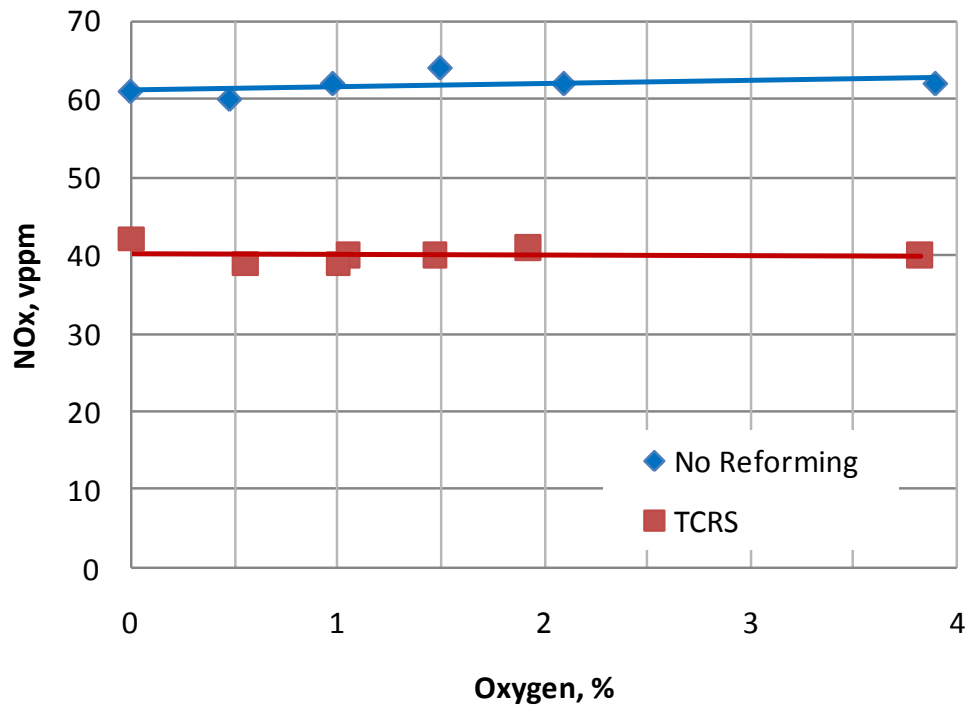


Figure A21. NO_x Emissions (dry)
(FGR/NG=3.34, Residence time 10 sec)

Carbon Dioxide (CO₂)—Since carbon dioxide is a direct function of the fuel combusted, the reduction in fuel usage of 21% translates to a nominal projected pounds of CO₂ per ton of reheated steel reduced from 185 lb of carbon dioxide per ton of steel reheated to 146 lb of carbon dioxide per ton of steel reheated.

Carbon Monoxide (CO)—One additional finding shown in Figure A22 is that for those operating periods where excess oxygen in the flue gas from the reheat furnace is 1% and lower there is a substantial reduction in carbon monoxide emissions.

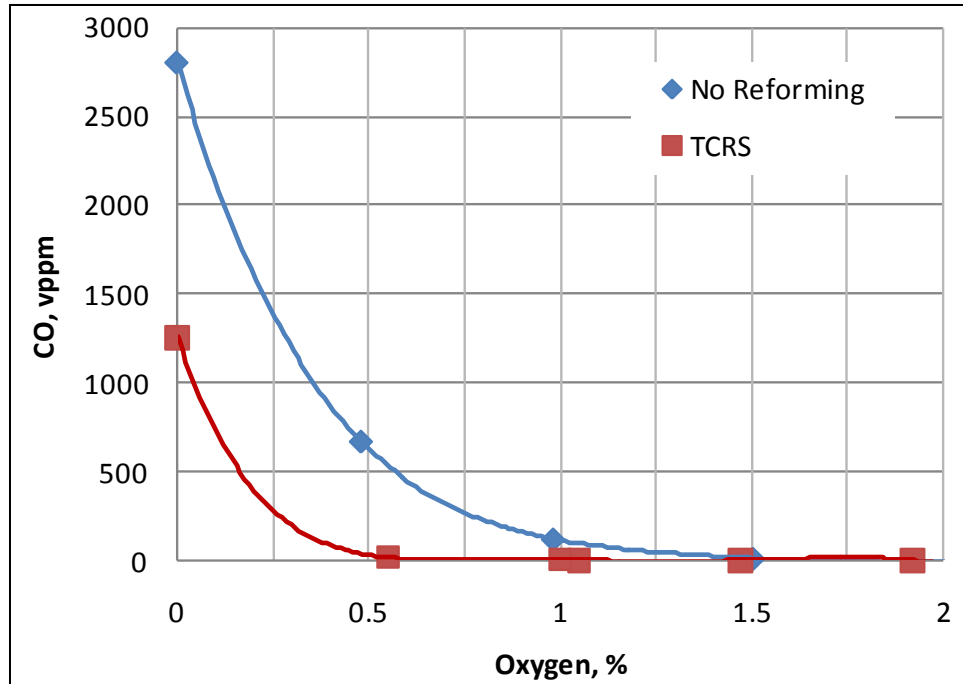


Figure A22. CO Emissions (dry) versus oxygen content in the furnace exhaust gas
(FGR/NG=3.34, Residence time 10 sec)

Recuperative Reformer Leakage Issue

The lab-scale TCR system test results indicated that internal leakage developed in the recuperative reformer. Notwithstanding that the test results were not compromised it was determined to be necessary to repair the reformer before further Durability Testing was undertaken. The recuperative reformer was partially disassembled (see Figure A23) by GTI staff and pressure tested to locate the leak(s). Leakage was confirmed but not located since further disassembling of the reformer unit by GTI would not be cost effective. A discussion was held with Thermal Transfer Corp. (TTC) on the cost and schedule for returning the reformer to TTC (leveraging their staff and equipment for cost effectiveness purposes). Approval by AISI was secured for GTI to proceed with this plan. The recuperative reformer was disconnected from the GTI experimental rig (see Figure A24) and shipped to TTC for repair(s). TTC disassembled and pressure tested the unit, and discovered several points of leakage (see Figure A25). TTC repaired the sources of leakage and shipped the unit back to GTI on 30 December 2011.



Figure A23. Partially Disassembled Recuperative Reformer at GTI Laboratory



Figure A24. Recuperative Reformer Prepared for Shipment to TTC

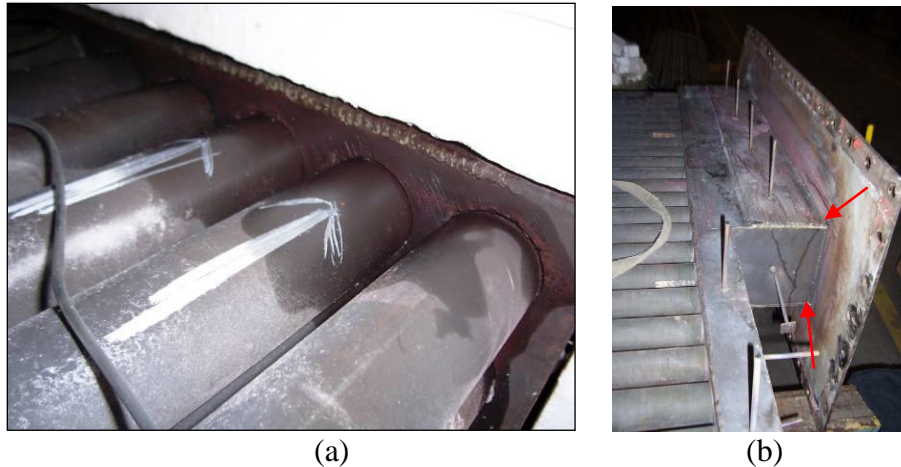


Figure A25. Leakage Locations at the Tube Sheet (a) and Plenum (b)

Durability Test Summary

Subsequent to the leaks being repaired by TTC and the return of the Recuperative Reformer, a Durability Test was undertaken to determine whether the methane reforming rate degradation that was observed during the planned Phase II tests was already asymptotic or leveled out at a lower level of methane reforming.

The Recuperative Reformer was reconnected and the TCRS was retested for approximately 48 continuous hours. Once the system reached thermal equilibrium, the same gradual reduction in methane reforming rate was observed. An additional phenomenon was observed in that periodically the percent H₂ would increase and then decrease over a short time interval (several minutes) without any changes in the process by the staff operating the lab set up. Once it was evident that the methane reforming rate was still decreased and was not asymptotic, several changes to the process variables were intentionally made to attempt to retard or reverse this effect. See Appendix A3 for several graphical representations of the durability test results.

- Decreased Flue Gas to Natural Gas (FGR/NG) Ratio in several steps down to FGR/NG~3.3
- Drove the static pressure of the flue gas within the RR from negative to positive to avoid air infiltration into the flue gas.
- Increased the flue gas temperature entering the RR from an average of 1625°F to 1700°F. Insufficient time was available to increase the temperature to 1800°F and 1900°F
- Operated the test furnace at near stoichiometric such that the flue gases supplied to the RR contained < 1% oxygen.

None of the above process changes had a material effect on retarding the decrease in the methane reforming rate. During these changes it was also found that at certain conditions (at a low FGR/NG ratio ~3.3, etc.) the methane reforming rate became unstable and had begun changing from low to very high values. The hydrogen content in the reformed fuel was changing from 2% to 18% (see Figure A26) which is indicative of large changes in the methane reforming rate.

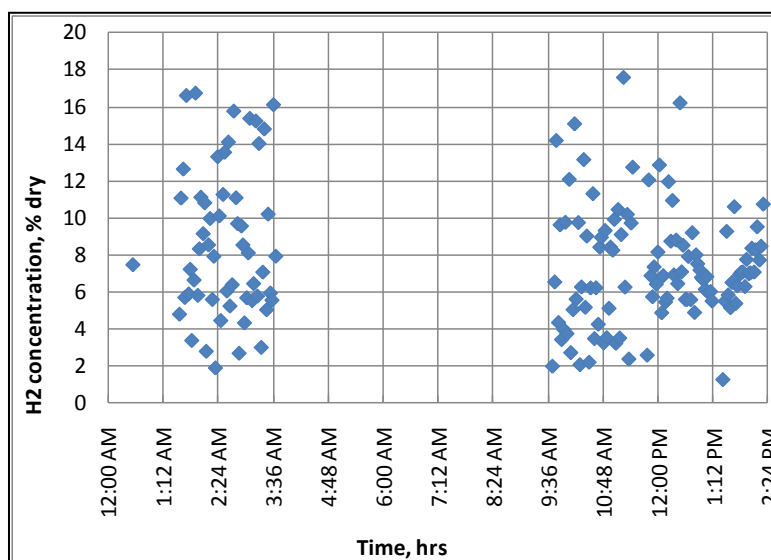


Figure A26. Hydrogen Content in the Reformed Fuel versus Time

Conclusions

GTI's preliminary conclusions are that the mechanism(s) producing the MRR decrease is (are) not entirely known or understood. The nature of the chemical kinetics that is triggering the mechanism and/or the other mechanisms described above is still necessary to be evaluated. Other possibilities include: stratification of the natural gas and flue gas downstream of the mixer within the preheater; and/or stratification of a portion of the flue gas/natural gas mixture and the complement of the flue gas/natural gas mixture for part of the residence time within the reformer-reactor.

Recommendations

Since the results of the endurance tests confirmed that the reforming process is gradually retarded over time due to one or more of the above mechanisms the TCR field experiment as outlined in Phase III is recommended to be postponed and a broader series of lab testing the TCR system to be approved with a revised test matrix based on a General Scope of Work for Extended Phase II TCR Testing that was prepared (see Appendix A4) with the technical objectives being to identify the mechanism(s) that are preventing a sustained methane reforming rate; devise and implement a solution to sustain the methane reforming rate.

GTI staff have discussed the above internally and believe that the following is a reasonable alternative given that (1) Proof-of-concept has been verified and; (2) More importantly a well-designed and operational TCR system residing in the GTI combustion laboratory is capable of further testing to evaluate which and how the above mechanisms are retarding the methane reforming rate. Once fully understood, necessary alterations to the reformer design can be made.

Accordingly, the teams' consensus is to capitalize on the considerable amount of data acquired from modeling and physical testing by proposing a revised scope of work that will focus on identifying the mechanism(s) that are co-opting methane reforming efficiency for long-term

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operation of TCR as a viable waste heat recovery technique. The revised scope of work will consist of kinetic modeling; adding instrumentation to more fully extract additional operating information (For example, sampling the flue gas/natural gas mixture at several points within the recuperative reformer. Currently the flue gas/natural gas mixture is sampled before entry into the recuperative reformer and the reformed fuel is sampled after exiting the recuperative reformer.) from the existing system that will enable the team to identify the mechanism(s) of MRR retardation; to conceive of the necessary modifications to the design; to build and to retrofit one or more modifications to the RR; iteratively retest the retrofitted RR until the RR achieves and sustains the predicted methane reforming rate for extended hours of operation. The revised schedule for the above revised Scope of Work is currently estimated as six months.

TCRS Performance Validation

Based on the physical test data obtained from the lab-scale experiments, the TCRS performance potential evaluated in Phase I was revised accordingly. Figure A27 shows the furnace thermal efficiency with combustion air recuperation and TCR system. The blue line represents furnace thermal efficiency for an air recuperated furnace. The red line, which is the ideal, shows TCR system evaluated in Phase I based on chemical equilibrium calculations; green line portrays the furnace thermal efficiency for the TCR system evaluated in Phase II based on the experimental results for the lab-scale test furnace at the achieved methane reforming rate with no degradation. As one can see from Figure A27 the revised thermal efficiencies of the furnace are lower compared to the equilibrium predictions, i.e. approximately 61%. This should be taken into account when fuel savings and capital expenditures are estimated.

Figure A28 shows fuel savings with combustion air recuperation and TCRS. As one can see from the figure, actual fuel savings using the non-catalytic reformer at 1200°F would be approximately 21% compared to the fuel consumption in the furnace with combustion air recuperation at 800°F. It would require approximately 1500°F combustion air preheat to achieve the same fuel savings as for the TCRS at 1200°F.

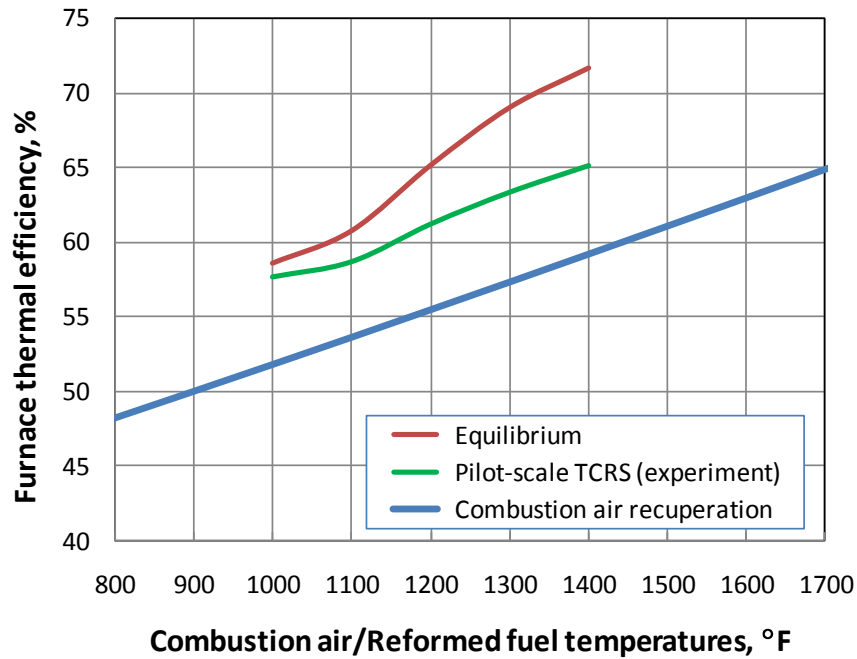


Figure A27. Furnace Thermal Efficiency Versus Combustion Air/Reformed Fuel Temperatures

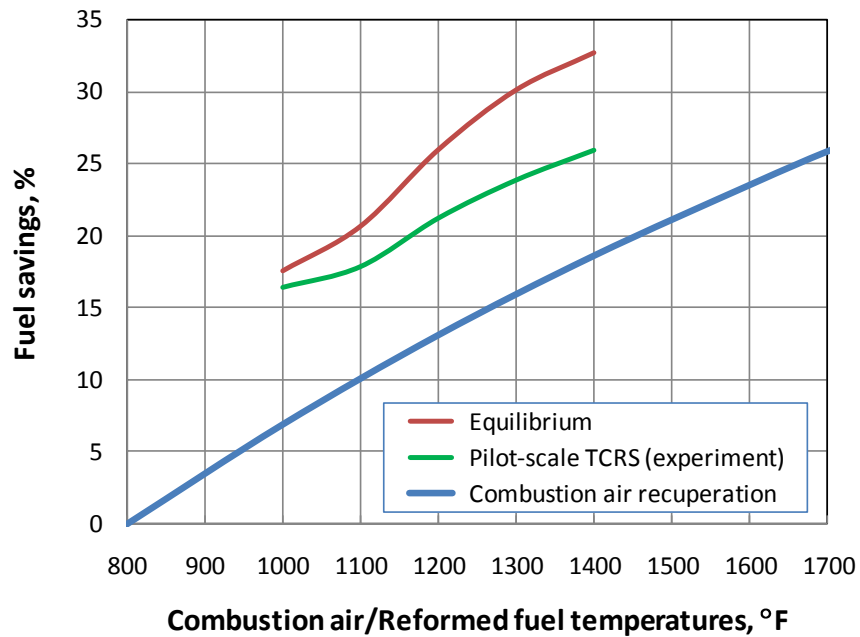
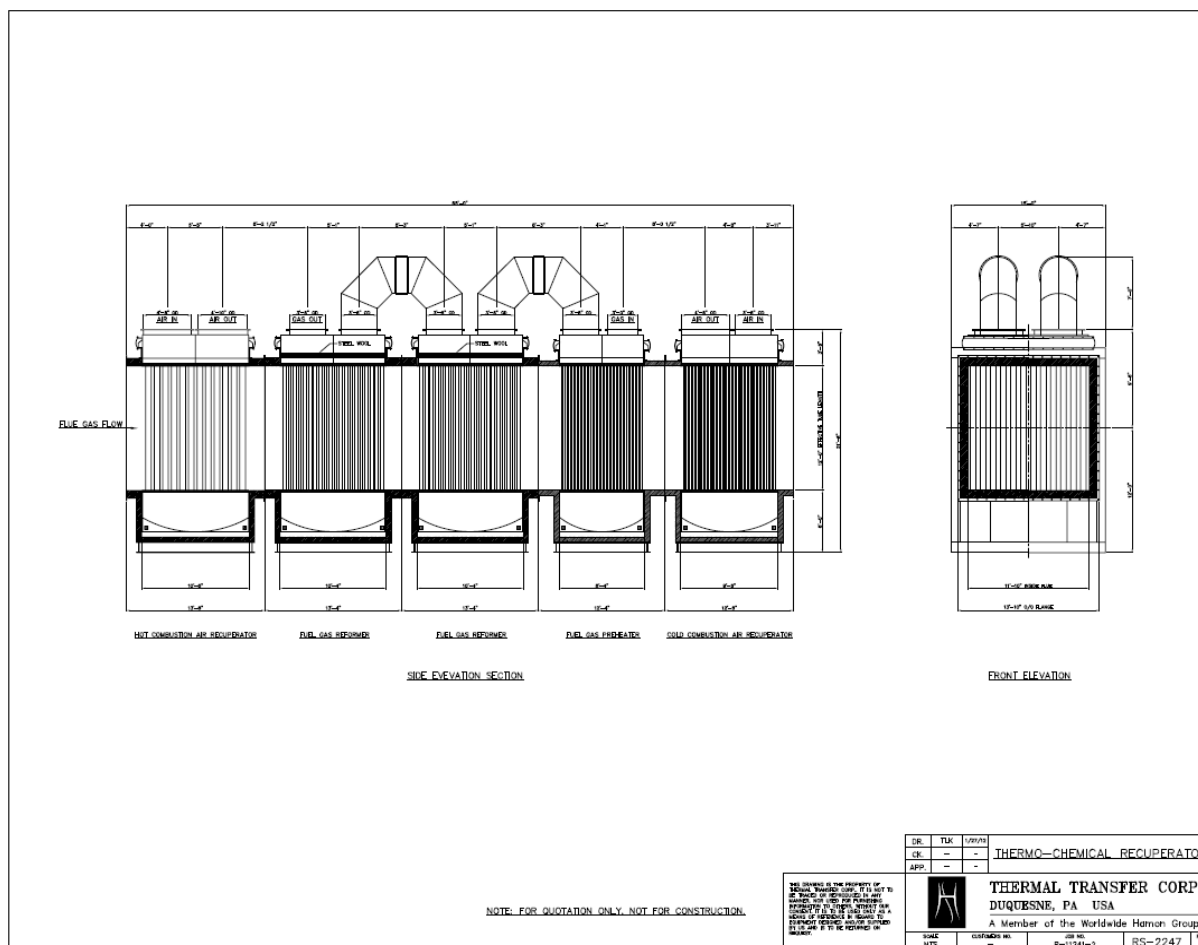


Figure A28. TCRS Fuel Savings Compared to Fuel Consumption at 800°F Air Recuperation

Revised TCR System Information Based on Phase II Test Results

The optimum three-stage TCR System configuration resulting from Phase I analysis was re-evaluated as a result of the physical lab testing carried out in Phase II. On this basis, additional technical information was provided to Thermal Transfer Corporation for obtaining a revised budgetary estimate and new physical dimensions and heat transfer module arrangement.

Figure A29 is a drawing showing the revised recuperative reformer based on Thermal Transfer Corporation's revisions per the Phase II results. Once major difference from the previous preliminary design is the preheater for the flue gas/natural gas mixture is not integrated into the recuperative reformer is now a separate module.



**Figure A29. Full Scale TCRS -Air Recuperation (AR)
and Thermochemical Recuperation (TCR)**

AR & TCR Footprints

For the AR

The length, width and height were established as 14.2 feet long \times 15 feet wide \times 21.5 feet in height given revised parameters from lab testing:

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- Combustion air preheat temperature $\approx 800^{\circ}\text{F}$
- Nominal furnace firing rate ≈ 335 MMBtu per hour
- Nominal waste gas flow $\approx 285,100$ pounds per hour
- Furnace thermal efficiency $\approx 48\%$

Note: the dimensions include the tube bundle and the outer shell.

For the TCRS

The length, width and height were established as 65 feet long x 15 feet wide \times 21.5 feet in height given the revised parameters from lab testing:

- Combustion air preheat temperature $\approx 1200^{\circ}\text{F}$
- Reformed fuel temperature $\approx 1200^{\circ}\text{F}$
- Nominal furnace firing rate ≈ 245 MMBtu per hour
- Nominal waste gas flow $\approx 261,324$ pounds per hour
- Furnace thermal efficiency $\approx 61\%$

Note: the dimensions include the tube bundle and the outer shell.

CAPEX and Simple Payback Based on Phase II Results

For purposes of comparison, the CAPEX values in Table A2 and Table A3 were established based on the Phase II results and revised budgetary estimates from Thermal Transfer Corporation.

It should be noted that the estimated cost of the TCRS increased by 100% whereas the estimated cost of an ARS increased by 42%. Although both utilize 304SS and 310 SS, the TCRS contains additional heat transfer surface areas consisting of these stainless steel grades. We believe additional opportunities to reduce and minimize reliance on this metallurgy may become evident when Extended Phase II TCR Testing is carried out, subject to approval.

Figure A30 and Figure A31 illustrate the revised capital expenditures (CAPEX) and simple paybacks for TCRS compared to a recuperated furnace with 800°F Air Preheat (Retrofitted Furnace). As can be seen, the TCRS option has a much lower capital expenditure level and lower simple paybacks compared to conventional air recuperation at matching furnace thermal efficiencies.

Table A2. Estimated CAPEX for the reference Air Recuperation System

Combustion air temperature, °F	800
Heat exchanger estimate	\$ 593,100
Direct Cost estimates	
Equipment f.o.b. price	\$ 1,627,507
Materials used for installation	\$ 466,031
Direct labor	\$ 422,743
Total direct materials and labor	\$ 2,516,280
Indirect Cost estimates	
Freight, insurance, taxes	\$ 106,331
Construction overhead	\$ 294,051
Contractor engineering expenses	\$ 180,249
Total indirect project costs	\$ 580,630
Bare module capital	\$ 2,228,911
Contingency/Fee estimates	
Contingency	\$ 336,116
Fee	\$ 69,596
Total contingency and fee	\$ 405,711
Total module capital	\$ 2,634,622
Auxiliary facilities	\$ 790,387
Total Estimated Costs	\$ 4,293,009

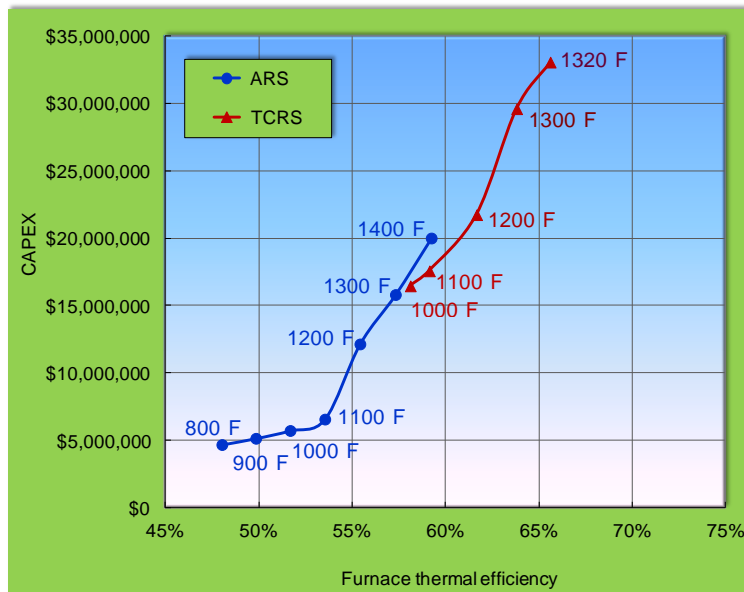


Figure A30. CAPEX for Air Recuperated System (ARS) and TCRS

Table A3. Estimated CAPEX for the current TCRS configuration

Air/Reformed fuel temperature, °F	1200
Heat exchanger estimate	\$ 3,077,700
Direct Cost estimates	
Equipment f.o.b. price	\$ 4,581,132
Materials used for installation	\$ 2,443,627
Direct labor	\$ 2,197,004
Total direct materials and labor	\$ 9,221,763
Indirect Cost estimates	
Freight, insurance, taxes	\$ 519,839
Construction overhead	\$ 1,528,116
Contractor engineering expenses	\$ 915,396
Total indirect project costs	\$ 2,963,351
Bare module capital	\$ 11,317,113
Contingency/Fee estimates	
Contingency	\$ 1,706,800
Fee	\$ 353,671
Total contingency and fee	\$ 2,060,471
Total module capital	\$ 13,377,584
Auxiliary facilities	\$ 4,013,275
Total Estimated Costs	\$ 18,258,860

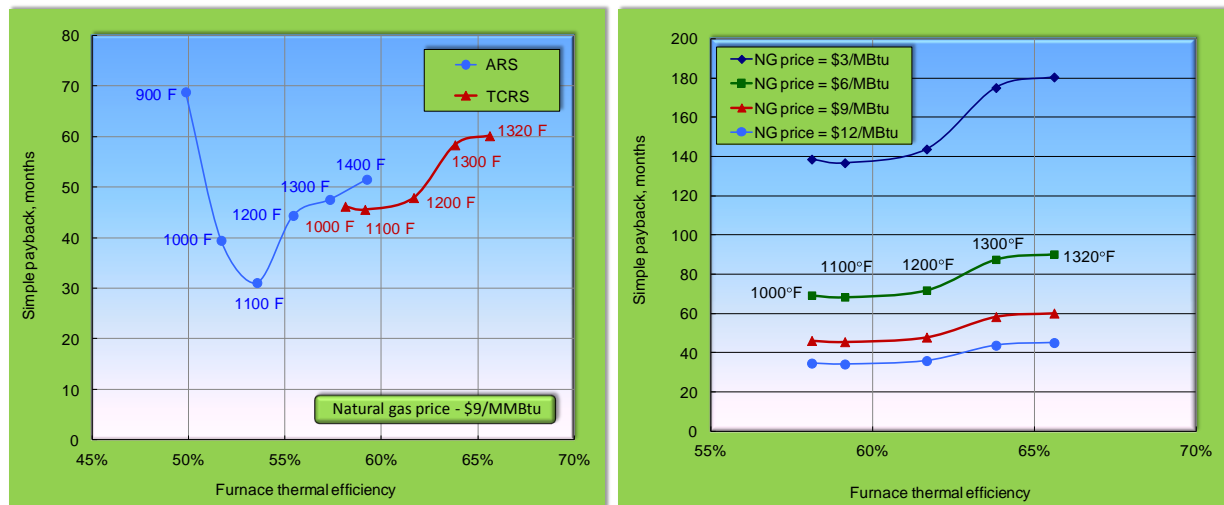


Figure A31. Simple Paybacks for TCRS Compared to a Recuperated Furnace with 800°F Air Preheat

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List of Acronyms

Acronym	Description
AISI	American Iron and Steel Institute
GTI	Gas Technology Institute
TCR	ThermoChemical Recuperation
CAPEX	Capital Expenditures
MMBtu	Million British Thermal Units
NPV	Net Present Value
TTC	Thermal Transfer Corporation
ARS	Air Recuperator System
TCRS	ThermoChemical System
WVPS	Water Vapor Pump System
T_{RF}	Reformed Fuel Temperature
FGR	Flue Gas Recirculation
CO_2	Carbon Dioxide
NO_x	Oxides of Nitrogen
CH_4	Methane
RR	Recuperative Reformer,
T_A	Temperature of Combustion Air
RF	Reformed Fuel
U	Heat Transfer Coefficient
ε	Relative Air Preheat
T_{ARI}	Temperature of Combustion Air – First Stage Air Recuperator
T_{ARII}	Temperature of Combustion Air – Second Stage Air Recuperator

Appendix A1 – Energy and Emissions Reductions and Cost-Benefit Effects on Steel Industry Reheat Furnace Population in Using TCRS

The efficiency step change validated in this Phase I work of increasing the reference reheat furnace (recuperated) thermal efficiency to 61% from 48% requires an air recuperator capable of producing preheated air at a temperature of 1700°F. The implications of the metallurgical requirements of the heat transfer tubes; the additional engineering considerations with respect to piping, valving, etc. due to 1700°F preheat temperature would, in GTI's opinion preclude this option being selected over that of a TCRS due to the increased cost of even higher grade tube materials and reduce longevity of the heat exchanger due to higher tube wall temperatures.

CAPEX and estimated Return on Investment: The cost estimates were established on the basis of three major categories that would make up retrofitting costs. Estimated Direct Costs, Estimated Indirect Costs and Estimated Contingencies and Fees for 1) The base case of retrofitting a reheat furnace with a recuperative system, and; 2) The three-unit TCRS that was optimized and validated in Phase II.

For retrofitting an ARS on the reference reheat furnace without recuperation, the estimated installed cost was approximately \$4.3 million, the annual fuel savings were \$9.2 million, the simple payback was 4 months and the ROI was \$31 million (NPV at a 7% discount rate over six years of cash flow).

In summary, for retrofitting the optimally designed three-unit TCR System on the reference reheat furnace without recuperation the estimated installed cost was approximately \$18.3 million, the annual fuel savings were \$14.3 million, the simple payback was 15 months and the ROI was \$38 million (NPV at a 7% discount rate over six years of cash flow).

For retrofitting the optimally designed three-unit TCR System on the reference reheat furnace with recuperation the estimated installed cost was approximately \$14 million, the annual fuel savings were \$14.3 million, the simple payback was 12 months and the ROI was \$6.4 million (NPV at a 7% discount rate over six years of cash flow).

The fixed natural gas cost for the above estimates was assumed as a nominal \$9 per million Btu.

It should be noted that no consideration was given for the complete or partial reuse of the existing recuperator of the reference steel reheat furnace which would further improve return on investment. There may be further reductions in the CAPEX as close inspection of Table D4 reveals that estimated Indirect Costs and Contingency and Fees are over 50% of the Installed cost of the optimized three-unit TCRS. We believe that these estimates are conservative and can be managed such that indirect costs and contingencies/fees can be reduced considerably.

Reduced Carbon Footprint and Oxides of Nitrogen: The reference recuperated furnace was estimated as producing 185 pounds of carbon dioxide per ton of steel reheated and 0.8 pounds of oxides of nitrogen per ton of steel reheated. Retrofitting the reference reheat furnace with the three-unit TCRS would reduce the emissions intensities of carbon dioxide and oxides of nitrogen

to 146 pounds per reheated ton and 0.54 pounds per reheated ton respectively. On an annualized basis the metric tons of CO₂ and NO_x produced by the three-unit TCRS reheat furnace would be an estimated 111,000 metric tons and 406 metric tons representing reductions of 30,000 metric tons per year of CO₂ and 200 metric tons per year of NO_x.

*Imputing results to 50% of the U.S. steel reheat furnace population:*¹ In order to benchmark the potential to the retrofitting of steel reheat furnaces, an estimated projection for frame-of-reference purposes only is included as summarized below. To remain conservative, 50% of the recuperated furnace population (approximately 80 steel reheat furnaces) was assumed as the steel reheat furnace market in the U.S.

Table A4. Imputed Future Fuel Usage Reductions – MMBtu per Ton

Flat/Long Plants		Recuperated Furnaces – MMBtu per Ton	
Recuperated	TCR	Current	Future
Integrated		1.18	0.93
Minimills		1.11	0.88
Converter/Specialty		1.40	1.11

The energy intensities (EIs) of each of the three steel segments (See table at the right), Integrated, Minimills and Converter/Specialty that making up the Flat and Long product plants representative composite or aggregate of EIs of the furnace populations within each segment. The approach employed was to scale back the energy intensities (composite energy intensities) of recuperated furnaces in three steel segments (see) on a prorated basis using the percent improvement in thermal furnace efficiency of the base case recuperated furnace in this study when equipped with a three-unit TCRS recognizing that the level of precision in making these projections will not be as high as in this report for the reference furnace studied since the furnaces making up 50% of the U.S. population were not studied in detail as the reference steel reheat furnace was for this study.

Finally, below are two tables summarizing the imputed reductions in energy consumption and emissions reductions for the ultimate equipping/retrofitting of 50% of the recuperated furnace population with TCRS. The reductions were projected by the imputed future energy intensities shown in the table above.

¹ 2003 North American Hot Strip & Plate Mill Market Study (*Customized Final Report*), prepared for Gas Technology Institute by AIM MARKET RESEARCH

Table A5. Imputed Future Fuel Usage Reductions – TBtu per Year

Plants	Current	Future	Savings
Flat and Long	TBtu	TBtu	\$-mill
Integrated	26.6	21	50.4
Minimills	16.0	12.6	30.6
Converters/Specialty	2.9	2.3	5.4
Totals-cum	45.6	36	86.4

Table A6. Imputed Emissions Reductions – Tons (metric) per Year

Emissions	Current	Future	Reductions
CO ₂	3,300,000	2,500,000	700,000
NO _x	14,000	9,500	4,700

Appendix A2 – Experimental Evaluation of Residence Time for Non-Catalytic Reformer

Testing Objectives

The numerous variables in the lab-scale TCRS testing require a multifactor design of the test matrix and large number of experiments with different initial conditions (levels) to augment/optimize the main body of testing and reduce the number of experiments in the lab-scale TCRS tests.

Optimized the number of experimental conditions was initiated by a short preliminary test that was conducted using another existing TCRS (experimental rig) at GTI combustion laboratory. The existing experimental rig installed on a GTI heat treat furnace contains a preheater and a recuperative reformer. The recuperative reformer design allows testing the reformer with and without a catalyst. The experimental rig is very flexible, allows changing reforming temperature, reforming fuel flow rate, and other parameters of the TCRS.

The existing recuperative reformer was used to confirm residence times required to reform natural gas with flue gas. The additional knowledge about the residence time for non-catalytic reforming allows reducing the number of experiments in the lab-scale test by eliminating conditions (levels) with too low or too high values of residence time. For example, the residence time low level can characterize experimental conditions when the reforming reaction rate is lower than 10% of theoretical prediction by equilibrium. The residence time high level can be limited by 90% of theoretical prediction by equilibrium or limited by the reformer dimensions. The higher residence time requires a larger reformer.

Experimental Setup and Measuring Equipment

Laboratory tests were conducted using the GTI natural gas-fired heat treat furnace which is equipped with several burners. One of the burners (see Figure) was used both as a high temperature flue gas source and heat source for the reformer; the other burners were not used. Produced reformed fuel was flared.

Flue gas from the burner simulated the lab-scale furnace exhaust and was controlled by natural gas/combustion air flow ratio. Flue gas composition was specified to provide comparable conditions with the lab-scale furnace and maintained close to the following values (by volume): $\text{CO}_2=8.1\%$; $\text{H}_2\text{O}=16.1\%$; $\text{O}_2=4\%$; $\text{N}_2=71.8\%$. The flue gas temperature was in the range of 1230°F - 1670°F . Desulfurized, line natural gas was used for reforming. Its composition was approximately the same during all tests. Typical values of the natural gas major components were (mole fraction, %): $\text{CO}_2=1.0\%$, $\text{N}_2=1.2\%$, CH_4 (methane) = 95%, C_2H_6 (ethane) = 2.4%, C_3H_8 (propane) = 0.3%, $i\text{-C}_4\text{H}_{10}$ (i-butane) = 0.05%, $n\text{-C}_4\text{H}_{10}$ (n-butane) = 0.05%. The lower heating value of the natural gas was approximately 20,320 Btu/lb.

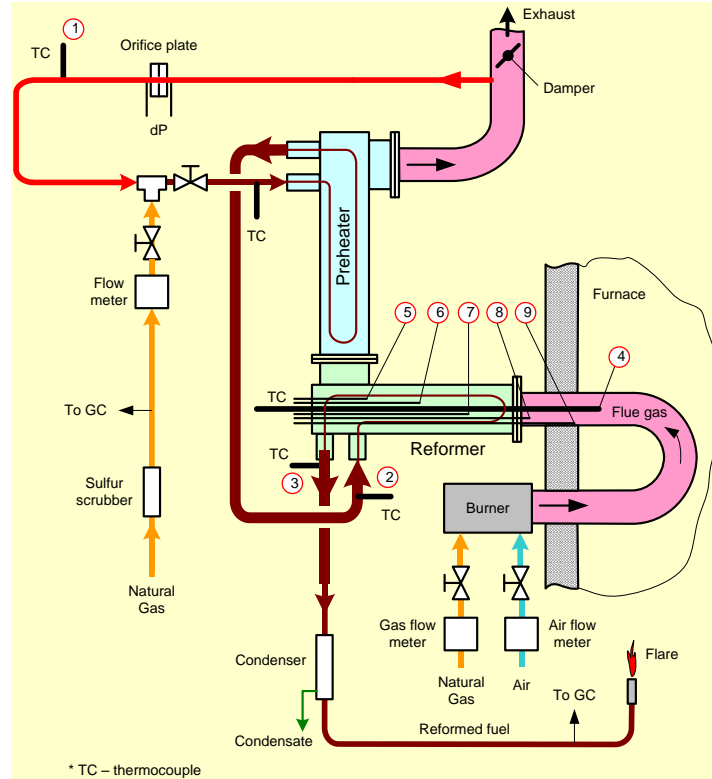


Figure A32. Laboratory Setup for Flue Gas/Natural Gas Reforming

The Eclipse 4" Therm-Thief Bayonet-Ultra Recuperator (see Figure A33) was used as the recuperative reformer. It is a tubular type heat exchanger with five heat exchange double tubes. Removable inserts (metal or catalytic) can be placed inside inner tubes (see Figure A34) and inspected after each test in order to observe if carbon deposited on the metal or catalytic surface.

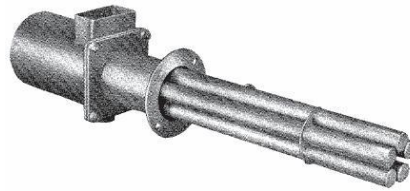


Figure A33. Eclipse Therm-Thief Bayonet-Style Recuperator Used as a Reformer

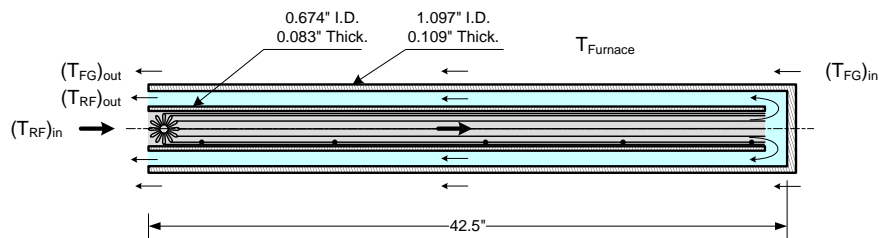


Figure A34. Tube Exchange Tube with Metal Mesh inside Inner Tube

A metal mesh (see Figure A35) as extended surface for the reforming reaction was used in some of the tests. The mesh material is Monel.



Figure A35. Metal Mesh inside Reformer Tubes

Thermocouples were installed inside inner tubes of the reformer between the tube wall and catalyst at different locations (see Figure A36) in order to measure temperature profile of the reforming gas.

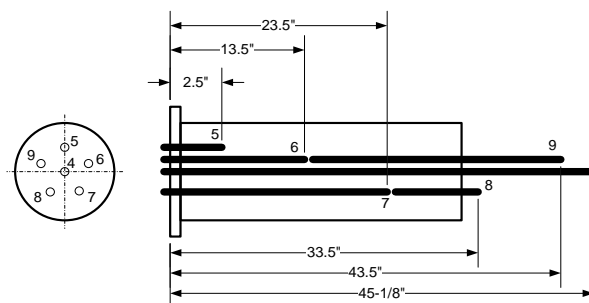


Figure A36. Thermocouple Position in Heat Exchange Tubes

A photograph of the test setup is shown in Figure A37. The burner on the left and burner in the middle were not used. Burner No. 1 is partially obscured behind the insulated pipe exiting one of the recuperators. Both recuperators are bayonet-style Eclipse Therm-Thiefs, model BU, shown in Figure A33. Each of the five cylinders contains interior parts for heat exchange. Two recuperators were needed to raise the temperature of the natural gas plus flue gas mixture enough to allow reforming. The schematic in Figure indicates the direction of flows in the setup. Burner No. 1 burns natural gas to simulate hot flue gas exiting a real furnace; the flue gas then exits the U-tube and transfers heat through two recuperators to reform the fuel. Downstream of the recuperators, part of the flue gas is added to the natural gas for reforming.

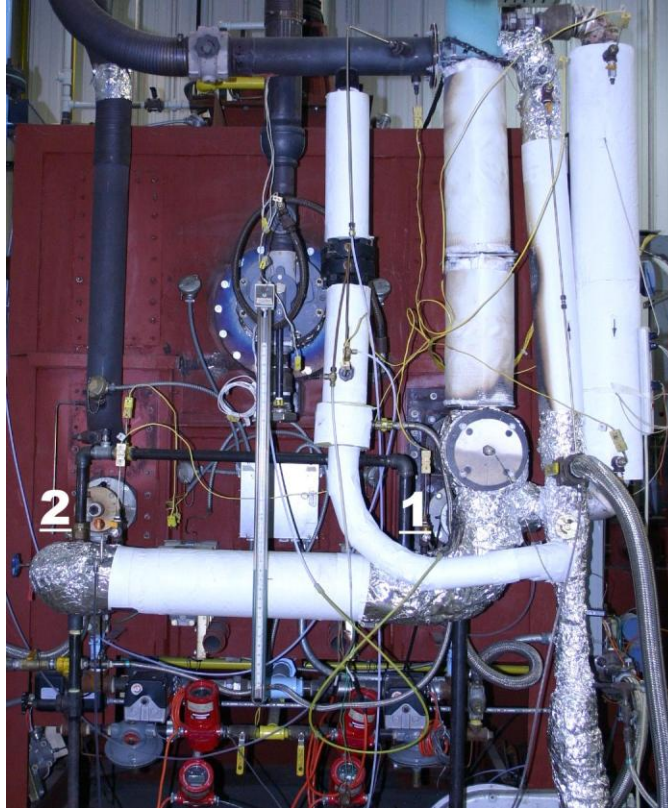


Figure A37. Laboratory Setup with Burner No. 1 Firing Natural Gas

The following parameters were estimated during the test:

- Temperature of the exhaust gas
- Inlet and outlet temperatures of the reforming mixture
- Composition of exhaust gas
- Composition of natural gas
- Composition of the reformed fuel
- Natural gas flow rate for reforming
- Exhaust gas flow rate for reforming

Instruments used in the laboratory tests are listed in Table A7. A Horiba portable gas analyzer was used to measure flue gas composition, with house gas composition presumed constant. The house gas composition was sampled once on three different days, analyzed in GTI's chemical laboratory by ASTM D1945-96(01), and the sample average was used for calculations. The Varian micro gas chromatograph was used to measure the composition of reformed fuel at the reformer outlet. Temperature data was collected periodically by the data acquisition system attached to the furnace.

Table A7. Instruments Used

Measurement Device	Measured parameter
Horiba PG-250 portable gas analyzer	Flue gas composition just before exhausting
Varian CP 4900 gas chromatograph	Reformed fuel composition at the reformer outlet
Laboratory gas chromatograph	Natural gas composition over three days
K-type thermocouples	Temperature at various locations in the process
Sierra mass flow meters	Natural gas flow rate and air flow rate
U-tube manometer and orifice plates	Flow rate of process flue gas

Key TCRS process parameters are temperature and residence time of mixture inside reformer. The process temperature was measured by 2 thermocouples installed at the reformer inlet and reformer outlet. Other thermocouples (5) were installed inside each of recuperator's heat exchange tubes (with installation depth varied from 2.5" to 45.125"). Installation depth was measured from the outer surface of recuperator's flange (see Figure A36).

Residence time was evaluated from reaction mixture flowrate, process temperature and recuperator's geometry (see Figure A38).

The volume used for residence time estimation consisted of (1) recuperator's inlet plenum, (2) volumes of heat exchanging tubes and annuluses, (3) recuperator's outlet plenum and (4) outlet pipe from recuperator to flare (straight horizontal insulated pipe in Figure A37).

Volumes of reformer's components were estimated as follows:

- Reformer's inlet plenum: 94.7 in³
- HX tubes and annuluses: 202.0 in³
- Reformer's outlet plenum: 38.6 in³
- Outlet pipe from reformer to flare: 325.3 in³

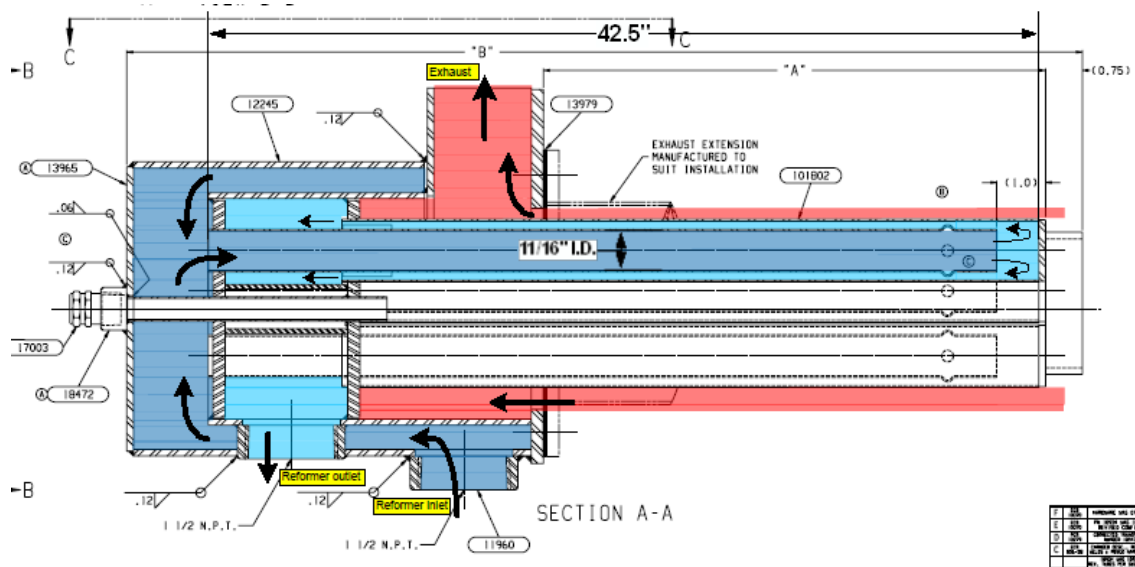


Figure A38. Recuperator/Reformer Geometry

Based on total volume and process temperature 1200°F, reaction mixture flowrate through reformer should be 136 ACFH (43.4 SCFH) to achieve a residence time of 10 s. Assuming flue gas (FG) to natural gas (NG) ratio of 3.5, flowrates of FG and NG should be 33.7 SCFH and 9.6 SCFH correspondingly.

From the shakedown tests, it was found that, due to low gas flowrate in the reformer, temperature distribution in the reformer is very uneven, except temperature inside HX tubes and annuluses. Typical values are shown in Table A8. Thermocouple in tube 1 is inserted at 3" from outer reformer flange, so it actually measures temperature in the inlet plenum (see Figure A35). Based on the measured results, due to low temperature in reformer plenums and outlet pipe, only the volume inside HX tubes should be considered to calculate the residence time.

Tests 1 through 7 shown in the table were conducted without any inserts in the reformer tubes. Tests 8 and 9 (two last columns in Table A8) were conducted with the metal mesh inserted into heat exchange tubes (see Figure A35) of the recuperative reformer. In all the tests except test No. 6 the average reforming temperature in reformer tubes was maintained approximately the same in the range of 1205°F-1228°F. The average reforming temperature in the test No. 6 was 1504°F.

Results and Discussion

Hydrogen content in the reformed fuel can be used for qualitative analysis of the TCRS efficiency and reforming reactions rates. As we can see from Table A8 there is low hydrogen content in the reformed fuel when the residence time is lower than seven seconds (Tests No. 1 and No. 3). Increasing the residence time to thirteen seconds allows achieving more hydrogen content in the reformed fuel (Tests Nos. 2, 3, 4, 5, and 7) which is evidence of higher fuel reforming rate and higher TCRS efficiency. It is obvious that the reforming rate is higher at higher reforming temperature (Test No. 6).

Metal mesh in the heat exchange tubes of the reformer promotes the reforming reactions and leads to higher hydrogen content in the reformed fuel (Test Nos. 8 and 9). Thus, hydrogen content in the reformed fuel is increased from ~3.8% (Test No. 4) to ~9% (Tests Nos. 8 and 9) when the mesh was inserted into the tubes.

Based on the obtained results we can conclude that the residence time in the reformer should be at least seven seconds or higher. Extended metal surface should be used in the reformer to promote the reforming reactions. This can be done by increasing the heat transfer surface area of the reformer or putting inserts in the reforming fuel flow.

Table A8. Test Results

Test #			1	2	3	4	5	6	7	8	9
Test date			11/11/2010	11/11/2010	11/11/2010	11/11/2010	11/23/2010	12/3/2010	12/3/2010	12/20/2010	12/20/2010
Temperatures	Hot flue gas (pos.4, Figure 1)	F	1313	1345	1354	1361	1327	1668	1397	1231	1237
	Preheater inlet mixture	F	548	512	522	518	623	738	710	587	583
	Tube 1, pos.5	F	813	765	766	700	823	965	834	711	716
	Tube 2, pos.6	F	1223	1224	1219	1227	1230	1519	1235	1229	1233
	Tube 3, pos.7	F	1237	1240	1236	1240	1231	1536	1232	1247	1249
	Tube 4, pos.8	F	1142	1153	1150	1154	1131	1403	1127	1153	1154
	Tube 5, pos.9	F	1218	1237	1240	1245	1231	1558	1316	1271	1274
	Outlet mixture (pos.3, Figure 1)	F	589	496	434	406	617	756	588	495	464
	HX average	F	1205	1214	1211	1217	1206	1504	1228	1225	1228
Flue gas composition	CO2	%	9.57	9.75	9.7	9.77	9.61	9.91	10.33	11.62	11.58
	O2	%	5.1	4.8	4.86	4.78	5.07	3.03	2.22	0.62	0.72
	NO	ppm	57.3	52	53	53.2	66	92	50	60.8	61.1
FG florate		scfh	34	16	16	12	12	12	12	12	12
NG flowrate		scfh	9.6	3.2	6	3.2	3.3	3.3	3.3	3.3	3.3
residence time in reformer		s	5.6	12.9	11.3	16.5	15.9	13.7	15.6	16.3	16.3
Residence time in HX tubes		s	3.5	8.0	7.0	10.2	9.8	8.4	9.6	10.0	10.1
Reformed fuel composition	H2	%	0.20	0.61	1.22	3.76	4.8	25.4	18.09	8.91	9.07
	O2	%	0	0	0	0	0	0	0	0	0
	N2	%	58.33	59.74	44.89	45.00	47.58	41.21	50.54	52.21	50.24
	CH4	%	34.09	32.07	47.95	44.25	42.49	17.87	19.83	31.31	33.38
	CO	%	0.00	0.00	0.00	1.04	0.8	7.05	6.38	2.04	2.18
	CO2	%	7.36	7.55	5.90	5.93	6.33	8.08	5.25	6.76	6.51
	C2H6	%	0.02	0.04	0.03	0.03	0.33	0	0.14	0.38	0.39

Appendix A3 – 48-Hour Durability Test – Graphical Results

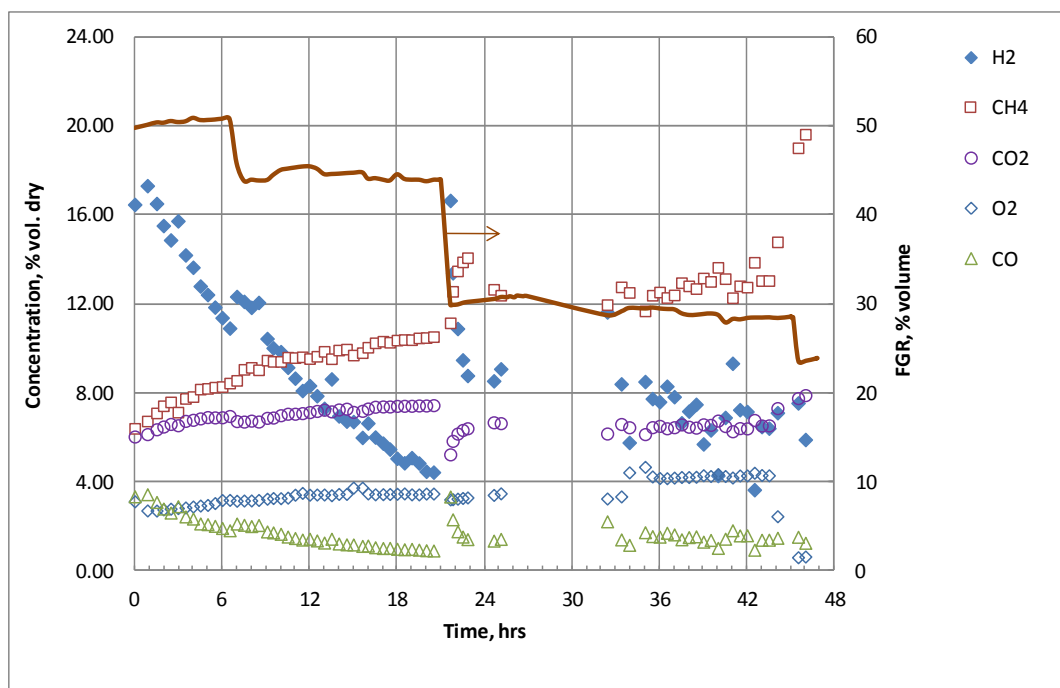


Figure A39. Reformed Fuel Components (dry) – 48 Hours

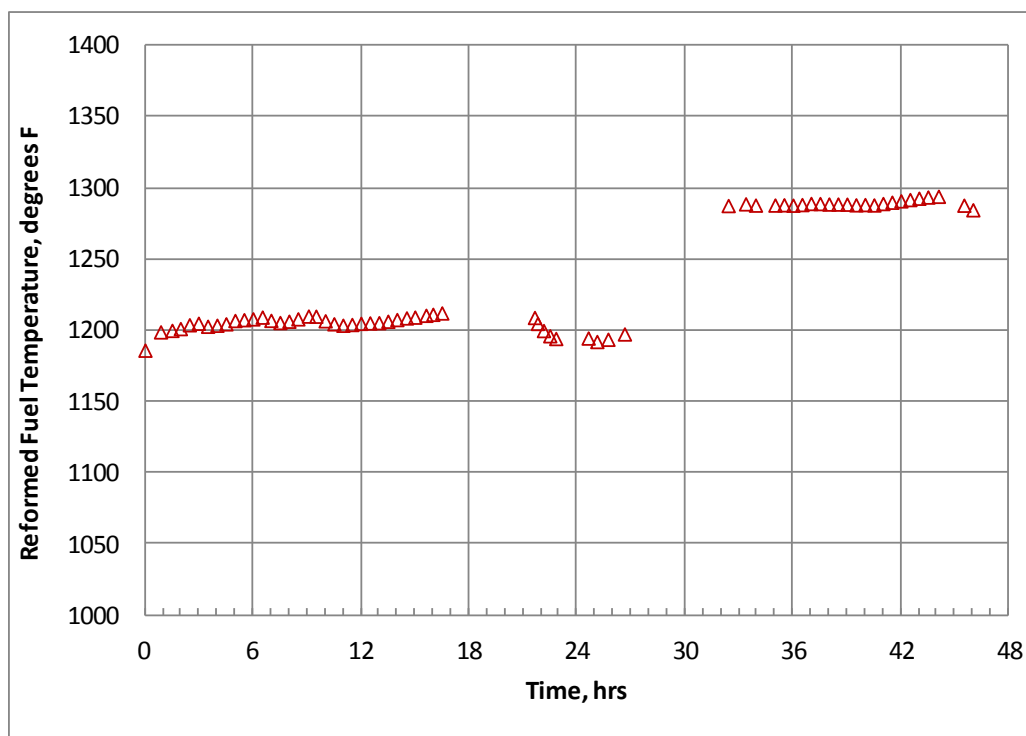


Figure A40. Reformed Fuel Temperature – 48 Hours

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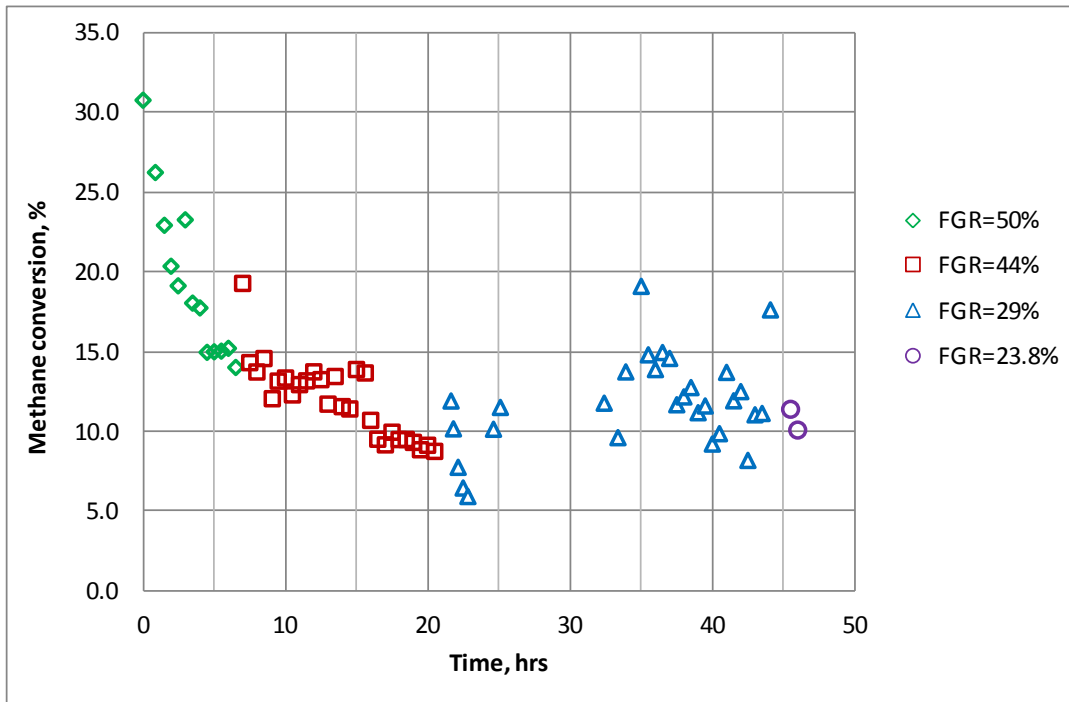


Figure A41. Methane Conversion Rate -48 Hours

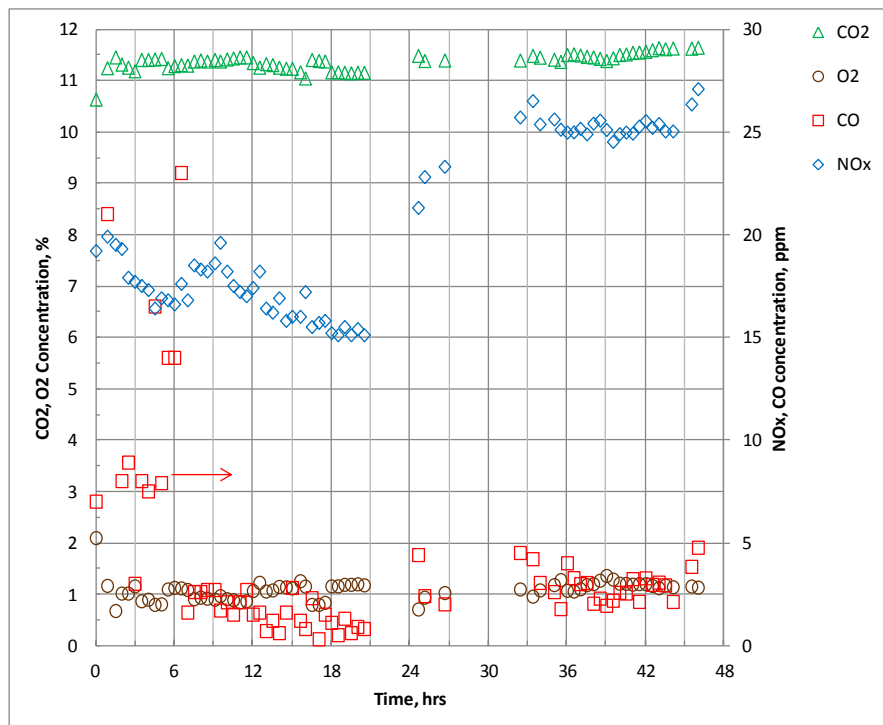


Figure A42. Furnace Exhaust Gas Composition (dry) – 48 Hours

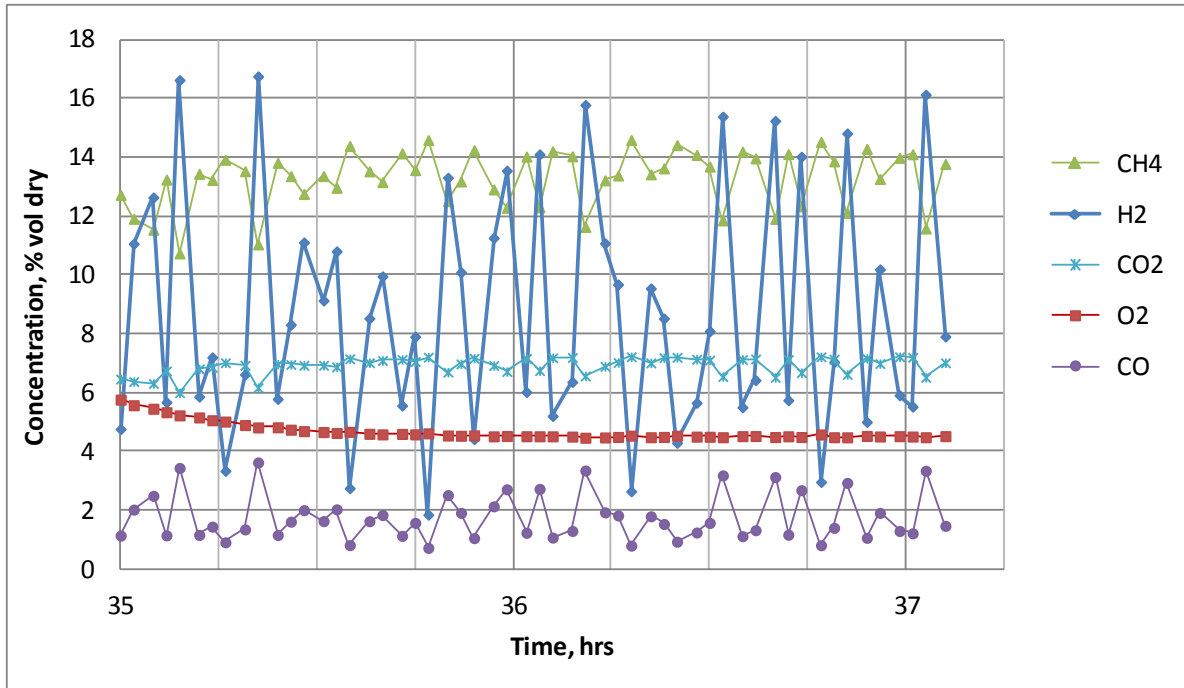
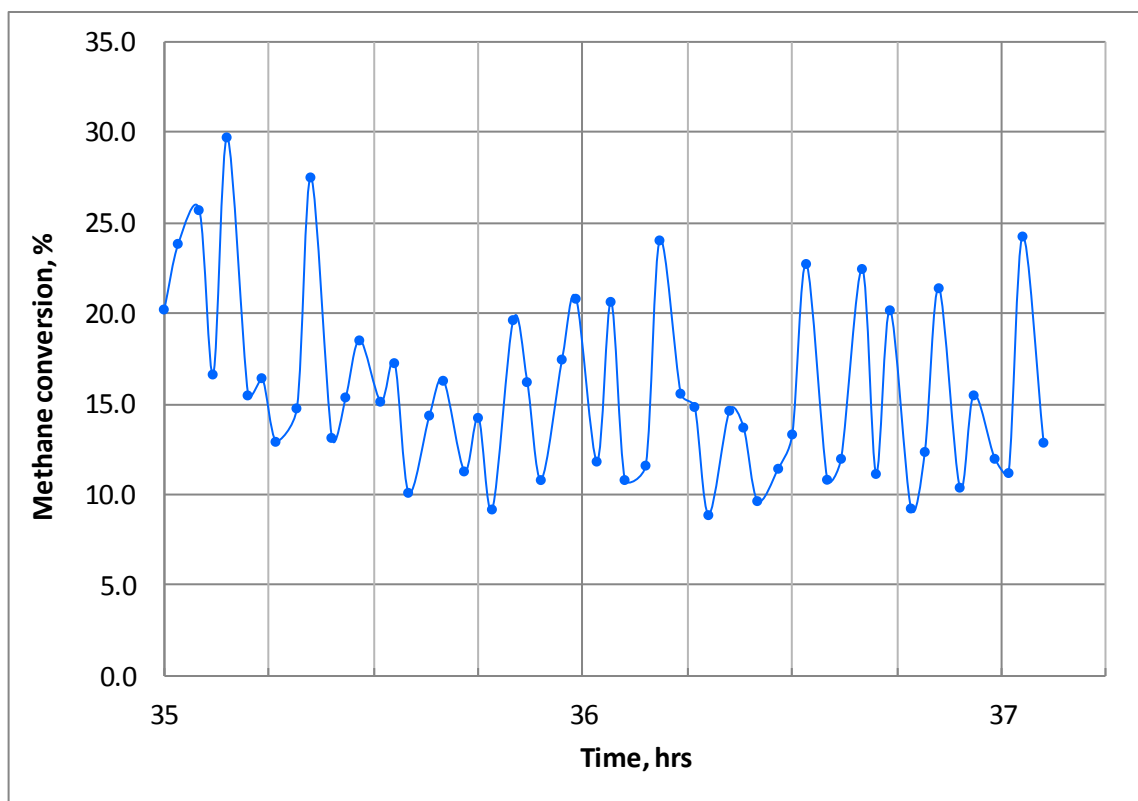


Figure A43. Instability of Reformed Fuel Composition (dry, FGR = 29% of Total Furnace Flue Gas) During a Portion of the 48 Hour Test

Note in Figure A43 that CO directly tracks H₂; and CH₄ inversely tracks both CO and H₂ which is indicative that the existing instrumentation was accurately detecting and measuring the varying levels of reforming that were occurring. Instrumentation/internal sampling was lacking to detect and measure the extent of the reactions/kinetics that were occurring within the recuperative reformer.

Figure A44 is complementary to that of the data shown in Figure A43 in that the methane reforming with increases and decreases in hydrogen, carbon monoxide and methane. The methane reforming rate was previously defined in this report and is restated here.

$$\text{Reforming process completeness} = \frac{(\text{measured methane conversion rate})}{(\text{calculated equilibrium methane conversion rate})}$$



**Figure A44. Instability of Methane Conversion Rate
During a Portion of the 48 Hour Test
(FGR=29% of Total Furnace Flue Gas)**

Appendix A4 – Extended Phase II TCR Testing

Proposed Scope of Work

Task 1 - Forensic Analysis—Conduct independent short-duration simulation modeling of the Lab Recuperative Reformer process over a range of operating conditions.

- Develop a system of equations describing chemical reaction kinetics within the Lab Recuperative Reformer
- Conduct Sensitivity Analyses of the process that includes the following independent variables: (Flue gas temperatures supplied; components of flue gas supplied; carbon to steam ratios; physical volume of the RR; and a range of specified space velocities consistent with a range of specified reforming mixtures.).

Task 2 - Conduct iterative testing of current Lab RR under both broader and new test conditions.

- Maintain <1% excess oxygen in furnace flue gasses to RR.
- Eliminate potential ambient air leakage into flue gas for mixing—Remove ID fans and reconfigure piping for direct connection of flue gas to mixer. Retain/ revise RFG cooler.
- Prepare two FG sampling ports—1) Inlet of water cooler; 2) and inlet of gas mixer.
- Maintain positive pressure on flue gas side of Lab TCR during operation of TCRS.
- Use two Horiba analyzers: one to measure flue gas components at exit of furnace; and one to sample oxygen readings at various points in the system and for back up.
- Use two GCs; one to simultaneously sample 1 – 3 intermediate points from within the RR; and one to sample reformed fuel supplied to burner. Both units to be set for minimum dwell times, i.e., 1- 2 minutes sampling.
- Arrange for 4 – 6 grab samples of reformed fuel to be taken each morning of operation, until GC calibrations are confirmed, for GTI analytical lab to provide same-day results.
- Variables to be varied in re Test Matrix
- Flue gas temperature entering RR—set at 1700°F, hold and capture all data; set at 1800°F, hold and capture all data;
- FG:NG ratio for each of the four FG inlet temperatures above—set at ~10, hold and capture all data; set at ~5, hold and capture all data; and set at ≤ 2 , hold and capture all data.
- Reform with steam in lieu of flue gas—use high/mid/low ratio points
- Preheat natural gas with electric heater to achieve FG+NG or STM+NG temperatures into RR of 600°F; 700°F and 800°F.

Task 3 - Depending on test results, devise any necessary changes to the RR design to sustain CH₄ Reforming Rate (MRR) and implement changes.

- Confer with TTC on implementation of changes
- Return RR to TTC for changes
- Return RR to GTI and reinstall

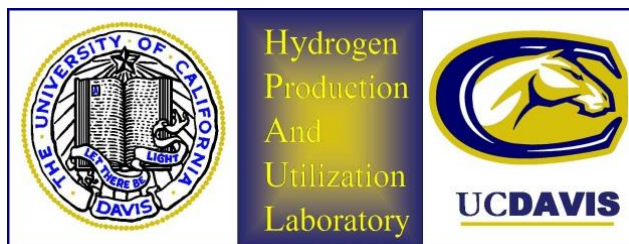
Task 4 - Conduct iterative testing of modified/retrofitted Lab RR under varying test conditions to confirm sustained CH₄ Reforming Rate (MRR).

Proposed Schedule and Budget

Table A9. Proposed Schedule and Budget

Tasks	2012 - Months						Budget (\$) by Task
	1	2	3	4	5	6	
1 Modeling Simulation							\$ 41,058
2 Iterative testing of Lab RR							155,090
3 Implement changes to RR design							94,409
4 Re-conduct iterative testing / Prepare Report							89,308
Total							\$379,864

Appendix B – UC Davis Technical Report



Parametric Study to Simulate/Evaluate Noncatalytic Reforming of Natural Gas in a Recuperative Reactor Final Report

Prepared for Gas Technology Institute
Project Period: 02/01/13 – 05/15/13

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Summary

This study investigates non-catalytic, reforming using various oxidized and non-oxidized feedstocks. The investigation utilized a steam-methane reforming facility previously constructed in the Hydrogen Production and Utilization Laboratory at the University of California, Davis under the leadership of Dr. Paul A. Erickson. For the purposes of this study, two reactor configurations were constructed: Baseline and Inserts.

Subsequent information is included in Appendix B1. Extreme care was taken to reduce the amount of variables when testing. All results presented are an averaged value over a 10-minute steady state period, unless otherwise noted.

Interpretation of results is discussed for each test individually, with overall conclusions discussed at the end of the report. Test results are presented chronologically. It is important to place them in this order, as the results from one test often led to the motivation behind the next. Ultimately, it was concluded that for our system: the presence of 800H strips did not aid reforming, and that sustained reforming could not be achieved (higher temperatures are likely needed).

Testing Apparatus

This project utilized a reforming facility constructed in the Hydrogen Production and Utilization Laboratory at the University of California, Davis. Shown in Figure 1, the experimental facility was built with the intention of studying multiple reactor types and sizes, but more specifically autothermal reforming (ATR) and steam reforming type reactors. The testing apparatus for this facility is composed of several pieces of hardware including a scale, pump, gas flow controllers, vaporizers, a gas heater, superheater, interchangeable reforming reactors, condensing units, and a gas analyzer. Instrumentation for measurement and control of heater temperatures and feedstock flows was utilized and managed via a computer control station. Electrical equipment was powered by one of two power relay boxes.



Figure B1: Reforming facility at the University of California, Davis Hydrogen Production and Utilization Laboratory (Photo courtesy of Jason Greenwood).

This steam methane reformer (SMR) testing apparatus operated by flowing a pre-heated, steam:carbon ratio specific, gaseous/water feedstock through a single reformer. For this project, the feedstock setup was expanded to allow specialty gas (described later), air, and carbon monoxide to also flow into the reformer. As shown by the reactor schematic in Figure B2 (a simplified version of this can be seen in Appendix B1), this was done by first metering and electrically heating the feedstocks individually. The separate feedstock flows were then mixed and could either flow through the electric superheater or bypass directly to the condensing unit, without going into the reactor (depending on the specific valve arrangement). This is important when bypassing the reactor is necessary, such as during warm up of water feedstock.

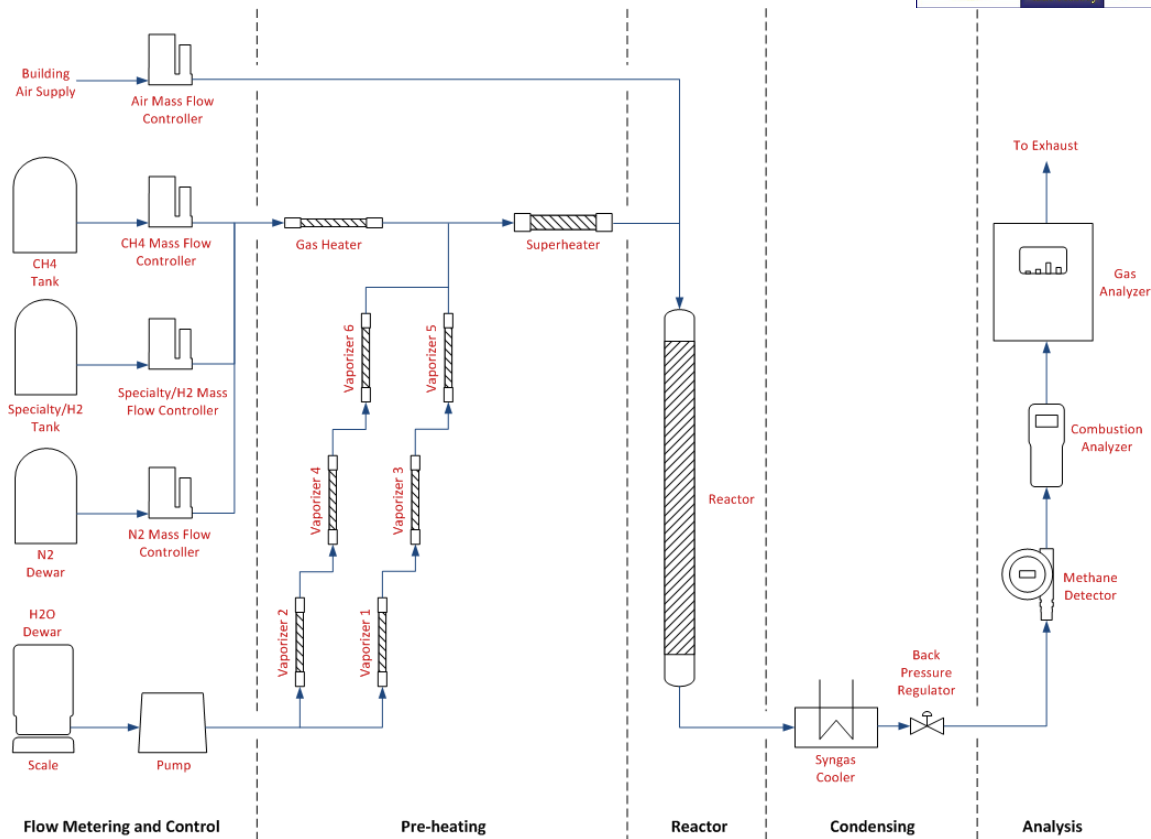


Figure B2: Simplified schematic of the methane steam reforming facility used for this project.

Should the mixed feedstock be routed through the superheater, the flow would then enter into a single, electrically heated reactor tube. This reactor tube would house an inner tube with or without inserts depending on the particular installation and mode of testing. After passing through the reactor, the reformed feedstock would then be routed to the main condensing unit (syngas cooler) to remove the bulk amount of heat and water from the reformed stream. The reformed stream, then a dry gas, could either be routed directly to exhaust or through the backpressure regulator depending on the specific arrangement. Through the backpressure regulator, the majority of reformed was exhausted, while a smaller sample stream was run to the gas analyzers. Following gas analysis, this sample was also exhausted. A nitrogen purge was also utilized in a similar manner to the methane feed to ensure no oxygen entered the facility, when not in use.

For organizational and operational purposes, the entire experimental facility was separated into subassemblies. These subassemblies include the *metering and pumping subassembly*, the *pre-heating subassembly*, the *reactor subassembly*, the *condensing subassembly*, *analysis subassembly*, and the *control subassembly* (not pictured). The metering and pumping subassembly is characterized by its function to meter and control flow of feedstock into the facility; it includes the feedstock reservoirs, gas flow controllers, water scale, and water pump. The pre-heating subassembly heats and regulates the feedstock temperature prior to the reactor inlet. This subassembly includes the water vaporizers, air/gas heater, and the superheater. The

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reactor subassembly contains the reactor housing and associated contents. The condensing subassembly cools the reformed stream for exhaust as well as provides dry gas for gas analysis; it includes the main condensing unit and back pressure regulator. The analysis subassembly acquires and reports the outgas composition; it includes the Nova gas analyzer, RKI methane detector, and UEi combustion analyzer. The control subassembly provides measurement and control logic for the entire process, and includes the operations computer and associated instrumentation for measurement and control. The reactor housing, instrumentation/control subassembly and analysis subassembly shall be described in further detail in the following sections. All other subassemblies are described in greater detail in Appendix B1 and were omitted here due to length.

Reactor Construction

Two reactors were constructed for this study, referred to as the “Baseline” and “Inserts” reactors. As shown in Figure B3 below, the main volume of each housing was composed of a 1.32 m (52 in.) type 316 stainless steel pipe (101.6 mm (4 in.) ID, 6.4 mm (0.25 in.) wall thickness). The reactor tubes were sealed at both the upper and lower ends by welding type 304 stainless steel end caps to complete the housings. The upper reactor caps were adapted to accept the inflow of feedstock via 6.4 mm (0.25 in.) stainless steel piping, as well as utilize gauges for measuring reactor pressure (0-1 MPa (0-145 PSI)). The bottom reactor caps were adapted to eject the reformed stream of each reactor to 6.4 mm (0.25 in.) stainless steel piping.

Each reactor configuration was heated by 18 individual electric 1100 W heat bands. Each heat band was clamped around the 114.3 mm (4.5 in.) outer diameter of the reactor housing and measured 45.7 mm (1.8 in.) in axial length. A 9.7 mm (0.38 in.) spacing was kept between each heat band to prevent damage from thermal expansion during operation. Control and instrumentation of these heaters will be discussed later on in the report.



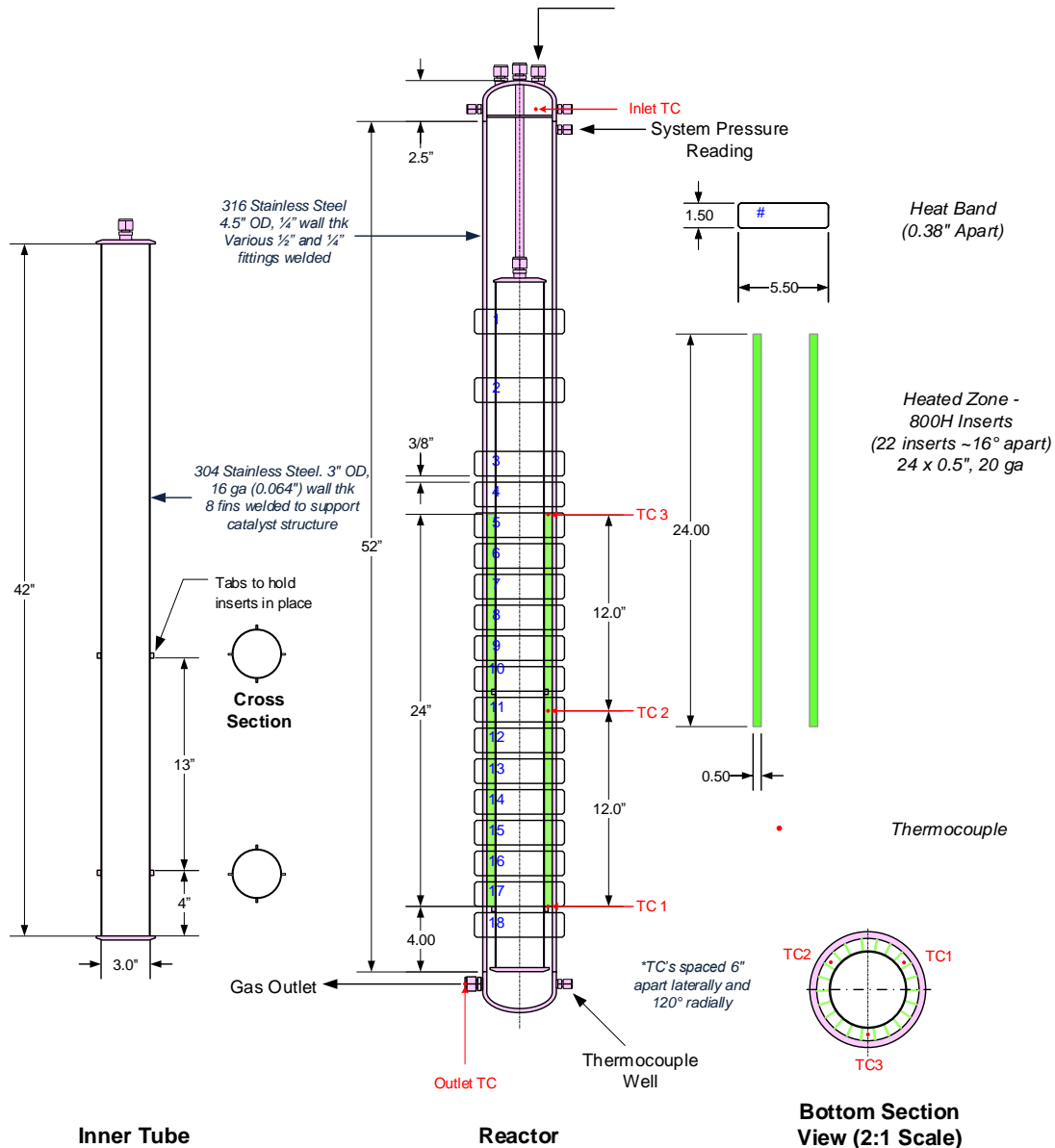


Figure B4: Detailed schematic of the Inserts reactor used for this project.

Each reactor contains a 1 m (42 in.) type 316 stainless steel tube (76.2 mm (3 in.) OD, 16 gauge wall thickness) inside the main reactor tube supported above from the top cap. Seen in the above schematics and photographs below, this tube remained sealed during installation/uninstallation and operation. (Figure B5) It should be noted that at the bottom of the reactor, an adapter was machined into the end cap to allow for the fitting of a thermowell. These thermowells allowed for the placement of internal thermocouples and consisted of 6.4 mm (0.25 in.) steel tubes. These ungrounded, stainless steel sheathed K type thermocouples were placed inside the reactor at locations specified by the schematics above. Three thermocouples were strategically placed within the reactor to obtain the most accurate average "bed" temperature. (Figure B6)

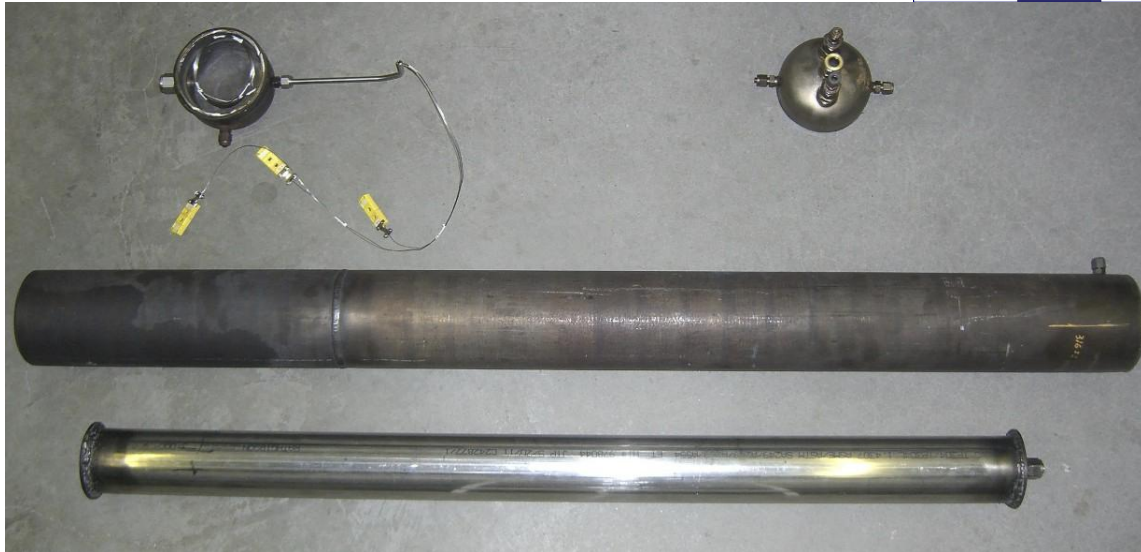


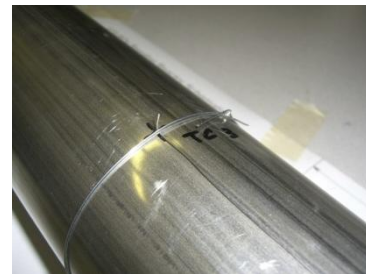
Figure B5: Photograph of inner tube, top cap, bottom cap (with thermowell and thermocouples), and outer tube which compose the Baseline reactor housing



(a)



(b)



(c)

Figure B6: Close-up photographs of inner thermocouples (a) 1, (b) 2, and (c) 3 secured to inner tube using 24 ga. stainless steel wire. Note how tips are bent into the process gas stream.

The two reactors are identical, except for the 800H alloy inserts present in the “Inserts” reactor. These 22 inserts (24 x 0.5 in., 20 ga.) were attached vertically to the inner tube using 24 ga. stainless steel wire and stainless steel hose clamps. (Figure B8) The inserts were installed such that they remained parallel to the flow at all times. It should be noted that the thermocouple placement differs slightly between the Baseline and Inserts reactors. For the Baseline reactor, the thermocouples are spaced 6 in. apart laterally, whereas for the Inserts reactor they are 12 in. apart. This is because a decision was made to double the heated length from 12 in. to 24 in. so that flow rates may be doubled to better suit the testing apparatus. However, this was not decided until after the Baseline reactor had already been constructed and welded, therefore its thermocouples do not reflect this configuration change.



Figure B7: Photograph of thermocouple placement along inner tube. Note, thermocouples are 60° apart axially, 6" apart laterally (Baseline reactor) and 12" apart laterally (Inserts reactor)

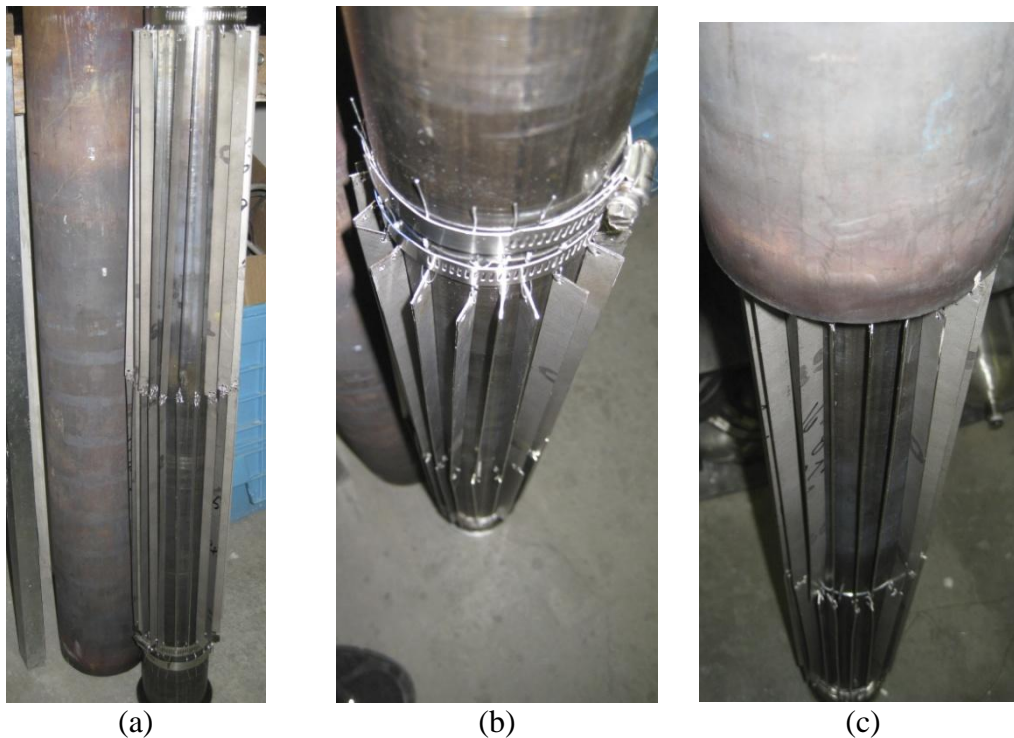


Figure B8: (a) Reactor inner tube with inserts installed, (b) hose clamps used to secure inserts and thermocouples to inner tube, (c) installation of inner tube/inserts into outer tube.

Instrumentation and Control Subassembly

The instrumentation and control subassembly served the purpose of controlling all operations of the steam methane reformer, as well as recording specific data in regards to principle aspects of the entire system. A closed loop scheme was designed for control of the reformer while an open loop scheme was implemented for the instrumentation. Both of these schemes were monitored

and controlled using a National Instruments LABView program. A schematic illustrating the input and output signals of these schemes is shown below.

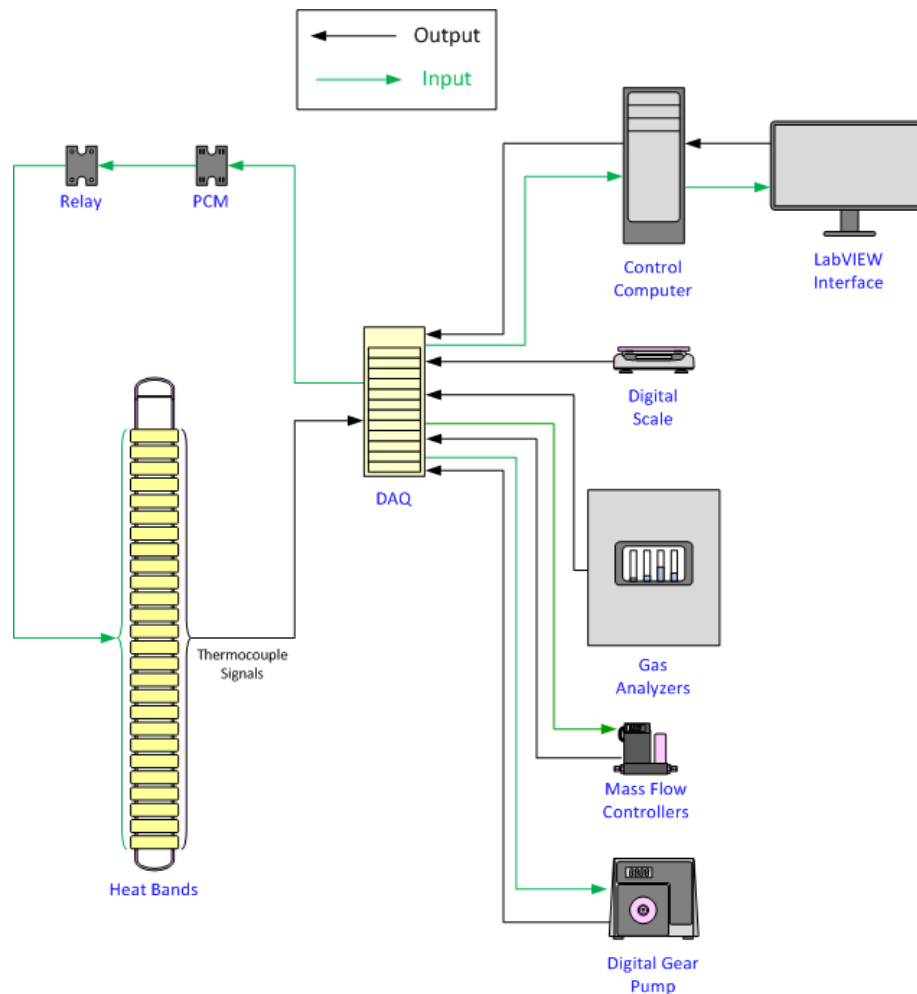


Figure B9: Input and output signal diagram

Reactor Subassembly

Thermocouples:

All temperature measurements in the reforming apparatus are measured using Omega K-type thermocouples. The sensor of a K-type consists of a chromel-alumel junction, and is chosen based on wide operating range and fast response time. For this experiment, two sizes of thermocouples were used: 0.020" and 0.062". All thermocouples are stainless steel sheathed and ungrounded. It is also important to note the operating conditions of internal thermocouples: 1) thermocouples are in direct contact with process gas stream, with little shielding present, 2) very low flow rates were utilized for this study, and 3) thermocouples are very close (0.25 in) from heated tube wall. These conditions mean that radiation error may be present in internal thermocouple readings. For principle of operation, please see the Instrumentation Report.

Table B1: K-type thermocouple specifications

Manufacturer	Omega Engineering, Inc.
Part no.	KMQXL-020U (0.020"), KQXL-062U (0.062")
Range	-328 to 2282 °F (-200 to 1250 °C)
Resolution	0.225°F (0.125°C)
Accuracy	±2.2°C or 0.75% above 0°C (whichever is greater), ±2.2°C or 2.0% below 0°C (whichever is greater)
Response Time	0.5 seconds or less
Output	-6.458 - 54.886 mV

Analysis Subassembly

Nova Gas Analyzer:

Analysis of carbon monoxide, carbon dioxide, and hydrogen was performed using a Nova Gas Analyzer. The analyzer was calibrated a minimum of twice per week, and typically before every new test. Calibration of the Model 7904CM gas analyzer took place by utilizing a span gas with known mixtures of carbon monoxide, carbon dioxide, methane, and nitrogen as well as a “zero” gas. For this study, the analyzer was calibrated using a span gas consisting of 9% carbon monoxide, 9% methane, 37% nitrogen, and 45% carbon dioxide. The zero gas consisted of 100% hydrogen. Both gases was regulated to 34.5 kPa (5 PSI) and fed into the analyzer. Using the analyzer’s user interface, the known mixture of the span gas was programmed in and the analyzer would calibrate itself based on its own programming. For principle of operation, please see the Instrumentation Report.

Table B2: Nova gas analyzer specifications

Manufacturer	Nova Analytical Systems
Part no.	7904CM
Method of Detection	Separate NDIR (infrared) detectors for CO, CO ₂ and CH ₄ . Thermal conductivity cell for H ₂ .
Ranges	0-10.0% CO [only 10%?], 0-50.0% CO ₂ , 0-20.0% CH ₄ , 0-100% H ₂
Resolution	0.1% for all gases
Accuracy	± 2% FS
Repeatability	± 2% FS
Response Time	20-30 seconds, not including sample transport time to analyzer
Operating Environment	32 to 120°F (0 to 50°C)
Power	115VAC 60Hz
Output	4-20 mA for each gas measured

RKI M2 Methane Detector:

Due to the limited range of the methane sensor in the Nova Gas Analyzer, a standalone methane detector is used to monitor methane content. The methane detector was calibrated prior to all testing, as it is recommended to re-calibrate every 6 to 12 months. Calibration took place by utilizing a calibration gas consisting of 50% methane, 50% nitrogen. Using the analyzer’s user interface, the known mixture of the span gas was programmed in and the analyzer would

calibrate itself based on its own programming. For principle of operation, please see the Instrumentation Report.

Table B3: RKI M2 methane detector specifications

Manufacturer	RKI Instruments
Part no.	65-2628RK-CH4
Method of Detection	Infrared Sensor
Range	0 - 100% Vol.
Resolution	1%
Accuracy	± 5% of reading or ± 2% of full scale (whichever is greater)
Response Time	30 seconds or less, not including sample transport time to analyzer
Operating Environment	-4 to 122°F (-20 to 50 °C), 5 - 95% Relative Humidity
Power	19 - VDC
Output	4 – 20 mA signal, corresponding to 0 - 100%

UEi C75 Combustion Analyzer:

Analysis of oxygen was performed using a handheld UEi C75 Combustion Analyzer. The combustion analyzer self-calibrates each time it is powered on, as long as it is exposed to atmospheric air. It assumes the atmospheric air consists of 20.9% oxygen, 0% carbon dioxide, and 0 ppm CO. For principle of operation, please see the Instrumentation Report.

Table B4: UEi combustion analyzer specifications

Manufacturer	Universal Enterprises, Inc. Test Instruments
Part no.	C75
Method of Detection	Electrochemical Cell
Range	0 - 21%
Resolution	0.1%
Accuracy	± 0.2%
Response Time	20 - 30 seconds
Operating Environment	32 to 104°F (0 - 40°C)
Power	9 VDC
Output	N/A

Test Results

Test results are presented in chronological order. Each test consists of a day's worth of experiments, separated into data points. Each data point has specified operating conditions, results, and is accompanied by a description, summary table, summary plot, and brief interpretation of results. Please note that all results in the summary table are averaged values for the final ten minutes of each data point (unless otherwise specified). Furthermore, reactor warm up is omitted from the reported test results.

Baseline Reactor Test 1

Test Date: Mar 02 2013

The first test performed with the baseline reactor utilized methane, water, and specialty gas (87.8% N₂, 11% CO₂, 1.2% O₂) in an attempt to reform simulated flue gas (specialty gas and

water) and methane. Data Points 1 – 4 utilized only methane and water (S:C = 1.86), with two space velocities and two bed temperatures. Data Points 5 – 8 introduced specialty gas while maintaining the same space velocities and bed temperatures. The operating conditions and results are as follows:

Table B5: Baseline Reactor Test 1 Operating Conditions

Pt #	Flue:CH ₄ Ratio [SLPM/SLPM]	S:C Ratio [mol/mol]	GHSV [1/h]	Spec. Gas Flow [SLPM]	CH ₄ Flow [SLPM]	H ₂ O Flow [mL/min]
1	0.00	1.87	360	0	4.4	6.60
2	0.00	1.85	720	0	8.8	13.11
3	0.00	1.86	720	0	8.8	13.14
4	0.00	1.86	360	0	4.4	6.58
5	4.64	0.66	720	18.4	4.0	3.17
6	2.78	0.45	360	8.2	3.0	1.40
7	2.70	0.46	360	8.9	3.1	1.37
8	4.39	0.63	720	17.6	0.0	3.08

Table B6: Baseline Reactor Test 1 Results

Pt #	H ₂ [%]	CO [%]	CO ₂ [%]	CH ₄ [%]	O ₂ [%]	Internal 1 [°C]	Internal 2 [°C]	Internal 3 [°C]	Avg Bed Temp [°C]
1	1.0	0.1	0.1	92.8	0	630.0	664.5	663.3	652.6
2	0.0	0.1	0.1	88.6	0	628.7	658.6	657.4	648.2
3	0.0	0.1	0.1	87.5	0	684.4	715.3	713.9	704.5
4	0.0	0.1	0.1	86.4	0	683.5	716.6	715.4	705.2
5	0.0	0.1	8.3	16.4	0.3	684.0	716.7	715.6	705.4
6	0.0	0.1	6.8	25.4	0.2	682.8	717.2	715.8	705.3
7	0.0	0.1	6.8	24.7	0.2	628.2	661.1	660.1	649.8
8	0.1	0.1	8.2	17.4	0.5	628.3	660.1	658.7	649.0

Very little reforming occurred for all data points. Originally, these data points were to serve as half of the testing matrix, while identical tests with the Inserts reactor would serve as the other half. Ultimately, different operating conditions were chosen in order to obtain more substantial results. After this first test, the specialty gas was not used again.

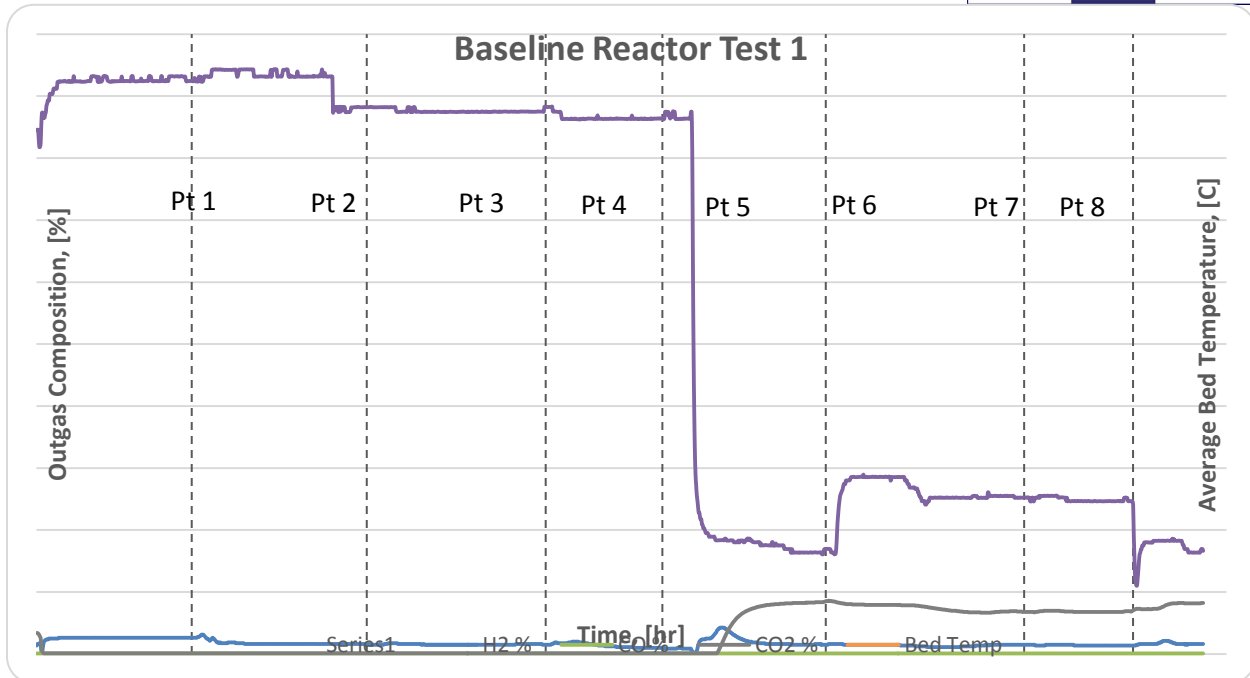


Figure B10: Baseline Reactor Test 1 Summary Plot

Baseline Reactor Test 2

Test Date: Mar 6 2013

The second test performed with the baseline reactor utilized methane, steam, and air. Because the results of the previous test were mostly unvaried, it was postulated that increasing the oxygen content would give more meaningful results. Therefore, air was used in the place of specialty gas for its higher oxygen content. The purpose of this test was to investigate the maximum temperature and lowest space velocity for the system, and to determine how and if the presence of air would affect the reforming process. The operating conditions and results are as follows:

Table B7: Baseline Reactor Test 2 Operating Conditions

Pt	O ₂ %	O ₂ :C Ratio	S:C Ratio	GHSV	H ₂ O Flow	CH ₄ Flow	Air Flow
#	[O ₂ /H ₂ O+Air]	[mol/mol]	[mol/mol]	[1/h]	[mL/min]	[SLPM]	[SLPM]
1	0	-	3	360	8.04	3.3	0
2	0	-	3	180	3.80	1.6	0
3	0	-	3	180	4.90	1.6	0
4	0	-	3	180	3.74	1.7	0
5	1	0.03	3	180	3.54	1.6	0.2
6	2	0.06	3	180	3.41	1.5	0.5
7	4	0.14	3	180	3.15	1.4	0.9
8	6	0.23	3	180	2.87	1.3	1.4
9	0	-	3	180	3.73	1.6	0.0
10	10	0.53	3	180	2.22	1.0	2.5
11	0	-	3	180	3.72	1.6	0.0
12	12	0.78	3	180	1.87	0.9	3.1

Table B8: Baseline Reactor Test 2 Results

Pt	H ₂	CO	CO ₂	CH ₄	Internal 1	Internal 2	Internal 3	Avg Bed Temp
#	[%]	[%]	[%]	[%]	[°C]	[°C]	[°C]	[°C]
1	1.5	0.1	0.1	93.3	683.3	716.5	716.4	705.4
2	1.6	0.1	0.1	92.2	681.7	717.0	717.3	705.3
3	2.0	0.1	0.1	91.8	709.5	744.5	745.2	733.1
4	2.2	0.1	0.1	86.3	737.4	773.9	773.1	761.5
5	1.9	0.1	0.1	86.5	739.2	774.0	773.6	762.3
6	0.0	0.1	2.1	69.0	739.4	776.0	775.0	763.5
7	0.0	0.2	2.8	50.6	739.3	775.8	775.4	763.5
8	0.0	0.3	3.0	38.0	739.3	775.9	775.8	763.7
9	1.9	0.1	0.1	86.7	738.7	775.2	774.5	762.8
10	0.0	0.1	3.8	14.8	739.7	777.9	776.9	764.8
11	1.9	0.1	0.1	83.1	737.4	774.9	773.9	762.1
12	0.0	0.3	3.6	12.0	737.9	778.6	776.3	764.3

Data Points 1 – 4 were used to investigate operating ranges for the system. It was found that a space velocity of 180 hr⁻¹ and a bed temperature of 760 °C were the stable operating limits of the testing apparatus. Points 5 – 12 maintained the same space velocity and temperature while introducing more and more air each time. Air was not observed to aid the reforming process, however it should be noted that when air was introduced a spike in hydrogen production occurred, followed by a rapid tail off. After enough time, this tailed off to 0, even if more air was introduced. In order to replicate the spike, steam and methane only were introduced during points

9 and 11. The points that followed (10 and 12) also saw a spike in hydrogen when air was added. However in both cases, hydrogen concentration eventually fell to zero.

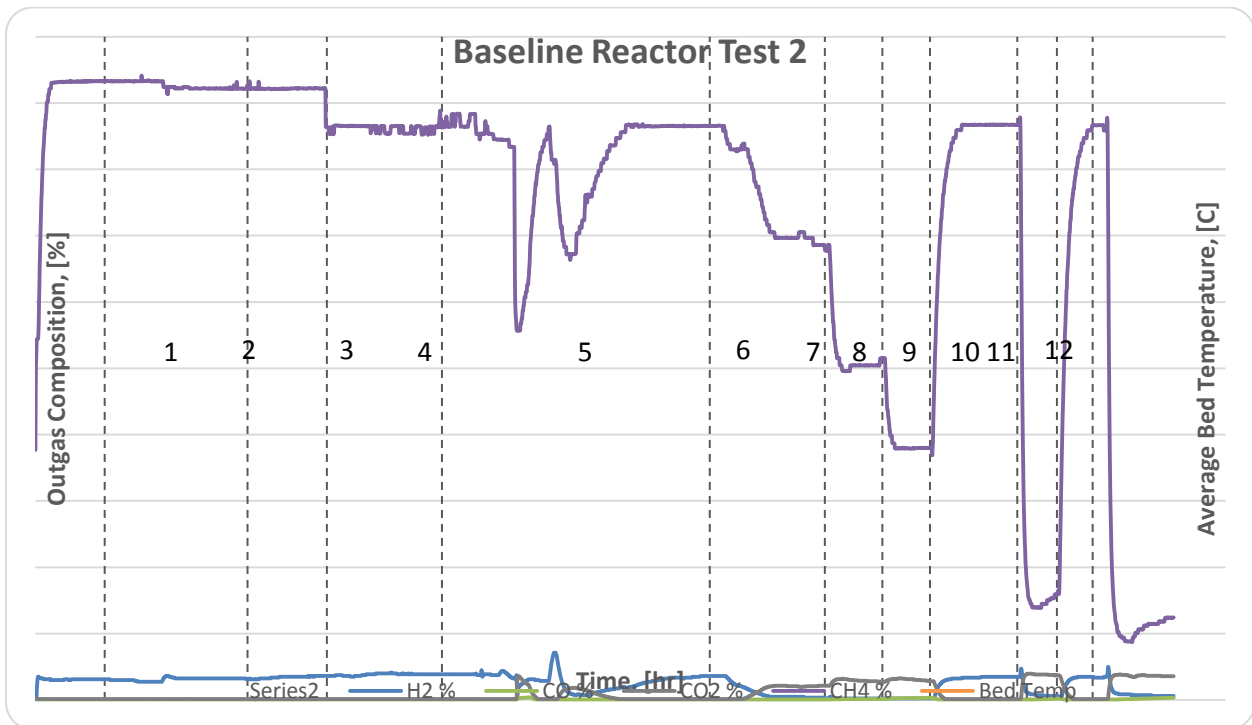


Figure B11: Baseline Reactor Test 2 Summary Plot

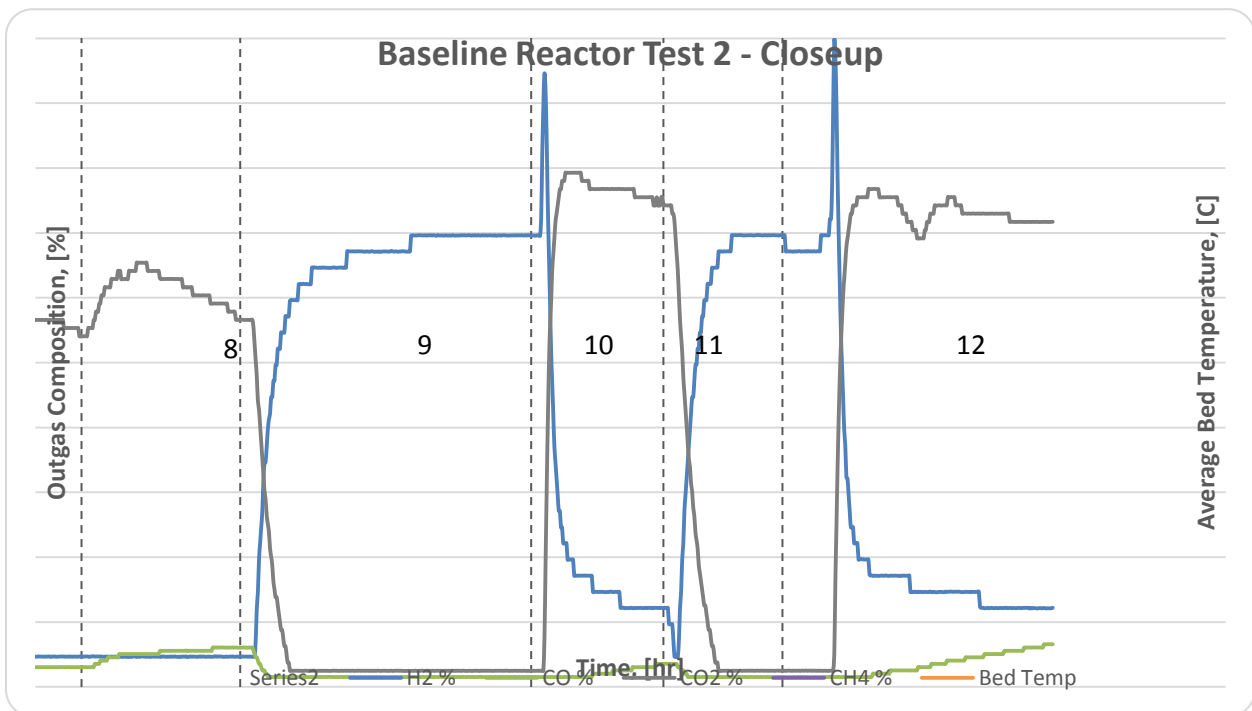


Figure B12: Baseline Reactor Test 2 Close-up

A carbon balance was also requested for this test, which was performed by observing the flowrate of methane in versus the concentration of methane and carbon dioxide out. Only a small difference in carbon was found between reactant and product. It should be noted, however, that the reactant carbon was a calculated value from the flow controllers, while the product carbon was an observed value from the gas analyzers.

Table B9: Baseline Reactor Test 2 Carbon Balance

		REACTANT				PRODUCT			
Pt	Tot. Molar Flowrate	CH ₄ Molar Flowrate	Air Molar Flowrate	Gas molar flow rate	Sum C	C molar Flowrate	CH ₄ output	CH ₄ conversion	Carbon molar difference
#	[mol/min]	[mol/min]	[mol/min]	[mol/min]	[%]	[mol/min]	[mol/min]	[%]	[mol/min]
1	0.54	0.1481	0.0000	0.1481	93.5	0.1384	0.1	6.7	0.0096
2	0.27	0.0720	0.0000	0.0720	92.4	0.0666	0.066	7.8	0.0054
3	0.27	0.0721	0.0000	0.0721	92.0	0.0663	0.066	8.2	0.0057
4	0.27	0.0741	0.0000	0.0741	86.5	0.0641	0.064	13.7	0.0100
5	0.27	0.0708	0.0089	0.0798	86.7	0.0692	0.069	2.6	0.0016
6	0.27	0.0687	0.0201	0.0888	71.2	0.0632	0.061	10.8	0.0055
7	0.27	0.0633	0.0411	0.1044	53.6	0.0559	0.053	16.6	0.0074
8	0.27	0.0574	0.0634	0.1208	41.3	0.0498	0.046	20.1	0.0076
9	0.27	0.0721	0.0000	0.0721	86.9	0.0627	0.063	13.3	0.0094
10	0.27	0.0448	0.1116	0.1564	18.8	0.0293	0.023	48.2	0.0154
11	0.27	0.0721	0.0000	0.0721	83.3	0.0601	0.060	16.9	0.0120
12	0.27	0.0383	0.1402	0.1785	15.9	0.0284	0.021	44.1	0.0100

Inserts Reactor Test 1

Test Date: Mar 6 2013

The first test performed with the Inserts reactor utilized steam and methane. Its purpose was to investigate the reforming capabilities under conditions identical to those in Baseline reactor test 2. The operating conditions and results are as follows:

Table B10: Inserts Reactor Test 1 Operating Conditions

Pt	S:C Ratio	GHSV	H ₂ O Flow	CH ₄ Flow
#	[mol/mol]	[1/h]	[mL/min]	[SLPM]
1	3	360	7.27	3.3
2	3	180	3.71	1.6
3	3	180	3.71	1.6
4	3	180	3.73	1.6

Table B11: Inserts Reactor Test 1 Results

Pt	H ₂	CO	CO ₂	CH ₄	Internal 1	Internal 2	Internal 3	Avg Bed Temp
#	[%]	[%]	[%]	[%]	[°C]	[°C]	[°C]	[°C]
1	1.6	0.1	0.1	93.9	695.2	713.2	-	704.2
2	2.0	0.1	0.1	94.0	695.1	713.6	-	704.4
3	2.6	0.1	0.1	94.3	723.9	742.6	-	733.2
4	3.4	0.1	0.1	93.9	751.5	770.8	-	761.2

*Note: Only internal thermocouples 1 and 2 were used to define average bed temperature in the inserts reactor, as they correspond to internal thermocouples 1 and 3 in the baseline reactor.

The Inserts reactor performed nearly identical to Baseline reactor, producing roughly 1% more hydrogen for all data points (a negligible amount). Therefore, it was observed that the presence of the 800H strips did not have a significant effect on reforming capabilities, under these operating conditions.

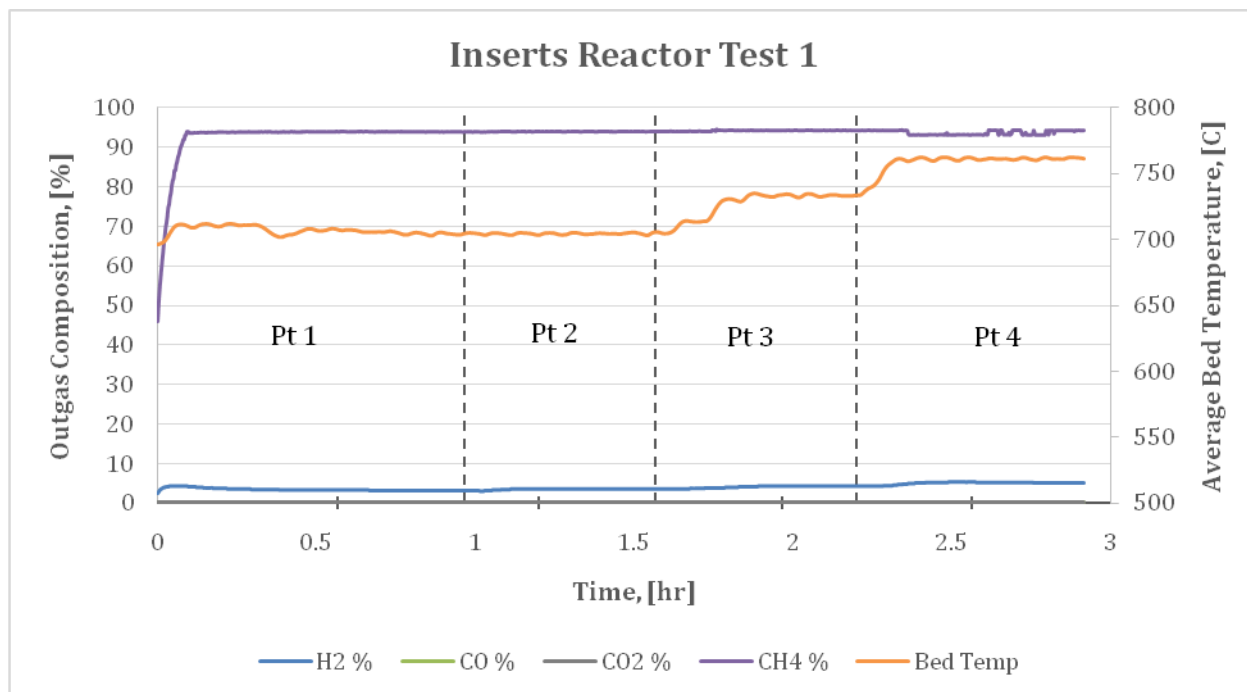


Figure B13: Inserts Reactor Test 1 Summary Plot

Inserts Reactor Test 2

Test Date: Mar 13 2013

The second test performed with the Inserts reactor utilized methane, steam, and air. The purpose of this test was to investigate the effect of air on the reforming process, similar to Baseline reactor test 2. The operating conditions and results are as follows.

Table B12: Inserts Reactor Test 2 Operating Conditions

Pt	O ₂ %	O ₂ :C Ratio	S:C Ratio	GHSV	H ₂ O Flow	CH ₄ Flow	Air Flow
#	[O ₂ /H ₂ O+Air]	[mol/mol]	[mol/mol]	[1/h]	[mL/min]	[SLPM]	[SLPM]
1	1	0.03	3	360	3.52	1.59	0.21
2	2	0.06	3	180	3.46	1.54	0.45
3	4	0.13	3	180	3.15	1.42	0.90
4	6	0.23	3	180	2.82	1.29	1.38
5	10	0.53	3	180	2.25	1.00	2.47
6	0	-	3	180	3.72	1.61	0.0

Table B13: Inserts Reactor Test 2 Results

Pt	H ₂	CO	CO ₂	CH ₄	O ₂	Internal 1	Internal 2	Internal 3	Avg Bed Temp
#	[%]	[%]	[%]	[%]	[%]	[°C]	[°C]	[°C]	[°C]
1	2.6	0.1	0.1	94.1	0.3	754.0	766.7	-	760.3
2	3.0	0.1	0.1	93.6	0.3	754.1	767.1	-	760.6
3	2.0	0.1	0.7	92.9	0.3	754.6	766.8	-	760.7
4	0.2	0.2	3.9	70.0	0.3	754.4	767.0	-	760.7
5	0.2	0.2	6.7	37.6	2.8	757.1	768.9	-	763.0
6	3.0	0.1	0.1	93.5	0.3	754.5	766.7	-	760.6

The presence of air had an adverse effect on output hydrogen concentration. That is, as more air was added, less hydrogen was produced.

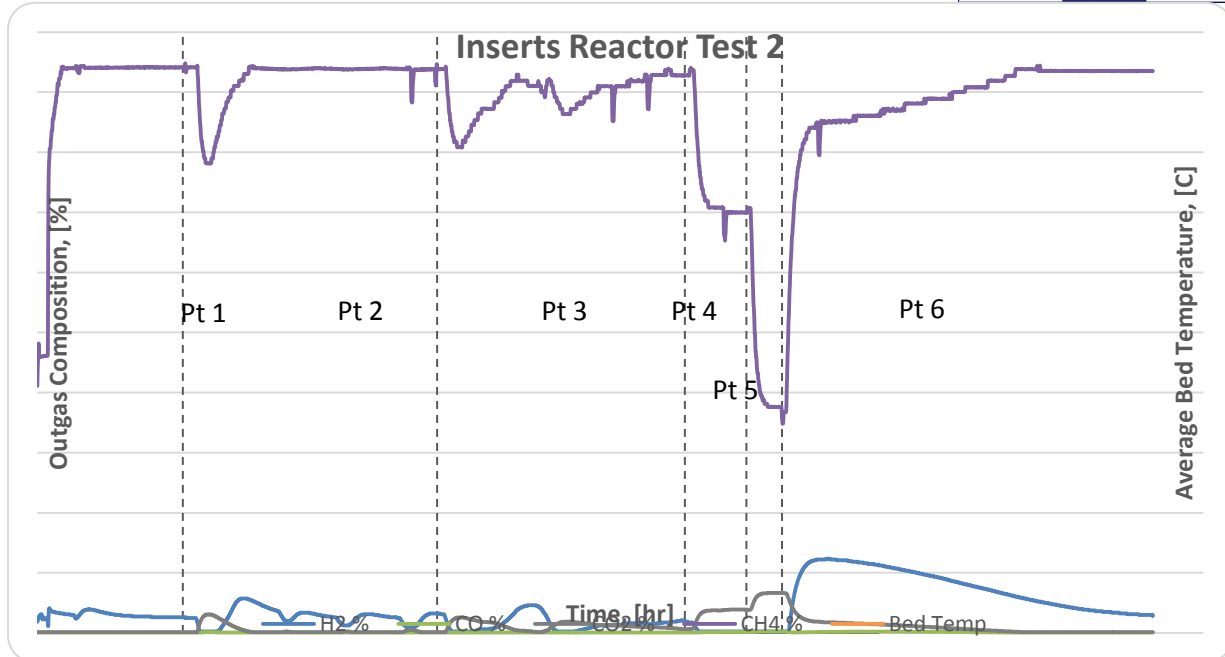


Figure B14: Inserts Reactor Test 2 Summary Plot

Another important observation was apparent “swinging” of hydrogen with air present. For the first 3 data points, 10-minute averages could not be recorded, as hydrogen would repeatedly swing up and down without settling.

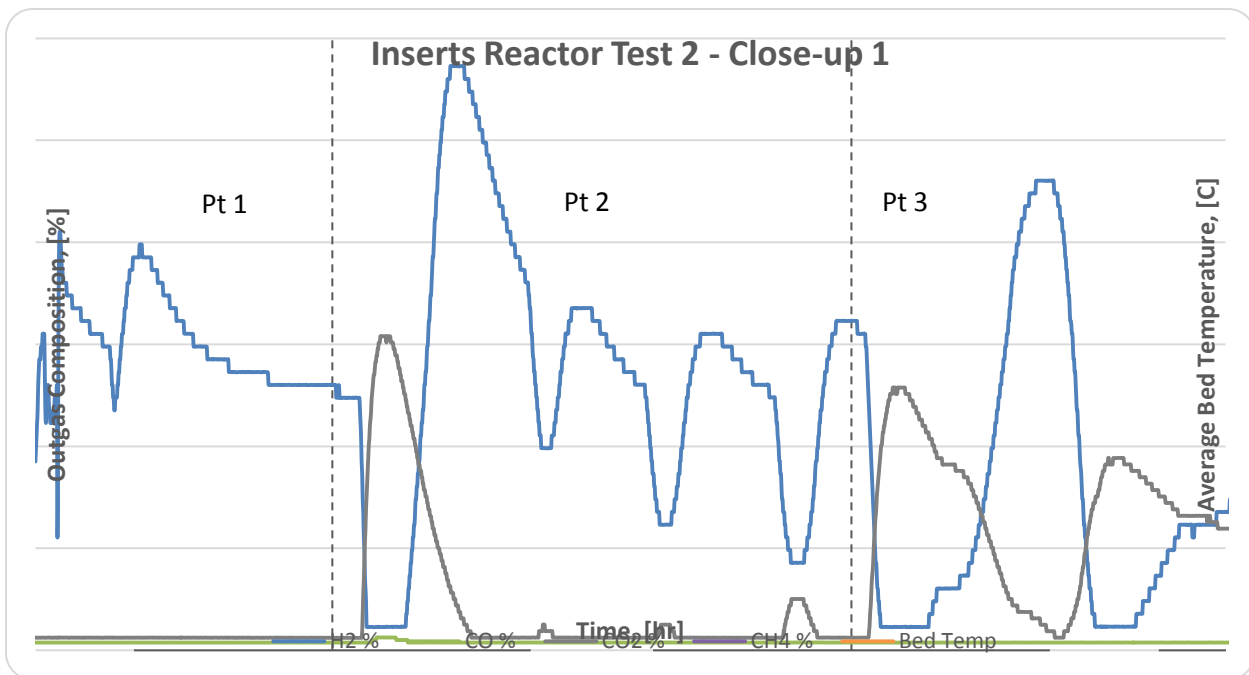


Figure B15: Inserts Reactor Test 2 close-up on hydrogen “swinging”

For Data Points 4 and 5, no hydrogen was produced. For data point 6, the final data point from Inserts reactor Test 1 was replicated, with nearly identical results.

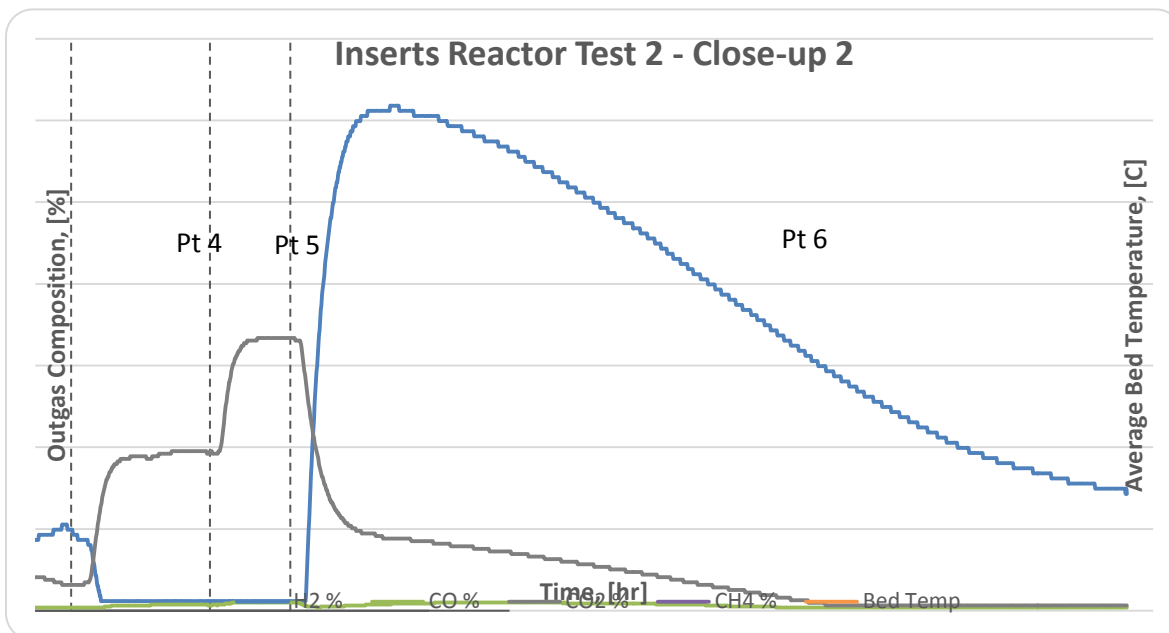


Figure B16: Inserts Reactor Test 2 close-up on final data points

Inserts Reactor Test 3

Test Date: Mar 15 2013

The third test performed with the Inserts reactor utilized methane, water, and introduced a reduction procedure. The purpose of this test was to determine whether or not a reduction procedure would aid in the reforming process. The operating conditions and results are as follows:

Table B14: Inserts Reactor Test 3 Operating Conditions

Pt	S:C Ratio	GHSV	H ₂ O Flow	CH ₄ Flow
#	[mol/mol]	[1/h]	[mL/min]	[SLPM]
1	3	180	3.72	1.61

Table B15: Inserts Reactor Test 3 Results

Pt	H ₂	CO	CO ₂	CH ₄	O ₂	Internal 1	Internal 2	Internal 3	Avg Bed Temp
#	[%]	[%]	[%]	[%]	[%]	[°C]	[°C]	[°C]	[°C]
1	2.1	0.1	0.1	93.7	0.3	753.2	765.5	-	759.3

The reduction procedure used can be seen in Figure B17 below. The reduction consists of controlled amounts of nitrogen and hydrogen being introduced to the reactor for at least one

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hour. As reduction proceeds, the temperature and amount of hydrogen are slowly raised. When the change in hydrogen fed equals the change in hydrogen measured, the reduction process is considered complete.

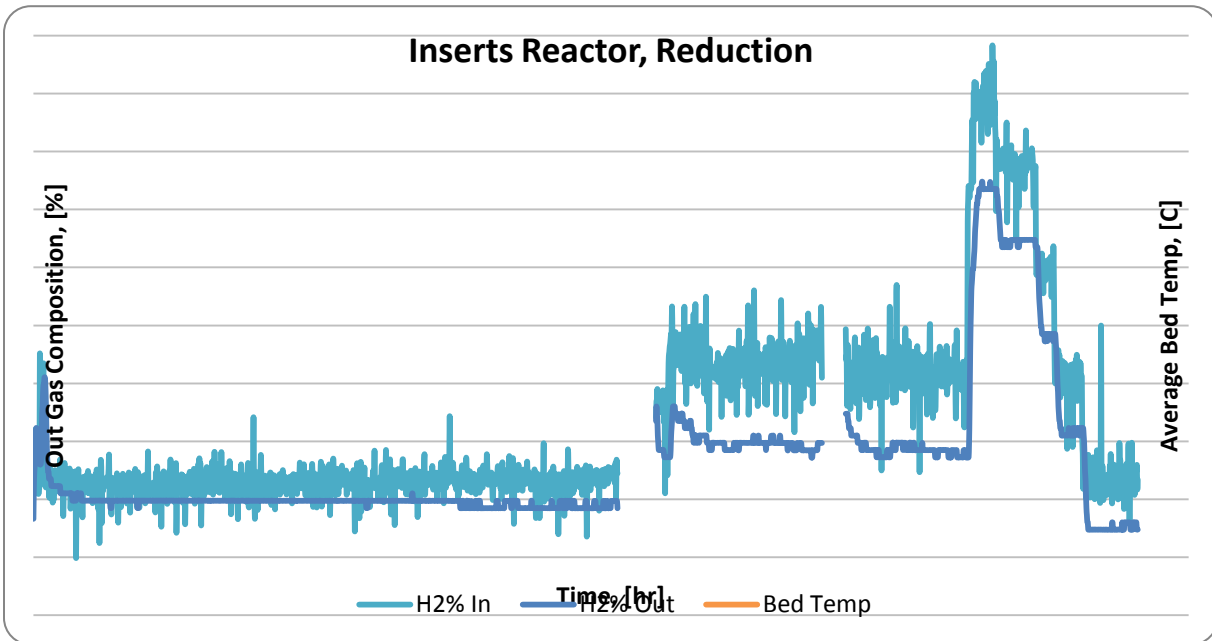


Figure B17: Inserts Reactor Test 3 Reduction Procedure

After the reduction process was complete, reforming was performed with identical operating conditions as previous tests. The hydrogen concentration was found to spike much higher (32% versus 12%) during reforming after a reduction procedure has been performed. However, as with all other previous tests reforming could not be sustained, and over time the hydrogen concentration fell to similar low concentrations.

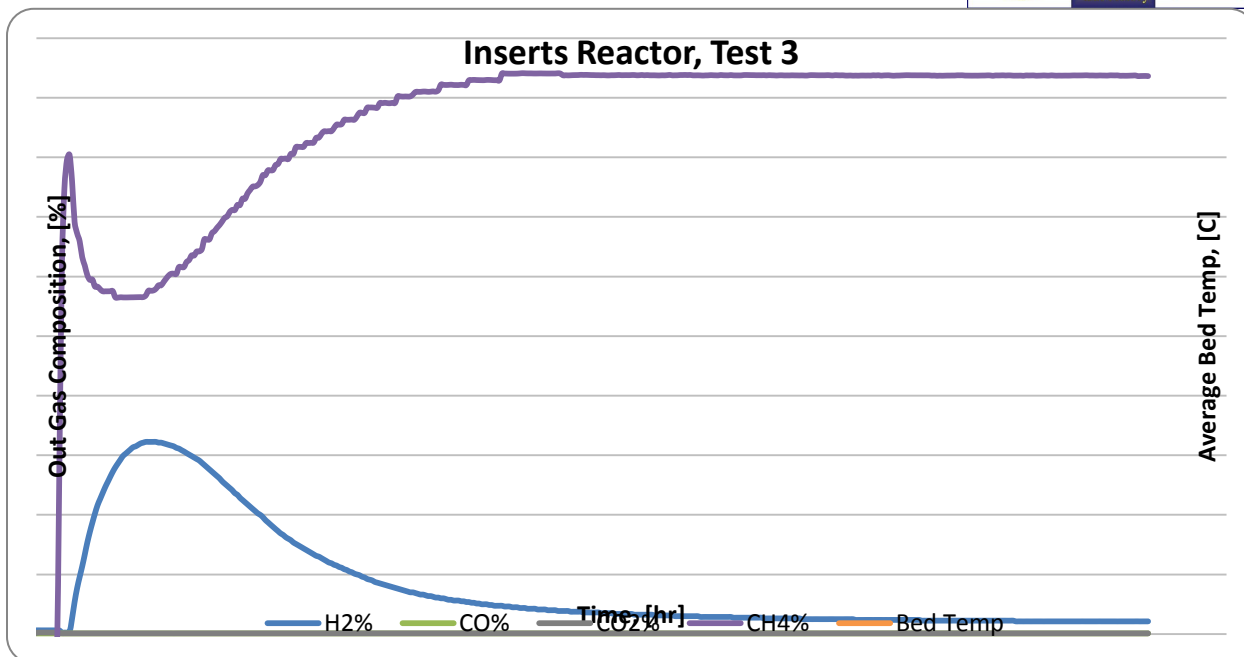


Figure B18: Inserts Reactor Test 3 Summary Plot

Inserts Reactor Test 4

Test Date: Mar 18 2013

The fourth test performed with the inserts reactor utilized methane, steam, and hydrogen. The purpose of this test was to determine if flowing hydrogen along with steam and methane would help propagate further reforming reactions. The operating conditions and results are as follows:

Table B16: Inserts Reactor Test 4 Operating Conditions

Pt	S:C Ratio	GHSV	H ₂ O Flow	CH ₄ Flow	H ₂ Flow
#	[mol/mol]	[1/h]	[mL/min]	[SLPM]	[SLPM]
1	3	180	3.55	1.53	0.00
2	3	-	3.68	1.61	0.53

Table B17: Inserts Reactor Test 4 Results

Pt	H ₂	CO	CO ₂	CH ₄	O ₂	Internal 1	Internal 2	Internal 3	Avg Bed Temp
#	[%]	[%]	[%]	[%]	[%]	[°C]	[°C]	[°C]	[°C]
1	2.0	0.1	0.1	93.7	-	754.9	766.7	-	760.8
2	5.5	0.1	0.1	92.5	-	754.4	765.8	-	760.1

After a reduction procedure lasting 4 hours (omitted from plot), steam and methane were introduced to the reactor with nearly identical results to the last test. Once settled, a reduction procedure lasting 1 hour was performed, and then steam, methane, and hydrogen were

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introduced. The hydrogen concentration spiked 3.6% higher than the previous data point, but also settled 3.5% higher. From these results, hydrogen did not seem to aid in sustaining reforming.

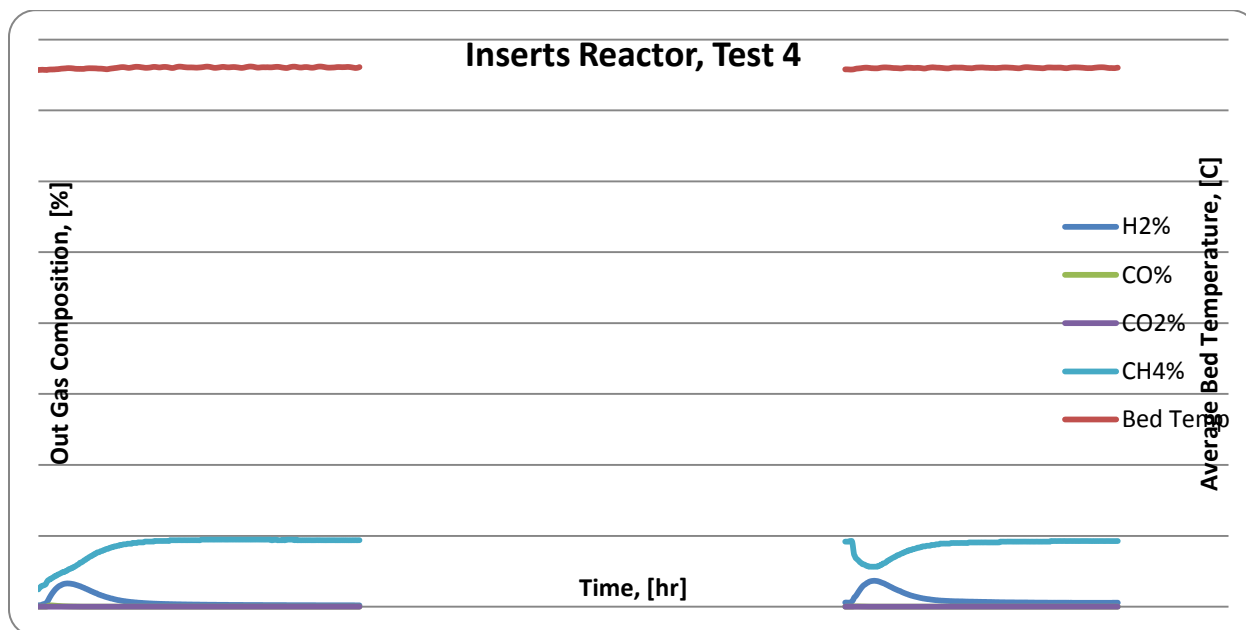


Figure B19: Inserts Reactor Test 4 Summary Plot

Inserts Reactor Test 5

Test Date: Mar 19 2013

The fifth test performed with the Inserts reactor utilized steam, methane, and hydrogen. The purpose of this test was to replicate the previous test and investigate the effect of shutting off methane flow for 30 minutes as the hydrogen concentration decays. The operating conditions and results are as follows:

Table B18: Inserts Reactor Test 5 Operating Conditions

Pt	S:C Ratio	GHSV	H2O Flow	CH4 Flow	H2 Flow
#	[mol/mol]	[1/h]	[mL/min]	[SLPM]	[SLPM]
1	3	180	3.74	1.61	0.43

Table B19: Inserts Reactor Test 5 Results

Pt	H2	CO	CO2	CH4	O2	Internal 1	Internal 2	Internal 3	Avg Bed Temp
#	[%]	[%]	[%]	[%]	[%]	[°C]	[°C]	[°C]	[°C]
1	8.6	0.1	0.1	1262.5	-	753.0	764.4	-	758.7

Test conditions identical to those for Inserts reactor Test 4 were performed. Halfway down the decay of hydrogen concentration, methane flow was stopped. During this time, the only gas reaching the analyzer was hydrogen, as water was condensed out downstream. A steady rise in hydrogen was seen, however the hydrogen did not saturate the analyzer, as the flow rate was very low. After 30 minutes, methane flow was resumed. A small spike in hydrogen was seen followed by a rapid decay identical to previous values.

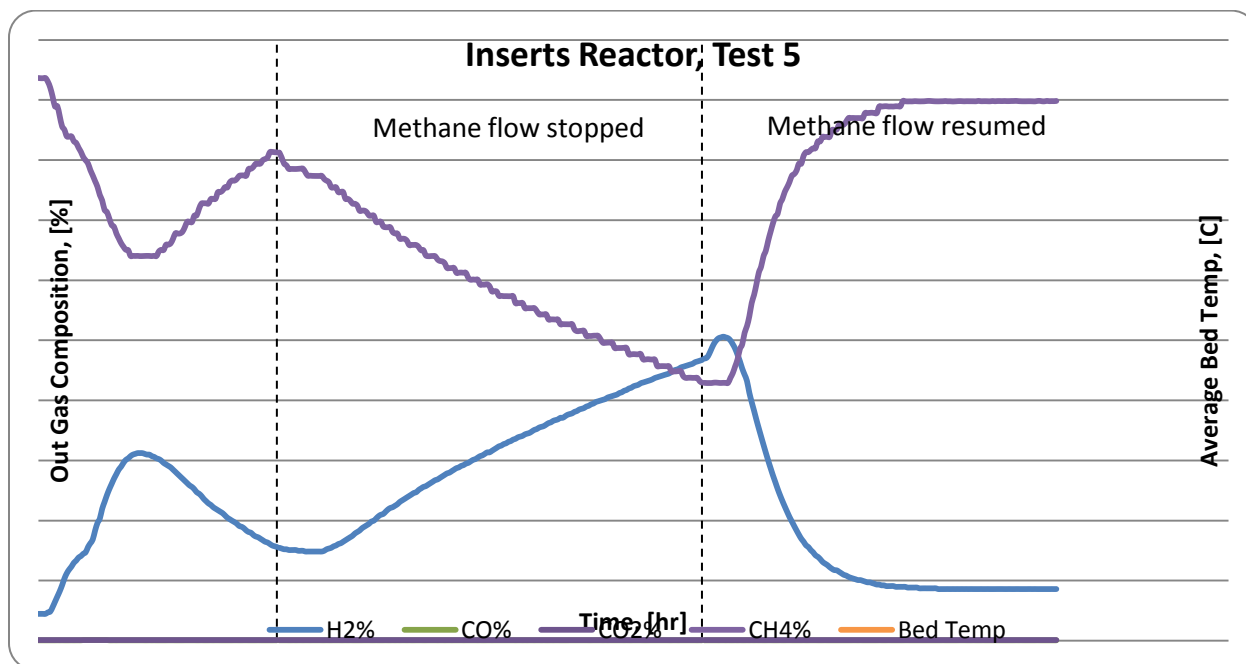


Figure B20: Inserts Reactor Test 5 Summary Plot

Baseline Reactor Test 3

Test Date: Mar 21 2013

The third test performed with the Baseline reactor utilized methane, steam, and a reduction procedure. The purpose of this test was to apply reduction procedures not yet applied to the Baseline reactor and compare the results to the Inserts reactor. The operating conditions and results are as follows:

Table B20: Baseline Reactor Test 3 Operating Conditions

Pt	S:C Ratio	GHSV	H2O Flow	CH4 Flow	N2 Flow	H2 Flow
#	[mol/mol]	[1/h]	[mL/min]	[SLPM]	[SLPM]	[SLPM]
(Reduction)	-	-	0.0	24.9	24.9	2.9
1	3	180	3.7	1.6	0.0	0.0
(Reduction)	-	-	0.0	18.6	18.6	2.1
2	3	180	3.7	1.6	0.0	0.5

Table B21: Baseline Reactor Test 3 Results

Pt	H ₂	CO	CO ₂	CH ₄	Internal 1	Internal 2	Internal 3	Avg Bed Temp
#	[%]	[%]	[%]	[%]	[°C]	[°C]	[°C]	[°C]
(Reduction)	9.0	0.1	0.1	-5.9	759.8	764.9	767.3	764.0
1	2.0	0.1	0.1	93.9	754.6	763.2	763.5	760.4
(Reduction)	8.2	0.1	0.2	-5.6	755.1	767.2	770.2	764.2
2	9.4	0.1	0.1	88.1	755.0	763.5	763.8	760.8

After a reduction procedure, Data Point 1 was performed using steam and methane. The results were nearly identical to those from Inserts reactor Test 4. A reduction procedure was performed for another hour, and then Data Point 2 was performed using steam, methane, and hydrogen. The results were also nearly identical to those from the Inserts reactor. From these results, it is seen that a reduction procedure was as effective for the Baseline reactor as it was for the Inserts reactor in aiding reforming. In both cases, sustained reforming could not be achieved.

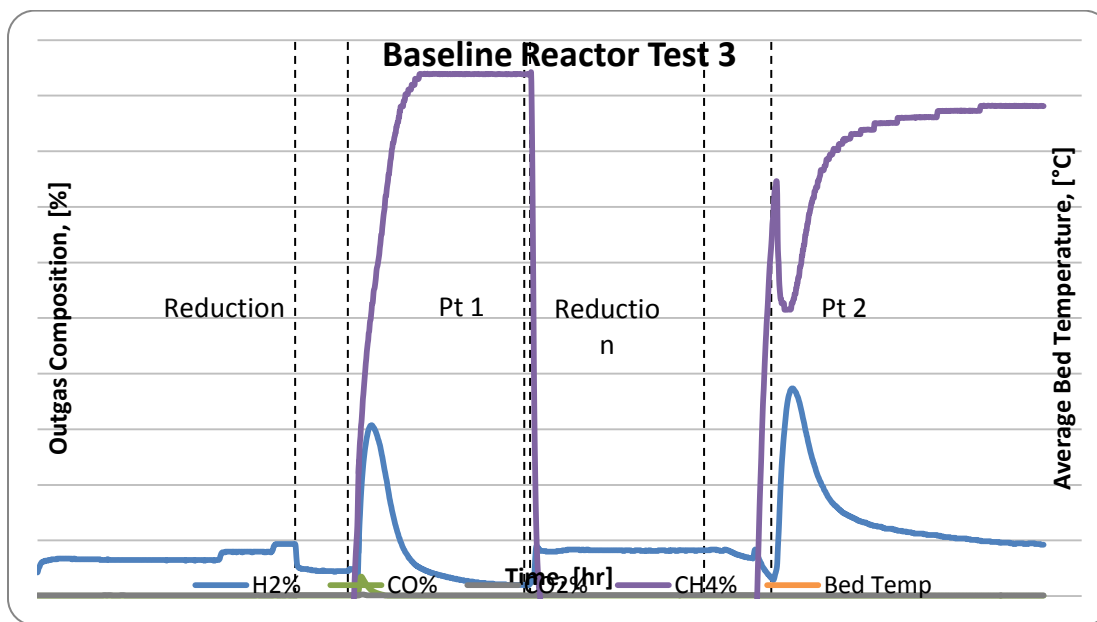


Figure B21: Baseline Reactor Test 3 Summary Plot

Baseline Reactor Test 4

Test Date: May 3 2013

The fourth test performed with the Baseline reactor utilized methane, steam, carbon monoxide, and reduction procedures. The purpose of this test was to investigate the effect of carbon monoxide present during reforming. The operating conditions and results are as follows:

Table B22: Baseline Reactor Test 4 Operating Conditions

Pt	S:C Ratio	GHSV	H ₂ O Flow	CH ₄ Flow	N ₂ Flow	H ₂ Flow	CO Flow
#	[mol/mol]	[1/h]	[mL/min]	[SLPM]	[SLPM]	[SLPM]	[SLPM]
(Reduction)	-	-	0.0	0.0	19.9	1.0 – 3.0	0.0
(Add CO)	-	-	0.0	0.0	20.0	0.0	3.1
1	3	180	3.7	1.6	0.0	0.0	0.0
(Reduction)	-	-	0.0	0.0	18.8	1.0 – 3.0	0.0
(Add H ₂ /CO)	-	-	0.0	0.0	18.5	1.5	1.6
2	3	-	3.7	1.6	1.6	0.0	0.0

Table B23: Baseline Reactor Test 4 Results

Pt	H ₂	CO	CO ₂	CH ₄	Internal 1	Internal 2	Internal 3	Avg Bed Temp
#	[%]	[%]	[%]	[%]	[°C]	[°C]	[°C]	[°C]
(Reduction)	13.7	0.1	0.2	-5.8	762.6	769.9	769.4	767.3
(Add CO)	0.2	10.8	0.7	-5.9	762.5	768.2	770.7	767.1
1	1.4	0.1	0.1	93.9	755.5	764.0	764.2	761.3
(Reduction)	13.5	0.1	0.2	-5.6	754.3	762.3	761.7	759.4
(Add H ₂ /CO)	6.7	3.9	0.6	-5.6	754.0	760.8	761.7	758.9
2	1.3	0.1	0.1	93.6	755.4	764.0	764.4	761.3

For this test, a reduction procedure was performed for one hour using nitrogen and hydrogen. Afterwards, similar amounts of carbon monoxide were introduced for half an hour, and then reforming occurred. Afterwards, another reduction procedure was performed. Next, the hydrogen flow was halved and replaced with carbon monoxide, and then reforming occurred. In both cases, CO seemed to have no effect on subsequent reforming, as hydrogen concentration spikes were nearly identical in both magnitude and behavior to the previous test.

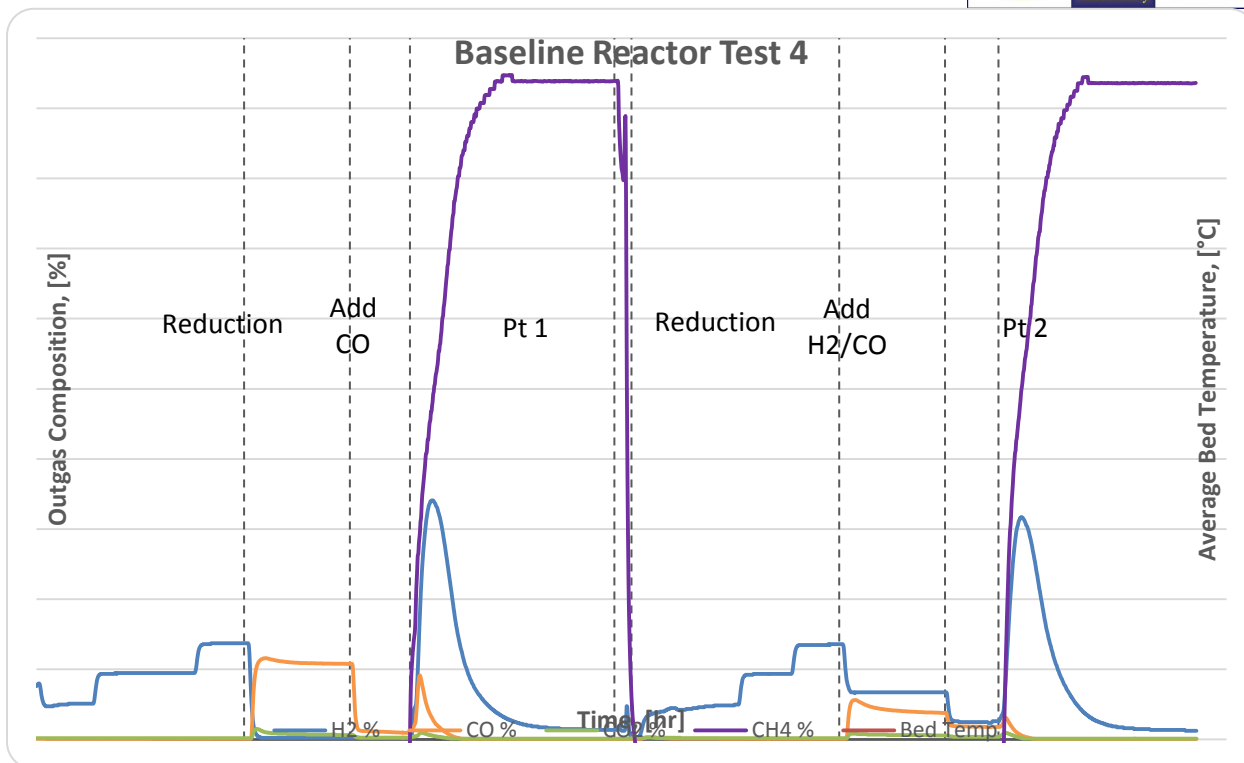


Figure B22: Baseline Reactor Test 4 Summary Plot

Baseline Reactor Test 5

Test Date: May 17 2013

The fifth test performed with the Baseline reactor utilized methane, steam, and nitrogen. The purpose of this test was to mimic reduction procedure, but replace hydrogen with methane and observe the results. The operating conditions and results are as follows:

Table B24: Baseline Reactor Test 5 Operating Conditions

Pt	S:C Ratio	GHSV	H ₂ O Flow	CH ₄ Flow	N ₂ Flow
#	[mol/mol]	[1/h]	[mL/min]	[SLPM]	[SLPM]
(100% CH ₄)	-	360	0.0	13.1	0.0
(50% CH ₄)	-	360	0.0	6.6	6.7
1	1	360	4.9	6.6	0.0

Table B25: Baseline Reactor Test 5 Results

Pt #	H ₂ [%]	CO [%]	CO ₂ [%]	CH ₄ [%]	Internal 1 [°C]	Internal 2 [°C]	Internal 3 [°C]	Avg Bed Temp [°C]
(100% CH ₄)	3.2	0.1	0.1	88.9	758.4	764.7	764.8	762.6
(50% CH ₄)	2.0	0.1	0.1	48.7	758.0	765.1	765.5	762.9
1	1.1	0.1	0.1	90.4	758.8	765.4	766.2	763.5

For this test, pure methane was introduced to the reactor for one hour. It should be noted that during this time, hydrogen concentration rose to about 8% then decayed. This implies some dissociation occurred, but could not be sustained similar to the reforming process. After one hour, methane flow was reduced by half and replaced with nitrogen. Reforming followed and a hydrogen spike very similar in magnitude and behavior to those previous was observed. It should be noted, though, that a spike in carbon monoxide was also seen.

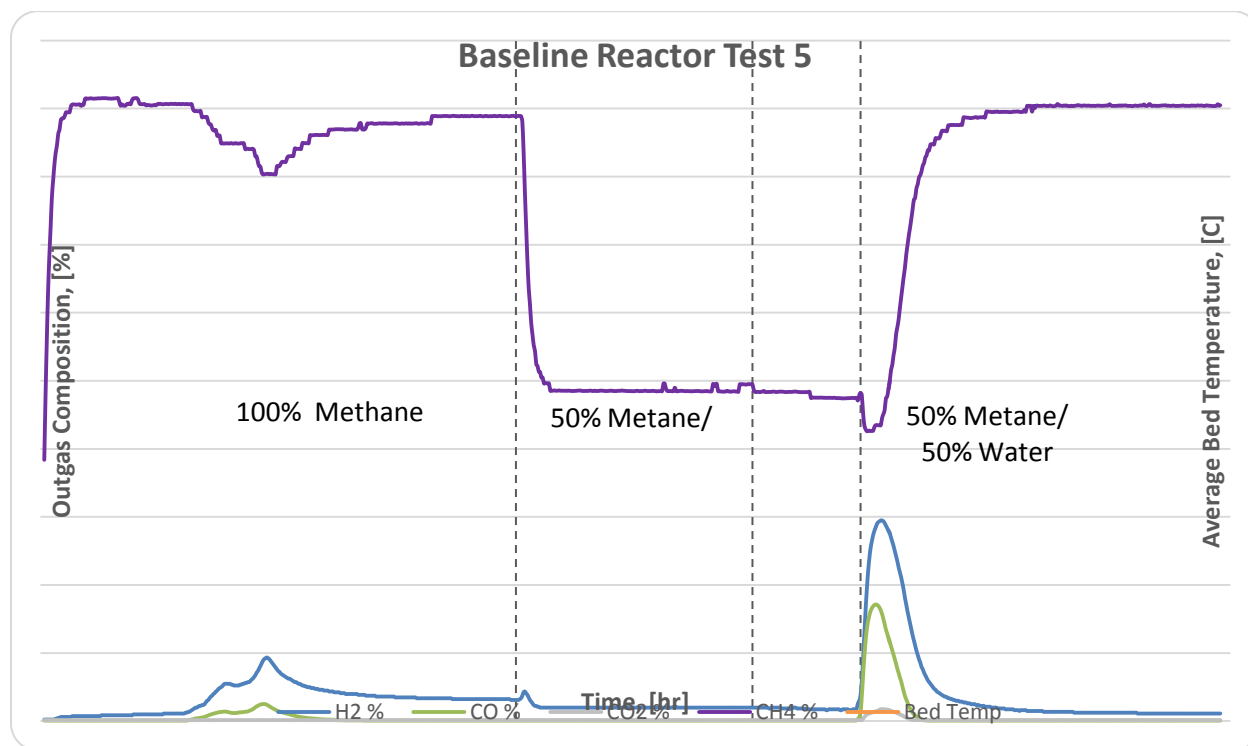


Figure B23: Baseline Reactor Test 5 Summary Plot

Conclusions

Key observations:

- For the operating conditions used, the presence of 800H strips did not aid reforming.
- The presence of air did not aid reforming.
- Regardless of reactor tested or operating conditions used, sustained reforming could not be achieved.
- Despite this, higher temperatures and lower space velocities did result in relatively larger spikes and (though very low) higher settled values of hydrogen concentration.
- For both reactors and under all test conditions, reduction procedures with hydrogen and methane greatly aided subsequent reforming.

Periods of sustained reforming results could not be replicated at our testing facility. In order to achieve sustained, non-catalytic reforming at our facility, higher temperatures are most likely needed. In order to achieve this, electrical heating of the reactor would no longer suffice and a revamping of the heat source would be required.

The importance of reduction procedures must also be stressed. For all tests, spikes in hydrogen concentration were only seen after reduction procedures were performed. These results indicate the possibility of surface activation. However, if surface activation is present there may also be deactivation, as reforming could not be sustained under any operating conditions. It must be stressed that this is only speculation at this point, and is contingent upon further research.

Appendix B1 – Detailed Description of Testing Apparatus

The following sections further details the experimental facility utilized in this study.

Metering and Pumping Subassembly

The metering and pumping subassembly consisted of two separate flow streams for the methane and water feedstock. Each flow stream served the purpose of supplying, controlling, and measuring the flow from their respective reservoirs. As shown in Figure B24, the water feedstock was supplied from a 16 liter (4 gal.) polyethylene dewar. This dewar sat upon a scale and fed directly to a gear pump via 6.4 mm (0.25 in.) vinyl tubing. The mass contained in the water reservoir was measured using a Veritas L16001 scale with 0.1g accuracy. The water feedstock was injected into the reforming facility using a Micropump A-75211-30 gear pump with attached EQ-73003-14 head. This particular pump configuration was capable of flowing 0.092 mL/rev.

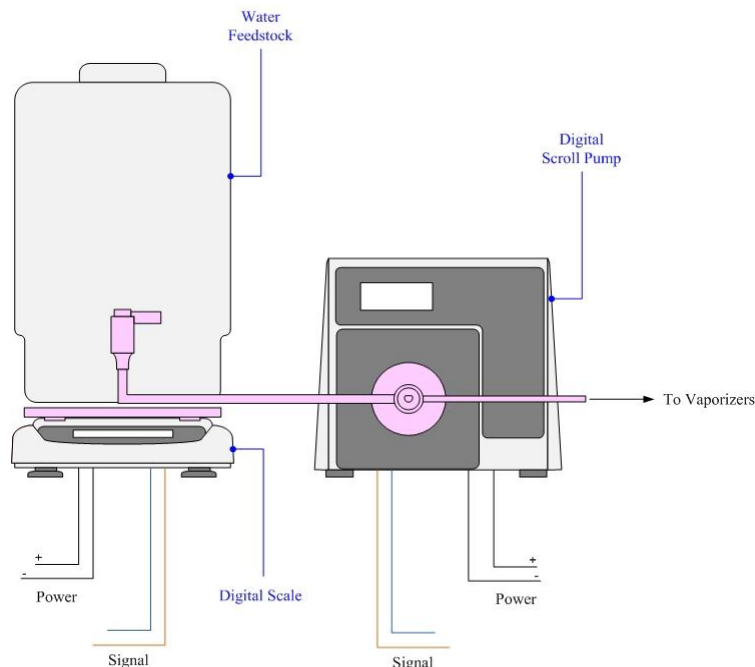


Figure B24: Simplified schematic of the water metering and pumping assembly

Flow of the water feedstock was regulated using the variable volumetric flow rate of the pump. However, mass flow rate was recorded using the mass change as reported by the scale and used as the controlling parameter for the pump flow rate.

The methane feedstock was supplied via a methane reservoir held at 13.8 MPa (2000 PSI) and regulated to 0.52 MPa (75 PSI). The reduced pressure methane was then fed to an Aalborg GFC57 mass flow controller (MFC) which monitored and controlled the flow of the feedstock. A simplified schematic of the MFC can be found in Figure B25. Both the water supplied from the

gear pump and the methane from the MFC were fed, separately, via 6.4 mm (0.25 in.) steel piping to the pre-heating subassembly.

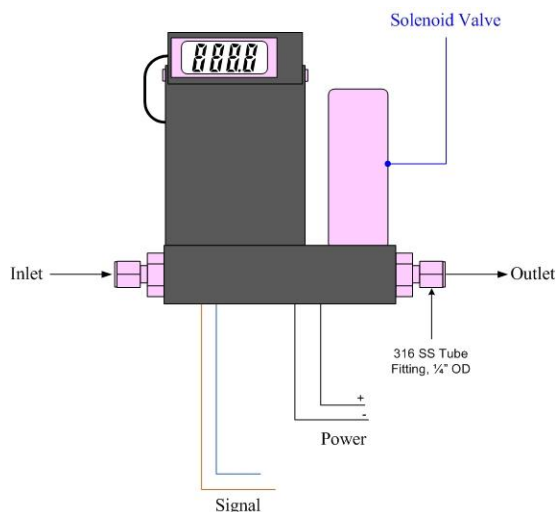


Figure B25: Simplified schematic of Aalborg GFC57 MFC

Pre-Heating Subassembly

The pre-heating subassembly served to: vaporize the incoming water feedstock, heat the methane feedstock, combine and mix the two streams, and regulate the main stream temperature before insertion into the reactor subassembly. Vaporization of the water occurred using two series trains of three vaporizers as seen in the simplified schematic of the overall reactor system. As shown in the Figure B26, each vaporizer consisted of a 254 mm (10 in.) stainless steel pipe (0.5 in. nominal diameter, schedule 40), which was used as the vaporizer housing. This vaporizer housing was machined to utilize a 254 mm (10 in.), 750 W cartridge heater (6.4 mm (0.25 in.) diameter) as its heating element. Each vaporizer was also designed to accept and feed into 6.4 mm (0.25 in.) stainless steel piping at its entrance and exit. In addition, each vaporizer utilized two stainless steel sheathed K-type thermocouples for measuring heater surface and vaporizer exit temperatures. The placement of these thermocouples is also shown in Figure B26.

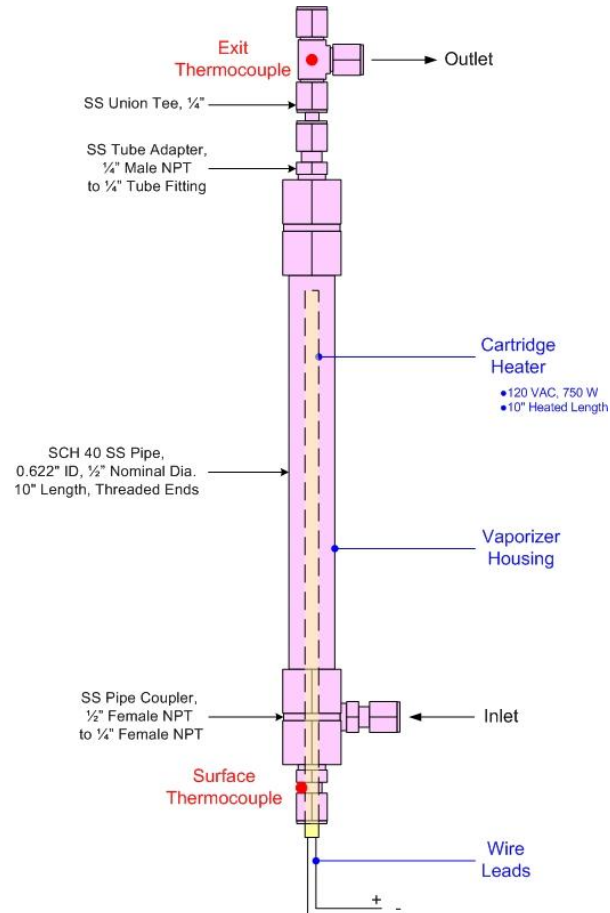


Figure B26: Detailed schematic of single vaporizer

Heating of the methane occurred using a single air/gas heater, also shown as the methane heater as shown in the simplified reactor schematic. As shown in Figure B27, the methane heater housed a 140 mm (5.5 in.), 750 W ceramic heater inside a 152.4 mm (6 in.) stainless steel pipe (19 mm (0.75 in.) diameter). Similar to the vaporizers, the methane heater was adapted for surface temperature and exit temperature K-type thermocouples. It was also adapted for 6.4 mm (0.25 in.) diameter stainless steel entrance and exit piping.

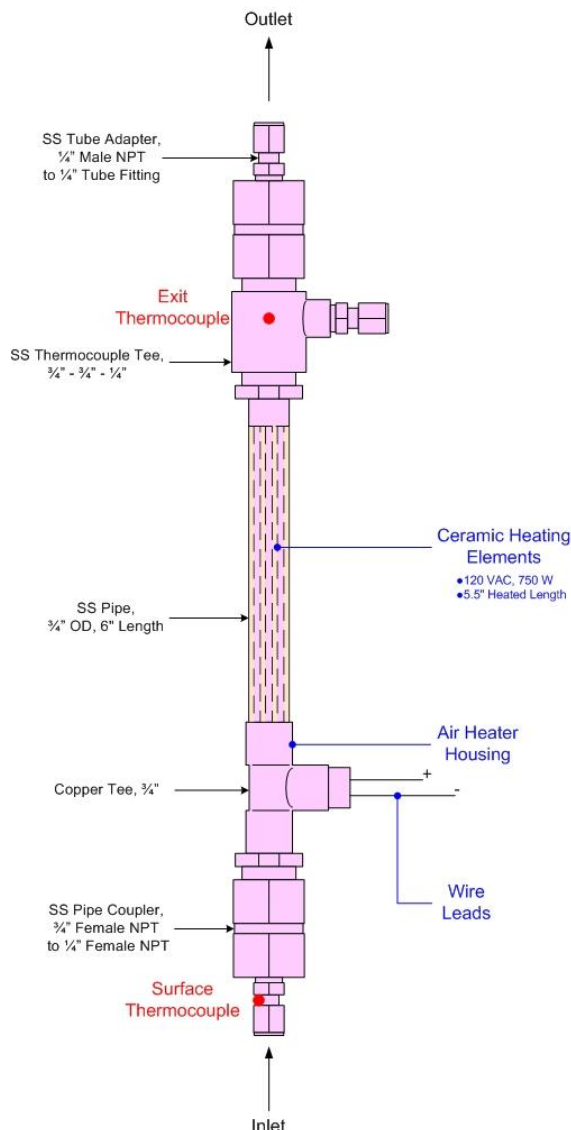


Figure B27: Detailed schematic of methane (air/gas) heater

Exit streams from the vaporizers and air/gas heater were combined, and mixed, using a stainless steel 6.4 mm (0.25 in.) union cross fitting and then fed to the superheater. Similar in construction to the vaporizers, the superheater was built using a 254 mm (10 in.) stainless steel pipe (0.5 in. nominal diameter, schedule 40) as the housing. This housing also utilized a 254 mm (10 in.), 750 W cartridge heater (6.4 mm (0.25 in.) diameter) as one of its heating elements. Like the vaporizer and the air/gas heater, the superheater was also designed to accept and feed into 6.4 mm (0.25 in.) stainless steel piping at its entrance and exit. The superheater also utilized three stainless steel sheathed K-type thermocouples for measuring the two heater surface temperatures as well the exit temperature. A detailed schematic of the superheater is shown in Figure B28. Upon exit from the superheater, temperature regulated feedstock was routed directly to the reactor subassembly.

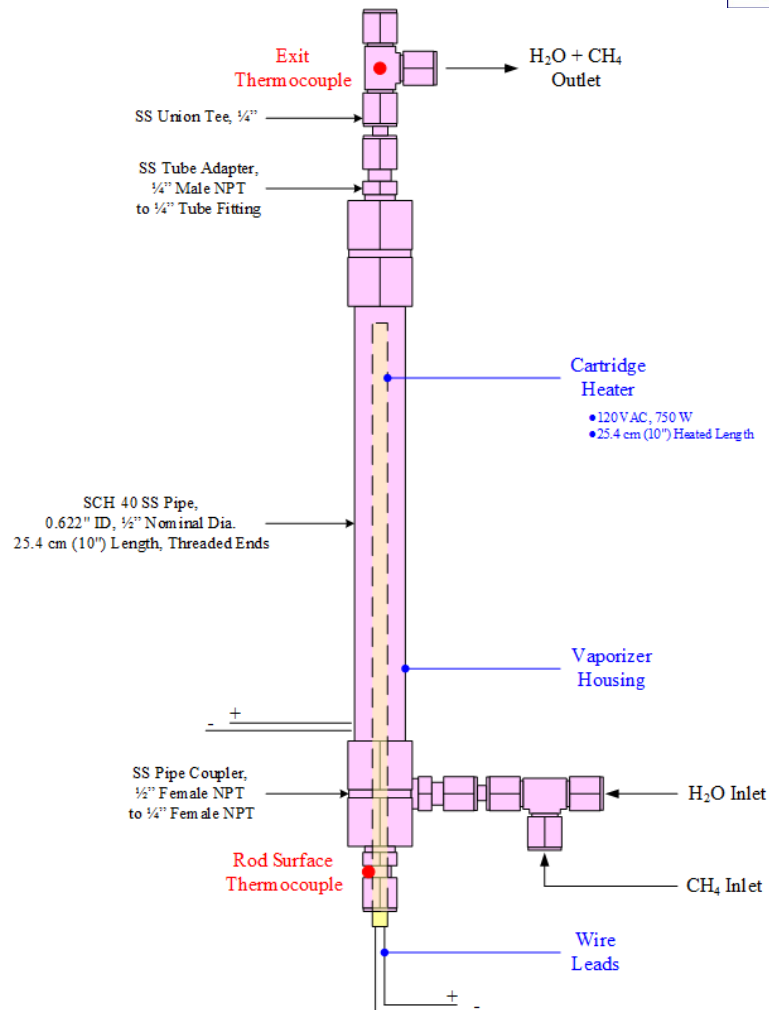


Figure B28: Detailed schematic of the superheater

Condensing Subassembly

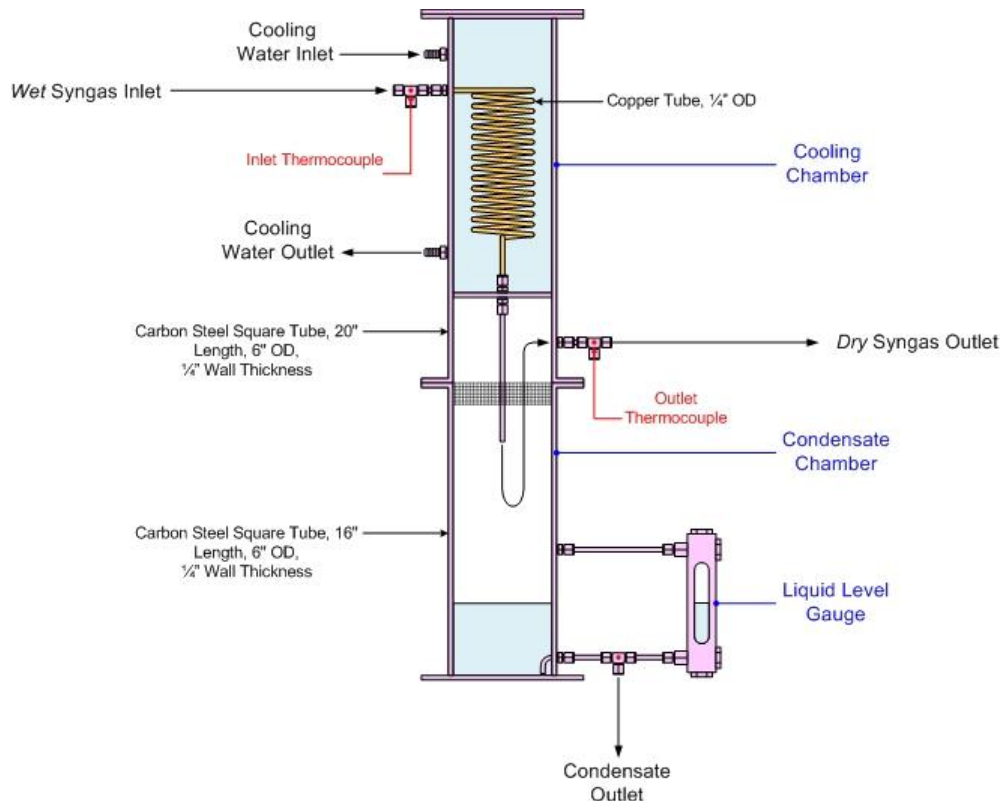


Figure B29: Detailed schematic of the main condensing unit

Closed Loop Control

A closed loop control scheme was designed to manage the water flow and temperature elements of the steam methane reformer. In regards to the temperature control, these elements included the heat bands, cartridge heaters, and superheater heat tape; and in regards to the water flow, included the gear pump. The thermocouple signals utilized in the temperature elements were processed using the NI SCXI-1303 Terminal Block and an operations computer. This computer, using the LabVIEW program, was then able to acquire and process the signals required to operate the steam methane reformer. The 4 to 20 mA signal utilized by the gear pump was monitored using a National Instrument I/O connector block and SCB-68 data acquisition board. This board was isolated from the thermocouple signals and SCXI chassis, but utilized the same computer and LabVIEW program. The front panel and block diagram of this program can be found in Appendix B2. The control logic used in the program was categorized as proportional-integral-derivative (PID) control. This controller utilized three separate parameters, a proportional term, an integral term, and a derivative term, to calculate the error between a measured data point or signal and the desired set point. The proportional (P) term was calculated based on the present error, the integral (I) term based on past errors, and the derivative (D) term was based on the prediction of future errors. The sum of these terms was then used to adjust the control signal sent to the controlled element. A block diagram of this process can be found in Figure B30. It should be noted that the methane and nitrogen mass flow controllers were also under closed loop control; however, their PID loops were internal to the equipment. All that was

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required for their use was a corresponding analog amperage signal (4-20mA) to be sent from the same SCB-68 DAQ board for the desired gas flow rate.

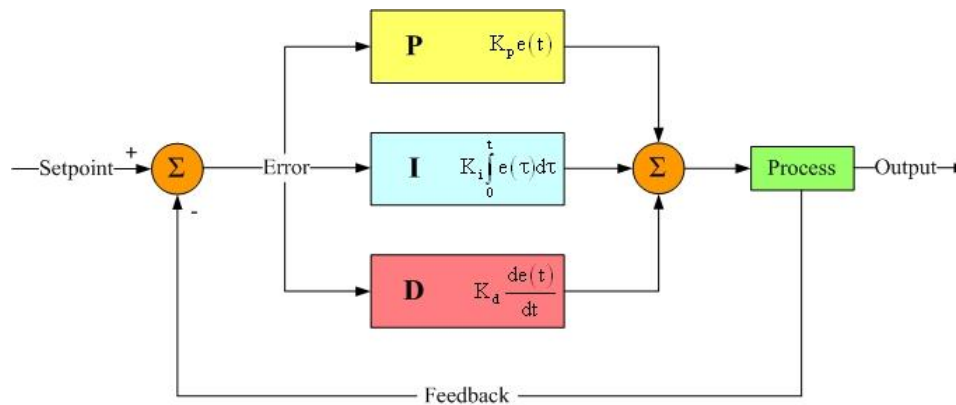


Figure B30: Diagram of a PID controller logic

As shown in Figure B30, the proportional, integral, and derivative terms are calculated to adjust the control signal of the process being governed. The proportional term created a proportional response to the time dependent signal based on the proportional gain, K_p . The integral term adjusted the output signal according to the magnitude and duration of the error, resulting in the accumulated error. The magnitude of this accumulated error could be further adjusted by multiplying with the integral gain, K_i . The derivative term adjusted the output signal using the slope of the error over time. The magnitude of this derivative term was adjusted by multiplying that rate of change of the slope with the derivative gain, K_d . Proper tuning of the proportional, integral, and derivative gains for each controller was required to ensure stable responses. This was done manually by setting K_p to 1 and the K_i and K_d to 0. K_p would then be increased just prior to the point of signal instability and held there. This process was repeated for integral and derivative gains, respectively.

The temperature PID controllers output analog voltage signals (0-5V) to be utilized in conjunction with 2 power relay boxes. These relay boxes, which supplied the power requirements for the reformer heaters, evenly distributed 7 circuits of 120V to each heater. To control the temperature output of each heater, their supplied voltage was adjusted from 0-120V based on the analog signal sent by the PID controller. As shown in Figure B31, this was done by utilizing a phase control module to systematically cycle a solid state relay on and off. By cycling the solid state relay at a certain rate, the effective voltage sent to a temperature element could be varied.

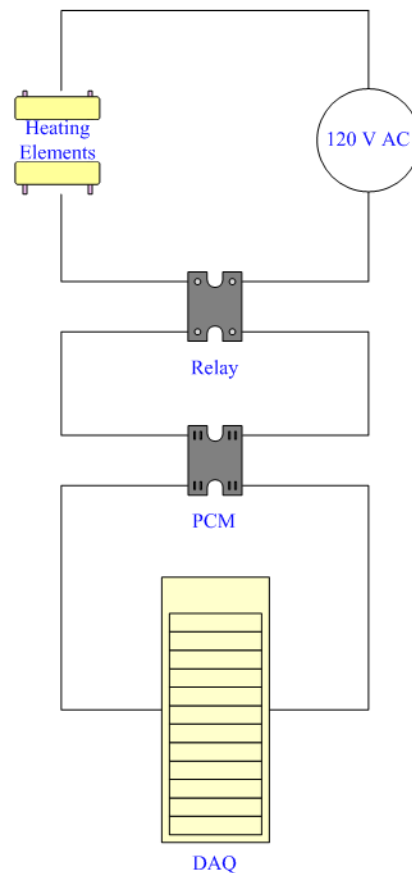


Figure B31: Simplified schematic of control circuit for heating elements.

The gear pump used to flow water into the steam reformer was built with an internal PID controller for its volumetric flow rate. However, it was preferred to use the water scale as a more accurate means to judge the rate change of mass entering the reformer. Therefore, an external PID loop was required to control the analog amperage signal (4-20mA) sent to the internal PID loop of the gear pump. A simplified schematic for this control loop is shown in Figure B32.

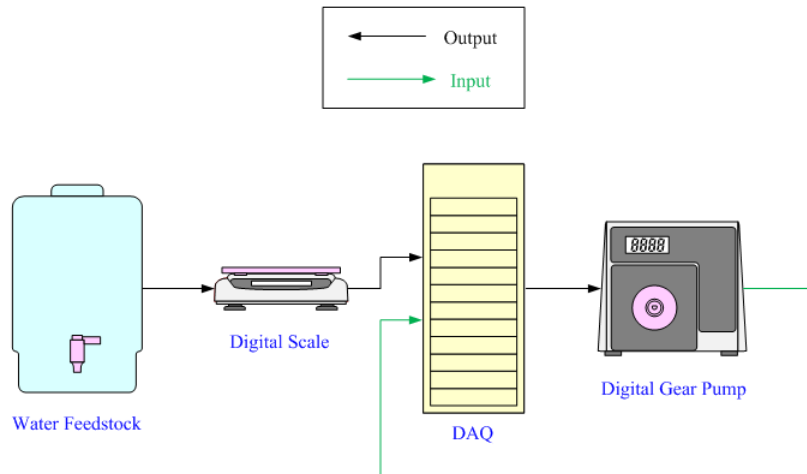
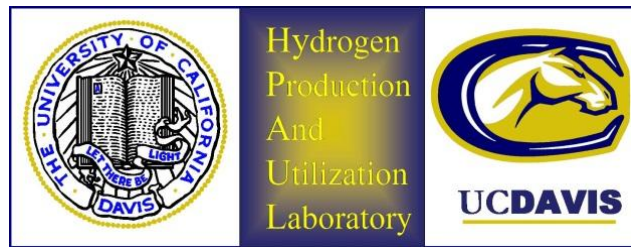


Figure B32: Schematic of control circuit for water pump

Open Loop Instrumentation:

Open loop instrumentation was implemented for the purpose of recording specific data in regards to principle aspects of the steam methane reformer. The elements included in this instrumentation were the digital scale, used for measuring the water mass, and the gas analyzer. The digital output signal from the scale was monitored and recorded by LabVIEW using the scale's RS-232 port connected to the SCB-68. The gas analyzer's analog amperage output signals (4-20mA) were acquired also using the SCB-68. They were subsequently processed and converted to their respective volumetric percentages in the LabVIEW program.

Appendix B2 – Instrumentation Report



Prepared for Gas Technology Institute
28 May 2013
Professor Paul A. Erickson

Introduction

This report summarizes the instruments utilized to conduct reformation experiments in the UC Davis Hydrogen Production and Utilization Laboratory. The reforming apparatus is separated into five subassemblies: Flow Metering and Control where the feedstock is supplied, Pre-heating where the mixed feedstock is heated, Reactor where syngas is produced, Condensing where the syngas is cooled before being analyzed, and Analysis where the gas composition is measured and analyzed.

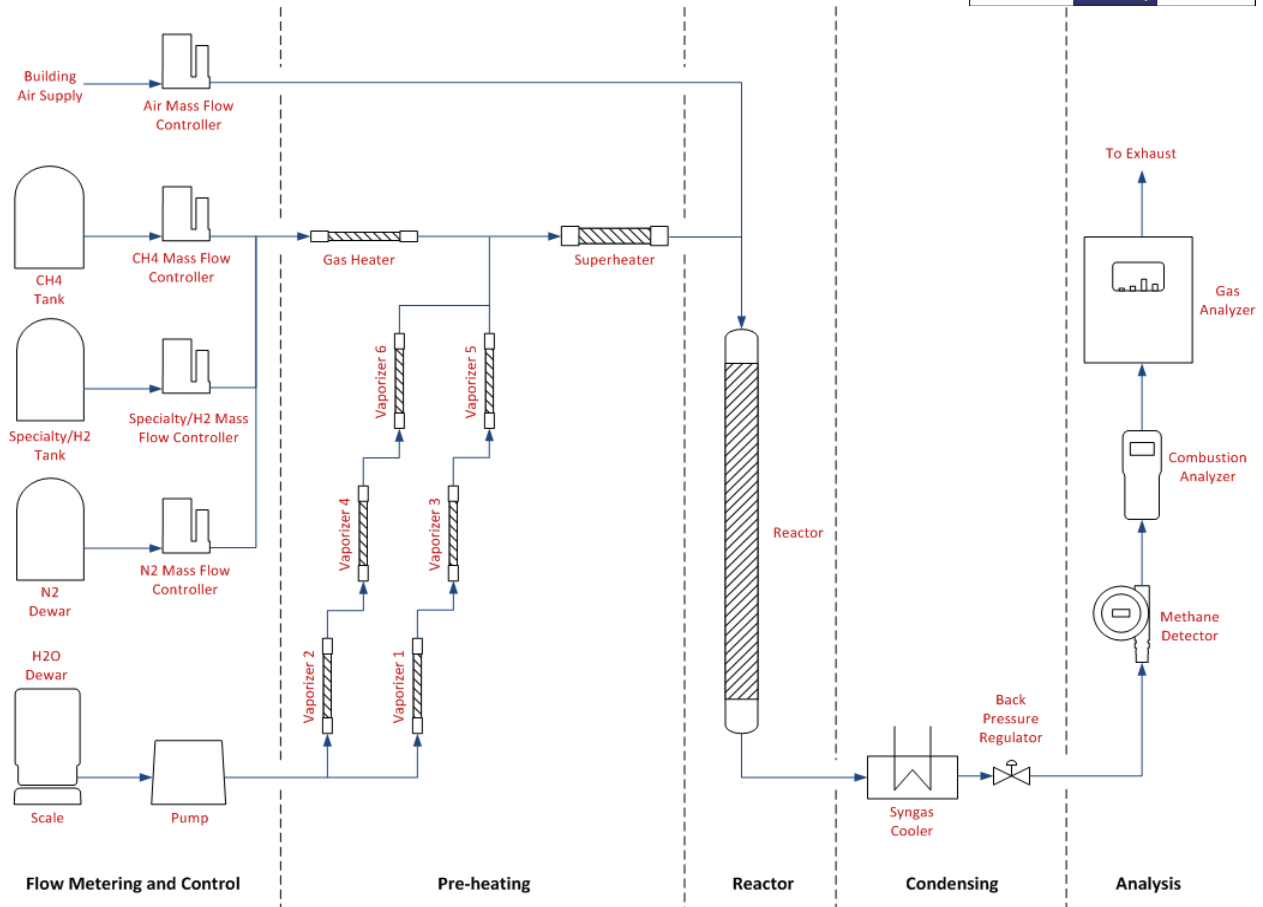


Figure B33: Schematic of the steam methane reforming apparatus

This report will focus on the *Flow Metering and Control*, *Reactor*, and *Analysis* subassemblies. *Pre-heating* and *Condensing* subassemblies are not discussed due to lack of notable instruments. Each instrument will be described by role in the system, principle of operation, detailed specifications (range, resolutions, accuracy, etc.), and input/output signals. (See figure below for signal diagram)

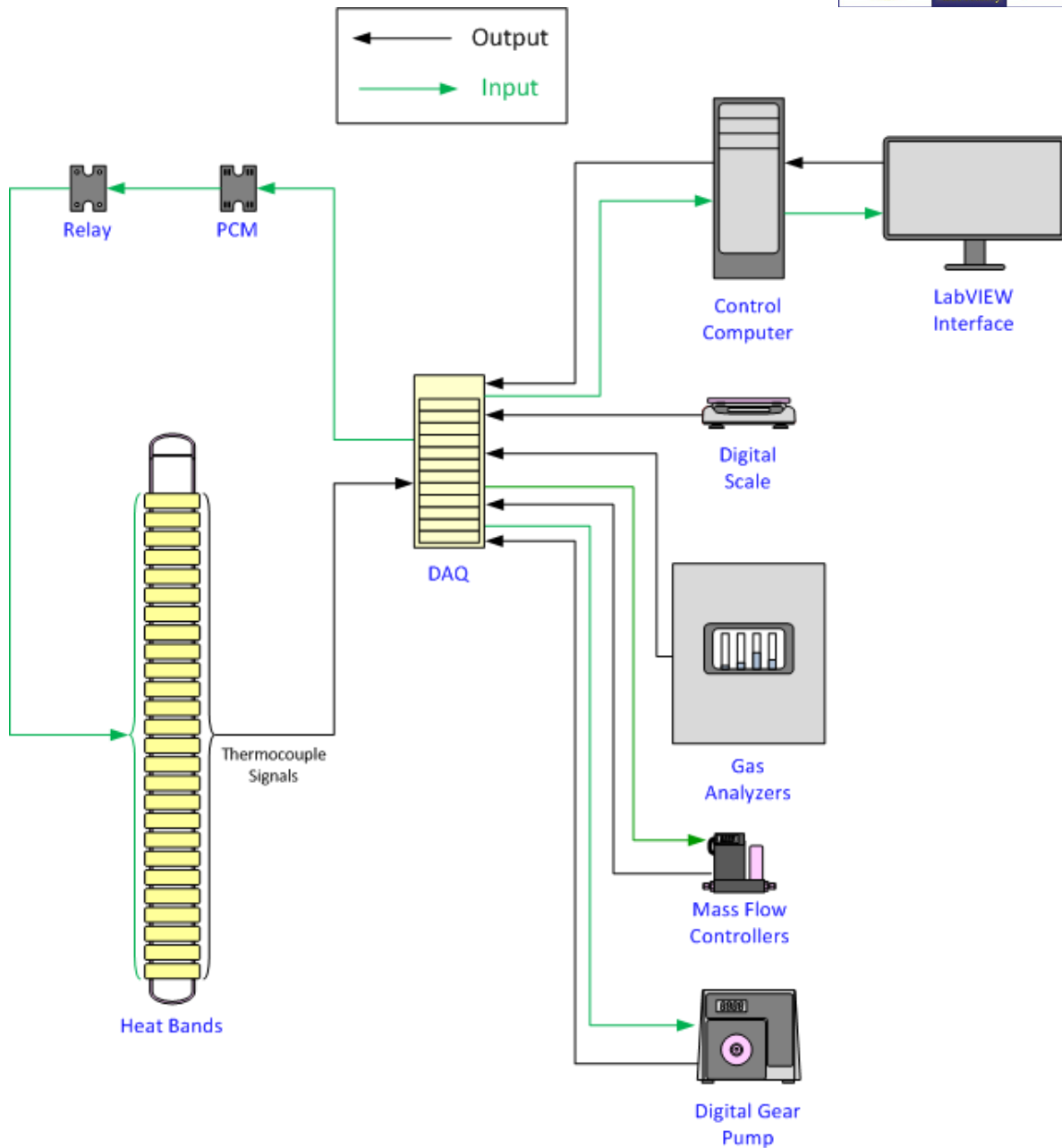


Figure B34: Input and output signal diagram

Metering and Control Subassembly

The metering and control subassembly consists of feedstocks, mass flow controllers, pump, and scale. This subassembly is responsible for supplying, controlling, and measuring the flow of reactants into the system.

Mass Flow Controllers

Gas flow into the system is metered and controlled by electronic mass flow controllers (MFCs). Their principle of operation is as follows:

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- The stream of gas entering the Mass Flow transducer is split by shunting a small portion of the flow through a capillary stainless steel sensor tube. The remainder of the gas flows through the primary flow conduit. The geometry of the primary conduit and the sensor tube are designed to ensure laminar flow in each branch. According to principles of fluid dynamics flow rates of gas in two properly sized laminar flow conduits are related to one another. Therefore, the flow rates measured in the sensor tube are directly proportional to the total flow through the transducer.
- In order to sense the flow in the sensor tube, heat flux is introduced at two sections of the sensor tube by means of precision wound heater-sensor coils. Heat is transferred through the thin wall of the sensor tube to the gas flowing inside. As gas flow takes place heat is carried by the gas stream from the upstream coil to the downstream coil windings. The resultant temperature dependent resistance differential is detected electronically. The measured gradient at the sensor windings is linearly proportional to the instantaneous rate of flow taking place.
- An output signal is generated that is a function of the amount of heat carried by the gases to indicate mass-molecular based flow rates.

Four MFCs were used in this project, three of which are manufactured by Aalborg Instruments & Controls, Inc., and one of which is manufactured by Omega Engineering, Inc.



(a)



(b)

Figure B35: Photos of (a) Aalborg Mass Flow Controller, and (b) Omega Mass Flow Controller

MFC specifications vary based on operating range and gas. Because of this, some specifications are given in percent of full scale (% FS), as seen in the table below. Unless otherwise specified, these specifications apply to both Aalborg and Omega MFCs.

Table B26: General MFC specifications

Resolution	0.1 SLPM
Accuracy	±1 % FS (Aalborg), ±1.5 % FS (Omega)
Repeatability	±0.25 % FS
Linearity	±1 % FS
Response Time	2 sec to ±2 % final value (Aalborg), 1 sec to 63 % final value (Omega)
Operating Environment	32 to 122°F (0 to 50°C)
Power	12 VDC
Input	0 - 5 VDC
Output	0 - 5 VDC

Each MFC is manufactured with a specified range and gas. The MFC can be used for other gasses, so long as a K factor correction is applied to correct for differences in density and specific heat.

Table B27: Relevant K-Factors

Gas	K Factor relative to N ₂	Density, [g/L]
Air	1.000	1.293
Hydrogen, H₂	1.0106	0.0899
Methane, CH₄	0.7175	0.715
Carbon Monoxide, CO	1.000	1.25
Nitrogen, N₂	1.000	1.25
Specialty Mixture (87.8% N₂, 11% CO₂, 1.2% O₂)	0.963	1.33

The MFC used to flow specialty gas and hydrogen is an **Aalborg 0-100 SLPM H2 MFC**. Its specifications can be found in the table below.

Table B28: Specialty Gas/H2 MFC specifications

Manufacturer	Aalborg Instruments & Controls, Inc.
Part no.	GFC47
Range	0 - 100 SLPM (H2), 0 - 96 SLPM (Specialty)
Resolution	0.1 SLPM
Accuracy	±1 SLPM (H2), ±0.96 SLPM (Specialty)
Repeatability	±0.25 SLPM (H2), ±0.24 SLPM (Specialty)
Linearity	±1 SLPM (H2), 0.96 SLPM (Specialty)

The MFC used to flow methane and carbon monoxide is an **Aalborg 0-20 SLPM N2 MFC**. Its specifications can be found in the table below.

Table B29: Methane MFC specifications

Manufacturer	Aalborg Instruments & Controls, Inc.
Part no.	GFC37
Range	0 - 14.4 SLPM (CH ₄), 0 - 20 SLPM (CO)
Resolution	0.1 SLPM
Accuracy	±0.14 SLPM (CH ₄), ±0.2 SLPM (CO)
Repeatability	±0.04 SLPM (CH ₄), ±0.05 SLPM (CO)
Linearity	±0.14 SLPM (CH ₄), ±0.2 SLPM (CO)

The MFC used to flow nitrogen is an **Aalborg 0-500 SLPM N2 MFC**. Its specifications can be found in the table below.

Table B30: Nitrogen MFC specifications

Manufacturer	Aalborg Instruments & Controls, Inc.
Part no.	GFC67
Range	0 - 500 SLPM
Resolution	0.1 SLPM
Accuracy	±5 SLPM
Repeatability	±1.25 SLPM
Linearity	±5 SLPM

The MFC used to flow air is an **Omega 0-50 SLPM Air MFC**. Its specifications can be found in the table below.

Table B31: Air MFC specifications

Manufacturer	Omega Engineering, Inc.
Part no.	FMA-1900
Range	0 - 50 SLPM
Resolution	0.1 SLPM
Accuracy	±0.5 SLPM
Repeatability	±0.125 SLPM
Linearity	±0.5 SLPM

Digital Gear Pump

Water flow into the system is metered and controlled by an electronic digital gear pump. The pump's specifications vary based on the pump head attached. Because of this, the specifications given are in percent of full scale (% FS), as seen in the table below.

Table B32: General pump specifications

Range	50 - 3600 rpm
Resolution	0.1 mL/min
Accuracy	± 0.25 %FS
Repeatability	± 0.25 % FS
Linearity	± 0.25 % FS



(a)



(b)

Figure B36: Photos of (a) Digital gear pump, and (b) Pump head

The pump head used for this experiment is a Micropump EW-07002-25 which provides 0.017 mL/rev. Correcting for this pump head, the specifications are as follow.

Table B33: Pump specifications correcting for pump head

Manufacturer	Cole-Parmer
Part no.	75211-30
Range	0.85 - 61.2 mL/min
Resolution	0.1 mL/min
Accuracy	± 0.15 mL/min
Repeatability	± 0.15 mL/min
Linearity	± 0.15 mL/min
Response Time	30 sec or less
Operating Environment	32 to 104°F (0 to 40°C)
Power	115 VAC
Input	0 - 10 VDC
Output	0 - 10 VDC

Digital Scale

Though the volumetric flow rate is controlled by the pump, the mass flow rate is recorded using a digital scale. This mass flow rate is used as the controlling parameter and feedback for the pump flow rate. A density of 1 g/mL is assumed at all times.



Figure B37: Photo of BEL Engineering digital scale

The scale specifications can be seen in the table below.

Table B34: Digital scale specifications

Manufacturer	BEL Engineering
Part no.	L16001
Range	0 - 16000 g
Resolution	0.1 g
Accuracy	±0.05 g
Repeatability	±0.05 g
Linearity	±0.2 g
Response Time	3 sec or less
Operating Environment	41 to 95°F (5 to 35°C)
Power	115 VAC
Output	0 - 9 VDC

Reactor Subassembly

Thermocouples

All temperature measurements in the reforming apparatus are measured using Omega K-type thermocouples. The sensor of a K-type consists of a chromel-alumel junction, and is chosen based on wide operating range and fast response time. Their principle of operation is as follows.

- Thermocouples consist of two different types of metals, joined together at one end. When the junction of the two metals is heated or cooled, a voltage is created that can be correlated back to temperature. This is known as the thermoelectric or Seebeck effect.
- The voltage is not generated at the junction of the two metals of the thermocouple but rather along that portion of the length of the two dissimilar metals that is subjected to a temperature gradient. Because both lengths of dissimilar metals experience the same temperature gradient, the end result is a measurement of the difference in temperature between the thermocouple junction and the reference junction.
- Thermocouples measure the temperature difference between two points, not absolute temperature. To measure a single temperature one of the junctions—normally the cold junction—is maintained at a known reference temperature, and the other junction is at the temperature to be sensed.



Figure B38: Photo of omega K-type thermocouple

For this experiment, two sizes of thermocouples were used: 0.020" and 0.062". Their specifications are can be seen in the table below.

Table B35: K-type thermocouple specifications

Manufacturer	Omega Engineering, Inc.
Part no.	KMQXL-020U (0.020"), KQXL-062U (0.062")
Range	-328 to 2282 °F (-200 to 1250 °C)
Resolution	0.225°F (0.125°C)
Accuracy	±2.2°C or 0.75% above 0°C (whichever is greater), ±2.2°C or 2.0% below 0°C (whichever is greater)
Response Time	0.5 seconds or less
Output	-6.458 - 54.886 mV

Analysis Subassembly

Nova Gas Analyzer

Analysis of carbon monoxide, carbon dioxide, and hydrogen was performed using a Nova Gas Analyzer. It's principle of operation is as follows:

- The Nova gas analyzer has the ability to simultaneously analyze concentrations of hydrogen, carbon dioxide, carbon monoxide, and methane based on a small amount of dry gas (which is continuously sampled from the exhaust stream). To determine the concentrations of carbon dioxide, carbon monoxide, and methane in the sample gas, a Non-Dispersive Infra-Red (NDIR) detector is used. The microprocessor based detector utilizes an infra-red (IR) source beam to pulse through a sample cell and be simultaneously read by an IR detector. The infra-red detector, opposite the IR lamp, monitors the specific gas wavelengths based on their discrete absorption characteristics. Analysis of the quantity and types of wavelengths absorbed corresponds to the composition and concentrations of the gases detected. To determine the concentration of hydrogen in the sample gas, a temperature controlled thermal conductivity (TC) cell is used. This TC cell determines the amount of hydrogen contained within the sample by comparison of a pair of heated thermistors. One thermistor is surrounded by the sample gas while the other surrounded by the reference gas, air. The hydrogen concentration is then determined by comparison of the heat transferred in regards to the two thermistors.



Figure B39: Photo of Nova Gas Analyzer

The analyzer was calibrated a minimum of twice per week, and typically before every new test. Calibration of the Model 7904CM gas analyzer took place by utilizing a span gas with known mixtures of carbon monoxide, carbon dioxide, methane, and nitrogen as well as a “zero” gas. For this study, the analyzer was calibrated using a span gas consisting of 9% carbon monoxide, 9% methane, 37% nitrogen, and 45% carbon dioxide. The zero gas consisted of 100% hydrogen. Both gases were regulated to 34.5 kPa (5 PSI) and fed into the analyzer. Using the analyzer’s user interface, the known mixture of the span gas was programmed in and the analyzer would calibrate itself based on its own programming.

The gas analyzer specifications can be seen in the table below.

Table B36: Nova gas analyzer specifications

Manufacturer	Nova Analytical Systems
Part no.	7904CM
Method of Detection	Separate NDIR (infrared) detectors for CO, CO ₂ and CH ₄ . Thermal conductivity cell for H ₂ .
Ranges	0-10.0% CO, 50.0% CO ₂ , 0-20.0% CH ₄ , 0-100% H ₂
Resolution	0.1% for all gases
Accuracy	± 2% FS
Repeatability	± 2% FS
Response Time	20-30 seconds, not including sample transport time to analyzer
Operating Environment	32 to 120°F (0 to 50°C)
Power	115VAC 60Hz
Output	4-20 mA for each gas measured

RKI M2 Methane Detector

Due to the limited range of the methane sensor in the Nova Gas Analyzer, a standalone methane detector is used to monitor methane content.



Figure B40: Photo of RKI M2 methane detector

The methane detector was calibrated prior to all testing, as it is recommended to re-calibrate every 6 to 12 months. Calibration took place by utilizing a calibration gas consisting of 50% methane, 50% nitrogen. Using the analyzer's user interface, the known mixture of the span gas was programmed in and the analyzer would calibrate itself based on its own programming. The methane detector specifications can be seen in the table below.

Table B37: RKI M2 methane detector specifications

Manufacturer	RKI Instruments
Part no.	65-2628RK-CH4
Method of Detection	Infrared Sensor
Range	0 - 100% Vol.
Resolution	1%
Accuracy	± 5% of reading or ± 2% of full scale (whichever is greater)
Response Time	30 seconds or less, not including sample transport time to analyzer
Operating Environment	-4 to 122°F (-20 to 50 °C), 5 - 95% Relative Humidity
Power	19 - VDC
Output	4 – 20 mA signal, corresponding to 0 - 100%

UEi C75 Combustion Analyzer

Analysis of oxygen was performed using a handheld UEi C75 Combustion Analyzer.



Figure B41: Photo of UEi C75 Combustion Analyzer

The combustion analyzer self-calibrates each time it is powered on, as long as it is exposed to atmospheric air. It assumes the atmospheric air consists of 20.9% oxygen, 0% carbon dioxide, and 0 ppm CO. The combustion analyzer specifications can be seen in the table below.

Table B38: UEi combustion analyzer specifications

Manufacturer	Universal Enterprises, Inc. Test Instruments
Part no.	C75
Method of Detection	Electrochemical Cell
Range	0 - 21%
Resolution	0.1%
Accuracy	± 0.2%
Response Time	20 - 30 seconds
Operating Environment	32 to 104°F (0 - 40°C)
Power	9 VDC
Output	N/A

Appendix C – Phase III – Field Experiment Options (Proposed)

Background

Per Amendment No. 1 to the subcontract between AISI and GTI (6/24/2012), a pilot scale field experiment of a TCR system with a revised/reduced test matrix, a technical objective and budget or a single zone of a steelmaking reheat furnace was held out as a guide to the scope of work for Phase III.

Phase I work was initiated based on a 250 MMBtu per hour reheat furnace that served as a representative furnace. Republic Steel and ArcelorMittal provided specifications for several operating furnaces from which the reference furnace was selected. Phase II lab-scale TCR work was predicated on Phase I results and the 250 MMBtu per hour reference furnace.

Based on Phase 2 test results, several alternative field experiment site options should be considered, particularly sites that have connected inputs ranging from 250 MMBtu per hour to 50 MMBtu per hour. The proposed options for consideration are:

1. Existing production furnace connected capacity of ~250 MMBtu/h,
2. Existing production furnace connected capacity of ~100 – 200 MMBtu/h, and
3. Existing production furnace connected capacity of ~50 – 100 MMBtu/h.

Summary of Proposed Phase III Options

Option No. 1 – Production Furnace w/ connected capacity ~250MMBtu/h

This option would consist of an air preheater and a recuperative reformer (three module design) as a Full Scale TCRS - Air Recuperation (AR) and Thermochemical Recuperation (TCR) to be designed, built and installed.

Option No. 2 – Production Furnace w/ connected capacity ~150MMBtu/h

This option would consist of an air preheater and a recuperative reformer (three module design) as a Reduced Scale TCRS - Air Recuperation (AR) and Thermochemical Recuperation (TCR) to be designed, built and installed.

Option No. 3 – Production Furnace w/ connected capacity ~75MMBtu/h

This option would consist of an air preheater and a recuperative reformer (three module design) as a Further Reduced Scale TCRS - Air Recuperation (AR) and Thermochemical Recuperation (TCR) to be designed, built and installed.

Phase III – Field Experiment Scope of Work for either Option

GTI is of the opinion that the lab recuperative reformer design remains as the basis for scale up purposes. Since the TT Tests have successfully confirmed that sustained MR Rates can be

achieved by fine tuning the design of the lab recuperative reformer, the three-module TCRS design still holds for the basic design to scale up.

The subtasks making up Phase III that were originally proposed can serve as the basis for a SOW for any one of the options above. The subtasks consist of:

1. TTC, GTI and Host Site – Design and Engineer a Prototype TCR System/Recuperative Reformer System
2. GTI and Host Site – Conduct Baseline/Prep Install Plan
3. TTC, Host Site and GTI – Fabricate Prototype TCR System/Recuperative Reformer System
4. Host Site, TTC, GTI – Install and Shakedown Prototype TCR System/Recuperative Reformer System
5. GTI and Host Site – Capture performance information; reduce and analyze data
6. GTI – Prepare a Final Project/Phase III Technical Report

Details of Proposed Phase III Options

Option No. 1 – Production Furnace w/ connected capacity ~250MMBtu/h

This option would consist of an air preheater and a recuperative reformer (three module design) as a Full Scale TCRS - Air Recuperation (AR) and Thermochemical Recuperation (TCR) to be designed, built and installed.

Discussion

This option is equivalent to what was originally proposed for this project. The scope of supply would include designing and engineering a TCRS that is scaled up from the current lab recuperative reformer design, with several adjustments to be determined from lessons learned during the Task 2.5 tests.

Advantages:

- Waste heat recovery Synergy realized
 - 1200°F Air/1200°F RF equivalent to 1700°F Air
- Comprehensive field experiment for finalizing commercial TCRS for deployment
- Commercialization of TCRS sooner

Disadvantages:

- ,Hot air/hot Fuel piping and insulation required
 - Full Instrumentation package required
 - Full demolition and site prep
 - Full installation labor
 - Full Engineering

- Full TCR System design engineering
- Burner mods for air/fuel required
- Large Footprint
- Risk-Momentary production derate
- Installation and start up shoehorned in to planned R&M shutdown

Option No. 2 – Production Furnace w/ connected capacity ~150MMBtu/h

This option would consist of an air preheater and a recuperative reformer (three module design) as a Reduced Scale TCRS - Air Recuperation (AR) and Thermochemical Recuperation (TCR) to be designed, built and installed.

Discussion

Reduced budget requirements relative to Option No. 1 due to lower connected capacity affecting TCRS heat transfer area and dimensions including specifics below.

Advantages:

- Reduced diameter hot air/hot Fuel piping and insulation
- Reduced demolition and site prep
- Reduced TCR System design engineering
- Reduced Engineering
- Reduced footprint
- Waste heat recovery Synergy realized
 - 1200°F Air/1200°F RF equivalent to 1700°F Air
- Comprehensive field experiment for finalizing commercial TCRS for deployment
- Commercialization of TCRS sooner

Disadvantages:

- Full Instrumentation package required
- Risk-Momentary production derate
- Installation and start up shoehorned in to planned R&M shutdown

Option No. 3 – Production Furnace w/ connected capacity ~75MMBtu/h

This option would consist of an air preheater and a recuperative reformer (three module design) as a Further Reduced Scale TCRS - Air Recuperation (AR) and Thermochemical Recuperation (TCR) to be designed, built and installed.

Discussion

Further reduced budget requirements relative to Options No. 1 and No. 2 due to lower connected capacity affecting TCRS heat transfer area and dimensions including specifics below.

Advantages:

- Reduced diameter hot air/hot Fuel piping and insulation
- Reduced demolition and site prep
- Reduced TCR System design engineering
- Reduced Engineering
- Reduced footprint

Disadvantages:

- Full Instrumentation package required
- Risk-Momentary production derate
- Installation and start up shoehorned in to planned R&M shutdown

Proposed Phase III Project Schedule and Plan

The Activities/Tasks to Be Performed for Phase III (24 months) to build and test a prototype are detailed below and in the Project Management Plan – Detail:

- Using the results of the modeling from Phase I, the lab-scale tests of the TCR system during Phase II work, the data compiled on typical steel reheat furnace operation, and engineering assistance from the project team, a prototype TCR system will be designed. Drawings for fabrication of the reformer and recuperator and installation drawings will be prepared.
- Base-line measurements of reheat furnace operation at the steel company site. GTI will bring its field instrumentation to the selected site to collect efficiency and emission data. Also compiled will be operational data from the candidate steel reheat furnace. Specific issues regarding the installation of the TCR system on the target furnace will be reviewed between the project partners and the host site.
- Fabricate TCR system and ship to site including other ancillary components Induced Draft Fan, Jet Pump, and instrumentation package components.
- Install the prototype TCR system at the steel company site and shakedown the TCR system. After installation, it is anticipated that during the startup period the operation of the various components of the TCR system will be verified.
- Capture performance information. A week-long campaign to collect performance (efficiency and emissions) data and compile operational data for the steel reheat furnace TCR system. After a period of continued operation of the TCR system, a follow-up data collection campaign is planned.

- Reduce and analyze field results. The data from the baseline measurements and the data collection campaigns will be reduced, analyzed, and compared to calculate the performance improvements.
- Prepare technical report. The results from Phase III will be compiled into a report that includes the relevant data needed for sound investment decisions by the steel industry and its process equipment suppliers. A meeting between the project team and sponsors will be held to review the results of the prototype testing and determine future commercial system configuration and testing requirements.
- Develop a licensing arrangement (Memorandum of Understanding and licensing terms) with commercialization partner. After completion of the project, it is expected that a follow-on successful demonstration of the commercial version of the concept will lead to signing a licensing agreement with first commercial units ready for installation in 2016.

Table C1. Estimated Schedule and Plan

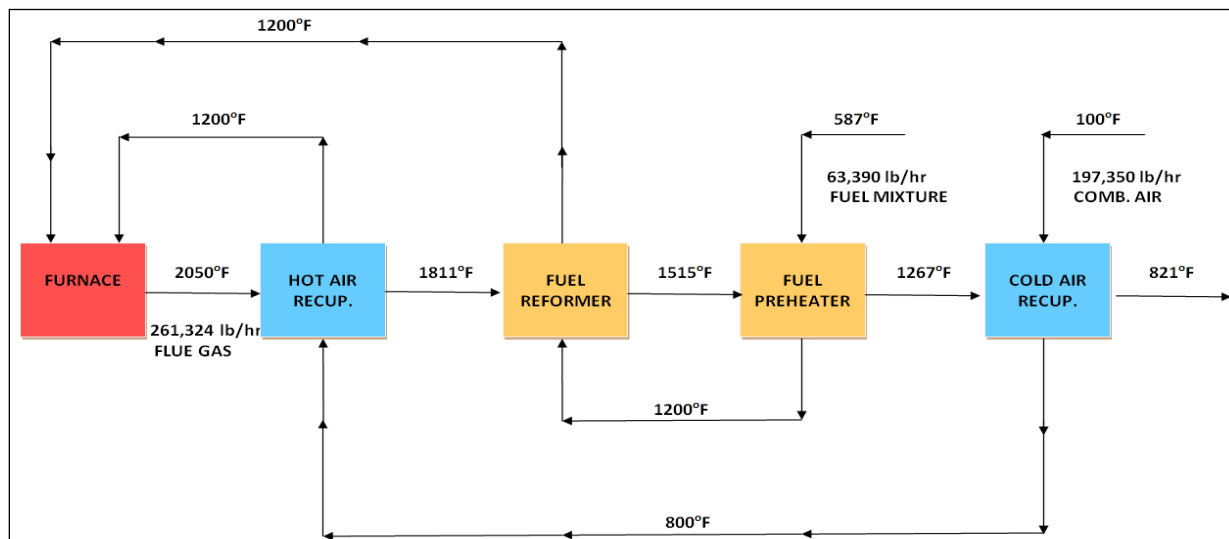
Project Management Plan - Detail

DE-FG36-08GO18130																														
Year	2013						2014												2015											
Month	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12
Go / No-Go Decision																														
Phase III Prototype TCR Build and Test																														
3.1 Design and Engineer Prototype TCR System																														
3.2 Conduct Base Line Test at Selected Steel Site and Prepare Installation Plan																														
3.3 Fabricate Prototype TCR System																														
3.4 Install Prototype TCR system at steel company site and shakedown TCR system																														
3.5 Capture performance information; Reduce and analyze data																														
3.6 Prepare Draft and Final Technical Report																														
Project Management and Reporting																														

Projected Budgets for Proposed Options

Thermal Transfer Corporation (TTC) provided preliminary estimates for the three options for both the respective combustion air heat exchangers and the recuperative reformer that make up the GTI three-module TCRS to be employed in the proposed Phase III Field Experiment. Also provided by TTC, and shown below is a single-line diagram for Option 1 (~250MMBtu/h production reheat furnace) in terms of mass flows and corresponding temperatures.

**Figure C1. Option No. 1 – Flows and Temperatures
Corresponding to a ~250MMBtu/h TCRS Retrofit**



TTC has advised that for estimation purposes, only the flows would change for Options 2, and 3. For example, any or all of the flows would be reduced for Option No. 2 by dividing 150MMBtu/h by 250MMBtu/h and multiplying each flow by 0.6.

Preliminary budgets for each proposed option including estimated cost sharing by the host site are provided in Table C2.

Table C2. Phase III Preliminary Budgets for Proposed Options

Cost Category	Original Budget (2008)	Budgets- PROPOSED PHASE III OPTIONS		
		Option 1	Option 2	Option 3
AISI Project Management	559,212	840,901	840,901	840,901
GTI:				
Design and Engineer Prototype TCR System	243,808	263,786	263,786	263,786
Conduct Baseline/Prep Install Plan	59,282	64,140	64,140	64,140
Fab Prototype TCR System	1,601,290	3,379,576	2,482,375	1,634,738
Install and Shakedown Prototype TCR System	88,715	95,984	95,984	95,984
Capture performance info; reduce and analyze data	57,887	62,630	62,630	62,630
Prep Draft and Final Technical Report	65,382	70,739	70,739	70,739
Phase 2 Additional costs	-	50,168	50,168	50,168
Total GTI	2,116,364	3,987,023	3,089,822	2,242,185
Co-Funding				
Suppliers	440,682	627,000	493,950	368,250
Host Site - In-kind	699,990	1,270,520	1,016,416	762,312
Industry Oversight	6,000	32,333	32,333	32,333
GTI Co-Funding	-	142,000	142,000	142,000
Total Co-funding	1,146,672	2,071,853	1,684,699	1,304,895
Total Budgets	\$ 3,822,248	\$ 6,899,777	\$ 5,615,422	\$ 4,387,981

Estimated Budgets for Each Option

As can be seen, estimates/projections for the Key Tasks and cost of the Prototype TCRS that make up the Phase III field experiment estimates range from of \$4.4 million to \$6.9 million with the largest projected expenditure of each option attributed to the TCR system fabrication; and Design and Engineering of the TCR system the second largest expenditure. As previously noted above, the fabrication of the TCRS for all three options were based on updated preliminary estimates from TTC; the other tasks were updated from the original estimates by applying a CPI index factor; and finally the Total Cost Share and Host Site In-kind correspond to, and are a function of, the size of the production furnace of each option.

Anticipated Schedule for Proposed Options

The schedule of 24 months for a full field experiment as described for all three options is considered as a reasonable basis for consideration. Thermal Transfer Corporation has advised that based on their business experiences, the typical lead time for fabricating and delivering waste heat recovery equipment at the sizes proposed can be as long as six to seven months depending upon material availabilities and other projects in the queue. The expansion or contraction of the schedule will be strongly dependent upon the Phase III Option ultimately agreed upon.

Appendix C1 – Host Site Risk

The explanation for the Derating cost share is as follows:

Each steel company partner was asked to provide basic information about one of their representative reheat furnaces. It is well understood that any retrofit of a major piece of equipment such as a TCR system on a reheat furnace will have the potential for temporarily derating the furnace for a period of time during the shakedown period following the installation due to “tuning” of operating parameters of the TCR System to operate optimally. The derating will come about for the following primary reasons:

- Fuel to Air ratios will be required to be optimized in regards to settings for low, mid-range, and high fire.
- Flue Gas recirculation settings for low, mid-range, and high fire will be required to be optimized.
- An optimized balance(s) between heat abstraction of Reformer and Air Recuperator will be required for purposes of controlling flame luminosity which effects heat transfer in the interior of the furnace.

The calculation for determining the value of the risk requires assuming 10 shakedown days of 24 hours each and a nominal derating of 1%. The other factors are specific energy intensity, nominal furnace rating in MMBtu per hour, a throughput rate and a selling price of the finished product which are all specific to each steel company partner.