



Gas-phase propane combustion in the freeboard of a fluidized bed



Jean-Philippe Laviolette^a, Gregory S. Patience^a, Concetta La Marca^b, Jamal Chaouki^{a,*}

^a Department of Chemical Engineering, École Polytechnique de Montréal, P.O. Box 6079, Succ. "CV", Montréal, Québec, Canada H3C 3A7

^b DuPont Company, DuPont Engineering Research & Technology, DuPont Building, Wilmington, DE 19898, USA

HIGHLIGHTS

- We conducted C₃H₈ combustion experiments in the freeboard of a fluidized bed.
- Solids flux, chemical composition, temperature and pressure were measured.
- For $T_B > 833$ K, C₃H₈ autoignition occurred within 0.06 m of the bed surface.
- Six microkinetic models underestimated the reaction rate above the bed surface.
- Accounting for H₂O₂ production in the bed increased the calculated reaction rates.

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ABSTRACT

Propane combustion experiments were conducted in the freeboard of a fluidized bed of sand particles at temperatures between 818 K and 923 K and at superficial gas velocity twice the minimum fluidization velocity. The freeboard region was characterized by simultaneous measurements of solids flux, chemical composition, temperature and pressure. Autoignition was recorded within 0.06 m of the bed surface for bed temperatures greater than 833 K. Propane conversion predicted by six different microkinetic mechanistic models were compared to the experimental measurements: all six models underestimated the reaction rate above the bed surface. However, accounting for the production of intermediate species and H₂O₂ during in-bed combustion significantly increased the calculated reaction rates and resulted in a better agreement between predicted and measured propane conversion.

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1. Introduction

Gas-phase homogenous combustion is a major constraint in attaining high yields, particularly selectivity, in processes involving heterogeneous catalysis and specially as applied to partial oxidation reactions. Together with product yield losses, combustion represents a significant safety hazard in the case of reactions involving molecular oxygen and hydrocarbons. Chemical processes requiring molecular oxygen are widespread in the industry. Also, new processes are currently under development for chemicals production and power generation in the context of increasing oil prices and global warming: selective oxidation of alkanes, biomass gasification, and combustion of non-conventional feedstocks, for example. Fluidized bed reactors are currently being developed for several of these processes due to their high heat transfer characteristics.

In order to increase productivity, fluidized bed processes may operate within the explosion envelope while feeding the oxidant

and hydrocarbon separately into the bed. This can be achieved due to the ability of the solids phase to suppress the homogeneous reactions (combustion) and at the same time promote selective heterogeneous reactions. However, due to operational constraints, the processes may be operated under conditions of partial conversion. In the case of selective oxidation reactions, for example, the selectivity has been shown to decrease at high conversion due to the increase in the rate of product decomposition [1–4]. Therefore, downstream of the bed – in the freeboard, cyclones and associated piping – the effluent gas phase composition is potentially explosive, characterized by high hydrocarbon and oxygen concentrations, elevated temperatures and an insufficient solids volume fraction to quench non-selective homogeneous reactions [5,6]. Minimizing the risk of gas-phase combustion–deflagration in these regions remains an important design issue.

Several explosion criteria, such as explosion limits, autoignition temperatures and induction time correlations [7–17] have been published in the scientific literature for gas-phase homogeneous systems. Hesketh and Davidson [18] showed that induction time correlations can be adequate to predict ignition delays above a fixed bed with $T_B \leq 973$ K and with negligible combustion in the

* Corresponding author. Tel.: +1 514 340 4711x4469; fax: +1 514 340 4159.

E-mail address: jamal.chaouki@polymtl.ca (J. Chaouki).

Nomenclature

d_p	average particle size (μm)	T_B	fluidized bed temperature (K)
G_{SU}	solids upward flux or entrainment flux ($\text{kg}/\text{m}^2 \text{ s}$)	U_g	superficial gas velocity (m/s)
r	radial position (m)	U_{mf}	minimum fluidization velocity (m/s)
R	reaction radius (0.2 m)	Y_i	volume fraction of species i (vol%)
τ_B	average gas residence time in fluidized bed (s)	Z	axial position (m)
T	temperature (K)	Z_F	axial position in the freeboard (m)

bed. However, extrapolating these correlations to fluidized bed reactors introduces uncertainties since the entrained solid particles inhibit gas-phase reactions downstream of the fluidized bed. Furthermore, the axial and radial distribution of solids above the bed surface is non-homogeneous: solids entrainment decreases exponentially from the bed surface until it reaches a steady value above the transport disengagement height [19,20]. Together with heterogeneous solids distribution, axial and radial temperature gradients may exist in the freeboard region as well as species concentration gradients. Finally, partial reactant conversion in the fluidized bed region produces reaction intermediates and free radicals that may influence the reaction kinetics in the freeboard region.

To accurately predict induction time and the rate of combustion of a hydrocarbon/oxygen mixture in the freeboard for a wide range of operating conditions, a combustion model that combines the gas/solids hydrodynamics, reaction microkinetics, temperature gradient and correct initial boundary condition must be developed. Steady state freeboard reaction models have been developed by De Lasa and Grace [21], Chen and Wen [22], Walsh et al. [23], Sotudeh-Gharebagh and Mostoufi [24], Dounit et al. [25], and Hartman et al. [26] for various reactions. However, these models have relied on global kinetic mechanisms, and were unable to model the free radical chemistry and induction time. Furthermore, they used correlations to estimate solids volume fraction, which may introduce significant errors.

Elementary step level free-radical kinetics models are necessary to characterize induction time and to account for the effect of intermediate products on reaction times. Several homogeneous gas-phase microkinetic models for propane oxidation are available in the literature for the low ($T < 600 \text{ K}$) [27], intermediate (650–1000 K) [28,29] and high temperature ($T > 1000 \text{ K}$) regions [30–33]. Some of these models have been previously modified to account for the quenching effect of solid particles on free radicals [34,35]. A gas-phase microkinetic model was previously used by Hutchenson et al. [4] to predict the oxygen conversion in the freeboard of a lab-scale fluidized bed (0.128 m I.D.) of vanadyl pyrophosphate (VPP) catalyst during n-butane selective oxidation. The calculated conversions were compared to experimental measurements: the predicted conversions were significantly lower than the measured values. Two possible explanations were given for this discrepancy: (1) some important heterogeneous/homogeneous reactions may not have been included in the model and that and (2) the production of free radicals in the bed was not taken into account. However, this study relied on a limited characterization of the freeboard region: temperature and species volume fractions were measured at one position such that the freeboard was assumed to be perfectly mixed.

The reaction model should be better validated with experimental data of hydrocarbon combustion in the freeboard of a fluidized bed if the parameters that affect the reaction are carefully characterized, namely the mixture composition, solids volume fraction and temperature. Furthermore, since these parameters are coupled, they should be measured simultaneously in the freeboard, even though this task is very challenging.

In the present study, non-premixed propane fluidized bed combustion experiments were conducted in a pilot-scale reactor (I.D. = 0.2 m) at low bed temperatures ($818 \text{ K} \leq T_B \leq 923 \text{ K}$), which resulted in low in-bed conversion and autoignition in the freeboard region. Sand particles ($d_p = 290 \mu\text{m}$) and a low superficial gas velocity of 0.17 m/s ($U_g = 2.1 \times U_{\text{mf}}$) were used for all experiments to limit solid entrainment into the freeboard region. The steady-state combustion process in the freeboard region was characterized by simultaneous measurements of solids entrainment flux, chemical composition, pressure and temperature. A gas-phase reaction model with elementary step level free-radical kinetics was developed and compared to the experimental data. Six well-established microkinetic models from the literature were used [28–33].

2. Experimental

The experiments were conducted in a fluidized bed reactor with an inner diameter of 0.2 m in the bed and freeboard regions. Sand particles (Geldart group B, $\rho_s = 2650 \text{ kg}/\text{m}^3$, $d_p = 290 \mu\text{m}$ and $U_{\text{mf}} = 0.08 \text{ m/s}$) were used as the bed material and air was the fluidizing media. Propane was injected separately through a downward-facing sparger whose tip was located at 0.1 m above the distributor. For all experiments, a low superficial gas velocity of 0.17 m/s ($U_g = 2.1 \times U_{\text{mf}}$) and low bed temperatures ($818 \text{ K} \leq T_B \leq 923 \text{ K}$) were used. The fluidized bed surface and freeboard region were characterized by simultaneous measurements of solids entrainment flux, chemical composition and temperature. Solids and gas were sampled simultaneously from the reactor using a non-isokinetic probe. The solids flux was measured from the mass of the solids samples and the gas was analyzed with a gas chromatograph and a CO/CO₂ analyzer for the following chemical species: C₃H₈, C₃H₆, C₂H₆, C₂H₄, CH₄, CO, CO₂, N₂, O₂ and H₂.

Temperature was measured with 10 thermocouples (Omega® type K and 1/4 inch O.D.) positioned along the reactor's length at a distance of generally 5–6 cm and no greater than 10 cm apart. The thermocouples were positioned inside the reactor with their tip located at the centerline. However, tests were also performed while moving the thermocouples along the radial axis to determine if a radial temperature gradient was present and if the presence of the thermocouple affected the chemical reactions in the freeboard region. Finally, Omega® reports a measurement error less than $\pm 2.2 \text{ }^\circ\text{C}$ for the thermocouples and no correction for radiation and conduction was made on the temperature measurements: this will be discussed further in Section 4.1.

3. Kinetic modeling in the freeboard

A gas-phase reaction model with elementary step level free-radical kinetics was developed and compared to the experimental data. Propane is known to undergo a transition from a low temperature reaction regime ($T < 600 \text{ K}$) to an intermediate reaction re-

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