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Effect of Biomass Feed Position on the Kinetics of Devolatilization in a Fluidized Bed

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The main aim of the current investigation is to compare the kinetics of devolatilization of wood spheres introduced at the top and close to the base of a fluidized bed gasifier. The experiments were performed in an externally heated batch reactor filled with olivine particles and fluidized with nitrogen. A known mass of wooden spheres with a diameter equal to 0.005 m was fed into the bed operated at 973, 1,073 and 1,173 K. The molar flow rate of H_2, CO, CH_4 and CO_2 as a function of time was determined with gas analyzers equipped with infrared or thermal conductivity detectors. A devolatilization model was suggested to explain the observed experimental increase of the gas yield when the particles were introduced close to the bottom of the bed. It accounts for the believed transient catalytic conversion of tar. It supposes that a catalytic decomposition of tar at the surface of olivine particles controls the rate of a three step catalytic mechanism. A comparison between experimental and calculated transient results of molar flow rate of formed gas species confirmed the reliability of the suggested model in both the examined circumstances, that is, when biomass was introduced at the top and close to the base of the bed. The results reveal that the olivine particles alter drastically the selectivity of the gasification, since only CO_2 was formed due to the heterogeneous catalytic decomposition of tar.

1. Introduction

Gasification presents high efficiency of energy conversion, in particular when it is coupled with integrated gasification combined cycle (IGCC) (Engelen et al., 2003). The almost ideal mixing between the devolatilization gas and biomass (Bridgewater, 1995) is the main reason for the good results in terms of gas yield and low tar content (Barba et al., 2011). However, there are evidences in the literature that tar production is reduced and gas yield is increased if the fluidized bed is filled with olivine particles (Rapagnà and Mazziotti di Celso, 2008), a mineral containing ferric oxide and silicon ($Mg_{1,78}$, $Fe_{0.13}$ SiO_4) (Devi et al., 2005) that is believed to present catalytic properties (Corella et al., 2004).
In this study, kinetic results of molar flow rate of major species formed during gasification of wood spheres were obtained in a fluidized bed filled with olivine particles. In particular, a supposed catalytic activity of olivine particles was evaluated by comparing these results when biomass was introduced at the top and close to the base of the fluidized bed. A simplified model was suggested to describe the non-catalytic and catalytic decomposition of biomass.

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2. Materials and Methods

2.1 Experiments

The gasification experiments were performed at 973 K, 1,073 K and 1,173 K in a bed made of stainless steel partially filled with olivine particles (equivalent diameter=4.8×10^{-4} m). Nitrogen at the mentioned temperatures was used to fluidize a mass between 2.4×10^{-3} kg and 3.15×10^{-3} kg of wooden (*Ostrya carpinifolia*) spheres with a diameter equal to 5×10^{-3} m. They were placed in two positions of the bed formed with olivine particles: i) at the top and; ii) close to the base (0.1 m above the gas distributor). In both the examined cases, a cold and clean sample of gas mixture leaving the gasifier was continuously pumped into a IR and TCD online analyzers in order to determine the volume composition of H_2, CO, CH_4 and CO_2 as function of time. Several thermocouples, a pressure transducer and two mass flow meters were used to measure the temperature, pressure and flow rates of fluidized gas, respectively. A detailed description of the experimental apparatus and procedure is presented in the literature (Rapagnà and Mazziotti di Celso, 2008).

2.2 Modelling

The suggested kinetic model for biomass gasification is summarized in Table 1. It involves a single (reaction r1) and a four step mechanism (reaction r1 to r4) to describe the decomposition of biomass at the top and when it was initially close to the base, respectively. In the first case, an irreversible first-order non-catalytic thermal decomposition of biomass to form the major measured species (H_2, CO, CH_4 and CO_2) is suggested. However, when the biomass was introduced into the bed of olivine, catalytic activity of olivine is believed to favor the chemical conversion of tar. Based on such a premise, a simplified kinetic model to describe the catalytic decomposition of tar is presented (reactions r2 to r4). It considers that tar is firstly adsorbed at the surface of the olivine particles, then tar decomposition takes place to produce CO_2, and finally there is a step of desorption of the residual liquid. A reaction rate in terms of tar concentration in the fluid phase was written by assuming that the overall catalytic mechanism of CO_2 production is governed by the step of tar decomposition (reaction r3).

Table 1: Simplified kinetic mechanism of (non-catalytic) biomass and (catalytic) tar decomposition

Number	Reaction
r1	$CH_{1.471}O_{0.810} \rightarrow 0.0937H_2+0.153CO_2+0.270CO+0.0921CH_4+0.597(C_{0.812}H_{1.533}O_{0.392})$
r2	$C_{0.812}H_{1.533}O_{0.392}+X \leftrightarrow (C_{0.812}H_{1.533}O_{0.392})X$
r3	$(C_{0.812}H_{1.533}O_{0.392})X \rightarrow 0.068CO_2+(C_{0.744}H_{1.533}O_{0.256})X$
r4	$(C_{0.744}H_{1.533}O_{0.256})X \leftrightarrow C_{0.744}H_{1.533}O_{0.256}+X$

Based on the supposed kinetic mechanism presented in Table 1, a system of algebraic-differential equations is presented. It was solved by the numerical method of Euler with a computational routine written in FORTRAN. Eq (1) is the rate for an irreversible first order reaction of biomass, where n_A is the number of moles of biomass (A=biomass), t is time and T is the average temperature of the particle. Eq (2) is rate of catalytic devolatilization of tar, where n_B is the number of moles of tar (B=tar) in the fluid phase. Eq (3) is the analytical solution of the transient one-dimensional problem of heat conduction in a sphere, where T_s is the temperature at the surface of the sphere, T_i is the initial temperature of the biomass (298 K), d is the diameter of the wooden spheres and α is its thermal diffusivity (1.6×10^{-7} m^2 s^{-1}) (FPL, 2010). Eqs (4) to (7) were from mass balances for H_2, CO, CH_4 and CO_2 in the batch reactor. They involve the stoichiometric coefficients for the examined species presented in reaction r1 and reaction r2.

$$\frac{dn_A}{dt} = -36.9\,exp\left(-\frac{5875}{T}\right)n_A \tag{1}$$

$$\frac{dn_B}{dt} = \frac{-4.57\,exp(-2541/T)n_B}{n_B-0.12} \tag{2}$$

$$T = T_s + \frac{6(T_i - T_s)}{\pi^2}\sum_{j=1}^{\infty}\left\{\frac{1}{j^2}exp\left[-\left(\frac{2j\pi}{d}\right)^2 \alpha t\right]\right\} \tag{3}$$

$$n_{H2} = -0.0937\frac{dn_A}{dt} \tag{4}$$

$$n_{CO} = -0.270\frac{dn_A}{dt} \tag{5}$$

$$n_{CH4} = -0.0921\frac{dn_A}{dt} \tag{6}$$

$$n_{CO2} = -0.153\frac{dn_A}{dt} - 0.068\frac{dn_B}{dt} \tag{7}$$

The parameters in Eq (1) are the frequency factor (-36.9 s^{-1}) and the ratio between the energy activation and universal gas constant (5875 K^{-1}) for reaction r1, respectively. These parameters and the stoichiometric coefficients in reaction r1 were tuned simultaneously on a set of kinetic results of molar flow rate of H_2, CO, CH_4 and CO_2 measured when wooden particles with diameters equal to 0.005 and 0.015 m were introduced at the top of the bed at 1073 K. The parameters in Eq (2) are defined by Eqs (8) to (10), where k_s is the rate constant for reaction r2, K_B designates the adsorption equilibrium constant for B (tar), K_C is the desorption equilibrium constant for C ($C_{0.744}H_{1.533}O_{0.256}$), m is the mass of olivine particles, C_m expresses the molal concentration of total sites, E_{a3}/R is the ratio between the energy activation and universal gas constant (5,875 K^{-1}) for reaction r3 and V is the bed volume.

$$\frac{k_s C_m K_B}{m(K_B - K_C)} = 4.57 \tag{8}$$

$$\frac{E_{a3}}{R} = 2541 \tag{9}$$

$$\frac{V}{K_B - K_C} = -0.12 \tag{10}$$

The parameters whose meaning is given in Eqs (8) to (10) and stoichiometric coefficient for CO_2 in reaction r3 were tuned simultaneously on a set of experimental results of molar flow rate of CO_2 for the case that wooden spheres 0.005 m in diameter were introduced into the bed of olivine operated 973 K. In both the tuning procedures, the simplex method of optimization was applied in order to minimize the sum of the squared differences between experimental and calculated molar flow rate of the already mentioned species.

3. Results and Discussions

Figure 1 shows a comparison between the experimental and calculated molar flow rate of hydrogen for both the examined circumstances, *i.e.*, when biomass was fed at the top (a1, a2 and a3) or it was initially fed close to the bottom of the bed (b1, b2 and b3). A rapid analysis of the experimental results at an identical temperature evidences no significant effect of biomass feed position on the amount of released hydrogen. For instance, the case of n_{H2} in Figure 1a1 and 1b1 at 973 K, Figures 1a2 and 1b2 at 1073 K, or Figures 1a3 and 1b3 at 1173 K. So, it seems that there was no hydrogen produced from a supposed catalytic conversion of tar. In fact, the non-catalytic model, which involves only Eq(1), (3) and Eq(4) for n_{H2}, correctly reproduced the experimental results in Figure a1 to a3, as well as in b1 to b3.

It is important to highlight that the negligible increase of hydrogen in Figures 1b1 compared to 1a1 is attributed to the slight greater initial mass of wooden spheres (m_{Ai}) always found when the wooden particles were initially at the base of the bed (*see* the caption for Figure 1). For the same reason a residual difference between the results of n_{H2} in Figures 1a2 and 1b2, or in Figures 1a3 and 1b3, is observed.

In Figures 2 and 3 the experimental results of molar flow rate of carbon monoxide and methane are reported, respectively. Anyway, there is again no evidence that a decomposition reaction takes place at the olivine surface to produce gas species. The reliability of the non-catalytic model to reproduce the experimental results of n_{CO} and n_{CH4} under all the examined conditions of gasification confirm it.

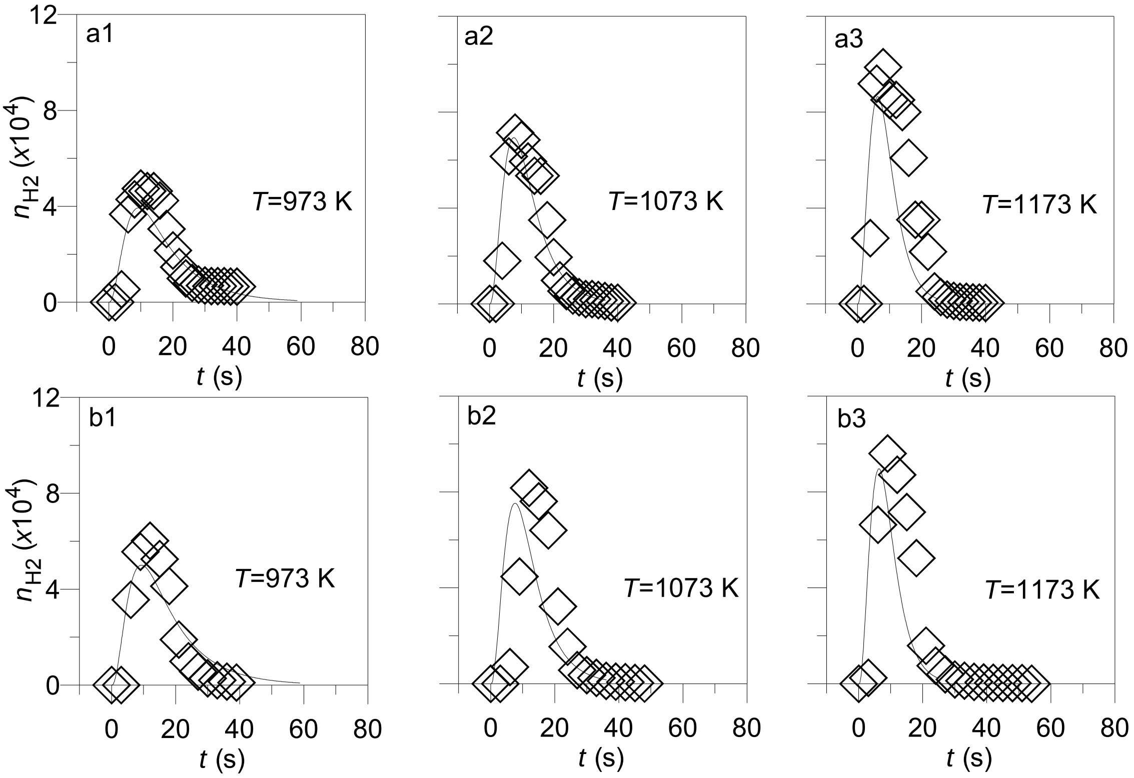

Figure 1: Molar flow rate of hydrogen when the biomass was at the top (a1, a2 and a3) and close to the base (b1, b2 and b3) of the bed. Operating conditions: m_{Ai}=2.40×10^{-3} kg (a1); m_{Ai}=3.05×10^{-3} kg (b1); m_{Ai}=2.90×10^{-3} kg (a2); m_{Ai}=3.15×10^{-3} kg (b2); m_{Ai}=2.70×10^{-3} kg (a3); m_{Ai}=2.80×10^{-3} kg (b3)

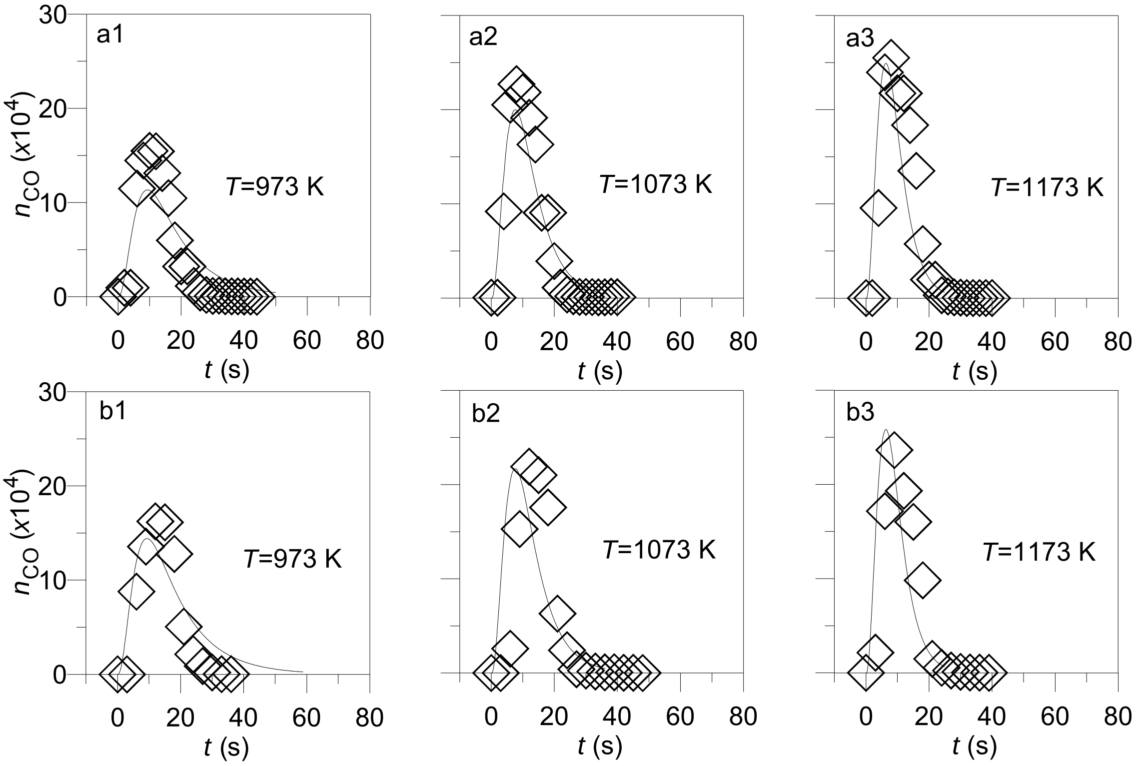

Figure 2: Molar flow rate of carbon monoxide when the biomass was at the top (a1, a2 and a3) and close to the base (b1, b2 and b3) of the bed

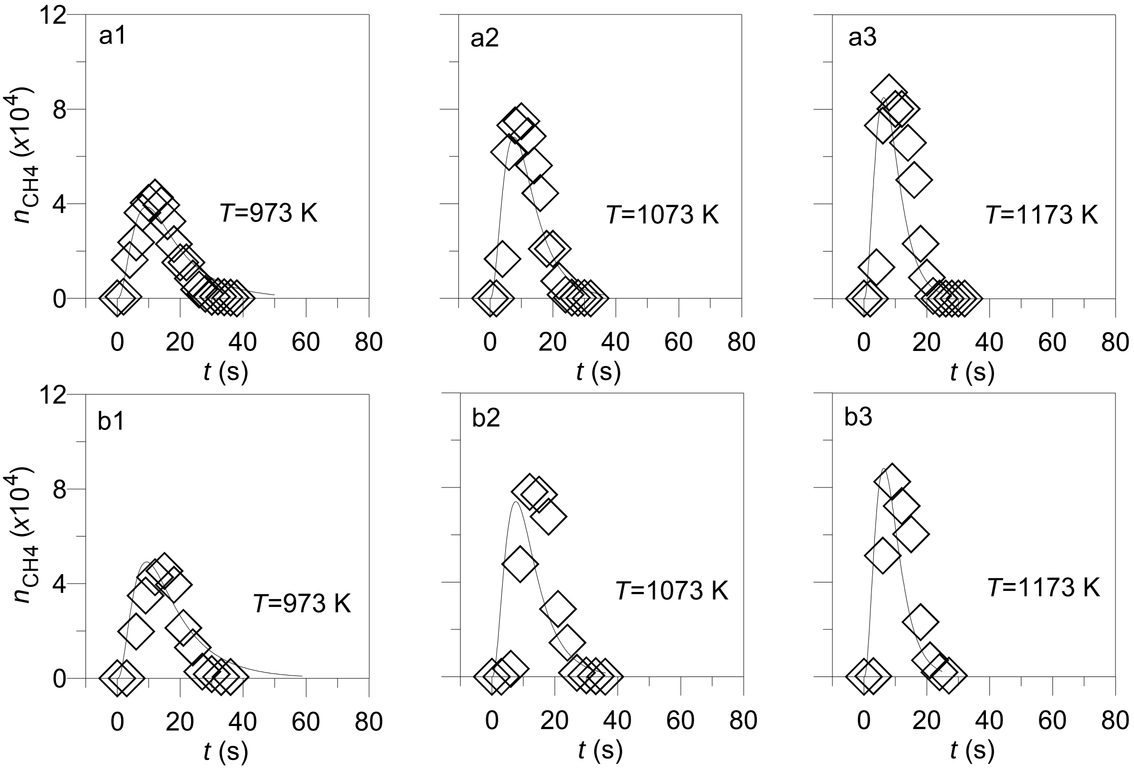

Figure 3: Molar flow rate of methane when the biomass was at the top (a1, a2 and a3) and close to the base (b1, b2 and b3) of the bed

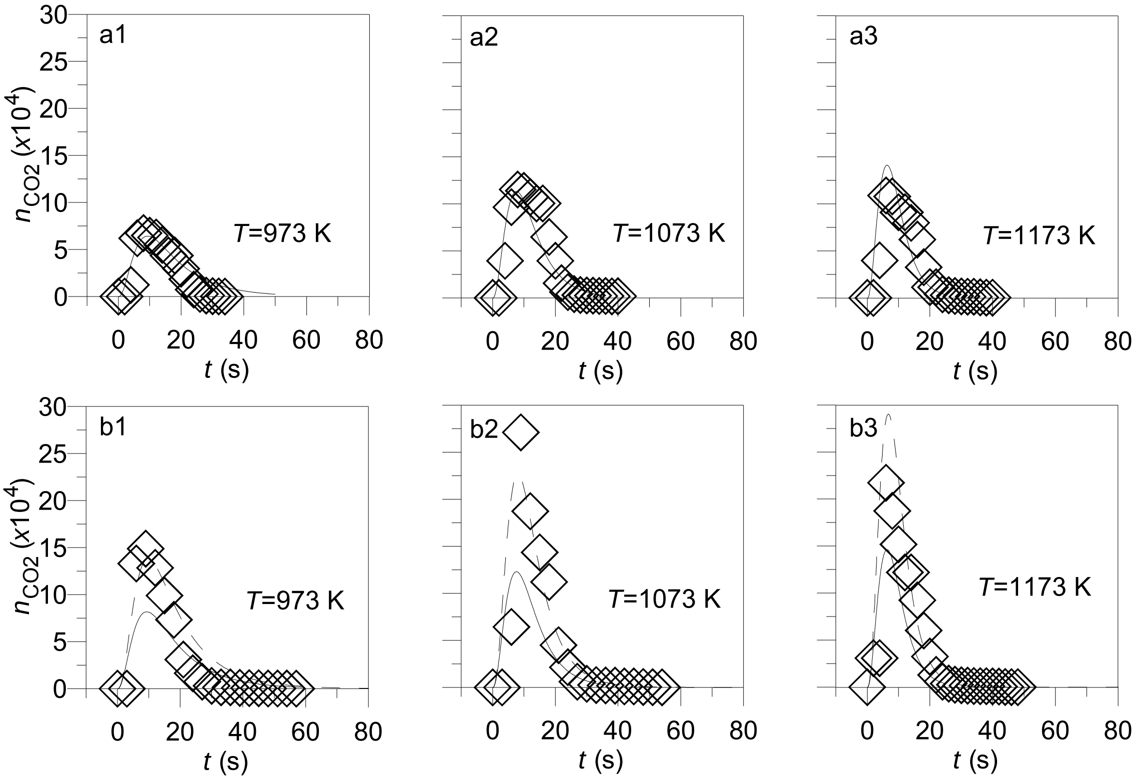

Figure 4: Molar flow rate of carbon dioxide when the biomass was at the top (a1, a2 and a3) and close to the base (b1, b2 and b3) of the bed

Figures 4a1 to 4a3 show the results of molar flow rate of carbon dioxide when the biomass was fed at the top of the bed of olivine particles. Figures 4b1 to 4b3 present the same kind of data, but when the particles were initially fed close to the base. A comparison between these different group of figures at an identical temperature promptly reveals that a large amount of CO_2 is released when the biomass was introduced into the bed. In this particular case, the non-catalytic model represented by a solid line in Figures 4b1 to 4b3 is not able to reproduce the molar flow rate of carbon dioxide. However, when the model accounts for a catalytic effect of olivine on the kinetics of CO_2 production, a good agreement between experimental and calculated results is noticed. Based on the presented evidences, it seems that olivine particles cause a selective catalytic conversion of tar to carbon dioxide, which is responsible for enhancing the gas yield.

Figure 5 presents the experimental results of gas yield. It represents the mass ratio of total released gas per dry and free of ash biomass introduced into the bed. Both the experimental and calculated results show that the gas yield is increased when the biomass was initially at the base of bed formed with particles of olivine. Such a result is fully in agreement with the evidences emerged from the transient results of molar flow rate for the major measured species.

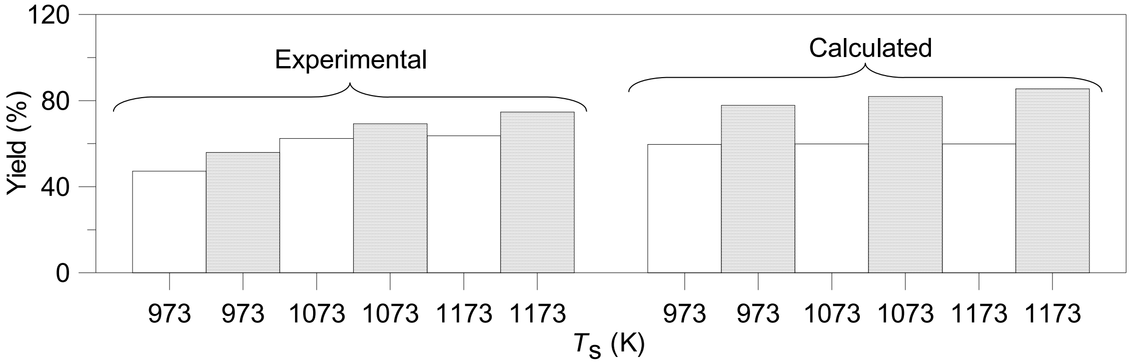

Figure 5: Gas yield for the case of biomass introduced into the bed of olivine particles (dark bars) and at the top (white bars) of the fluidized bed

4. Conclusions

The kinetic experimental results of molar flow rate of H_2, CO, CH_4 and CO_2 shown that tar is catalytically and selectively converted into carbon dioxide. From a practical point-of-view, it means that better results in terms of gas yield are expected when the gasifier, or the operation of gasification, is designed to promote a good contact between olivine particles and biomass. A simple solution toward such an objective is to introduce the biomass close to the base of the bed. The suggested chemical kinetic catalytic model is able to reproduce the increase of released carbon dioxide due to the conversion of tar, as well as the enhance of gas yield observed when the particles are initially close to the base of the bed of olivine particles.

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