Fuel 105 (2013) 523–534

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

A comparative experimental study of the interactions between platinum and a range of hydrocarbon fuels

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HIGHLIGHTS

- The reactivity of four different alkanes ranging from C_1 to C_4 is tested over platinum.
- The platinum plate temperature peaks at moderately rich ethane/air mixtures.
- The reactivity limits of ethane/air mixtures broaden in the presence of platinum.
- Compressed natural gas show higher selectivity towards CO and H_2.
- Two distinct reactive zones are observed in the streamwise and transverse directions.

ARTICLE INFO

Article history:
Received 19 June 2012
Received in revised form 10 August 2012
Accepted 13 August 2012
Available online 29 August 2012

Keywords:
Catalytic combustion
Reactivity limits
Homogeneous and heterogenous reactions
Micro-combustion

ABSTRACT

This paper presents the reactivity of different alkanes ranging from C_1 to C_4 over platinum. The four fuels used are compressed natural gas (CNG), liquefied petroleum gas (LPG), butane, and ethane. Experiments are performed to study the effects of varying the temperature of the incoming mixture (T_{jet}), its equivalence ratio (φ) and the Reynolds number (Re), on the reactivity limits and species distributions. Platinum surface temperatures as well as species profiles streamwise and transverse to the plate are investigated. The reactivity limits of ethane over platinum are discussed in details.

For flameless combustion (defined by the the presence of reactions on the plate without a gaseous flame), it is found that the plate temperatures of ethane/air peak at moderately rich mixtures ($\varphi = 1.3$) and the reactivity limits broaden in the presence of platinum plate compared to the gaseous flammability limits. The main products of burning these four hydrocarbon fuels over platinum are CO_2 and H_2O while CNG showing the highest selectivity to CO and H_2. Species such as methane (CH_4), acetylene (C_2H_2), ethane (C_2H_6), dimethyl ether (C_2H_6O), propylene (C_3H_6), and propane (C_3H_8) appear in the products when burning LPG and butane over platinum. The streamwise profiles of species indicate the presence of two reacting zones along the plate which are described as: (i) the leading edge zone where high gradients of species mole fractions are observed and (ii) the trailing zone where the profiles are more flat and stable. The transverse profiles highlight the presence of two reactive layers: (i) the inner boundary where peaks of CO, CO_2, and H_2 occur and (ii) the outer layer where formation of the other hydrocarbons is observed. Heavier alkanes result in oxygen/fuel ratio near the plate higher than those injected in the free stream and this may be largely due to differential molecular as well as thermal diffusion.

1. Introduction

A thorough understanding of the interactions between gaseous and surface chemistries is a necessary prerequisite for the development of stable and efficient micro-combustors that may be used in micro-power generation [1–4] or in the replacement of batteries in portable electronic devices [1,5]. Such knowledge would also be extremely useful in fuel processing technologies where the range of working temperatures is lower [6–9]. While the fuels and catalysts used vary depending on the application, the key difficulties are common in that the fluid–solid interface involves a complex exchange of homo–heterogeneous reactions and heat management is vital considering the large surface to volume ratios that dominate micro-reactors.

It is convenient here to classify micro-reactors nominally in two broad categories: flaming and non-flaming. Flaming micro-combustors involve the stabilization of either a premixed [10–12] or

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http://dx.doi.org/10.1016/j.fuel.2012.08.021

diffusion flames [1,13,14] and operate at relatively high temperatures leading to significant heat losses and issues with flame stability. In the case of diffusion flames, mixing fuel and oxidant is a challenge that requires special configurations for the fluid streams considering that the flow is laminar and mixing rates are controlled mainly by molecular diffusion [1,13,15]. Non-flaming micro-reactors generally make use of catalytic surfaces and operate in lower temperature ranges as dictated by the process and the catalyst. The focus of this paper is on the latter category using platinum with a range of gaseous hydrocarbon fuels.

Earlier research on non-flaming micro-combustors has studied a range of flow geometries [15] such as stagnation flow [16], axisymmetric tube [17,18], rectangular channels [14], and flat unconfined plate [19,20], but remains limited to fuels such as hydrogen, carbon monoxide, methane and propane. Channel flows sandwiched between two parallel catalytic plates were studied using propane [21–23], hydrogen [11,16,24], methane [25–27] as well as CO–H_2/air mixtures [28]. In Stefanidis and Vlachos [23] the bulk inlet velocity of the (lean) fuel/air mixture was varied as well as the separation between the plates and their conductivities. It was concluded that while low inlet velocities favor surface reactions, homogeneous gas chemistry continued to play a role, albeit decreasing, with decreasing gap size, to separations as low as 200 μm. The stability limits for methane were found to be wider than propane and this was attributed to the Lewis number effects which enhance "transverse transport towards the catalytic surface".

Mantzaras and his group [21] performed detailed laser diagnostics measurements of species concentrations using LIF-Raman scattering confirming their calculations and showing that the reactor stability improves at higher pressure [21]. Also, Heatwole et al. [29] conducted experiments with lean methane/air mixtures and used an FTIR-based spectroscopic technique that exploits silicon's transmissivity in the infrared to make nonintrusive measurements of species concentration and temperature profiles in micro-combustors. Volchko et al. [30] studied the reactivity of methane/air mixtures with equivalence ratios that are richer than the flammability limits obtained in platinum micro-tubes. They showed that catalytic reactions could support combustion in mixtures even when gas-phase chemistry does not play a significant role. Also, Spadaccini et al. [31] fabricated a three-wafer catalytic combustor for a micro-scale gas turbine engine and reported efficiencies in excess of 40% for ethylene/air and propane/air combustion.

Maruta [32] have investigated the stability limits of methane/air mixtures within a Swiss roll micro-reactor. Ahn et al. [33] have found that using the same configuration (Swiss roll), the reactive limits of propane over platinum are broad and cover the equivalence ratio range of 0.2–40 [33]. This broadening has been attributed to the reactivity of propane/air mixtures over platinum, especially the enhancement of O_2 desorption at low Reynolds numbers [33]. Smyth et al. [19] have used methane to study its interaction with platinum on a simple configuration of a flat plate positioned in a co-flowing premixed fuel/air mixture. They measured temperature as well as selected species sampled from the plate's proximity and concluded that the reactive layer along the plate can be nominally split into three zones [19]. Zone I is very close to the leading edge where sharp temperature increases are noted accompanied by fast depletion of the gaseous reactants. Zone II is towards the middle where the surface temperatures plateau at a high value and reactant concentrations remain low. Zone III is towards the trailing edge where extinction of the non-adiabatic reaction is experienced and a replenishment of reactants from the free stream was observed. More recently, Smyth and Kyritsis used the same set-up but with the propane fuel to report novel flow-field as well as composition measurements in the vicinity of the plate [20].

This study adopts a flow configuration similar to that reported in Smyth et al. [19]. In an earlier paper [34], compressed natural gas (CNG), liquefied petroleum gas (LPG), commercial butane and dimethyl ether (DME) reacting on a platinum surface were studied over a range of equivalence ratios, temperatures and velocities. Measured surface temperatures were reported for all four fuels but numerical calculations, using detailed surface and gas chemistries were performed for methane only. It was concluded that: (i) the reactive limits of all fuels studied here on platinum are much broader than those of the gas-phase alone, (ii) the surface chemistry is largely controlling the heat and species release and (iii) the plate surface temperature peaks at moderately rich mixtures for all fuels except CNG where it peaks at stoichiometry. This paper extends the study to include detailed measurements of species sampled at varying distances from the plate. Additional results are reported and compared for the following fuels: compressed natural gas (CNG), ethane, liquefied petroleum gas (LPG), and butane.

2. Experimental set up

The configuration adopted here uses a premixed fuel/air mixtures co-flowing around a flat vertical unconfined platinum plate. Four hydrocarbon fuels with increasing carbon content from C_1 to C_4 are studied here. A schematic of the experimental apparatus is shown in Fig. 1 and more details may be found in [34]. The 30 cm long heater (TEMPCO) consists of a ceramic shell containing a heating coil with a diameter of 8 cm surrounding a 24 mm-OD and 23 mm-ID stainless steel tube. The fuel/air mixture flows over baffle plates positioned inside the stainless steel tube to increase the heat transfer and achieve exit temperatures up to 600 °C for Reynolds numbers based on the jet exit diameter ranging from 250 to 1500 and with equivalence ratios that range from $\varphi = 0$ to $\varphi = \infty$. The Reynolds number Re_d is calculated at the jet exit temperature (T_{jet}) and since the choice of the reference length scale is arbitrary so the corresponding approach velocities are also provided for convenience. An arrangement of meshes is used within the tube and a sintered bronze plate is placed at the exit plane to keep the flow exiting the tube laminar ($Re_d < 2000$) and uniform in both temperature and velocity. Gas issuing from the 23 mm-ID stainless steel tube flows over both sides of the platinum plate, which has a width of 6 mm, length of 20 mm and a thickness of 0.25 mm. The platinum plate is held by two pointy ceramic pins as shown in Inset A of Fig. 1. It should be noted that the ceramic was machined to minimize the area of contact with the platinum plate so that the heat losses are negligible.

This region over which flow from the tube extends without being affected by the laboratory air is referred to here as the "valid region". It is important that the entire platinum plate remains in this "valid region" surrounded by the mixture being studied and not be subjected to laboratory air. To ensure this, it was found from an earlier study that a Reynolds number of more than 200 should be used. All measurements reported here ensured that the platinum plate is fully engulfed by the mixture issuing from the jet so that the results are neither dependent on the separation from the leading edge of the nozzle nor on the nozzle diameter. A PID controller (Novus N1200) is used to regulate the temperature of the mixture at the exit plane of the burner which is measured using a type-K thermocouple. The temperature of the gases exiting the tube can be varied within the range from ambient up to 600 °C. Tylan and Bronkhorst mass flow controllers are used to control the flow rates of fuels and air, respectively.

Four different fuels, namely compressed natural gas, liquefied petroleum gas, butane, and ethane have been tested over platinum at various conditions. The parameters varied during the experiments are (i) the equivalence ratio, φ of the fuel mixture co-flowing over the platinum, (ii) its temperature at the jet exit plane, T_{jet}, and