

**PROGRESS IN CATALYTIC IGNITION FABRICATION,  
MODELING AND INFRASTRUCTURE:**

**(Part 1) Catalytic Ignition Studies**

**Final Report**



**TranLIVE**

**J. Steciak, S. Beyerlein, R. Budwig, D. Cordon, D. McIlroy**

**February 2014**

## DISCLAIMER

The contents of this report reflect the views of the authors, who are responsible for the facts and the accuracy of the information presented herein. This document is disseminated under the sponsorship of the Department of Transportation, University Transportation Centers Program, in the interest of information exchange. The U.S. Government assumes no liability for the contents or use thereof.

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle Progress in Catalytic Ignition Fabrication, Modeling and Infrastructure (Catalytic Ignition Studies)		5. Report Date February 2014	
		6. Performing Organization Code KLK907	
7. Author(s) Steciak, J., Beyerlein, S., Budwig, R., Cordon, D., McIlroy, D.		8. Performing Organization Report No. N14-09A	
9. Performing Organization Name and Address  TranLIVE NIATT/University of Idaho 875 Perimeter Dr MS 0901 Moscow, ID 83844-0901		10. Work Unit No. (TRAIS)	
		11. Contract or Grant No. DTRT12GUTC17	
12. Sponsoring Agency Name and Address  US Department of Transportation Research and Special Programs Administration 400 7th Street SW Washington, DC 20509-0001		13. Type of Report and Period Covered Final Report: January 2012 – February 2014	
		14. Sponsoring Agency Code USDOT/RSPA/DIR-1	
15. Supplementary Notes:			
16. Abstract  Progress was made in measuring the temperature coefficient of thermal resistance. Thermal shielding improved results at high temperatures. Convective mixing was implemented to improve low temperature results. The temperature coefficient of thermal resistance is needed to measure the catalyst temperature at which surface reactions initiate.  A separate report was prepared on the development of a multi-zone engine model simulated using MATLAB software.			
17. Key Words catalytic ignition, infrastructure		18. Distribution Statement  Unrestricted; Document is available to the public through the National Technical Information Service; Springfield, VT.	
19. Security Classif. (of this report)  Unclassified	20. Security Classif. (of this page)  Unclassified	21. No. of Pages 11	22. Price ...

**TABLE OF CONTENTS**

EXECUTIVE SUMMARY ..... 1  
DESCRIPTION OF PROBLEM..... 2  
APPROACH AND METHODOLOGY ..... 3  
FINDINGS; CONCLUSIONS; RECOMMENDATIONS ..... 5  
REFERENCES ..... 10

**FIGURES**

Figure 1: Four-wire setup..... 5  
Figure 2: Setup inside furnace (sans shielding). ..... 6  
Figure 3: SourceMeter to furnace. .... 6  
Figure 4:  $\alpha$  as a function of temperature, 295 K reference. .... 8  
Figure 5:  $\alpha$  as a function of temperature, 273 K reference. .... 8  
Figure 6: Average  $\alpha$  with error bars, 273 K reference. .... 9

**TABLES**

Table 1: Changes in Pt Resistance with Conditioning..... 7

## **EXECUTIVE SUMMARY**

Platinum has been recognized as a viable combustion catalyst for use in transportation engines operating at fuel-lean conditions. Its change in electrical resistance with temperature has been used to measure light-off temperatures and rates of heat generation for various fuel-oxygen mixtures at the University of Idaho. In an attempt to maximize the surface area for these reactions to occur, platinum-coated nanosprings have been manufactured. A reliable method of determining an effective temperature-dependent temperature coefficient of resistance ( $\alpha(T)$ ) for the nanosprings assembly has been developed and verified using pure platinum. Measured values of  $\alpha(T)$  for platinum were matched against literature data at 373 and 1100 K. A linear fit was assumed for the gap between these temperatures; measurements made with platinum at intermediate temperatures were in good agreement. Using the same methodology,  $\alpha(T)$  for the nanosprings assembly will be determined, which will allow for further research of the nanosprings in catalytic combustion.

## **DESCRIPTION OF PROBLEM**

Catalytic igniters allow for lower ignition temperatures of lean mixtures in homogeneous charge, catalytically-assisted compression ignition engines. These systems have been the subject of much research at the University of Idaho, including both real-world setups to measure the power output and emissions of catalytic engines [Cherry, 1992; Cordon, 2002, 2006, 2008; Olberding, 2005], and laboratory setups to explore the catalytic effects of platinum and platinum-rhodium wires with various fuels [Elgan, 2012; Gibson, 2009; Leichliter, 2010; Lounsbury, 2007; McGary, 2011; Mehaffey, 2011]. Increasing the surface area of the wire increases its effectiveness as a catalyst, as shown with previous experiments in which the wire was coiled within the testing apparatus. For a greater increase in surface area, platinum-coated nanospring wire created at the University of Idaho will be used in coming research [McIlroy, 2001, 2004; Morton, 1999; Timalisina, 2010; Wang, 2006; Zhang, 2003]. This research requires the ability to measure the temperature of the wire to find the temperature at which surface reactions initiate, as well as the heat caused by these reactions. Knowing the temperature-dependent coefficient of thermal resistance,  $\alpha(T)$ , allows for the calculation of temperature from known voltage and current values.

To determine  $\alpha(T)$  of the nanospring wire, a method had to be verified using known values. Literature data was found for platinum at 273-373 K and 1100-1900 K, and a linear fit was assumed for the gap. An experimental setup was constructed, and platinum wires were tested to establish proper procedure.

## APPROACH AND METHODOLOGY

The relationship between temperature and electrical resistance can be described by

$$R(T) = R_a[1 + \alpha(T)(T - T_a)]$$

where  $R_a$  is the resistance at ambient temperature  $T_a$  [Scorzoni, 2004]. A single value for  $\alpha(T)$  for 273-373 K is given in the literature as  $0.0039 \text{ K}^{-1}$  [Butler, 1957]. Glazkov [1985] gives an equation for  $\alpha(T)$  for 1100-1900K as follows:

$$\left(\frac{1}{R_{273}}\right) * \left(\frac{dR}{dT}\right) = A + BT + \left(\frac{C}{T^2}\right) \exp\left(-\frac{H}{kT}\right)$$

where  $A = 4.21\text{E-}3 \text{ K}^{-1}$ ,  $B = -1.08\text{E-}6 \text{ K}^{-2}$ ,  $C = 3.78\text{E}7 \text{ K}$ ,  $H = 1.6 \text{ eV}$ , and  $k$  is the Boltzmann constant [Glazkov, 1985]. If  $\alpha(T)$  was a constant, and if the reference resistance was taken at  $T_a = 273 \text{ K}$ , the left hand side of the second equation would equal  $\alpha(T)$  in the first equation. This second definition of  $\alpha(T)$  [ $\alpha(T) = (1/R_{273}) * (dR/dT)$ ] was used. Between 1100 and 1200 K, Glazkov's equation approaches linear. This linearity was extended to 273 K to serve as the expected values for measurements.

For the heating element, a Thermolyne furnace (350 cubic inch, SSP, 120 V, Model F48025-60) was chosen. Short lengths of 127  $\mu\text{m}$ -diameter platinum wire were tested in a four-wire resistance test (Figure 1). The steady current connections were placed outside of the voltage-measuring connections to eliminate contact resistance errors [Kreider, 2009]. The four wires used to supply current and measure voltage were run through the vent on the top of the furnace. The back wall of the furnace was modified with two steel plates to secure a propeller shaft near the furnace's thermocouple. Figure 2 shows this modification, as well as the 2.5" model boat propeller that was run by a flex-cable motor to promote mixing within the furnace. A metal propeller was chosen to withstand the heat of the furnace and did not off-gas. Stainless steel foil was used as radiation shielding and stood between the exposed furnace coils and both the tested wire and furnace's thermocouple.

A Labview program controlled the current output and measurement timing of a Keithley 2440 5A SourceMeter (Figure 3). Measurements were taken with 0.1 amp current, 0.5 seconds apart for ten seconds with a four-second current head-start to avoid spikes. The reference temperature and resistance were taken before all other measurements; ambient temperature was 293-295 K. To remain well within the various temperature limits of all materials involved, a maximum temperature of 1000 K was chosen, and the oven was run to 993 K. To promote consistency and to reduce the effects of radiation, the oven was allowed to cool to 973 K before the first measurement was taken. The oven was then reheated to 993 K and allowed to cool to 973 K five times to condition the wire such that the change in resistance between successive measurements was less than 0.75%. No imaging or other testing has been done to discover what physical changes occur during this conditioning phase, but hypotheses include changing grain boundaries. After these five resistance measurements at 973 K, the oven was allowed to cool without periods of reheating, and further data points were taken approximately every 20 K down to 593 K.

**FINDINGS; CONCLUSIONS; RECOMMENDATIONS**

It was found that the resistance of the wire changed with successive runs to 993 K. Table 1 shows a representative sample of 973 K measurements (taken March 10). Between each pair of measurements, the oven was reheated to 993 K. Percent difference is calculated using the last measurement as the true value.

The fifth measurement taken at 973 K showed a change of only 0.56% for this particular wire, so the wire was deemed sufficiently conditioned and the oven was allowed to cool for further testing.



**Figure 1: Four-wire setup.**



**Figure 2: Setup inside furnace (sans shielding).**



**Figure 3: SourceMeter to furnace.**

**Table 1: Changes in Pt Resistance with Conditioning**

% Difference in Successive Max Temp Runs		
Temp (K)	Resistance ( $\Omega$ )	% Difference
973	0.971032143	4.734943
973	0.991634524	2.713705
973	1.004665143	1.435310
973	1.013548143	0.563826
973	1.019295190	

Figure 4 shows the  $\alpha(T)$  of several runs versus the temperature compared to the linear approximation and literature data. The literature data was taken with a reference temperature of 273 K, which accounts for some of the difference shown. Figure 5 shows the  $\alpha(T)$  of the same runs calculated with an estimated reference resistance corresponding to 273 K. Figure 6 shows this same data condensed into an average value with error bars of 1.96 standard deviations.

Using the estimated reference resistance, the data appears close to the assumed linear approximation for the range 593-833 K. The data is somewhat more curved than the assumed linear approximation. At higher temperatures, deviations from expected values may be due to insufficient radiation shielding or conditioning. Too few data points at lower temperatures do not allow definite conclusions to be made for that range.

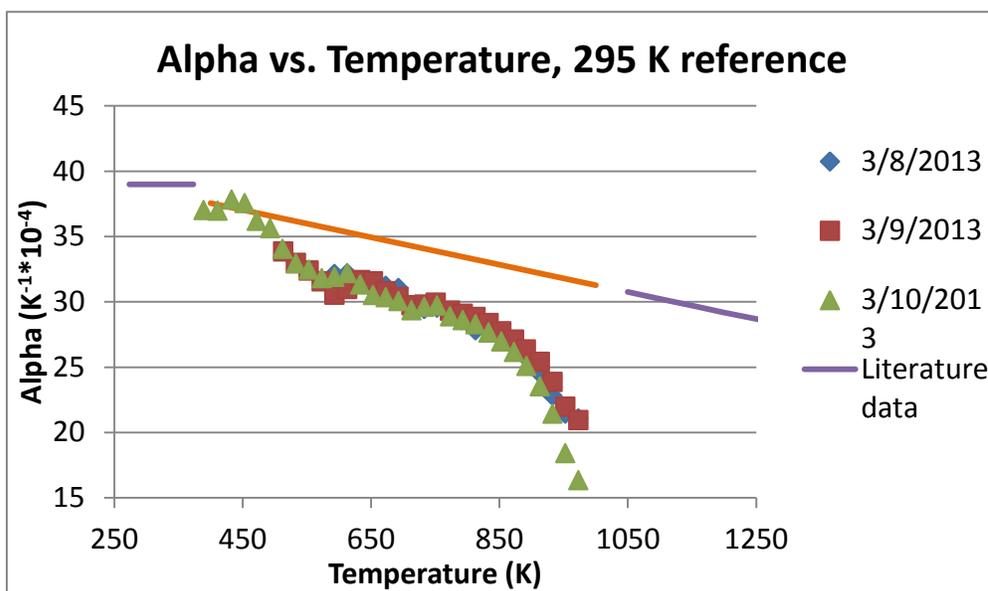


Figure 4:  $\alpha$  as a function of temperature, 295 K reference.

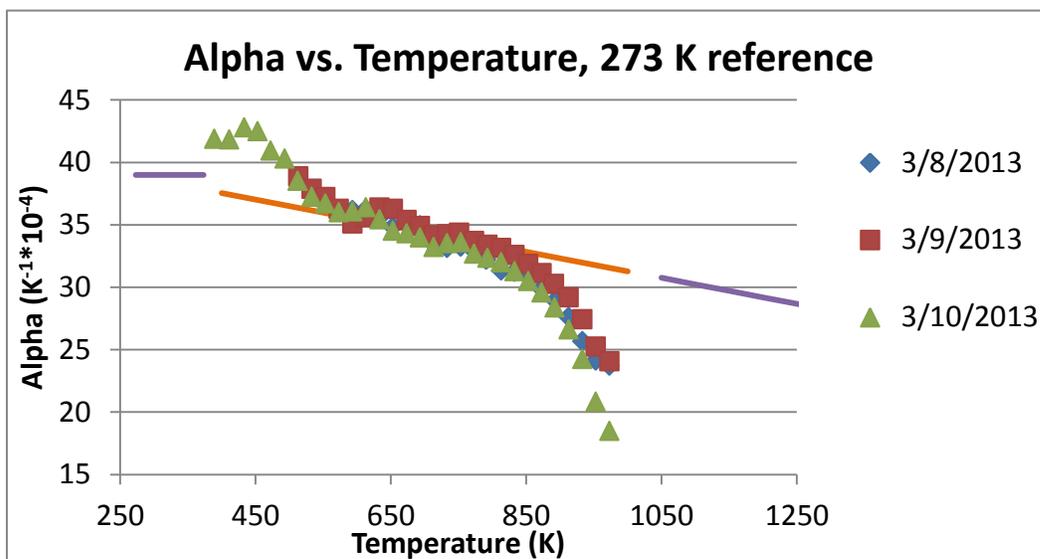
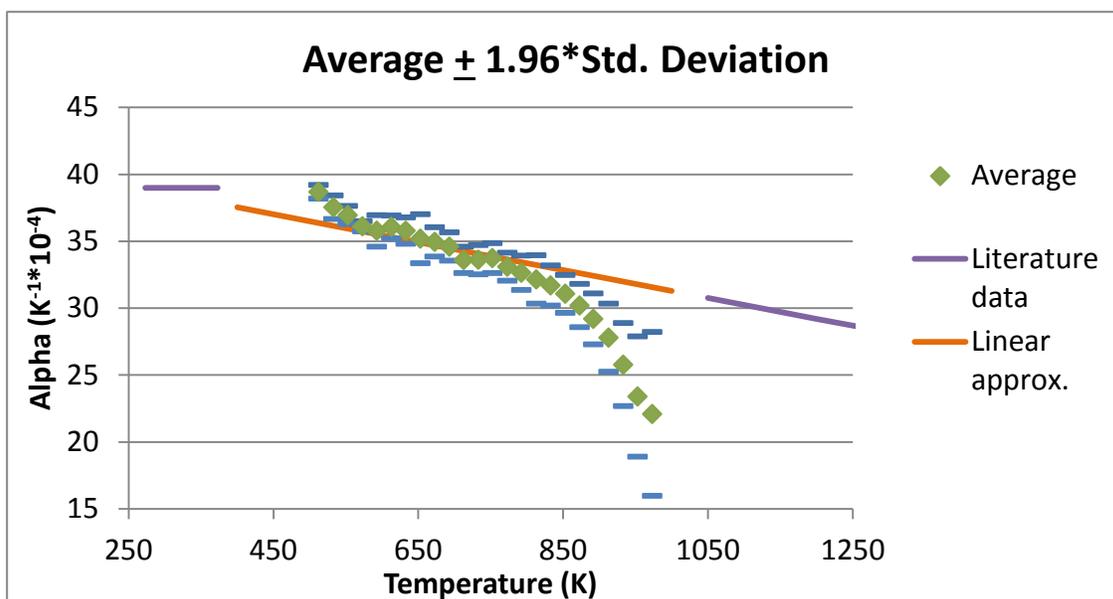


Figure 5:  $\alpha$  as a function of temperature, 273 K reference.



**Figure 6: Average  $\alpha$  with error bars, 273 K reference.**

In summary, for the range 593-833 K, the current method outputs a reasonable approximation of  $\alpha(T)$ , within two standard deviations. At lower temperatures and higher temperatures, however, the values deviate from the expected. Further testing is required to address this issue before research on nanospring wires may begin. These conclusions are based on an estimated reference resistance corresponding to 273 K; testing to determine this value is required for accurate data.

**REFERENCES**

Butler, J. (ed), "Physical Properties of the Platinum Metals," *Platinum Metals Review*, 1957, 1, (2), 61.

Cherry, M. A., Morrisset, R., and Beck, N., "Extending the Lean Limit with Mass-Timed Compression Ignition using a Plasma Torch," *SAE Paper*, 921556, 1992.

Cordon, D., Clarke, E., Beyerlein, S., Steciak, J. and Cherry, M., "Catalytic Igniter to Support Combustion of Ethanol- Water/Air Mixtures in Internal Combustion Engines," *Society of Automotive Engineers Paper 2002-01-2863*, 2002.

Cordon, D., Walker, M., Beyerlein, S., Steciak, J., and Cherry, M., "*Catalytically Assisted Combustion of JP-8 in a 1 kW Low-Compression Genset*, SAE, 2006-32-0024, 2006.

Cordon, D., Beyerlein, S., Steciak, J., and Cherry, M., "Conversion of a Homogeneous Charge Air-Cooled Engine for

Operation on Heavy Fuels," *Society of Automotive Engineers Paper 2008-32-0023*, 2008.

Elgan, D.J., *Catalytic Ignition Properties of Methane-Oxygen-Nitrogen Mixtures on Platinum*, Master's Thesis, University of Idaho, 2012.

Gibson, J.G., *Catalytic Ignition Properties of Ethanol-Oxygen-Water-Nitrogen Mixtures over Platinum*, Master's Thesis, University of Idaho, 2009.

Glazkov, S., "Point-Defect Formation and Temperature Coefficient of Electrical Resistivity of Platinum and Platinum-(10 wt%) Rhodium Alloy Range 1100-1900 K," *International Journal of Thermophysics*, Vol. 6, No 4, 1985.

Kreider, K., Ripple, D., Kimes, W., "Thin-film resistance thermometers on silicon wafers," *Measurement Science and Technology*, Vol. 20, 045206, 2009.

Leichliter, K., Steciak, J., Beyerlein, S., Budwig, R., "Measuring Ignition Temperature and Heat Generation from Moist Propane-Oxygen Mixtures on Platinum", *ASME, IMECE-38861*, 2010.

Lounsbury, B.L., *Catalytic Ignition Temperatures of Propane-Oxygen-Nitrogen Mixtures over Platinum*, Master's Thesis, University of Idaho, 2007.

McGary, B.S., *Catalytic Ignition Properties of Canola-Methyl-Ester and Soybean-Methyl-Ester in Oxygen-Nitrogen Mixtures over Platinum-Rhodium*, Master's Thesis, 2011.

McGary, B., Steciak, J., Budwig, R., and Beyerlein, S., "Ignition of Evaporated Biodiesel-Oxygen Mixtures on Platinum and Platinum-Rhodium," *ASME IMECE-65917*, 2011.

McIlroy, D.N., Zhang, D., Kranov, Y., Norton, M. Grant. Nanosprings, *Applied Physics Letters* 79, 1540, 2001.

McIlroy, D.N., Zhang, Daqing, Alkhateeb, A., Aston, D.E., Marcy, Andrew C., and Norton, M. Grant. Nanospring Formation – Unexpected Catalyst Mediated Growth, *J. Phys: Condens. Matter* 16, R415-R440, 2004.

Mehaffey, D., Steciak, J., Budwig, R., Beyerlein, S., “Catalytic Ignition of Ethanol-Oxygen-Nitrogen Mixtures over 90% Platinum-10% Rhodium in Comparison with Pure Platinum”, *ASME, IMECE-63931*, 2011.

Morton, A., Munoz-Torrez, G., Beyerlein, S., Steciak, J., McIlroy, D., and Cherry, M. "Aqueous Ethanol Fueled Catalytic Ignition Engine." *SAE Paper 99SETC-5*, 1999.

Olberding, J., Cordon, D., Beyerlein, S., Steciak, J., and Cherry, M., “Dynamometer Testing of an Ethanol-Water Fueled Transit Van,” *Society of Automotive Engineers Transactions, Journal of Fuels and Lubricants*, V114-5, pp. 1253 – 1264, No. 2005-01-3706, 2005.

Scorzoni, A., Baroncini, M., Placidi, P., “On the relationship between the temperature coefficient of resistance and the thermal conductance of integrated metal resistors,” *Sensors and Actuators A*, Vol. 116, pp 137-144, 2004.

Timalsina, Y.P., Oriero, D., Cantrell, T., Prakash, T., Branen, J., Aston, D.E., Noren, K., Nagler, J.J., Rastogi, S., McIlroy, D.N., and Corti, G., “Characterization of a vertically aligned silica nanospring-based sensor by alternating current impedance spectroscopy,” *Journal of Micromechanics and Microengineering*, vol. 20, 095005, 2010.

Wang, L., Major, D., Paga, P., Zhang, D., Norton, M.G., and McIlroy, D.N. High Yield Synthesis and Lithography of Silica-Based Nanospring Mats, *Nanotechnology* 17, S298, 2006.

Zhang, D., Alkhateeb, A., Han, H., Mahmood, H., McIlroy, David N., and Norton, M.G. Silicon Carbide Nanosprings, *Nano Letters* 3, 98, 2003.