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Influence of steam on the flammability limits of premixed natural gas/oxygen/steam mixtures

Matthew J. Degges [a,*], J. Eric Boyer [a], Kenneth K. Kuo [a], Luca Basini [b]

[a] The Pennsylvania State University, University Park, PA 16802, USA
[b] Eni R&M Division, Via Maritano, 26, 20097 San Donato Milanese (MI), Italy

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ABSTRACT

Synthesis gas (Syngas) is an intermediate in a variety of industrial processes. Its production is energy and capital intensive and any improvement of existing technologies allowing simpler and economic production is of great interest. Recently, a new method known as short contact time-catalytic partial oxidation (SCT-CPO) has been developed into a commercial technology [1–4]. SCT-CPO is an entirely heterogeneous catalytic process converting premixed flammable feedstocks inside a very small reactor. In order to ensure safety and a high selectivity towards CO and H_2 it has been important to determine and understand flammability properties of the gaseous reactant mixtures. Here we report on the results obtained within a windowed tube reactor equipped with multiple photodetectors and pressure transducers that has allowed the study of ignition, flame propagation, and explosion characteristics of gas mixtures similar to those used as reactants in the SCT-CPO reactor. The tests were conducted at various pressures with different amounts of steam and two different compositions of natural gas (NG). A flammability boundary for each mixture, based on normalized pressure and mole fraction of steam, was determined. The results conclude that these mixtures' flammability could be suppressed in two very different ways. Depending on the adiabatic flame temperature of the mixture, suppression could be caused by steam's chemical influence increasing chain-termination or by a large amount of steam decreasing the reaction zone temperature.

1. Introduction

The main objective of this study is defining the flammability boundaries of natural gas (NG), steam and oxygen mixtures in conditions very close to those that could be adopted in industrial short contact time-catalytic partial oxidation (SCT-CPO) processes [1–4]. The effects of steam on combustion processes is an increasingly important issue not limited to the SCT-CPO case but also for other technologies; for instance steam can affect the combustion processes in exhaust gas recirculation in I.C. engines, in nuclear power plant accident suppression systems, and in the operation of combined cycle gas turbine (IGCC) fed with synthesis gas [5]. It is important to determine the suitable amount of steam used in a SCT-CPO reactor for the mixture to be non-flammable, as a safety precaution, as well as being an important reactant in the creation of Syngas. The main objective of this study is to characterize the flammability boundaries of two types of natural gas simulants combined with steam and oxygen.

In this work the flammability characteristics of the premixed SCT-CPO reactant mixtures were determined in turbulent reactant flows with Reynolds number greater than 2×10^4 at normalized pressure level varying between $P_{c,i}/P_{ref} = 0.1–1.5$. The flammability limits of these flows were experimentally determined inside a tubular test apparatus designed for sustaining the rapid pressurization process caused by ignition. Furthermore the apparatus allowed inlet flow temperatures varying between 298 and 450 K to be achieved through a pre-heating of the reactant gas mixtures. The pre-heated gases were then mixed in top of the reactor within a well-stirred mixer.

It is here noted that, despite its relevance in synthesis gas production (particularly with autothermal reforming and non-catalytic partial oxidation technologies), there is a lack of detailed information and experimental knowledge on the effect of steam on the flammability of gaseous mixtures at high pressures. Instead there is a general knowledge on the possibility of reducing the flammability limits in the presence of steam [6–9]. Previous studies indicated that the steam serves as an energy sink for absorbing heat generated by the gaseous chemical reactions. Moreover it was defined that the presence of steam affects the flammability proper-

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* Corresponding author at: 139 Research Building East, The Pennsylvania State University, University Park, PA 16802, USA. Tel.: +1 870 219 5768; fax: +1 814 863 3203.
E-mail address: mjd1027@psu.edu (M.J. Degges).

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ties of the mixture mainly due to its heat absorption characteristics rather than its chemical reactivity [5]. This conclusion was based on the conservation of energy that the rate of pressure increase in the reactor is caused by the increase of thermal enthalpy due to chemical reactions overcoming heat losses by conduction. Clearly the addition of steam to a flammable mixture can affect both the enthalpy and the heat conduction terms. However, in case of highly energetic mixtures, the addition of steam would have a small effect on the enthalpy variations caused by the chemical reactions. For this reason, the steam addition on flammability limits in relatively energetic mixtures concerns mainly the heat losses term rather than chemical effects term.

To the purpose of the present work, it is relevant to summarize some points concerning the role of steam addition on the chemistry of the hydrocarbon/oxygen mixtures. A first point is made by observing that the hydrogen oxidation mechanism [10,11] is at the core of alkane combustion chemistry. The driving chain-branching reaction is:

$$H + O_2 \rightharpoonup OH + O \tag{R1}$$

The alkanes in the mixture break down into hydrocarbon radicals, which then produce a pool of hydrogen radicals through beta-scission. These hydrogen radicals combine with the oxygen in the mixture and create hydroxyl radicals and oxygen atoms, thus branching the reaction paths and releasing thermal energy. The reaction which is chain terminating at pressures less than about 1.32 MPa, along a 450 K isotherm in the classical hydrogen oxygen flammability limit, is:

$$H + O_2 + M \rightharpoonup HO_2 + M \tag{R2}$$

(R2) competes with (R1) for the pool of hydrogen radicals as pressure is increased, as the 3rd body reactions (M) occur more frequently at higher pressures. The terminating reaction (R2) produces the hydroperoxy radical (HO_2) which is a heavy radical that can diffuse to the wall and not propagate the reaction at pressures less than 1.32 MPa and temperatures at 450 K, according to the classical flammability limits of H_2–O_2. At pressures greater than 1.32 MPa, along the 450 K isotherm, the hydroperoxy radical will no longer diffuse to the wall, but can propagate reactions in the mixture through the following overall chain propagating path:

$$HO_2 + H \rightharpoonup H_2O_2 \tag{R3}$$

$$H_2O_2 + M \rightharpoonup 2OH + M \tag{R4}$$

The hydroperoxy radical combines with the hydrogen radicals to produce hydrogen peroxide (R3) which easily decomposes to hydroxyl radicals (R4). (R3) and (R4) form an overall chain propagating reaction causing the mixture to be flammable above 1.32 MPa along the 450 K isotherm. In summary, the classical hydrogen oxygen flammability limit, which is at the core of alkane chemistry, shows that mixtures are non-flammable above 0.25 kPa and below 1.32 MPa along a 450 K isotherm and flammable at pressures higher than 1.32 MPa along the same isotherm. In this study, it is expected that the reactions dependent on 3rd body interactions ((R2) and (R4)) do not only occur due to the 3rd body reactions (M) associated with increasing pressure, but also from the active 3rd body role of H_2O in their collision with the similar HO_2 and H_2O_2 molecules. Steam has a high chaperon efficiency which makes 3rd body reactions more effective than other diluent gases [5]. From this theory, the flammability boundaries of this work were expected to demonstrate a non-linearity due to the change in reaction path with increasing pressure and steam mole fraction.

If enough steam is added to a reactive mixture, the steam can lower the reaction zone temperature by decreasing the quantity of other heat releasing reactions. This diluent or physical effect changes the reaction kinetics as some reactions are less likely to occur at lower temperatures due to their higher activation energies. Petersen et al. [12] shows that as an inerting agent, like steam, is added to a reactive mixture the reaction zone temperature is lowered and the dominant reaction mechanism shifts from a relatively fast branching reaction to a slower reaction that depends on third body reactions that produces formaldehyde as the final product. A significant amount of formaldehyde in the product exhaust indicates that the reaction is close to its flammability limit and is in its multiple ignition or cool flame regime [13].

Table 1
Composition of Mixture 1 and Mixture 2 without steam.

Parameter	Mixture 1	Mixture 2
O_2	38%	57%
CH_4	56%	23%
C_2H_6	4%	1%
H_2	2%	–
C_3H_8	–	12%
C_4H_{10}	–	7%
ϕ	3.33	2.69

The flammability of the mixtures considered in this study were very sensitive to relatively small changes in equivalence ratio (ϕ). Table 1 shows the compositions of the two different mixtures being studied.

A NASA-CEA2 calculation [14] was performed for each mixture, without steam, at 1.01 MPa and the adiabatic flame temperatures were calculated as 1375 K and 2159 K for Mixture 1 and Mixture 2, respectively. From the large differences in T_f, it is anticipated that these two mixtures have drastically different flammability limits.

2. Experimental setup

In this study, a tube reactor with a 40-mm diameter bore was used to study ignition, flame propagation, and explosion characteristics of the two simulated NG mixtures considered as inputs to the SCT-CPO reactor. The composition of NG delivered to the pilot plant can vary, so multiple compositions were investigated [15]. Variation in the initial chamber pressure and gaseous flow rates were also studied.

The reactor (shown in Fig. 1) is equipped with multiple ports housing fast-response photodetectors and dynamic pressure gauges to verify the onset of ignition and to measure flame propagation rate. The initial pressure was measured with static diaphragm pressure gauges. The test rig is also instrumented with multiple K-type thermocouples to verify the temperatures of all the reactants individually, before mixing. The temperature of the gaseous mixture was measured at different locations: the mixer, top, and

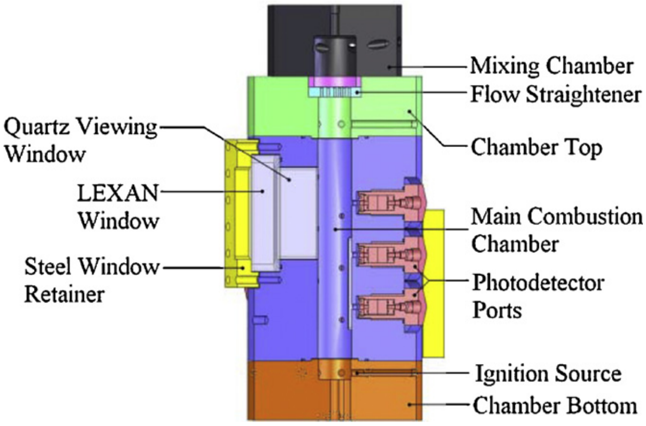

Fig. 1. 135° Sectional view of the high pressure tube reactor.

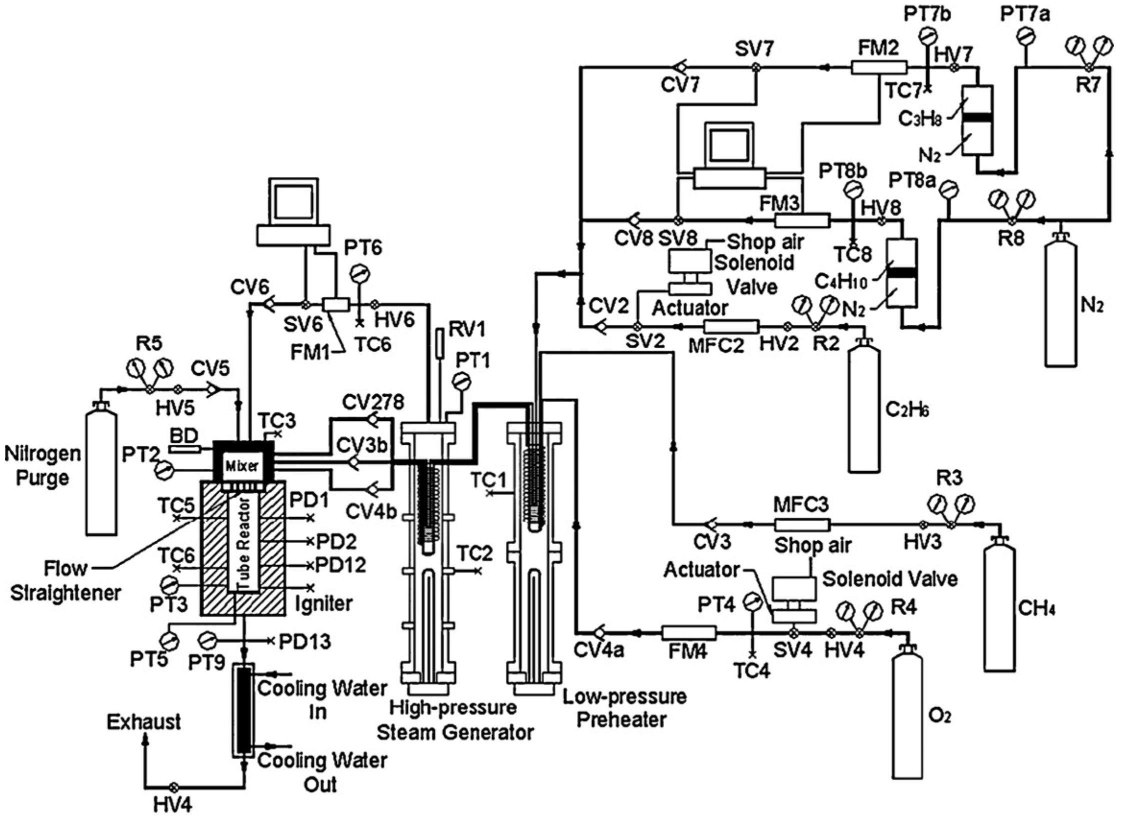

Fig. 2. Process flow diagram for flammability study of hydrocarbon/steam/oxygen mixture.

bottom of the reactor. The reactor was made of a stainless steel thick-walled cylinder and the reactor portion of the chamber is lined with a Pyrex glass tube to ensure a chemically inert test environment. Through two slit windows, flame propagation process was viewed with a high-speed camera. The process flow diagram of the experimental setup is shown in Fig. 2. The components of the mixtures are pre-heated through the steam generator heat exchanger and the pre-heater to the temperature of 450 K. The gaseous flow rates were set by multiple flow meters and controlled by computer actuated valves. After steady flow rates were established, an electric match was triggered at the bottom of the test rig. The multi-channel data acquisition system was synchronized with the ignition switch to activate and acquire signals from all instrumentation.

Of the 75 tests performed, three different regimes of combustion rate (rapid, intermediate, and slow) were observed and defined according to the time required to reach the maximum pressure recorded by the dynamic pressure transducers. When a mixture was ignited, the pressure in the reactor rose to levels significantly above the initial chamber pressure. Fig. 3 shows three *P*–*t* traces from Tests 53, 54, and 55. These traces were recorded by the dynamic pressure transducer at the bottom of the reactor, near the igniter.

For all tests with flammable mixtures, the time to peak pressure from the initiation time was measured. The average time duration was determined to be $\overline{t_m} = 0.051$ s. This value was used to normalize the time to peak pressure $(t_{m,i})$ of the *i*th test. A dimensionless time (τ_i) was defined as $\tau_i \equiv t_{m,i}/\overline{t_m}$ (2). If $\tau < 0.5$, it is considered a rapid rate. If $0.5 < \tau < 1$, it is considered an intermediate rate. If $\tau > 1$, it is considered a slow rate.

In the intermediate *P*–*t* trace, in Fig. 3, a plateau in pressure was observed. During this plateau time frame, 0.3–0.7 dimensionless time units, the radical pool had grown to a concentration that generated chemical energy which was balanced by physical losses. At 0.7 units, the physical losses were overcome by an increase in exothermic reactions and a rapid pressurization was observed. This plateau represents the thermal induction time of the ignition process. This thermal induction time is characterized by the combustion rates defined above. If the physical losses are competitive with the chemical energy generated, lower pressurization rates will be recorded. If the pressurization rate is very slow and small in magnitude, a “cool flame” phenomenon could be observed. Also, as the flow field and heat transfer become more competitive with the chemical reactions, unusual flame spreading could be seen, as diffusion gradients would not be as clearly defined as in a rapid

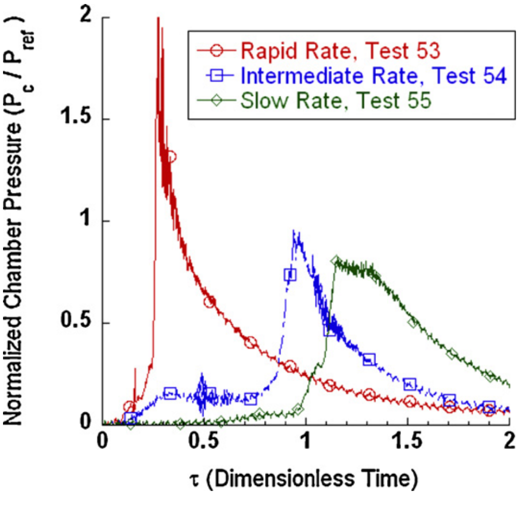

Fig. 3. Representative *P*–*t* traces recorded from the tube reactor.

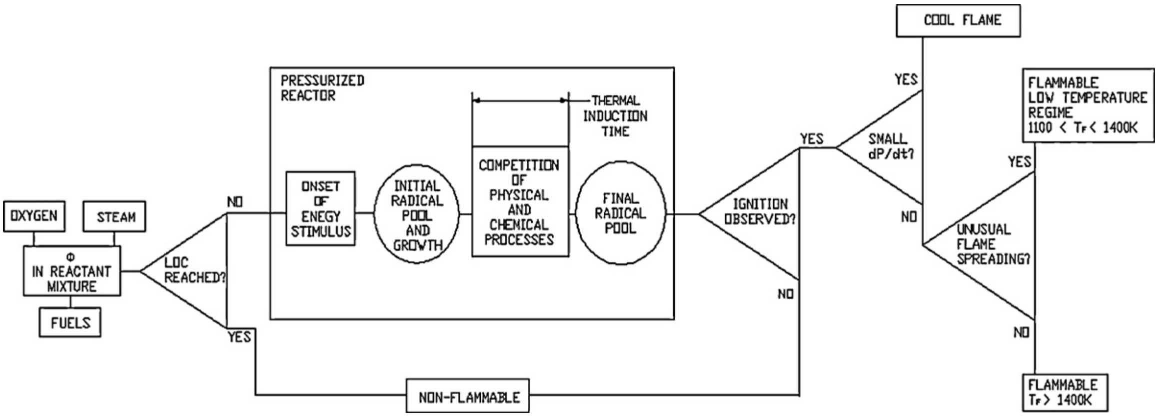

Fig. 4. Conceptual flammability model.

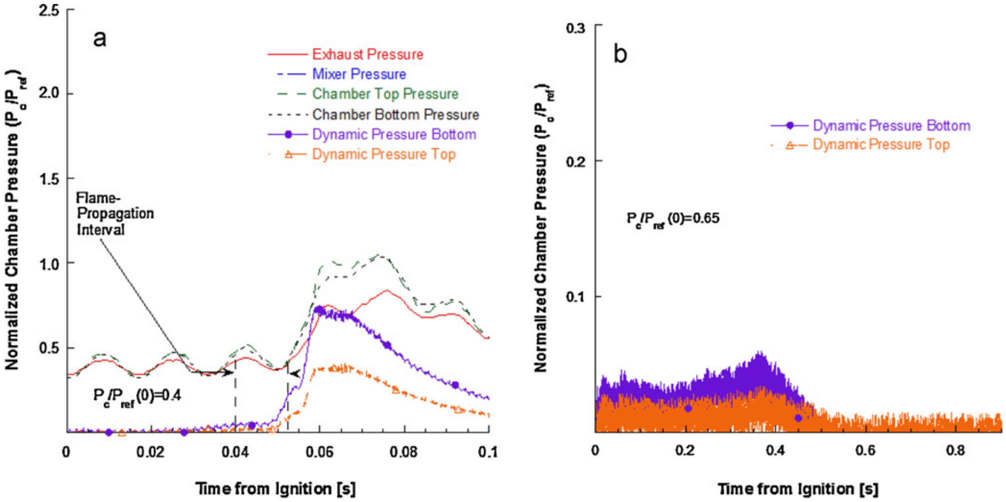

Fig. 5. Pressure–time trace changes with increasing steam: (a) 25% steam by vol. (b) 70% steam by vol.

rate reaction. A model of the physical and chemical processes that govern ignition and observations of these experiments is shown in Fig. 4.

In addition to the slow, intermediate, and rapid regimes of combustion rate, two phenomena, the "cool flame" and multiple ignition, were observed as the mixture approached its flammability limit [13]. As steam is added to the mixture, the dynamic pressure time traces reduce in pressurization rate and maximum pressure as seen in Fig. 5, which shows two plots of dimensionless pressure vs. time from ignition. Fig. 5a shows a slow rate reaction with a smaller amount of steam. Fig. 5b shows a "cool flame" reaction, which has a very low pressure rise over a much longer time from ignition.

Fig. 6 shows the turbulent ($Re_D = 20{,}000–40{,}000$) premixed flame front propagating up the reactor tube at a rapid rate of reaction.

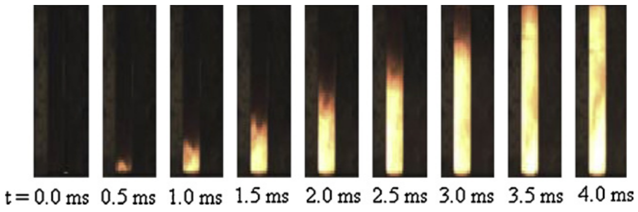

Fig. 6. High-speed camera visualization of turbulent premixed flame front.

The flame spreading rate was also measured with 12 photodetectors, spaced at 16.1 mm between adjacent detectors. PD1 is located at the top and PD12 at the bottom of the reactor. An example of the results is shown in Figs. 7 and 8. Fig. 8 shows the turbulent flame speed deduced from the data in Fig. 7.

Knowing the spacing between each photodetector, the relative turbulent flame speed of the ignited mixture can be calculated by the slope of the line in Fig. 8. The flow velocity is added to the relative turbulent flame speed to determine the absolute turbu-

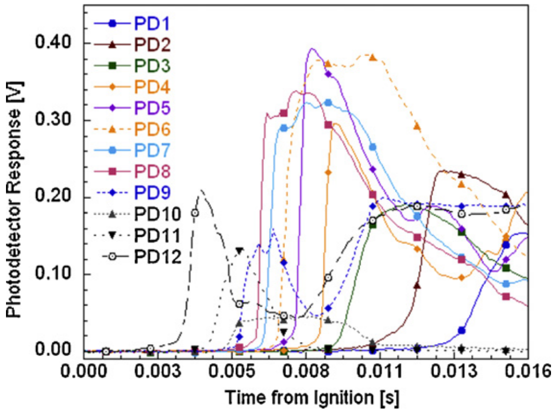

Fig. 7. Representative photodetector intensity-time traces.

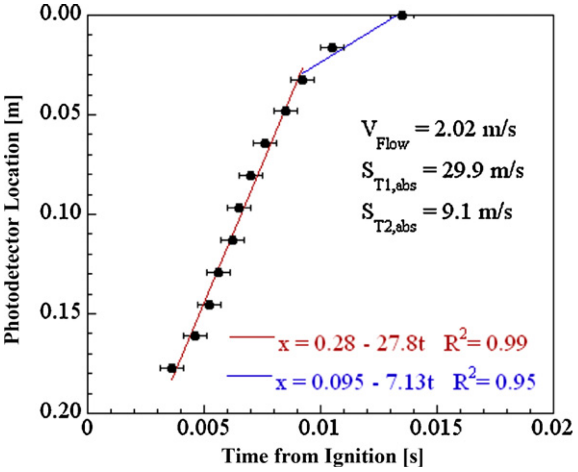

Fig. 8. Representative linear fit of flame-propagation speed.

lent flame speed. The initial absolute turbulent flame speed from the reactor bottom ($S_{T1,abs}$) was determined to be 29.9 m/s. When the flame approached the mixer exit the flame speed decreased to 9.1 m/s due mainly to the effect of the multi-perforated discharge plate at the exit.

It is important to note that as the steam content was increased beyond 25% by vol., odd flame spreading was observed in that the photodetectors did not register signals in ascending order, from the bottom to the top of the reactor. This odd flame spreading is a sign of the reaction zone temperature decreasing and changing the reaction kinetics from the typical progressively upward flame spreading seen in Fig. 7. Because of this phenomenon, flame speed measurements could not be deduced with steam content greater than 25% by vol.

3. Discussion of flammability results

Before presenting experimental results, potential errors in the flow rate measurements of different gaseous components are presented. The uncertainties in the initial conditions of the experiments are due to the instrumentation uncertainties of pressure gauges and flow meters. The inherent uncertainty of the static diaphragm pressure gauges is ±0.13% of full scale. The inherent uncertainty of the flow meters varies for different groups of tests, as shown in Table 2. Table 2 also shows average flow field parameters for each test group at the bottom of the table.

Mixture 1 (shown in Table 1) was used in Tests 1–38. In these tests, the orifice of the steam flow meter was changed, beginning with Test 11, to allow for less steam flow. This change increased the uncertainty of the steam flow measurement. Mixture 2 was used in Tests 39–76. During these tests, the steam flow meter orifice was changed back to its original configuration to allow for more steam flow. At Test 56, the steam generator reached its maximum steam production limit, but the Mixture 2 experiments had not exhibited a non-flammable data point. To reach a non-flammable condition, all of the Mixture 2 flows, except steam, were reduced by half, allowing for larger steam-to-hydrocarbon fuel ratios. After Test 59, the Mixture 2 reactant flows were again reduced by half. In Tests 60–76, the majority of the non-ignitions were observed. As the Mixture 2 flows were reduced, the error increased as the flow meters were sized to flow, more accurately, at higher rates. The flow rate of the ethane and methane was reduced to a level that lies in the lower limit of the flow meter's control capability. This resulted in relatively high error of the methane and ethane flow rates in Tests 57–76. The error in the measurement of ethane has a small effect on the flammability of the mixture as it constitutes a very small fraction of the mixture. The maximum error on the equivalence ratio of the mixture was found to be 3.87% in Tests 60–76.

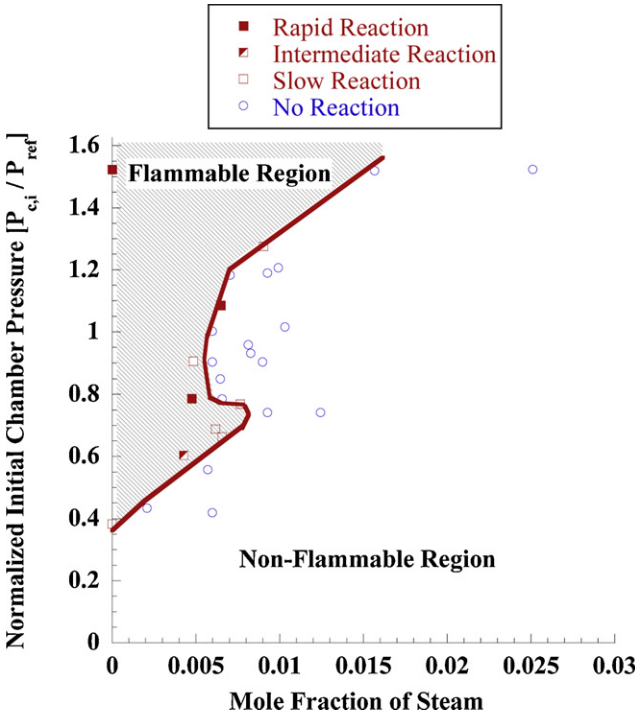

Fig. 9. Flammability limits of Mixture 1.

Fig. 9 shows the Mixture 1 flammability boundary on the plot of pressure vs. mole fraction of steam. This flammability limit shows that a very small amount of steam (less than 2%) is needed to create a non-flammable mixture. The limit shows highly non-linear

Table 2
Percent uncertainty in various components of the mixture for different tests. Average flow field parameters for different tests.

Test	1–10	11–38	39–48	49–56	57–59	60–76
O_2	1.67%	1.67%	1.58%	1.58%	3.20%	6.30%
CH_4	1.12%	1.12%	3.90%	3.90%	8.00%	16.0%
C_2H_6	1.20%	1.20%	5.51%	5.51%	11.0%	20.0%
H_2	1.20%	1.20%	–	–	–	–
C_3H_8	–	–	1.00%	1.00%	1.00%	1.00%
C_4H_{10}	–	–	1.00%	1.00%	1.00%	1.00%
H_2O	1.60%	2.70%	2.70%	1.60%	1.60%	1.60%
ϕ	0.07%	0.07%	0.25%	0.25%	1.05%	3.87%
V (m/s)	1.24	1.98	2.47	3.22	3.21	1.46
m (g/s)	23.01	23.00	22.94	27.26	17.44	10.84
Re_D	27,300	27,300	27,200	32,400	20,700	12,870

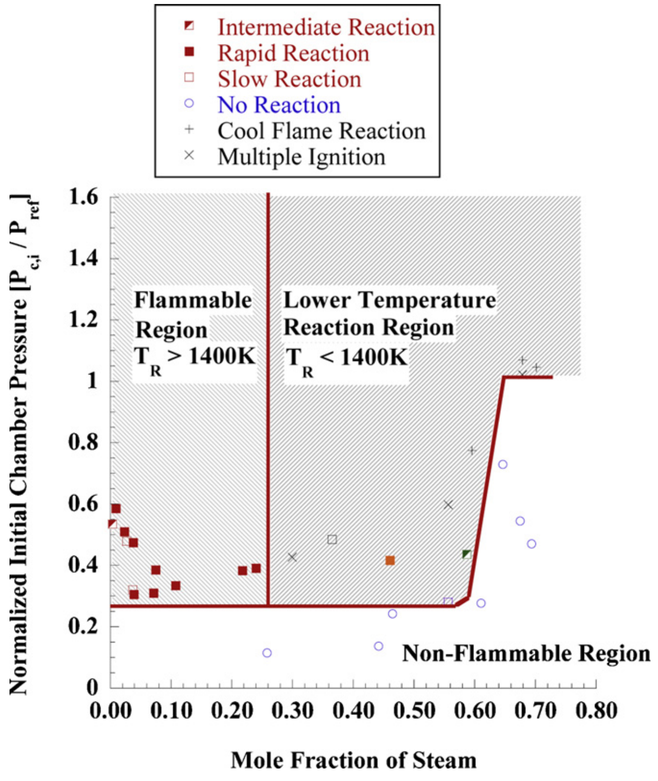

Fig. 10. Flammability limits of Mixture 2.

behavior with increasing pressure. This is similar to the non-linear trends found in the flammability limits of hydrocarbon combustion discussed in the Introduction.

Fig. 10 shows the Mixture 2 flammability limits on the plot of pressure vs. steam mole fraction.

As indicated in Section 1, it was anticipated that Mixture 1 would require less steam to be non-flammable than Mixture 2. This is verified experimentally, by comparing the scale of steam mole fraction between Figs. 9 and 10. The required steam mole fraction for Mixture 2 to be non-flammable is about 35 times higher than that of Mixture 1. No ignitions were observed below $P_{c,i}/P_{ref} = 0.25$. This could be due to the dependency of the rich limit on pressure. For both Mixture 1 and Mixture 2 the test results indicated that steam can be used to control the flammability. Mixture 1 required a very small amount of steam to suppress the reactions. This small of an amount of steam would not lower the reaction zone temperature significantly, but could only cause suppression by a chemical mechanism. It is suggested that the chain-terminating reaction of $2CH_3 + M \Rightarrow C_2H_6 + M$ overcomes the chain branching reactions, causing suppression of Mixture 1. Petersen et al. [12] suggests that this reaction is the dominant terminating reaction for high pressure, fuel-rich, diluted hydrocarbon mixtures. While this chain-terminating reaction does exist in Mixture 2 reaction kinetics, it is not effective in suppression of Mixture 2. Mixture 2 is more energetic than Mixture 1 and can only be suppressed by the physical mechanism. The reaction zone temperature of Mixture 2 is clearly lowered as steam is increased until a flame can no longer be sustained. The change of the reaction zone temperature could be inferred from the data collected by photodetectors and dynamic pressure transducers.

4. Conclusions

The highly non-linear flammability boundaries for two different hydrocarbon/oxygen/steam mixtures were determined through a series of tests performed at operating conditions close to those adopted in a SCT-CPO reactor. The tests demonstrated that steam can be used to control and suppress the flammability of hydrocarbon/oxygen mixtures. For mixtures with lower adiabatic flame temperature (Mixture 1), less steam is required to achieve a non-flammable condition. The pressure threshold was observed from these flammability tests, below which a self sustained ignition was not possible due to insufficient energy release at lower initial pressures. Most importantly this research showed that flammable hydrocarbon/oxygen mixtures can be suppressed by steam in two separate ways. Mixture 1 was suppressed by a chain-terminating reaction and Mixture 2 was suppressed by steam lowering the reaction zone temperature. This shows that the physical effect steam has on a flammable mixture is not always dominant over the chemical effect.

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