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Autothermal Reforming of Natural Gas to Synthesis Gas

Reference: KBR Paper #2031

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Abstract

This Project Final Report serves to document the project structure and technical results achieved during the 3-year project titled Advanced Autothermal Reformer for US Dept of Energy Office of Industrial Technology. The project was initiated in December 2001 and was completed March 2005. It was a joint effort between Sandia National Laboratories (Livermore, CA), Kellogg Brown & Root LLC (KBR) (Houston, TX) and Süd-Chemie (Louisville, KY). The purpose of the project was to develop an experimental capability that could be used to examine the propensity for soot production in an Autothermal Reformer (ATR) during the production of hydrogen-carbon monoxide synthesis gas intended for Gas-to-Liquids (GTL) applications including ammonia, methanol, and higher hydrocarbons. The project consisted of an initial phase that was focused on developing a laboratory-scale ATR capable of reproducing conditions very similar to a plant scale unit. Due to budget constraints this effort was stopped at the advanced design stages, yielding a careful and detailed design for such a system including ATR vessel design, design of ancillary feed and let down units as well as a PI&D for laboratory installation. The experimental effort was then focused on a series of measurements to evaluate rich, high-pressure burner behavior at pressures as high as 500 psi. The soot formation measurements were based on laser attenuation at a view port downstream of the burner. The results of these experiments and accompanying calculations show that soot formation is primarily dependent on oxidation stoichiometry. However, steam to carbon ratio was found to impact soot production as well as burner stability. The data also showed that raising the operating pressure while holding mass flow rates constant results in considerable soot formation at desirable feed ratios. Elementary reaction modeling designed to illuminate the role of CO_2 in the burner feed showed that the conditions in the burner allow for the direct participation of CO_2 in the oxidation chemistry.

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Executive Summary

Introduction

The Introduction of this report begins with a description of the project motivation and goals as originally stated in the proposal submitted to the US DOE in May 2000. As supporting background information, a brief description of the current technological methods used in the chemical industry for the production of synthesis gas follows. The relationship between these methods, largely variations of steam methane reforming, and the potential advantages of a high pressure ATR approach are illustrated. The next subsection describes the specific technical issues associated with the high pressure ATR approach especially when combined with carbon dioxide recirculation. The need for experimental research is highlighted by noting that the available computational tools are insufficient to draw any firm conclusions on either the probability or the magnitude of soot formation throughout such a unit, and that testing is required to develop definitive data for commercial design. A brief summary of the energy and environmental benefit analysis that was included in the original proposal is presented next where it is stated that the two main environmental benefits in an ATR-based approach relative to existing technology originate from the significant reduction in NO_x and reduced net CO_2 emissions. It also notes that the power savings associated with a 1000 TPD plant relative to existing technology is approximately 20 MW. The next three subsections describe the project plan, team members, and technology transfer approach. The final section outlines the way the project took its course through first an ambitious and original idea of a building a miniature complete ATR equipped with optical access to the final project experimental work that was completed with the available budget. The project history subsection ends with a brief outline of the aims of the project when it refocused on exploring the soot formation characteristics of high pressure partial oxidation (POX) within the limits of a bench scale annular burner.

Phase 1 Design

The Phase 1 design section summarizes the development of the ATR system that KBR focused on during the early stages of the project. This section illustrates the level of detail that was developed and shows that the sophistication of the design was sufficient to ensure successful operation of the test unit, had sufficient funds been available. Although never built, KBR retains considerable know-how in addressing this fairly complex heat transfer engineering challenge. The detailed P&ID calls out all of the required pressure equipment and control and measurement components needed for installation. This section also includes a description of the development of a unique steam generator and high pressure superheater that delivers steam based on a prescribed mass flowrate independent of pressure rather than maintaining a setpoint pressure as typical commercial units operate.

Bench Scale Burner

This subsection describes in detail the design and operation of the high pressure partial oxidation burner that was used to generate the experimental data that is the core result of the project. The subsection is broken down into number of topics including 1) pressure equipment, 2) the laser attenuation view cell and experimental principles for soot content detection, 3) test operation scheme, and 4) specifics regarding POX flame measurements and data collection

Experimental Results.

This Results subsection presents the data that supports the several quantitative conclusions that the project generated on high pressure partial oxidation flames and soot formation. This section also highlights the complicated nature of the pulse flame approach, wherein there are data interpretation considerations surrounding the formation of deposits on the windows and heavy transient soot formation during flame ignition/extinction. The data suggests that, as anticipated, steam, oxygen equivalence ratio, and pressure all contribute to soot formation. Specifically, at 250 psi, gas to oxygen ratios of greater than 2.0 tend to produce a lot of soot, whereas at gas to oxygen ratios of 1.6, very little soot is produced even with low steam content. The relatively small amount of data collected at 500 psi suggests that flames at these pressures produce soot at a gas to oxygen ratio of 2.0 regardless of the steam content.

Reaction Chemistry Modeling

This subsection describes the results generated in this project from the direct kinetics modeling of partial oxidation flames using a high pressure soot precursor mechanism. The results show that there is indeed something special about gas to oxygen ratios greater than 2.0 that can lead to persistent soot precursors in the flow. These calculations also show that the direct incorporation of CO_2 into the gas feed results in a significantly changed flame product spectrum and indicate clearly that these partial oxidation flame conditions are capable of directly converting CO_2 into product syngas CO well upstream of the shift/ reforming catalysts in an ATR. These calculations also show that the presence of CO_2 in the feed gas alters the behavior of the soot precursor chemistry.

Introduction

Project Motivation and Goals

This project was designed to address a key technical issue surrounding the advanced autothermal reforming of natural gas and carbon dioxide to synthesis gas (H_2/CO) for use in the production of liquid hydrocarbons including ammonia, methanol, and heavier hydrocarbons. The project period was three years. The technical issue to be resolved focused on determining the optimum conditions for maximizing syngas production while avoiding the production of soot. This proposal was targeted to address the Topical Area of "Alkanes and C1 Compounds as Feedstocks" cited in a March 2000 DOE laboratory call for proposal by providing a needed advance in reforming in an especially energy efficient single-unit operation, the Autothermal Reformer (ATR). ATRs have the potential to significantly improve the energy efficiency and technical reliability of the overall conversion of C1 compounds to liquid hydrocarbons. The implementation of ATR technology to the production of synthesis gas for Fischer-Tropsch conversion to liquid hydrocarbons hold the promise of reducing the cost of this key reforming step to a level that makes the use of C1 compounds (in this case methane as natural gas) economically viable as feedstocks.

The most common method for the production of synthesis gas is steam-methane reforming. [1] Various configurations of this method are used at perhaps as many as a thousand installations worldwide. Although autothermal reforming is an old idea, to date there are only a few commercial sites. ATRs can be used to achieve low H_2/CO ratios by directly adding carbon dioxide to the gas feed while simultaneously reducing the steam content. However, the limited experience in plants and even laboratory-scale reactors employing this approach has shown that these conditions may lead to the formation of soot to a degree that can adversely affect the overall unit operation. [2,3]

The primary goal of this work is to generate a map of process variables that define the boundaries of soot formation. These variables include feed composition, pressure, mixing configuration and selection of reforming catalyst. Elementary reaction modeling of the chemical kinetics of the gas phase partial oxidation in an ATR suggest that the presence of large amounts of CO_2 in the feed has only a minimal effect on the combustion characteristics and experimental work conducted several years ago confirmed these calculations.[1] However, the details of soot formation under these conditions, specifically high CO_2 recirculation, are not understood. At the temperature present in such a system it is likely that soot precursors are formed, but the rate controlling steps including nucleation and particle growth and possible subsequent re-oxidation cannot be quantitatively modeled at this time. As a result, to speed commercialization of this energy efficient and environmentally friendly gas-to-liquids (GTL) technology, direct experimental measurements in a small-scale reactor that permits a wide range of operating conditions are required.

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[1] Experiments conducted by Southwest Research Institute and calculations conducted by M. Frenklach (U. of California, Berkeley) for KBR.

Synthesis gas and ATR technical basics

The first step in a GTL scheme is to make synthesis gas from the feedstock. This is true regardless whether the final liquid product is ammonia, methanol, or higher hydrocarbons. Synthesis gas is a mixture of hydrogen and carbon monoxide with the ratio varying depending on the desired product. The synthesis gas also usually contains inert compounds such as argon, methane, nitrogen, carbon dioxide, and so forth. Synthesis gas can be made in a variety of devices, but is almost always made by reforming natural gas.

The reforming of natural gas is sometimes referred to as steam-methane reforming as natural gas is predominately composed of methane. Reforming uses a nickel-based catalyst to promote the reaction. It proceeds in parallel with the water-gas shift reaction according to the following reactions:

$$CH_4 + H_2O = 3H_2 + CO \qquad \text{(Reaction 1)}$$
$$H_2O + CO = H_2 + CO_2 \qquad \text{(Reaction 2)}$$

Steam-methane reforming, reaction 1, is highly endothermic. The water-gas shift, reaction 2, is slightly exothermic and therefore the overall reaction is endothermic. In industrial practice, near equilibrium yields are achieved using a variety of reactor designs. Important design considerations are system pressure, steam to carbon ratio in the feed, composition of the natural gas, the method of supplying the heat of reaction, and amount of carbon dioxide recycle. Carbon dioxide recycle may be used to lower the ratio of H_2/CO in the synthesis gas as it forces reaction 2 in the reverse direction.

Steam-methane reforming is practiced industrially using several different reactor designs. The most popular design, the primary steam-methane reformer (SMR), has more than 500 and perhaps as many as 1000 installations. It consists of catalyst-filled tubes that absorb heat via a radiant heat transfer mechanism inside a fire box. Secondary reformers, used mostly in ammonia plants, accomplish reactions 1 and 2 by partially combusting the effluent from the primary reformer with air to supply the heat. Some methanol plants use secondary reformers if oxygen is available as the oxidant. The combustion products are equilibrated over a catalyst bed contained in the same vessel underneath the combustion zone. There are about 400 secondary reformers that have been built. Kellogg Brown & Root LLC (KBR) has a long history of development of secondary reformers, particularly with the combustion chamber. [4]

Pre-reformers have gained industrial importance in the last ten years. A pre-reformer is a catalyst-filled vessel that operates adiabatically. It depends on the heat content of the incoming reactants to furnish the heat of reaction. Higher hydrocarbons in the feed are converted to methane plus a relatively small amount of hydrogen and carbon oxides. Pre-reformers are used to debottleneck existing primary reformers, convert heavy feedstocks to methane and lighter components, and to accommodate swings in natural gas composition. [5] There are perhaps 10 to 20 pre-reformers in industrial applications.

Reforming exchangers are reactors that can replace the primary reformer when used in combination with an autothermal reformer or secondary reformer. Instead of supplying the heat of reaction by burning fuel in a radiant heat transfer zone, the heat is supplied indirectly by exchange with a hotter stream. This hot stream is usually the effluent from the secondary reformer or from an autothermal reformer. The reforming catalyst is contained in packed tubes with the hot stream on the shell side. This design has been offered by various licensors for a number of years, each with its own variation. There are a dozen or so reforming exchangers in operation, all on a relatively small scale. Two of the largest operating reforming exchangers were designed by KBR. One was installed at a plant in Kitimat, British Columbia, Canada in 1995. [6] A second, three times larger KBR Reforming Exchanger System (KRES™) was successfully commissioned at an ammonia plant in Liaohe, China in late 2003.

Partial oxidation (POX) reactors are sometimes used to generate synthesis gas. POX is a non-catalytic process in which the feed is partially combusted with air, oxygen, or enriched air to make synthesis gas. Feed to these reactors can be almost any carbonaceous material, from natural gas through liquid feeds such as fuel oils and gas oils as well as coal. We estimate there are about fifty such units that have been built and operated on various feedstocks.

The autothermal reformer (ATR) concept has been around for many years. A schematic with flow streamlines is pictured in Figure 1. An ATR reactor contains a combustion zone at the top and a catalyst filled bed at the bottom. The feedstock is mixed with a sub-stoichiometric amount of oxidant and burned in the combustion zone. There is an intermediate conical recirculation section where the hot gases continue to react, but are far from equilibrium. The resultant gases are passed over the catalyst in the bottom section to achieve as close to an equilibrium mixture as possible. ATRs are attractive when used in combination with a reforming exchanger. They are also suited for making large volumes of synthesis gas, especially with relatively low hydrogen/carbon monoxide ratios such as 1.5/1 – 3/1. These lower ratios are desirable for synthesis of higher molecular weight hydrocarbons. To achieve the low end of the H_2/CO range, recycle of carbon dioxide is required. ATRs have limited commercial experience. There are only a handful of sites that use this technology. One such site is SASOL in South Africa, which uses ATRs licensed by Lurgi out of Germany. As stated above, KBR-designed ATRs have been installed in ammonia plants in Kitimat, Canada and Liaohe, China. There are a handful of other ATRs installed in commercial operation.

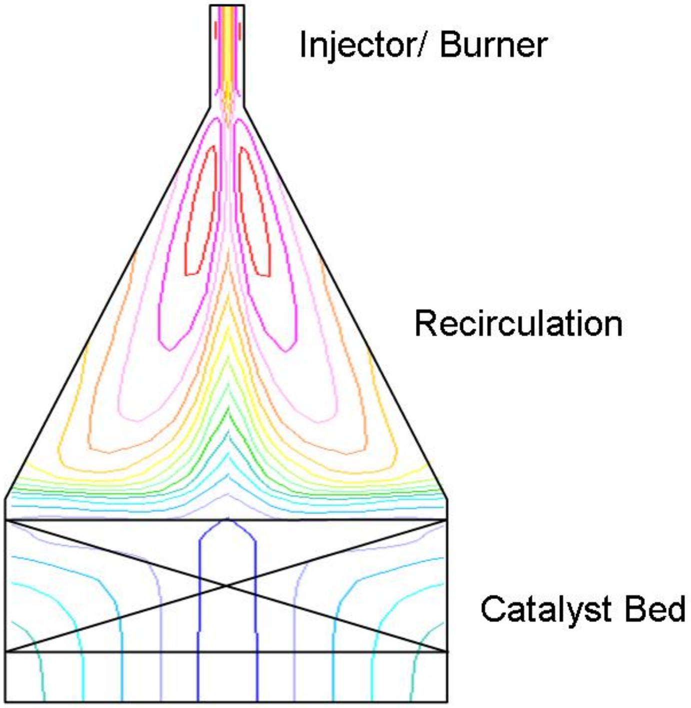

Figure 1. Schematic cross section of an ATR reactor vessel.

Autothermal reformer technical Issues

Although ATRs are similar to secondary reformers used in ammonia and methanol plants, there is one important difference. The feed to an ATR is unreacted natural gas and so it has a higher concentration of combustible components in its feed than a secondary reformer. Therefore, the potential for forming soot is greater than in a secondary reformer. Soot is suppressed by adding steam to the feed, but adding steam increases capital and operating expenses.

Although the mechanical integrity of the basic ATR approach has been well established, operating experience is lacking at the large carbon dioxide recycle rates required to reduce the ratio of hydrogen-to-carbon monoxide in the product gas to the low levels needed for Fischer-Tropsch synthesis. The high carbon dioxide fraction raises concerns with respect to its impact on the combustibility of the feed gas to the ATR and, more importantly, on soot formation in the combustion zone of this unit. Furthermore, with increasing carbon dioxide flows, the actual steam-to-carbon ratio of the fuel is, in essence, much lower than that found in a typical unit which operates with virtually no carbon dioxide in the recycle.

Using a kinetics-based combustion model, it can be shown that the carbon dioxide feed is predicted to have a very minute impact on the combustibility characteristics of the system. For example, the ignition delay for the largest carbon dioxide recycle (to yield $H_2/CO = 1.5$), is about five percent greater than that calculated for a normal (no CO_2) case. From proprietary KBR-sponsored combustion tests conducted by Southwest Research Institute in 1991 and in 1993 at conditions commensurate with the operation of an ATR, the autoignition temperature was estimated. Although ignition delays as high as 20 seconds were observed at the autoignition temperature, these investigations clearly indicated that combustion is essentially instantaneous when the induction temperature exceeds autoignition by at least 110 °C. Although the latter measurements focused solely on CO_2-free ATR feeds, the appreciable margin and small computed increase in the ignition delay due to carbon dioxide indicates that combustion should take place readily at the specified design conditions, particularly in light of the combustion zone residence time provided in an ATR design.

On the other hand, conclusions with respect to soot formation are not as straightforward. There are published reports that others have operated successfully at steam to carbon ratios as low as 0.6. [7] KBR experience is that soot can form at steam to carbon ratios substantially higher than this.

Many questions on the physical and chemical details of soot formation remain unanswered. It is generally agreed that the growth of soot, which is a complex polyaromatic hydrocarbon, is fostered in a combustion environment at temperatures exceeding 1000 °C. Although peak temperatures in the range of 1325-1400 °C are attained in the ATR combustion zone, soot has not been observed unless the steam to carbon ratio is too low. At these high temperatures, the precursors to soot are likely formed, but the rate-controlling steps – soot particle nucleation, coagulation and surface growth by acetylene addition – are highly dependent on the system dynamics, particularly the speed and quality of the fuel-oxidant mixing and subsequently, the residence time. We suspect that sooting is not normally detected under high steam-to-carbon ratio operating conditions, because it is probably suppressed by the high efficiency mixing achieved in the combustion zone of the ATR. Furthermore, it is plausible that any soot particles formed by combustion are totally re-oxidized due to the abundance of steam present in the high-temperature reaction zone of the ATR when operating at high steam-to-carbon ratios. With a lower steam rate, it follows that the rate of coke oxidation will be diminished.

A thorough search of the literature revealed very little pertinent information on this matter. Many of the publications are directed toward diesel engine technology and combustion fuel studies. The reported data are at generally low pressure, up to a few bars. Moreover, reported feed rates of carbon dioxide and steam are well below those encountered in designs of interest for this project. In many instances, the fuel-oxidant mixture was steam and carbon dioxide free.

In the course of earlier investigations by KBR, Prof. Michael Frenklach at the University of California at Berkeley consulted on the potential for sooting. Using his state-of-the-art soot formation mechanism, Frenklach made estimates for the maximum carbon dioxide recycle rate ($H_2/CO = 1.5$.), an intermediate case, and no carbon dioxide recycle at 580 °C and 46 bar. His results clearly show that carbon dioxide enhances sooting. The predicted soot volume fraction at maximum carbon dioxide recycle was almost double that calculated at no carbon dioxide recycle. These trends are reasonable, because steam rates are increased as the CO_2 recycle is decreased, and with more steam there is a greater OH radical concentration and hence, more oxidation of the generated soot precursors, especially acetylene. These unpublished results on methane are supported by published calculations on C2 species as well as experiments reported in Ref. 3. [8]

On the other hand, the quantitative significance of the foregoing results must be questioned, because Frenklach's mechanism was formulated primarily from low-pressure data with very little steam and, particularly, little carbon dioxide in the fuel-oxidant combustion mixture. Also, his model assumes that the feed induction temperature is quite high. Moreover, when applied to KBR's commercial design conditions, Frenklach's model reproduces the observed system behavior with respect to changes in the steam rates and other parameters, but unfortunately predicts soot generation at operating conditions which are clearly soot free. In essence, while the trends may be qualitatively correct, the model cannot be considered a robust tool for the design.

Lacking the available tools, therefore, to draw any firm conclusions on either the probability or the magnitude of soot formation, testing is required to develop definitive data for commercial design.

Energy and environmental benefit

The initial energy and environmental benefit analysis that was submitted in the proposal to the DOE in 2000 was a sound and objective evaluation based on industrial knowledge of the operation of ammonia and methanol plants. There are few, if any, basic processes within the entire petrochemical industry that would produce greater worldwide or domestic energy and environmental benefit than an improved method to convert stranded natural gas to liquid fuels.

The two main improvements in environmental impact when comparing an ATR-based reforming technology approach relative to conventional steam methane reformer (SMR) technology originate from the significant reduction in NOx and reduced net CO_2 emissions. The NOx emissions can be reduced to 27% of the conventional technology of a gas-fired tubular reformer, and the CO_2 recirculation can result in a further reduction to 25% of the NOx emissions from conventional SMR-based reforming technology. The energy benefits are also significant. In a case study for methanol production an approach using an autothermal reformer versus a conventional reformer the following results were obtained:

- Emissions
    - A 1,000 STPD methanol plant (with conventional reformer and ultra low NOx burners) will produce about 728 STPD of CO_2 and 0.235 STPD of NOx emissions.
    - A 1,000 STPD of methanol plant based on Advanced Autothermal Reformer is expected to produce about 291.4 STPD of CO_2 and 0.094 STPD of NOx emissions
- Energy Savings
    - $5x10^{11}$ BTU/yr for a 1,000 STPD methanol plant (~20,000 KW)

Project plan

The project as initially proposed was divided into four Phases: I) Engineering, procurement and construction (EPC) of the test unit; II) Validation of burner design; III) ATR test unit operation; and IV) Commercial Design. Phases I and II were to consist of design, fabrication, and preliminary operation of a laboratory scale ATR testing unit. It would be capable of 100 bar and 1400 °C and contain both combustion and catalytic reforming sections. It would be equipped with a flow cool down section and optical access to permit light scattering/extinction measurements of the soot content of the flow. Phase III encompassed the operation of the test unit at a variety of conditions. The data that these measurements yield were to be the heart of the project. Phase IV consisted of incorporation of the Phase III quantitative information into a preliminary design for a non-sooting ATR operating at low steam/hydrocarbon feed ratios suitable for the energy-efficient production of ammonia and liquid hydrocarbon fuels.

Project team

The project team consists of two industrial partners, Kellogg Brown & Root LLC (KBR) (Houston, TX) and Süd-Chemie (Louisville, KY) and Sandia National Laboratories' Combustion Research Facility (Livermore, CA). The structure of the team was designed to use the respective strengths of the individual organizations to lead to the commercial application of ATRs in gas-to-liquids within a five year time frame. KBR, a subsidiary of Halliburton Company, is an industrial engineering and construction firm with experience in a variety of technologies for the synthesis of numerous commodity chemicals including high volume products such as ammonia, hydrogen, and methanol. KBR has particular experience in the development of ATRs for synthesis gas and has conducted research and technology development in this arena both internally and with outside organizations for over a dozen years. Süd-Chemie is a global supplier of catalysts, among other industrial activities for numerous applications and has worked closely with KBR on many processes which use reforming catalysts. Sandia National Laboratories' Combustion Research Facility (CRF) is a DOE User Facility engaged in a variety of basic and applied research projects related to combustion and energy intensive industrial processes. The CRF has developed a wide range of experimental and computational methods to explore complicated reacting flow at conditions including the extreme pressures and temperatures present in an ATR.

The project was planned as a $720K effort. With costs shared equally between the industrial partners and the US DOE. KBR participated in the cost share at the amount of $100K/yr. In Phase I, Engineering Procurement and Construction, the KBR cost share was in the form of services to the project including providing reactor design and fabrication specifics. In Phases II and III, the cost share was to be represented by data analysis and direct participation in the experimental activities through the Combustion Research Facility's Visitor Program. In Phase IV, KBR was committed to a conceptual design of a commercial system based on the results of this project. Süd-Chemie was to participate at the amount of $20K/yr with the cost share in the form of services and test material. Süd-Chemie was to supply catalysts for use in the experimental work to be conducted at Sandia. In addition, Süd-Chemie focuses on inventing new materials designed to be more compatible with the low H_2/CO ratio environment in an ATR than are available in present reforming catalysts. Süd-Chemie was to supply data analysis support on these materials in relationship to the performance of these catalysts in sooting environments.

Sandia's role was to provide the facilities and primary experimental capability for the measurements to be conducted in Phases II and III. Sandia participated in the reactor design in Phase I and constructed the test facility with its funding resources. In Phases II and III Sandia was to lead the test program, disseminate the results to the industrial partners, and coordinate the data analysis. Funding for the Sandia contribution ($360K) is supplied by the DOE.

Technology transfer plan

Sandia National Laboratories negotiated a Cooperative Research and Development Agreement (CRADA) with KBR and Süd-Chemie. Those negotiations recognized that Sandia is a government-owned-contractor-operated facility operated by the Sandia Corporation for the U.S. Department of Energy under a Management and Operating (M&O) Contract DE-ACO4-94AL85000. As a DOE M&O Contractor, Sandia Corporation is obligated to follow specific fairness stipulations which require Sandia to offer the type of services described in this proposal to any non-federal entity that wishes to acquire these services through the DOE. The CRADA negotiations recognized that the provision of these services is subject to DOE review and approval. Both KBR and Süd-Chemie have major business units located in the United States. Therefore, the CRADA met paragraph (f)(1)(i) of Section I of Sandia's M&O Contract Clause 130. DEAR 970.5204-40 TECHNOLOGY TRANSFER MISSION wherein resulting design and development will be performed in the United States and resulting products, embodying parts, including components thereof, will be substantially manufactured in the United States.

Project history

The original project budget as stated in the proposal that was sent to the DOE in May, 2000 was for $360K with an equivalent cost share from the industrial partners as described above. Sandia, the project lead, received a letter in December, 2000 indicating the project would be funded once a CRADA was in place. Regrettably, it took 11 months to get the CRADA in place, however, the project team held its kickoff meeting in December 2001 with the assumption that the project was for three years with a total funding level as described at $720K.

At the kickoff meeting it became abundantly clear to the project team that a more sophisticated and realistic ATR test unit, as opposed to the small burner-oriented device that was proposed, could provide significantly more useful data and insight into the soot formation process. KBR embarked on an ambitious design which was presented to the OIT Chemicals Team at a review in New Orleans in March, 2002.[2] The review team acknowledged the value of this research but expressed concern that the project was mismatched with the Chemicals Team focus and felt that it would be more appropriately placed within the domain of Fossil Energy, a separate DOE program office. In response to these reviewers' concerns, the project team provided an overview of the importance of ATR technology for both GTL applications as well as ammonia manufacturing as ammonia was recognized as being a product chemical rather than a fuel. This brief white paper is included in Appendix A.

As an additional result of the preparation for the March 2002 review, it became clear that the cost of this test unit would be significantly larger the original amount budgeted in the May 2000 proposal. So, prior to obtaining formal quotes for major reactor components, the team requested that the project be supplemented an additional $100K from the DOE. This cost increase was to cover increased fabrication expense associated with the larger pressure vessel size and an internal inductive heater. In May 2002, the Chem Team agreed to provide and additional $50K to the project, with the expectation that the industrial partners would make up the $50K shortfall.

The project team met in Houston at KBR in July 2002 and decided to continue on this more ambitious design plan and proceed with an eye to stay within this new budget, presumably $820K. Additional design refinements were introduced by the KBR design team and a final reactor package was sent out for quotes in September 2002. In the meantime, Sandia began preparing the laboratory facility for housing the ATR.

The fabrication quotes were returned over the next six to eight weeks, revealing that the cost of this unit would be approximately $250K. Since this cost was to be covered out of the Sandia (now) $410K, it appeared that the lab-scale ATR design was not within the existing funding

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[2] Over the course of the project, the DOE Office of Industrial Technologies was redefined as a program within EERE.

scope of the project, even with the additional $50K from the DOE. KBR readdressed the unit design, and by February 2003 it had been determined that the inductive heating could be removed and that other vessel shape and configuration modifications could produce considerable savings. A new design was reached in June 2003 and based on the experience gained from responses to the previous design KBR believed the cost of this unit was likely to be $100K-$125K.

During the September 2002 to June 2003 time period, Sandia had completed much of the lab preparation encompassing: 1) reconfiguring half of a laboratory; 2) designing and fabricating two unique >1000 psi flow-metered steam generators; 3) modifying the laboratory gas manifolds to deliver regulated high pressure flows of oxygen/enriched air, natural gas/methane and carbon dioxide; 4) designed and obtained parts for he optical windows need for the direct in situ monitoring of the soot formation; and 5) acquired analytical test apparatus including on-line gas chromatography.

In June of 2003, at the 19-month point in the 36 month project, it was revealed that the project funding on the DOE side was limited to the $300K that had been already received. As stated above, at that time the project planning was based on the terms that the total DOE project funding was $410K ($360K + $50K). With only the $300K of the funds in, the project was now faced with insufficient resources to be completed despite the efforts that KBR had put forth to engineer a much more inexpensive test bed. Had the anticipated additional $110K been in the works for FY04, the project would still have had a difficult time proceeding, but could have been successful with the full ATR configuration, albeit with a more limited experimental scope.

KBR invested a great deal of effort in developing this unique test reactor. Throughout the design activity, the project's other industrial partner, Süd-Chemie Inc., remained ready to supply their share of support once the experiments were operating, as outlined in the project's original proposal. As a result of the funding shortfall, there was no choice but to commit the remaining funds that Sandia had available for FY2004 to meeting the original goals of the project as proposed within the constraints of a much smaller bench-scale system. The technical targets of this remaining work were to: 1) establish a 100-1000 psi experimental reactor that could mimic conditions of an ATR burner; 2) conduct proof-of-principle tests to demonstrate the applicability of the laser attenuation method as quantitative measurement of soot formation in rich flames; and 3) begin the development of a soot map for this burner configuration.

Phase 1 Design

KBR ATR design

Although the original lab-scale reactor was not constructed due to budget constraints, considerable work was invested in developing a versatile test unit that could indeed mimic the thermal, convective mixing, and catalytic characteristics of a full scale ATR. A schematic of the 1st generation design of this unit is shown in Figure 2. As shown, the total weight of the ATR reactor (designed for 1200 psig pressure) is approximately 2200 lbs. The reactor has three separate sections which can be lifted one at a time. The topmost section (which has a 1/4" internal diameter by 18" long mixing chamber) was to be used in the first phase of the research. However, it was to be replaced by a much shorter top section as different burners were developed. The top section detached at the base of the burner inlet. The intent of this feature was to be able to explore significantly different inlet configurations without the need to reconfigure the entire reactor. The second flange permits disassembly midway in the catalyst bed. In this way, the catalyst could be changed if it becomes poisoned by soot. In addition, this facilitates the testing of new soot-tolerant catalysts as they are developed as part of the Süd Chemie contribution to the project.

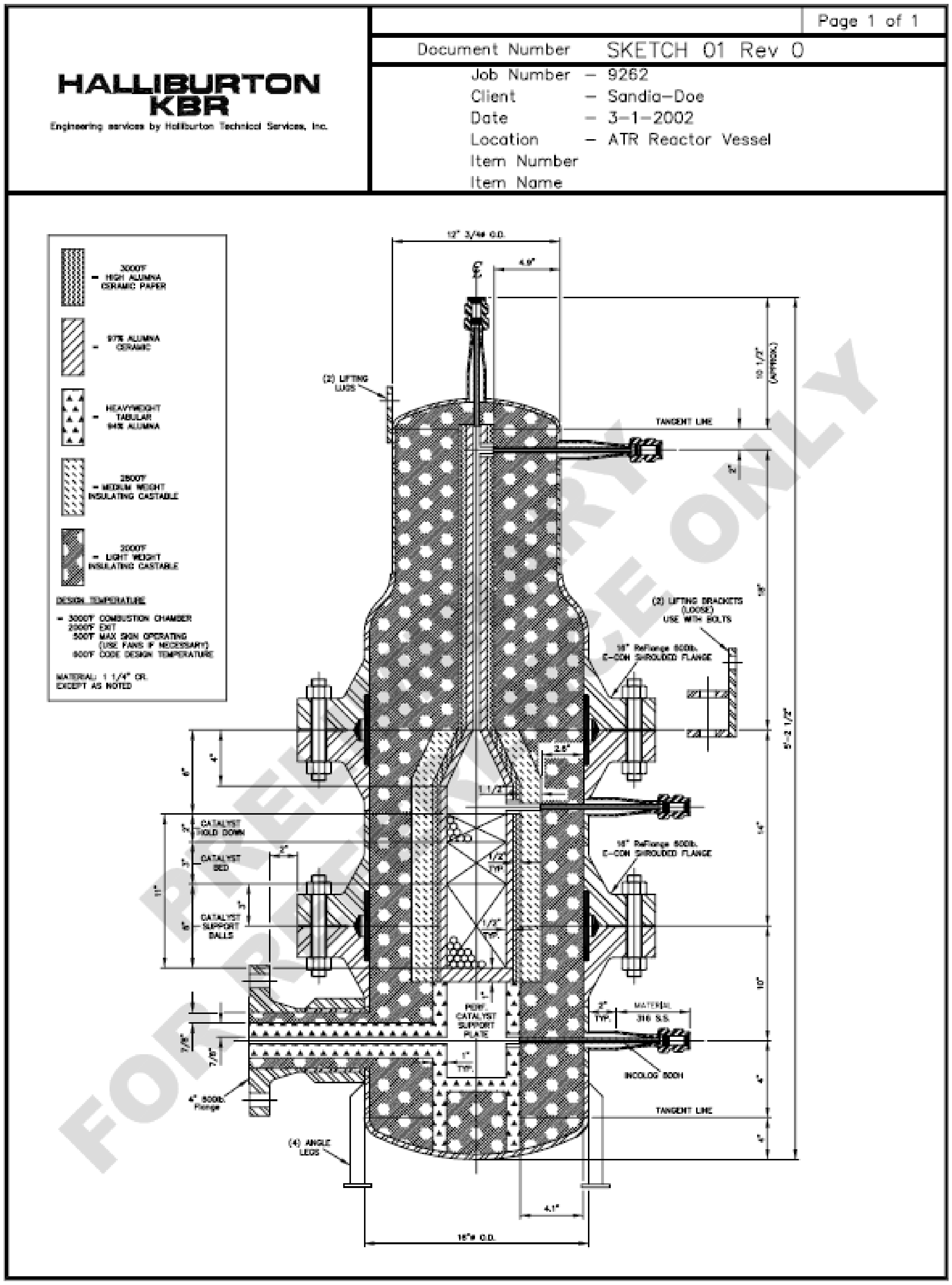

Figure 2. KBR design of Lab-scale ATR as of March 2002.

This original design worked out many of the heat balance issues associated with the sizing of the reactor. However, within the heat transfer estimates, it could not be made certain the heat losses would not be greater than acceptable and thus the internal temperature of the ATR would be too low.

A second design evolved from this first approach. The design relied on the presence of an internal inductive heater to be able to maintain the high temperature that would be found in a full scale unit. The heater's function was to offset the net heat loss to the laboratory surroundings through the internal refractory. In a plant scale unit, there are consider heat transfer economies as a simple result of a more favorable surface to volume ratio maintaining high internal temperatures in the reaction zone. This design is presented in Figure 3.

This second approach removes the lower flange, a major source of heat loss, and therefore makes servicing the catalyst more difficult. However, when combined with the inductive heating coil, identified by the small circles imbedded in the mid section of the ATR in the cross sectional sketch in Figure 3, the full scale internal temperatures could be maintained within the conical recirculation zone and well as within the catalyst bed. The inductive heater added considerable cost to the design. The catalyst can be accessed by removing the upper section of the reactor and then removing the ceramic cone insert.

This plan was carried forth to a complete set of schematics that included not only the reactor but several other components as well that would be necessary for installation in the lab. Other key components included an exit gas cooler, shown in Figure 4, and a water knock-out drum. A detailed P&ID was generated to guide the gas supply manifold design that was taking place at Sandia. This P&ID is shown in Figure 5. The overall system would consist of:

1) a high pressure gas manifold delivering gas, oxygen or enriched air, carbon dioxide, and steam, all preheated to as high at 575 °C and at pressures approaching 1200 psi.
2) The ATR itself, equipped with optical ports to permit the detection of soot in the burner or recirculation zone and optical pyrometry to measure temperature.
3) high pressure gas cooler
4) water knock out drum
5) ventilation

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Page 1 of 1

Document Number 401D1 Rev 0
Job Number - 9262
Client - Sandia-Doe
Date - 09 AUGUST 2002
Item Name - ATR Reactor Vessel
Item Number
Location

○	= BUBBLE
▨	= 97% ALUMNA CERAMIC
⁘	= HEAVYWEIGHT TABULAR 94% ALUMNA
▧	2800°F =MEDIUM WEIGHT INSULATING CASTABLE
▨	2000°F = LIGHT WEIGHT INSULATING CASTABLE
▩	= SUSCEPTOR SOLID MOLYBONUM

DESIGN TEMPERATURE
= 3000°F COMBUSTION CHAMBER
2000°F EXIT
500°F MAX SKIN OPERATING
(USE FANS IF NECESSARY)
600°F CODE DESIGN TEMPERATURE

MATERIAL: 304SS
EXCEPT AS NOTED

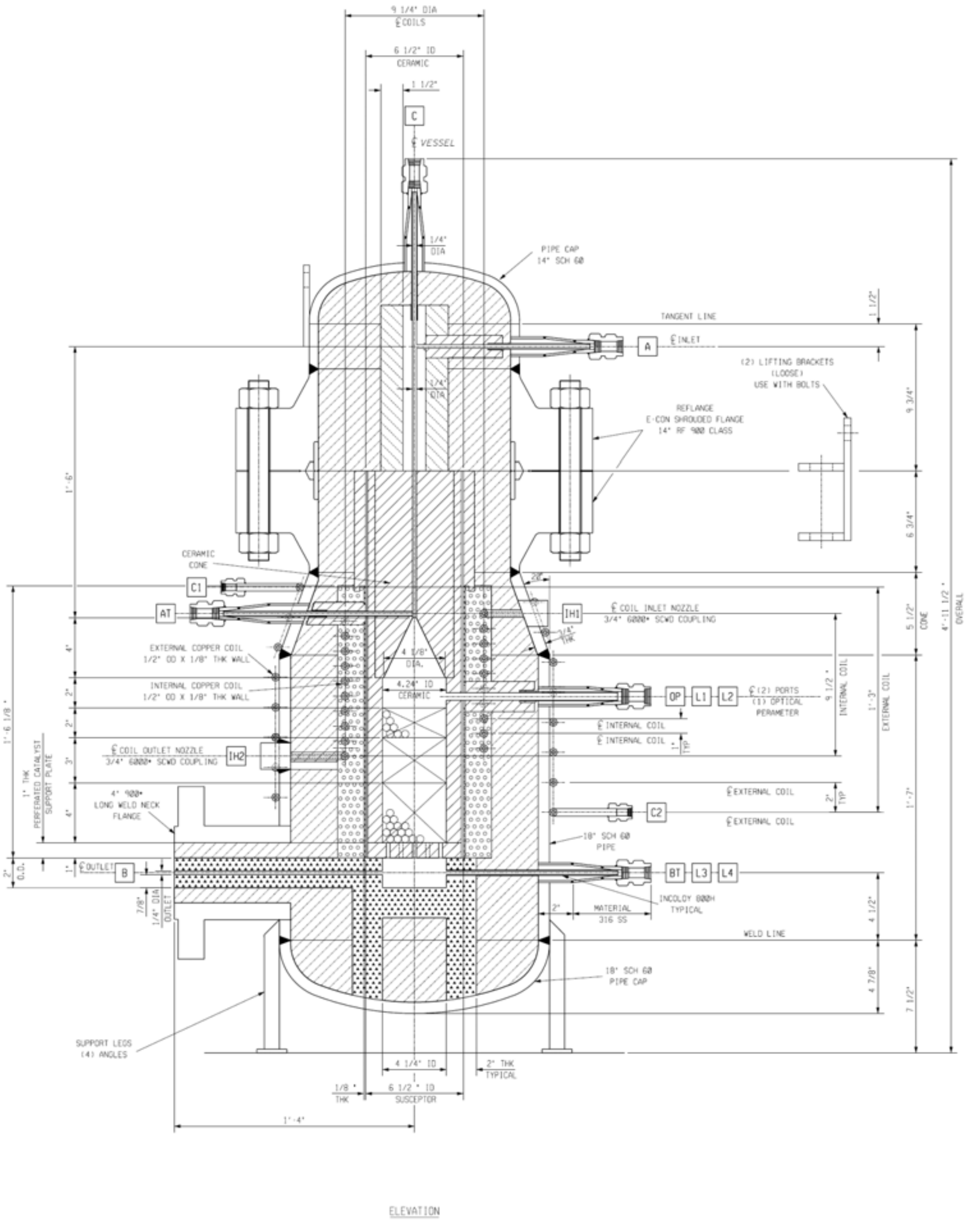


Figure 3 Second generation lab-scale ATR with internal inductive heater.

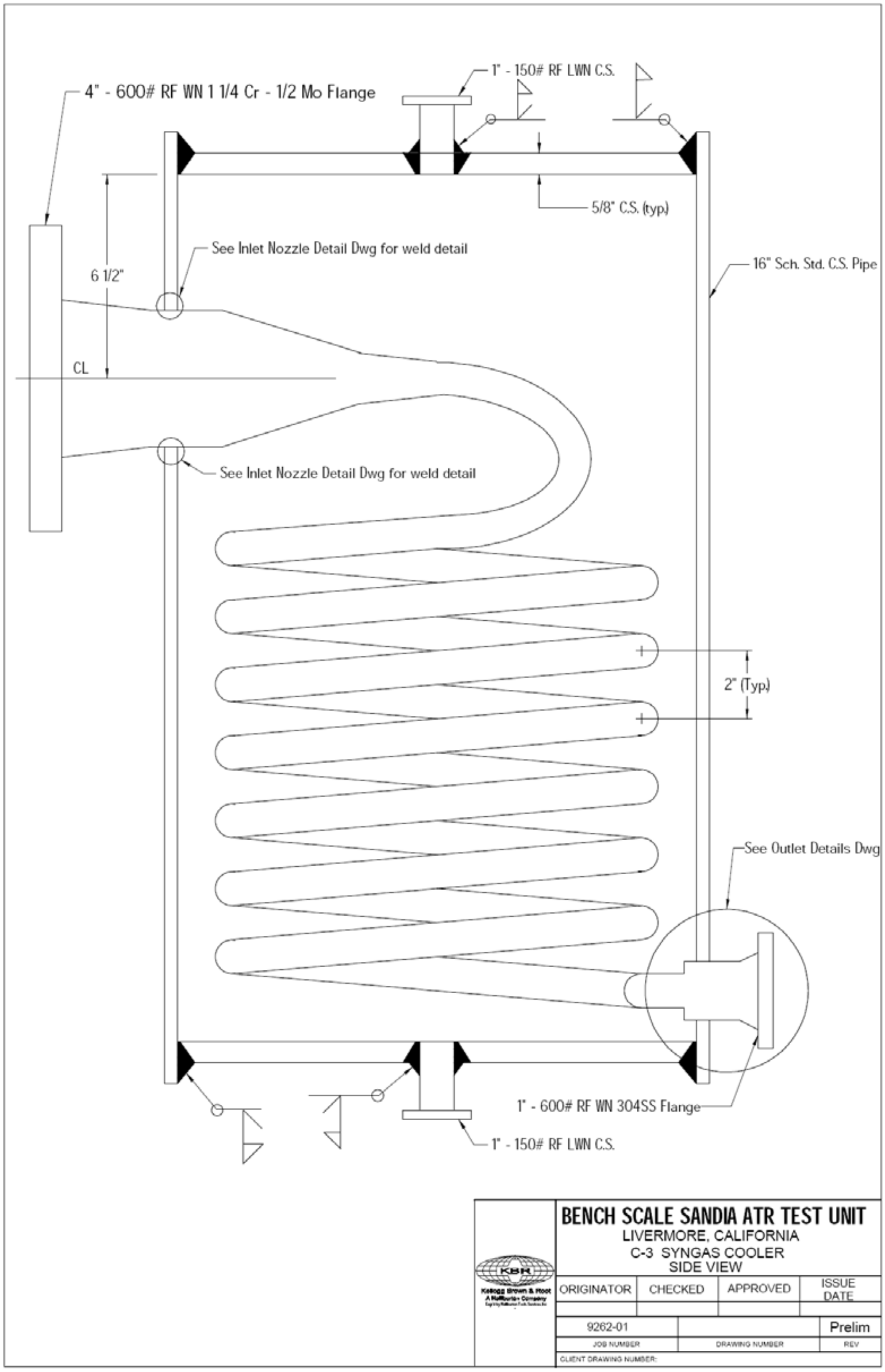


Figure 4. Product syngas cooler.

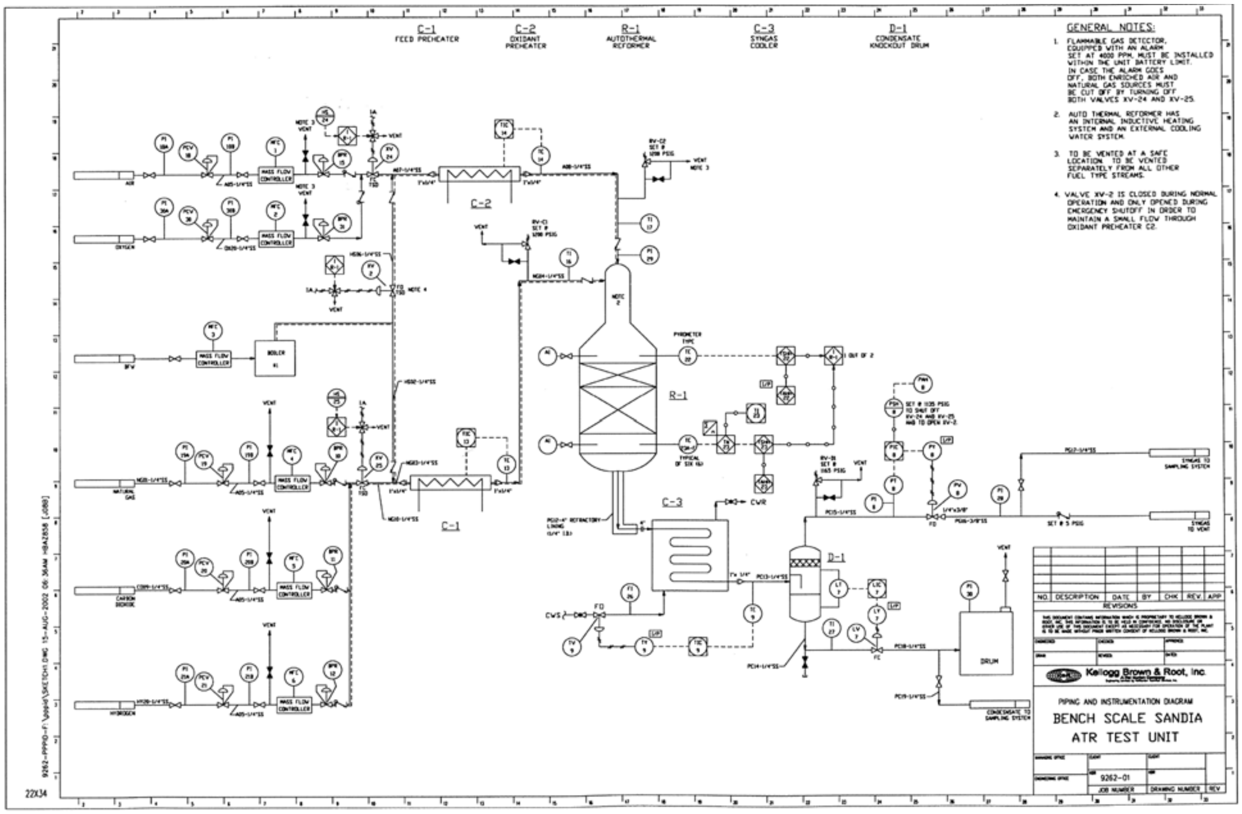


Figure 5. P&ID of the lab scale system as of August 2002.

SNL gas manifold and steam system

Considerable upgrade to the existing in-lab gas delivery system at Sandia was required to meet the higher flow rates intended for this ATR. The gas manifold consists of high pressure feed lines for fuel gas, oxygen/enriched air, carbon dioxide, and steam. All gases except carbon dioxide had to be delivered at pressures up to 1200 psi and preheated to 575 °C. For the initial phase of experiments, CO_2 pressure would be limited to somewhat below the liquid vapor pressure of 830 psi. A warm gas compressor would be added later if especially high pressure experiments were warranted. This sort of equipment is readily available at a range of delivery rates from suppliers that cater to the supercritical CO_2 industry.

Much of the gas delivery high pressure tubing and flow control was off-the-shelf equipment although a new laboratory manifold was required to bring the gases into the lab at such high pressures. The only special items required were high pressure flow regulators capable of regulating flow at 1200 psi with only a small pressure drop (~50 psi) across the regulator itself and maintaining calibration over a wide operating pressure range. The high pressure gas heaters as well as a 1200 psi steam system that can deliver steam at a controlled flow rate up to several grams per second are both unique items.

Commercial steam systems are designed to provide steam at a fixed pressure, not fixed flow rate. These high pressure boilers are controlled by a pressure-based control loop. As such, the steam delivery rate in an overall mixed gas configuration cannot be varied in a deliberate fashion independent of the other gas flow rates. Consequently, the basic approach that was chosen for both the steam generators was to regulate the gas flows upstream prior to heating and then construct flow heating units to bring the gases and steam to the appropriate preheat temperature. In this way, the steam flowrate is controlled by a high pressure dosing pump and subsequently converted to steam in the preheater.

The basic design of the preheaters is a series 12 ft lengths of 1/8 in OD seamless high-pressure stainless steel tubing (40,000 psi) wrapped helically around 6-in long, ¾-in diameter, 500 W (@120V) rod heaters (Watlow Firerod). A typical rod assembly has approximately 40 windings. A single component is shown in Figure 6. This assembly is placed in an 8-in long, 2 in nominal pipe nipple and insulated with alumina blanket material (Fiberfrax®) shown in Figure 7. These heaters are linked in series and placed in an insulated box,

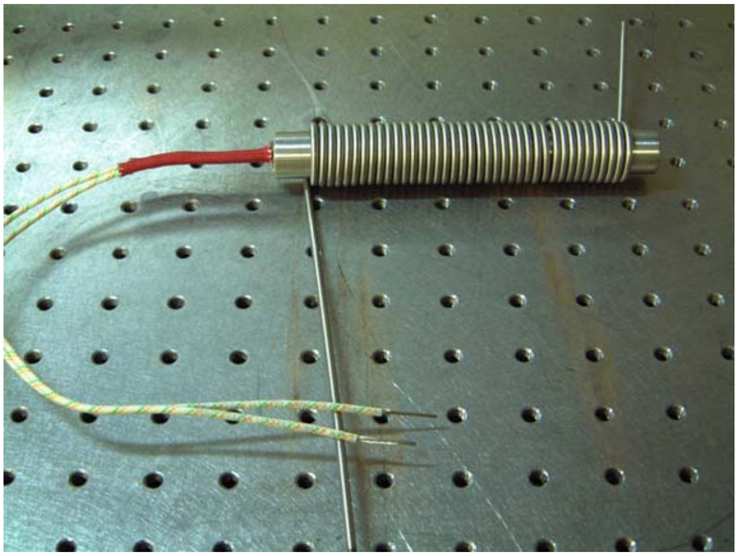


Figure 6. Firerod and coiled tube heater sub-unit.

Figure 7. Heater assembly installed in insulated pipe nipple. Six of these are installed in the insulated box.

Heating the expected gas flows from ambient to near 600 °C is not too difficult. For example, the planned experimental test plan called for methane/CO_2 flows of typically 24 SLPM, corresponding to approximately 1 mole/minute. With $C_p(CH_4, CO_2) \sim 0.035$kJ/mole-K, the power required is only about 350 W. Even at these high flow rates, six 500 W units like these in Figure 6 can easily get the gas feed to the preheat temperature.

Heating the water into high pressure superheated steam is much more difficult. With a nominal feed of as much as 2 g/s of steam, this will require nearly 8KW of power. A second separate steam generator was developed. This unit has 12 Firerod cartridges similar to the gas preheater, but uses 240V rated heaters. Using the laboratory 208V power, each unit can supply near 1800W. The very high heat transfer coefficient of pressurized boiling water enables much of this 21 KW to be power available to the water.

Window design

The high pressure windows for the ATR are based on a design strategy that was developed at Sandia for a variety of combustion and reacting flow applications. Details of this method were reported by Rice et al. a number of years ago. [9] The primary challenge in window assembly design is to maintain a high pressure seal of a brittle optical material such as sapphire or fused silica (quartz) to a port made of metal at elevated temperatures. This is achieved by using a 0.010 in thick gold foil gasket as the seal between the a sapphire window and the body of the optical port in conjunction with a spring washer assembly to enable a constant load on the window at elevated temperatures despite the mismatch in thermal expansion characteristics of the steel vessel and the brittle crystal window. A particular requirement in this instance is the need to be able to routinely remove the window between reactor test operations to clean them. To meet this requirement, the entire window assembly is built into a standard pressure fitting. A schematic of this window design is shown in Figure 8. This fitting is used as the cap on the tubes extending radially from the ATR vessel in Figures 2 and 3.

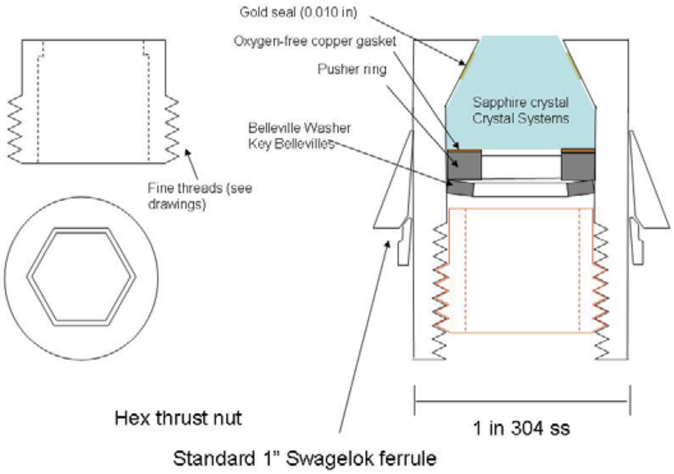


Figure 8. Schematic of window fitting.

Soot measurement

The measurement of the presence of soot in the reacting flow is based on the attenuation of transmitted light by scattering and absorption by fine soot particles, sometimes called extinction. This technique has been developed over the past several decades in the combustion research field. Although there remains ongoing debate over the precise quantitative applicability of the laser attenuation approach, the ability to simply detect the presence of soot is fairly straightforward. [10]

The basic apparatus in simply a low power HeNe laser, some steering mirrors and a photodiode detector. The laser is aimed though one optical port, though the reacting flow in the ATR, out another port on the opposite side of the vessel and onto a photodiode detector. Some care must taken to ensure that the port tubes are well-aligned during construction of the pressure vessel. The beam can be split such that a second detector is used as a reference. The two detector outputs are ratioed to get the fraction of the light that is transmitted by the reacting flow, I/Io.

A relevant assessment of this approach is to estimate what is the minimum amount of soot that can be detected via the extinction measurements. This can be found in the review by Sorenson in Ref. 10 (Eq. 102a). The fraction of the light transmitted is related to the pathlength, l_p, and the extinction cross section, σ_e. This expression assumes a homogenous composition of the probed volume, which probably is not actually the case in a burner, but this will serve to estimate whether the method can detect a reasonably small amount of conversion to soot.

$$I/Io = \exp(-\sigma_e l_p) \qquad \text{(Equation 1)}$$

where the extinction cross section is the sum of the two terms originating from both light scattering and absorption.

$$\sigma_e = \sigma_s + \sigma_a \qquad \text{(Equation 2)}$$

If we assume the dominant process is absorption and not scattering, the total cross section is related the complex index of refraction of soot

$$\sigma_e = (6\pi E(m)/\lambda) \times f_v \qquad \text{(Equation 3)}$$

f_v = particle volume fraction
$E(m) = -\,\mathrm{Im}\{(m^2 - 1) / (m^2 + 2)\}$
$m = n - i\kappa$, 1.57 - 0.56i, complex index of refraction of soot [11]

Assuming that a 5% reduction in transmittance can be detected, I/Io = 0.95, l_p = 10 cm, λ = 628 nm (6.3×10^{-5} cm, and $6\pi E(m) \sim 5$, the extinction cross section is $\sigma_e = 5\text{x}10^{-3}$ and

$f_v = 6.3\times10^{-8}$, Volume fraction measurable = 63 ppb soot

Soot has a density of about 1.8 g/cm^3 (0.15 mole carbon)/cm^3) corresponding to a detectability limit of 9×10^{-8} moles/cm^3. At ATR conditions of 250 psi and 1500 °C, the reacting gas flow is about 1.28×10^{-4} mole/cm^3 placing the molar detectability at 73 ppm. With methane making up somewhat less than half of the feed (on a molar basis) combined with the increase in product moles in the partial oxidation reaction, it can be conservatively concluded that if approximately

0.3 % of the carbon is converted to soot, this method will detect it. It is important to note that the 95% transmittance detectability is a lower limit for nearly instantaneous response (0.3 s time constant) Given longer measurement times (perhaps a minute or more) it may be possible to improve this to 99%, or even better, resulting in an improvement in detectability to 0.03%.

Bench-Scale Burner

Equipment

The bench scale burner embodies the core of the original research plan as it was proposed in April 2000. After the lab-scale ATR in Phase 1 was abandoned, the challenge remained to conduct a subset of the intended research program by directing the remaining funds to gain, at a minimum, proof of the utility of the extinction method at these conditions, as well as some preliminary quantitative results regarding simple trends in burner operation as a function of gas composition, oxidation stoichiometry, and pressure.

Figure 9 shows a simplified schematic of the apparatus. The bench scale system would be forced to be able to function within the flow range of the flow meters for the larger scale system. As it turned out, several pieces of equipment already in Sandia's Industrial Chemistry Laboratory enabled rapid installation of the burner and soot diagnostics. These key pieces of equipment were: 1) a high pressure view cell; 2) an HPLC pump; and 3) a lock-in amplifier. Along with a variety of ancillary items including a laser, photodiodes, band and cable heaters, high pressure heat exchangers, and back-pressure let down valves, the burner cell assembly was constructed. The availability of much of this equipment was what initially kept the cost of the proposal down.

Figure 10 shows the power panel for the steam and gas heaters. The top row are simple displays of the temperature of the gases in the burner immediately downstream of the flame mixing point, (chamber analog out). The second row has controllers for the cable heaters that wrap the lines running from the large preheater boxes to the burner cell, the band heaters on the cell itself (chamber), and heaters on the downstream tube (post chamber). The power controllers for the smaller oxidizer preheater and the larger steam/fuel preheater are located on the lower levels.

Figure 11 shows the bench scale set up without the insulation on the cell or feed lines. At the far left of the photograph is the computer monitor with the LabVIEW (by National Instruments) software display that automatically runs and records the experiment. It controls the oxidizer solenoid timing and records flow rates and temperature as well as the laser detector output voltage. The two aluminum boxes behind the computer on the bench are the gas preheater and larger superheated steam boiler. The burner unit on the bench consists of the two rectangular high pressure fittings that feed the cylindrical optical cell to their right, which is wrapped with two parallel band heaters. In front of the cell are laser pointing optics, the light chopper that works with the lock-in, and the 15 mW helium-neon laser. The large blue knob is the back pressure regulator that sets pressure for the system and vents product to the exhaust line. The lower deck contains the HPLC pump on the left, the lock-in amplifier, and the gas cooler (copper coil). The cooler coil, which is commercial-made by Parker, consists of a copper water jacket tubing coil surrounding an inner length of ¼ in OD Inconel 600 tubing. A 1L water collection vessel is located at the lower right of the photo. The high-pressure gas manifold (not visible in the photo) is located on the wall above the apparatus.

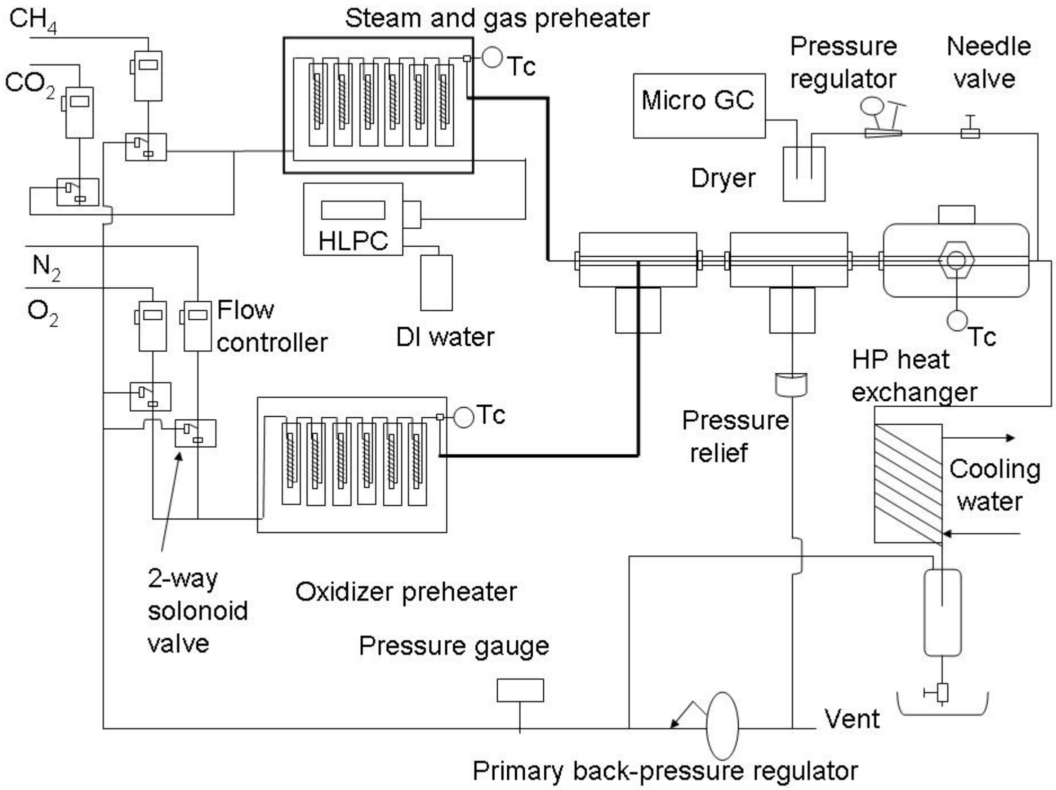


Figure 9. Schematic of the bench-top high pressure burner system.

Figure 10. Power controller box.

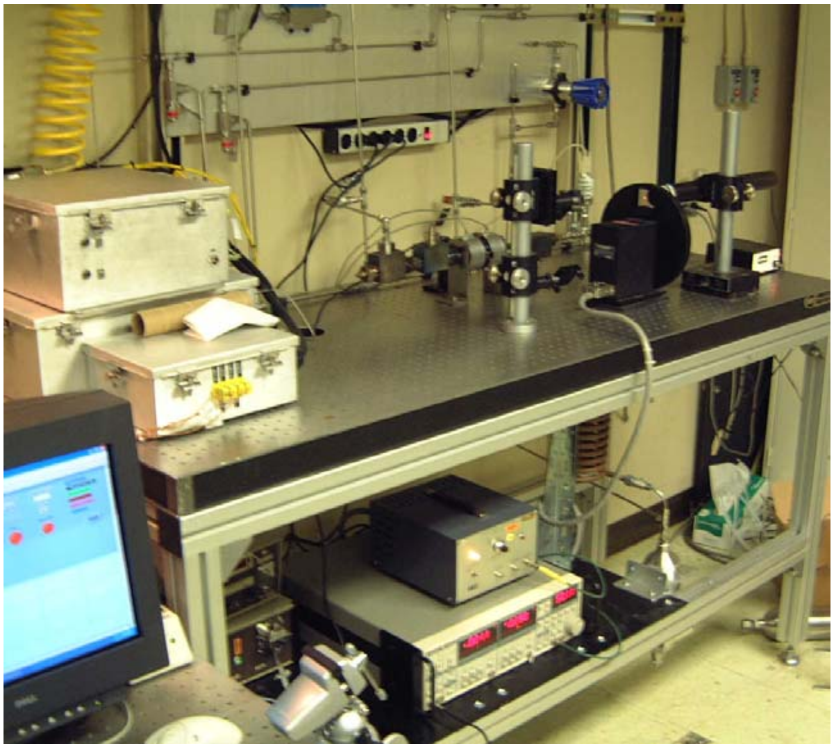


Figure 11. Photograph of the bench-top burner system without insulation.

Burner assembly and view cell

The design of the burner is simple. A mixture of steam and fuel gas (methane or a mostly-methane natural gas mixture) was supplied in the inner tube of a tube-in-tube annular burner with pure oxygen in the outer tube. The hardware consists of heater-traced, insulated feed lines from the two preheaters fitted onto two adjoining Inconel 625 high pressure "T" unions (Autoclave Engineers). See Figure 9. The fuel burner line is a 1/16 in Inconel 625 tube that runs down the center of the assembly. The unions are joined together by 9/16 in OD 3/16 in ID Inconel 625 high pressure nipples. The position of the burner can be repositioned relative to the window by adjusting the length of the 1/16 in. fuel tube.

The view cell was identical to one that had been used in this laboratory for experiments in supercritical water at pressures as high as 4000 psi and temperatures as high as 500 °C. It is constructed from a piece of Inconel 625 bar stock and is equipped with three sapphire windows. The design of the high pressure window is discussed in an earlier report.[9] Figure 12 shows the view cell without insulation and Figure 13 shows the insulated cell during an experiment using the HeNe laser. The cell is surrounded by a Lexan® composite bullet-proof Lexguard® case (General Electric) to provide operator protection should one of the windows fail under pressure. The metal screen insulates the hard Lexan® composite from melting. A thermocouple is positioned radially along with the windows, from the bottom (not shown), and is used to indicate the presence of exothermic reaction. A short length of heated 9/16 in tubing downstream (covered in insulation) can be charged with reforming catalyst to accommodate experimental work focusing on soot formation on various catalysts as well as conversion and selectivity measurements. The product gases can be sampled through a leak valve that leads to a Micro GC (Agilent 3000).

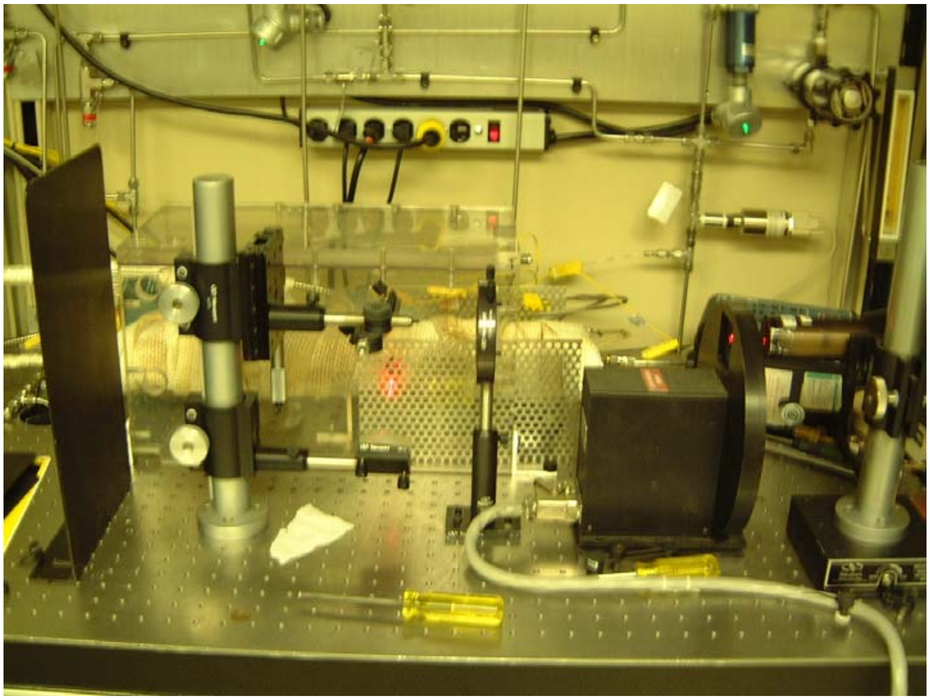


Figure 12. Burner assembly during operation

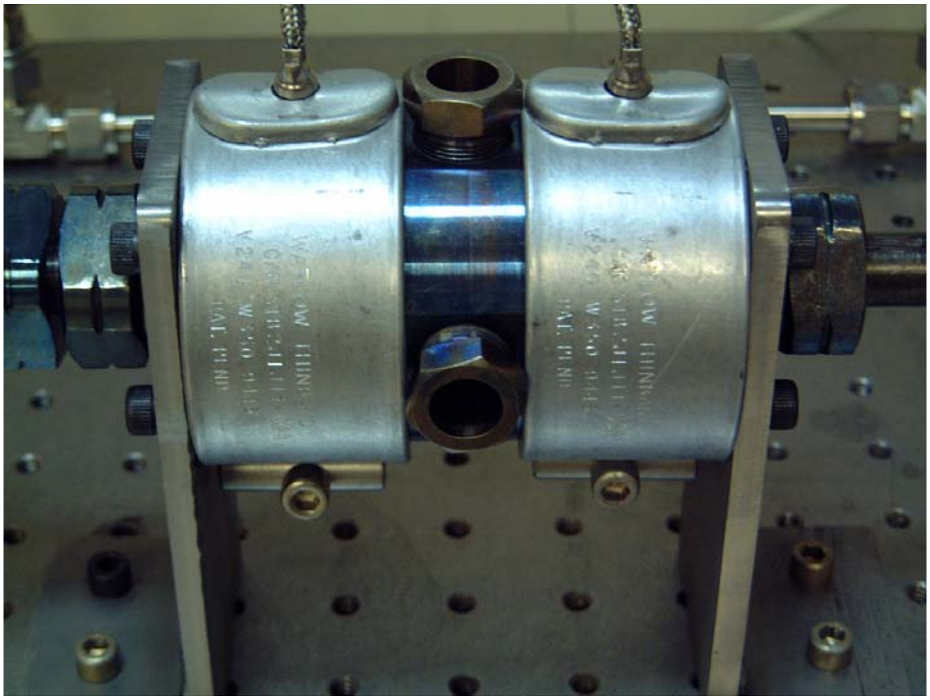


Figure 13. View cell.

Equipment operation and experimental methods

The basic experimental method for operating the burner consisted of setting a number of initial conditions (described below), waiting for flow and temperature stabilization, and then introducing oxygen in place of nitrogen in the oxidizer line. The oxygen and nitrogen flows were interchangeable on the oxidizer preheat and feed line, controlled by two solenoid valves. Each line has a bypass such that the gases were both always flowing into the high pressure system but only one flowed into the preheater. When not in use, the second gas was fed into the reactor downstream of the experimental region. In this way the flows remained stable as did the system pressure when oxygen was switched for nitrogen in the burner.

Initial conditions were established by first pressurizing the system with a slow flow of nitrogen and setting the manual back pressure regulator to establish operating pressure. Nitrogen flow was then increased to a value near the flow rate expected for the exit gases. At this point the HPLC pump was started at a typical water flow of 1.0 ml/min and the preheaters and cell heaters were switched on. Typical heating time was a little over one hour to achieve steady conditions at 565 °C in the burner. It was not unusual to need to make small adjustments of the manual back pressure regulator as conditions lined out to maintain the target pressure. Once gas and steam flow were established at temperature, the fuel gas was introduced into the steam line and the flow settings were adjusted to the desired test conditions, including an oxygen flow to match the nitrogen flow shunted past the reactor. When steady conditions were reestablished at the desired steam, gas, and nitrogen flow rates, the oxidizer pulse sequence was entered into the computer and initiated. This initiates the nitrogen line to switch to the bypass shunt mode, briefly bypassing nitrogen around the reactor, and introducing a pulse of oxygen flow into the reactor. A typical oxygen flow pulse duration was 120 s.

Depending on the chosen flow rate for the oxygen, flame ignition in the burner assembly is delayed until oxygen moves through the preheater into the annular burner tube where it mixes with fuel gas. This ignition delay was typically 60-90 seconds at our nominal startup conditions of 0.8 SLPM CH_4, 0.4 SLPM O_2, and 0.016 ml/s H_2O and 250 psia. When the oxygen reached the burner, a flame would always spontaneously ignite if the preheater temperature was above 550 °C. If the preheater temperature was below 550 °C ignition was erratic and below 530 °C ignition did not occur.

Over the course of the experimental campaign hundreds of test flames were operated over a range of feed conditions. The following procedure was used for all test flame experiments:

1) Steady flows of steam, fuel gas (plus carbon dioxide, if used), and nitrogen were established at predetermined conditions. Two fuel gas compositions were used – either pure methane or a natural gas mix that contained mostly methane with small amounts of butane, propane, ethane and hydrogen.

2) The duration of the oxygen flow pulse (typically 120 s, but as high a 600 s) was entered into the control program. At conditions where the O_2 flow was low, a longer pulse period was implemented as the low flow tended to mix more with the nitrogen in the line (non plug-flow conditions) producing longer “edge effects” (unstable combustion periods) at the beginning and end of the oxygen flow pulse.

3) The oxygen flow pulse sequence was initiated on the computer and the computer automatically controlled the simultaneous opening of the O_2 flow valve into the reactor and the

switching of the N_2 bypass valve which diverted N_2 flow around the combustion chamber cell. At the end of the O_2 pulse period, the control program switched the N_2/O_2 line back to the standby condition with nitrogen flow and no oxygen flow to the burner.

Experimental Results

Typical data

Figure 14 illustrates the characteristics of a typical sooting flame for a 120 s oxygen pulse. Approximately 90 s after the oxygen flow pulse is initiated, the oxygen has made its was through the approximately 100 ft of tubing in the gas heater and reaches the burner. The temperature monitored by the thermocouple in the well below the flame view port spikes upward by 110-130 °C as it registers the combustion exotherm. The adiabatic flame temperature itself is more like 1500 °C, but the monitoring thermocouple is recessed from the combustion flow and therefore registers much lower than the actual flame temperature. The flame ignites as the oxygen fraction goes from zero to the prescribed stoichiometry. During this brief interim period (where oxygen and nitrogen have mixed due to dispersion in the flow in the preheater) the flame is very rich and much more soot is formed than the at quasi steady-state conditions during the period that a stable flame is present in the burner. This is evidenced by the sharp drop in the transmittance followed by a quick recovery as pure oxygen is established in the burner. As the flame continues to burn over the next 120 s, the transmittance decreases due to build-up of soot deposits on the windows. As the flame extinguishes there is another brief period of very rich conditions and high signal attenuation from the detector monitoring HeNe laser light transmittance through the view cell windows. After the flame is out, the remaining attenuation in the laser transmittance is due to the soot deposits on the view windows. Note that the brackets show that at the beginning and end of the flame period, the amount of attenuation due to the soot entrained in the flow through the flame zone is nearly constant.

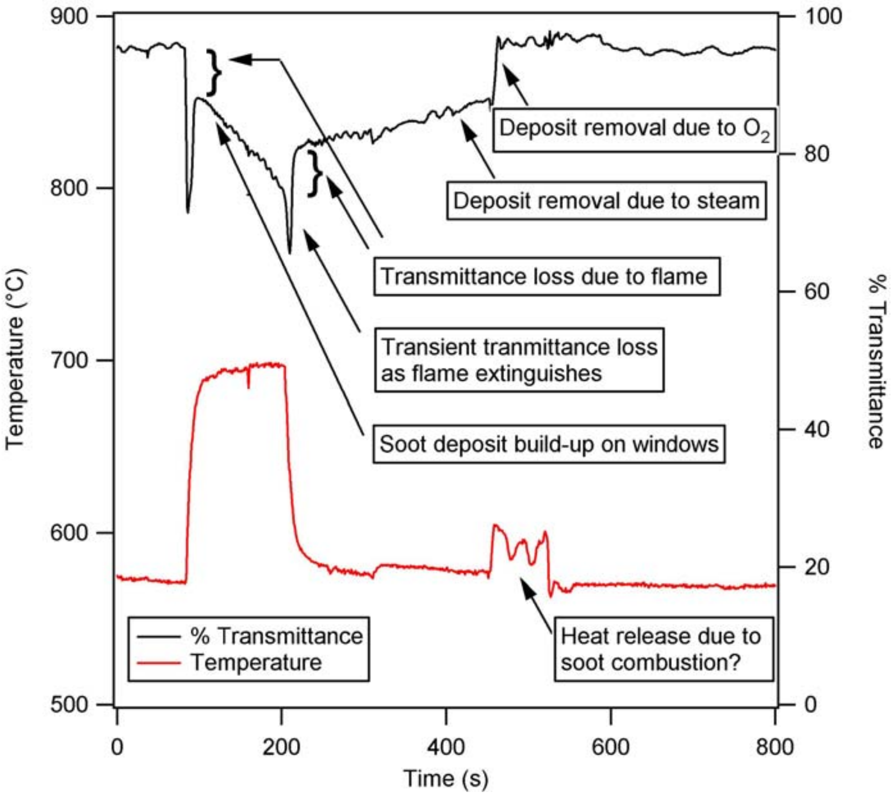


Figure 14. Temperature and laser transmittance signals during a typical sooting flame.

At time, t = ~ 200 s, (80 s after the initial oxygen pulse ends) the methane feed is turned off upstream and, then, 100 s later, a second oxygen pulse lasting approximately 120 s is introduced. From t = ~220 s to 420 s the soot deposits on the burner cell view windows are slowly removed solely by the high pressure steam in the gas mixture flowing through the burner view cell as evidences by the increasing laser transmittance trend. At t = ~420s, the second oxygen pulse arrives at the burner, but there is no longer any methane accompanying the steam flow. The presence of this oxygen with no fuel gas apparently results in the very rapid burning of the remaining soot deposits, and the overall laser transmittance returns to the previous high baseline value. Note the small erratic exotherm beginning a t = 450 s when the second oxygen pulse first arrives. This is likely due to exothermic combustion of soot, perhaps deposited on the thermocouple. However, it may be due to combustion of a very small amount of methane still entrained in the steam flow line to the burner.

Figure 15 shows another example of a heavily sooting flame with a unique characteristic. In this experiment at 505 psi, the flame is exhibiting oscillatory behavior with a period of about 5.5 s. (This was not entirely uncommon and proved to a recurring difficulty throughout the experimental program. It may have been related to the behavior of the single-piston HPLC pump.) At t = 190 s the oxidizer solenoid valve switched from O_2 to N_2 upstream. This causes a very brief discontinuity in the upstream pressure and the flame briefly extinguishes and reignites with inexplicable significant reduction in the sooting oscillation. No attempt was made to interpret data from these non-steady flames..

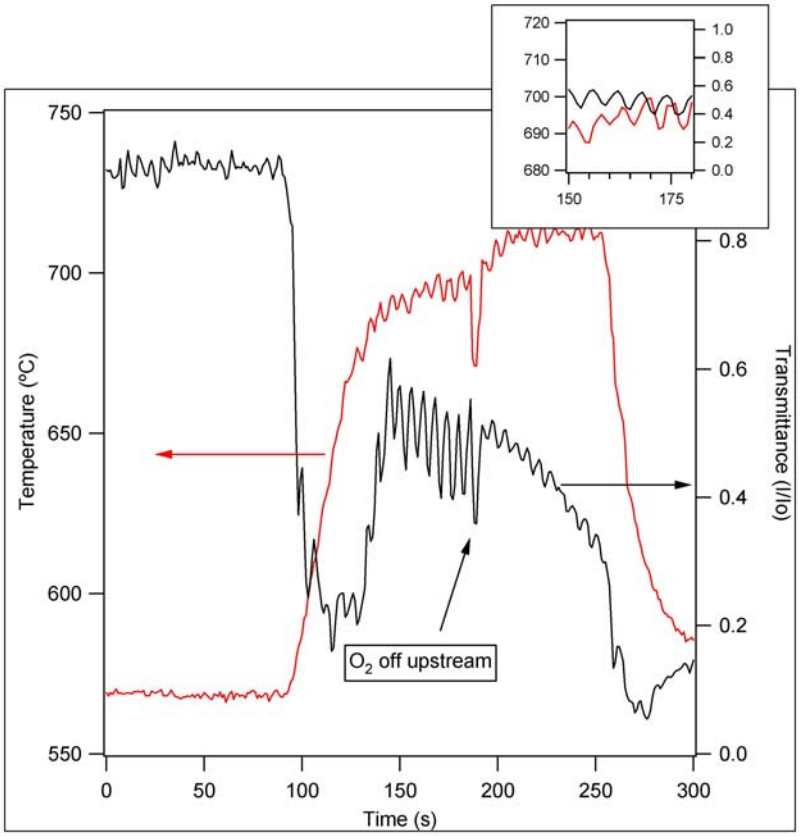


Figure 15. 500 psi flame showing oscillatory behavior.

Figures 16 and 17 are photographs of two different flames. Figure 16 is a flame that is forming very little soot and exhibits negligible attenuation of the probe laser. Figure 17 is a modestly sooting flame and clearly shows the orange incandescence of hot particulates. Figure 18 shows the laser transmittance record for two modestly sooting flames. These two flames were produced at 250 psi for a 180s duration and correspond to two different steam flow conditions. Flame "A" produces an attenuation of about 6% and only a very small amount of build-up of deposits on the view cell windows. Flame "B" produces an initial attenuation of closer to 10% and is characterized by considerable build up of deposits that contribute to a residual attenuation of the laser even after the flame is extinguished.

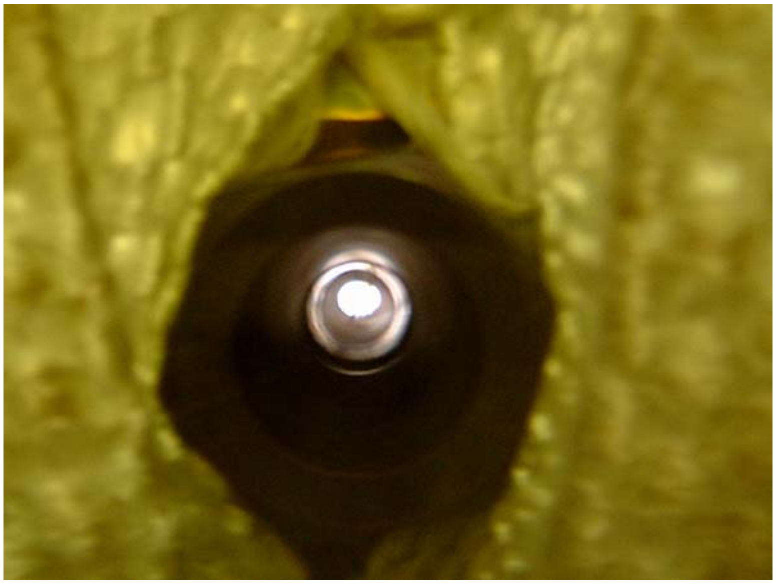


Figure 16 . Non-sooting flame

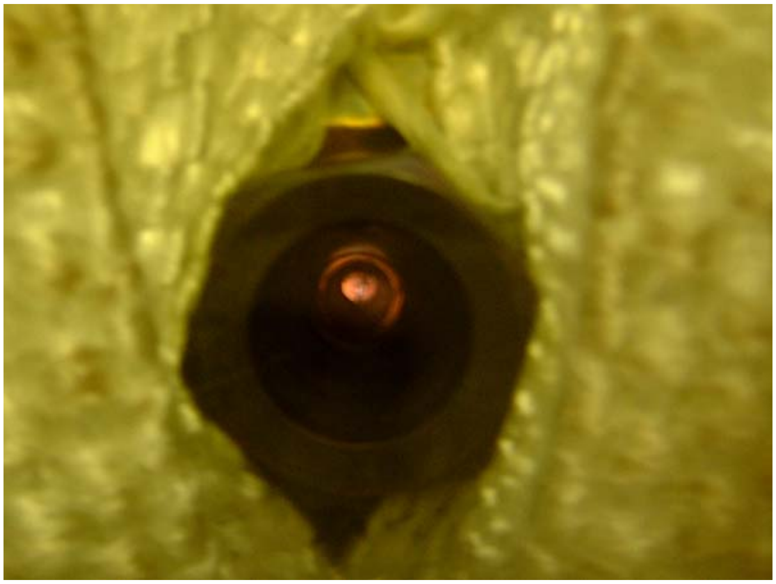


Figure 17. Moderately sooting flame.

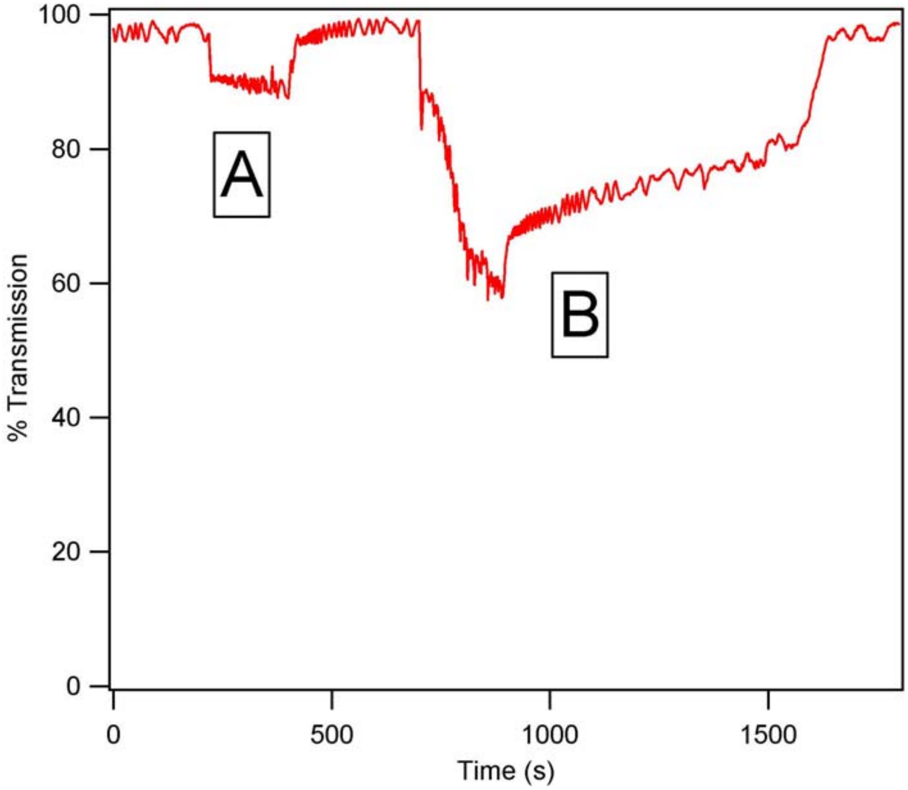


Figure 18. Transmittance records for lightly sooting (A) and moderately sooting (B) flames at 250 psi.

Data trends

The quantitative results obtained during the survey of ATR reformer flame conditions are presented in Figure 19 and Figure 20. Figure 19 shows the raw data for a number of oxidation stoichiometries and steam ratios. Figure 20 shows these same results calculated as the amount of soot per unit volume converted using Equation 1-3 with an assumed path length of 0.5 cm. The data were analyzed to compare the relative effects of: steam to carbon ratio, oxidation stoichiometry and pressure. Several observations can be made. To summarize:

1) At a pressure of 250 psi and a CH_4/O_2 ratio of 1.6, there is little or no difference in sooting behavior in flames produced using either pure methane fuel gas or a natural gas mixture that contains mostly methane and small amounts of heavier hydrocarbons.
2) When feeding natural gas, increasing the CH_4/O_2 ratio from 1.6 to 2.0 at a constant pressure of 250 psi resulted in substantially more soot formation at H_2O/CH_4 ratios below about 1.5:1. In other words, when feeding natural gas at a methane to oxygen ratio of 2.0, increasing the steam to methane ratio from 0.25 to 1.5 dramatically reduced the amount of soot formation.
3) When feeding natural gas, increasing the operating pressure from 250 to 500 psi at a constant methane to oxygen ratio of 1.6 resulted in significantly more soot formation (2.2 g/cm^3 soot at 500 psi vs. <0.4 g/cm^3 at 250 psi).
4) Soot formation at a methane to oxygen ratio of 1.6 with either pure methane or natural gas feed is not affected or decreases slightly as steam to methane ratio is increased from 0.25 to 1.75.

5) At 500 psi and using natural gas as the fuel gas, only heavy sooting conditions existed even at CH_4/O_2 = 2.0. There was an effect due to steam however, such that with CH_4/H_2O >1, the sooting in the flames was so severe that window coating with soot occurred so rapidly that is was not possible to separate the attenuation effect of soot particles in the flame from attenuation due to soot deposits as described above and illustrated in Figure 15.
6) As illustrated in Figures 19 and 20, all flame experiments conducted in this experimental program produced some level of laser signal attenuation indicating the presence of soot. It is possible that low levels of attenuation of only a few percent were caused not by the presence of soot but by slight changes in the density or opacity of the flowing gas when oxygen and a flame are present in the burner view cell.

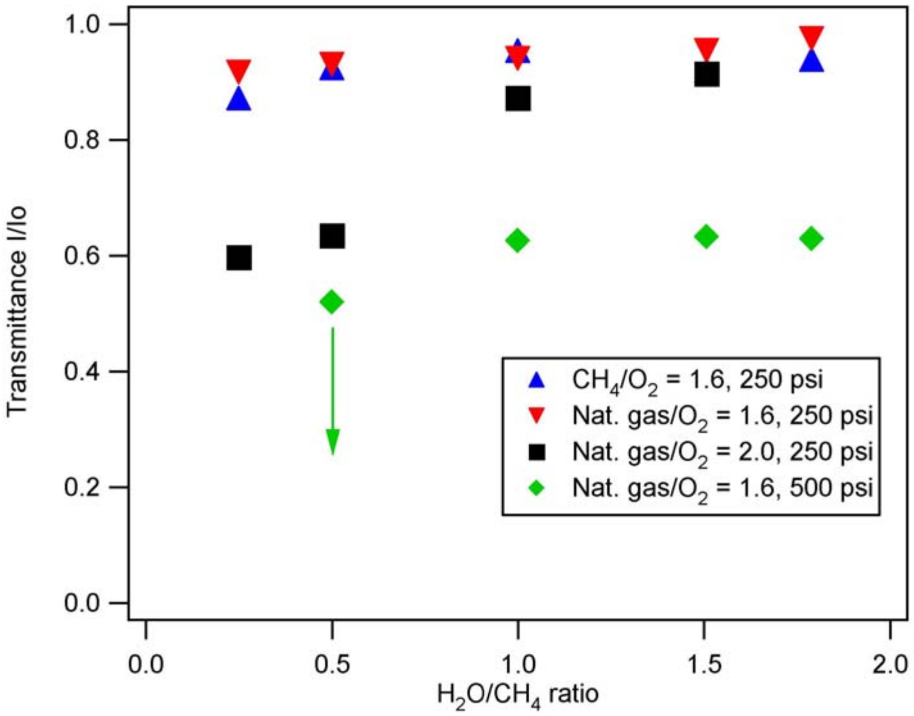


Figure 19. Summary of laser transmittance data for a variety of conditions.

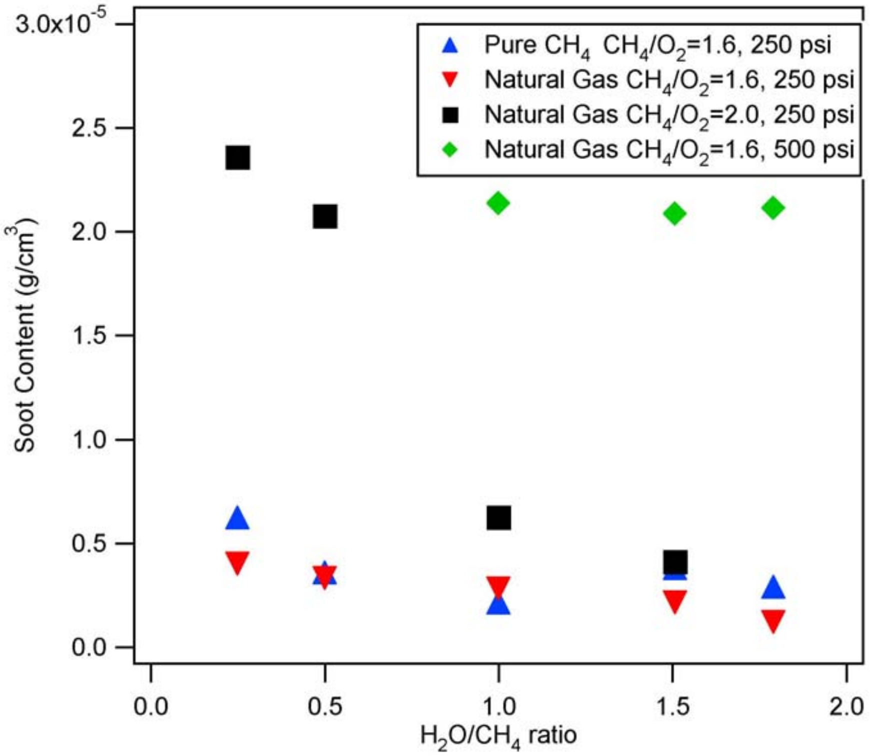


Figure 20. Transmittance data in Figure 19 converted to soot content via Equations 1-3.

Reaction Chemistry Modeling

Soot precursor modeling

Modeling the relationship between combustion chemistry and the formation of soot particles is a very active field of research and many researchers have developed models to capture the behavior of the various stages.[12-14] These stages include precursor formation, polycyclic aromatic hydrocarbon (PAH) formation, aggregation of PAHs to particulates, and subsequent reoxidation of soot particles. The experimental emphasis in this particular project has been on identifying the effects of water vapor and elevated pressure on the production of soot in a rich high pressure laminar flow burner. Recently, similar work along these lines for POX production of hydrogen has been reported by Glumac and co-workers. [15]

However, one of the additional goals of the project was to assess the effects of carbon dioxide recirculation in the ATR burner. As discussed in the introduction of this report, CO_2 recirculation offers a way to potentially lower the overall steam-to-carbon ratio in the ATR thereby producing a product gas mix that is more amenable to GTL applications. The experimental apparatus is capable of mixing CO_2 into the gas and steam input stream. A number of experiments were conducted with CO_2 in this stream. However, due to the budget constraints on the project, no detailed quantitative results were obtained either with respect to soot production tendencies or ignition delay.

Nevertheless, it remains important to know, at a minimum, whether it is possible for CO_2 to participate in the flame chemistry in such a burner and what effects this participation has on prompt soot formation. As a result, an attempt was made to address this question via direct kinetics modeling of the rich flame.

Simple elementary reaction modeling calculations for a premixed flow system were conducted as part of this project to examine the relationship between the experimental trends and the formation of soot precursors such as benzene and naphthalene. The calculations were performed using the CHEMKIN® 4.0 suite of programs assuming a premixed feed preheated uniformly to 550 °C. The mechanism used for these calculations is the most up-to-date version from the work of Miller and co-workers [16]. All of the calculations assumed adiabatic conditions. Typical flame temperatures were 1300-1600 °C.

Typical behavior of the premixed plug flow system at $CH_4/O_2/H_2O$ ratio of 2:1:4 is shown in Figure 21 and at a ratio of 2:0.5:4 in Figure 22. The pressure in these calculations was 17 atm (~250 psi). The ignition and consumption of the fuel occurs within a handful of milliseconds. During the brief flame period, benzene and naphthalene are formed in both cases at comparable peak concentrations, but at 2:1 the soot precursors are subsequently consumed within a few hundred milliseconds. In the richer flame (4:1), benzene and naphthalene soot precursors are not consumed immediately, and they have the opportunity to continue pyrolytic reactions. Note the evidence of some induction chemistry producing a significant amount of CO prior to the rapid and nearly instantaneous flame that produces hydrogen. Approximately 75% of the methane is converted.

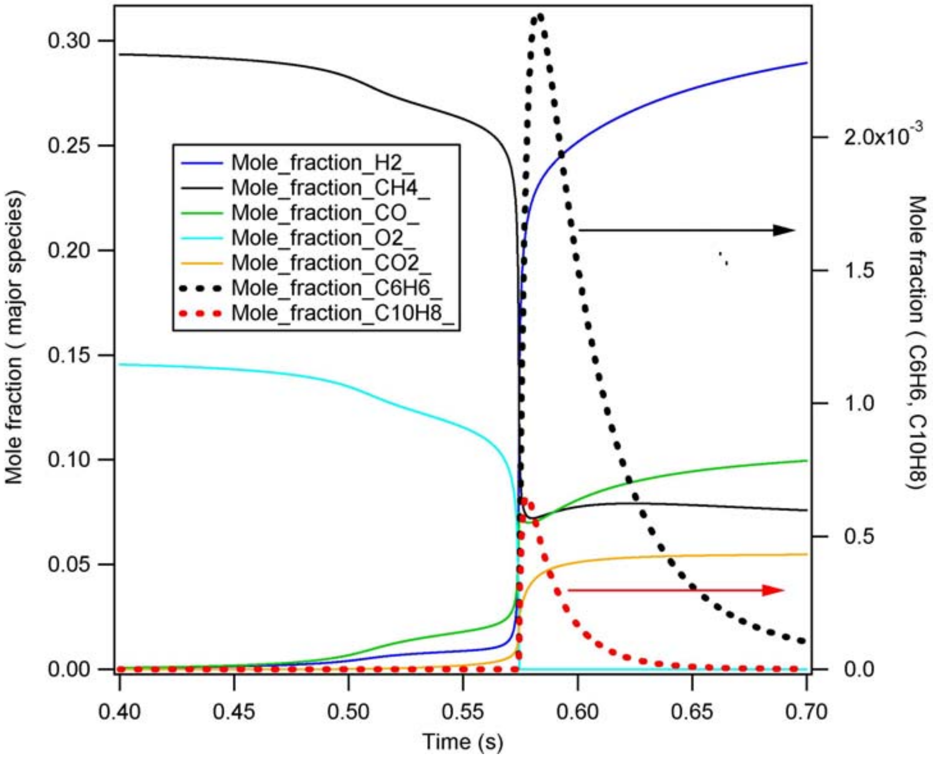


Figure 21. Reaction chemistry at 2:1 CH_4:O_2 feed ratio.

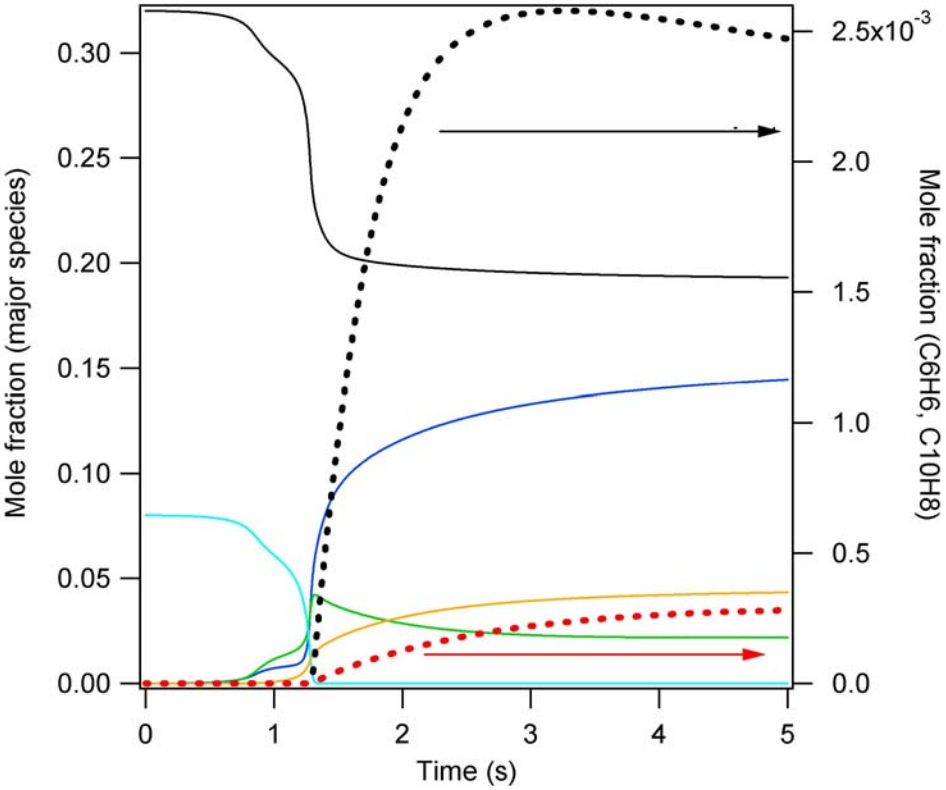


Figure 22. Reaction chemistry at 4:1 CH_4:O_2 feed ratio. Same graphics code as in Figure 21.

Figure 23 shows benzene and naphthalene maximum concentrations at 17 and 51 atm (250 and 750 psi) as a function of steam supply with CH_4:O_2 = 2. The most striking result here is that the mechanism used does not suggest an increase in soot precursors as a function of increasing pressure. In fact, it suggests a slight decrease. As expected, increasing the steam to methane ratio at constant operating pressure reduces the mole fraction benzene and naphthalene soot precursors. Table 1 summarizes the results of many calculations at different equivalence ratios.

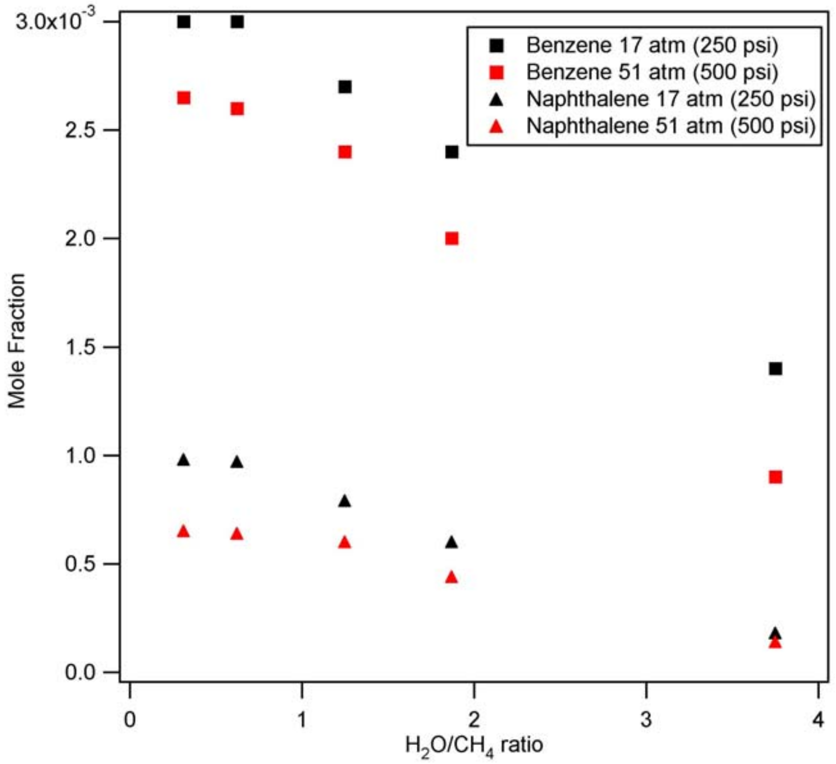


Figure 23. Predicted pressure effects on soot precursor formation

Table 1. Summary of equivalence ratio effect

CH_4:O_2	Soot precursor behavior
1:1	Essentially no precursors are formed; the only aromatic hydrocarbon present is phenol at a mole fraction of approximately 10^{-9}
1:1- 2:1	Benzene and other aromatics mole fractions increase from negligible to approximately 0.001 - 0.003.
2:1-6:1	Additional reduction of oxygen supplied does not result in significant increases in soot precursor concentrations but does affect their persistence.
> 6:1	Flame has difficulty igniting spontaneously

A secondary but interesting result of these calculations illustrates some of the flame ignition phenomena that was observed experimentally. Figure 24 shows flame ignition time vs. pressure and steam-to-carbon ratio with a preheat temperature of 550 ºC and CH_4:O_2 = 2. These calculations agree with experimental observations at 17 atm (250 psi) in that H_2O:CH_4 ratios greater than four would not ignite. Note that at H_2O:CH_4 = 3.75 the 17 atm ignition delay is beginning to increase nonlinearly at pressures of 17 atm (250 psi) and 34 atm (500 psi) At higher pressures of 51 and 68 atm, ignition time increase linearly as steam to methane ratio is increased from 0.25:1 to 3.75:1.

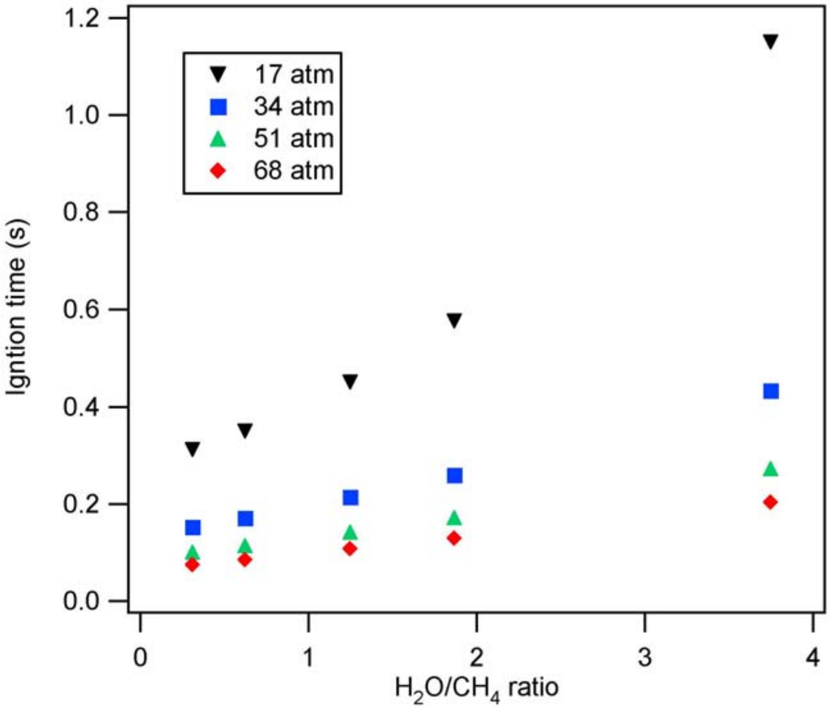
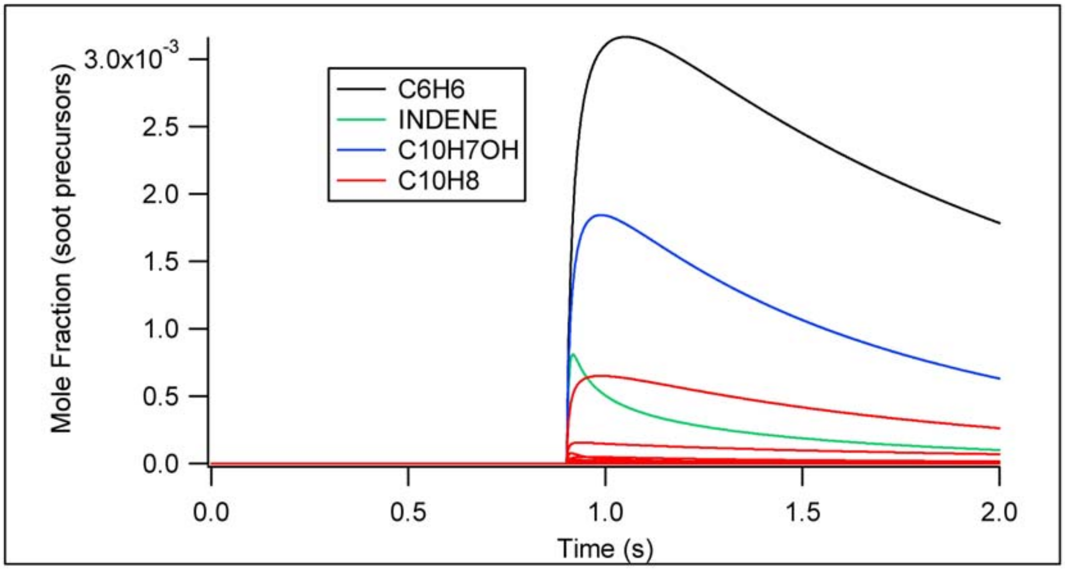


Figure 24. Effect of steam-to-carbon ratio and pressure on ignition delay.

Carbon dioxide recirculation

A second important question surrounding CO_2 recirculation addresses whether or not CO_2 participates directly in the combustion chemistry in the ATR burner or whether its effect on product gas composition in an ATR is largely the result of the water-gas shift chemistry in the catalytic bed. In principle, this topic can be addressed with the experimental burner apparatus when combined with product gas analysis via the Micro GC. Again, a systematic study was not executed experimentally, but it was possible to address some of the characteristics of this sort of rich combustion chemistry computationally.

Figure 25 shows the evolution of chemical species concentrations with CO_2 added to the fuel feed with steam and Figure 26 shows the results of a similar calculation in the absence of supplemental steam. In both cases it is clear that CO_2 participates in the reaction chemistry and methane reforming occurs simultaneously with CO_2 reduction. Note that the soot precursors are somewhat more persistent than in Figure 21. The presence of CO_2 significantly raises the mole fraction of CO relative to hydrogen and does so in the burner section of the ATR.



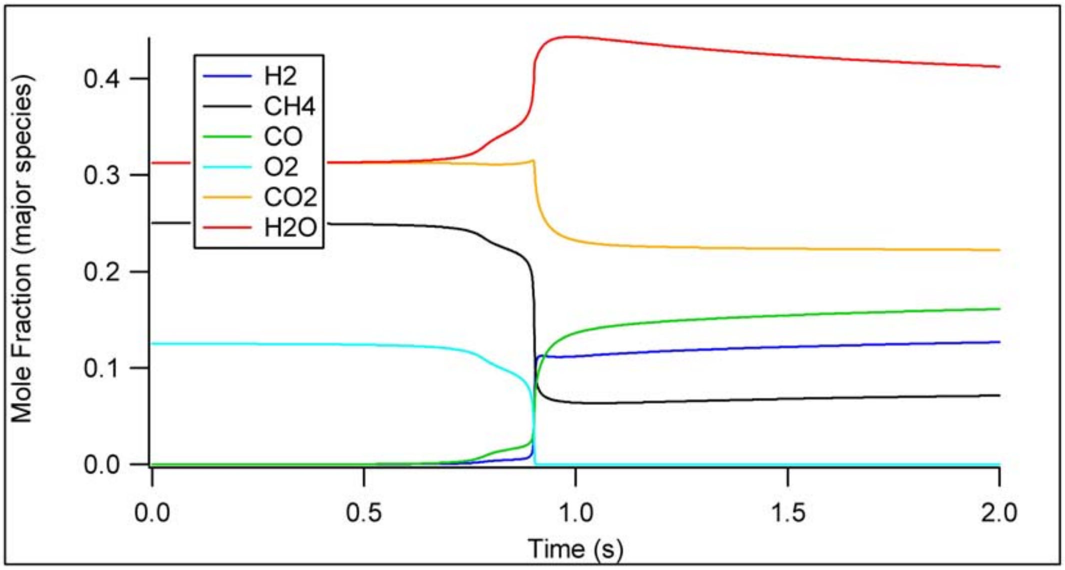


Figure 25. High pressure flame at 17 atm and CH_4:O_2 = 2 with CO_2 in the gas feed substituting for some of the steam. Top) soot precursors, Bottom) syngas products.

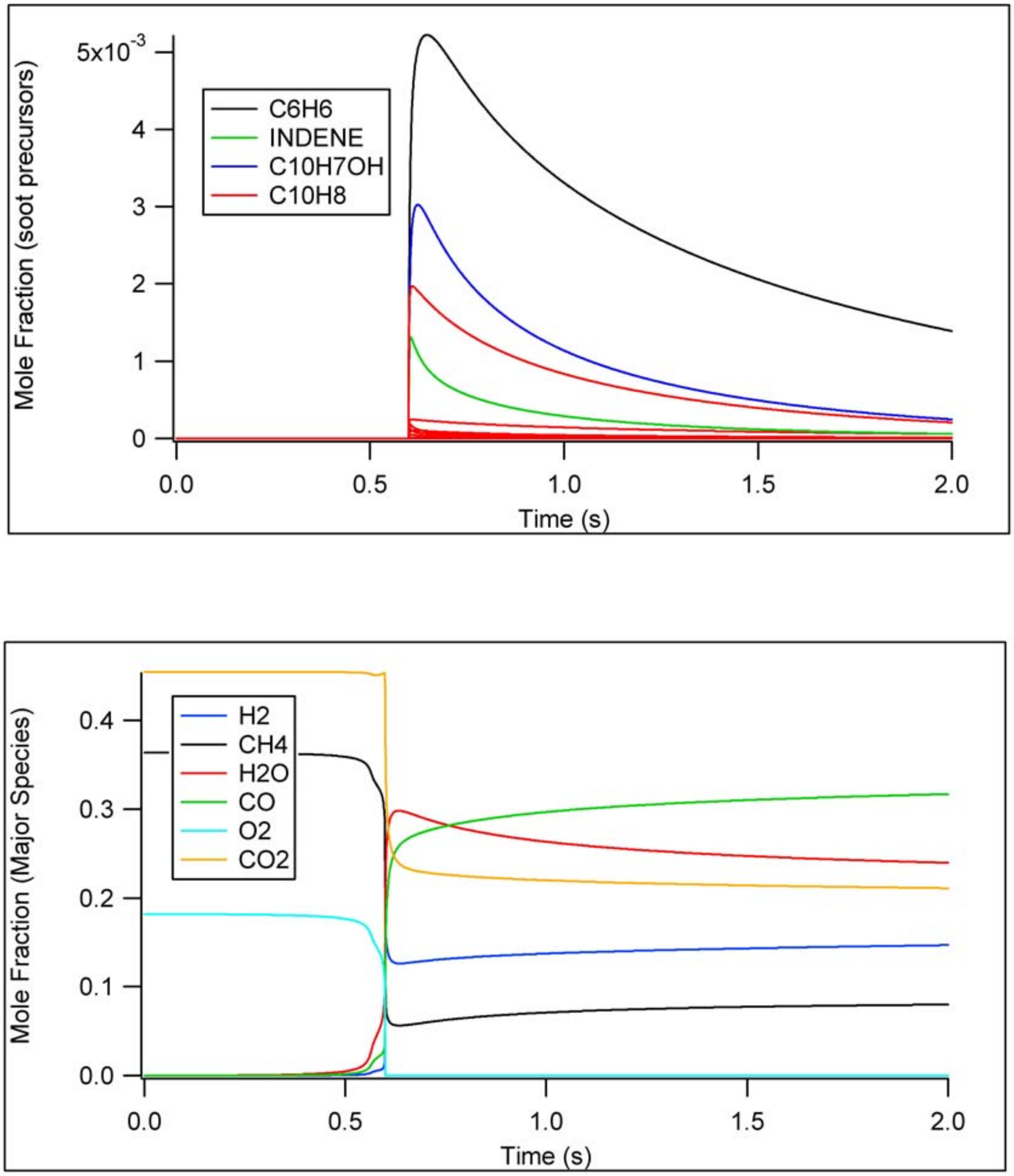


Figure 26. High pressure flame at 17 atm and CH_4:O_2 = 2 with CO_2 in the gas feed with no steam. Top) soot precursors, Bottom) syngas products.

Summary

The project successfully met, at least partially, many of the goals as proposed in May 2000. A high pressure ATR-like burner was constructed and soot formation measurements were carried out demonstrating the applicability of the laser extinction method to make in-situ measurements at practical conditions. The experiments showed that both oxidation equivalence ratio and steam fraction play important roles in the behavior of the burner, affecting soot formation and ignition characteristics in feed ranges relevant to desirable operating conditions. The attempts to build a lab-scale ATR test bed were unsuccessful due to insufficient budget for the effort and not due to inherent engineering constraints related to the scaling of heat transfer considerations. The KBR effort showed that a lab-scale unit can be designed to produce realistic ATR conditions throughout the burner, the recirculation zone, and the catalyst bed, provided sufficient attention is paid to heat management details.

Parallel to the associated experiments, the calculations reveal there are many degrees of freedom within this system that can affect the overall chemistry. These include preheat temperature, pressure, and the many combinations of relative feed concentrations. It is recognized that an annular burner (as used in the experiments in this report) is not as efficient as a premixed commercial ATR burner and that examining the production of precursors does not encompass the entire soot production process. Nevertheless, calculations based on modern reaction modeling software (CHEMKIN® 4.0) and the most recent soot formation mechanisms developed by Miller, et. al. [16] indicate that oxidation stoichiometry is the dominant parameter in determining the degree to which soot precursors are formed and that steam, pressure, and CO_2 are less important factors in soot precursor formation. The results from the experiments discussed in this report support these reaction chemistry modeling calculations to some extent, showing that at a CH_4:O_2 ratio much less than 2.0, soot is generally not formed at 250 psi and increasing steam to methane ratio from 0.25:1 to 3.75:1 results in only slightly less soot formation. However, in contradiction to the results of modeling calculations, experiments conducted with natural gas at a higher pressure of 500 psi resulted in substantially more soot formation than observed at a 250 psi operating pressure.

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Appendix A

Advanced Autothermal Reforming of Natural Gas to Synthesis Gas and Hydrogen and Future Energy Savings in the U.S. Chemical Industry

Support information for the development of an ATR test reactor at Sandia National Laboratories' Combustion Research facility, a DOE User facility.

Steven Rice
Sandia National Laboratories

James Richardson
Süd Chemie Inc.

David Mann
KBR

Synthesis gas use in the Chemical Industry

Synthesis gas is produced from various fuels such as natural gas, oil, and coal. The most common fuel used to produce synthesis gas in the chemical industry is natural gas. Synthesis gas is a mixture of hydrogen and carbon monoxide at a variety of ratios typically ranging from 5:1 H_2/CO to as low as 1.7:1 H_2/CO. It functions as the starting material for ammonia, hydrogen, and methanol manufacturing, as well as for other processes, including oxo-alcohols, acetic acid, acetic anhydride, phosgene, and acrylates. It is used as the source of hydrogen for hydrocracking, hydrotreating, and hydrodesulfurization in petroleum refining.

The production of synthesis gas is growing worldwide. This growth is expected to continue for years. There are indications that the current demand for ammonia may begin to increase significantly as a result of the increase in the production of fertilizer for dent corn production. This growth in the agricultural sector stems from an anticipated dramatic increase in the use of ethanol as a fuel oxygenate or as a new fuel itself (E85). In fact, as a result of this anticipated demand, the U.S Dept of Energy has set as a goal to reduce the cost of ethanol production by as much as $0.60/gal by the year 2015.

Presently, synthesis gas for methanol and ammonia production is produced in a number of ways, but by far the most common method is steam-methane reforming (SMR). Steam-methane reforming is practiced industrially using several different reactor designs. The most popular design, the primary reformer, has more than 500 and perhaps as many as 1000 installations. It consists of catalyst-filled tubes that absorb heat via a radiant heat transfer mechanism inside a firebox. Primary reformers are fed steam and natural gas (methane) in a steam to carbon molar ratio of typically 3.2 to 3.4. Primary reformers can be made more energy efficient by operating them at lower steam to carbon ratio, but they cannot be successfully operated at lower steam to carbon ratios due to fouling of the catalyst with carbon or soot. The chemical reactions that take place in the primary reformer are as follows:

1. $CH_4 + H_2O = CO + 3H_2$
2. $CO + H_2O = CO_2 + H_2$

The manufacture of ammonia requires nitrogen as a raw material in addition to the synthesis gas. Nitrogen is produced in secondary reformers by partially combusting the effluent from the primary reformer with air. The reactions that take place in the secondary reformers include the following reactions in addition to reactions 1 and 2 listed above:

3. $CH_4 + O_2 = CO + H_2O$
4. $2H_2 + O_2 = 2H_2O$

Some methanol plants also use secondary reformers if oxygen is available as the oxidant. In this application, secondary reformers are used to produce additional synthesis gas instead of nitrogen.

In both applications (ammonia and methanol), secondary reformers consist of a partial combustion (oxidation) zone and a catalyst bed. The products of partial combustion (oxidation) are equilibrated over a catalyst bed contained in the same vessel underneath the partial combustion zone.

Synthesis gas is also produced using reforming exchangers and autothermal reformers. Reforming exchangers are reactors that replace the primary reformer. Instead of supplying the heat of reaction by burning fuel in a radiant heat transfer zone, the heat is supplied indirectly by exchange with a hotter gas stream. This hot stream is usually the effluent from an autothermal reformer (ATR). In the reforming exchanger, the reforming catalyst is contained in packed tubes with the hot stream on the shell side. This design (combination of ATR and reforming exchanger) has been offered by various licensors for a number of years, each with its own variation.

Despite the many different ways of producing synthesis gas, it is generally agreed that the future of synthesis gas production will be based on autothermal reforming. The capital cost of building an ammonia or methanol plant based on an ATR is less than the capital cost of a plant based on a primary reformer. A recent development in the ATR area, successful operation at low steam to carbon molar ratio, has made ATR the most efficient way of producing synthesis gas. Future ammonia and methanol plants will use ATRs instead of primary reformers. The autothermal reformer design is very similar to secondary reformer design. An ATR reactor contains a partial combustion zone at the top and a catalyst filled bed at the bottom. The feedstock is mixed with a sub-stoichiometric amount of oxidant and burned in the combustion zone. The resultant gases are passed over the catalyst in the bottom section to achieve as close to an equilibrium mixture as possible. ATRs are attractive when used in combination with reforming exchangers.

Due to their compact design and low steam to carbon ratios, ATRs are also suited for making large volumes of synthesis gas, especially with relatively low hydrogen/carbon monoxide ratios such as 1.5/1 – 3/1. To achieve the low end of the H_2/CO range, recycle of carbon dioxide is required. Used in this way, ATRs have limited commercial experience. There are only a handful of sites that use this technology. One such site is SASOL in South Africa, which uses ATRs licensed by Lurgi and Haldor-Topsoe. One of our industry partners (KBR) has a relatively small ATR unit installed at the Kitimat site in Canada. There are a handful of other ATRs installed in commercial operation.

Energy savings in methanol and ammonia production through ATR technology

Energy savings due to implementation of the Advanced ATR technology will be about 1.5 MM Btu's/Short ton of ammonia or methanol produced. A conventional ammonia or methanol plant consumes about 30 - 33 MM Btu's/Short ton of ammonia or methanol produced. Energy savings will be due to two reasons, lower steam to carbon ratio and production of syngas at high pressure (1075 psig). Most existing conventional ammonia and methanol plants that are typically designed for steam to carbon ratio of 3.3 or higher and syngas production at 350 psig can be either retrofitted or replaced with new ATR technology.

There are also environmental benefits of an Advanced ATR technology. Carbon dioxide emissions can be reduced from 0.728 ST to 0.291 ST per short ton of ammonia or methanol production and the NOx emissions can be reduced from 0.47 Lb to 0.19 Lb per short ton of ammonia or methanol production.

There will also be a reduction in capital costs of a methanol or ammonia plant associated with advanced ATR. New ammonia or methanol plants based on KBR's Advanced ATR and KRES (Kellogg Reforming Exchanger System) technologies will reduce capital cost for ammonia and methanol plants by about 5 percent. This capital savings will enhance the rate at which it appears beneficial to retrofit existing plants and thus speed both energy conservation benefits as well as the environmental benefits described above.

Methanol and ammonia demand

With the anticipated phase out of MTBE as the primary oxygenate in gasoline, the demand for methanol may decrease over the next few years. However, the addition of oxygenates, especially dimethyl ether, to diesel fuel will be on the rise in the future, and as a result, the need for efficient low H_2/CO ratio synthesis gas will remain. We anticipate the need for approximately one 1500 MTPD methanol or similar fuel additive plant to be added per year. If half of the new plants that will be built by year 2020 use advanced ATR technology, the energy savings realized by 2020 will be 50 trillion BTUs (approximately 0.7 trillion BTU/year per ATR plant).

Ammonia demand is more difficult to predict. Presently, the amount of NH_3 currently produced in the US is approximately 12 MM tons per years. About 80 % of domestic ammonia production is used to manufacture fertilizer for crop production. Between 2002 and 2010, we would estimate that the fertilizer requirement solely for food crop production will increase at a rate paralleling the projected growth in U.S. GDP of about 1-1.5% per year. However, it is a substantial increase in fertilizer production connected to corn-based ethanol production that drives the future ammonia production outlook.

According to the website Ethanol.org, 1.8 Billion gallons of ethanol were produced in the United States during 2001, consuming 667 Million bushels of corn. The renewable fuels mandate in the new Energy legislation will increase ethanol production up to 5 Billion gallons per year by 2012. Assuming 2.7 gallons of ethanol per bushel of corn, the additional 3.2 Billion gallon requirement by 2012 will consume an additional 1.2 Billion bushels of corn. It is reasonable to assume that if this mandate is successful the use of ethanol will continue to expand through 2020.

Per *Fertilizer Markets* (29 March 2002 issue), it takes about one pound of NH_3 to produce a bushel of corn. Therefore, production of an additional 1.2 Billion bushels of corn per year will consume 600,000 tons/year of NH_3. Assuming that this can be produced by incremental capacity increases in existing plants and idled plants located in the US, which are retrofitted with advanced high pressure ATR technology, a production increase of 600,000 tons/year represents a potential savings in energy demand of 1 x 10^{12} BTU/yr. Thus, between 2005 and 2012 approximately 5 trillion BTUs will be saved.

Assuming success of the shift to ethanol as a fuel continues through 2020 at a similar rate established in the 2005 – 2012 timeframe, the demand for corn-derived ethanol will have reached nearly 9 billion gallons by 2020. This translates to an energy saving of 2.0 trillion BTU/year by 2020 through the implementation of ATR technology in ammonia production. Integrating this increase in demand from 2005 through 2020 results in a total energy savings in ammonia production alone of 17 trillion BTUs.

Other applications for field corn as a commodity chemical feedstock source are on the horizon. For instance, in the 8 April 2002 edition of PetroChemical News it is reported that the new Dow-Cargill plastics resin plant is now in operation. It alone will use 15 million bushels of corn per year.

Hydrogen production for the hydrogen economy

Much of the future potential for ATRs actually lies outside the manufacture of commodity chemicals such as ammonia and methanol. In fact, ATRs represent one of the better methods for the production of a high-pressure hydrogen stream, suitable for use as a transportation fuel in the hydrogen economy of the future.

The direct partial oxidation of hydrocarbon fuels to hydrogen-rich synthesis gas offers promising alternatives to hydrogen production by steam reforming. By replacing endothermic steam reforming with fast exothermic oxidation reactions, gains in overall efficiency are realized through better utilization of process enthalpy. However, direct oxidation reactions are much more difficult to manage because dominant chemical pathways driven by nonselective reactions create fully oxidized products (water, carbon dioxide) or solids (carbon deposits/soot).

ATR technology offers the most efficient way to circumvent the energy costs associated with steam reforming methods, but presents one demanding technical challenge. In order to realize the energy savings by removing excess steam, the hydrogen-to-carbon ratio must be dropped, even to produce 3:1 H_2:CO_2. Successful introduction of ATRs into a distributed hydrogen supply network will require developing the know-how associated with small and compact units; much smaller than existing design technology. Achieving improved energy efficiency while reducing unit size is a daunting initiative. However, it is the precise control of the flow characteristics and feed mixing methods that will lead to the development of 1000 psi ATRs that will be both efficient and compact.

Summary

The implementation of advanced high pressure ATR technology for new or retrofitted ammonia plants and new fuel additives for gasoline and diesel based on synthesis gas as the primary feed will result in a total energy savings of approximately 67 trillion BTUs by the year 2020. Additionally, there are significant environmental benefits associated with advanced ATRs in relation to industrial gaseous pollutants.

NH_3 production is directly related to food production as well as energy self sufficiency in the United States. Anytime we can reduce our energy costs in a large-scale economic endeavor, we improve energy self-sufficiency.

The need for a complete understanding of the optimal operating range of an ATR is acute. We envision an applicability of a laboratory scale ATR test unit to have enduring utility beyond the life of this high-pressure soot-map project. Specifically, very little work has explored the possibility of using feedstocks other than methane or natural gas. This test unit can be seen as a research investment to extend ATR design technology specifically to the production of hydrogen from heavier hydrocarbons (naphtha, pyrolized biomass), using a combination of cracking, reforming, and water-gas shift chemistry in a compact, integrated system.

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