Reducing Ultra-Clean Transportation Fuel Costs with HyMelt® Hydrogen

Quarterly Report

July 1 – September 30, 2005

October 2005

Work Performed Under Cooperative Agreement No. DE-FC26-02NT41102

For

U.S. Department of Energy
National Energy Technology Laboratory
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By

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DISCLAIMER

ABSTRACT

This report describes activities for the twelfth quarter of work performed under this agreement. The design of the vessel for pressure testing has been finalized. We have initiated the purchasing process for the vessel and related equipment. Siemens Westinghouse Power Corporation completed computational fluid dynamics modeling and chemical reaction modeling of catalytic combustion of HyMelt product gases.

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1.0 PROJECT OBJECTIVES, SCOPE AND DESCRIPTION OF TASKS

1. Introduction

EnviRes and DOE executed the cooperative agreement for this work on September 19, 2002. This document is the twelfth quarterly progress report under this agreement. Kvaerner, MEFOS and Siemens Westinghouse will conduct most of the significant tasks in this project through subcontracts with EnviRes.

1.1 Scope of Work

Phase I of the work to be done under this agreement consisted of conducting atmospheric gasification of coal using the HyMelt technology to produce separate hydrogen rich and carbon monoxide rich product streams. In addition smaller quantities of petroleum coke and a low value refinery stream were gasified. Phase II of the work to be done under this agreement, consists of gasification of the above-mentioned feeds at a gasifer pressure of approximately 5 bar. The results of this work will be used to evaluate the technical and economic aspects of producing ultra-clean transportation fuels using the HyMelt technology in existing and proposed refinery configurations.

1.1 Phase I Task Description

Task 1.1 Project Management and Planning

This task includes all project planning; experimental test plans; risk analysis; implementation of a bridge loan and project funding, purchasing, contracting and accounting systems with requisite auditing; and execution of contracts with MEFOS, Kvaerner and Siemens Westinghouse. On January 15, 2005 we entered into a Memorandum of Agreement between Murray State University, and the Western Regional Center for Emerging Technology Inc., in conjunction with Kentucky Consortium for Energy and the Environment, MOA No. OSP 2005-19 proposing an additional $250,000.00 in funding for support of this project. On March 29, 2005 we were notified that our MOA had been accepted and funded for the requested amount.

Robert H. Wombles, formerly Vice President Technology at Koppers, Inc., accepted an offer to become CEO of EnviRes replacing Thomas M. Ward. This change becomes effective August 1, 2005.

Task 1.2 Preparation and Shipment of Feedstock Materials

This task consists of procuring 25 tons of coal, 15 tons of petroleum coke and 48 – 55 gal drums of aromatic extract oil; transporting the coke and coal to a pulverizing facility; pulverizing, drying and loading the coke and coal into bags; and shipping the feedstocks to MEFOS in Lulea, Sweden. EnviRes completed this task

Task 1.3 Predictive Modeling of the HyMelt Process

This task consists of generating detailed reactor energy and material balances for each feedstock using the Fact Sage pyrometallurgical thermodynamic modeling program. Kvaerner will perform detailed process simulation using the Aspen Plus process simulator. Kvaerner, MEFOS and EnviRes will evaluate and analyze the results of predictive modeling. This has been completed.

Task 1.4 Combustion Modeling and Analysis

Siemens Westinghouse will perform combustion turbine modeling using fuel gas conditions and compositions provided by task 1.3. Siemens Westinghouse is nearing completion of the first phase of this work.

Task 1.5 Design and Fabrication of Pilot Plant Specific Molten Iron Bath Apparatus

MEFOS will design and fabricate all solid feeding systems and oxygen injection systems required by the testing. EnviRes will assist MEFOS in designing the petroleum liquid feed system. MEFOS will design the shell of the high-pressure reactor. MEFOS and EnviRes completed the originally planned injection system for this task. MEFOS and EnviRes designed and fabricated a tuyere for submerged injection. MEFOS and EnviRes designed and fabricated a commercially feasible tuyere for testing in December 2003. We performed the testing as planned.

Task 2.0 Project Testing

Task 2.1 HyMelt Atmospheric Pressure Testing in a Molten Iron Bath

MEFOS designed and fabricated the petroleum liquid feed system. This injection system was tested in a cold flow environment. The injection systems were hot commissioned. Any equipment revisions indicated by cold flow testing and hot commissioning were made. Process performance testing was performed for each feed. MEFOS and EnviRes completed execution of this task.

Task 2.4 Above Atmospheric Pressure Testing in a Molten Metal Bath

MEFOS completed a preliminary design for this work. MEFOS and EnviRes met on September 12, 2005. The design of the pressure vessel was finalized and the purchase of the pressure vessel and related materials was initiated.

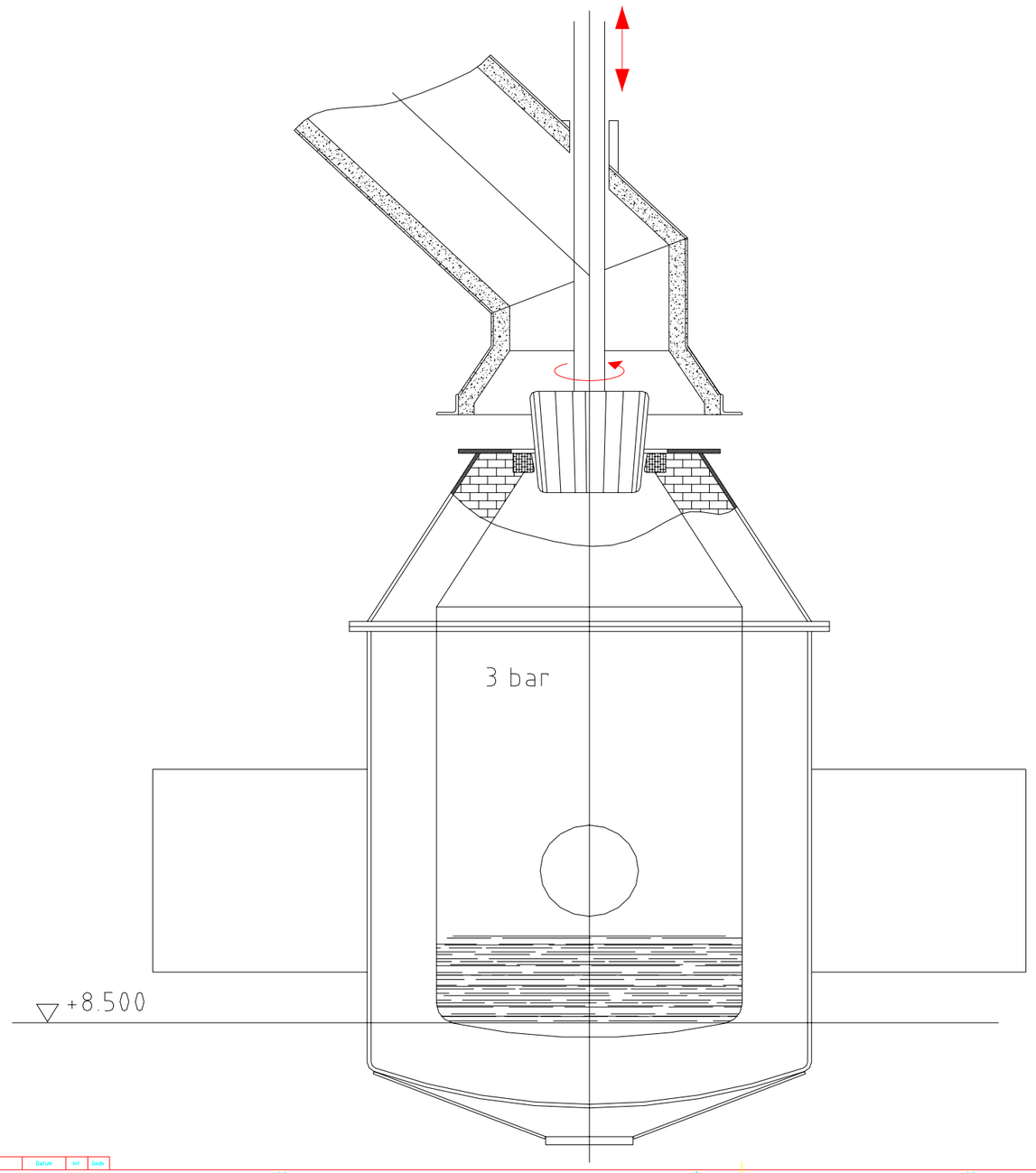
2.0 EXECUTIVE SUMMARY OF WORK DONE DURING THIS REPORTING PERIOD

EnviRes, Aker Kaeverner and Siemens Westinghouse Power Corporation have completed agreements to extend the performance period for their subcontracts to run through September 30, 2006.

3.0 Experimental

MEFOS Activities

EnviRes and MEFOS finalized the design of the pressure vessel. Figures 1 and 2 depict this design. A tapered, rotating ceramic plug maintains pressure in the vessel. The tapered plug can be moved closer or farther from the vessel opening. By virtue of its rotation, the problem of slag or metal splashing onto the plug and freezing it to the vessel opening is avoided. The hollow stem of the plug allows product gases to be sampled at pressure. The product gases drop to atmospheric pressure when the gases flow through the annular space between the plug and the vessel. As the gases exit the annular space they are captured by the vessel hood and processed in the same way as gases normally exiting an atmospheric pressure vessel.



MEFOS
BOX 812, S-971 25 LULEÅ SWEDEN
TEL +46 920 28 79 00 FAX 920-25 58 32

Ritn nr.: TRYCKS.–KONV.1
Skala: 1:20
Datum: 04–01–20
Godkänd:

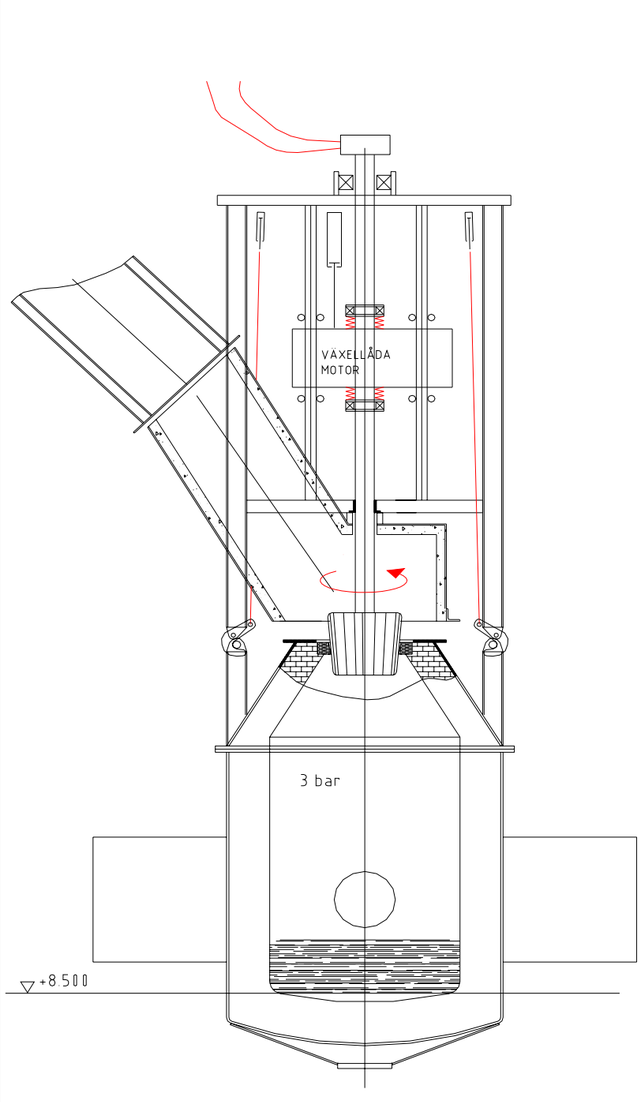
Konstruktionstjänst AB
Ratagrand 11 Tel 0920-249688 Fax 0920-249689
972 42 LULEÅ 070-6249688

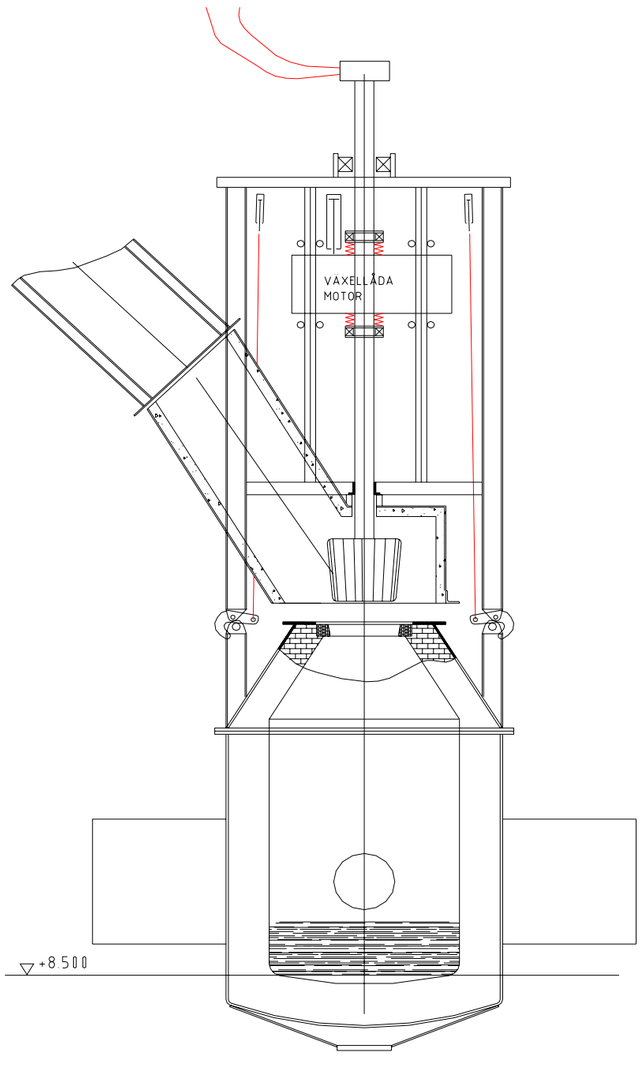
Ritad av: AST
Granskad av:
Konstruerad av: AST
Avdelning: MF

Benämning:
FIGURE_1.
HYMELT_TRYCKSATT_KONVERTER
FÖRSLAGSRITNING

Antal	Pos	Mtrl Ben Dim	Mod nr. / Art nr.	Vikt kg/st
—	—	—	–	—

Nr	Ant	Ändring och/eller medd.-nr	Datum	Inf.	Godk.


VÄXELLÅDA
MOTOR
3 bar
+8.500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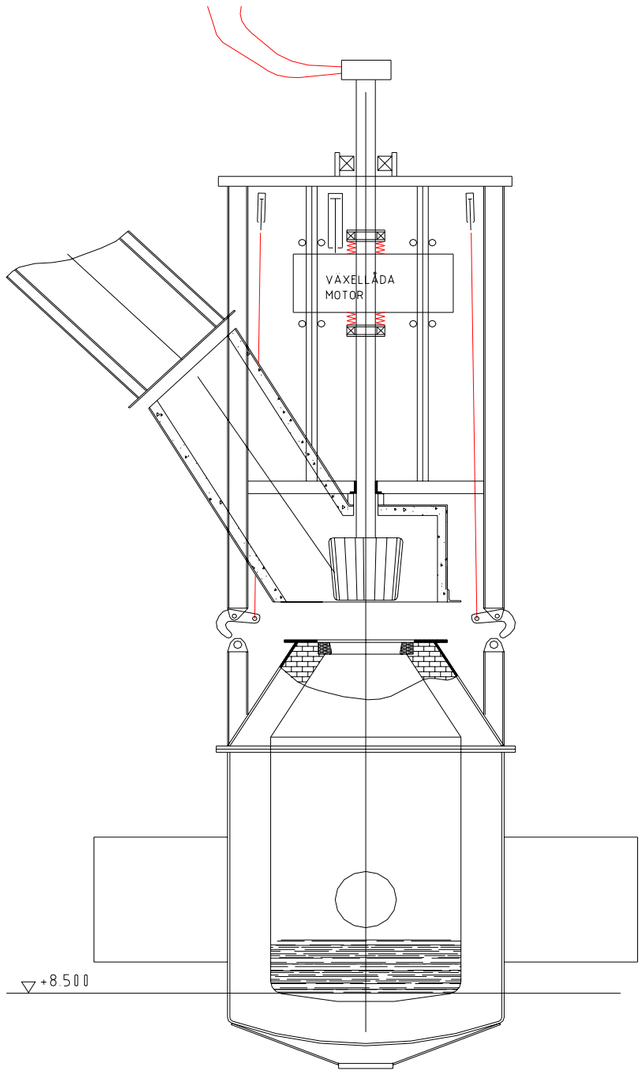
VÄXELLÅDA
MOTOR
+8.500

Figure 2

We have invoiced the funds made available by the Kentucky Consortium for Energy and the Environment through Murray State University. The vessel must be paid for in advance. We anticipate having the funds by early November. If this schedule is maintained, the pressure vessel and refractory lining should be delivered to MEFOS by December 2005.

Kvaerner Activities

EnviRes and Kvaerner discussed extending Kvaerner's subcontract.

Siemens Westinghouse Power Corporation Activities

EnviRes extended the subcontract with Siemens Westinghouse Power Corporation (SWPC) through September 30, 2006. EnviRes received a report from SWPC titled "Results of Subtask 6.1, Combustion Analysis/Modeling Chemical Reactor Modeling of Siemens Westinghouse Catalytic Combustors". This report can be found in Appendix I.

4.0 Results and Discussion

Modeling activities described above by SWPC in Appendix I showed that combustion of carbon monoxide rich fuel such as that produced by the HyMelt process emit slightly more to slightly less carbon monoxide in the flue gas for a combustor outlet temperature of 1127°C (2060°F) to 1149°C (2100°F) with 15% Oxygen in the flue gas compared to natural gas at the same conditions. Oxides of nitrogen were 50% lower for the carbon monoxide rich fuel compared to those from natural gas over the same conditions. The report also gives temperature and velocity profiles within the combustor.

5.0 Conclusions

Carbon monoxide rich fuels used with SWPC's catalytic combustor appear to offer significant advantages in emission rates compared to natural gas at conditions of commercial interest.

6.0 References

None

7.0 PLAN FOR THE NEXT QUARTER

We plan for MEFOS to take delivery of the pressure vessel shell and refractories by December 2005. The vessel will be installed in the Universal Converter station along with the pressure control system. Planning for experimental activities should begin before the end of the year.

Appendix I

Results of Subtask 6.1, Combustion Analysis/Modeling

Chemical Reactor Modeling of Siemens Westinghouse Catalytic Combustors

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July 25, 2005

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FIGURES AND TABLES

Acronyms

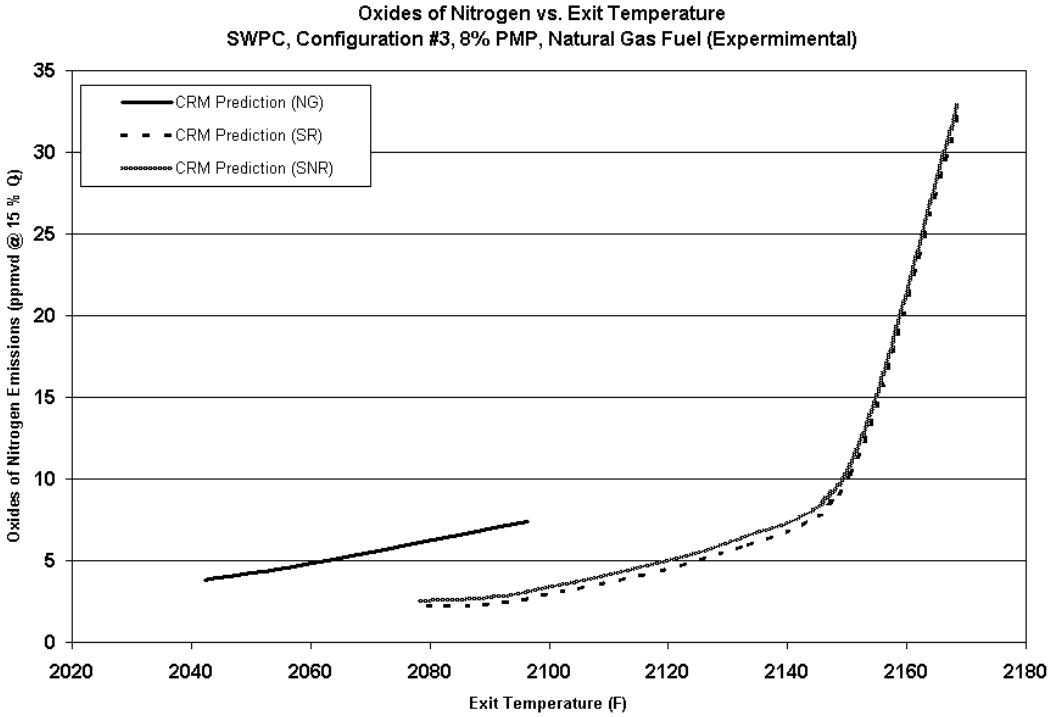
AFR Air-Fuel Ratio
CET Combustor exit temperature
CFD Computational fluid dynamics
CRM Chemical Reactor Modeling
CSE Combustion Science and Engineering, Inc.
GRI Gas Research Institute
GTE Gas Turbine Engine
NG Natural Gas
NO_x Oxides of Nitrogen, nitric oxide and nitrogen dioxide
PFR Plug Flow Reactor
PMP Pre-Mixed Pilot
PSR Perfectly Stirred Reactor
SNR Syngas combustion with No catalytic Reaction
SR Syngas combustion with catalytic Reaction
SWPC Siemens Westinghouse Power Corporation
UHC Unburned hydrocarbons

Summary

The objective of Subtask 6.1 is to determine the catalytic combustion characteristics of HyMelt syngas burned in a W501D5A gas turbine. This analytical task was accomplished by modeling the partial combustion in the catalytic zone and the complete combustion of the remaining gases in downstream zones. The analytical approach included the following steps.

1. Conceptually divide the geometry of the combustor into a pilot zone, a catalytic combustion zone, and hot, warm, and cold downstream zones.
2. Represent the fluid flow and chemical reactions in each zone as analytical models consisting of plug-flow reactors, perfectly stirred reactors, and mixers.
3. Calibrate the analytical models using data from previous natural gas combustion tests. Establish the flow rates in each zone for fuel, combustion air, cooling air, and combustion products.
4. Model the partial combustion of HyMelt syngas in the catalytic zone.
5. Using the combustion products from the catalytic model and downstream combustion parameters determined in the calibration step, calculate the combustion characteristics of HyMelt syngas, including emissions.
6. Repeat the syngas combustion calculations, except without any combustion in the catalytic section, to see the effects of this “worst case” on catalytic combustor performance.

The analytical results from Task 1 showed satisfactory combustion performance with HyMelt syngas in a catalytic combustor. Figure 1 and Figure 2 show the estimated NOx and CO emissions, respectively, for combustor exit temperatures between 2080 and 2170 ^{o}F (1140 to 1190 ^{o}C). Each chart contains a dotted line representing expected performance, a solid line near the dotted line representing "worst case" performance without catalytic reactions, and a solid line to the left representing calibration with natural gas combustion. The expected combustor exit temperature is



around 2130 to 2140 ^{o}F (1165 to 1170 ^{o}C), with 6-7 ppmvd NOx and 40-45 ppmvd CO.

Figure 1 – Calculated NOx Emissions from Catalytic Combustion of HyMelt Syngas

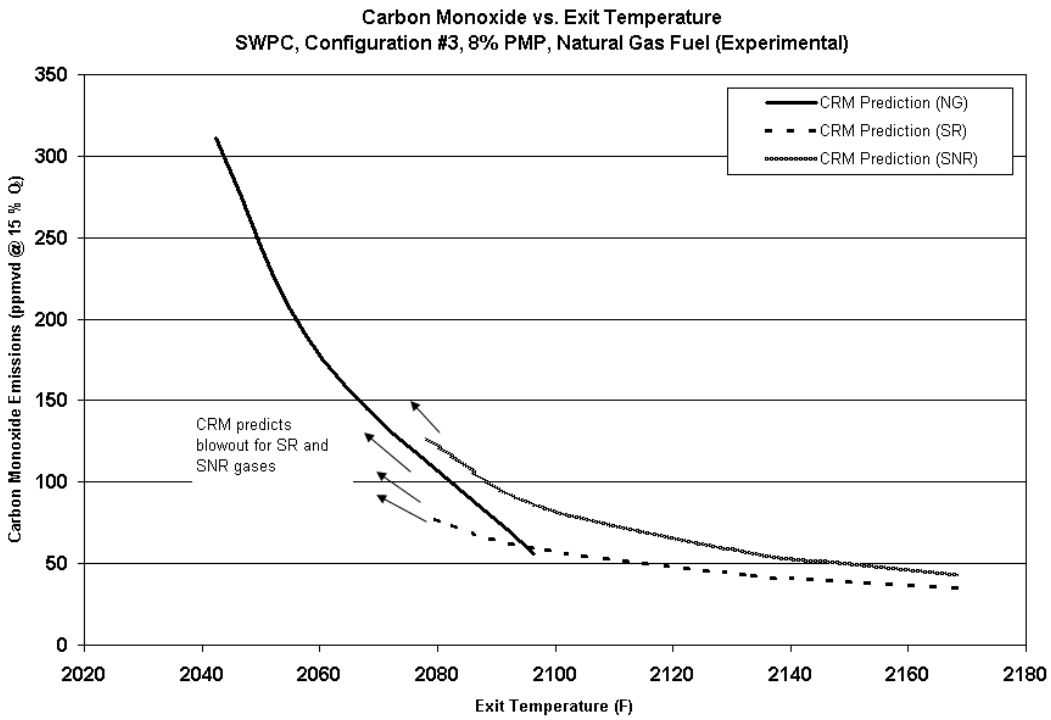


Figure 2 – Calculated CO Emissions from Catalytic Combustion of HyMelt Syngas

Introduction

The goal of this project is to study the effects of fuel switching on emissions of carbon monoxide (CO) and oxides of nitrogen (NOX). Computational fluid dynamics (CFD) and chemical reactor modeling (CRM) are used in concert to form a model of the SWPC combustor. Although CFD is a useful tool in predicting fluid structures, it is not robust enough to incorporate a detailed chemical kinetics model. The use of a detailed chemical kinetics model is necessary to accurately predict emissions, because it takes into consideration the multitude of pathways in which combustion reactions occur. Through the CRM model, detailed chemical kinetics is used to predict emissions from the SWPC combustor. A CRM model approximates the combustor fluid dynamics as a network of perfectly stirred (PSR) and plug flow (PFR) reactors. The CRM model allows rapid design studies, but the CRM must be tuned to some experimental data, in this case provided by SWPC.

CRM Modeling Process

The CRM process uses mathematical models that approximate sections of a combustor as chemical reactors. The CRM model is built using a network of PSR, PFR, and non-reacting flow mixers. PSR and PFR are commonly used to describe the re-circulation and CO burnout zones, respectively, of a combustor. The theory of operation of each reactor is described below, and their application to the SWPC combustor is also explained.

PSR: Perfectly Stirred reactors

A PSR is one in which stirring is so efficient that the contents are always uniform in composition and temperature throughout the reactor [1]. The initial part of a gas turbine combustor, where fuel is locally burned using a re-circulation zone, can be readily described as a PSR. PSR inlet conditions are characterized by temperature, pressure and inlet composition, and the reactor is characterized by residence time, temperature and pressure. PSRs are considered to be controlled by the flow parameters. In the SWPC combustor the pressure is constant throughout the combustor. All PSRs in the SWPC combustor are assumed to be adiabatic. Residence times of PSRs are determined through particle tracking post processing from a CFD solution.

PFR: Plug Flow Reactors

A PFR is one in which elements of the homogeneous fluid reactant move through a tube as a uniform mass parallel to the tube axis. It is assumed that no mixing occurs in the axial (flow) direction, but that mixing is perfect in the transverse direction [1]. The CO burnout zone of a combustor can be accurately described as a PFR. PFR inlet conditions are characterized by temperature, pressure and inlet composition and the reactor is characterized by residence time, physical dimensions, heat loss rate, wall temperature profile, and pressure. PFRs are considered to be controlled by the kinetic rates of the chemical reactors. All PFR's in the SWPC combustor are assumed to be adiabatic. The residence times are approximated by the following equation: distance / average bulk velocity = time.

MIX Subroutine

MIX subroutine solves for the mass and energy balances when two or more streams of non-reacting fluids mix. Mass, temperature and species composition inputs are specified.

Subroutines for PSR and PFR calculations can be found through Sandia National Laboratories. Manuals on the CHEMKIN suite of subroutines used to build the CRM model are available at http://www.ca.sandia.gov/chemkin/docs.html.

CFD: Computational Fluid Dynamics

Previously, CSE has performed detailed CFD analysis on the SWPC combustor using reduced chemical kinetics with large-eddy-breakup combustion sub-model. The results from the CFD modeling process are used as a starting point for the CRM modeling of the SWPC combustor. CFD results provide detailed information about the fluid dynamics inside the combustor. In the case of the SWPC combustor, we can locate the recirculation zone around the PMP by looking at a velocity vector plot created through CFD. Throughout the combustor, air is added at locations as prescribed in the Configuration #3 to cool the combustor liner. Particle tracking is used to determine the penetration depths of various flow streams.

Kinetic Submodel

The CRM uses GRI Mechanism 3.0 to model the detailed chemical kinetics. GRI Mechanism 3.0 is a detailed chemical kinetics mechanism for combustion of methane, comprising of 325 elementary chemical reactions utilizing 53 species. This mechanism can be found at http://www.me.berkeley.edu/gri_mech/. GRI Mechanism 3.0 has sub-mechanisms for CH_4, C_3H_8, CO, and H_2 combustion.

SWPC CRM Model

Previous CFD modeling of the SWPC combustor was used to gain detailed information about the fluid dynamics inside the combustor. Figure 3 shows the axial velocity profile in the combustor. By analyzing temperature, velocity, species concentration, and species production rates, the combustor can be divided into zones that are represented by PSRs and PFRs in a CRM model, as shown in Figure 4. Recirculation zones, such as the premixed pilot zone, are represented as PSRs. Dilution and quench air feeds match those used in the March 7, 2003 test run with Configuration #3.

The downstream portion of the combustor is represented as a network of interconnected PFRs. These PFRs allow for bulk transport of mass from center of the combustor to the edge of the combustor and vice versa. The CRM model theorizes three zones in the combustor. The innermost zone, along the axial centerline of the combustor, is the hottest zone. As flow from the catalyst exit reacts with the premixed pilot, the centerline of the combustor generates the hot (the hottest) products of combustion. Penetration of cold air streams into the hot zone is accounted for in the model. The outermost zone contains cold air from various dilution flows and some of the hot flow (from the inner hot zone) that has migrated to the outer edge of the combustor. In the outermost zone, the hot flow mixes with the cold flow, lowering the temperature to levels below which CO oxidation to CO_2 can take place. Therefore, the outermost zone is the main source of the CO emissions.

Figure 4 shows the CRM network model for the SWPC combustor. The three catalyst flows and the three core flows leaving the head end are connected to the inner, middle, and outer sections downstream, as indicated by the shape symbols shown near the streams. The catalyst flow is added in stages, percentages of which were determined through tracing the catalyst flow from the catalyst exit to the turbine inlet. Figure 5 shows the CRM overlay on the CFD temperature solution and the spatial orientation of the reactors.

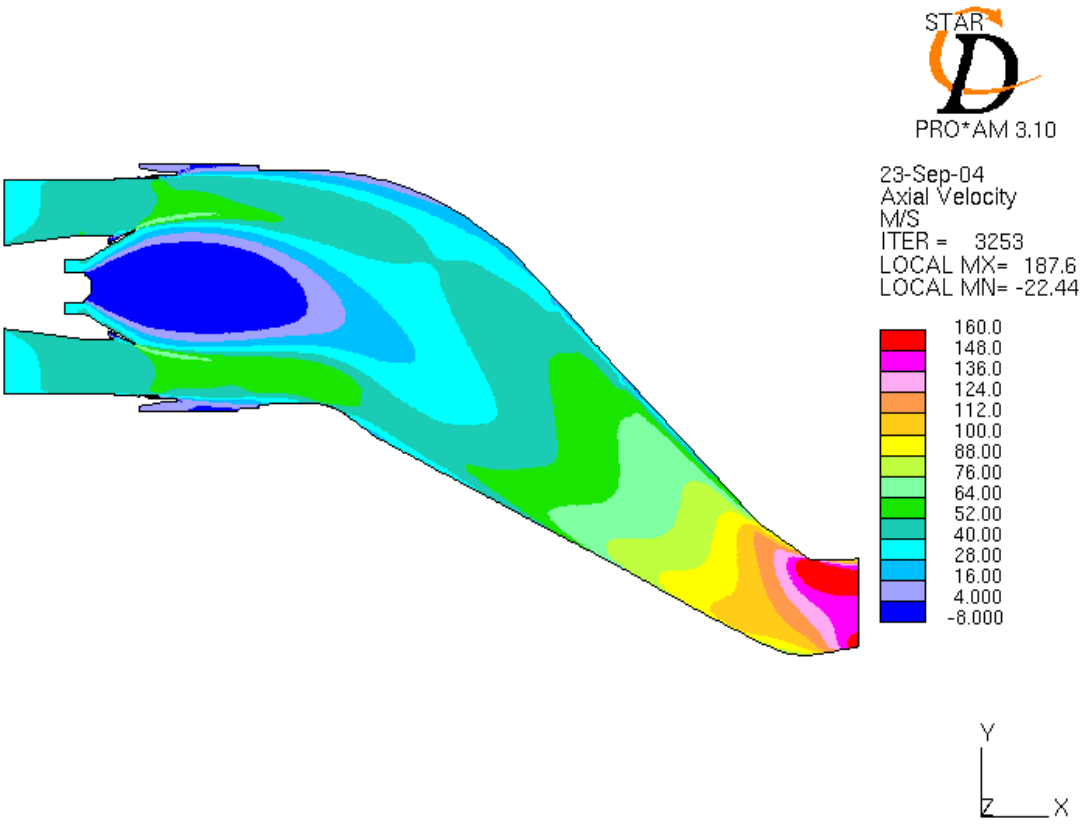


Figure 3. Axial Velocity Profile Created Through CFD Modeling of the SWPC Combustor

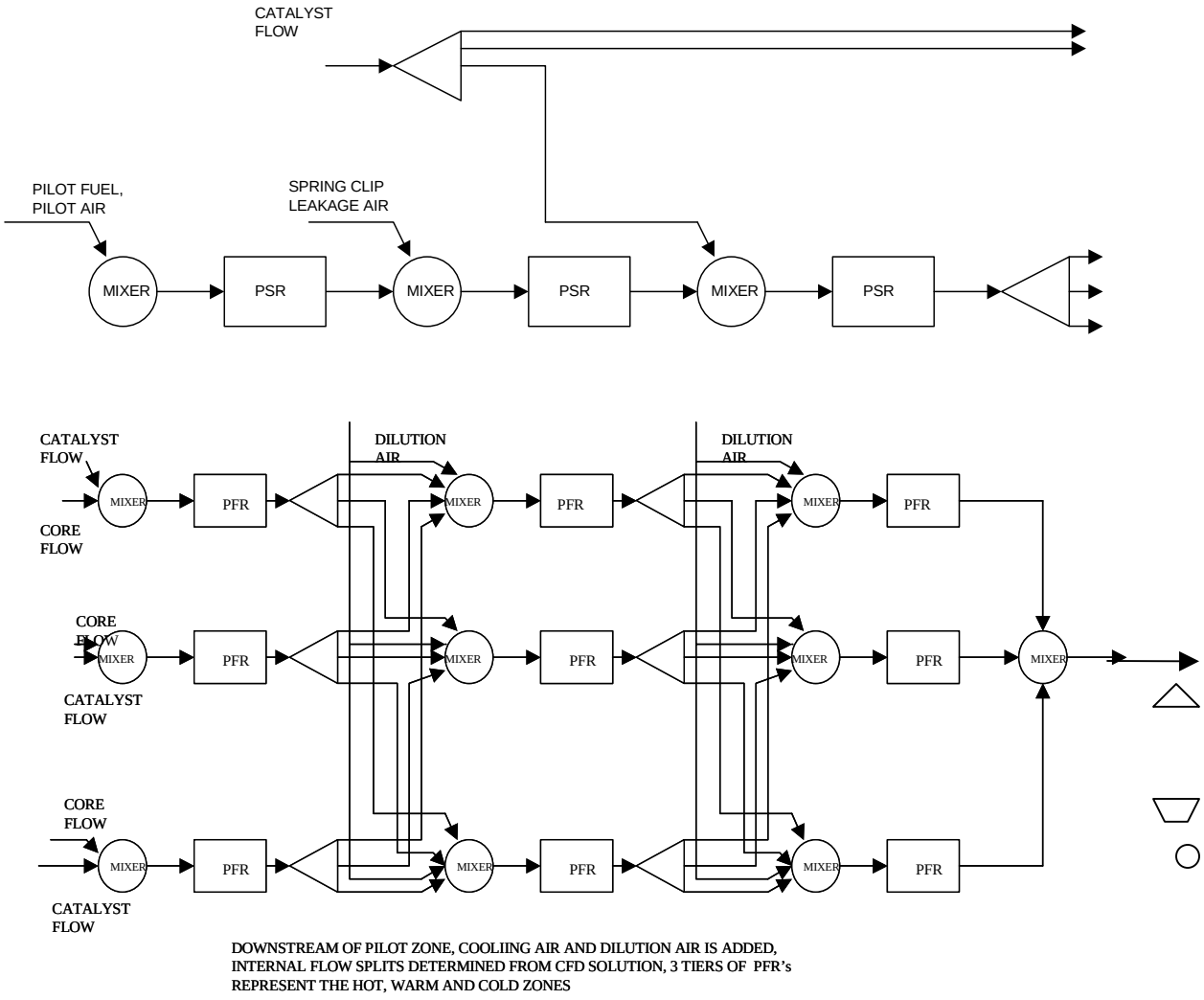


Figure 4. CRM Model Representation of the SWPC Combustor.

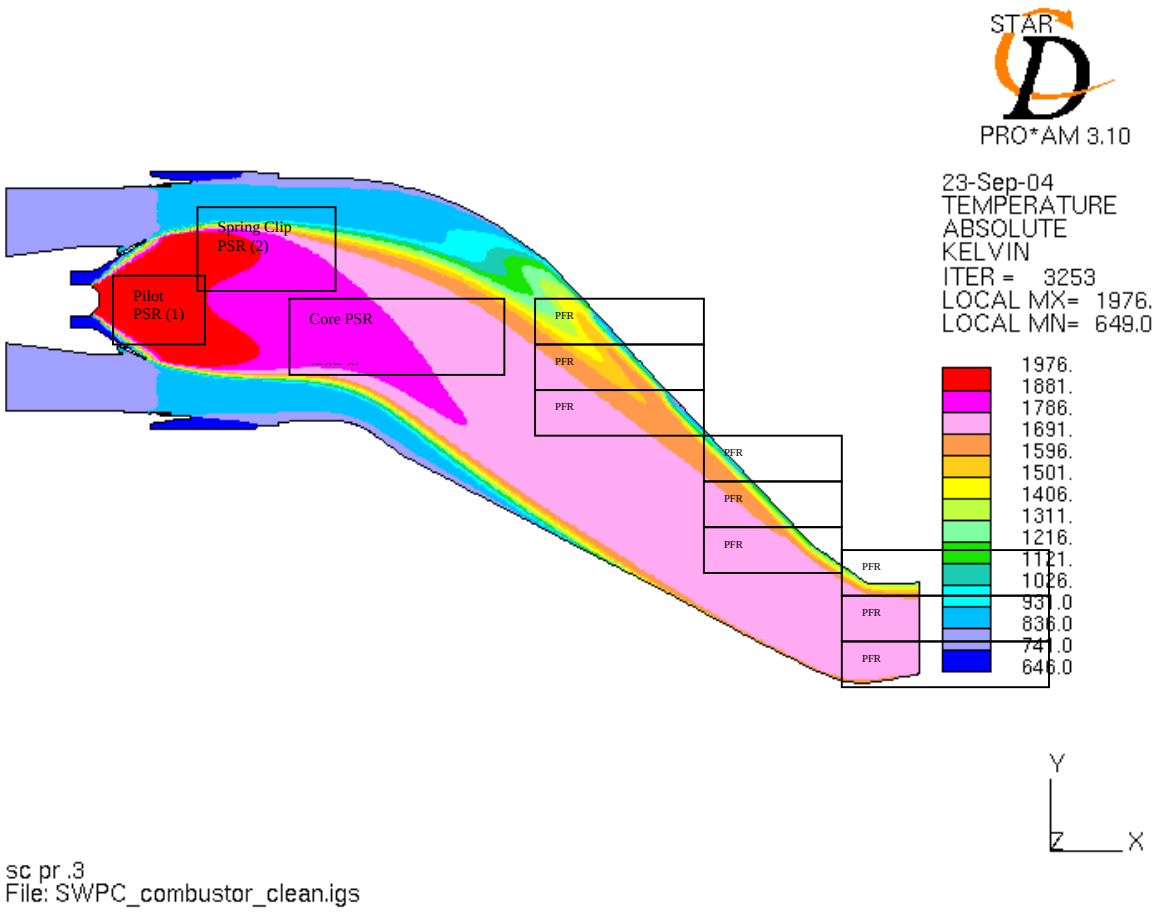


Figure 5. CRM Overlay on CFD Temperature Solution

Boundary Conditions

The combustor inlet conditions are specified below:

- Pressure = 14.2 atm, (208.7 psi)
- Air Temperature = 649.5 K (709.4 °F)
- Catalytically Combusted Fuel Temperature = See Table 1
- 8% Fuel split to the premixed pilot
- Dilution along the combustor
- Fuel = natural gas, syngas with reaction, syngas without reaction

Fuel Properties

Fuel properties are provided in the table below. The mole percentage of each component of the fuel is provided, as well as the temperature of each stream (added with the appropriate air stream). Note the lower SNR catalyst exit temperature, since the SR has reacted through the catalyst and heat has been liberated through the reaction with the catalyst.

Table 1. Fuel Composition and Temperatures Specified by SWPC

	Natural Gas (NG)		Syngas without Reaction (SNR)		Syngas with Reaction (SR)	
	Pilot	Catalyst Exit	Pilot	Catalyst Exit	Pilot	Catalyst Exit
Temperature (F)	733.00	952.00	733.00	665.60	709.43	1013.04
Ar	0.00%	0.88%	0.00%	0.81%	0.00%	0.82%
CH_4	98.00%	3.32%	0.07%	0.01%	0.07%	0.01%
C_2H_6	0.60%	0.02%	0.00%	0.00%	0.00%	0.00%
CO	0.00%	0.02%	75.72%	9.03%	75.72%	7.45%
CO_2	0.00%	0.73%	3.92%	0.49%	3.92%	2.16%
H_2	0.00%	0.01%	19.96%	2.38%	19.96%	2.26%
H_2O	0.00%	2.61%	0.30%	1.13%	0.30%	1.28%
N_2	1.40%	73.99%	0.03%	67.93%	0.03%	68.54%
O_2	0.00%	18.42%	0.00%	18.22%	0.00%	17.48%
* all mole percents						

Experimental Data

The experimental data is provided in Figure 6.

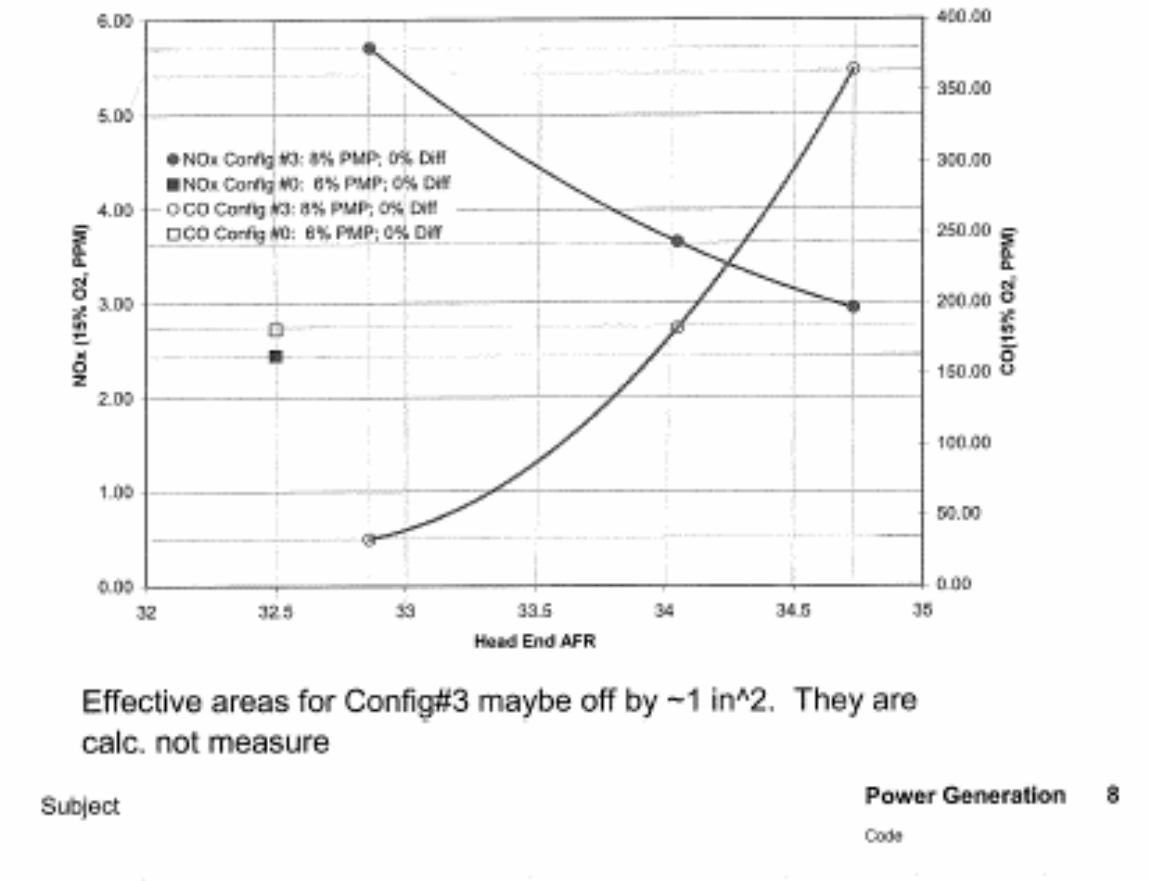


Figure 6. Experimental CO and NO_X Emissions data for the 8% PMP, Configuration #3

The experimental data provided by the testing of Configuration #3 (a representative case) is shown in Figure 6. Natural gas fuel properties, combustor temperature and pressure listed in the boundary conditions section, and internal gas flow splits determined from CFD analysis provide all other pertinent boundary conditions.

Results

Figure 7 shows the CO emissions as a function of the head-end air-fuel ratio, which is the total amount of air to the catalyst and the pilot divided by the total amount of fuel to the catalyst and the pilot. The CRM predicts the absolute values and trends close to experimental CO emissions fairly well over the range of head-end air-fuel ratios modeled. An increase in load (corresponding to a higher exit temperature) facilitates the higher temperature required for a faster rate of CO burnout. The calculated theoretical combustor exit temperature (CET) is also listed for each experimental point. The CET is used to compare the results of the natural gas with the syngas, which will be discussed later.

Figure 8 shows the NO_X emissions as a function of the head-end air-fuel ratio. As with CO emissions, experimental NO_X trend and absolute values are matched by the CRM model. The CET is also listed. The trend in NO_X emissions is due to changing head-end air-fuel ratio. An increase in air-fuel ratio results in a lower primary zone temperature for the primary premixed pilot, which causes lower NO_X emissions.

Figure 9 compares the CO emissions from the three fuels modeled. Based on the current CRM model, a higher CO emissions output is predicted for the syngas fuels, when compared to the natural gas. This can be attributed to the freezing of CO in the outer boundary layer where cold air for dilution and quenching is introduced. When comparing the two syngas fuels, syngas without reaction is predicted to have higher CO emissions. A higher mole fraction of CO

at the exit of the catalyst (syngas without reaction, Table 1) translates to a higher CO emissions value at the exit of the combustor. The figure also shows that syngas fuels reach blowout at a higher CET than natural gas fuel.

Figure 10 compares the NO_X emissions from the three combustion gases modeled. Syngas with reaction has slightly higher NO_X emissions than syngas with reaction. Natural gas has higher NO_X emissions than syngas for the same exit temperature. The premixed pilot has a higher flame temperature for natural gas due to the changes in fuel mass required to balance exit temperature, therefore NO_X production in the premixed zone is higher for the natural gas fuel.

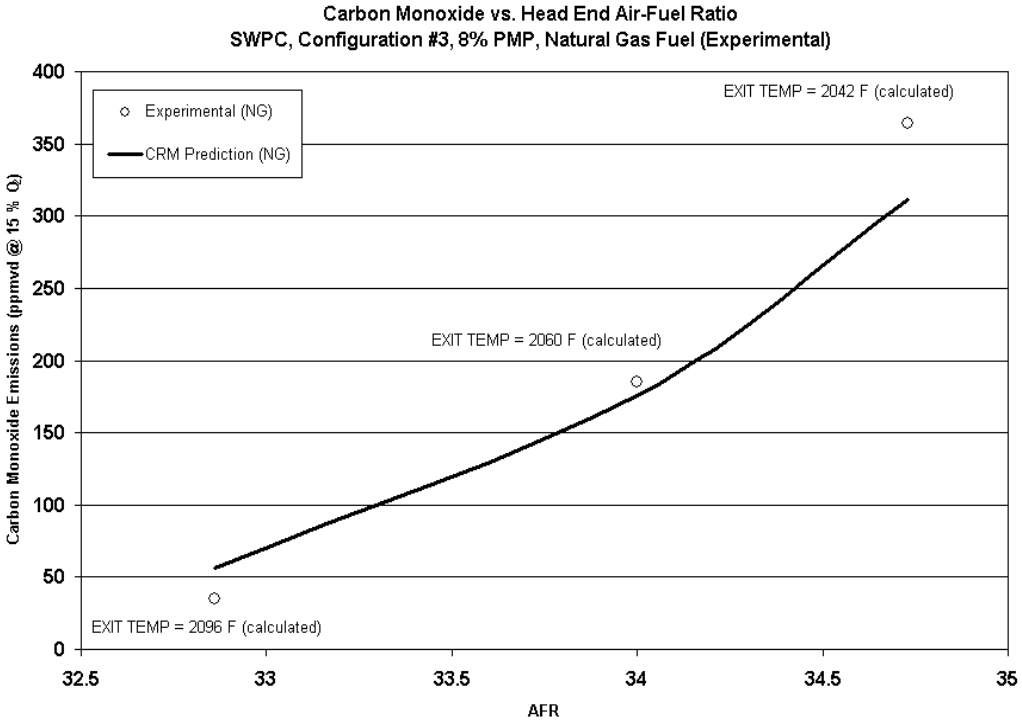


Figure 7. CO vs. Head-End Air-Fuel Ratio for Natural Gas: Experimental vs. CRM Model

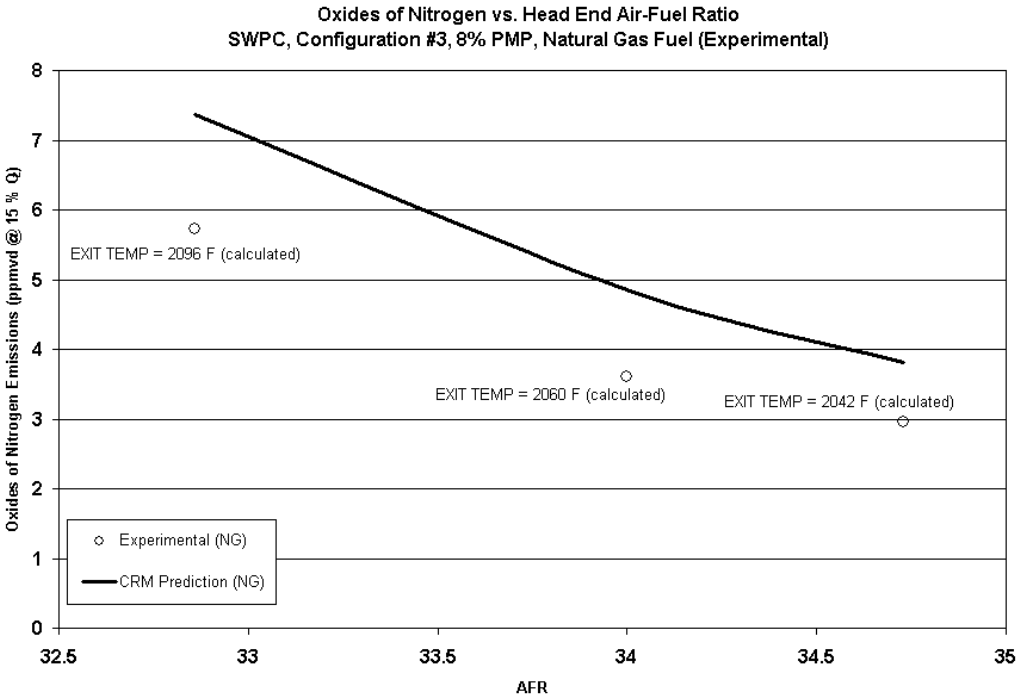


Figure 8. NO_X vs. Head-End Air-Fuel Ratio for Natural Gas: Experimental vs. CRM Model

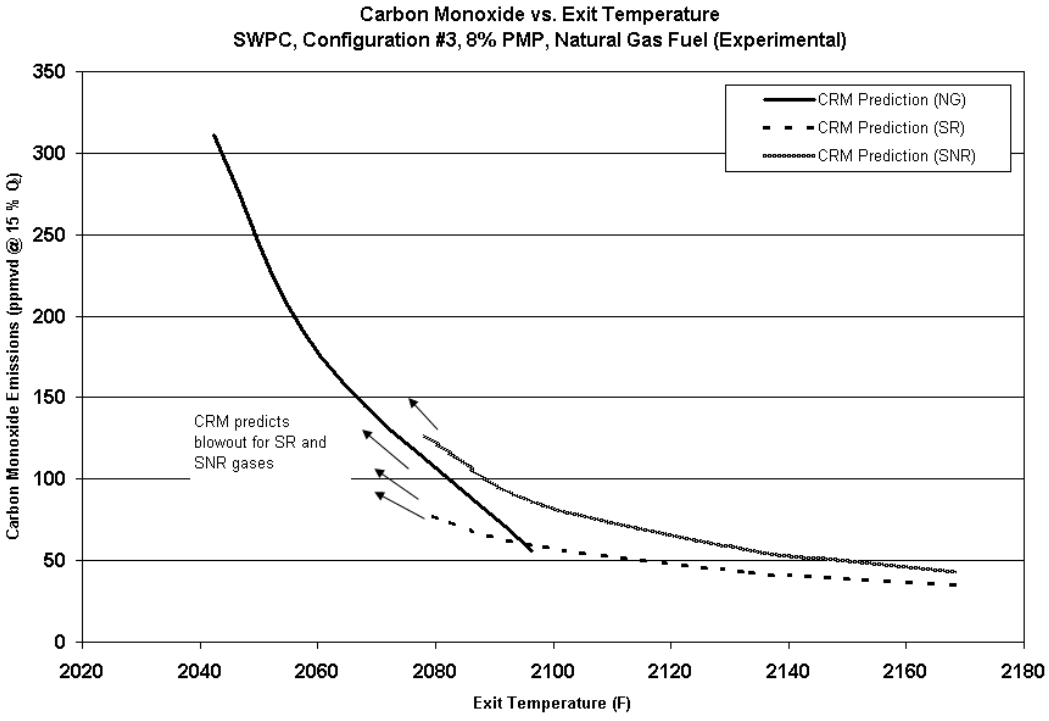


Figure 9. CO vs. Combustor Exit Temperature for All Fuels: CRM Model

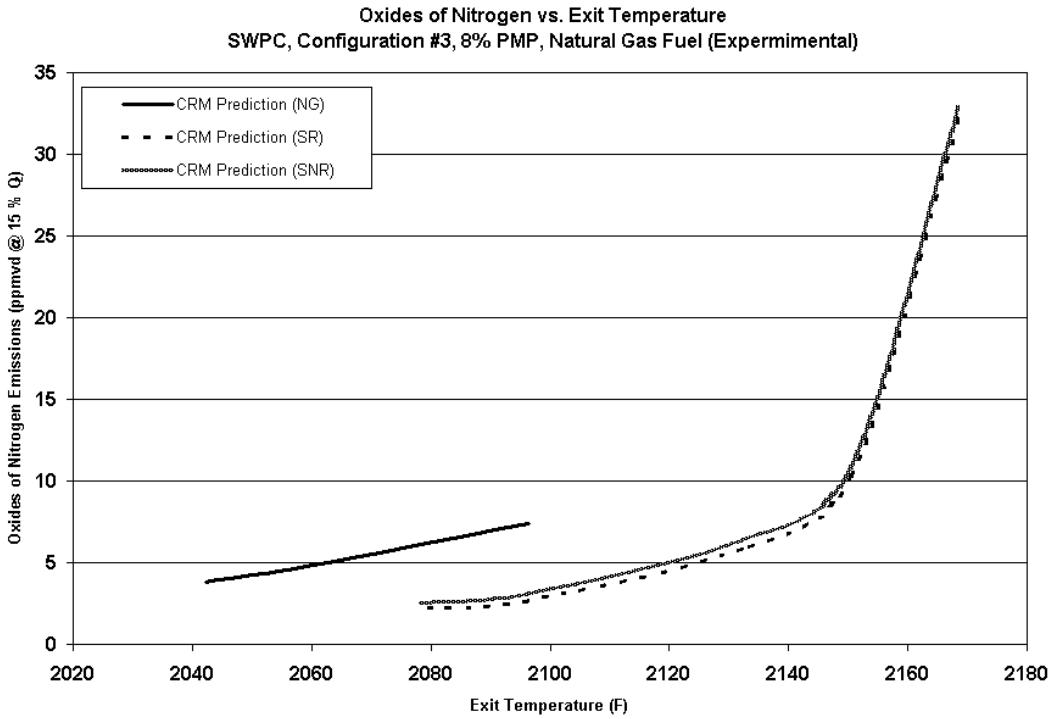


Figure 10. NO_X vs. Combustor Exit Temperature for All Fuels: CRM Model

Conclusions

A CRM tool is created to perform parametric studies aiding in the combustor design cycle. Through the CRM model, full chemical kinetics analysis is used to predict emissions from a SWPC engine.

Good agreement with the 8% premixed pilot experimental data is found with the natural gas fuel. Syngas fuel with reaction (SR) gives lower CO emissions than syngas fuel without reaction (SNR) for the same CET. Syngas fuels (both SNR and SR) give lower NO_X emissions than natural gas for the same CET. Blowout is predicted to occur at a higher CET temperature for syngas fuels than for natural gas fuel. These conclusions are based on modeling the combustor for a limited set of experimental data collected for natural gas combustion.

Reference

1. Hill, Charles, G. *An Introduction to Chemical Engineering Kinetics and Reaction Design.* New York, Wiley, 1977.