FLUIDIZED BED COMBUSTION OF C1-C4 N-ALKANES

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Abstract: The non-premixed combustion of C_1 to C_4 n-alkanes was investigated inside a bubbling fluidized bed of inert sand particles at intermediate temperatures: 923 K (650°C) ≤ T_B ≤ 1123 K (850°C). Lower (T_1) and upper (T_2) critical transition bed temperatures were measured for ethane, propane and n-butane as 923 K (650°C) and 1073 K (800°C), respectively. The values for methane were significantly higher with T_1 = 1023 K (750°C) and T_2 > 1123 K (850°C). Alkane conversion was accurately modeled with first-order kinetics and C_2 to C_4 n-alkanes combustion rates were characterized by a uniform Arrhenius expression: $r = (2.59 \times 10^7) C_i e^{-127800/RT}$. The reaction rate of methane was significantly slower with: $r_{CH4} = (1.99 \times 10^{12}) C_{CH4} e^{-261008/RT}$.

Keywords: combustion, fluidized bed, methane, propane, ethane and n-butane

1. Introduction

The combustion of methane, LPG and propane in fluidized beds of inert particles has been the subject of several studies in premixed [1-10] and non-premixed modes [11-16]. Fluidized bed temperature has been reported as a key parameter that determines in-bed fuel conversion: combustion is initiated deeper inside the fluidized bed with increasing temperature. In premixed combustion, increasing temperature has been shown to move the combustion front towards the distributor - the combustion front moves first from the freeboard to the bubbles bursting at the upper surface of the bed, then to bubbles igniting in the bed and finally to small bubbles where ignition occurs practically at the level of the distributor and the process appears flameless [7, 9]. While some studies have suggested that combustion did not occur to any significant extent inside the emulsion phase [9], methane and propane combustion have been observed in fixed beds of sand particles at temperatures above 1023 K (750°C) and 973 K (700°C), respectively [1, 17].

Two critical transition temperatures have been defined for fluidized bed combustion in inert particles. Below the lower critical temperature (T_1), combustion only occurs above the bed surface. Between T_1 and the upper critical temperature (T_2), combustion begins to move inside the bubbles within the bed. Finally, above T_2, combustion takes place entirely within the bed and close to the distributor. For methane combustion in inert sand particles, the values of T_1 and T_2 reported in the literature range between 823-1018 K (550-745°C) and 1133-1250 K (860-977°C), respectively [18]. For propane, T_2 was measured in a shallow bed (H_B ≈ 0.1 m) of sand particles as 1123 K (850°C) [2, 9]. Investigations on the fluidized bed combustion of other alkanes in inert particles are scarce.

In-bed conversion for specific operating condition can also be estimated by reaction models that combine gas/solids hydrodynamics and reaction kinetics. Several microkinetic and first-order global kinetics schemes are available in the literature for gas-phase systems [5, 6, 19]. Gas-phase microkinetic models have also been modified to account for the "quenching" effect of solids particles on the free radicals [17, 20]. However, microkinetic models are very complex, while global kinetic models are valid only for a specific range of operating conditions such that both types of models may yield significant uncertainties. Furthermore, using global kinetics

schemes for different hydrocarbons from various sources and measured under different experimental conditions may result in further errors in the modeling results.

It may be possible to express the first-order kinetics and conversion of C_2 and higher alkanes in terms of a single expression or correlation. Studies have reported similarities between the combustion chemistry of n-alkanes: their combustion rate is controlled by the same main chain branching path, which can be summarized by the following elementary reactions at intermediate temperatures (~ 850 K (577°C) to 1200 K (927°C)) [21-24]:

$$H + O_2 + M \rightarrow HO_2 + M \tag{1}$$
$$RH + HO_2 \rightarrow R + H_2O_2 \tag{2}$$
$$H_2O_2 + M \rightarrow OH + OH + M \tag{3}$$

In the above equations, RH is an alkane, R is an alkyl radical and M is a third body. Saxena *et al.* [23] have demonstrated that the high temperature induction time of propane and higher alkanes can be accurately estimated by employing rate parameters of elementary steps (2) to (4).

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{4}$$

Consequently, the induction time of C_2 and higher n-alkanes have been shown to exhibit similar dependence on temperature, pressure and mixture composition such that it may be calculated from a single correlation with an uniform activation energy [21-22]. Methane, on the other hand, has been observed to yield significantly higher induction times, which can be explained by the production of a methyl radical in equation (2), which recombines to form ethane, resulting in chain termination. If the combustion chemistry and induction time correlations among C_2 and higher n-alkanes show such similarities, it seems reasonable to think that a parallel may also be made between the global reaction kinetics and conversion.

In the present study, the non-premixed combustion of methane, ethane, propane and n-butane was studied in a fluidized bed of sand particles at temperatures ranging from 923 K (650°C) to 1123 K (850°C). The flow of each hydrocarbon was adjusted to obtain a constant heat release rate of 3.8 kW and critical bed temperatures were measured for each hydrocarbon. Furthermore, a reaction model with first-order reaction kinetics was developed and compared to the experimental results. The first-order kinetic parameters were measured for each n-alkane and compared.

2. Experimental

The experiments were performed in a fluidized bed reactor with an inner diameter of 0.2 m and a height of approximately 1.0 m. Inert sand particles (d_p = 290 μm and U_{mf} = 0.08 m/s) were used as the bed material. The bed was fluidized with air, which was injected through the distributor, and the hydrocarbon fuels (methane, ethane, propane and n-butane) were separately injected through a downward-facing sparger whose the tip was located at a distance of 0.1 m above the distributor. Prior to each experiment, the fluidized bed reactor was heated to the desired temperature with a natural gas burner connected to the windbox.

The experiments were conducted at a superficial gas velocity of 0.4 m/s and at five bed temperatures: 923 K (650°C), 973 K (700°C), 1023 K (750°C), 1073 K (800°C) and 1123 K (850°C). The temperature was measured at 9 different axial positions with thermocouples. Gas was sampled at six axial and five positions. The sampled gas was analyzed by a CO/CO_2 analyzer and a micro-GC connected in series to measure the volume fraction of the following species: H_2, CH_4, C_2H_4, C_2H_6, C_3H_8, n-C_4H_{10}, O_2, N_2, CO and CO_2. At each axial position, a cross-sectional average of species volume fraction was calculated from the measurements. The mixed-cup volume fraction at the injector tip was adjusted for each hydrocarbon to obtain a

constant heat release rate of 3.8 kW. For methane, ethane, propane and n-butane, the mixed-cup volume fraction was 5.1%, 2.5%, 1.9% and 1.3%, respectively.

3. Results and discussion
3.1 Critical transition fluidized bed temperatures

Lower (T_1) and upper (T_2) critical transition bed temperatures were measured for methane, ethane, propane and n-butane. Figure 1a shows the axial profile of conversion for ethane, propane and n-butane inside the fluidized bed reactor at a bed temperature of 923 K (650°C). The corresponding axial profile of CO_2 volume fraction is presented in Figure 1b. The bed height was 0.55 m and it is shown on both figures as a dashed line. At 923 K (650°C), ethane, propane and n-butane conversion was not significant inside the fluidized bed: conversion fluctuated between 0-4%, 0-18% and 10-27% for ethane, propane and n-butane, respectively. Furthermore, the CO_2 volume fractions in the fluidized bed remained low at approximately 0.7%. Combustion occurred mainly at the bed surface and inside the freeboard as conversion reached 92%, 93% and 96% at 0.2 m above the bed surface (Z = 0.75 m) for ethane, propane and n-butane, respectively. This was accompanied by a significant increased in the CO_2 volume fraction, which reached approximately 5.5% for all alkanes. Complete conversion was obtained at Z = 0.97 m. Since in-bed conversion was limited and most hydrocarbons burned inside the freeboard, the lower critical temperature (T_1) was defined as 923 K (650°C) for ethane, propane and n-butane.

As the bed temperature was increased to 973 K (700°C), the combustion front moved upstream inside the fluidized bed for ethane, propane and n-butane. Figures 1c and 1d show the axial profile of conversion and CO_2: combustion was initiated within 0.15 m (Z = 0.25 m) of the injector tip where a conversion of 24%, 57% and 61% was measured for ethane, propane and n-butane, respectively. Conversion increased steadily in the fluidized bed and partial in-bed conversions of 60%, 79% and 84% were measured at 0.1 m below the bed surface (Z = 0.46 m) for ethane, propane and n-butane. The unconverted hydrocarbons burned inside the feeboard region and complete conversion was observed at 0.2 m above the bed surface (Z = 0.75 m). The measured conversion in the fluidized bed and freeboard regions was accompanied by a corresponding increase in the CO_2 volume fraction, which reached approximately 3.8% at 0.1 m below the fluidized bed surface (Z = 0.46 m) and 6.0% in the freeboard region at Z = 0.97 m.

Figures 1(e) and 1(f) show the axial profile of CO_2 and conversion for the three n-alkanes as the bed temperature was increased further to 1023 K (750°C). Near complete fuel conversion occurred in the fluidized bed with ethane, propane and n-butane: conversion reached 95%, 95% and 98%, respectively, only 0.36 m (Z = 0.46 m) downstream of the injector. At that position, the CO_2 volume fraction reached about 6.0%, which corresponded approximately to the theoretical value at 100% combustion. Complete conversion was observed 0.2 m over the bed surface (Z = 0.75 m).

At a bed temperature of 1073 K (800°C), the conversion of ethane, propane and n-butane, conversion reached 99% within 0.25 m of the sparger tip (Z = 0.35 m): this temperature was defined as the upper critical temperature (T_2). This value is lower than the 1123 K (850°C) previously reported for propane [2, 9]. However, this discrepancy may be explained by the fact that conversion was not measured at a bed temperature of 1073 K (800°C) – experiments were performed at bed temperatures of 1023 K (750°C) and 1123 K (850°C) [2, 9].

Methane fluidized bed combustion required significantly higher bed temperatures compared to ethane, propane and n-butane. Figure 2 shows the axial profile of methane conversion at four bed temperatures: 973 K (700°C), 1023 (750°C), 1073 (800°C) and 1123 K (850°C). At a bed temperature of 973 K (700°C), no methane conversion was measured in the fluidized bed and

combustion occurred entirely in the freeboard region: methane conversion increased from 37% at 0.06 m above the bed surface ($Z = 0.61$ m) to 99% at $Z = 0.97$ m, respectively.
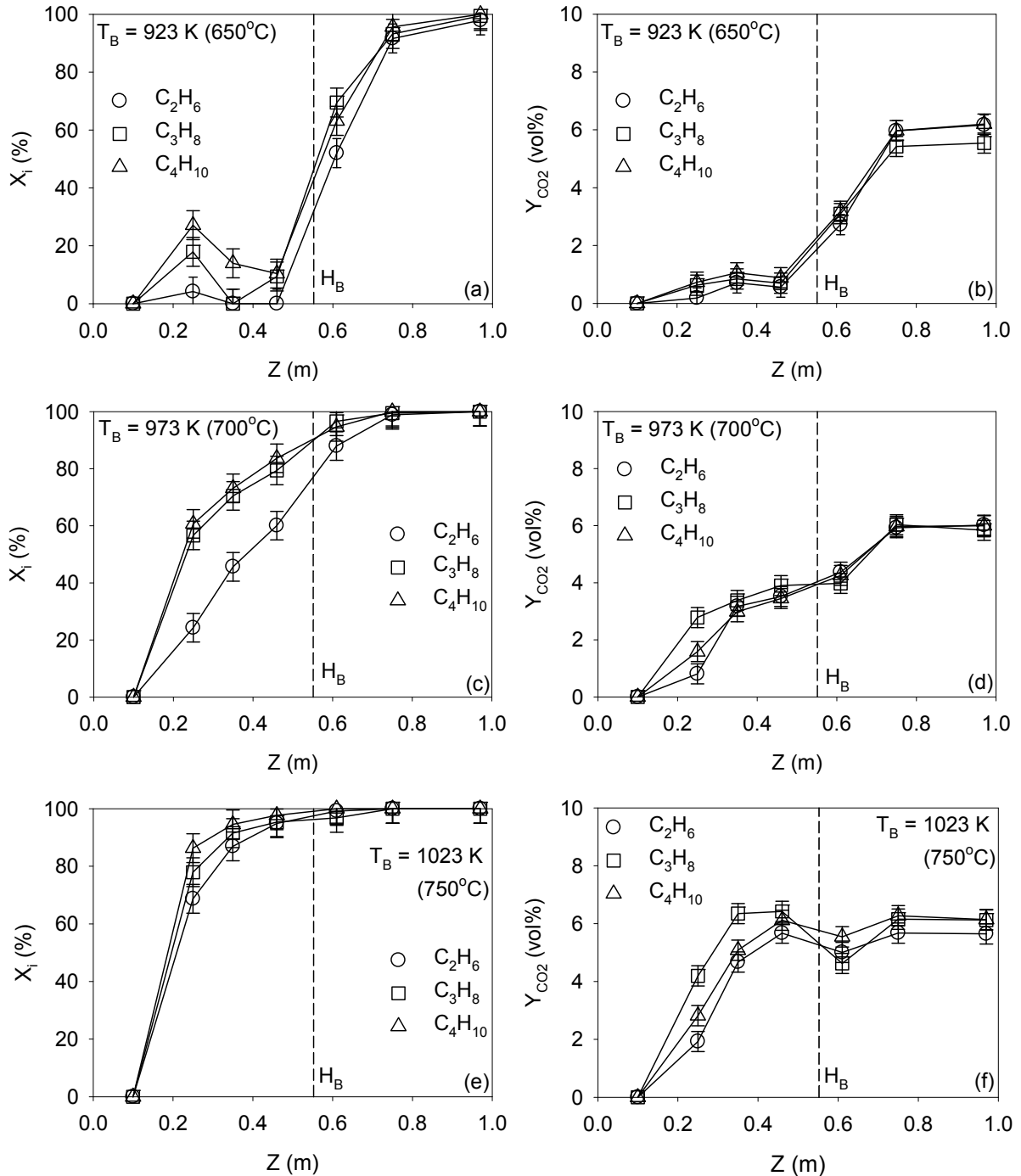

Figure 1: Conversion and Y_{CO2} axial profiles at 923 K and 973 K

As the temperature was increased to 1023 K (750°C), figure 2 shows that the methane in-bed conversion was small – the measured conversion fluctuated between 0% and 12% and the CO_2 volume fraction reached about 2.0%. Combustion mainly occurred at the bed surface –

conversion increased to 64% at 0.06 m (Z = 0.61 m) above the bed surface. This was accompanied by a significant increase in the volume fraction of CO_2 in the freeboard. Complete methane conversion was observed at Z = 0.97 m. A bed temperature of 1023 K (750°C) was defined as the lower critical temperature (T_1), which is similar to the observations of previous studies [18].

At a higher bed temperature of 1073 K (800°C), significant in-bed conversion was observed: conversion reached 23% at a distance of 0.15 m downstream of the sparger (Z = 0.25 m) and increased to 40% at Z = 0.46 m. The unconverted methane burned in the freeboard and complete conversion was obtained at Z = 0.97 m.

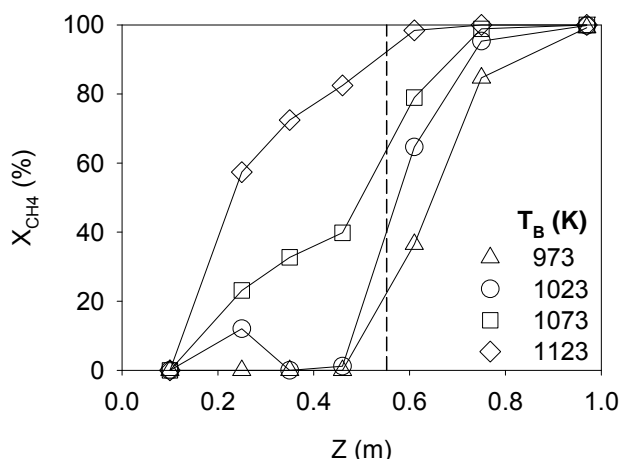Figure 2: X_{CH4} axial profiles at various fluidized bed temperatures

The bed temperature was increased further to 1123 K (850°C) and metane conversion increased to 83% at 0.1 m below the bed surface (Z = 0.46 m). The unconverted methane burned inside the freeboard region and within 0.2 m of the bed surface. The upper critical temperature (T_2) for methane is higher than 1123 K (850°C) and this agrees with the reported values in the scientific literature [18].

3.2 C$_1$-C$_4$ n-alkanes global reaction rates

A reaction model was developed and compared to the experimental measurements. The fluidized bed gas-phase hydrodynamics and reaction kinetics were modeled as a plug flow reactor and a first-order reaction, respectively. The hydrocarbon conversion was calculated from equations (5) and (6):

$$X_i = 100 \left(1 - e^{-k'\left(Z_{inj} - b_i\right)}\right) \tag{5}$$

$$k' = \frac{Ak_0}{v} e^{-E_A/RT} = k_0' e^{-E_A/RT} \tag{6}$$

In equation (5), the parameter b_i represents an induction delay: b_i increases with induction time. Furthermore, Z_{inj}, k, A, v, E_A and R corresponds to the height above the sparger tip (Z_{inj} = 0 m corresponds to Z = 0.1 m), the kinetic constant, the fluidized bed cross-sectional area, the volume flow rate in the fluidized bed, the activation energy and the universal gas constant. The use of this simple reaction model is consistent with the work of Lorences *et al.* [25], which have shown that the gas-phase hydrodynamics in fluidized beds are very close to plug flow when $U_g \leq 6 \times U_{mf}$. Also, several fluidized bed combustion studies have reported that fuel-lean combustion can be accurately represented as first order with respect to hydrocarbon concentration [17, 26-27].
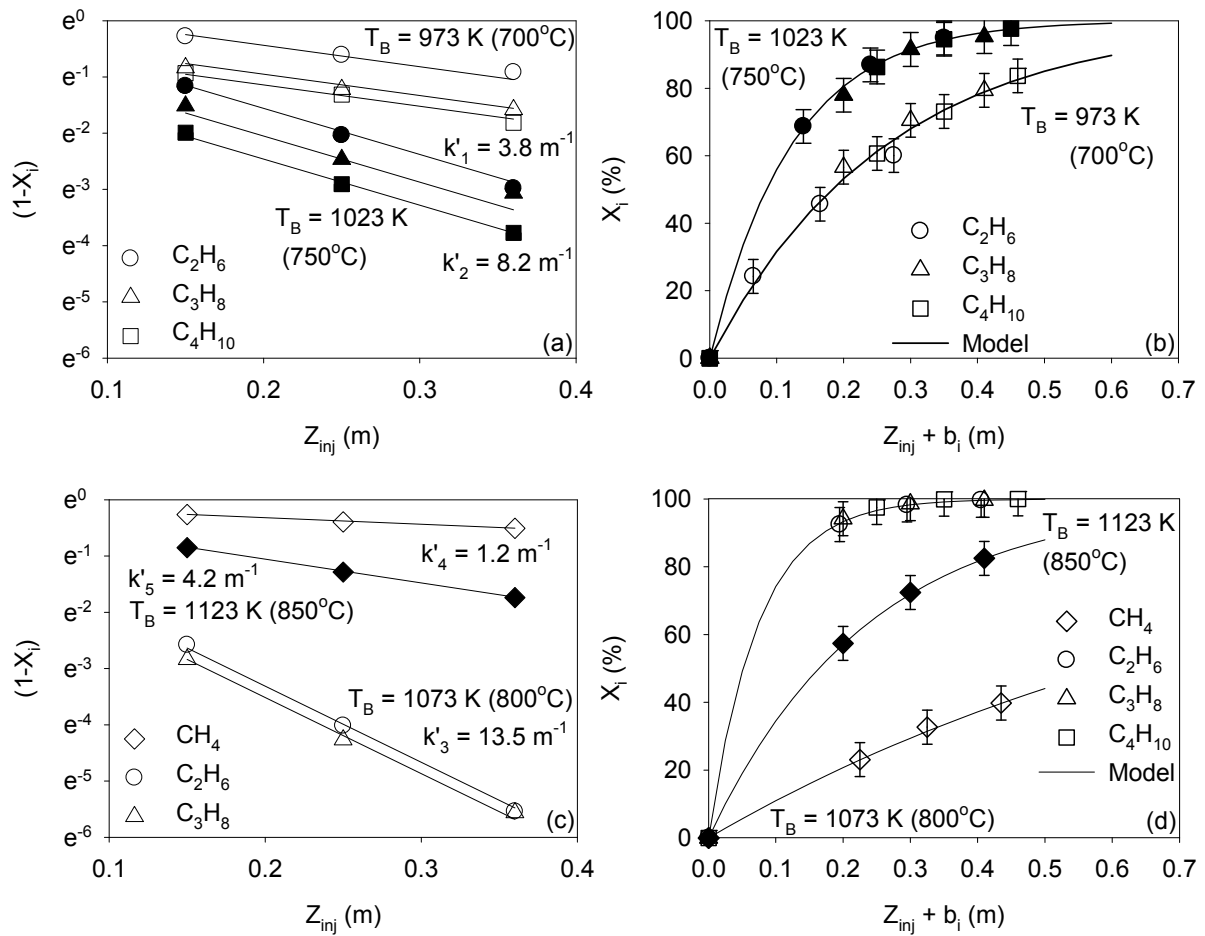
Figure 3: Comparison between the model and experiments at 973, 1023,1073 and 1123 K

Figure 3a shows the in-bed conversion of ethane, propane and n-butane as a function of Z_{inj} on a natural logarithmic scale for two bed temperatures: 973 K (700°C) and 1023 K (750°C). A linear relationship is observed between the ordinate [$\ln(1-X_i)$] and Z_{inj}, which indicates that the model agrees well with the experimental results. The slope of the curve represents the first order reaction rate (k'): the same reaction rate was measured for ethane, propane and n-butane. For bed temperatures of 973 K (700°C) and 1023 K (750°C), k' was measured as 3.8 m^{-1} and 8.2 m^{-1}, respectively. Therefore, the temperature dependence of the reaction rate was uniform for C_2 to C_4 n-alkanes, which implies that the activation energy (E_A) was also the same. However, the parameter b_i in equation (6) was not uniform among C_2 to C_4 n-alkanes. Table 1 lists the different values of b_i measured at the different bed temperatures and used in the fluidized bed combustion model. Figure 3b compares the measured and predicted conversion of ethane, propane and n-butane as a function of ($Z_I + b$): the agreement between the model and the experimental results is very good.

Similar observations were made at higher bed temperatures. Figure 3c shows the in-bed conversion of methane, ethane and propane as a function of Z_{inj} on a natural logarithmic scale for two bed temperatures: 1073 K (800°C) and 1123 K (850°C). The first-order global reaction

rate for ethane and propane was measured as 13.5 m^{-1} at 1073 K (800°C). N-butane conversion reached 100% and could therefore not included in Figure 3c. For methane, however, the reaction rate was significantly lower compared to C$_2$-C$_4$ n-alkanes: k' rose from 1.2 m^{-1} to 4.2 m^{-1} as the bed temperatures was increased from 1073 K (800°C) to 1123 K (850°C). Figure 3d compares the measured and predicted conversion of methane, ethane, propane and n-butane in the fluidized bed: at these higher bed temperatures, the agreement is also very good.

It is observed in Table 1 that the magnitude of b$_i$ decreased with increasing alkane carbon number at a constant bed temperature. For methane and ethane, b$_i$ decreased linearly with temperature, which is consistent with induction time studies: induction time decreased with increasing temperature. For ethane, b$_i$ decreased from 0.085 m at 973 K (700°C) to -0.045 m at 1073 K (800°C). A negative b$_i$ can be explained by a significant hydrocarbon conversion near the injector tip at high bed temperatures. Studies have shown that the jet originating from an injector enhances mixing, which can lead to significant conversion in that region when the mixture induction time is sufficiently low [18]. For methane, b$_i$ decreased from 0.075 m at 1073 K (800°C) to -0.05 m at 1123 K (850°C). For propane and n-butane, b$_i$ remained approximately constant at -0.05 m and -0.1 m, respectively.

The global reaction rates can be expressed in the Arrhenius form:

$$k'_{CH4} = (1.99 \times 10^{12})\, e^{-261008/RT} \tag{7}$$

$$k'_{C2H6} = k'_{C3H8} = k'_{C4H10} = (2.59 \times 10^{7})\, e^{-127800/RT} \tag{8}$$

The reaction rate constant and the activation energy for methane were calculated from the reactions rates measured at bed temperatures of 1073 K (800°C) and 1123 K (850°C). On the other hand, the parameters for ethane, propane and n-butane were calculated from the reactions rates at 973 K (700°C) and 1023 K (750°C). Equation (8) overpredicts the global reaction rate at 1073 K (800°C) and yields 16.4 m^{-1} compared to the measured value of 13.5 m^{-1}. This discrepancy can be explained by the fact that the in-bed conversions were very high at this temperature (in the order of 93% to 100%). At these high conversions, a variation of 1.0% in the measured value greatly affected the measured slope in Figure 3c. The precision in the conversion measurements was estimated for the present study as ±5% absolute.

Table 1: Parameter b$_i$ at the different bed temperatures (T$_B$)

n-Alkane	b$_i$ (m)	Range (K)
CH$_4$	-0.0025 T$_B$ + 2.76	1073-1123
C$_2$H$_6$	-0.0013 T$_B$ + 1.35	973-1073
C$_3$H$_8$	-0.05	973-1073
n-C$_4$H$_{10}$	-0.1	973-1073

The fact that ethane, propane and n-butane have the same global kinetics is consistent with previous studies, which have shown that the induction times of C$_2$ and higher alkanes are of similar magnitude and are governed by the same temperature dependence or activation energy [21-22]. Methane is also known to be significantly less reactive than higher n-alkanes [22,24]. Table 1 shows that the parameter b$_i$ increased with increasing number of carbons in the

n-alkane molecule, which suggests that the mixture reactivity increased (and induction time decreased) with increasing fuel molecule size. This trend is consistent with previous studies [21-22] except for ethane, which was reported by Burcat *et al*. [22] to show the highest reactivity among C_1 to C_5 n-alkanes. This was also supported by Westbrook [24] with kinetic considerations. This discrepancy between the present results and the scientific literature can not be explained and the ± 5% (absolute) error in the measured conversion may be at cause.

4. Conclusions

The non-premixed combustion of methane, ethane, propane and n-butane was investigated in a fluidized bed of inert sand particles. The bed temperature was varied between 923 K (650°C) and 1123 K (850°C) while the superficial gas velocity was kept at 0.4 m/s. Critical transition bed temperatures (T_1 and T_2) were measured for each fuel. For ethane, propane and n-butane, combustion occurred mainly in the freeboard region at bed temperatures below: T_1 = 923 K (650°C). On the other hand, complete conversion occurred within 0.2 m of the injector at: T_2 = 1073 K (800°C). For methane, the measured values of T_1 and T_2 were significantly higher at 1023 K (750°C) and above 1123 K (850°C), respectively. A reaction model with first-order kinetics was developed and compared to the experimental measurements. The reaction rate of C_2 to C_4 n-alkanes could be characterized by a single kinetic expression and a uniform reaction rate constant and activation energy. On the other hand, the methane reaction rate was significantly slower with a higher activation energy.

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