Progress in Catalytic Ignition Fabrication and Modeling: Modeling Part 2

Final Report

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16. Abstract

The ignition temperature and heat generation from oxidation of methane on a platinum catalyst were determined experimentally. A 127 micron diameter platinum coiled wire was placed crosswise in a quartz tube of a plug flow reactor. A source meter with a 4-wire measurement capability measured the resistance and current to calculate the average temperature of the surface reaction. Light-off temperatures varied from 730-780K for methane for a fuel-oxygen equivalence ratio of 0.3 to 1.0 at fuel percentages of 2-5% by volume. A model of the experimental system was created using Fluent coupled with Chemkin to combine an advanced chemistry solver with flow simulation. The experimental data was compared to the model results, which includes heat transfer and the surface reaction kinetics of methane on platinum. The heat transfer model obtained values close to experimental data for temperatures between 400K and 700K. At temperatures greater than 700K the model deviated with temperatures greater than the experimental results.

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EXECUTIVE SUMMARY

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DESCRIPTION OF PROBLEM

This research investigates the effects of methane-oxygen-nitrogen mixtures over a heated platinum catalyst. Methane is one of the only fuels for which surface reaction mechanisms on platinum have been made available. In order to create a computer model of the heat generated from the chemical surface reactions, the catalyst temperature at which surface reactions initiate (ignition temperature) is needed for comparison. Other data collected includes the overall heat generated from the surface reactions.

This report contains the experimental results of the ignition temperature and heat generation data for methane on a platinum catalyst using fuel to oxygen equivalence ratios of 0.1 to 1.0. In addition, the progress in meshing and modeling the heat transfer model and surface reaction kinetics is presented. Future work may involve additional adjustments to the model to more closely fit the experimental data.

This study is used in the further development of catalytic igniter technology for use in lean burning internal combustion engines [1,2,3]. It will help to determine the average heat flux from a platinum surface and the power input necessary to initiate combustion. Without sacrificing power, the igniters permit extremely fuel-lean, cold combustion that prevents nitrogen formation via the thermal mechanism and the dissociation of carbon dioxide back to carbon monoxide within the cylinder of an internal combustion engine. This study leads to better understanding of the ignition process without the complexities of engine dynamics.

Prior work has focused on the combustion of ethanol/water/air in engine platforms [4,5], catalytic ignition properties of propane/water/air [6,7], ethanol/water/air mixtures [8,9], and catalytic ignition properties of biodiesel/air mixtures [10]. The work presented here represents progress toward studying the effects of catalysts exposed to fuel, nitrogen, and oxygen mixtures.

APPROACH AND METHODOLOGY

A plug-flow reactor was used to determine ignition temperatures of non-flammable methane/oxygen/nitrogen mixtures over a coiled platinum wire catalyst. The experimental setup is shown in Figure 1.

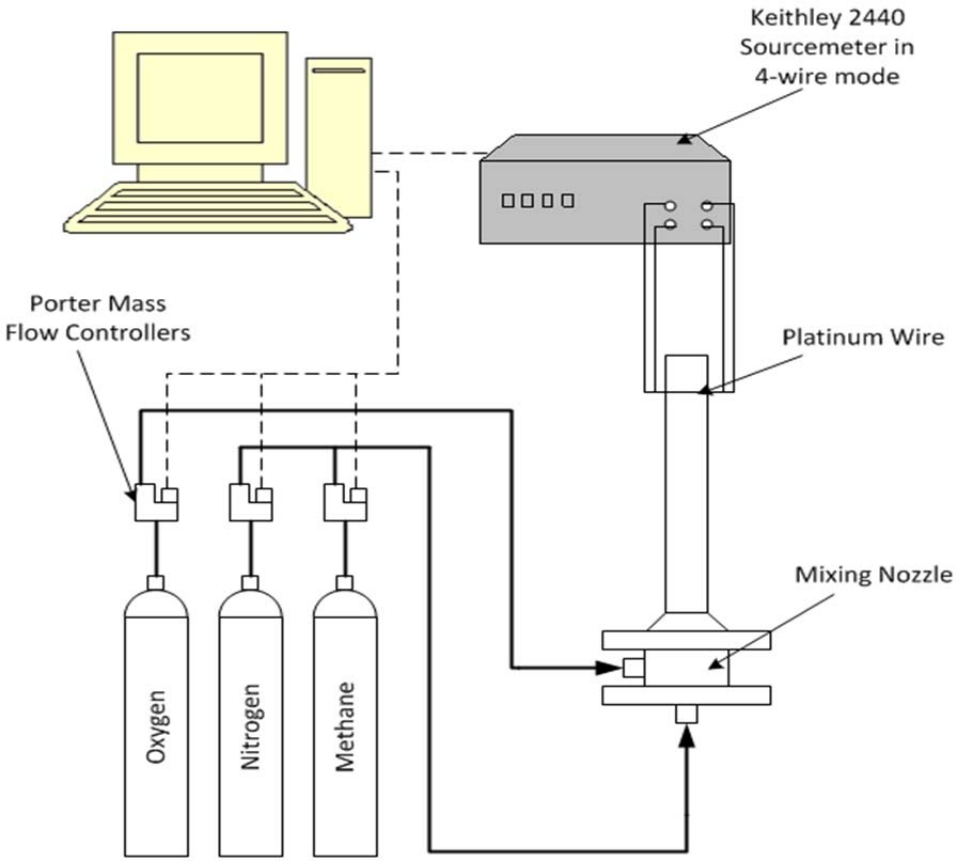

Figure 1: Experimental setup.

The reactor consists of two gas inlets, a mixing nozzle, and a quartz tube with an inside diameter of 2.73 cm. The reactor mixes inlet streams of methane, nitrogen, and air that pass through a quartz tube in a manner that achieves plug flow conditions at approximately 3 to 11 diameters downstream from the reactor nozzle [6]. A 127 micron diameter platinum coiled wire catalyst with a total length of 15.3 cm was placed in cross-flow through the reactor tube to allow the fuel mixture to uniformly pass over the wire in cross-flow. The platinum wire is connected to a Keithley 2440 source meter that conducts a specified range of current through the wire while measuring the voltage and resistance. Data was collected for fixed volume percentages of methane from 2% to 5% in 1% increments. All experiments were run through an equivalence ratio, φ, from 0.1 to 1.0 in 0.1 increments, all while maintaining a non-flammable mixture at a total volumetric flow rate of 5 L/min. For these experiments, φ is defined as the ratio of the mass of methane to oxygen divided by an equivalent stoichiometric ratio. At each equivalence ratio, the multi-meter was used to measure the voltage drop across the wire, from which the resistance

and the average wire temperature were determined. These temperatures were plotted with respect to the power input to the wire and then compared to the average temperature with a non-reactive flow. With this comparison, the heat generation due to surface reactions could be calculated by the process shown in Figure 2.

In Figure 2, the post ignition curve is created by fitting a line to the slope of the temperature after reaching steady state and is somewhat parallel to the baseline curve when extended. The ignition curve is fit to the line where the temperature is rapidly increasing. Where the ignition curve intersects the baseline curve is the point of ignition (Point 1). Point 2 is the intersection of the methane response curve and the post ignition curve, also known as the leveling off steady-state burn point. Point 3 is found by drawing a line parallel to the x-axis over from Point 2 until it intersects the baseline curve. The distance on the x-axis from Point 1 to Point 3 is the rate of heat generation by the reacting fuel. This is referred to as Q_{gen}. In other words Q_{gen} is the power it would take to heat the wire to the temperature at Point 2 with a non-reacting flow. Hence, the measurement of the average wire temperature also provides the rate of heat generation, which is useful for catalytic igniter development.

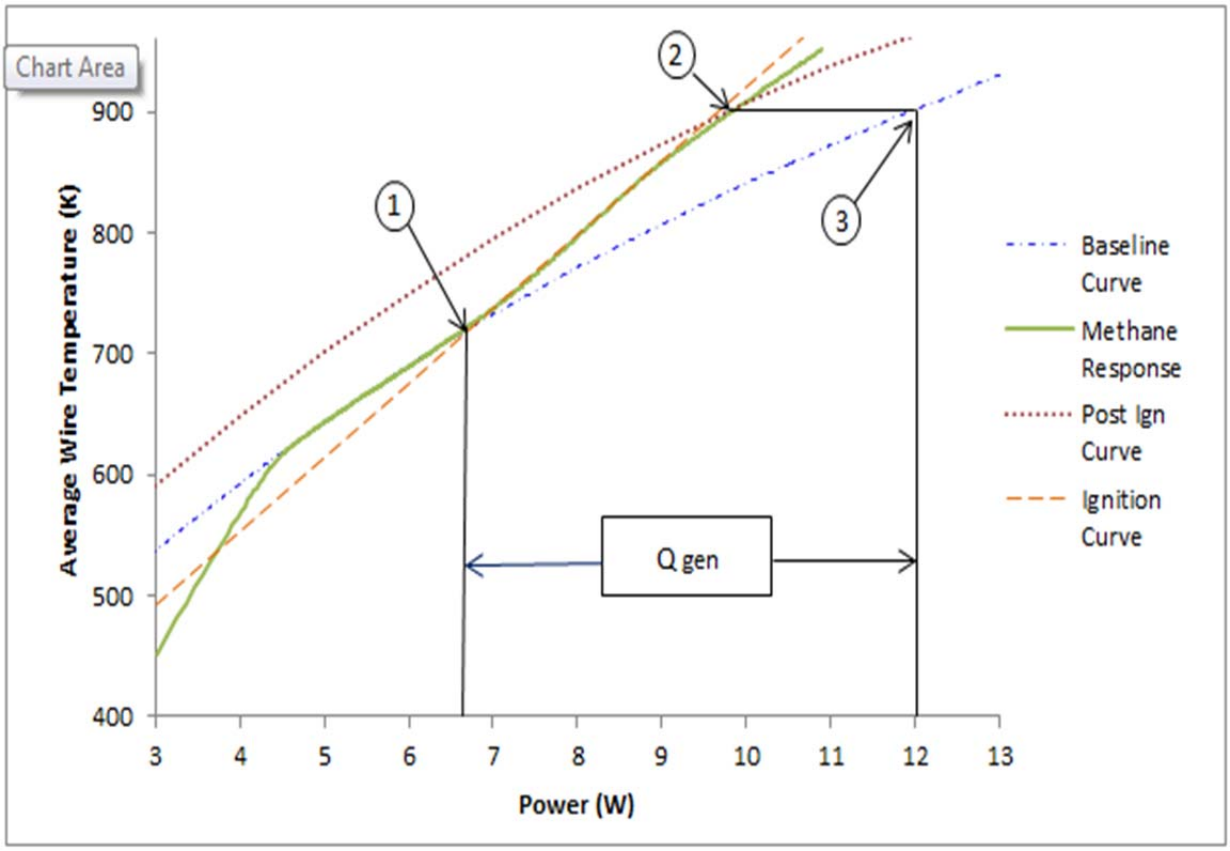

Figure 2: Temperature vs. power for a standard ignition line.

Modeling Methods

The Ansys CFD package was used to create the geometry, mesh and compute a solution with Fluent. Chemkin was used as plugin for Fluent to solve the surface reaction chemistry. The surface reaction mechanisms and thermodynamic data were obtained from the GriMech 3.0 database initially provided by Quincino et al [11]. The data was for the most part already available in the compatible Chemkin format. All of the unnecessary species and reactions were removed from the files to reduce computational time.

Boundary conditions for the model were set to be as close to the experimental conditions as possible. The inlet fluid flow was set to be a steady state inviscid flow with zero shear stress at the tube walls to simulate plug flow. A constant source term was applied to the platinum wire with an energy balance applied at the interface of the fluid and coil wall. This was to account for the conduction, convection, and radiation heat transfer from the wire to the surrounding fluid.

Geometry and Meshing

Two basic geometry designs were used for the computer modeling. A simple straight wire drawing and a coiled wire drawing similar to the experimental setup is shown in Figure 3.

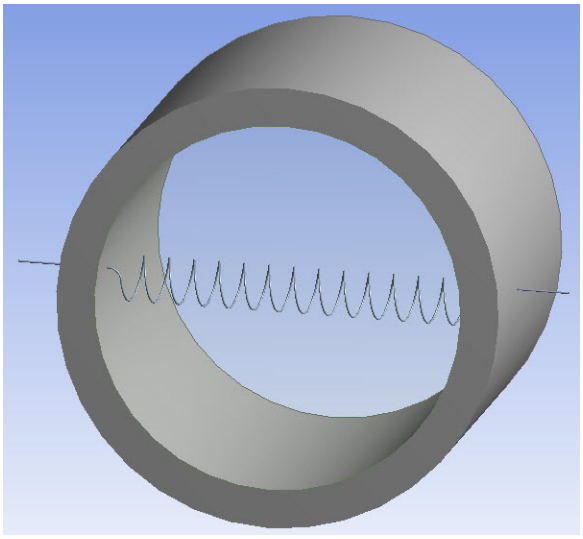

Figure 3: Coiled wire geometry.

The simple straight wire model was created to more easily resolve meshing, boundary condition, and surface chemistry issues. The model geometries were created using Ansys Design Modeler and represents the section of reactor tube where the fuel-oxygen-nitrogen mixture passes over the platinum wire catalyst. The tube had an inside diameter of 2.73 cm and an outside diameter of 3 cm. The coiled wire had a length of 15.3 cm and a diameter of 0.127 mm. The fluid was created by creating caps over the tube ends and filling the void with the fluid geometry.

The surface of the platinum wire is the focus of this study so it is desirable to create a mesh of close grid points about the wire. In the case of this model, the wire is very thin with respect to the surrounding quartz tube and is arranged in a helical profile which creates complicated surfaces to mesh requiring a larger number of grid points.

The mesh was created by using a hexahedral sweep method for the wire and a patch conforming tetrahedral method for the fluid body and the tube. The patch conforming method first meshes

the edges, then surfaces, and finally the volumes of the geometry bodies. The resultant mesh can be seen in Figure 4.

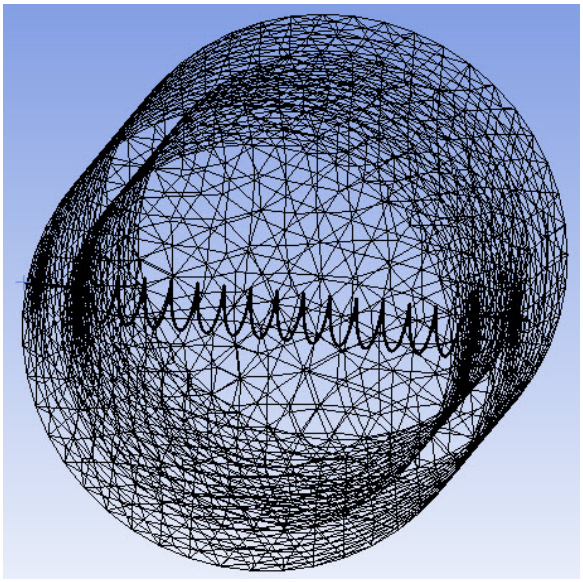

Figure 4: Coiled wire mesh.

To ensure that heat will transfer properly from the solid region to the fluid region, it was important to ensure that the wire surface in contact with the fluid region and the fluid surface in contact with the wire was a conformal mesh. This ensures that each grid point on the wire surface matches a grid point in the fluid region in contact with the wire. The conformal mesh was done by inserting a face sizing element for the wire end and specifying the same maximum and minimum grid sizes for the sweep method and the patch conforming method. In addition, it was necessary to insert virtual topology for the two boundaries where the wire passes through the tube.

Preprocessing and Solver Parameters

Ansys Fluent was used to read the mesh and perform the computations for the heat transfer model. A pressure-based (segregated) solver was used for this model since there is a very low Reynolds number flow through the tube. Material properties for platinum were added to the database and the specific heat and thermal conductivity for air was modified from constants to polynomial functions of temperature for improved accuracy. Radiation properties were added for

each material. These properties included the absorption coefficient, scattering coefficient, scattering phase function, and refractive index.

Boundary conditions were specified for the inlet, outlet, tube wall, and wire walls. The inlet was specified as a velocity inlet and given a value of 0.173 m/s with an initial temperature of 298K. The outlet was set as a pressure outlet and left with the default value of 0 gage pressure and 298K. The tube wall was assigned a zero shear stress to simulate plug flow and the coil wall left with the default no slip condition. The coil ends were fixed at 298K because they extend out beyond the tube in the surrounding atmosphere. All other boundary conditions remained at default. A source term was specified for the coil body cell zone in W/m3 to simulate the wire heating. Fluent material property and boundary condition settings are summarized in Table 1.

Table 1: Summary of Fluent Model Settings

Property	**Platinum**	**Quartz**	**Air**
Density (kg/m^3)	21450	2620	1.225
Specific Heat (J/kg*K)	130	830	1050-0.365T+8.5E^{-4}T^2-3.7E^{-7}T^3
Thermal Conductivity (W/m*K)	71.6	1.46	-3.93E^{-4} +1.02E^{-4}T-4.86E^{-8}T^2-1.52E^{-11}T^3
Viscosity (kg/m*s)	- -	--	1.79E^{-5}
Absorption Coefficient (1/m)	1	4.5	--
Index of refraction	2.33	1.46	1
Model	**Settings**		**Notes**
Solver	Pressure-based 3-D Steady-state Implicit		Inlet velocity from pressure gradient Three dimensional model
Energy Equation	On		Heat transfer occurs in the model
Viscous	Laminar		Low Re number
Boundary Conditions			
Velocity Inlet	velocity = 0.173 m/s T = 290K		Inlet air velocity Inlet air temperature
Pressure Outlet	P = 0 gauge		Flow exit
Coil Cell Zone	Source Term		Input current in W/m^3 for coil heating

Surface Chemistry Modeling

The species needed for methane surface reactions were limited to CH_4, O_2, H_2, H_2O, CO, CO_2, HO, OH, and N_2. As CH_4 reacts with the surface of the platinum catalyst, it breaks down with a series of surface reactions as shown in the following mechanism.

$CH_4 + 2PT(S) \Rightarrow CH_3(S) + H(S)$

$CH_3(S) + PT(S) \Rightarrow CH_2(S) + H(S)$

$CH_2(S) + PT(S) \Rightarrow CH(S) + H(S)$

$CH(S) + PT(S) \Rightarrow C(S) + H(S)$

Hence, intermediate species including CH_3, CH_2, CH, and C that result from surface reactions are not required as input data.

It should be noted that the designation of a surface reaction species should be differentiated from a gas phase species. Chemkin does this by additional annotation of the surface species with (S) after the species.

In addition to the Gas-Phase Chemkin Mechanism file, the Gas-Phase Thermodynamic Database file is required. The first line of this file identifies it as containing thermodynamic data, while the second line provides the three temperatures used in the fitting process, a low temperature, break temperature, and high temperature. The remaining input consists of four lines for each species containing the elemental composition information and fitting coefficients for calculating specific heat, enthalpy, and entropy. The surface mechanism file and transport database were also selected to complete the import process. Once imported, the material properties change to where the fluid consists of a “Chemkin imported mixture” rather than just air.

The inlet boundary conditions must be modified to specify the mole fractions of each incoming species. These values vary with each equivalent ratio and fuel percentage. For this study, a fuel percentage of 4% and equivalent ratio of 1.0 was chosen. This corresponded with mole fractions of CH_4, O_2, and N_2 as 0.04, 0.08, and 0.88 respectively.

The absolute tolerance for the surface species was changed to 1e-12 and the relative tolerance for the surface species was changed to 1e-5. To tell Fluent to calculate reactions on the surface of the

platinum wire, the boundary conditions for the wire wall needed to be modified as well. This was done by checking the "Reaction" box under the species tab for the wire wall boundary conditions. All other settings in Fluent remained the same as the heat transfer model.

Initial attempts at using Chemkin were done with a straight wire simple model to more quickly troubleshoot errors. The problem with the straight wire model is that it was not possible to collect experiment data to validate the results because of the small surface area exposed to reacting flow. It was made to just test model settings since convergence with the coiled wire model took several hours. To set the source term in W/m^3, both the volume and the power setting had to be adjusted to account for the smaller wire. The new wire volume is calculated either by hand or by clicking on the wire body in Ansys Design Modeler where the physical properties are displayed. The power setting also needs to be adjusted accordingly or else the resulting source term value will be much higher for a smaller wire resulting in inaccurately high temperatures.

FINDINGS; CONCLUSIONS; RECOMMENDATIONS

Figure 5 is a plot of ignition temperatures from experimental data using methane volume percent of 2-4% and equivalence ratios of 0.3 to 1.0. The ignition temperatures varied from 730K to 785K for all three data sets. As the equivalent ratio increases, the ignition temperature decreases. This suggests that as the fuel concentration increases in the mixture, it becomes easier to initiate surface ignition. In addition, decreasing ignition temperature with increasing fuel content suggests that oxygen is first covering the catalyst surface [12]. When compared to ignition temperatures of propane for a similar experiment, this data shows similar trends but with ignition temperatures of about 330K greater [6,13].

Figure 6 shows the experimental data for the average calculated heat generation using methane volume percentages of 2-4% and equivalence ratios of 0.3 to 1.0. It is shown that as the equivalence ratio increases, the rate of heat generation also increases and has a range of 4.8 W/cm^2 to 11.2 W/cm^2. The trend is quite linear for fuel volume percentages of 3% and 4% whereas with 2% the heat generated is only linear up to equivalence ratio 0.7. Overall, more heat is generated as the fuel mixture becomes more rich. This upward trend is consistent when compared to a similar experiment using propane for a fuel volume percent of 2% [6]. However with propane, the heat generation rate was about 15 W/cm^2 at stoichiometric, a considerable increase from the value of 8 W/cm^2 using methane.

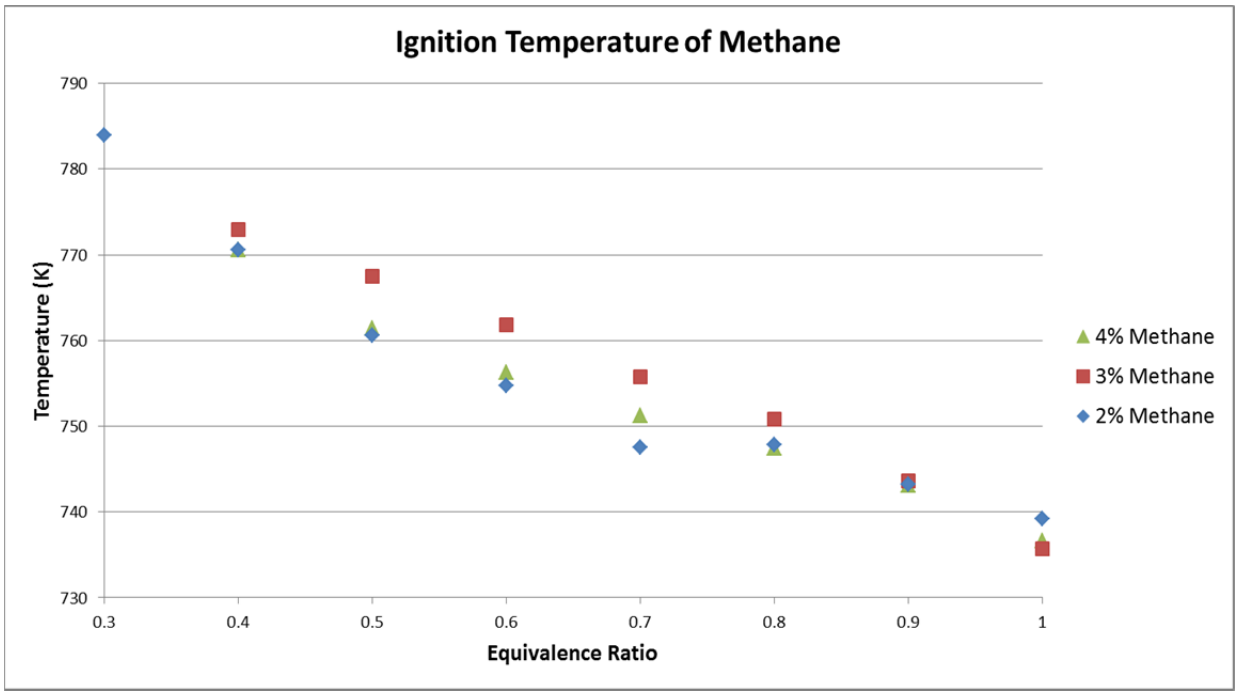

Figure 5: Ignition temperature vs. equivalence ratio at different fuel percentages.

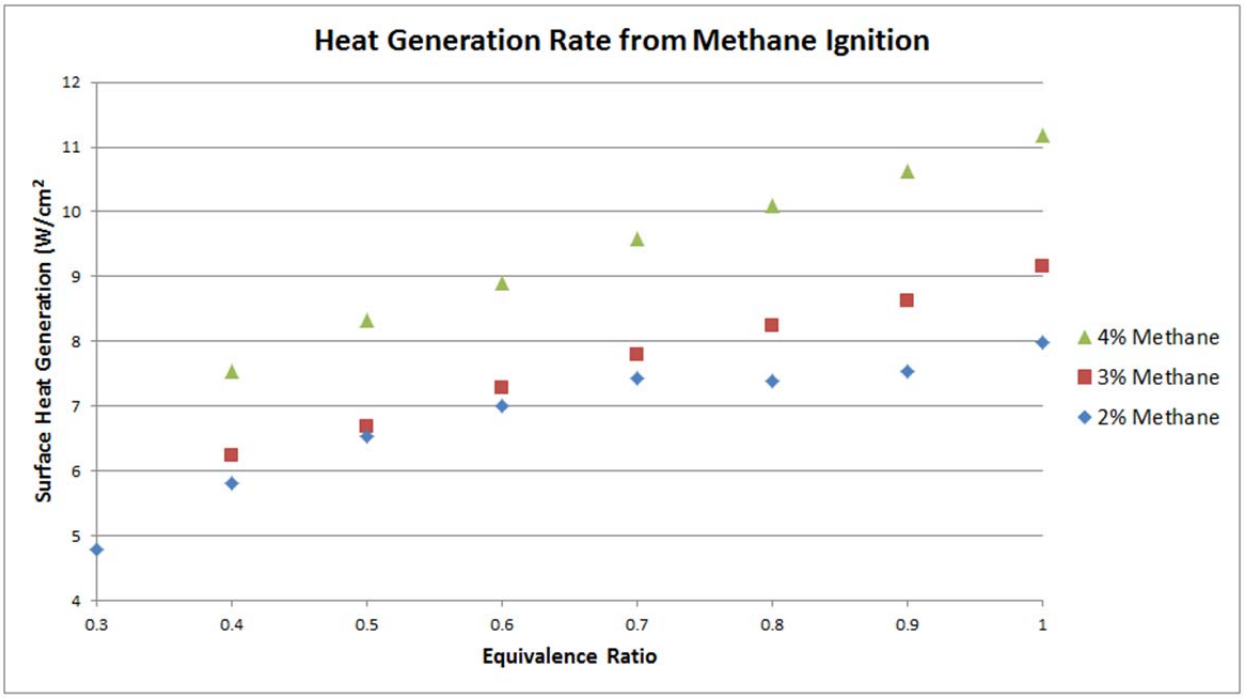

Figure 6: Heat generated vs. equivalence ration at different fuel percentages.

Fluent calculated a solution for each watt of power being assigned as a source term from 1W to 12W in increments of 1W. The volume averaged wire temperature, contours of temperature, and wire temperature profile plot could be reported for each calculation. Contours of temperature and wire temperature profile plots are shown in Figure 7 and Figure 8. These plots are useful to ensure that heat is being transferred to the surrounding fluid in an expected manner. The wire temperature profile plot shows that the upstream side of the coil is at a higher temperature than the downstream side and the ends of the wires approach room temperature which was set as a boundary condition in Fluent. Other plots such as velocity and pressure contours are also useful to determine if model parameters are working properly. The volume averaged wire temperature report calculates the average wire temperature by taking a weighted average by volume of the temperatures of each grid point in the wire. This temperature value is used to compare to the average wire temperature calculated for the experimental data. Figure 9 shows the experimental wire temperatures plotted against the values generated by Fluent.

Looking at Figure 9 it is evident that there is a fairly close fit between the experimental data and the model data at wire temperatures below 700K. At the higher temperatures, there is a deviation from the experimental data. The reason for this deviation is not yet clear.

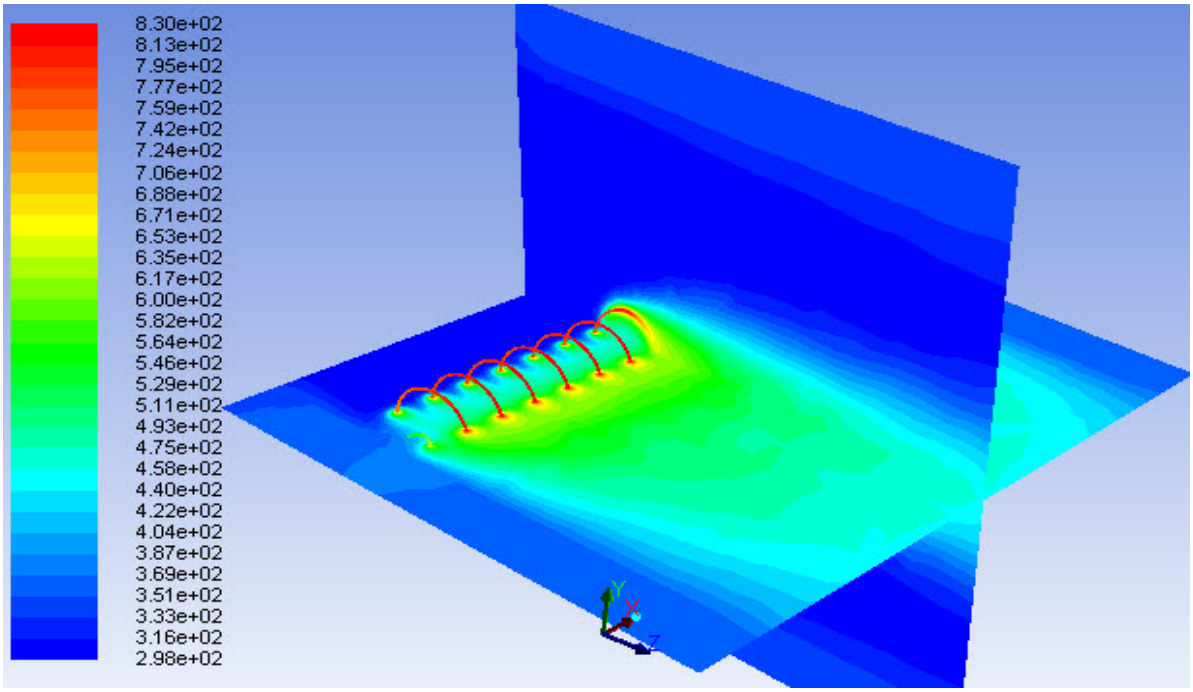

Figure 7: Coiled wire and flow temperature contours with power set to 10W.

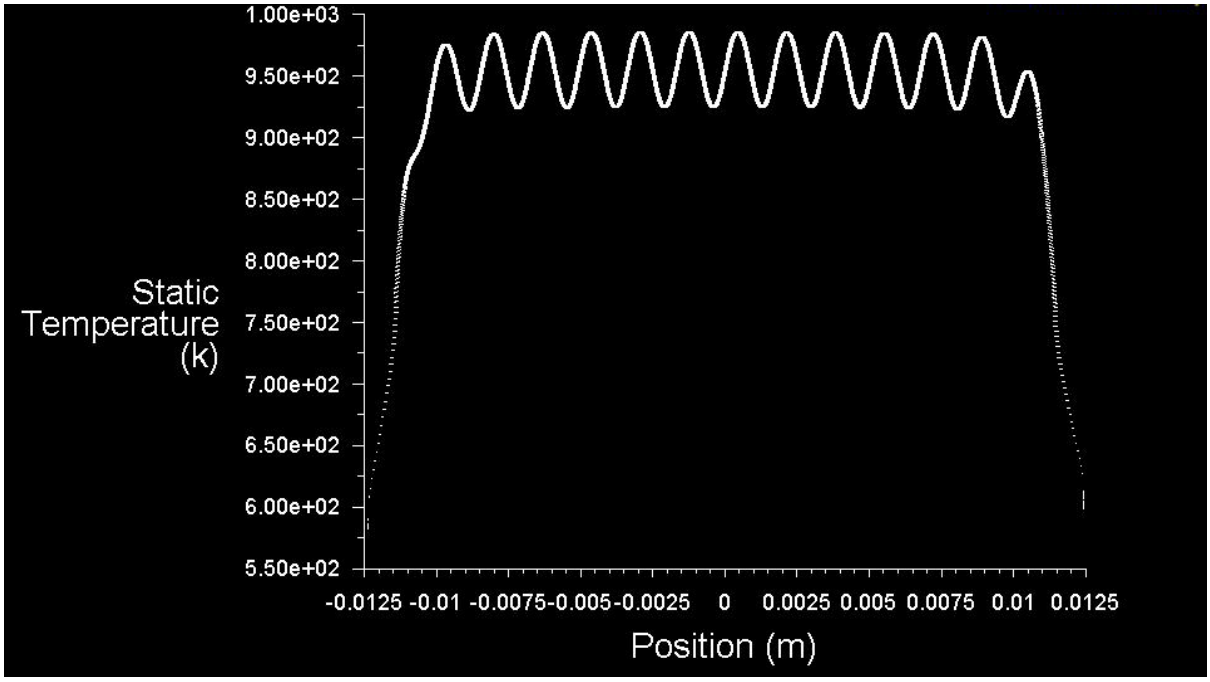

Figure 8: Temperature distribution of the coiled wire with power set to 10W.

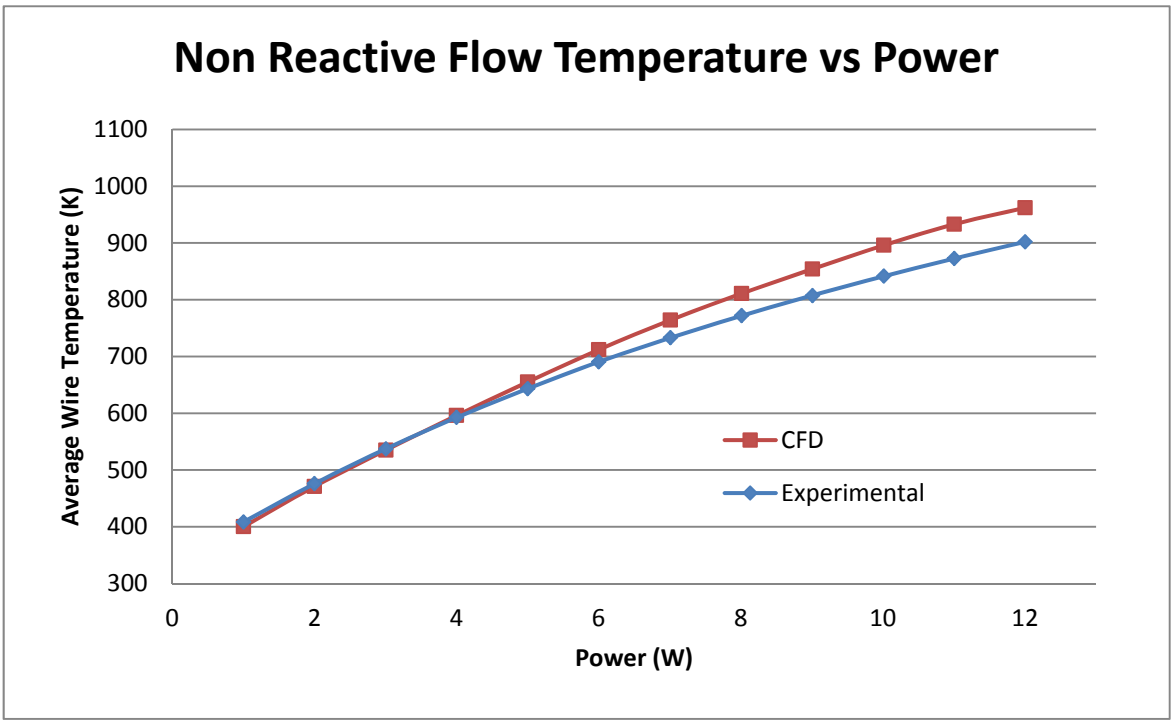

Figure 9: Average wire temperature vs. power plot.

The results for the straight wire model show a heat transfer temperature profile to be more linear than that of the coiled wire. This is likely because of the differences in heat transfer between the straight wire and the coiled wire. The surface area of the straight wire is about 1/3 that of the coiled wire, leading to increased convection from the coiled wire. The straight wire is in crossflow, whereas the coils see both crossflow and parallel flow. Also, thermal radiation exchange exists between adjacent coils of the coiled wire, whereas the straight wire cannot 'see' itself for radiation exchange. When the Chemkin solver was applied, the results show a temperature differential between the non-reactive flow and reactive flow of 24, 43, and 72 degrees Kelvin for 7, 8, and 9 Watts respectively. When referencing Figure 9 for 4% methane at 1.0 equivalence ratio, we see that when the baseline curve is at 800K, the surface reaction temperature is about 30K higher. When looking at Figure 10, there is a similar increase in temperature. While the correlation is encouraging, this only serves to check model settings and not validate data.

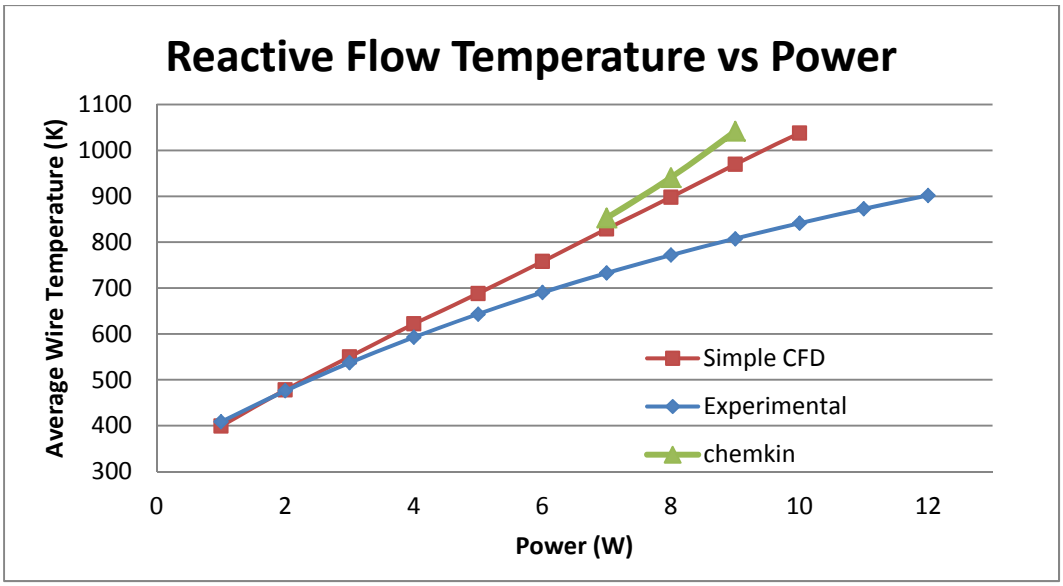

Figure 10: Temperature vs. power of simple Chemkin model.

When attempts were made to compute the model using the full 50 species gas-phase mechanism, the software was unable to compute a single iteration despite leaving the computer to run for 10 hours. After several attempts resulting in similar outcomes, it was determined that either the computer used had insufficient computational power (number of CPU cores and memory quantity) for the current 3D model or there was an unknown incompatibility with the gas-phase mechanisms and the current settings.

When testing only heat transfer from the wire, successful settings for the simple model worked on the coiled model as well with only much longer convergence time. It was assumed that once the simple model was working with Chemkin that the same settings would work with the coiled wire as well but that has thus far not been the case. Despite success using the simple model with Chemkin, there have not been successful results when working with coiled wire model. The reasons for this are not yet clear.

Summary and Conclusions

Experimental data was recorded for an electrically heated platinum coil in cross flow. The average wire temperature was calculated as a function of power input. A finite element model was created using Ansys Fluent. Model geometry, mesh, properties, and boundary conditions

were set. The program was run at each of 12 source terms that varied from 1W to 12W of power input, and the resulting average temperatures were recorded.

The model fit the experimental data fairly well from 400K to 700K and from 700K to 900K there was a slowly increasing discrepancy. This trend was also evident when the model was initially calculated using a more simple straight wire geometry. Chemkin calculations have been successful for the simple model but there have not been successful results when attempting to use Chemkin with the coiled wire geometry and mesh.

Future work may include refinement to the heat transfer model to try and minimize the temperature discrepancy. In addition, it is worthwhile to collect an independent temperature measurement of the catalyst using a high definition infrared camera. Additional work will be required to troubleshoot the reasons for the lack of convergence when using Chemkin with the coiled wire model.

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