

**Effect of wall thermal conductivity on the performance of  
Swiss roll combustors using ammonia pretreated Pt catalyst  
for catalytic reaction**

By

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the  
dissertation/thesis of CHIEN SHUNG LIN find it  
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**Effect of wall thermal conductivity on the performance of  
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ABSTRACT

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Washington State University  
MAY 2009

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Platinum based catalysts are well known as the most active ones among noble metals for oxidation of hydrocarbons as well as hydrogen. Ammonia, a strong reduction agent, creates a step-like structure on the surface of the Pt catalyst before and after hydrocarbon combustion tests. This change in structure significantly improves the performance of the catalyst.

A Swiss roll heat exchanger/combustor which has no moving part and can efficiently recycle a large proportion of the thermal energy at the cold junctions to eliminate sudden quenching was used to study on the extinction limits with different

thermal conductivity and comparison of results with and without ammonia pretreated Pt catalyst. At Reynolds number less than 45, the catalyst was required to sustain reaction. With the catalytic reaction, the self-sustain reaction could be obtained at Reynolds number of 4.2. Both lean and rich extinction limit were extended. The rich extinction limit was extended much further. At low Reynolds number, the lean extinction limit was rich of stoichiometric and rich extinction limit had equivalence ratio 20 in some cases. At higher Reynolds number which the catalytic reaction was not required, non-catalytic rich limits of nearly 2 times stoichiometric were also found.

Experiments with copper, steel, ceramic and polyimide combustors have demonstrated that reducing thermal conductivity leads to lower heat loss and a wider extinguish limit at fuel lean and rich conditions and increases operation temperatures, particularly at low Reynolds number. At these low Reynolds numbers with catalytic reaction, the lean extinction limit was rich of stoichiometric ( $\phi_{lim} \sim 3.5$ ) and rich extinction limit was extremely rich ( $\phi_{lim} \sim 25$ ). The minimum reaction of propane-air mixture at temperatures 62 °C was found.

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## Chapter I: INTRODUCTION

Hydrocarbon fuels provide 40 times more energy per unit mass (45 MJ/kg vs. 1.2 MJ/kg) than lithium-ion batteries. It is proven that the use of combustion process on generating energy has enormous advantages over batteries. In addition, a small-scale combustion generator could represent a great deal of improvement in battery-powered applications like cell phone and laptop computers [A.C. Fernandez-Pello 2002]. However, on the design of a micro-scale combustion generator, heat loss, friction, sealing, and assembly, are major factors that affect the total power generation.

Among the current micro-scale combustion generator concepts, fuel cells, static heat engines and dynamic engines have been developed to use hydrocarbon fuels to generate electrical power. However, heat and friction losses still have become the major issues. One approach to meliorate the usability of the concepts is to utilize the heat recirculation combustor first studied 30 years ago [Lloyd and Weinberg 1974]. It is also called excess enthalpy combustor because the thermal energy is transferred from the combustion products to the reactants via preheating without mass transfer and thus no dilution of reactants. Consequently, the total enthalpy of reactants (sum of thermal and chemical enthalpy) is higher than that of the incoming cold reactants and

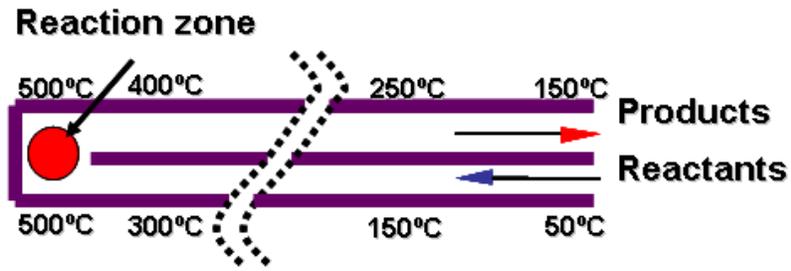
hence the combustion can be sustained even under more critical conditions of lean mixtures, small heating value fuels, or large heat losses. Figure 1 (a) shows a generic scheme of the counter-flow heat exchanger. Its large external surface area typically causes great amount of heat loss to ambience. In order to effectively eliminate the heat loss, the counter-flow heat exchanger can be wrapped up in a “Swirl roll” configuration (Figure 1 (b)) and thus the heat transfer between windings is integrated to the combustor design [Sitzki, Borer, Schuster and Ronney, 2001]. This characteristic leads the counter-flow spiral "Swiss roll" heat exchanger/combustor to the potential applications for micro-scale power generation.

Because of the increased surface area-to-volume ratio, an important issue in a small-scale combustor is the heat losses, which would cause flame quenching. This flame quenching can be significantly inhibited by catalytic combustion. With catalytic reaction, self-sustained combustion can be established at lower temperature and higher heat loss. The higher surface area-to-volume ratio at small scale makes area-limited catalytic reaction even more attractive comparing to volume-limited gas-phase reaction. Since chemical reactions only occur on the catalyst surface, its stationary heat source simplifies the heat transfer design while the gas-phase reaction is more complicated due to the unfixed reaction zone which may change in undesirable

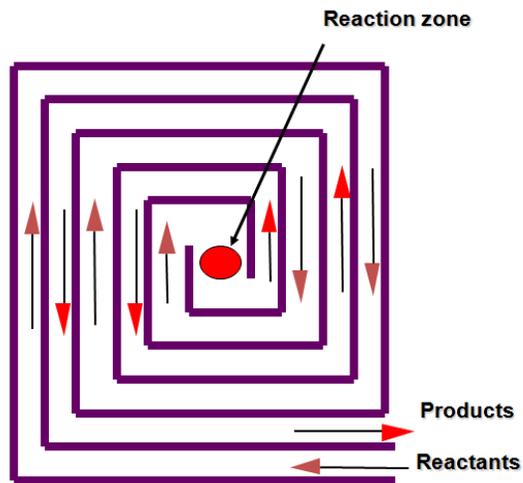
ways. In addition, catalytic combustion that allows to be sustained at lower temperature makes thermal stress and materials limitation less problematic.

Ammonia is well known as a strong reducing agent for catalyst treatment. The performance of the Pt catalyst pretreated with ammonia improves significantly, but only for low Reynolds number corresponding to the low reaction temperature. Ammonia pretreatment also creates step-like structure on the surface of catalysts. This change in structure increases the performance of the catalyst. This is not merely a surface area effect since increasing bulk catalyst area has almost no effect on combustion performance.

In particular, simulations [Ronney, Kuo, Yang, Tsai, Hung, 2008] showed that counter-current heat-recirculating combustors require thin walls with low thermal conductivity for maximum performance at small scale. Copper combustor ( $k \approx 400$  W/m-K at 300K) with similar geometry as steel combustor ( $k \approx 40$  W/m-K at 300K), ceramic combustor ( $k \approx 4$  W/m-K at 300K), and polyimide combustor ( $k \approx 0.4$  W/m-K at 300K) were constructed to test this hypothesis. Metallic and ceramic combustors can be operated at high temperatures, but the performance of metals is poor in small-scale devices due to high thermal conductivity. The thin wall ceramic plate is brittle and hard to fabricate, and it has marginally acceptable thermal conductivity



(a)



(b)

Figure 1. Schematics of the excess enthalpy combustors. (a) Counter-flow combustor with typical temperatures. (b) Linear device rolled up into a “2D” Swiss roll” combustor (Weinberg, 1970’s).

even though its performance is better than metal. Polyimide plastic has far lower thermal conductivity than metals and ceramics. The reaction in small scale combustors built by polyimide plastic can be achieved at very low Reynolds number in comparison with other combustors and hence is more suitable in micro scale applications because polyimide plastic combustors have low thermal conductivity ( $k \approx 0.4 \text{ W/m-K}$  at 300 K), and they are cheap and easy to fabricate. The objectives of this work are to examine the effect of ammonia treatment on Pt catalyst used for low  $Re$ , compare the extinction limits and thermal behavior of the “Swiss roll” combustor with or without catalyst, and evaluate the performance of the combustors by using different thermal conductivity materials with catalyst.

## CHAPTER II: EXPERIMENTAL APPARATUS

Due to the limitations of experiments with various conditions of the micro-scale devices, it is useful to develop macro- and meso-scale Swiss roll combustors such that their behaviors at low  $Re$ , which is the characteristics of micro scale combustors, can be easily understood by the measurement of appropriate parameters.

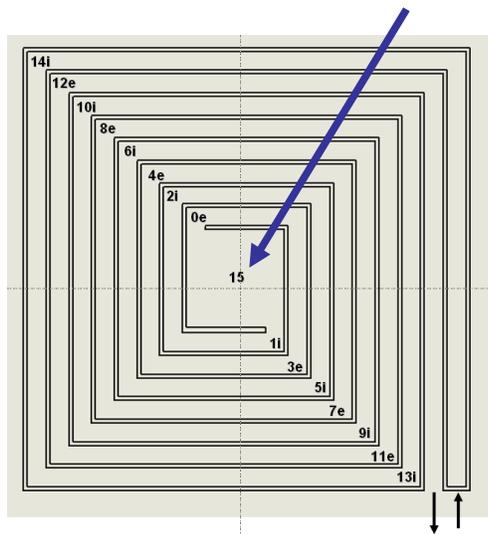
4-turn, macro-scale, spiral, and counter-flow Swiss roll combustors (Figure 2, Figure 3, Figure 4) were contrasted using thickness of 0.64 mm copper (thermal conductivity  $k \approx 400$  W/m-K at 300K), steel (thermal conductivity  $k \approx 40$  W/m-K at 300K), ceramic (thermal conductivity  $k \approx 4$ W/m-K at 300K) and polyimide plastic (thermal conductivity  $k \approx 0.4$  W/m-K at 300K). Due to the limitations of CNC milling, the thin-walled polyimide plastic, copper, and steel combustors were made by folding sheets of the materials into spirals. The brittle ceramic sheet was glued into spiral by using Heat Shield ceramic adhesive which can stand over 1500 °C. These combustors have 3.1 cm tall and the gap-width between each inlet and outlet is 3.18 mm. The center of each combustor has a cross-sectional area of 98 mm<sup>2</sup>.

The top and bottom of the ceramic and polyimide plastic combustors are sealed with a couple layers of fibrous ceramic blanket (approximately 8mm thick), backed by 6.6 mm aluminum plates. The bottoms of copper and steel combustors are secured

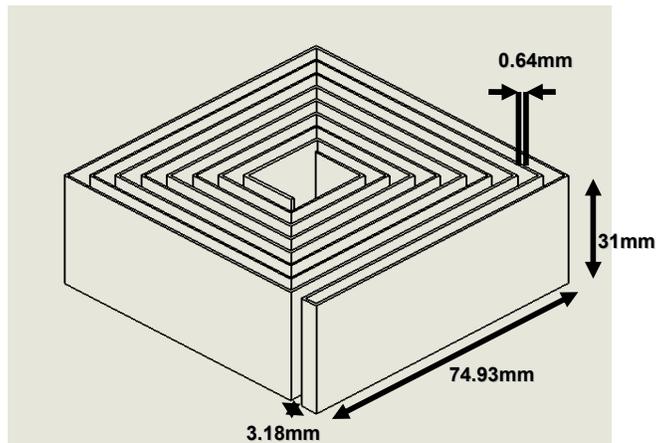
with Heat Shield ceramic adhesive, and the tops are also sealed with a couple layers of fibrous ceramic blanket. The 140 mm square aluminum plates on top and bottom are secured to one another with screws at four corners of the assembly. The fresh fuel-air mixture is pumped into a manifold attached to the inlet of the Swiss rolls.

For catalyst treatment, the 3.5- turn titanium (thermal conductivity  $k \approx 6 \text{ W/m-K}$  at 300K) Swiss roll combustor (Figure 5) is adopted. It is 5 cm tall, and the gap-width between each inlet and outlet is 5 mm. The center of the combustor has a cross-sectional area of  $250 \text{ mm}^2$ . Although bare metal platinum catalyst is unsuitable for practical applications, it was used in the experiment because it is a readily available standard material which was found to yield very reproducible results. The platinum catalyst can be operated over one week and yet its performance is only slightly degraded over operating period. In addition, it can be easily restored by polishing the foil and burning in hydrocarbon fuel to eliminate coking. In order to enhance the combustor performance at low Reynolds number, the bare platinum catalyst was placed along the corner of the reaction zone in the titanium combustor (Figure 5(a)), and the catalyst surface was treated by different sets of ammonia, a strong reducing agent, with different sets of time. To determine the best performance of the platinum catalyst with different sets of ammonia treatment, the DuPont<sup>TM</sup> Vespel<sup>TM</sup> polyimide combustor ( $k \approx 0.29 \text{ W/m-K}$  at 300K) Works<sup>TM</sup> CAD files. The outside dimensions of Vespel<sup>TM</sup>

Catalyst placement  
area = 28.51 cm<sup>2</sup>

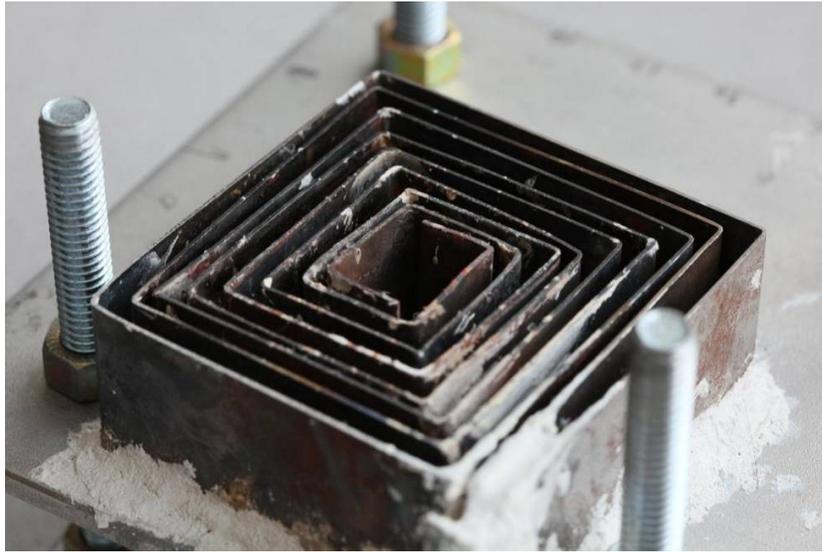


(a)



(b)

Figure 2: Schematic plane view of the Swiss roll combustor. (a) Platinum catalyst strips were placed as show when used. Thermocouples 0 – 15 were located in the exhaust 'e' and inlet 'I' turns as indicated. (b) 2 dimensional macro scale Swiss roll combustor.

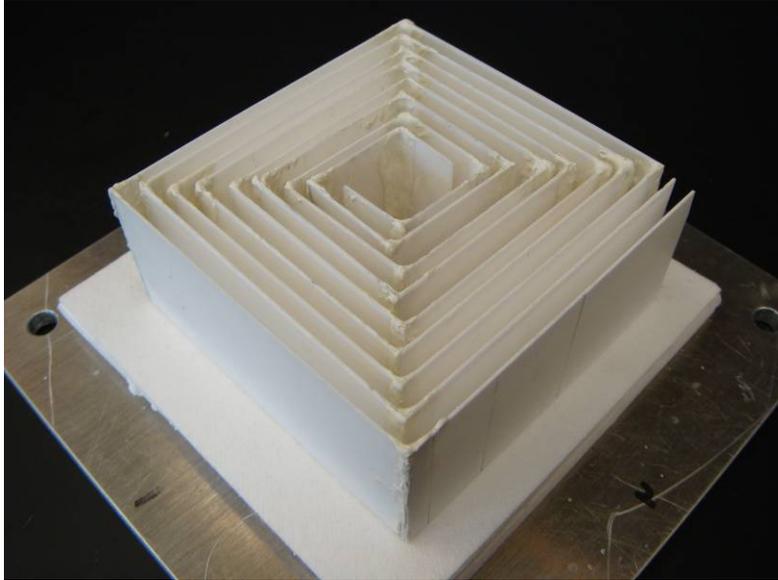


(a)

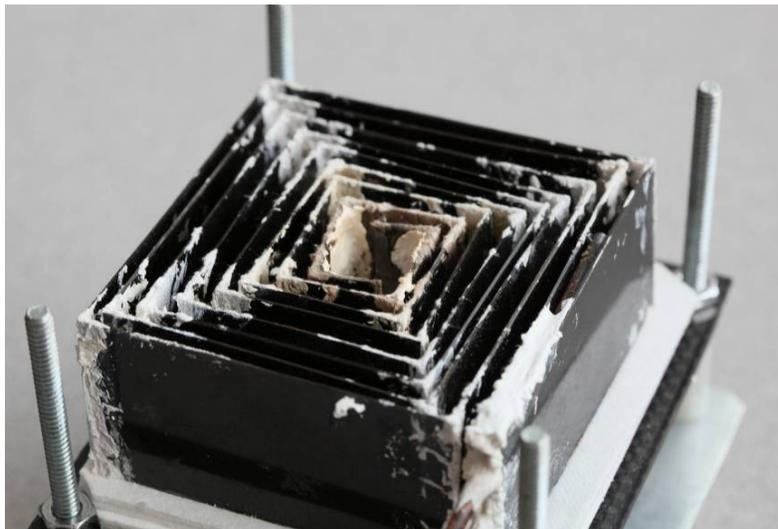


(b)

*Figure 3: (a) Macro scale steel Swiss roll combustor with top plate removed. (b) Macro scale copper Swiss roll combustor with top plate removed.*

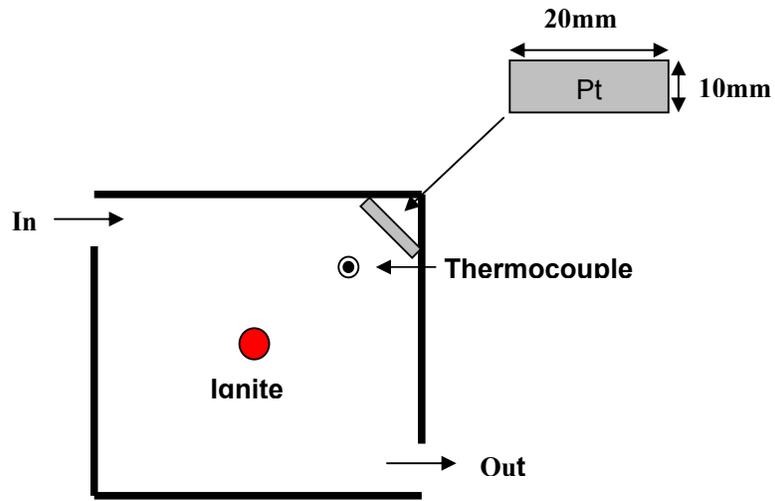


**(a)**

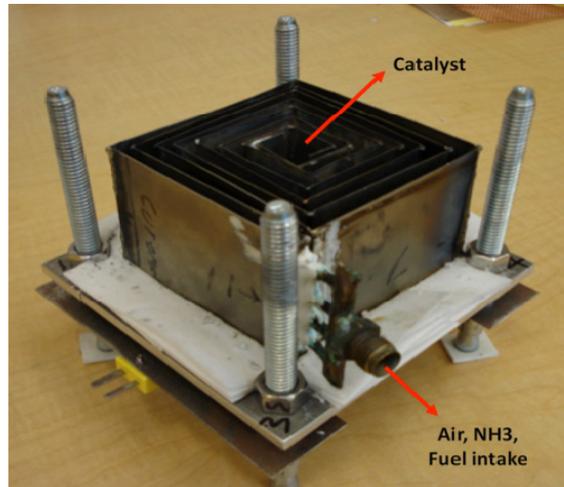


**(b)**

*Figure 4: (a) Macro scale ceramic Swiss roll combustor with top plate removed. (b) Macro scale polyimide Swiss roll combustor with top plate removed.*



(a)

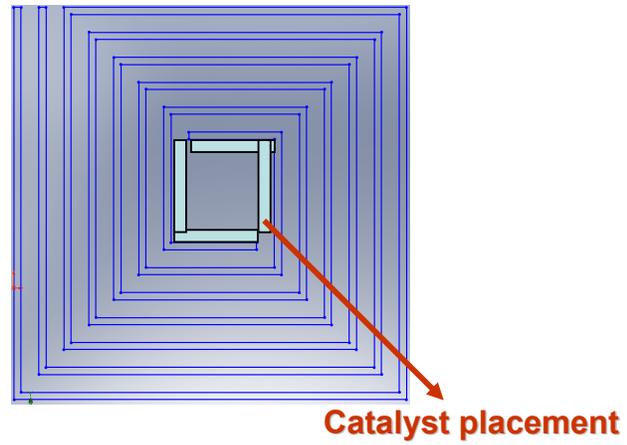


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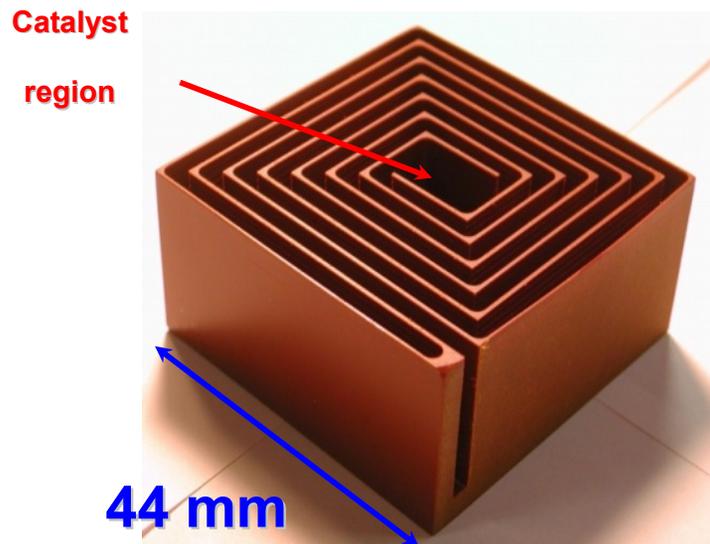
Figure 5: (a) Platinum catalyst strips were placed as show when treated with ammonia. Thermocouple was located in the corner of reaction zone. (b) Macro scale titanium Swiss roll combustor with top plate removed.

was applied (Figure 6). Vespel™ combustor was CNC milled automatically from Solid combustor are 44 mm wide by 44 mm deep by 16 mm height with 7 mm thick walls. The gap-width between each inlet and exhaust channel is 2 mm. The top is sealed with 0.5 mm fibrous ceramic blanket and backed by 1.5 mm carbon fiber plate. The center has a cross-sectional area of 32 mm<sup>2</sup>. It was instrumented with thermocouples at the center, the inlet, and the exhaust of central reaction zone (Figure 6(a)). Since the size of the Vespel™ combustor is smaller than other combustors, it only uses small amount of ammonia pretreated catalyst to test the performance of the catalyst. A Scanning Electron Microscope (SEM) was used to examine the changes on the surfaces of the catalyst before and after combustion tests. After determining the best condition to treat bare platinum catalyst with ammonia, strips of ammonia pre-treated platinum catalyst were then placed in the center of the copper, steel, ceramic and polyimide plastic combustors (exposed area ~ 28.51cm<sup>2</sup>) to test the performance of catalytic reaction. An electrically heated Kanthal wire wrapped in 1 mm diameter ceramic tube was placed in the central region of the Swiss roll for ignition. Sixteen thermocouples were evenly allocated at the center and at each inlet and exhaust turn (Figure 2(a)).

Each thermocouple was also supported by a 1 mm diameter ceramic tube with only its head protruding the top of the tube. Temperature measurements are repeatable to ± 20 °C. Commercial electronic mass flow controllers were used to control the



(a)



(b)

*Figure 6: Schematic plane view of the Swiss roll combustor to test the performance of pretreated catalyst. (a) Ammonia pretreated catalyst was placed in the center of DuPont Vespel SP-1 polyimide combustor. (b) Swiss roll combustor made of DuPont Vespel SP-1 polyimide.*

flow rate of the fuel and air into the manifold for mixture and then through the inlet channel into the central region of the Swiss roll for combustion. Labview data acquisition software was used to control the mass flow controllers and to record the temperatures of each thermocouple (Figure 7, Figure 8). Extinction limits was set to within 5% of the reported value.

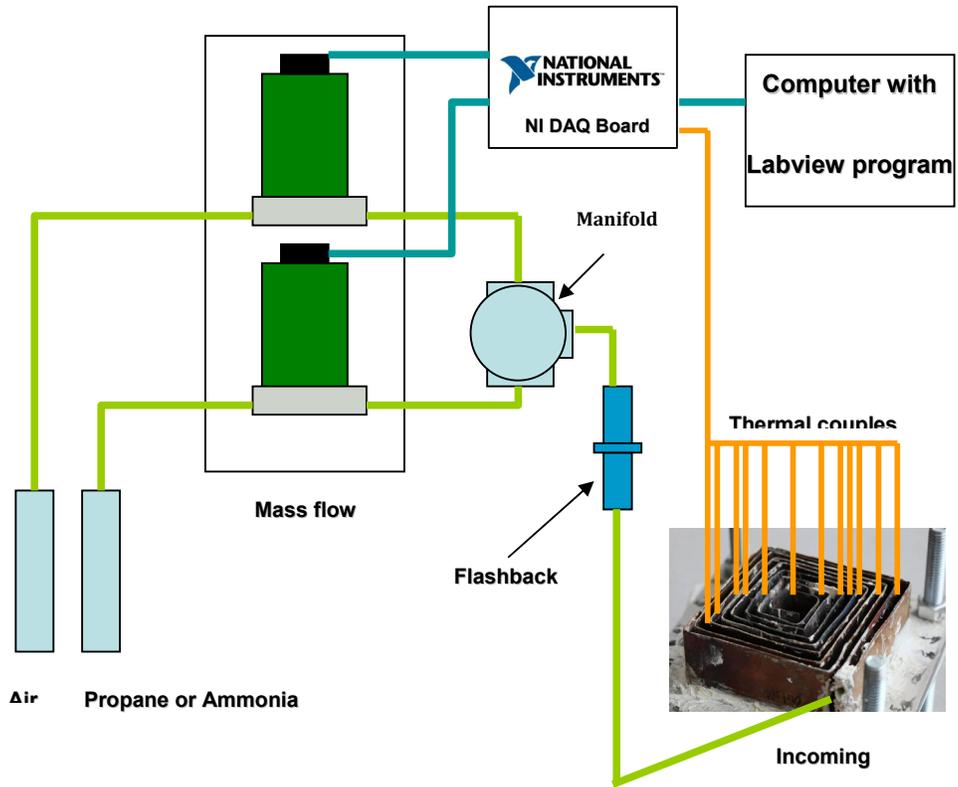


Figure 7: Schematics of the experimental setup.

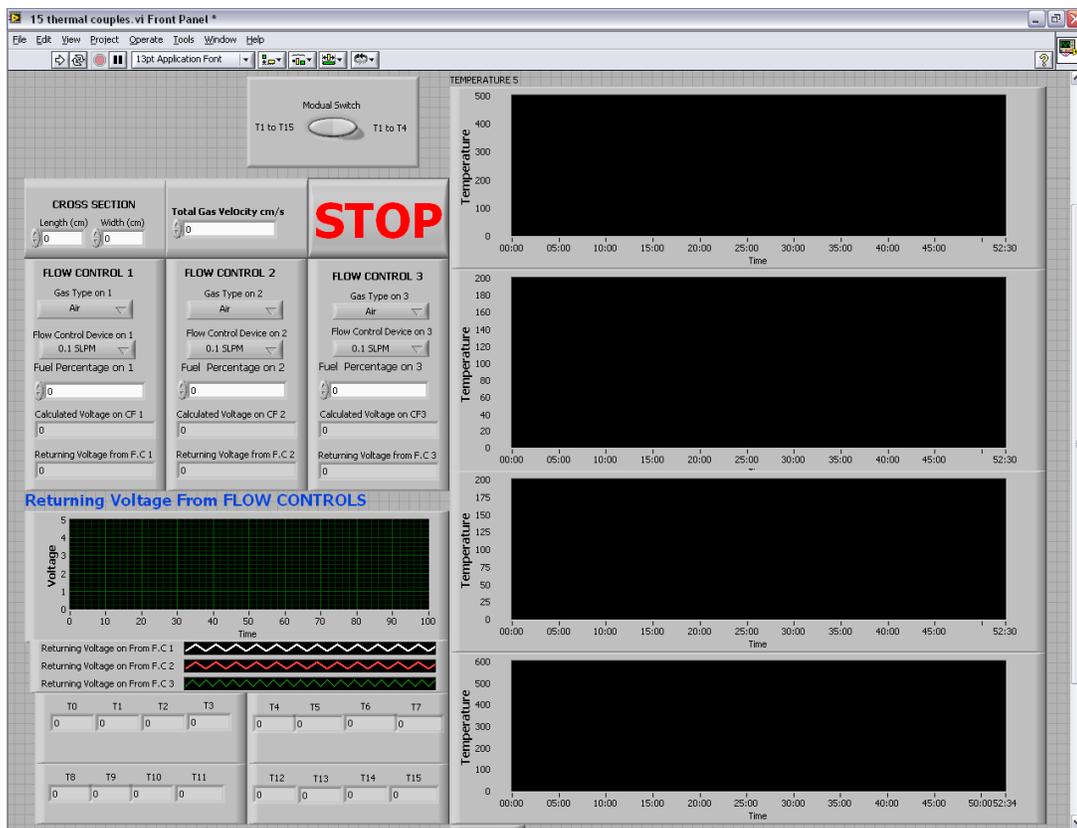


Figure 8: Labview program for controlling the mass flow controllers and recording the temperatures of the thermocouples.

## Chapter III: RESULT AND DISCUSSION

### 1. EFFECT OF AMMONIA TREATMENT ON PT CATALYST USED FOR LOW TEMPERATURE REACTION.

Table 1 shows the 12 different treatment conditions for treating bare foil platinum catalyst. The equivalence ratio ( $\phi$ ) is based on the ratio of fuel and air from the chemical equation,  $4NH_3 + 3O_2 \longrightarrow 6H_2O$  where Nitrogen is ignored. When the mixture contains 22 % of the ammonia, it reaches the equivalence ratio 1 which represents the complete reaction. When  $\phi < 1$ , the mixture is in fuel lean condition which contains excessive air and results oxidation of the catalyst. On the contrary, when  $\phi > 1$ , the mixture is in fuel rich condition which contains enough ammonia and results better performance of the catalyst. For a 15 minute treatment, it was 0.7 at 101 °C (sample 12) and 1.3 at 336 °C (sample 8) for the lowest and highest treatment temperatures respectively. To test the performance of the catalysts with different conditions of pre-treatment, Vespel<sup>TM</sup> Swiss roll combustor was adopted. Due to the conditions of treatment, sample Pt 008 and Pt 012 produced completely different results (Figure 10). Pt 008 catalyst treated with 25% of ammonia ( $\phi=1.25$ ) at high

Catalyst sample #	Ammonia (%)	Propane (%)	Velocity (cm/s)	Treatment time (min)	Reaction Temperature (°C)
1	15	0	10	30	212
2	18	0	10	30	230
3	22	0	10	30	217
4	25	0	10	30	227
5	30	0	10	30	263
6	25	0	5	30	214
7	25	0	15	30	185
8	25	0	10	15	336
9	25	0	10	45	240
10	25	0	10	60	216
11	10-15-20-25	0	10	15-15-15-15	115-215-334-354
12	25-20-15-10	0	10	15-15-15-15	231-215-142-101

*Table 1: Treatment conditions of catalyst.*

temperature for 15 minutes (Table 1) had the best performance when the reaction temperature was close to 200 °C at  $Re = 8$  (Figure 10). In contrast with Pt 008, Pt 012 treated in 4 segments starting with fuel rich condition and ending with fuel lean condition ( $\phi = 0.41$ ) for 15 minutes for each segment had the worst performance. It could be caused by oxidation when the catalyst was in fuel lean condition. Therefore, the best treatment method is to treat the catalyst in fuel rich condition so that it would not be oxidized. Samples Pt 008, Pt 009, and Pt 010 in Table 1 were treated with the same amount of fuel for different durations. Pt 008 has wider extinction limits and higher operation temperatures than other samples. Thus, a catalyst treated in fuel rich condition at low velocity for a short time has the best performance.

SEM was employed to examine the differences of Pt catalyst surfaces treated with ammonia before and after combustion tests. Bare Pt catalyst in Figure 11 (a) shows typical flat surface structure. For the samples treated with ammonia before combustion tests, SEM images (Figure 11 (b) ~ (d)) reveal varied surface structures on different catalysts. According to the images, ammonia creates step-like grain structure on the Pt catalyst surface after ammonia treatment. Some studies [McCabe and Borer, 1974] showed that ammonia reducing yields superior Pt catalyst performance due to an increase in surface area since ammonia etches the catalyst surface. However, this is not merely a surface area effect since increasing bulk area

had a little effect on combustion performance from earlier experiments performed by using four times more catalyst (total area  $\sim 112 \text{ cm}^2$ ) in the combustor center [Ahn and Ronney, 2005]. This change in structure with ammonia treatment is noteworthy in that it increases the performance of the catalyst, but only for low-temperature reactions [Ahn and Ronney, 2005]. Figure 12 shows the change of the Pt surface structure after the combustion tests. It is obvious that the ammonia-treated catalysts has the step-like grain structure which is a major factor to better catalyst performance. It is suggested that the increasing in performance of the catalyst is not due to the surface area but the differences of treatment conditions such as treatment temperature, fuel concentration, Reynolds number, and duration. As a result, the change of the structure on the catalyst surface due to ammonia treatment in fuel rich, low velocity, and short duration increases the performance of the catalyst at low temperature reaction, which is more desirable for meso- or micro-combustors.

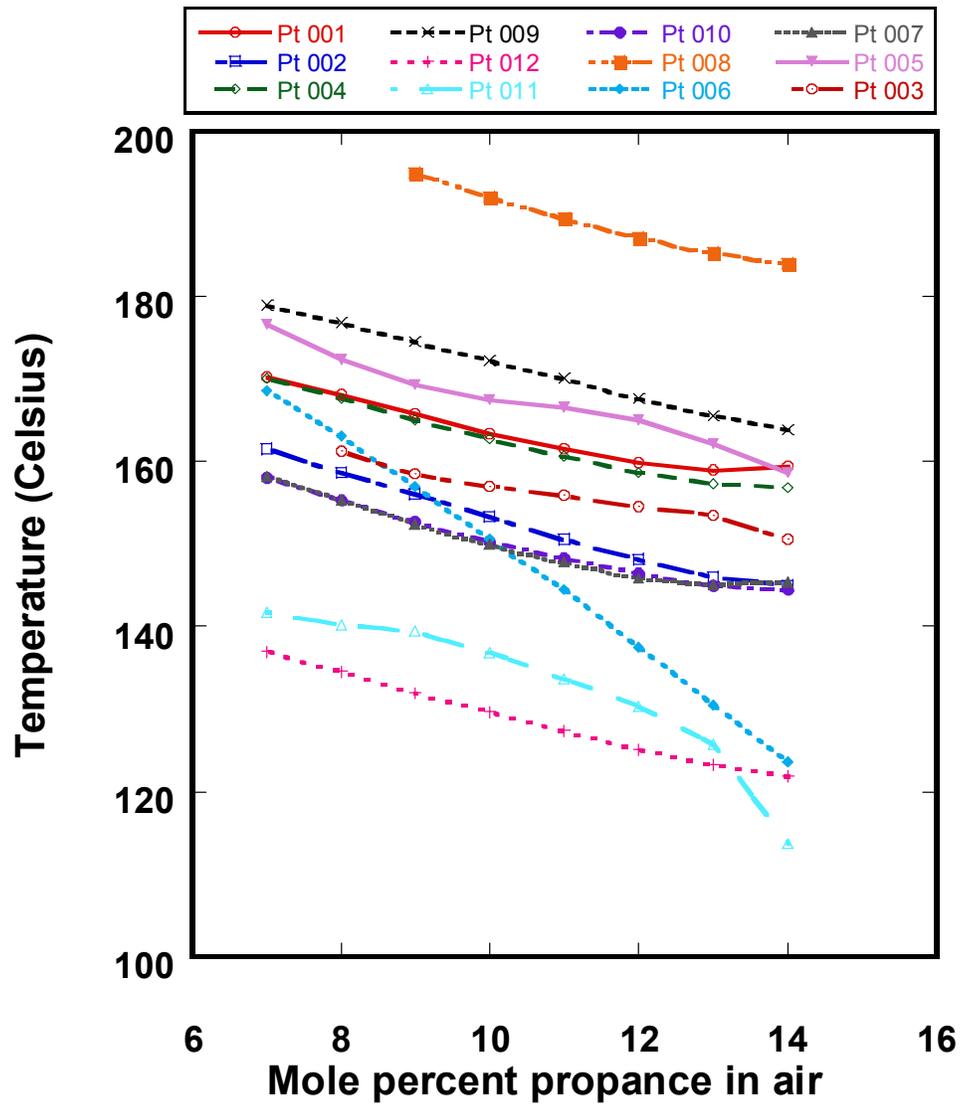
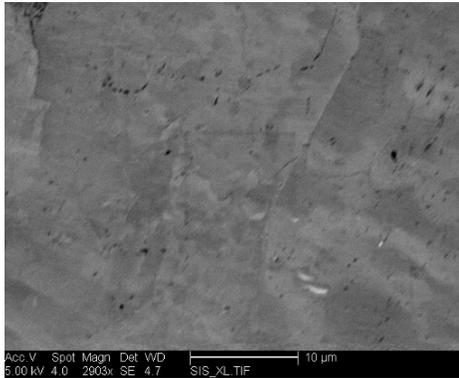
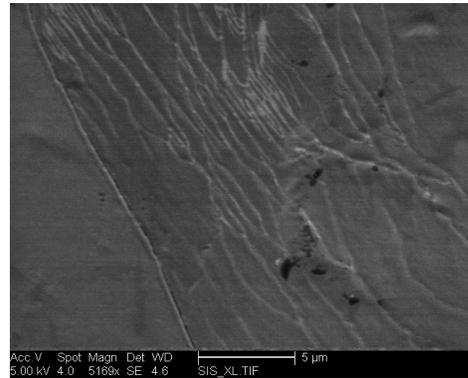


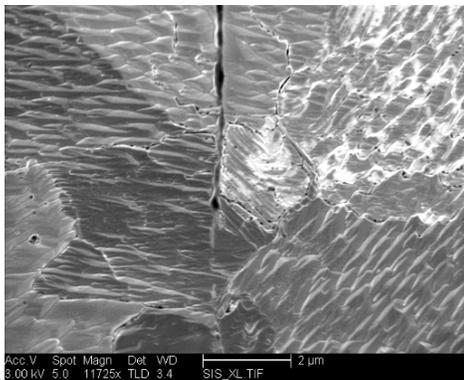
Figure 10: The performance of catalyses with different treatment in Vespel<sup>TM</sup> Swiss roll combustor at  $Re=8$ .



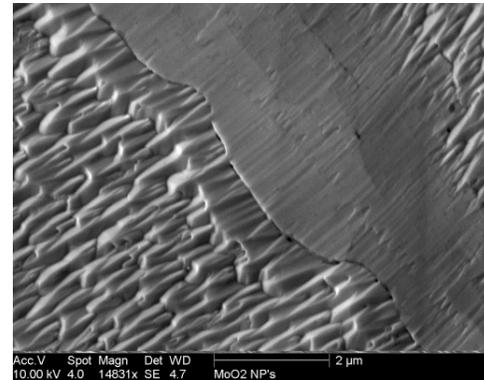
(a)



(b)

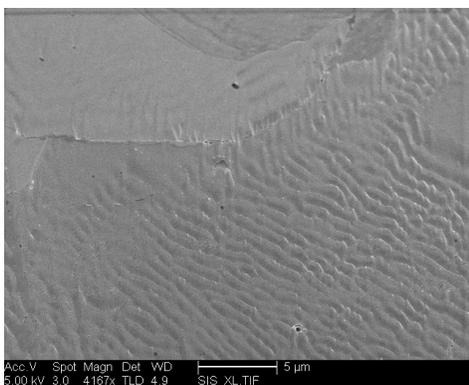


(c)

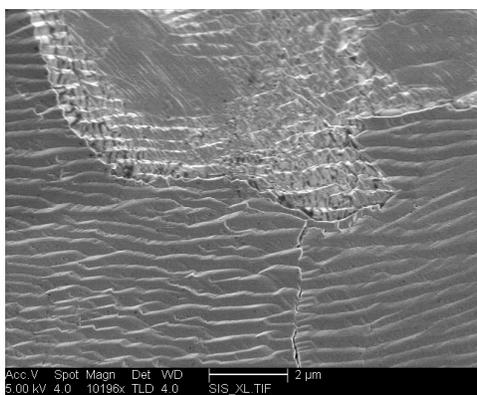


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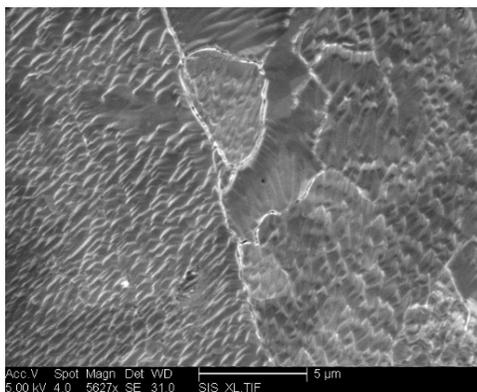
*Figure 11: (a) Bare untreated Pt. (b) Sample PT008 with NH<sub>3</sub> treatment. NH<sub>3</sub> create circle shape grand boundaries on Surface structure. (c) Sample PT009 with NH<sub>3</sub> treatment. Atomic step structure observed within certain grains. (d) Sample PT010 with NH<sub>3</sub> treatment.*



**(a)**



**(b)**



**(c)**

*Figure 12: (a) Sample PT008, with NH<sub>3</sub> treatment, after hydrocarbon combustion testing. (b) Sample PT009, with NH<sub>3</sub> treatment, after hydrocarbon combustion testing. (c) Sample PT010, with NH<sub>3</sub> treatment, after hydrocarbon combustion testing.*

## 2. EXTINCTION LIMITS

Lean and rich extinction limits are determined by starting from a steady burning state, then decreasing or increasing fuel concentration with the igniter off until the self-sustained chemical reaction stops and then the reaction temperature decreases to room temperature. These limits are independent of the path in mixture and are corresponding to Reynolds number. The Reynolds number is defined based on the area-averaged gas velocity at the inlet, the gas kinematic viscosity at the inlet, and the gap width. As the gas velocity increases, the reaction temperature increases proportionally due to the decreasing in gas density. At higher Reynolds number, turbulent flow near the inlet is very weak when it occurs [Ahn 2007]. Figure 13 shows three sets of lean and rich extinction limits for NH<sub>3</sub>- pretreated catalytic reaction, gas phase reaction, and the out-of-center reaction zone.”

Two types of extinction limits were identified in earlier studies [Jones et al. 1978, Maruta et al. 2002, Norton and Vlachos 2003, Ronney 2003]. The “blow-off” limit occurs at a high-Re where the extinction limit equivalence ratio ( $\phi_{lim}$ ) increases slightly as Re increases, and a low-Re limit where  $\phi_{lim}$  increases considerably as Re decreases, induced by heat loss [Jones et al. 1978, Maruta et al. 2002, Norton and

Vlachos 2003, Ronney 2003]. The heat loss limit which applies to most of the test conditions results because peak temperatures are only weakly dependent on  $Re$  and thus heat loss rates are almost independent of  $Re$ . Heat generation rates are proportional to mass flow and thus Reynolds number. On the contrary, as  $Re$  decreases, heat generation rates decrease and so the ratio of heat loss to heat generation rates increases. Consequently, as long as  $Re$  is sufficiently large, the ratio of heat loss to heat generation is small and hence the self-sustained chemical reaction can be held in Swiss-roll combustors. Figure 13 shows that the extinction limits in gas-phase reaction are nearly symmetric about stoichiometric, which yields the highest potential flame temperature. The difference of the lean limits in mixture composition between catalytic and gas-phase reaction is small. Non-catalytic rich limits of nearly 2 times stoichiometric were also found. The gas-phase reaction could not be sustained below a Reynolds number of approximately 45.

In the most test conditions (with or without catalyst), it was found that the combustion occurred in the center of the reaction zone was in a “flameless” mode which no visible flame could be observed [Ahn 2005]. Recently, other investigators [Katsui and Hasegawa 1998, Maruta et al. 2000, Wüning and Wüning 1997] had observed similar behavior in macro-scale combustors using highly preheated air. The region “out-of-center reaction zone” in Figure 13 shows that the sustained combustion

occurs around the inlet channel of the Swiss roll combustor. It corresponds to higher  $Re$  where the ratio of the heat loss to heat generation is lower, and the amount of heat in the out-of-center reaction zone is strong enough to yield propagating fronts without the benefit of the heat recirculation. Under these conditions, the visible flames can be observed near the combustor inlet [Ahn 2005]. In the gas-phase reaction, once the reaction shifts from the center of the combustor, it is impossible to be re-centered by adjusting the mixture of air and fuel. On the other hand, catalytic reaction can be easily retained at the center. This is plausible since the catalytic reaction temperature is much lower than the gas-phase reaction temperature; the difference is typically around 250 °C at the minimum sustained temperature in a steel combustor (Figure 14).

Figure 13 also shows that catalyst reduction using ammonia significantly improves the catalyst performance, which self-sustained reaction at  $Re \sim 5$  can be achieved. This corresponds to the condition in low maximum temperature due to heat loss and long residence time. However, with this catalyst, an additional driving force was needed to desorb O(s) via rich mixtures, and the behavior was very biased toward richer mixtures [Ahn 2007]. This led to lean limits rich of stoichiometric for Reynolds number approximately less than 15 with rich limit ( $\phi_{lim} > 10$ ). No such self-sustained reaction was found without catalyst. At higher  $Re$  where either catalytic or gas-phase reaction is possible the catalyst would enable slightly leaner

mixtures to be burned at much lower temperatures and therefore much lower fuel utilization.

### 3. THERMAL BEHAVIOR

Figure 14 shows the maximum temperatures at lean and rich extinction limits in catalytic reaction and gas-phase reaction with different Reynolds numbers using the steel Swiss-roll combustor. The maximum temperatures were measured at the center of the reaction zone where the temperature was the highest comparing to other turns (Figure 2 (a) and Figure 15). The minimum reaction temperatures in catalytic and gas-phase reactions were around 62 °C at  $Re = 5$  with average inlet gas velocity 1.5 cm/s and 400 °C at  $Re = 46$  with average inlet gas velocity 14.5 cm/s, respectively. Figure 14 also shows that the temperature in catalytic reaction is typically 250 °C lower. The gas-phase reaction cannot be sustained below  $Re = 46$ , and the ammonia pretreated catalysts can be used to continue the combustion for  $Re < 46$  to avoid insufficient fuel velocity. It suggests that the catalytic reaction is beneficial only when gas-phase reaction is not possible.

The temperatures at lean extinction limit in both catalytic and gas-phase reactions are higher than rich extinction limit due to the air-to-fuel ratio (Figure 14). The minimum mixture required in gas-phase reaction is 2.5 % of fuel with 97.5 % of air for the fuel lean condition and 7 % of fuel and 93 % of air for the fuel rich condition to

maintain the minimum self-sustained reaction. According to the chemical equation  $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$  with Nitrogen ignored, the ideal fuel to air ratio for the complete reaction (maximum reaction temperature occurs) is 4 % of fuel and 96 % of air. Figure 15 shows the temperature recorded by each thermocouple in the steel Swiss roll combustor for catalytic reaction using  $28.51 \text{ cm}^2$  of catalyst at  $Re = 30$ .  $T_{center}$  is the temperature recorded at the center of the combustor,  $TC_0$  recorded at the first exhaust turn, and  $TC_2$  recorded at the second inlet turn, etc (see also Figure 2 (a)). Temperatures shown in Figure 15 correspond to the fuel concentration. Chemical reaction only occurs on the catalyst surface, and it reaches the highest reaction temperature  $337 \text{ }^\circ\text{C}$  at the center of the reaction zone among all fuel concentrations. Thus, the location of the heat source is fixed. The lowest reaction temperature  $48 \text{ }^\circ\text{C}$  is at the outermost outlet turn. Consequently, the outward temperature gradient across the turns of the combustor is proportionally decreasing due to the heat loss.

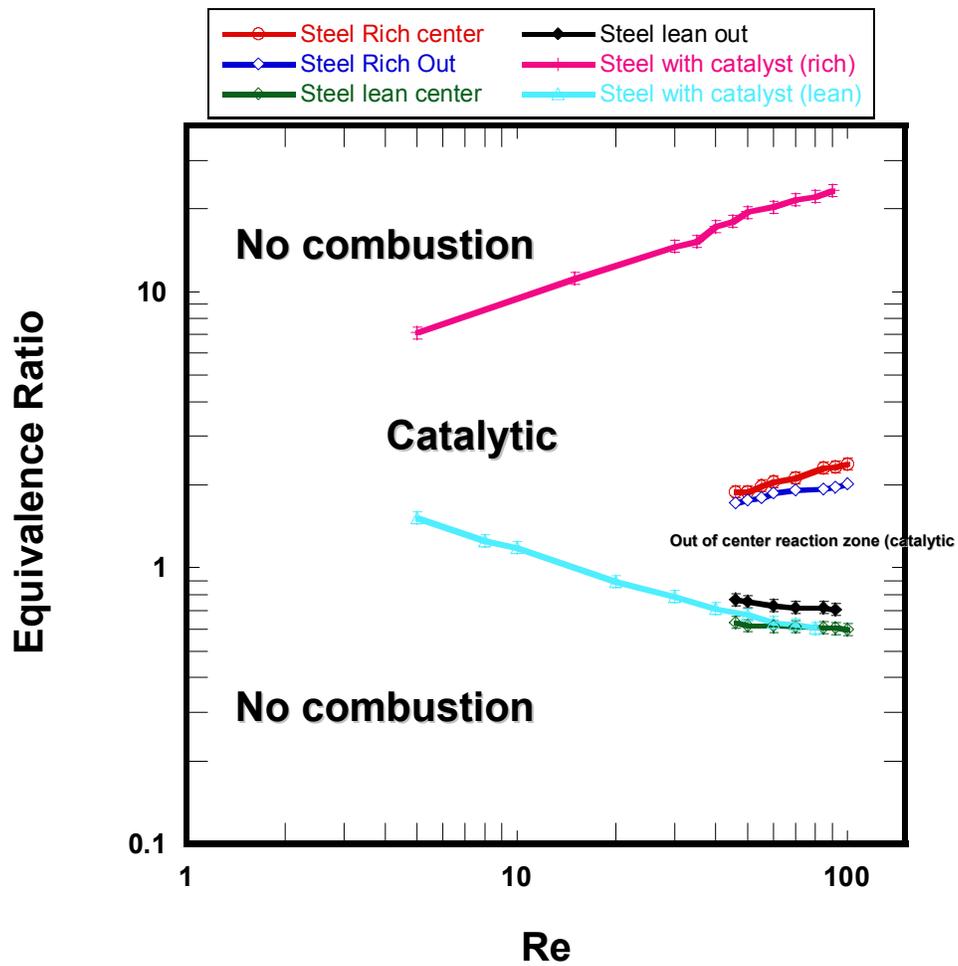


Figure 13: Extinction limit map for catalytic and gas phase combustion in the Swiss roll type heat exchanger made with steel.

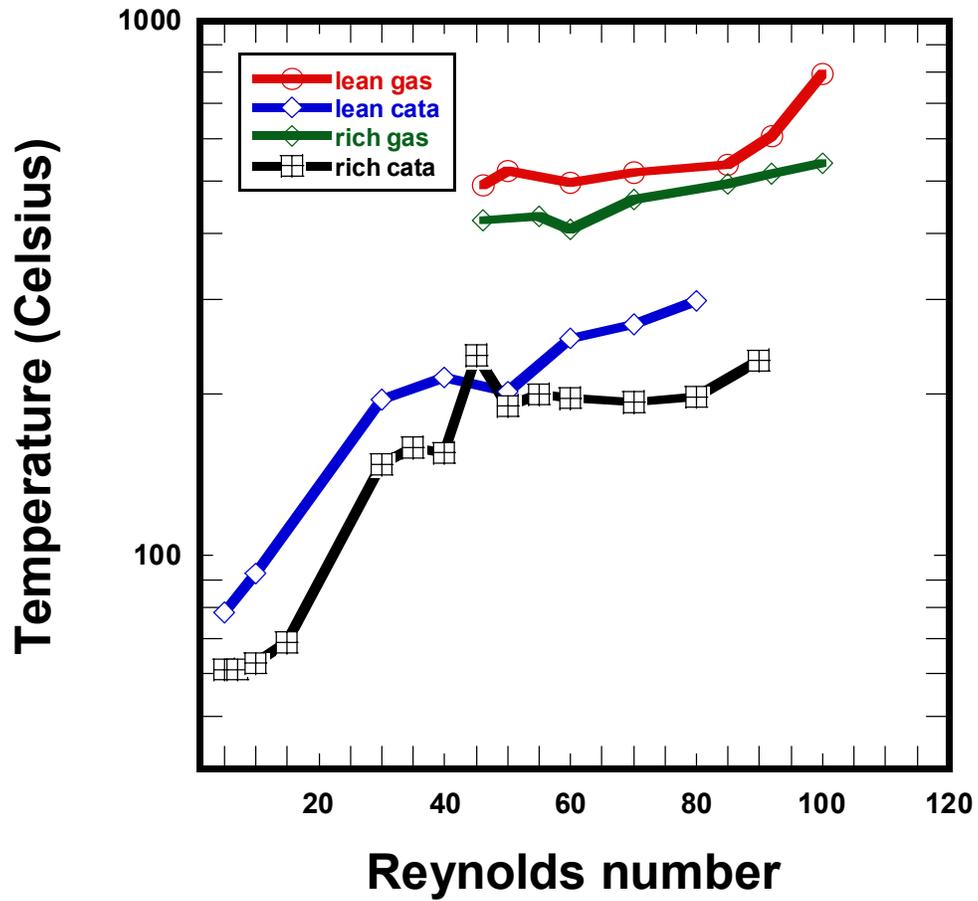


Figure 14: Maximum temperature at different extinction limit corresponds to Reynolds number in Steel Swiss-roll combustor. The temperature is measured in the center of the reaction zone.

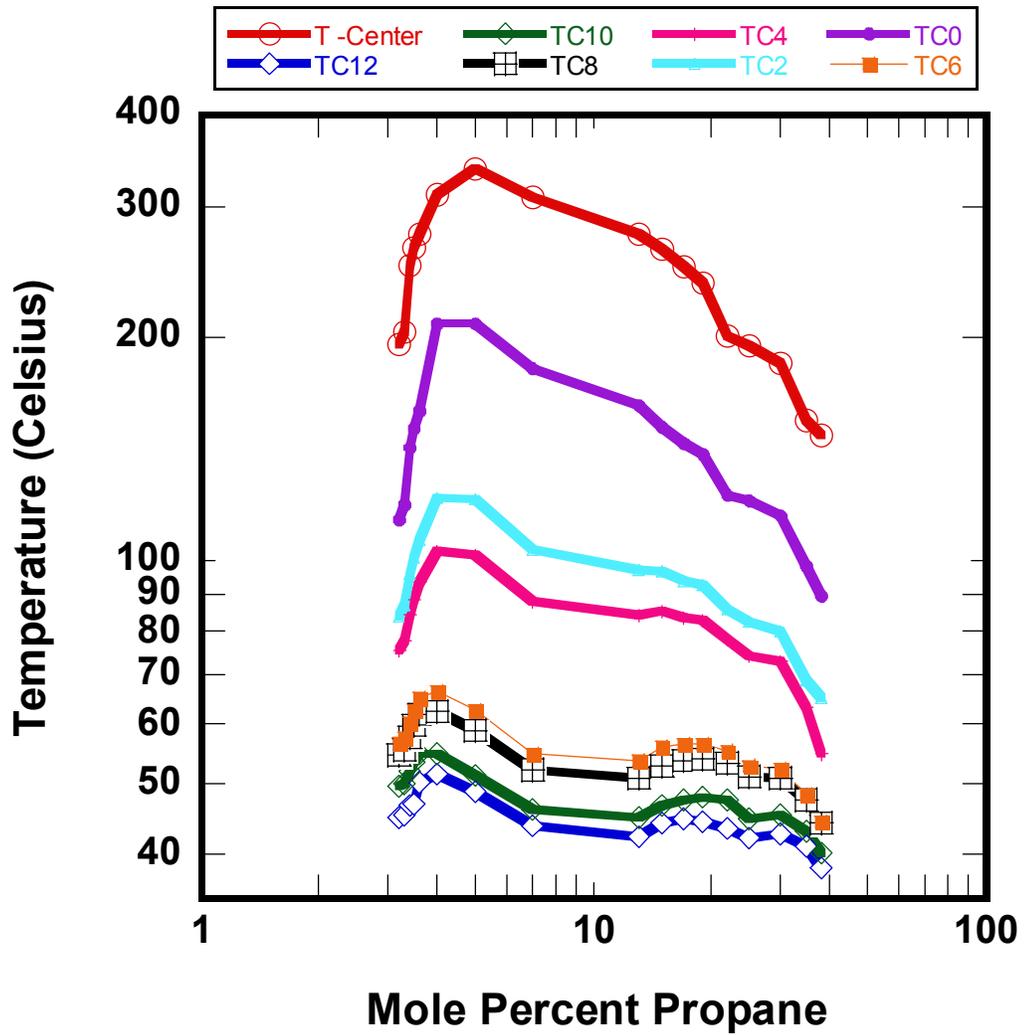


Figure 15: Maximum temperature for catalytic combustion at  $Re = 30$  in Steel Swiss-roll combustor. The temperature is measured in the center of the reaction zone.

#### 4. EFFECT OF THERMAL CONDUCTIVITY

Recently, other investigators' simulations [Ronney, Kuo, Yang, Tsai, Hung, 2008] showed that the heat conduction and the number of turns for the Swiss roll combustor has a major impact on the performance of Swiss roll combustor. In addition, they indicated that the optimal combustor performance requires thin wall with low thermal conductivity because the heat conduction effect is more efficient at smaller Reynolds number. Copper, steel, ceramic and polyimide plastic Swiss roll combustors made in four turns were constructed to verify the results. The thermal conductivity of copper, steel, ceramic and plastic is 400 W/m-K, 40 W/m-K, 4 W/m-K, and 0.4 W/m-K, respectively, at 300K. The lean and rich extinction limits are determined by starting a steady burning state, then decreasing or increasing fuel concentration with the igniter off until the self-sustained chemical reaction stops and then the reaction temperature decreases to room temperature.

Figure 16 and Figure 17 show the lean and rich extinction limits with different Reynolds numbers. Figure 16 shows the comparison between the copper and ceramic combustors for gas-phase extinction limits with different Reynolds numbers. It demonstrates that reducing wall thermal conductivity allows self-sustained reaction

being obtained particularly at low Reynolds number when heat loss becomes predominant. The “out-of-center reaction zone” in the Figure 16 corresponds to the conditions that the heat-recirculation is not required to sustain reaction. For this range of Reynolds numbers, as the mixture becomes increasingly rich or lean, the thin reaction zone moves toward the center of the Swiss roll until a broad centered flameless reaction zone appears. At very low Reynolds number or in very rich or lean mixtures, heat-recirculation is required.

In gas-phase reaction, copper combustor can not be sustained below  $Re = 48$ , but ceramic combustor can be sustained at  $Re = 45$  which is better than the copper combustor. Figure 17 shows the comparison between the catalytic extinction limits obtained by using both the copper and ceramic combustors. With ammonia pretreated catalyst, self-sustained reaction using ceramic and copper combustors can be obtained at  $Re = 5$  and  $6$ , respectively. For  $Re < 10$ , the lean extinction limits are actually rich of stoichiometric. The rich extinction limit is almost 16 times stoichiometric at  $Re = 10$  and is 10 times stoichiometric at the lowest  $Re = 5$ . Also non-catalytic rich limit is nearly 2 times stoichiometric according to Figure 17.

Figure 18 shows a comparison between the catalytic extinction limits with different Reynolds numbers obtained by using four combustors which have different thermal conductivities. With ammonia pretreated catalyst, self-sustained combustion

at Reynolds number as low as 4.2 can only be obtained in the polyimide plastic combustor. In the steel and ceramic combustors, catalytic reaction can not be sustained below  $Re = 5$ . The copper combustor can not be sustained below  $Re = 6$ . Since the polyimide plastic combustor has the lowest thermal conductivity, its heat loss is the smallest; therefore, the combustor can have the highest operation temperature and extend extinction limits widely. As a result, polyimide plastic combustor has the broadest extinction limits. On the contrary, copper combustor has the narrowest extinction limits.

The extinction limits at  $Re = 20$  recorded in Figure 19 indicates that when thermal conductivity decreases, the extinction limits of the combustor can be broadened. It also indicates that it is impossible to have heat recirculation when the thermal conductivity reaches zero, but it is possible to predict the extinction limits when thermal conductivity is not zero. Therefore, there must be an optimal thermal conductivity that can widely extend the extinction limits.

Figure 20 is the comparison of the operation temperatures between the polyimide plastic, copper, steel and ceramic combustors under the same condition of using ammonia pretreated catalyst at  $Re = 30$ . At this Reynolds number, reaction occurs at the center of the combustor is also in the “flameless” mode discussed previously [Ahn 2005]. The operation temperature increases due to low thermal

conductivity of the combustor which has small heat loss. Each temperature curve is corresponding to different thermal conductivity. The combustor which has lower thermal conductivity has broader operation temperature curves, which corresponds to the results shown in the previous figures.

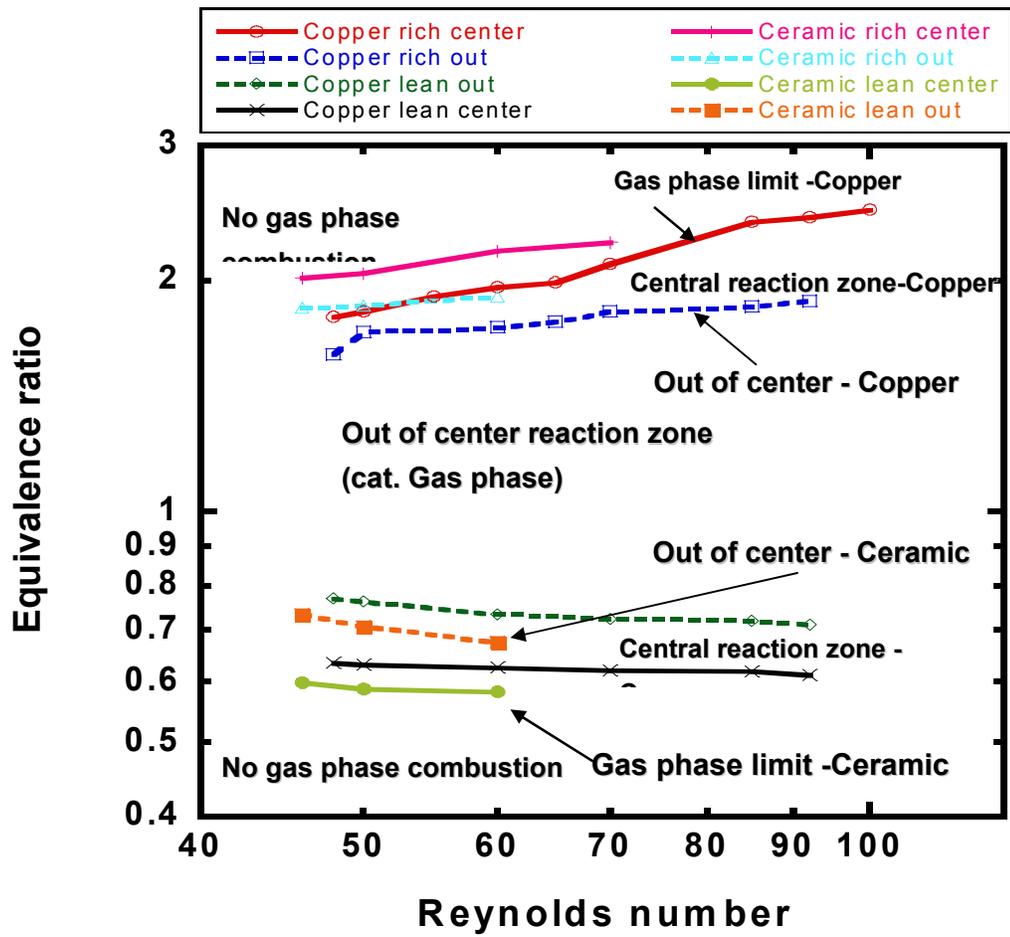


Figure 16: Comparison of extinction limits in gas-phase combustion between copper and ceramic Swiss roll combustors.

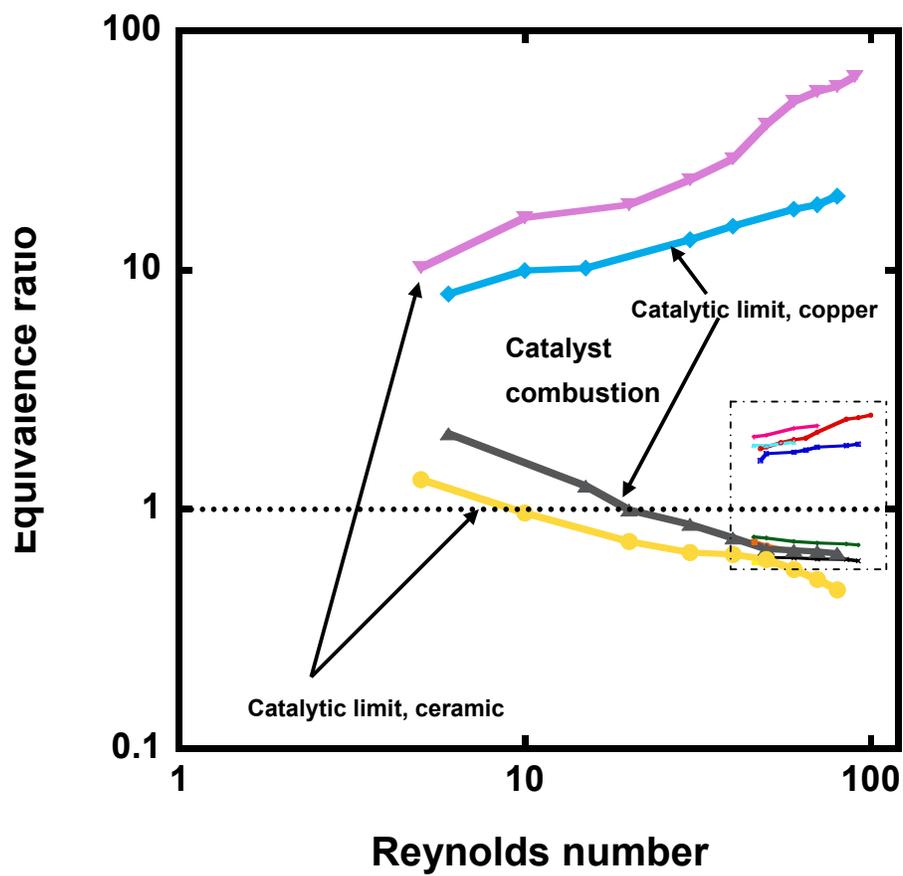


Figure 17: Comparison of extinction limits in catalytic reaction between copper and ceramic Swiss roll combustors.

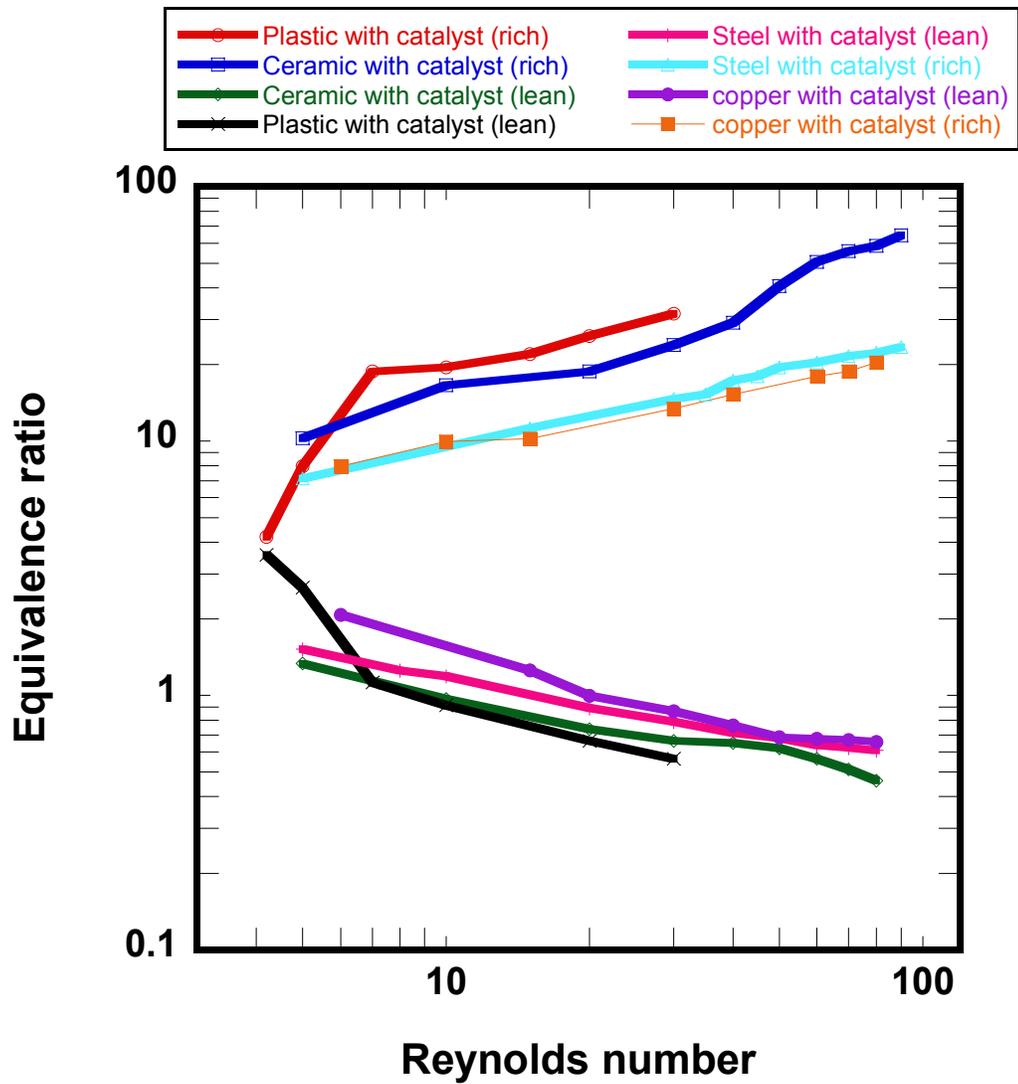


Figure 18: Comparison of extinction limits in catalytic reaction between copper, steel, ceramic and plastic Swiss roll combustors.

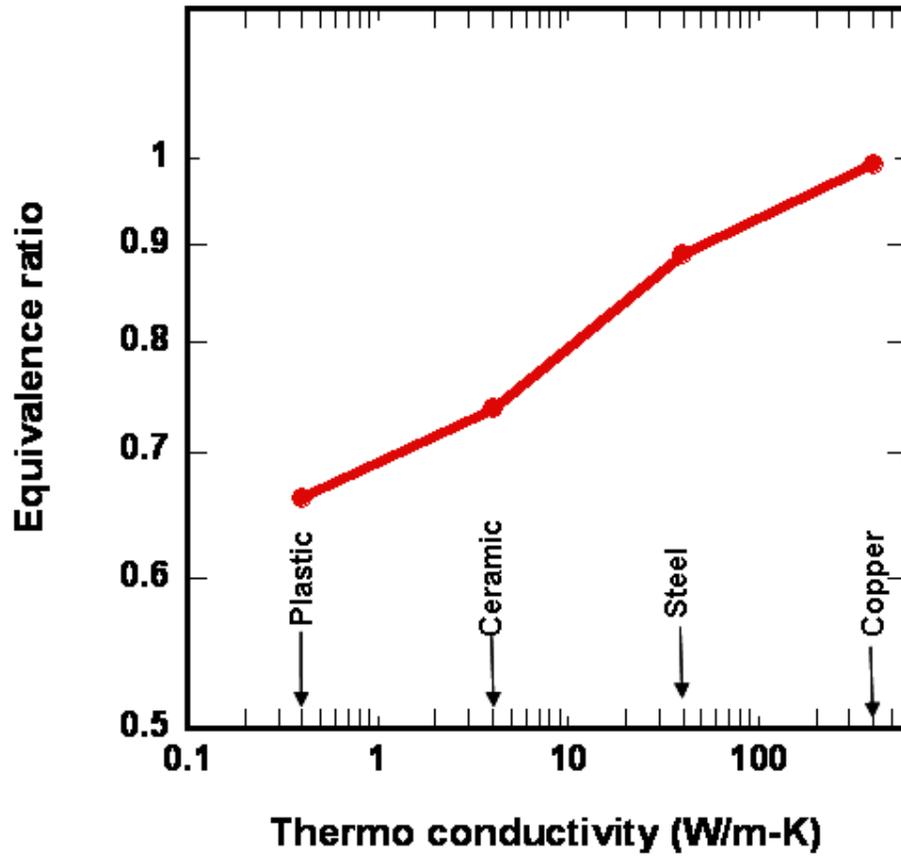


Figure 19: Comparison catalytic lean extinguish limits with different thermal conductivity at Reynolds number 20.

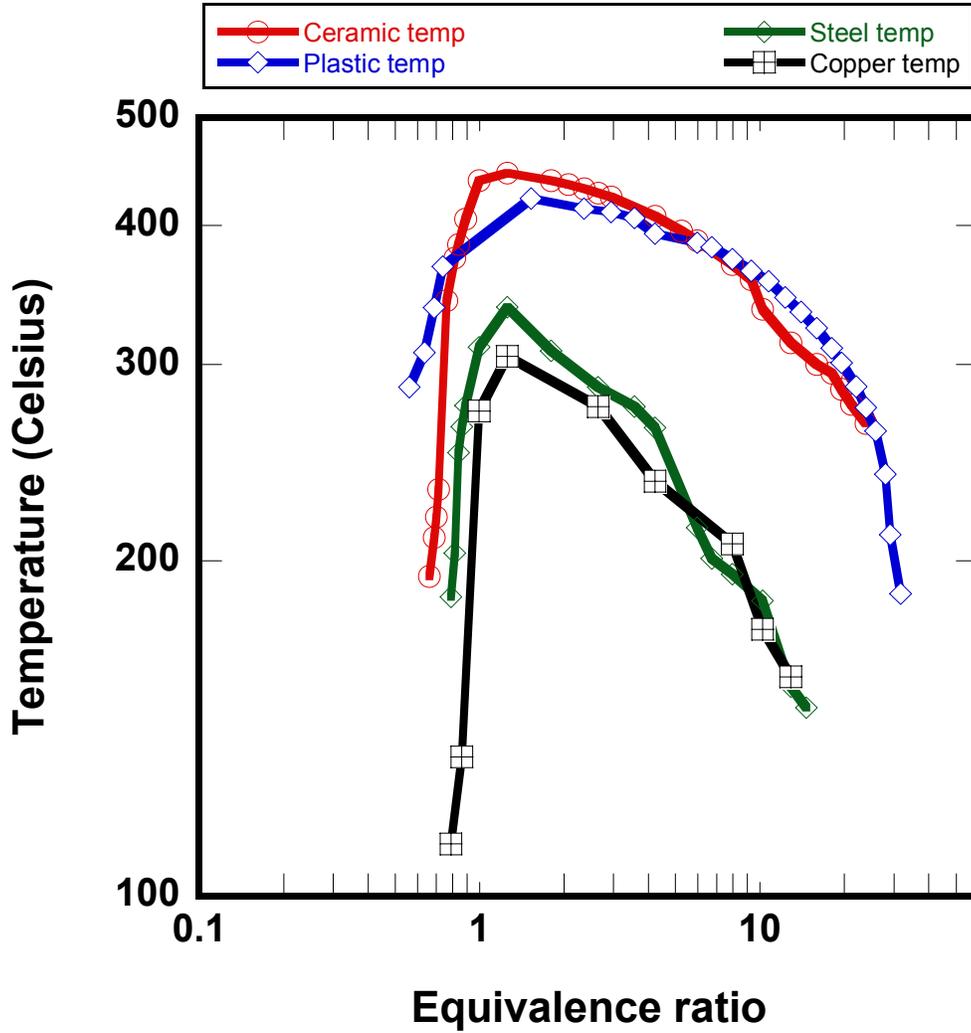


Figure 20: Comparison the temperatures obtain in copper, steel, ceramic and plastic combustors with catalytic reaction at Reynolds number =30.

## Chapter IV: CONCLUSION

Experiments performed at low Reynolds number indicate that combustion in a micro-scale combustor is possible, but it has to be catalytic reaction in Swiss roll shape or similar heat exchanger geometries. The heat recirculating combustor allows recycling enthalpy by conducting the heat from high temperature products to reactants via the walls of combustor. Also from the extinction limits of the Swiss roll, it can be seen that the Swiss roll can sustain the reaction under the conditions such as lean mixture and large heat loss with or without the catalyst but the performance is significantly different. Without catalysts (gas-phase reaction), the sustaining reaction can not be obtained with  $Re < 45$ . The extinction limits are nearly symmetric with respect to stoichiometric since stoichiometric conditions yield the highest potential flame temperature [Ahn 2008]. With the catalyst, the self-sustained reaction can be maintained at lower temperatures with lower Reynolds number which is less than 5, and the minimum sustained temperatures for all types of tested combustors are typically 300 °C lower than those without the catalyst. At these low Reynolds numbers, the lean and rich flammability limits are actually rich of stoichiometric. The results also show that catalyst reduction using ammonia significantly improves the catalyst performance, but only at low Reynolds number, corresponding to conditions

with low maximum temperatures. By employing ammonia pre-treated platinum catalyst in Swiss roll combustors, hydrocarbon (such as propane) reaction can be sustained at  $Re = 4.2$  (see Figure 19). Under this condition, low-temperature reaction (116 °C) of hydrocarbon fuels can be sustained. The ammonia pre-treatment etches the catalyst surface on the scale of few  $\mu m_s$ , and the surface structures are completely different from those without ammonia treatment. This change in structure increases the performance of the catalyst. However, it is not merely a surface area effect since increasing bulk catalyst area has almost no effect on combustion performance.

Experiments indicate that the optimal performance can be obtained by using combustors constructed with a material which has low thermal conductivity. Reducing wall thermal conductivity leads to less heat loss and increases the operation temperature. Thus, the combustors constructed by low thermal conductivity material result wider extinction limits at fuel lean and rich conditions, and the minimum sustained reaction can be obtained at very low Reynolds number. With catalysis and heat-recirculation, minimum self-sustained reaction at  $Re = 4.2$  can be obtained, and reaction occurred at the center of the combustor is in “flameless” mode. At low Reynolds number, the lean extinction limit is rich of stoichiometric ( $\phi_{lim} \sim 3.5$ ) and rich extinction limit is extremely rich ( $\phi_{lim} \sim 25$ ). Since reducing wall thermal conductivity will increase the operation temperature, the pick operation temperature at

$Re = 30$  for polyimide plaster combustor is  $437\text{ }^{\circ}\text{C}$  which is much higher than copper and steel combustors. Also the operation temperature curves corresponding to lower thermal conductivity combustors (see Figure 21) is broader than those with higher thermal conductivities. As a result, with low wall thermal conductivity, the heat loss can be reduced and the operation temperature can be increased since heat recirculation is sufficient to sustain the chemical reaction. Therefore, the polyimide plastic combustor has the best performance and is feasible for macro- or micro-scale thermochemical devices.

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