GENERIC BEHAVIOUR OF PROPANE COMBUSTION IN FLUIDIZED BEDS

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The typical behaviour of commercial propane combustion in a laboratory size fluidized bed of silica sand is described. Four different sizes of sand particles were used (−500 + 400, −400 + 315, −315 + 250 and −250 + 200 µm). The fluidized bed was heated from 400 to 900°C, while mixtures of air and propane with various equivalence ratios were blown into the bed through the distributor, and the mole fractions of CO₂, CO and O₂ in the flue gases leaving the fluidized bed were measured and recorded. Analysis of the experimental results, especially of the CO₂ evolution, revealed trends and a general classification for the experiments.

Keywords: combustion; propane; fluidized beds; bubble.

INTRODUCTION

When a batch of particles of coal is thrown into a hot fluidized bed, the particles release their volatile material and after devolatilization the remaining coke particles begin to burn. The volatiles released by coal particles consist mainly of H₂, CO, CH₄ and other higher hydrocarbons (Hesketh and Davidson, 1991). The combustion of these higher hydrocarbons begins with their fragmentation into smaller hydrocarbons like propane (Westbrook and Dryer, 1981), and because of this it is likely that the propane represents the volatile matter from coal. Consequently, the fuel used in this work was commercial propane with 91% (w/w) propane.

The combustion of propane and air mixtures was studied in a laboratory-scale fluidized bed. Explosions can occur either inside the bed, at an unknown distance above the distributor, or at or above the free surface of the bed (Dennis et al., 1982), depending on the temperature. The temperature of the fluidized bed at which combustion takes place when the bubbles reach the free surface of the bed is known as the critical temperature. For a bed which is above critical temperature (Dennis et al., 1982; Hayhurst, 1991; Ribeiro and Pinho, 1998; Hayhurst and Tucker, 1990), the bubbles burn inside the bed, while below the critical temperature the bubbles burn over the bed.

Bulewicz et al. (1997) determined the composition of the gases from shallow fluidized beds with a maximum depth of 15 mm by burning natural gas. They concluded that there is no relation between the composition of the flue gases and the sand size; that the CO concentration varied strongly with bed temperature at 900°C; and that the NO concentration varied with temperature, bed depth and excess air.

In the present article the combustion of mixtures air and propane was characterized in a laboratory deep fluidized bed. Accordingly, various mixtures of air and propane were introduced in the fluidized bed through the distributor, while the fluidized bed was being heated by an electrical resistance placed externally around the reactor, from 400 to 900°C; the mole fractions of CO₂, CO and O₂ in the off gases were measured. The gas sampling probe was placed about 100 mm above the free surface of the fluidized bed.

EXPERIMENTAL

The fluidized bed was contained in a refractory steel tube with an 80 mm internal diameter with a stainless steel plate distributor with 101 holes (0.3 mm diameter), drilled according to a 7 mm square pitch (Ribeiro and Pinho, 1998). The fluidized material was group B silica sand (Geldart, 1986), with four different sizes: −500 + 400, −400 + 315, −315 + 250 and −250 + 200 µm. The bed was heated by a 4.2 kW electrical resistance, placed around the reactor tube and inserted in refractory clay pieces. Two stainless steel-sheathed K-thermocouples were used to measure the temperature at two different locations in the fluidized bed, and were connected to a data acquisition system. Another identical K-thermocouple was connected to the temperature controller of the fluidized bed. The maximum uncertainty associated with these thermocouples was 2.2°C or 0.75% of the reading. To measure the composition of the combustion gases, CO₂,
CO and O₂ analysers were used. For the non-dispersive infrared CO₂ and CO analysers, their precision was 0.5% of the maximum scale reading; the scale maximum for the CO₂ analyser was 25% and for the CO analyser it was 5%. The O₂ paramagnetic analyser had better than 0.1% linearity; its precision was less than 0.1%, and the reading was affected by 0.05% at most by the battery charge.

The gas sampling and suction probe was made from stainless steel AISI 316, 4 mm inner diameter and 5 m in length. The collected gases were cooled to 50°C before reaching the analysers.

For the above mentioned sand sizes, five static bed heights were considered (10, 15, 20, 25 and 30 cm) and three different mass flow rates of reactants (Table 1), with 0, 10, 20 and 30% excess air, were tested, giving a total of 240 experiments. Each experiment was performed once.

During each experiment the fluidized bed was heated from 400 to 900°C, and the three flue gas analyser readings were cooled to 50°C before reaching the analysers. The following relations have been proposed (Darton et al., 1977), as criteria for defining the threshold for the appearance of slugs in a fluidized bed:

\[ \frac{(u - u_{mfl})}{0.35 \sqrt{gD_d}} > 0.2 \quad \text{and} \quad \frac{z}{D_d} > 3.5 \times \left( 1 - \frac{1}{\sqrt{N_{or}}} \right) \]

where \( D_d \) is the diameter of the distributor and \( N_{or} \) is the number of orifices of the distributor. In the reactor used \( D_d = 0.08 \text{ m} \) and \( N_{or} = 101 \), so according to the second inequality the slugs appear only for fluidized beds deeper than 0.252 m. According to the first inequality \((u - u_{mfl}) > 0.2 \times 0.35 \times (9.81 \times 0.08)^{1/2} \), and so it is possible to evaluate the minimum temperature required for slugs to form in the fluidized bed, since \( u \) and \( u_{mfl} \) are both functions of temperature (Tables 1 and 2). Thus, to obtain slugs a bed deeper than 0.252 m is required and simultaneously its temperature must be above that given in Table 3.

### Experimental Results

#### Auto-Ignition Temperature

It was noticed through analysing the dry mole fractions of CO₂, CO and O₂ that the combustion of propane usually accelerates for temperatures of reactant mixture above 500 or 600°C. Above this range, it is possible to detect four simultaneous phenomena: the generation velocities of CO₂ and CO accelerate sharply; the consumption of O₂ rises sharply; the noise level yielded by the combustion also increases sharply. These four phenomena occur into the fluidized bed, and equations for \( u(T) \). Table 2 presents the \( u/u_{mfl} \) (\( T \)) ratio for all experimentally studied situations.

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#### Hydrodynamics

The fluidized beds were hydrodynamically characterized, for a given temperature \( T \), and each sand size used, through velocities \( u(T) \), \( u_{mfl}(T) \), the \( u/u_{mfl}(T) \) ratio and also by the definition of the threshold temperature for the appearance of slugs. If it is assumed that the reactant mixture crosses the fluidized bed at atmospheric pressure and behaves like a perfect gas, the determination of the superficial velocity from the mixture flow-rate is straightforward.

For all sand sizes Table 1 gives the mass flow-rates, the mole fractions and \( u(T) \) for all situations experimentally studied.
owing to auto-ignition of reactant mixture in the fluidized bed.

In a closed vessel where there is a homogeneous mixture of air and propane at 1 atm, the auto-ignition temperature is 480°C (Monnot, 1978). However, in all 240 tests, the auto-ignition temperature was found to be higher. This happens because the free radicals in a fluidized bed are more likely to collide with a solid surface than inside a closed vessel. These wall collision reactions entail heterogeneous chain termination reactions (De Soete, 1976; Tums, 1996), disrupting the kinetic mechanism of combustion inside the bed (Dennis et al., 1982).

Table 3. Temperatures required for the appearance of slugs in the fluidized beds studied.

<table>
<thead>
<tr>
<th>Excess air (%)</th>
<th>Mass flow-rate (kg min⁻¹)</th>
<th>Temperatures required for appearance of slugs (K)</th>
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<tbody>
<tr>
<td></td>
<td>C₂H₆</td>
<td>-250 + 200 µm</td>
</tr>
<tr>
<td>0</td>
<td>1.073 x 10⁻³</td>
<td>1.628 x 10⁻²</td>
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<tr>
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</tr>
<tr>
<td>0</td>
<td>1.305 x 10⁻³</td>
<td>1.981 x 10⁻²</td>
</tr>
<tr>
<td>10</td>
<td>9.770 x 10⁻⁴</td>
<td>1.628 x 10⁻²</td>
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<tr>
<td>10</td>
<td>1.073 x 10⁻³</td>
<td>1.778 x 10⁻²</td>
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<td>9.040 x 10⁻⁴</td>
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<td>8.299 x 10⁻⁴</td>
<td>1.628 x 10⁻²</td>
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<tr>
<td>30</td>
<td>9.040 x 10⁻⁴</td>
<td>1.778 x 10⁻²</td>
</tr>
<tr>
<td>30</td>
<td>1.001 x 10⁻³</td>
<td>1.981 x 10⁻²</td>
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Figure 1. Curve types of dry mole fractions against the fluidized bed temperature.
Exhaust Gas Composition

The mole fractions of CO$_2$, CO and O$_2$ in the dried flue gases were measured and plotted towards the fluidized bed temperatures. The graphs were organized into four different types, according to the evolution of the CO$_2$, CO and O$_2$. Figure 1 schematically represents these four types of graphs, with the corresponding CO$_2$, CO and O$_2$ evolutions. In some cases, the values shown in the y-axis indicate the peak value that can be attained by the mole fraction considered. For curve types III and IV, there is a disturbance at around 750°C, which will be explained later.

Table 4 presents the types of curves obtained for all performed tests. The types of graphs in Figure 1 are mostly a function of the sand size and the depth of the fluidized bed. In Table 4 there are cells with more than one type of graph assigned. In such cases the frequency of appearance of the type of graph diminishes from left to right in the sequence contained in those cells.

Type I curves

Type I graphs are typical of situations when propane burns with smaller sand sizes and for $H_{mf} < 20$ cm (Table 4). One example of curves of the mole fractions of CO$_2$, CO and O$_2$ against the temperature of the fluidized bed is presented in Figure 2. The dry mole fraction of CO$_2$ increases with the temperature of fluidized bed after auto-ignition at 650°C. The dry mole fraction of CO drops to zero beyond 750°C. The dry mole fraction of O$_2$ decreases as the temperature increases, which is in line with the increase in CO$_2$ production as the temperature of the fluidized bed increases.

Table 3 shows that $n_{mf}$ diminishes and $n$ increases as the temperature of the fluidized bed rises. Thus, the volumetric flow-rate that crosses the bed as bubbles increases, while the volumetric flow-rate in the particulate phase decreases. It is plausible to assume that, in a fluidized bed, the kinetic mechanism of the combustion of a mixture proceeds within the bubbles and that in the particulate phase the same mechanism is quenched by the sand through radical–wall collision reactions (Dennis et al., 1982; Hayhurst, 1991; Ribeiro and Pinho, 1998; Hesketh and Davidson, 1991; Hayhurst and Tucker, 1990). Therefore, as the flow-rate of bubbles crossing the bed increases with the temperature of the bed, the mole fraction of CO$_2$ will also increase.

Furthermore, there is species transfer between bubbles and particulate phase. At low temperatures, many active radicals generated inside the bubbles and transferred to the particulate phase are transformed into stable species, while fewer return to the bubbles unchanged. As the temperature of the fluidized bed rises, the number of free radicals leaving the bubbles and escaping wall collision reactions in the particulate phase should also rise. Because of this, the mole percentage of CO$_2$ increases as the temperature of the fluidized bed is raised.

The low CO$_2$ mole fractions in off gases are explained by the dilution effect promoted by the unburned reactants coming from the particulate phase and by the quenching of combustion above the free surface of the bed.

Type II curves

Type II graphs are associated with the higher sand sizes and 10 < $H_{mf} < 20$ cm. Curves of mole fractions of CO$_2$, CO and O$_2$ against the temperature of the fluidized bed are presented in Figure 3.

The dry mole fraction of CO$_2$, at the moment of auto-ignition, rises sharply from 0 to 6%, and remains around 6% thereafter. The dry mole fraction of CO attains a peak at the temperature of auto-ignition and becomes almost zero for higher temperatures. The dry mole fraction of O$_2$ is 20.8% up to auto-ignition, drops abruptly to 11% and stays around this value after auto-ignition.

As sand size increases, the gas–solid contact surface in the particulate phase drops and the probability of free radicals generated inside the bubbles of avoiding wall collision reactions, after being transferred to the particulate phase, increases too. Since the number of radicals in the particulate phase increases, the acceleration effect of these radicals is enhanced when they re-enter the bubbles. Accordingly, the differences between Figures 2 and 3 become understandable in that the CO$_2$ mole percentage in the former graph must be lower.

<table>
<thead>
<tr>
<th>$H_{mf}$ (cm)</th>
<th>Curve types</th>
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<tr>
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<tr>
<td>25</td>
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<tr>
<td>20</td>
<td>III/III/IV</td>
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$H_{mf}$ (cm) | Curve types |
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<td>500 + 400</td>
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<td>315 + 250</td>
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<td>400 + 315</td>
<td>III/III/IV</td>
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<tr>
<td>500 + 400</td>
<td>III/III/IV</td>
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Generics behaviour of propane combustion due to CO$_2$, CO and O$_2$.

Figure 3. Mole percentage of CO$_2$, CO and O$_2$ against temperature. $H_{mf} = 10$ cm; sand size, $-500 + 400$ µm; air–propane mixture with 30% excess air–air, $1.778 \times 10^{-2}$ kg min$^{-1}$; propane, $9.040 \times 10^{-4}$ kg min$^{-1}$. $u/H_{mf} = 1.788 \times 10^{-3} \times T^{1.666}$, with $T$ in Kelvin.

Figure 4. Mole percentage of CO$_2$, CO and O$_2$ against temperature. $H_{mf} = 30$ cm; sand size, $-400 + 315$ µm; air–propane mixture with 30% excess air–air, $1.981 \times 10^{-2}$ kg min$^{-1}$; propane, $1.001 \times 10^{-3}$ kg min$^{-1}$. $u/H_{mf} = 2.091 \times 10^{-3} \times T^{1.666}$, with $T$ in Kelvin.

Type III curves
Type III graphs are related with $H_{mf} > 20$ cm. Curves of CO$_2$, CO and O$_2$ mole fraction against the temperature of the fluidized bed are shown in Figure 4. The dry mole fraction of CO$_2$ rises slightly after the auto-ignition of the mixture, around 620°C, to 5.5% attained at about 760°C. The dry mole fraction of CO increases with temperature from the auto-ignition to 680°C; at this temperature, the dry mole fraction of CO drops slightly, and resumes rising at 730°C to 780°C, where it attains a peak; beyond 780°C the dry mole fraction of CO decreases slightly with temperature until it becomes almost zero, above 850°C.

As seen in either type I or type II graphs, the peak of dry mole fraction of CO in the off gases coincides with the auto-ignition of the mixture. The most interesting feature of the type III graphs is that the peak of dry mole fraction of CO in the off gases occurs around 100°C above the auto-ignition temperature. This is probably a consequence of the appearance of slugs inside the fluidized bed, which entails a mixing of packs of sand among bed regions at different temperatures. The result is a sharp drop in the temperature of the fluidized bed in the formerly hotter zones and the partial quenching of the combustion. This explains the peak of dry mole fraction of CO about 100°C beyond the auto-ignition temperature. The graphs for type IV help to clarify this point.

Type IV curves
Type IV graphs only appear for beds with $H_{mf} \geq 25$ cm, Table 4. Curves of CO$_2$, CO and O$_2$ mole fraction against the temperature of the fluidized bed are shown in Figure 5. In this graph there is a feature not found in the previous situations: a disturbance that appears in the curves around 750°C. To clarify the source of that disturbance the curves of the temperature of the fluidized bed against the heating time are shown in Figure 6 for two fluidized beds, both with the same sand and crossed with the same mixture, but one 30 cm deep and the other 10 cm deep. The deeper bed in Figure 6 corresponds to the situation in Figure 5. For the deeper bed, when the temperature reaches 750°C its value drops steeply to 730°C, and thereafter it resumes increasing. This disturbance is due to the appearance of slugs whose ascensions induce transfer of portions of sand between hotter and colder zones of the fluidized bed. In the shallow fluidized beds there are no slugs, so the curve of temperature against heating time has a shape without disturbances.

In Table 3, for each of the studied situations, threshold conditions for the appearance of slugs were defined: $H_{mf} \geq 25.2$ cm and the temperature of the bed must at least be the value presented in this table. The fluidized bed reported in Figures 5 and 6, here with the ‘×’ symbol, had $H_{mf} = 30$ cm and the minimum temperature required for the appearance of slugs was 710°C, which is close to the measured value of 750°C. Such disturbances are then characteristic of fluidized beds with $H_{mf} \geq 25$ cm and occur at temperatures near those referred to in Table 3.

CO evolution
It was noticed that, for a given temperature, a fluidized bed yields more CO as its depth increases. All of the CO in flue gases is generated inside the bubbles, and is partially transferred by diffusion and advection from the
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Figure 5. Mole percentage of CO₂, CO and O₂ against temperature. 

Figure 6. Temperature against heating time; effect of slugs. For both fluidized beds sand size, -400 + 315 μm; air and propane with 30% excess air—air, 1.628 × 10⁻² kg min⁻¹; propane, 8.299 × 10⁻⁴ kg min⁻¹. 

Figure 7. Mole percentage of CO against temperature. 

bubbles to the particulate phase. If the hydrocarbons disappear inside the bubbles, then the existing CO will be converted to CO₂, while the CO which is in the particulate phase must remain unchanged owing to the quenching of reactions. Therefore, for a given temperature and provided the bubbles only explode above the free surface of the fluidized bed, the bed yields more CO as its height increases, because bubbles have more time to generate CO and to transfer it to the particulate phase. If a bubble explodes inside the fluidized bed its yield of CO will increase, as the time elapse increases, after its formation at the distributor until its explosion.

In Figure 7 CO yield is compared for two fluidized beds, both with the same sand and crossed with the same mixture, but for two different bed heights. For the deeper bed, higher CO yield is evident.

CONCLUSIONS

An overview of the curves of CO₂, CO and O₂ mole fractions with the fluidized bed operating conditions allowed the definition of four categories of operational conditions by taking into account common trends. Type I and type II curves are commonly found for low bed heights, \( H_{mf} < 20 \text{ cm} \). Type I are more frequent for -250 + 315 μm particle size, whereas type II curves are more frequent for -315 + 250 μm and -400 + 315 μm bed particle sizes. Type III and IV curves are more frequent for deeper beds, \( H_{mf} \geq 20 \text{ cm} \), and are related to the formation of slugs. To be more precise, type IV curves only appear for \( H_{mf} > 25 \text{ cm} \) and never for the smaller bed particle size, -250 + 200 μm.

The low CO₂ mole fractions in the flue gases are explained by the quenching of combustion and dilution of reactants in the particulate phase and also by the quenching of combustion in the free board of the bed. It was also found that, for a given temperature, a fluidized bed yields more CO as its depth increases, because bubbles have more time to generate CO and to transfer it to the particulate phase.
NOMENCLATURE

\[ \begin{align*}
D_d & \quad \text{distributor diameter, m} \\
g & \quad \text{gravity constant, m s}^{-2} \\
H_{mf} & \quad \text{incipient fluidization height, m} \\
N_{or} & \quad \text{number of orifices of the distributor} \\
T & \quad \text{temperature of the mixture, K} \\
T_{a.i.} & \quad \text{temperature of auto-ignition for bubbles, K} \\
u & \quad \text{average velocity of the fluid, m s}^{-1} \\
u_{mf} & \quad \text{incipient fluidisation velocity, m s}^{-1} \\
z & \quad \text{height measured from the distributor, m}
\end{align*} \]

REFERENCES


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