CATALYTIC IGNITION TEMPERATURES OF PROPANE-OXYGEN-NITROGEN MIXTURES OVER PLATINUM

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16. Abstract

The A platinum (Pt) wire was used to study surface reactions with fuel-lean mixtures of propane and oxygen in a plug flow reactor under low Re flow regimes. The average wire temperature, catalytic ignition temperature, power at ignition, and heat generation were determined by measuring the voltage of current supplied to 127 μm and 203 μm 'seasoned' Pt wires. The average wire temperature and catalytic ignition temperature are reported with a 3 percent error, while the average power and power at ignition are reported with an 8.5 percent error.

A one-step surface reaction model was used to find values of the ratios of the sticking coefficients SO2;O/SF;O = 5.25±12%, the pre-exponential constant for oxygen desorption, AO2;D = 1.99E12±165% (1/s), and the activation energy for oxygen desorption, EO2;D = 47±17% kJ/kmol, for propane-oxygen mixtures on Pt. These values were within the uncertainty reported for other hydrocarbon fuels. The model predicted the ignition temperature to within 1%. However, predicted rates of heat generation were as much as two orders of magnitude higher than measured.

The results will assist the design and modeling of catalytic igniters used in engines burning under fuel-lean conditions. Future research will introduce water and use aqueous ethanol.
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Catalytic ignition; demonstration projects; laboratory; fuels; environmental impacts

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EXECUTIVE SUMMARY

A platinum (Pt) wire was used to study catalytic surface reactions with non-flammable fuel-lean mixtures of propane and oxygen, in a tubular plug flow reactor under low Re flow regimes. The average wire temperature, catalytic ignition temperature, power at ignition, and heat generation have been calculated for a 127 μm and 203 μm Pt wire from experimental voltage measurements and current supplied to the wire. Trends in the data were consistent with that of prior researchers and proved that the apparatus and methods were accurate. New data has been obtained for propane-oxygen mixtures with "seasoned" Pt wires, wires that have been exposed to surface reactions. The average wire temperature and catalytic ignition temperature are reported with a 3percent experimental error, while the average power and power at ignition are reported with an 8.5 percent experimental error.

Progress was made in applying a one-step surface reaction model, the "Perger Model," to the ignition temperature data. The model was first used to find values of the ratios of the sticking coefficients $S_{O2;O}/S_{F;O} = 5.25\pm12\%$, the pre-exponential constant for oxygen desorption, $A_{O2;D} = 1.99E12\pm165\%$ (1/s), and the activation energy for oxygen desorption, $E_{O2;D} = 47\pm17\%$ kJ/kmol, for propane-oxygen mixtures on Pt. The values of these three parameters were within the uncertainty of those reported for other hydrocarbon fuels and propane. The model was then used to predict the ignition temperature and heat release from the Pt surface at ignition. Good agreement to within 1 percent was obtained between predicted and experimental ignition temperatures. The consistency of the predicted heat release varied with both equivalence ratio and wire diameter. Predicted rates of heat generation were as much as two orders of magnitude higher than measured. The best agreement, which was only four times greater than measured, was obtained for the 203 μm wire.

1. INTRODUCTION

The purpose of this project was to study the heterogeneous effects of a Pt catalyst exposed to propane-oxygen mixtures in extended operation, which will be referred to as a “seasoned” wire. The experimental data has been used to apply a one-step reaction rate model, the “Perger Model”, to predict the ignition temperature and heat release from the Pt wire. Despite the shortcomings found by application of the Perger Model in predicting the heat generation rate, it is a good first order model to begin the creation of a more accurate model. Better heat transfer rate characterization is one area of improvement for future use of the Perger Model. Upon successful modeling of the heterogeneous reactions with Pt, further experimental data will not be needed. The durability and catalytic data gained from this research the design of catalytic igniters designed to operate engines under homogeneous charge, catalytically assisted compression ignition (HCCCI).

A tubular plug flow reactor was used under low Re flow to study the interaction of propane-oxygen mixtures with a seasoned Pt catalyst [1]. A seasoned wire is one that has been exposed to heterogeneous reactions. The reactor was first tested to ensure plug flow conditions. Once the apparatus and initial conditions were satisfied, data was collected on a range of propane-oxygen mixtures that were maintained below flammable limits and with a 127 μm and 203 μm wire. The average wire temperature, catalytic ignition temperature, power at ignition, and surface heat generation were then calculated. The ignition temperature data collected was compared with that of Cho and Law [2]. Although the catalyst used in their work was continually cleaned, this work relates to catalyst performance under continual operation or with a seasoned wire. Nonetheless, this comparison gave confidence that the apparatus and methods were accurate. This work has formed a foundation upon which continued research can be conducted on alternative fuels, more specifically with the inclusion of steam to the propane-oxygen as well as ethanol-water-air mixtures.

1.1 Background and Motivation

Research has been conducted at the University of Idaho over the past several years relating to HCCCI of aqueous ethanol, Aquanol, a blend of 35 percent water and 65 percent ethanol. A catalytic plasma torch (CPT) igniter or Smartplug® was developed that uses an in-cylinder platinum/rhodium catalyst to ignite an aqueous ethanol mixture [3–5].

Research at the University of Idaho started with a Yanmar three-cylinder, direct-injection (DI) diesel engine by Morton [6]. The engine was modified for homogeneous charge combustion using CPT igniter technology. Advances in the design of the CPT igniter were made to increase durability and effectiveness. A 10 percent increase in maximum power output and a 10 percent reduction in NO_x emissions were found while using Aquanol as compared to diesel.

This work was followed by Clarke [7], who obtained two 20 hp Yanmar engines, a dynamometer, and a 5-gas analyzer enabling him to more easily compare the performance of Aquanol to diesel. One engine was converted to run on Aquanol and the other was left in the stock condition to be used for comparison. Clarke [7] modeled ignition timing and focused on parameters that affect ignition timing that in turn affect the design of the CPT igniter. He found that ignition timing was controlled by the igniter length, core temperature, compression ratio, and that water concentration had little effect. With this knowledge, more adjustments were made to the engine and igniter and a 50 percent increase in peak power and a 12 percent decrease in NO_x were obtained. An increase in hydrocarbon and carbon monoxide emissions was found, but oxidative exhaust catalysts can control these pollutants.

The natural progression of this research led to the desire to test an engine under real world conditions. Valley Transit of Lewiston, Idaho donated a 1985 Ford Econoline Van to the University of Idaho. Cordon [8] determined the intricacies of converting the van to a dual-fueled vehicle, capable of operating on Aquanol or gasoline, creating a van that could be switched between fuels in less than an hour. Due to this conversion even the gasoline fuel economy and emissions were greatly improved. Test protocols for the dynamometer, fuel handling systems, and emissions analyzer were also established such that future work could continue per a standard basis.

Williams [9] continued this work by subjecting the dual-fueled van to a modified urban driving cycle to compare the emission and power characteristics of the two fuels. As was found with the previous research by Morton [6] and Clarke [7], there was a significant decrease in NO_x emissions and an increase in peak power. Significant advances were made in resolving cold starting issues by adding an engine coolant heater and by boosting the igniter amperage. These additions increased the engine block temperature and igniter temperature, aiding in the catalytic ignition of Aquanol under cold-starting conditions.

All of the research to date at the University of Idaho has been based on a comparison of emissions between engines fueled by Aquanol, diesel, or gasoline. One extremely important design difference to this comparison is that the gasoline engines were operated with exhaust cleanup, i.e., a catalytic converter. However, due to the lower combustion temperatures of Aquanol and hence the lower exhaust temperatures, the light-off temperatures of the stock catalytic converters were too high. Therefore, they were not useful in oxidizing any of the exhaust products from Aquanol combustion. Even without exhaust cleanup there was a decrease in NO_x from all test apparatuses during combustion of Aquanol as compared to gasoline.

These studies concluded that there were several advantages of Aquanol combustion, but cold starting remained an issue. A tubular plug flow reactor, as outlined by Patel [1] and used in this research, was constructed to investigate heterogeneous reactions. The information gained from these studies such as the ignition temperature and power required to ignite various mixtures of Aquanol; with variations in flow velocity, equivalence ratio, and pressure will help improve cold starting. The first step in this process, however, was to use a gaseous fuel and compare experimental results with data obtained by prior researchers, in addition to developing new results from the use of a seasoned wire. This will ensure that the data collected is accurate and the methods are sound. The next step will be the addition of steam to the propane-oxygen mixtures, collecting valuable information on the effect of steam to heterogeneous reactions.

1.2 Literature Review

The heterogeneous and homogeneous ignition of gaseous fuels over a catalyst such as platinum, palladium, or rhodium has been extensively studied [2, 10–19]. This research was done with catalysts that were cleaned during experiments or where data was replicated with new catalysts; the study reported here involved a catalyst that is operated continually without treatment - a seasoned wire. Research conducted on the catalytic ignition of hydrocarbon fuels is in agreement with Veser, et al. [13], when they detailed:

> These diagrams showed a clear distinction between the behavior of the saturated hydrocarbons and the unsaturated hydrocarbons. While the alkane-air mixtures show a decreasing ignition temperature with increasing equivalence ratio up to a minimum ignition temperature near the fuel-rich surface flammability limit, the olefins (alkenes) ignite at much leaner mixtures and display their minimum ignition temperature well into the fuel-lean side of the bifurcation diagram.

Cho, et al. [2], Vlachos [20], Veser, et al. [13], Veser, et al. [11], and Dogwiler, et al. [15] concluded that this was due to the surface adsorption/desorption properties of each fuel type. They determined that the differences in ignition temperature were due to the platinum surface being covered by oxygen molecules or hydrocarbon molecules. This phenomenon of surface adsorption/desorption was further investigated by Perger, et al. [18], where analytical equations were used to predict the heterogeneous ignition temperature, if you knew the adsorption/desorption properties of the gases used and had information about the test apparatus. This was accomplished by performing a heat balance on the system and from the Frank-Kamenetskii condition [21]. The Frank-Kamenetskii condition states that if the Biot number, based on gas thermal conductivity, is greater than 1, then the temperature of the solid surface is equal to the temperature of the gas. For the experiments here, Bi is on the order of 1. The Frank-Kamenetskii condition was assumed in order to obtain a 1st order simplification.
Catalysts have the effect of inducing combustion at lower temperatures and with lower equivalence ratios. These two effects decrease the maximum combustion temperature, lowering harmful NO_x emissions.

Research has shown that platinum (Pt) is the preferred catalyst to use in the ignition of hydrocarbons in air [10, 11, 20]. It was shown that Pt was able to ignite the full spectrum of equivalence ratios of various hydrocarbon fuels. Of special interest is the ignition of fuel lean or extremely fuel lean mixtures. Fuel lean mixtures have the advantage of creating fewer pollutants, particularly related to the emission of NO_x and CO. Due to the lower temperatures of heterogeneous ignition, palladium (Pd) became polluted by oxides and created a stable oxide (PdO) inhibiting catalytic ignition, while Pt did not exhibit this affect [10]. Veser, et al. [13], discovered that Pt exhibited no oxide formation from alkenes ignited under fuel-lean conditions. Hence, Pt was chosen as the catalyst for this research.

A literature search revealed a number of efforts at creating models to predict the ignition temperature of gaseous fuels on catalytic surfaces while none of these models attempted to predict heat release from the surface [11, 13, 18, 19, 21, 23–27]. Rinnemo, et al. [19], used a kinetic model based on a three-step mechanism for CO oxidation on Pt, combined with time-dependent mass and heat transport. A cylindrical computation domain, using the governing equations in cylindrical coordinates, with application of a modified Lagrange transformation led to a one-dimensional governing equation eliminating convective terms for Deutschmann et al. [26], with CH_4, CO, and H_2. Behrendt, et al. [27], solved the Navier-Stokes equations describing the gas phase with boundary conditions, which yielded a differential-algebraic equation system that could be solved using LIMEX [28, 29], with CH_4 and H_2. A simplified heat transfer model using a Langmuir-Hinshelwood mechanism, as illustrated in Figure 1.1 for hydrogen oxidation on Pt, for the adsorption and desorption of simple alkanes was used by Veser and Schmidt [11, 13], for various fuels. Deshmukh and Vlachos developed a detailed microkinetic model using a computer-aided model reduction strategy that included reaction path analysis, sensitivity analysis, partial equilibrium analysis, and simple algebra to deduce the most abundant reaction intermediate and rate-determining step for fuel lean methane/air mixtures over rhodium (Rh). Perger et al. [18, 21], created a one-step reaction model from curve fitting ignition temperature data, which in turn could be used to predict the ignition temperature. This one-step reaction rate model presented by Perger, et al. will be used and expanded to include the heat release from the Pt surface at ignition. The ideas and apparatus used in their work more closely follows the apparatus and methods used in this work.

The predictions and experimental results outlined will be closely followed to ensure that the experimental apparatus is properly set up and is therefore consistent with the literature found in this review.

1.3 Catalysis

The Pt wire functions as a catalyst, constant temperature heater, ignition detector, and temperature transducer [2]. The wire initiates heterogeneous reactions with the addition of small amounts of fuel and electrical power. The electrical power is controlled by a variable power supply operated in constant current mode, thus maintaining a constant heat supply to the wire making the wire a constant temperature heater. The average wire temperature is then determined by monitoring voltage changes across the wire. Small changes in voltage, and thus temperature, when the wire is exposed to fuel mixtures, indicates or detects the point at which ignition occurs.

As discussed by Perger, et al. [18], when a catalyst such as platinum is introduced into a gaseous fuel and oxygen mixture the platinum surface is covered by either fuel or oxygen depending on the sticking coefficients for adsorption onto the surface. As the temperature of the wire is increased, the adsorbed species will begin to desorb from the wire surface or react and hence the ignition temperature is controlled by the rate at which the gas species adsorb and desorb from the Pt surface with wire temperature. Figure 1.1 demonstrates the oxidation of hydrogen on a Pt surface graphically [30, p 80].

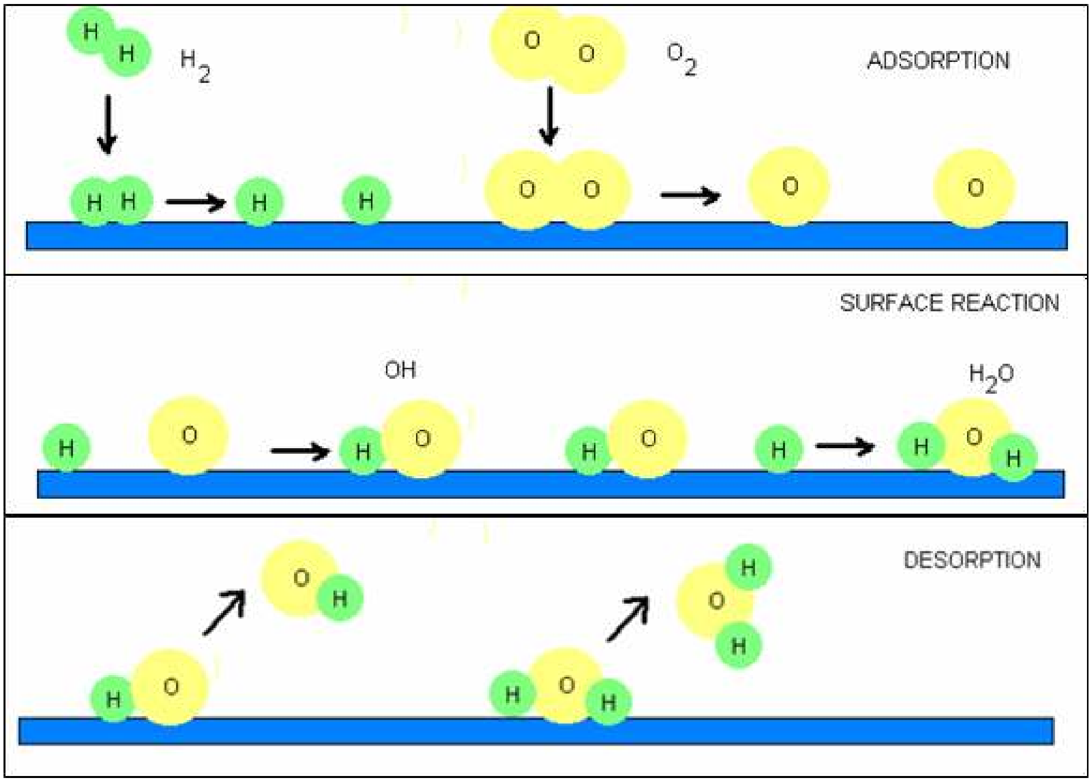

Figure 1.1: The process of hydrogen oxidation on platinum. Hydrogen and oxygen molecules adsorb onto the surface, dissociate, react, and products desorb.

This would be similar to what would occur for propane on Pt although this would be a much more complex reaction. This process can be describes as follows, for hydrogen oxidation on Pt.

1. Diffusion of H_2 and O_2 to the surface
2. H_2 and O_2 adsorb onto the surface and dissociate into 2H and 2O
3. OH formed in a surface reaction; OH and H surface reaction forms H_2O
4. Desorption of OH and H_2O from the surface
5. Diffusion into the gas phase

This process has been determined for methane oxidation on platinum [25]. The oxidation of propane on Pt has not yet been fully developed due to the complication of higher order heterogeneous hydrocarbon reactions.

1.4 Description of the Problem

The purpose of this research was to study heterogeneous reactions with seasoned Pt wires and attempt to model this data numerically. The data collected from seasoned wires will mimic the response of the CPT igniter or Smartplug under operation in an internal combustion engine. The wire temperature at which catalytic reactions occur and the amount of power that must be supplied to the wire to initiate these reactions will contribute to future CPT igniter designs and improve ignition timing models created at the University of Idaho.
Testing was done to enhance the available knowledge of wire seasoning, the effects of platinum surface geometry, the power required to ignite the mixture, the heat generated from catalytic surface reactions, and consequently led to the application of a one-step reaction rate model for the heterogeneous ignition of propane-oxygen mixtures over platinum.

The one-step model was used to predict the ignition temperature and heat release from the wire. The goal was to obtain a simple model capable of predicting the ignition temperature and heat release. This could potentially eliminate the need to collect experimental data. The experimental ignition temperature was then compared with a numerical model, the Perger Model, as outlined by Perger, et al. [18, 21], and the experimental work of Cho and Law [2]. This Perger Model was then extended to predict the heat release at ignition, which has not been performed based on a review of the literature.

Additional ignition temperature, ignition power, and heat release data was also collected for two different wire diameters. The experimental data collected and presented in this research relates to the catalytic effects of seasoned wires that also has not been performed based on a review of the literature.

2. METHODOLOGY

This section describes the apparatus and methods used to measure the average catalyst surface temperature and the ignition temperature, the power supplied to the wire at ignition and the heat generated from surface reactions. A tubular plug flow reactor was used as described by Patel [1]. Prior to experimental data collection, it was necessary to ensure that the nozzle and reactor were operating under plug flow conditions using a hot-wire anemometer as described below.

A plug flow reactor is defined as an ideal reactor with the following assumptions [22, p 200]:

1. Steady-state, steady flow.
2. No mixing in the axial direction. This implies that molecular and/or turbulent mass Diffusion is negligible in the flow direction.
3. Uniform properties in the direction perpendicular to the flow, i.e., one-dimensional flow. This means that at any cross section, a single velocity, temperature, composition, etc., completely characterize the flow.
4. Ideal frictionless flow. This assumption allows the use of the simple Euler equation to relate pressure and velocity.
5. Ideal-gas behavior. This assumption allows simple state relations to be employed to relate T, p, , Y_i, and h.

A hot-wire anemometer was used to determine the velocity profile throughout the length of the quartz reactor tube. The anemometer was setup as in Figure 2.1 such that the hot-wire probe was connected to the anemometer and an oscilloscope to measure voltage.

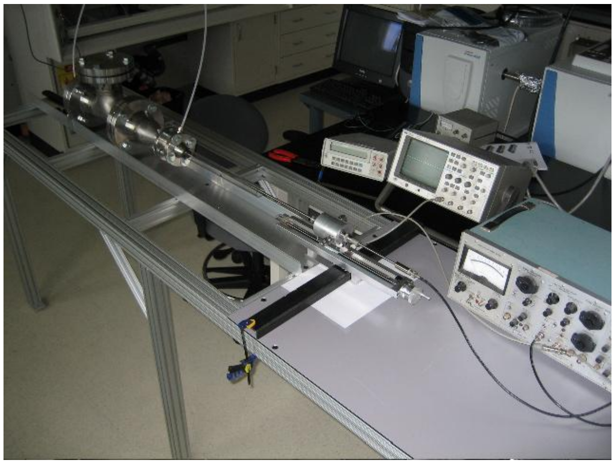

Figure 2.1: Hot-wire anemometer apparatus setup. The hot-wire probe is connected to the anemometer that is connected to an oscilloscope to monitor the voltage.

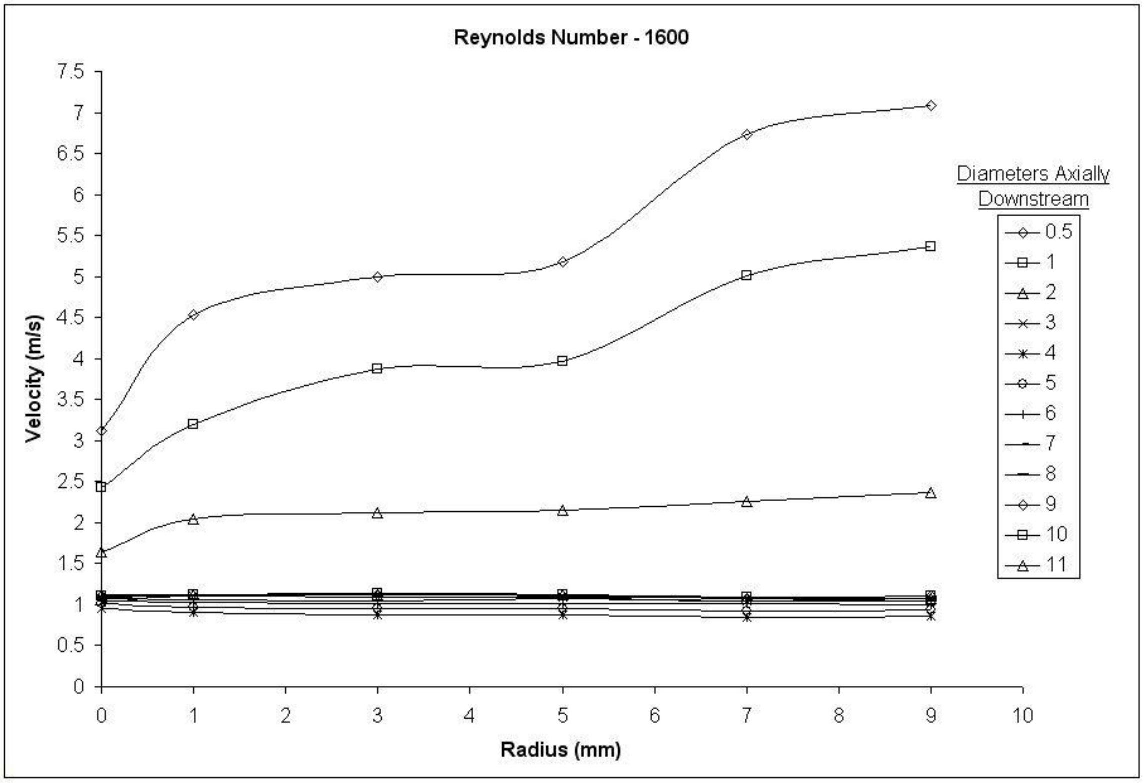

Figure 2.2: Velocity versus radius as a function of the diameters downstream. At approximately 3 diameters downstream of the mixing nozzle the gas velocity is constant across the diameter of the quartz tube.

The probe was attached to a uni-slide for stable and precise movement along the reactor tube. At each point where the probe was setup the voltage and hence the velocity of the flow could be determined as discussed by Lounsbury [34]. The probe was then moved in 2 mm increments radially across the tube and in integer numbers of diameters downstream. The flow velocity was changed from (2-45) $^{L}/_{min}$ to ensure that a constant velocity profile could be obtained under large variations in flow. It was found that from approximately 3 to 11 diameters downstream the velocity across the reactor was constant as seen in Figure 2.2. Hence, the reactor can be assumed to operate under plug flow conditions [22, p 200]. The data shown was collected for a Reynolds number of 1600, which corresponds to a flow velocity of 17 $^{cm}/_{s}$. Similar results were obtained for all tested flow rates.

All experiments were performed with propane-oxygen mixtures diluted with nitrogen at a total flow rate of 5 $^{L}/_{min}$. These mixtures were below the flammability limit due to the volume percentage of propane and oxygen as shown in Figure 2.3, Lewis and von Elbe [31]. The red zone in the figure corresponds to flammable gas mixtures and hence any other mixture of propane and air is non-flammable. Any flammable mixture could also be rendered inflammable with nitrogen dilution. The figure shows that with the addition of approximately 42 percent nitrogen, beyond that in air, any flammable mixture could be rendered non-flammable. It also shows that with approximately 12 percent or less oxygen in a given gas mixture the mixture will be non-flammable no matter what percentage of propane is available. The tip of the peninsula shaped curve is the point at which inflammation cannot occur. This means that if there exists more than 42 percent nitrogen, beyond that in air, or less than 12 percent oxygen in any propane air mixture the mixture will be rendered non-flammable.

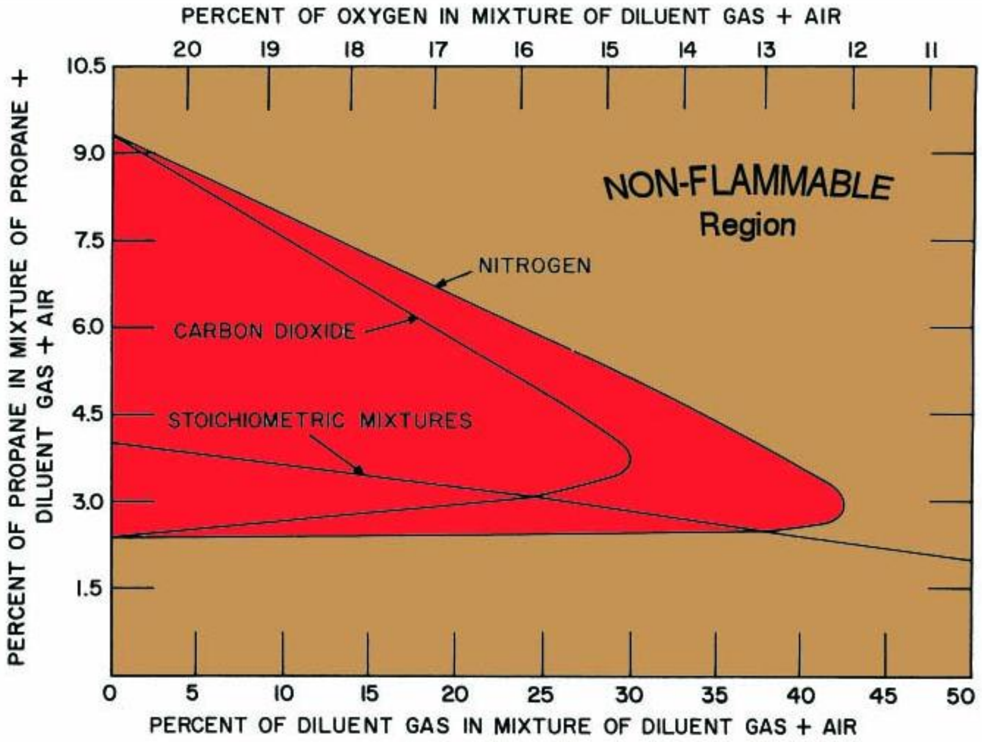

FIG. 352. Limits of flammability of propane in air diluted with CO_2 and N_2 (Coward and Jones). Room temperature and atmospheric pressure.

Figure 2.3: Flammability limits for propane-air mixtures diluted with nitrogen [31].

A modified equivalence ratio, φ, was used for all data sets and was defined as the ratio of the mass of propane to oxygen divided by an equivalent stoichiometric ratio. This was done so that an equivalent data comparison could be performed with Cho and Law [2].

2.1 Experimental Apparatus

Experiments were conducted with propane-oxygen mixtures with nitrogen as the diluent. The three gases were individually metered through Porter mass flow meters. As shown in Figure 2.4, propane diluted with nitrogen enters from the left and oxygen is introduced into the mixing nozzle near the center of the figure. The two gas streams then mix through the mixing nozzle and a steady stream of constant velocity gas mixture moves over the coiled platinum wire. The wire was electrically heated by an HP6673A variable power supply, operated in constant current mode. Changes in the voltage across the wire were manually recorded, using a four-point voltage measurement, with an HP3468A multimeter. This voltage measurement technique eliminated errors incurred by the resistance in the electrical leads, thus measuring only the voltage drop across the Pt wire.

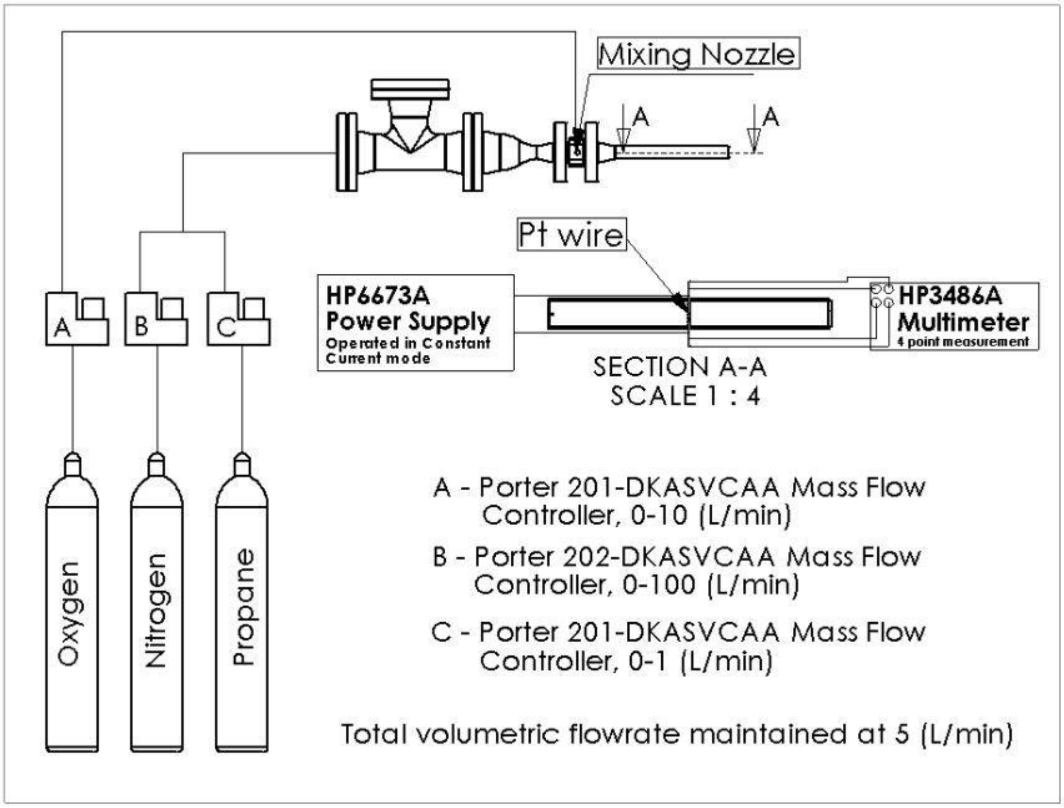

Figure 2.4: Experimental schematic. Propane and nitrogen enter the reactor from the left and oxygen enters at the mixing nozzle; the two gas streams then mix and a constant velocity gas mixture at 5 $^{L}/_{min}$ flows over the Pt wire. The wire is then heated by a constant current provided by the power supply and the voltage manually recorded using a 4 point measurement with the multimeter.

Data was collected for fixed volume percentages of oxygen, from $5\% \leq x_{O_2} \leq 20\%$ in 2.5% increments and for fixed volume percentages of propane, from $1\% \leq x_{C_3H_8} \leq 2\%$ in 0.5% increments. All experiments were run through an equivalence ratio from $0.1 \leq \varphi \leq 1$ in 0.2

increments, all while maintaining a non-flammable mixture at a total volumetric flow rate of 5 $^{L}/_{min}$. Once again, for these experiments, is defined as the ratio of the mass of propane to oxygen divided by an equivalent stoichiometric ratio. The gases were turned on and allowed a few minutes to reach a steady-state condition, as was the power supply, which required one hour to stabilize.

2.2 Experimental Methods

The Pt wire acts as a micro-calorimeter, monitoring small changes in heat flow due to voltage fluctuations. This simple voltage measurement enables the detection of the heterogeneous ignition temperature, ignition power, and surface heat generation as will be explained below. A constant current is being supplied to the wire, hence the change in resistance can be obtained by Ohm's Law

$$V = I\,R \tag{2.1}$$

by measurement of the voltage drop across the wire. The power required to maintain the wire at a given temperature in a non-reacting flow can then be determined from this new value for R and the current supplied to the wire

$$P = I^2 R \tag{2.2}$$

The new wire temperature is found by a linear correlation of the electrical resistance of the material with temperature [32, p 245]

$$R = R_o\left[1+\alpha\left(T-T_o\right)\right] \tag{2.3}$$

where R_o is the resistance at T_o and α is the linear temperature coefficient of resistance of the catalyst material, with α= 0.003927 for platinum. These three parameters can be calculated and are a function of the material and experimental conditions. More specifically, R_o is defined as

$$R_o = \frac{\rho_r l}{A} \tag{2.4}$$

where ρ_r is the electrical resistivity being 1.10E07 μm for platinum, l is the length of wire, and A the cross-sectional area. The length l was determined experimentally by applying a small amount of current through the wire ~0.01 A and calculating the average wire temperature. The theoretical length was then modified such that the average wire temperature was approximately room temperature for this small current value. This is assuming that the actual temperature of the wire remains constant at this current value. This was done because the actual length of the wire is not the same as that needed to calculate the initial resistivity. The length needed for calculation of the initial resistivity, is the wire length between the electrical clips supplying current to the wire that was not easily measured.

The wire was first heated in a stream of compressed air and the temperature of the wire determined as discussed above. Then the wire was exposed to various propane-oxygen mixtures and the average wire temperature determined once again. The point at which a clear difference in the power requirement for non-reactive and reactive mixtures was first observed, marked the critical point of catalytic ignition. This is shown in Figure 2.5. The electrical power or current to the wire was incrementally increased until at Point 1 reactions occurred at the Pt surface, and an immediate increase in overall power and temperature was observed. Thus, the temperature of the wire at Point 1 marked the critical point of catalytic ignition. The temperature at this point of heterogeneous ignition is what will be referred to as the "ignition temperature." Also, the power at this point will be referred to as the "ignition power."

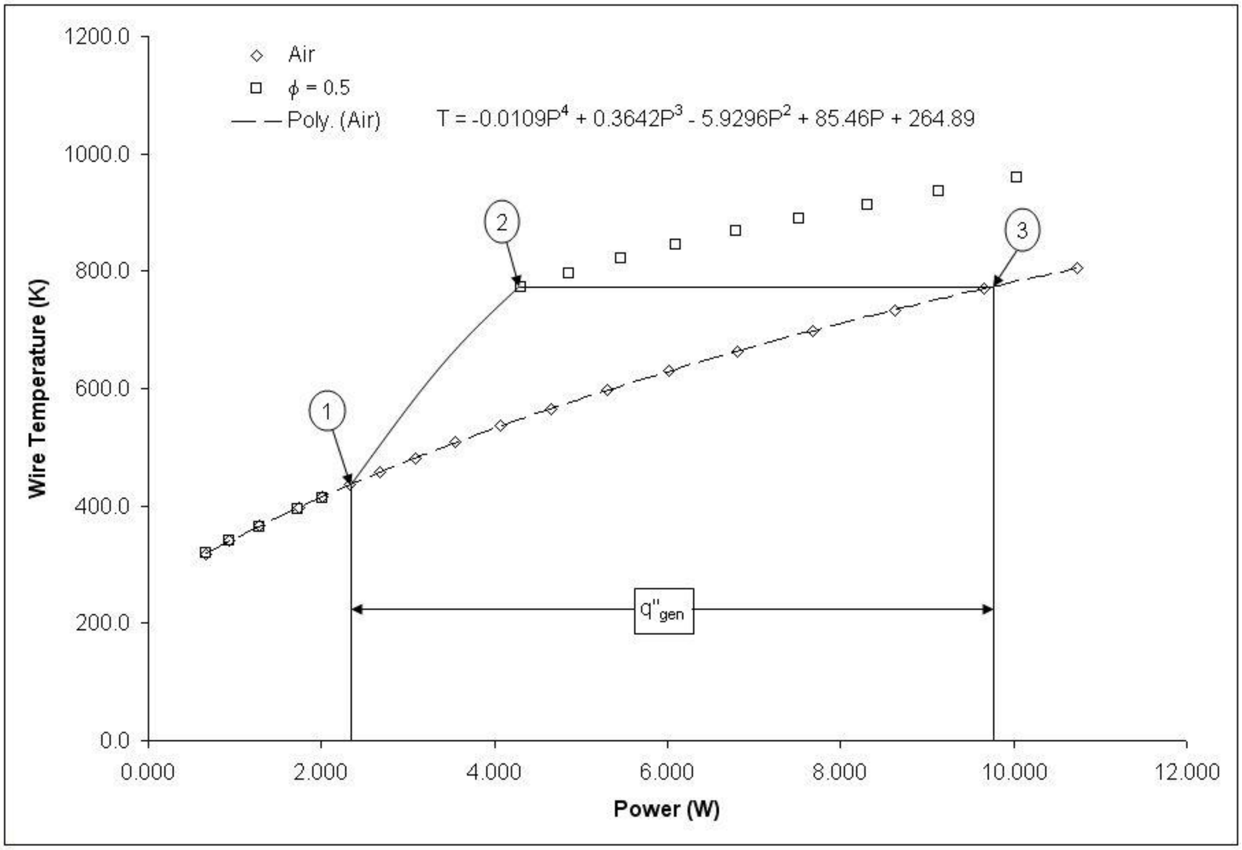

Figure 2.5: The process of calculating the heat generated from catalytic surface reactions, q_{gen}''. Power is incrementally increased until at Point 1 surface reactions occur and an increase in temperature and power is seen up to Point 2; the power required to maintain this new temperature in air is marked by Point 3. Therefore, the difference in power between Points 3 and 1 is therefore the heat generated from catalytic surface reactions.

The ignition temperature was based on an observed increase in power and temperature from that of non-reactive flows. The increase in the measured power from that of the wire in air, at the same temperature, is generated by catalytic surface reactions. The same amount of electrical power was supplied to the wire under non-reactive and reactive flows. Hence, the increase in power and temperature across the wire was the heat generation from catalytic surface reactions, q_{gen}''. Figure 2.5 shows how this is quantified. Point 1 represents the initiation of reactions on the surface, which caused an increase in power and temperature up to Point 2. If the wire were to be maintained at this new temperature in air, the power necessary would correspond to Point 3. The difference between Points 3 and 1 represent the heat generated from catalytic surface reactions. The power at Point 3 is calculated by substituting the temperature at Point 2 into the 4th order polynomial shown in Figure 2.5. Figure 2.5 shows this process for an equivalence ratio of 0.5 with 20 percent O_2 by volume. The process is identical for any equivalence ratio of interest.

3 EXPERIMENTAL RESULTS

The propane-oxygen mixtures were run with a total flow rate of 5 $^{L}/_{min}$ using either a coiled platinum wire 15.24 cm in length and 127 μm in diameter or 9.52 cm in length and 203 μm in diameter. The two different wires were used to determine if the ignition temperature, ignition power, or heat release were independent of wire geometry since the wires had equal surface areas. Data was first collected for air, to obtain the baseline comparison between the temperature of the wire in non-reactive versus reactive flows. Data was then collected for a fixed volume fraction of oxygen or propane. Only a few data points at lower equivalence ratios were collected for oxygen fractions above approximately 12 percent because as the equivalence ratio increased the gas mixture moved into the flammable region. The addition of 45 percent more nitrogen could have eliminated this limitation as shown in Figure 2.3. However, this would increase the total flow rate of the gas mixture and it was desired to maintain a flow rate not greater than 5 $^{L}/_{min}$.

The average wire temperature and calculated ignition temperature are reported with a 3 percent experimental error, while the average power supplied to the wire and the ignition power are reported with a 8.5 percent experimental error. This error is shown in Figure 3.1. However, it was not included in the remainder of the figures so that the data could be clearly presented.

3.1 Air Curves

The baseline air curve was generated by running purified compressed air at 5 $^{L}/_{min}$ and calculating the average wire temperature as discussed in Section 2.2. This curve forms the foundation for comparison of the average wire temperature in air with any propane-oxygen mixture. Data points were collected at various power levels and the wire temperature calculated. The results were plotted as average wire temperature versus power. Figure 3.1 shows, as expected, that as the power is increased across the wire, the temperature of the wire increases. The data points were then approximated by a fourth order polynomial to calculate the power at any wire temperature.

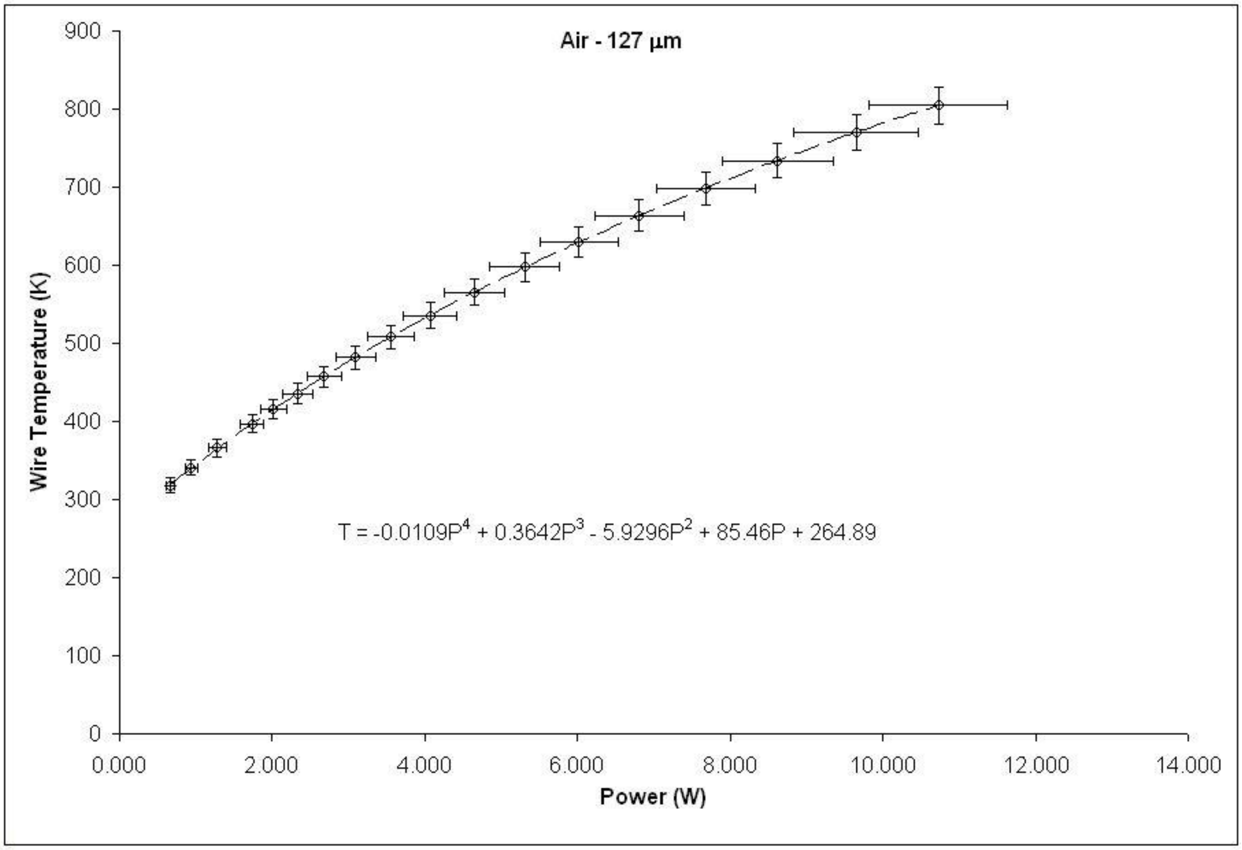

Figure 3.1: Wire temperature vs. power in air for the 127 µm wire. The data points were approximated by a fourth order polynomial as shown. A similar curve was obtained for the 203 µm wire [34]

3.2 Wire Temperature vs. Power

The work from Section 3.1 was then continued with either a fixed amount of propane or oxygen. Figures 3.2 and 3.3 show the change in wire temperature with respect to a fixed amount of oxygen for the 127 µm wire. Figures 3.4 and 3.5 show the same effect for a fixed amount of propane for the 127 µm wire. The power shown in these figures is a function of the constant current from the power supply and the heat generation from surface reactions. However, prior to observing surface reactions, it is based only on electrical input and the corresponding change in wire resistance.

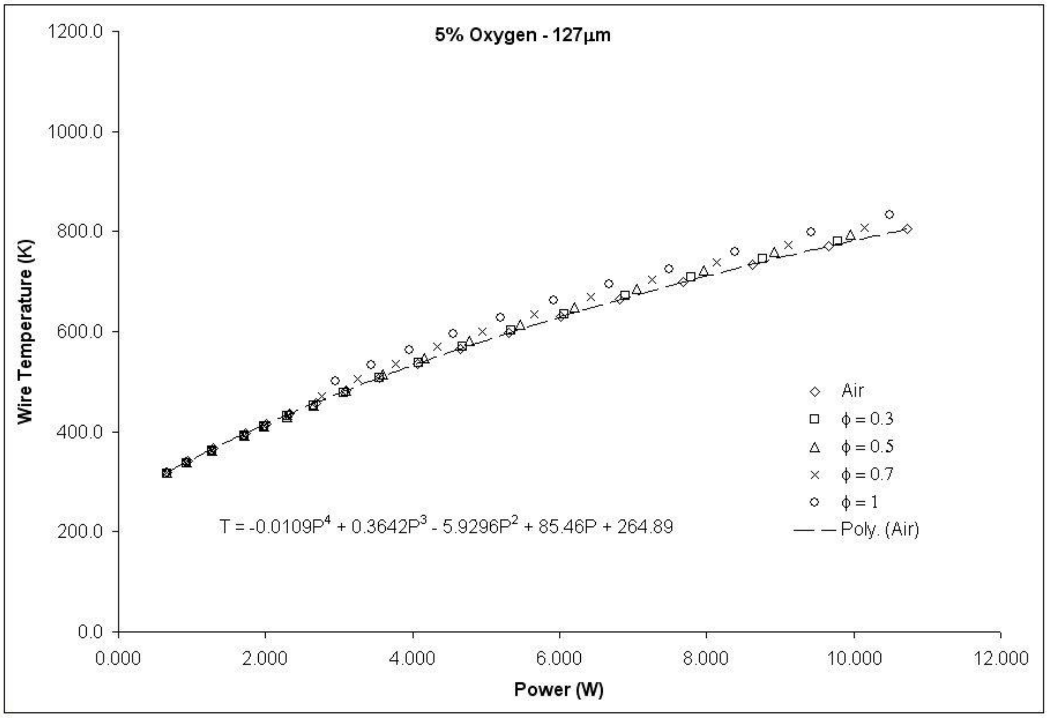

Figure 3.2: Wire temperature vs. power for 5 percent fixed oxygen with the 127 μm wire.

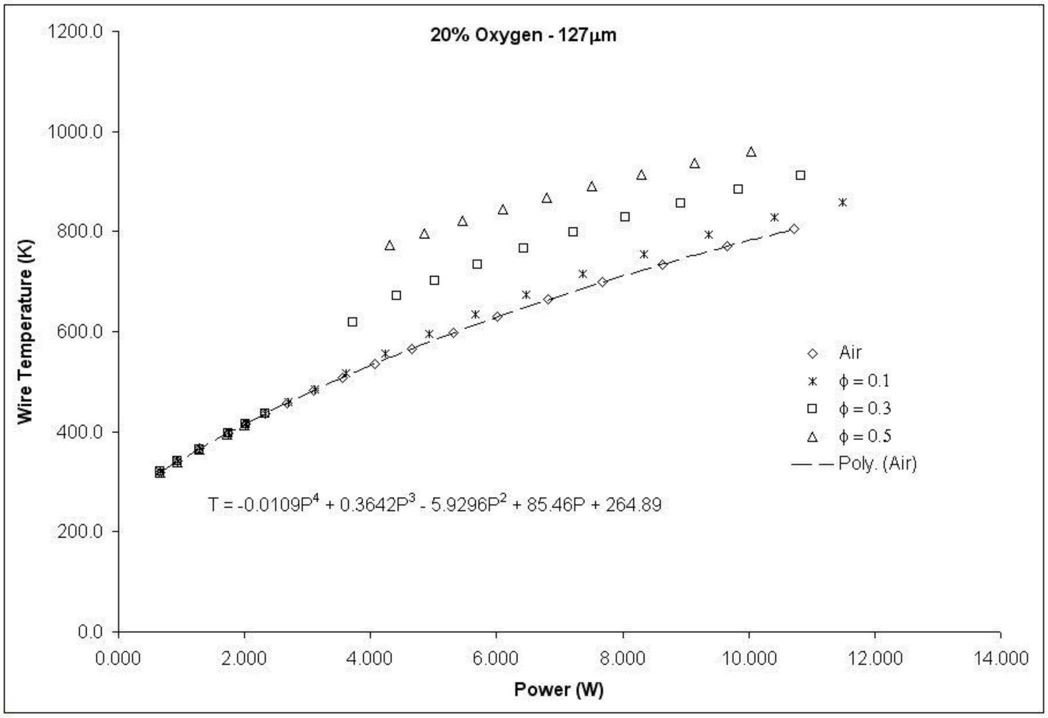

Figure 3.3: Wire temperature vs. power for 20 percent fixed oxygen with the 127 μm wire.

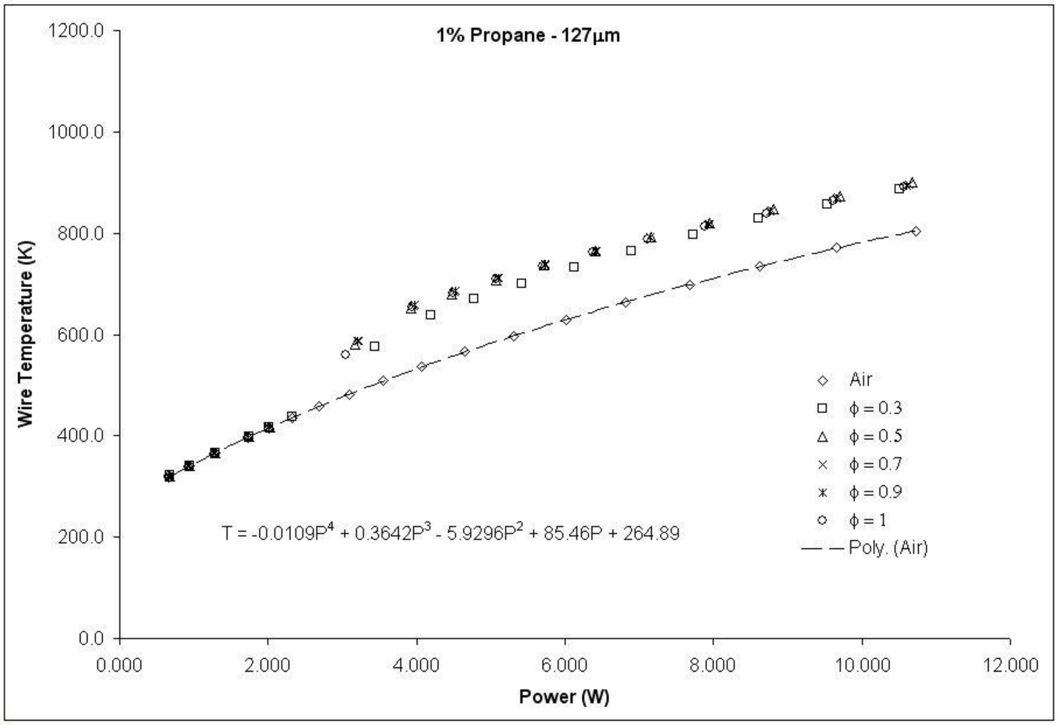

Figure 3.4: Wire temperature vs. power for 1 percent fixed propane with the 127 μm wire.

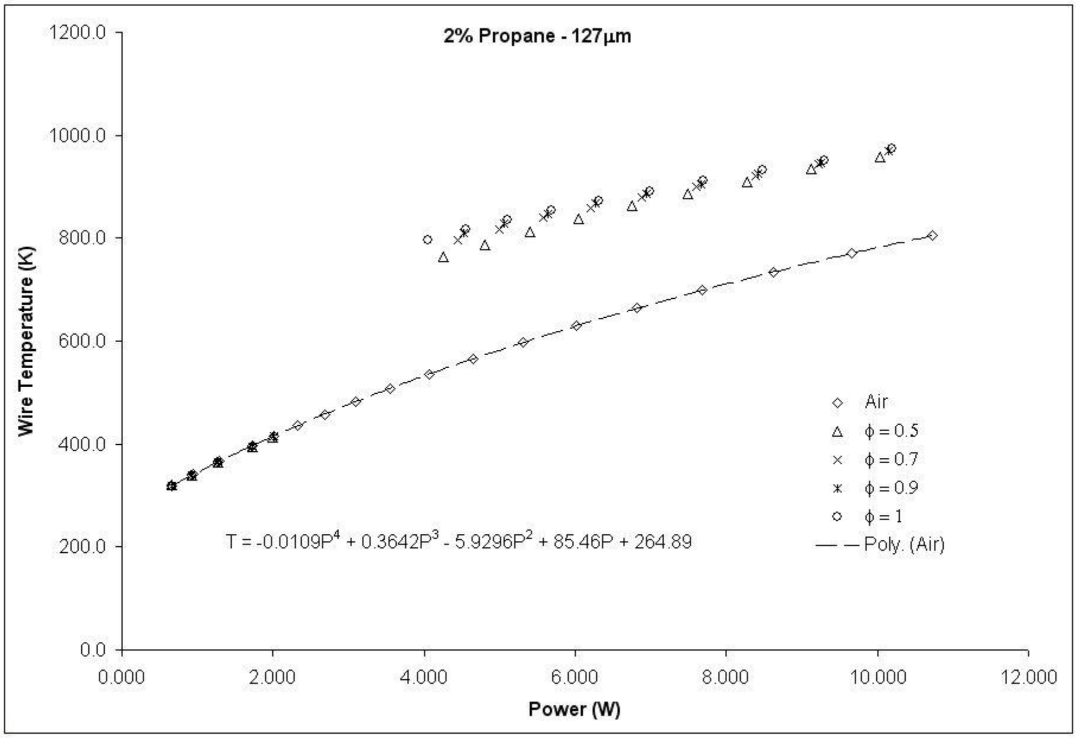

Figure 3.5: Wire temperature vs. power for 2 percent fixed propane with the 127 μm wire.

This data was then repeated for a wire with an equal surface area but a larger diameter of 203 µm, and hence a shorter length. The power shown in these figures is a function of the constant current from the power supply and the heat generation from surface reactions. However, prior to observing surface reactions, it is based only on electrical input and the corresponding change in wire resistance as previously discussed.

3.3 Ignition Temperature vs. Equivalence Ratio

The catalytic ignition temperature could then be determined and plotted as a function of equivalence ratio with respect to the percent oxygen or propane. Figure 3.6 shows the ignition temperature as a function of equivalence ratio with respect to the percent oxygen. For both wires, the ignition temperature decreases with increasing equivalence ratio. There is a direct correlation between the ignition temperature and the percentage of fuel in the mixture. The 127 µm wire seems to be more sensitive to different gas mixtures than the 203 µm wire. The smaller wire is able to ignite the mixture at a lower temperature for $\varphi = 0.5$ while the larger wire is not able to ignite the mixtures at a comparable temperature until $\varphi = 0.7$. The same behavior is also noted at the maximum equivalence ratio of $\varphi = 1$ where the 127 µm wire is able to ignite the 2 percent propane mixture at a lower temperature.

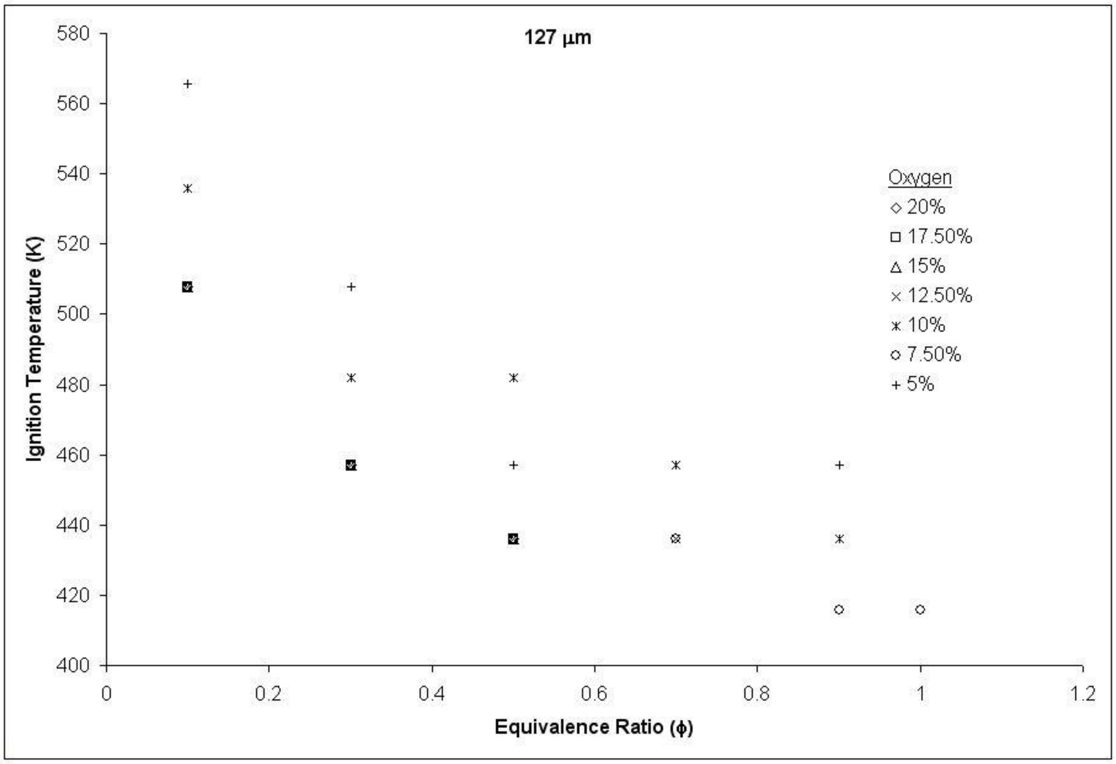

Figure 3.6: Ignition temperature vs. equivalence ratio with respect to fixed oxygen for the 127 µm wire. As the equivalence ratio increases the ignition temperature decreases since more fuel is available to react with the platinum.

3.4 Ignition Power vs. Equivalence Ratio

An important aspect of the data collected is the power required to ignite a given gas mixture. The power required to initiate a surface reaction decreases as the equivalence ratio increases. In other words, as the amount of fuel in the gas mixture increases the power required to initiate surface reactions decreases up to stoichiometry. The 127 µm wire is able to ignite leaner mixtures thus decreasing the amount of power required to initiate reactions. Also, at $\varphi = 1$ less power is needed for the 2 percent propane mixture to initiate surface reactions [34].

3.5 Surface Heat Generation vs. Equivalence Ratio

Figures 3.7 and 3.8 show the change in heat generation with fixed oxygen for the two different wire diameters. The heat generation change with fixed oxygen shows a nearly linear trend with increasing oxygen percentage. The heat generation increases with both equivalence ratio and the percent oxygen. The heat generation change with fixed propane shows more of a similarity to a parabola where a minimum is found at lower equivalence ratios and another dip is seen at φ = 1. This is more noticeable for the 127 μm wire. The 203 μm wire has a more linear response. As equivalence ratio increases there is only a slight gain in surface heat generation. The real increases in heat generated are found by increasing the amount of fuel in the mixture. A larger amount of heat is generated with the 127 μm wire as can be seen by comparing the two figures.

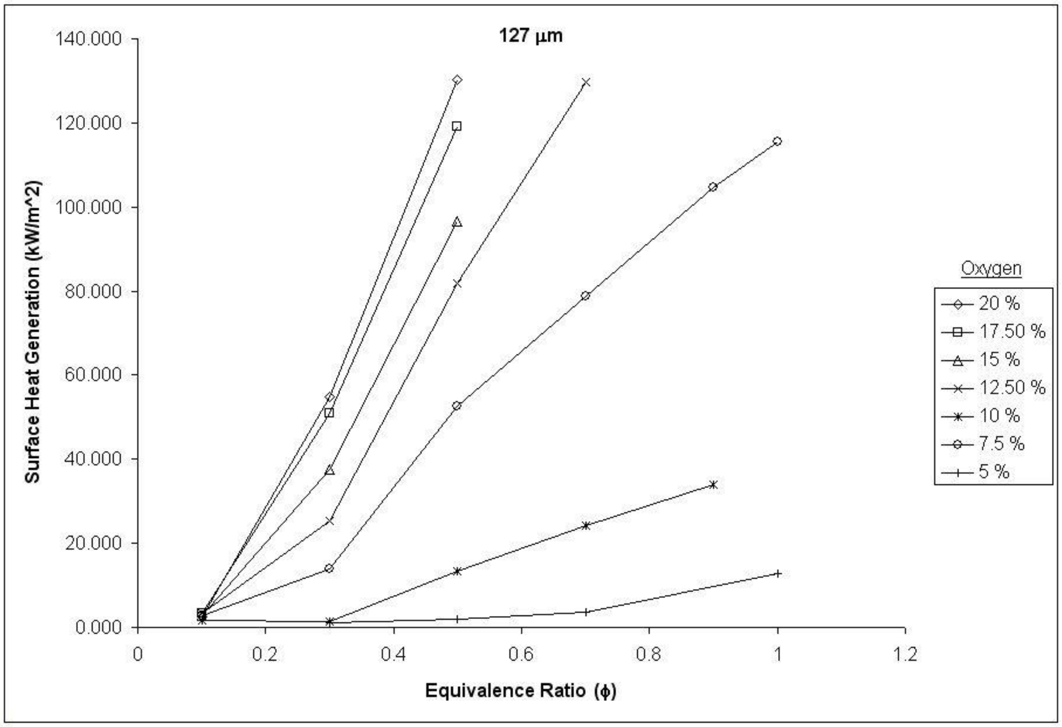

Figure 3.7: Surface heat generation vs. equivalence ratio with respect to fixed oxygen for the 127 μm wire. As the equivalence ratio increases the surface heat generation increases since more fuel is available to react with the platinum.

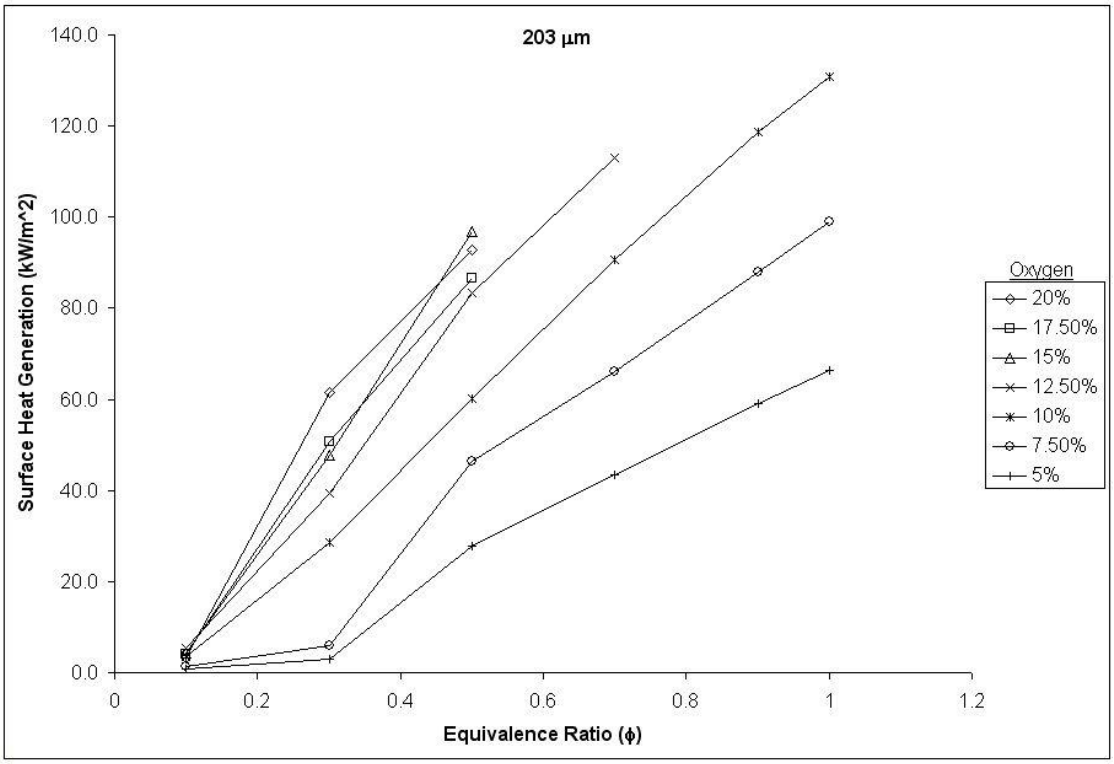

Figure 3.8: Surface heat generation vs. equivalence ratio with respect to fixed oxygen for the 203 µm wire. As the equivalence ratio increases the surface heat generation increases since more fuel is available to react with the platinum.

3.6 Wire Geometry

A comparison of the average ignition temperature of the two wires as a function of equivalence ratio is shown in Figure 3.9 for 7.5 (percentV) oxygen. The ignition temperature was found to not depend on geometry. An increase in ignition temperature was found at one equivalence ratio and then a decrease in ignition temperature at the next equivalence ratio. The change in wire diameters either increased or decreased the ignition temperature by approximately 10 K.

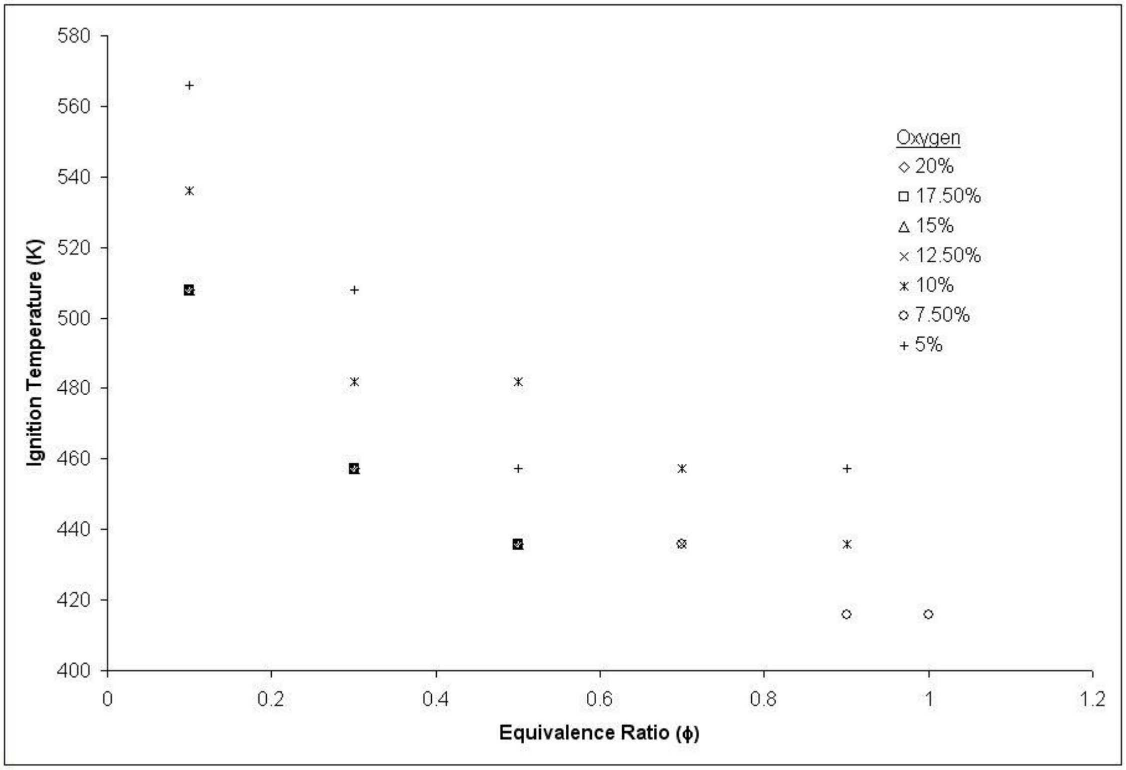

Figure 3.9: Ignition temperature versus equivalence ratio for the two different diameter wires at 7.5 percent oxygen. There is no clear distinction in behavior between the two wires.

However, as stated in the previous sections, the 127 μm wire was more responsive to changes in the gas mixture and produced larger amounts of heat.

4 ONE-STEP SURFACE REACTION KINETIC MODEL

The Perger Model is based on the basic chemistry of surface reactions described in Section 1.3 with consideration given to heat transfer, molecules adsorbing onto the surface, and desorbing from the surface. This seemed the most promising of the models to apply to the experimental data and attempt to extend it to predict not only ignition temperature but heat release as well. In the Perger Model the temperature of the wire was determined through a basic heat balance, assuming that the heat produced from electrical power and catalytic surface reactions are equal to the heat lost. It was also assumed that since the temperatures were moderately low that radiation heat losses could be neglected, and hence the heat loss from the wire is solely a function of conductive and convective heat transport. These assumptions could lead to errors at higher temperatures, but they allow for a first approximation of ignition temperature based on the volume fraction of fuel and oxygen in the gas mixture. Following this procedure lead to an equation for the heat balance for system of the form

$$r_F \Delta H_r + q''_{elec} = \frac{k_t}{L_c}\left(T - T_\infty\right) \tag{4.1}$$

where r_F is the fuel decomposition rate, H_r is the enthalpy of the overall reaction, q_{elec}'' is the electrical power input, k_t is the thermal conductivity of the gas, and L_c is the characteristic thermal length, L_c. This characteristic thermal length is a function of the experimental setup and can be calculated for a cylinder in cross-flow as [33]

$$L_c = \frac{d}{0.891 \times 10^2 \,\mathrm{Re}^{0.33}} \tag{4.2}$$

The rate constant for adsorption of species i is given by

$$k_{i,A} = \frac{S_i p_i}{\Gamma \sqrt{2\pi MW_i R_i T}} \tag{4.3}$$

where Γ, the density of active sites on the catalyst surface, is 2.7E05 $^{\mathrm{mol}}/_{\mathrm{m}^2}$ [21]. This is an average value for Pt. MW_i is the molar mass of species i, R_i is the ideal gas constant of species i, p_i is the partial pressure of species i in the bulk reacting flow, T is the temperature of the wire (average in this case), and S_i is the sticking coefficient for species i. The sticking coefficient is the probability that a molecule sticks when it collides with a surface.

The rate of desorption of species i is given by

$$r_{i,D} = k_{i,D}\theta_i^{n_{i,D}} \tag{4.4}$$

where the reaction order of desorption of species i is given by $n_{i;D}$. It was not necessary to determine this, as will be shown. θ_i is the surface coverage of species i, this was also not necessary to determine. $k_{i;D}$ is the rate constant for the desorption of species i, which follows an Arrhenius expression as

$$k_{i,D} = A_{i,D}\exp\left(-E_{i,D}/RT\right) \tag{4.5}$$

the pre-exponential constant $A_{i;D}$ and the activation energy $E_{i;D}$ can be determined from experimental data. Perger, et al. [21], used these expressions for a surface initially covered with oxygen, to derive the overall initial reaction rate or fuel decomposition rate, r_F, on the Pt surface

$$-\frac{d}{dt}\left[fuel\right] = r_F = \frac{\Gamma k_{O_2,D}}{\dfrac{k_{O_2,A}}{k_{F,A}} - a} \tag{4.6}$$

The constant, a, is the stoichiometric oxygen coefficient for the fuel-oxygen system. This can be calculated from combustion stoichiometry; stoichiometric combustion of propane and oxygen, a = 5.

By substituting Eqn's (4.3) and (4.5) for oxygen and fuel into Eqn (4.6) the following expression was obtained

$$r_F = \frac{\Gamma A_{O_2,D}\exp\left(-E_{O_2,D}/RT\right)}{\left(\dfrac{S_{O_2}}{S_F}\right)^b \dfrac{p_{O_2}}{p_F}\sqrt{\dfrac{MW_F}{MW_{O_2}}}} \tag{4.7}$$

Hence, to predict the rate at which fuel will decompose on the Pt surface, it was necessary to know b = $n_{O_2;A}$=$n_{F;A}$, the ratio of the reaction orders of adsorption for oxygen and propane; the ratio of the sticking coefficients S_{O_2}/S_F , the pre-exponential constant $A_{O_2;D}$ for the desorption of oxygen, and the activation energy $E_{O_2;D}$ for the desorption of oxygen. All of these can be obtained from the ignition temperature data gathered at different equivalence ratios.

Perger et al. [18], show that the reactivity of Pt catalysts depends on important characteristics of the fuel. If the reacting flow is fuel rich and/or the sticking coefficient for fuel adsorption is higher than that for oxygen, the surface will be dominated by fuel molecules. Simple fuels (CO_2 and H_2 for example) may desorb without reacting. This is called initial fuel coverage; fuels with this behavior will show an increase in ignition temperature as increases.

If, however, the reacting flow is fuel lean and/or the sticking coefficient for oxygen adsorption is higher than that for the fuel, the surface will be dominated by oxygen molecules. More complex fuels, including propane, are not likely to desorb from the surface intact. This is called initial oxygen coverage and is characterized by a decrease in the ignition temperature with increasing equivalence ratio. All the propane-oxygen ignition data on Pt exhibited this behavior.

The method used to obtain the one-step reaction rate model is taken from that outlined by Perger et al. [18, 21]. They show that the energy balance and kinetic reaction constant expressions can be combined into the following expression for initial oxygen coverage when b = 1

$$\frac{\Gamma \Delta H_r L_{cp} A_{O_2,D} E_{O_2,D} \exp\left(-E_{O_2D}/RT\right)}{k_t R T_{ig}^2 \left[\frac{x_{O_2}}{x_F} \sqrt{\frac{MW_F}{MW_{O_2}}} \left(\frac{S_{O_2,O}}{S_{F,O}} \right) - a \right]} = 1 \qquad (4.8)$$

A non-linear curve fitting technique (Levenberg-Marquardt) was used to fit the above expression to ignition temperature data to obtain S_{O_2}/S_F , $A_{O_2;D}$, and $E_{O_2;D}$. Perger et al. [21], give a more complex expression to determine b as well. It was determined that b ~1 for propane-oxygen mixtures with Pt. Hence, the simpler expression Eqn (4.8) was used for the rest of the calculations.

One of the Mathcad® worksheets for the Levenberg-Marquardt non-linear least square fitting algorithms is provided in Lounsbury [34] for 12.5 percent fixed oxygen with the 127 µm wire.

The Perger Model was fit to experiments with sufficient data conducted for both the 127 µm and 203 µm wires. The results are listed in Table 4.1.

Table 4.1: Results of the Levenberg-Marquardt non-linear least square fitting

d (m)	x_{O_2}	S_{O_2}/S_F	$A_{O_2;D}$ **(1/s)**	$E_{O_2;D}$ **(kJ/kmol)**	**RMS (%)**
127	0.050	5.447	5.10E10	39,830	0.7566
127	0.075	4.499	6.50E11	48,960	0.9194
127	0.100	5.345	1.30E10	35,520	0.5487
127	0.125	4.852	4.00E12	55,740	0.4554
203	0.075	6.456	8.72E12	58,780	0.9798
203	0.100	4.873	2.50E11	46,430	1.0938
203	0.125	5.245	2.50E11	45,540	0.8079
	Mean	5.25	1.99E12	47,257	0.7945
	Std. Dev.	0.63	3.29E12	8,208	0.2297
		12%	165%	17%	29%

The ratio of the oxygen-to-fuel sticking coefficients is 5.25±12%. This level of uncertainty is consistent with that expressed for other fuels including CO, H_2, CH_4, C_2H_4, and C_3H_6 on Pt [18, 21, 24]. The pre-exponential constant $A_{O_2;D}$ shows considerable variability, but is in agreement with Perger et al., who found that the application of their model was insensitive to values of $A_{O_2;D}$; hence this is not a reliable method of determining this value. The activation energy is 47 ±17% , this level of uncertainty is also consistent with prior research [18, 21, 24]. The relative quality of the curve fitting was assessed with a root-mean-square (RMS) calculation that was normalized by the mole fraction of fuel. RMS values averaged 0.8% ±29%, suggesting a reasonably good fit between the model and the experimental data.

To apply the one-step surface reaction model, the sticking coefficients ratio $S_{O_2;O}/S_{F;O}$, the pre-exponential constant $A_{O_2;D}$, and the activation energy $E_{O_2;D}$ must first be determined for the fuel and equivalence ratio of interest as described above. Then, the implicit expression Eqn 4.8 is solved for the ignition temperature, T_{ig},

A representative plot of the predicted ignition temperature with experimental data is shown in Figure 4.1 for 12.5% oxygen with the 127 µm wire.

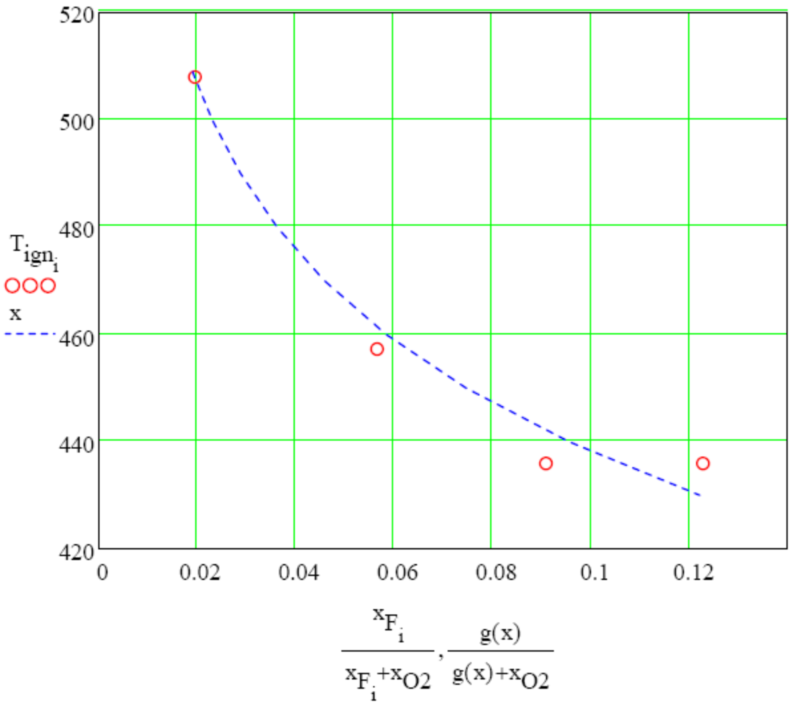

Figure 4.1: Predicted ignition temperature versus experimental data as a function of the percent fuel in the mixture for 12.5 percent oxygen with the 127 µm wire.

Good agreement to within 1 percent was obtained from the model.

The rate of heat generated due to surface reactions is calculated by multiplying the rate of fuel decomposition, r_F, by the enthalpy of the overall reaction, H_r. The enthalpy of the overall reaction is the difference between the enthalpy of decomposition products and the enthalpy of the reactants, and it is a function of the temperatures of the reactants and products.

The initial rate of fuel decomposition is calculated by

$$r_F = -\frac{d}{dt}\left[fuel\right] = \frac{\Gamma A_{O_2,D} \exp\left(-E_{O_2D}/RT\right)}{\left[\frac{x_{O_2}}{x_F}\sqrt{\frac{MW_F}{MW_{O_2}}}\left(\frac{S_{O_2,O}}{S_F}\right)-a\right]} \qquad \left[mol/m^2 s\right] \tag{4.10}$$

this can be used to calculate the heat release from the Pt surface by application of the enthalpy of the overall reaction, H_r.

Hence, the rate of heat generated on the surface at ignition is then found from

$$q''_{gen} = r_F \Delta H_r = \frac{\Delta H_r \Gamma A_{O_2,D} \exp\left(-E_{O_2D}/RT\right)}{\left[\frac{x_{O_2}}{x_F}\sqrt{\frac{MW_F}{MW_{O_2}}}\left(\frac{S_{O_2,O}}{S_F}\right)-a\right]} \qquad \left[W/m^2\right] \tag{4.11}$$

This value for q_{gen}'' can be used in connection with a thermal model that includes the rate of heat loss from the system.

Accuracy of the Perger Model can be checked by comparing the measured rate of heat generated with the calculated rate. An energy balance on the Pt wire shows that at steady state the rate of energy generated electrically and chemically must be lost to maintain steady-state conditions, hence

$$q''_{elec} + q''_{gen} = q''_{lost} \tag{4.12}$$

The ratios of q_{pred}'' calculated using the Perger Model and q_{gen}'' as measured in the experiments are listed in Table 4.2 at different values of and x_{O_2} for the two wires.

Table 4.2: The ratio of heat generation from the Perger Model and experimental. The predicted heat generation is much higher at lower equivalence ratios. A better prediction of heat generation was found with the 203 µm wire.

	q_{pred}''/q_{gen}''					
d (m)	**0.1**	**0.3**	**0.5**	**0.7**	**0.9**	**1**
127	806	565	200	80	-	-
127	239	42	10	10	5	5
127	-	753	630	101	45	23
127	223	22	6	5	-	-
203	370	47	11	4	4	4
203	206	11	9	4	4	4
203	157	9	7	4	4	-

In all cases, the calculated q_{pred}'' is greater than that obtained experimentally, sometimes by two orders of magnitude. The largest discrepancies are generally seen at lower values of and x_{O_2}.

5 OBSERVATIONS AND DISCUSSIONS

The first observation was a clear distinction in behavior between a "fresh" wire, one that has not been exposed to surface reactions, and a "seasoned" wire, one that has been exposed to surface reactions. This behavioral difference is shown in Figure 5.1 where it is clear that the seasoned wire initiates surface reactions sooner and much more vigorously.

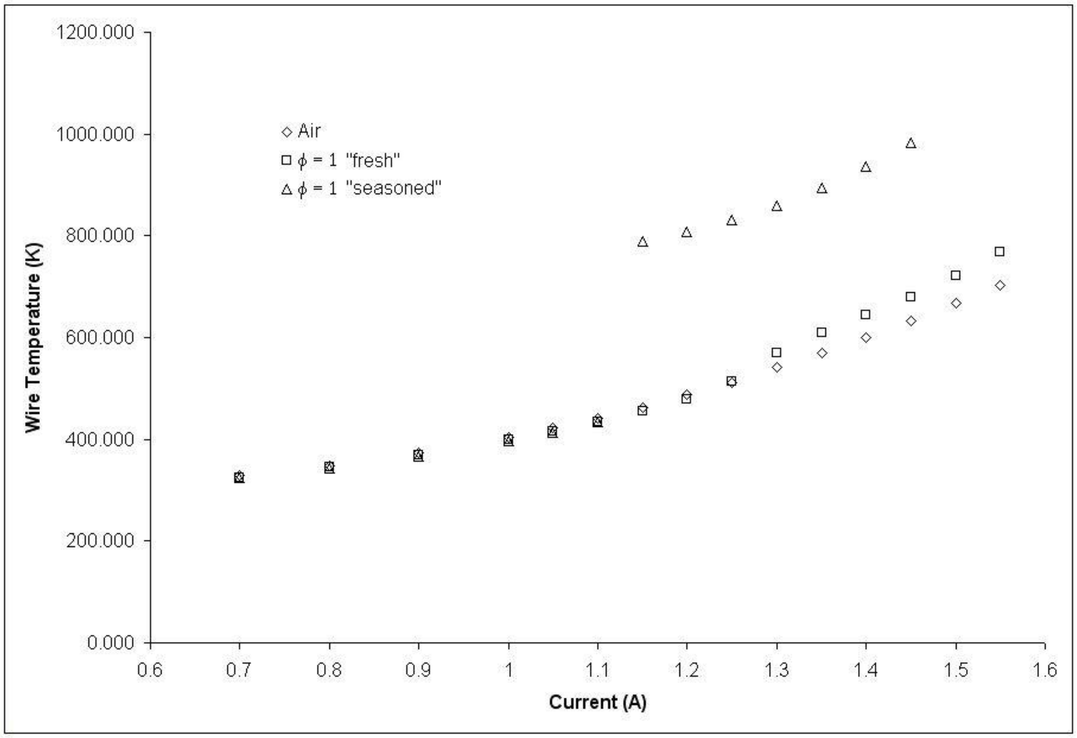

Figure 5.1: Wire temperature vs. current for a "fresh" and "seasoned" wire. The former being a wire that has not been exposed to catalytic surface reactions and the later the opposite.

Due to this difference it was desired to further investigate the effects of seasoned Pt wires. The change in reactivity between fresh and seasoned wires is an important aspect in the CPT igniter application. Hence, work will continue with data collected only with seasoned wires. At this time, it is not clear whether the increased reactivity is due to impurities of the fresh wire or whether a seasoned wire carries adsorbed gas species that initiate a faster response or whether erosion of the surface over time may be a contributing factor. Future work will examine each wire under scanning electron microscope to aid in these conclusions.

A comparison of calculated ignition temperatures with that of Cho and Law [2] is shown in Figure 5.2. The difference in ignition temperature observed, at this point, is assumed to be due to Cho and Law using only fresh wires or cleaning each wire between experiments. The research reported here relates to the continual use of a catalytic igniter in a consumer based environment where the igniter will not be fresh or cleaned while in operation. A practical igniter's catalyst surface would quickly lose its pristine state with many ignition events occurring during typical operation in an internal combustion engine.

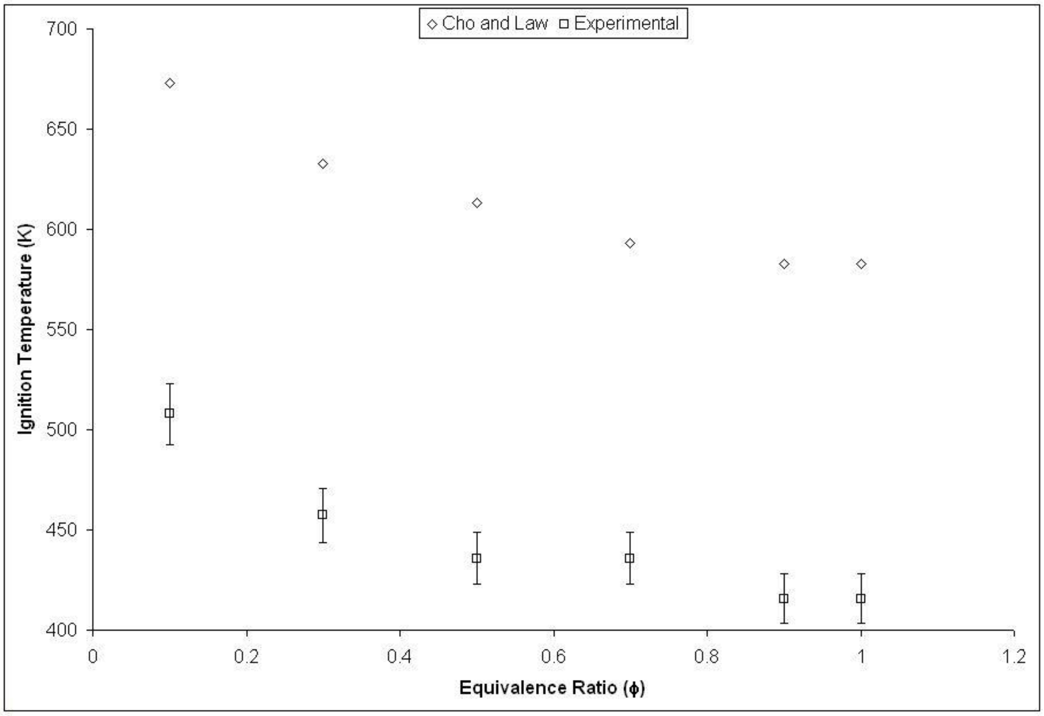

Figure 5.2: Catalytic ignition temperature versus equivalence ratio. A comparison of experimental ignition temperature data at 7.5 percent oxygen with that obtained by Cho and Law [2].

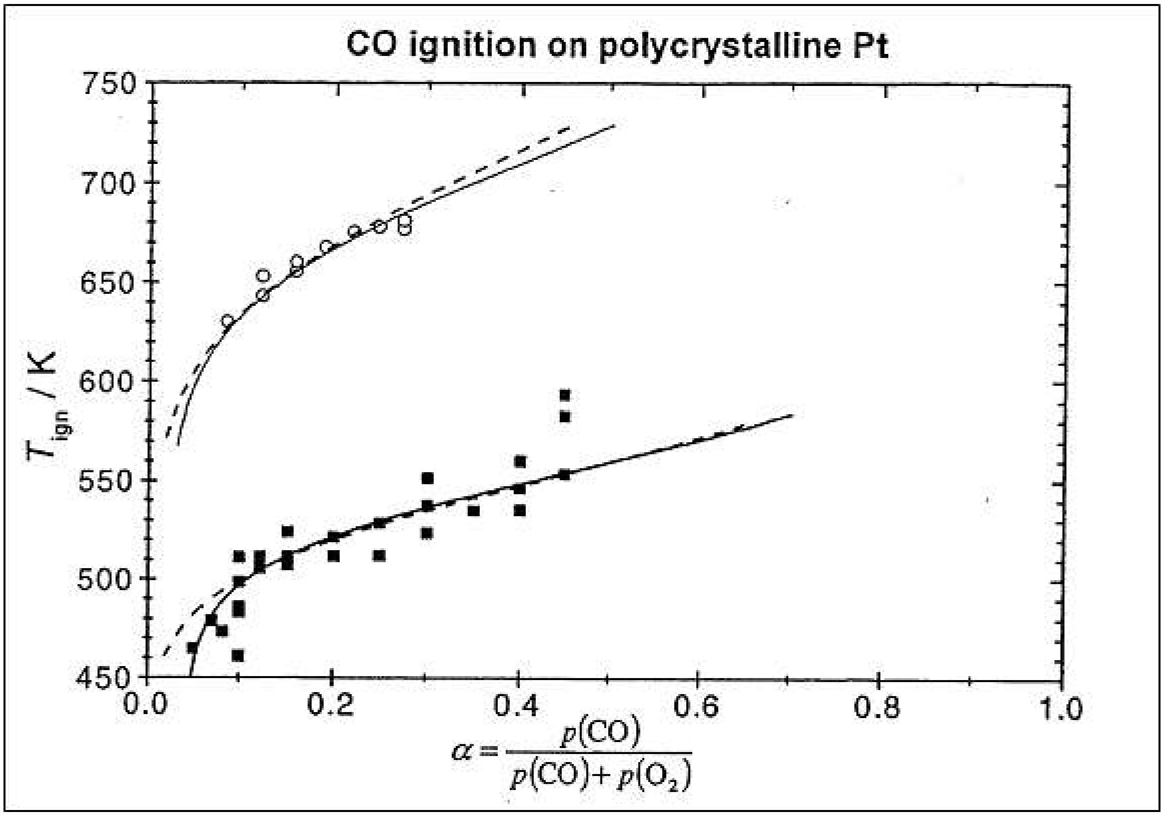

Figure 5.3: Comparison of the ignition temperature for CO over Pt as found by Cho and Law [2] the open circles and Rinnemo et al. [19] the solid squares. Referenced by Perger et al. [21] the dashed and solid lines represent their numerical curve fitting to these data sets.

A decrease in ignition temperature from that recorded by Cho and Law was also found by Rinnemo, et al. [19], for CO. A decrease of roughly 150 K was observed (Figure 5.3), which is comparable to the difference that was observed for propane in this work (Figure 5.2). Rinnemo et al., used a slightly smaller wire, 100 µm, positioned vertically with a much smaller volumetric flow rate than Cho and Law and this research. Therefore, the heat convected from the wire could be less, requiring less heating and resulting in a lower wire temperature required for ignition. They were also very careful to continually clean the wire to ensure consistent fresh ignition data. The variability in ignition temperature due to wire diameter, experimental apparatus, or wire cleanliness is not fully understood and further research is required. However, as shown in Figure

5.2 the data trends obtained are comparable to that of Cho and Law, which gives confidence that the apparatus and methods are reliable.

In the case of the 127 μm wire there is a strange reversal between 7.5 percent and 10 percent oxygen where more heat is generated with 7.5 percent oxygen than 10 percent oxygen. This is opposite of the expected behavior for an increase in oxygen and is shown clearly when looking at Figure 3.32, where a continual increase in the heat release is observed for every increase in oxygen, except for 7.5 percent and 10 percent. This change was not observed for the 203 μm wire. Cho and Law [2], also observed a decrease in ignition temperature for 1.5 percent fixed propane at approximately 7.5 percent oxygen. Figure 3.24 confirms this observation. Specifically, at an equivalence ratio of 0.9 the ignition temperature at 7.5 percent oxygen is less than that for 10 percent oxygen.

All other oxygen percentages show a consistent trend that as the percent oxygen is increased, the ignition temperature decreases and the heat release increases. Cho and Law state that this may be due to the ignition temperature dependence on oxygen or fuel for propane. They discovered that the ignition temperature was less dependent on the percent fuel and more dependent on the percent oxygen. This further demonstrates the adsorption/desorption phenomenon discussed by Perger et al. [18, 21], and discussed in Section 4, stating that fuels similar to propane will create a mostly oxygen covered catalyst, which explains the ignition temperature dependence on the percent oxygen in the mixture, rather than the percent fuel. This is even further confirmed by comparison of the figures in Section 3.3 for fixed oxygen or fixed propane. The fixed propane figures show less of a change in ignition temperature with equivalence ratio than fixed oxygen.

The discrepancies seen in Table 4.2 for q_{pred}'' may be because the rate of heat applied electrically was relatively large, and the rate of heat generated by surface reactions was relatively small in comparison, under the fuel-lean conditions that were tested. The discrepancies are reduced as equivalence ratio increases. As equivalence ratio increases the heat generated by surface reactions increases, thus minimizing the gap between electrical and surface heat generation. While the application of the Perger approach to finding $S_{O2;O}/S_{F;O}$, $A_{O2;D}$, and $E_{O2;D}$ seems satisfactory, the extension of the Perger Model to calculate the rate of heat generated at the surface at ignition, based on the ignition temperature, is much more inconsistent. An improved rate of heat transfer model may return better results. For example, in this application, the catalytic wire is coiled to increase the surface area of the wire exposed to the reacting flow. The characteristic thermal length of this physical arrangement is different than that of a single straight wire in cross-flow. Also, at some values of and x_{O_2}, the required temperature for ignition is higher and the Perger Model neglects thermal radiation, which increases at elevated temperatures.

The Perger Model is, however, a starting point for development of a one-step surface reaction model. The outcome of such a model would give users the capability of predicting T_{ig} and the heat generated q_{gen}'' at the surface of the CPT igniter. This information could increase knowledge of the point of ignition, and be used in ignition timing models to improve combustion efficiency.

6 CONCLUSIONS

A tubular plug flow reactor was used to study the detailed behavior of fuel-oxygen mixtures on a seasoned catalytic surface [1]. A coiled platinum wire was inserted along the mid-plane and near the midpoint of the plug flow region of the reactor. The wire was heated electrically in air and its average temperature determined experimentally. From the voltage data collected the power input to the wire was known and hence a plot of power vs. equivalence ratio could be generated and the data approximated by a fourth order polynomial as explained in Section 3.1. Non-flammable mixtures of propane and oxygen at different fuel-to-oxygen equivalence ratios, diluted with nitrogen, were then introduced into the reactor. The average temperature of the platinum wire when surface reactions occurred was determined experimentally and plotted once again as a function of average wire temperature versus power, see Section 3.2. This data was then used to determine the point at which catalytic ignition occurred (Section 2.2), the average heat generation (Section 2.2), and used in a one-step surface reaction kinetic model to numerically calculate the ignition temperature and heat release (Section 4).

The data trends found by Cho and Law [2], were replicated in this work. A 32 percent average decrease in ignition temperature was obtained as compared with Cho and Law for seasoned Pt wires. The ignition temperature decreased with increasing equivalence ratio (Figures 3.24 - 3.27). The analysis was further extended to include the power at which ignition occurred and the surface heat generation from catalytic reactions. The power at ignition followed the same trend as the ignition temperature, a decrease in power required to initiate surface reactions at higher equivalence ratios. It was also found that the 127 μm wire was more sensitive to ignition at lower equivalence ratios and higher fuel concentrations (Figure 3.30 and 3.31). The surface heat generation increased with both an increase in oxygen or propane percentage. These conclusions were expected and confirmed. This is explained by analyzing the flammability limits for propane (Figure 2.3). If the percentage of oxygen is increased for a fixed amount of fuel then the gas mixture will be move closer to the flammability limit. Also, if the percent fuel is increased for a fixed amount of oxygen the same trend is observed. The closer the gas mixture is to the flammability limits the more reactive or volatile the mixture is. Hence, a more excitable reaction was observed near these limits. In other words, a decrease in ignition temperature and power at ignition was observed while an increase in the heat release was found for either an increase in oxygen or propane percentage.

Progress was made in applying a one-step surface reaction model, the “Perger Model,” to the ignition temperature data. The model was first used to find values of the ratios of the sticking coefficients $S_{O_2;O}/S_{F;O}$, the pre-exponential constant for oxygen desorption, $A_{O_2;D}$, and the activation energy for oxygen desorption, $E_{O_2;D}$ for propane-oxygen mixtures on Pt (Table 4.1). The values of these three parameters were within the uncertainty of those reported for other hydrocarbon fuels and propane.

Good agreement was found between predicted and experimental ignition temperatures as shown in Figure 4.1. The model was expanded to calculate the rate of heat generated on the surface just after ignition. Predicted rates of heat generation were as much as two orders of magnitude higher than measured values for low values of and x_{O_2}. The best agreement, which was only four times greater than measured, was obtained for the thicker wire at higher values of and x_{O_2}.

An overall insight gained from this study was that a deceptively simple experiment, measuring the change in voltage of an electrically heated catalytic wire exposed to a reactive flow, provides a wealth of useful information:

- average electrical heating required to initiate surface reactions;
- average wire temperature when surface reactions initiate;
- average rate of heat generated when surface reactions initiate;
- estimates for the ratio of sticking coefficients of oxygen and fuel, activation energy for desorption of oxygen, and the pre-exponential constant for the desorption of oxygen,
- potential to predict the ignition temperature; and
- potential to predict the rate of heat generated when surface reactions initiate.

7 RECOMMENDATIONS

The experiments and data collected thus far have been a bit crude, although very insightful, in that care was not taken to ensure a clean platinum surface and the current supplied to the wire was not controlled in fine enough step increases such that a more exact ignition temperature could be determined. However, this data was very useful as related to the CPT igniter where wire cleaning and fine power input control is not realistic. Regardless of these concerns the data was consistent with that of previous researchers and has formed a foundation upon which further research with alternative fuels can be conducted with confidence that the methodology and apparatus are reliable.

Despite the shortcomings of the Perger Model in predicting the heat generation rate, it is a good first order model to begin the creation of a more accurate model. Better heat transfer rate characterization is one area of improvement for future use of the Perger Model, as discussed in Section 5.

A few items could prove to be beneficial to the continued research in this area:

- a microscope has recently been purchased and a scanning electron microscope is available that could aid in understanding the behavioral difference between a “fresh” and “seasoned” wire;
- a power supply capable of finer control of electrical current supply could help in determining a more exact ignition temperature along with the power required to initiate surface reactions;
- coupling of an improved surface heat release model with a simple gas-phase ignition model for use in CPT timing models;
- apply the experimental methodology outlined here to renewable transportation fuel;
- install an evaporator for experiments with fuels that are liquid at room temperature;
- explore the impact of water addition to propane-oxygen mixtures over platinum; and
- conduct experiments with catalytic wires exposed to ethanol-water-air blends.

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