Preliminary investigation of ignition and flame stabilization using catalytic treatment of propellants for scramjets

D. Paukner⋆*, M. Gurtner*⋆ *and H.-P. Kau*⋆†
⋆*Institute of Flight Propulsion (LFA), Technische Universität München (TUM), Germany*
Boltzmannstrasse 15, 85748 Garching

Abstract

The possibility to reduce autoignition temperatures of a hydrogen/air mixture using pre-injection catalytic treatment of the propellant is investigated. The reduction can be achieved by providing radicals within the mixture, which promote chain branching reactions. A test bench has been set up which allows to comparatively evaluate the ignition energy with and without catalytic treatment. Only fuel rich equivalence ratios outside the ignition boundaries have been evaluated in the reaction chamber. It was found, that initially adsorbed oxygen on the catalyst has a positive effect on ignition. Subsequent tests aimed at continuous promotion of ignition using hydrogen/air mixtures showed an inhibiting effect.

1. Introduction

Currently, supersonic combustion research is focused on steady state conditions at flight Mach numbers of 8. The final goal of most scramjet related projects is to create a supersonic civil aircraft capable of traveling at these velocities during cruise. To save weight and complexity, systems with a low number of different propulsion devices and combined cycle engines are preferred. Therefore, it is suitable to conduct the transition to ram/scramjet mode as soon as the thermodynamic cycle efficiencies allow more efficient operation than the propulsion systems used during the start and initial acceleration stages. This extension of the engine flight envelope towards lower transitional flight Mach numbers creates new challenges in terms of combustor efficiency, flame stability and auto ignition limits within the scramjet combustor.

Figure 1 shows the operational range of a generic scramjet combustor. The envelope boundary towards higher flight Mach numbers is given by the dissociation temperature of combustion reactants and products, while the limit at lower flight Mach numbers is limited by auto ignition, ignition delay and flame stabilization. The lower limit is directly related to the combustor entry temperature, which can be influenced for a given flight state by controlling the combustor entry Mach number. To do so, however, requires a complex system of movable surfaces to create a variable inlet geometry. Another possibility to extend the lower flight mach limit is to improve the chemical properties of the propellant mixture.

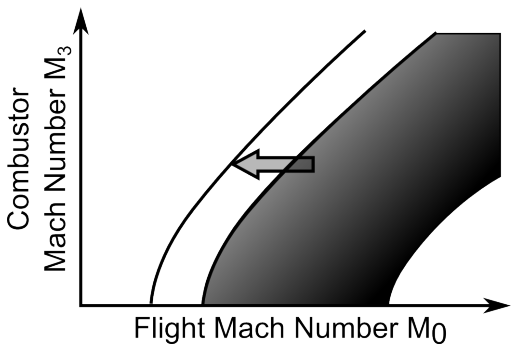

Figure 1: Operational boundaries of a generic scramjet

Research by Mitani et al on the effects of vitiated air in comparison to storage heated air showed a strong dependency of autoignition and combustion stability within a supersonic combustor towards facility air radical concentration

[1]. Analytical calculations using simplified models suggested a decrease of ignition delay time by 50% with an oxygen radical concentration of 100 ppm. Gas sampling measurements of the facility air heater using H_2-O_2 combustion showed a OH radical concentration of 80 ppm behind the facility nozzle, while no residual hydrogen was detected. This OH concentration was expected to be higher during actual testing conditions due to chemical quenching in the sample vessels. The comparison of combustion stability between vitiated and storage heated air showed better autoignition, flame holding and combustion stability for the vitiated air case. Additionally, a higher equivalence ratio could be achieved before the engine fell to the unstart condition. The inhibiting effects of H_2O were also considered by [1], but were determined to be negligible at the low static pressure of 25 kPa encountered during ignition in their test bench. These findings suggest that intentional radical production and injection into a scramjet combustor can significantly decrease the autoignition boundary and ignition delay times.

In order to produce and inject radicals and intermediate reaction products into a scramjet combustor, several concepts have been investigated in the past. For example, micro-ramjets within strut injectors [2] as well as the internal combustion of a pilot flame and subsequent freezing of the chemical reaction by acceleration through a laval nozzle were suggested. Additionally, a system with catalytic ignition, propagation of the reaction to the gas phase and ejection of the flame into the free stream was investigated [3, 4]. Other concepts include plasma torches or dielectrical barrier discharge setups [5]. All of these concepts, however, share the fact that an open flame has to be established within the injector geometry. This requirement limits the minimal injector size, as a cavity for the open flame has to be provided. Additionally, a fuel/air mixture within the ignition boundaries of the fuel has to be supplied in order to achieve combustion within the injector, which results in a high heat transfer onto the interior injector structure. Combined with the lost cooling effect of the fuel in the proximity of the injection port, this can lead to structural problems within the injector.

Due to the thermal loads linked with a gas phase combustion inside the injector, a partial, heterogenous combustion on a catalytic surface is chosen. The use of catalytic surfaces enables the continuous reaction of mixtures well outside the ignition boundaries. This allows to limit the heat release within the injection concept, which both improves structural integrity of the injection concept as well as the catalysts lifetime. Also, the space requirement is limited to the catalyst bed, which can be realized using a coated ceramic pipe or platinum wool stored inside a small cavity. This allows for significantly smaller injector geometries as compared to systems with internal gas phase combustion, where quenching at the walls requires a certain volume to be provided.

2. Chemical background

The heterogenous H_2-O_2-Pt_s reaction mechanism published in [6] is listed in table 1. It is commonly used to calculate the surface chemistry of platinum catalysts. While there is a desorption coefficient defined for OH(s), the sticking coefficients for atomic hydrogen and oxygen are selected as 1 and desorption of these species is disregarded. This

Table 1: Elementary heterogenous reaction scheme

#	Reaction			**A** $[mol \cdot cm \cdot s]$	**E** $[kJ/mol]$	S^0 $[-]$
	Adsorption Reactions					
1	H_2 + 2 Pt(s)	$\rightarrow$	2 H(s)	–	–	0.046
2	H + Pt(s)	$\rightarrow$	H(s)	–	–	1.0
3	O_2 + 2 Pt(s)	$\rightarrow$	2 O(s)	–	–	0.07
4	O + Pt(s)	$\rightarrow$	O(s)	–	–	1.0
5	H_2O + Pt(s)	$\rightarrow$	H_2O(s)	–	–	0.75
6	OH + Pt(s)	$\rightarrow$	OH(s)	–	–	1.0
	Surface Reactions					
7	H(s) + O(s)	$\rightleftharpoons$	OH(s) + Pt(s)	3.7×10^{21}	11.5	–
8	H(s) + OH(s)	$\rightleftharpoons$	H_2O(s) + Pt(s)	3.7×10^{21}	17.5	–
9	OH(s) + OH(s)	$\rightleftharpoons$	H_2O(s) + O(s)	3.7×10^{21}	48.2	–
	Desorption Reactions					
13	2 H(s)	$\rightarrow$	H_2 + 2 Pt(s)	3.7×10^{21}	$67.4-6\Theta_H$	–
14	2 O(s)	$\rightarrow$	O_2 + 2 Pt(s)	3.7×10^{21}	$213.2-60\Theta_O$	–
15	H_2O(s)	$\rightarrow$	H_2O + Pt(s)	1.0×10^{13}	40.3	–
16	OH(s)	$\rightarrow$	OH + Pt(s)	1.0×10^{13}	192.8	–

is, however, a simplification, as research into the thermal desorption of oxygen showed peaks in the desorption of atomic oxygen in the area of 600-800 K in a multi-component catalyst used in the partial combustion of hydrocarbons [7]. Such high temperatures can be achieved locally at active surface sites due to the heat release of the heterogenous

reaction. While the desorption rates of atomic species and molecular radicals are low in comparison to the rates of regular molecular species desorption rates, small amounts can have a significant impact, as stated before.

3. Reactor setup / Test bench

Before an injection system is implemented into our scramjet combustor facility [8], preliminary test runs with a separate catalytic reactor were conducted. The goal of the preliminary tests was to determine suitable mixtures for injection as well as quantify the achieved reduction in ignition energy. The reactor setup is shown in Figure 2 and is built upon a pressure vessel with a square interior cross-section of 12 mm. At the beginning of the flow path, 2 asymmetrically arranged injection holes for hydrogen and oxidizer as well as a nitrogen injection to flush the whole setup are located. The asymmetric injection helps to improve mixing in the following channel section of 30 mm length. The flow is then led through a monolithic Al_2O_3 catalyst bed of 20 mm length with a quadratic subchannel width of 1 mm and a catalytic coverage of 40 g/ft^3. The processed mixture exits the reactor through a central orifice of 0.5 mm diameter. Behind the ejection orifice, an electrically heated coiled filament heats and subsequently ignites the mixture. The power supplied to the filament is controlled using a pulse width modulation (PWM) and is increased during testing until ignition is achieved, which is detected using a thermocouple located behind the coiled filament. Since the electrical power, controlled by the duty cycle of the PWM, is in direct relation to the energy transfer to the fluid, a reduction in electrical energy necessary for ignition is equivalent to a reduction in activation energy of the processed mixture. To determine the actual influence of the catalyst onto the activation energy, the catalyst bed can be removed from the assembly and tests with air mixtures but without catalytic processing can be conducted. Inside the reactor on both sides of the catalyst, temperature and static pressure are measured. The thermocouples determine the temperature rise across the catalyst bed, which has to be taken into account when comparing test runs with and without catalytic processing, and are used to detect catalyst flame-off or flame propagation into the reactor, which result in a subsequent emergency shutdown and nitrogen flush of the system. The pressure taps are used to measure the partial pressures of both fuel and oxidizer to determine the mixture ratio. The volume flow of fuel and oxidizer can be controlled individually, but are kept constant during the respective test runs. First tests showed a limitation of the coiled filament as an ignition source, which limits the maximum mass flow through the reactor to an amount where ignition is still achievable. Therefore, low injection pressures in the range of 1 bar had to be used, which are unsuitable for a supersonic cross flow injection where approximately 20 bar are common. This needs to be kept in mind when transferring observations towards higher injection pressures, since the chemical equilibrium of catalytic reactions is pressure dependent. The possibility of a laser ignition has been considered, but was discarded due to difficulties in determining the actual amount of energy transferred to the fluid.

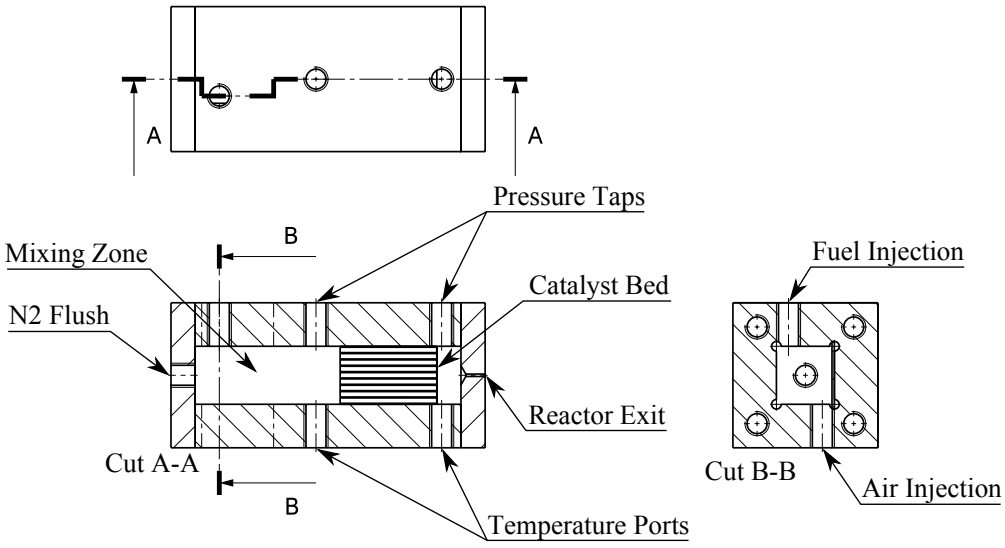

Figure 2: Schematic view of the reactor setup

4. Fuel only tests

A series of run-in tests was conducted in order to evaluate the test rig, where only hydrogen was supplied to the reactor. The tests were carried out as batches, where a series of runs is conducted while no catalyst is mounted inside the reactor. Several runs using the same values for fuel flow, initial duty cycle and duty cycle ramp are conducted until ignition is detected. The whole system is flushed with nitrogen after each successful ignition. Afterwards, the catalyst is mounted inside the reactor and a second batch of tests using the same values is conducted.
These test showed, that the respective first run of batches conducted with the catalyst mounted inside the reactor achieved ignition at lower PWM duty cycles, while consecutive runs of the respective batch required higher duty cycles and therefore more energy to achieve ignition. The effect can be seen in Figure 3, where the thermocouple temperature behind the coiled filament is plotted over the duty cycle. The moment of ignition is easily distinguishable by the sudden temperature rise.

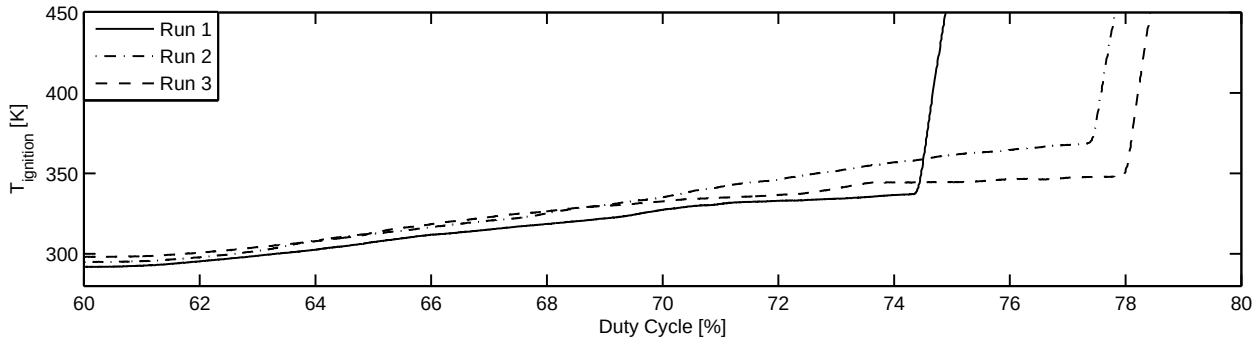

Figure 3: Ignition duty cycles with mounted catalyst, H2-injection

The phenomenon of reduced ignition energy appears despite initial nitrogen flushes of the system, but can not be observed in test runs without the catalyst mounted inside the reactor. This suggests, that it is caused due to residual oxygen adsorbed to the catalyst. A slight temperature rise within the reactor supports this assumption, as well as the fact that flushing the reactor with air and subsequently with nitrogen results in a comparable reduction. In figure 4, the respective graphs for a batch without a catalyst and a batch with air and nitrogen flushes before each run are shown. Here, it is also visible that ignition is not directly coupled to the temperature measured by the thermocouple, but rather to the localized energy transfer from the coiled filament to the flow. The effect of reduced ignition energy is also observable if the reactor is flushed with air, but no subsequent nitrogen flush is provided, which suggests the hydrogen injected into the reactor displaces the air instead of mixing and reacting with it on the catalyst.

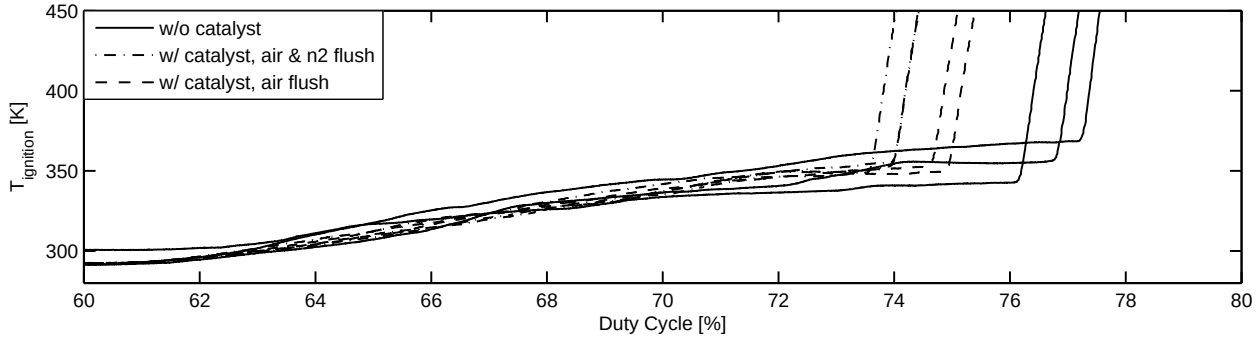

Figure 4: Ignition duty cycles without catalyst, with catalyst, air and nitrogen flush, and with catalyst and air flush

5. Fuel rich tests

While the reduced ignition energy was observable during test runs with adsorbed oxygen already provided on the catalyst, this method of ignition energy reduction is only viable for stable flames, as continuous support of the ignition can not be provided using this method. Therefore test runs with a fuel rich hydrogen/air mixture have been conducted.

The goal is to continuously provide a small amount of oxidizer to replenish the oxygen coverage, while staying well outside the equivalence ratios necessary for homogeneous ignition. The relative partial pressure of the hydrogen flow was set to 24 kPa, while the relative partial pressure of the air supply was set to 2,8 kPa ($\Phi = 4,29$). Again, tests with and without the catalyst mounted inside the reactor were conducted. It was expected the test batches with the catalyst mounted inside the reactor would again show reduced ignition energies, since both the preheating due to a partial reaction of the mixture on the catalyst, as well as the previously observed catalytic effect should promote ignition. The results, however, showed that ignition was inhibited instead. Figure 5 shows the measured ignition temperatures of the test batches with the fuel/air mixture. It can be seen that ignition for tests with catalytic conversion consistently occurs at higher energy outputs of the coiled filament.

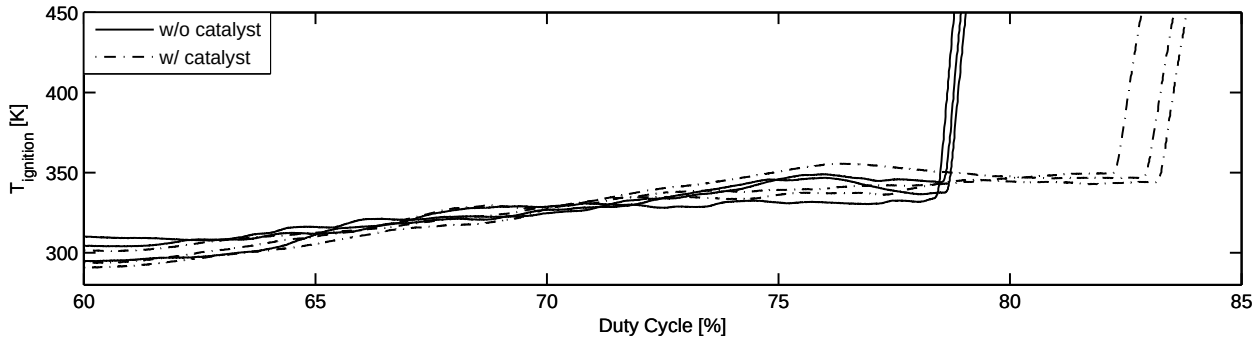

Figure 5: Ignition duty cycles with and without catalyst, fuel rich mixture ($\Phi = 4,29$)

Several possible explanations for this result have been investigated and evaluated. One possible explanation for this outcome is that water produced by the heterogenous reaction and subsequently desorbed, starts to act as a quenching agent and significantly suppresses ignition. This is done via the third-body radical recombination reaction $H + HO_2 + M \rightarrow H_2 + O_2 + M$, which acts as a chain breaking reaction. This reaction is greatly promoted if the third body M is water, as its efficiency in this reaction is about 30 times greater than tat of N_2. The assumption made by [1] that the quenching effect of water can be neglected at low pressures can not be applied, as the pressure in the reactor is one order of magnitude higher than in the combustor researched in the source.

Another possibility is that the reduced ignition energy observed in the tests with adsorbed oxygen on the catalyst is caused by a form of forced oxygen desorption, which is caused by hydrogen adsorbing to the catalyst. As every homogeneous reaction needs sufficient free surface sites for the educts to adsorb first and the catalyst can be expected to be initially covered entirely with oxygen, it needs to desorb before hydrogen can adsorb onto the surface and start reacting.

Another explanation for the reduced ignition energy in cases with adsorbed oxygen are superadiabatic temperatures. These unusually high surface temperatures occur on catalysts, if the diffusion rates of reactants result in a local surface equivalence ratio which allows higher reaction temperatures than the gas phase equivalence ratio would suggest. This is commonly observed in lean hydrogen/air mixtures, but can also occur due to the fact that oxygen is readily available at the surface and the fast diffusion rate of hydrogen provides a continuous supply of reactants, as long as the adsorbed oxygen is not yet consumed. The high temperatures occurring on the surface due to the rapid reaction can lead to radical desorption or gas phase reactions which promote ignition later on.

6. Conclusion and outlook

In order to reduce ignition delay in a supersonic combustor, a reactor has been constructed to investigate the possibility of catalytically supported radical production. Comparative measurements of ignition energy were conducted for test cases with and without a platinum catalyst present in the reactor. Preliminary tests with the catalyst exposed to oxygen before the test run showed significantly decreased ignition energies. Test runs with fuel rich hydrogen/air mixtures did not show an expected decrease in ignition energy, but actually showed an increase. This suggests adsorbed oxygen as the necessary initial condition for catalytic decrease of ignition energy.

The setup in its current condition can only promote ignition in a pulsed operation. This can be suitable for the expansion of the operational range of supersonic combustors, if the flame can be stabilized by additional means after ignition. If flame stabilization can not be achieved, a parallel setup of reactors, which are triggered cyclically, can provide a continuous support for ignition. As the ignition reduction appears to be linked to adsorbed oxygen on the catalyst, the next test campaign will focus on the investigation of lean fuel/air mixtures.

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