

GASIFICATION KINETICS OF CHAR FROM OLIVE TREE PRUNING WITH CO₂ AND H₂O IN FLUIDIZED BED

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ABSTRACT: Kinetics of gasification of char from olive tree pruning was measured in a fluidized bed at temperatures between 760 and 900 °C. Experiments were carried out using H₂O-N₂ and CO₂-N₂ mixtures to measure the rates of the gasification reactions with H₂O and CO₂ and to assess the inhibition effects of H₂ and CO. The reaction rates with H₂O were 3-4 times faster than those obtained with CO₂ and inhibition by CO and H₂ was observed to be significant, especially at low temperature. Langmuir-Hinshelwood kinetics was obtained for the two gasification reactions. Additional experiments were carried out with CO₂-H₂O-N₂ mixture to study the simultaneous gasification with CO₂ and H₂O. It was found that the char was converted slightly faster in a gas mixture containing both CO₂ and H₂O than in a gas with the same H₂O concentration but substituting CO₂ by N₂.

Keywords: biomass, gasification, kinetics, char, fluidized bed

1 INTRODUCTION

Gasification of char with CO₂ and H₂O is the rate limiting step in biomass gasification processes and therefore it is important to evaluate the kinetics of these reactions. Gasification of char from different coals and biomasses has been measured [1-8], but data regarding gasification of char from olive tree pruning (OTP) is lacking. OTP is an important biomass resource in the Mediterranean countries, having a heating value and composition that make it a suitable fuel for gasification applications.

Previous works have shown that the method employed to prepare the char affects its reactivity to a great extent. Chars generated at high heating rate have been found to be more reactive than chars obtained at low heating rate [3, 9-10]. Also the thermal history of the char affects its reactivity. [11].

Due to these aspects it is very important to produce the char under conditions similar to those in an industrial gasifier. In this work, the kinetics of char gasification is measured in a laboratory fluidized bed (FB) and the char employed is generated in situ in the reactor.

2 EXPERIMENTAL

2.1 Experimental setup

Experiments have been carried out in a laboratory fluidized bed (FB) reactor. The experimental setup is represented in Fig. 1. The reactor is made of stainless steel. It has a preheating section, an FB section with 51 mm internal diameter and a freeboard section with 82 mm internal diameter. The reactor is surrounded by a 10 kW electrical oven, with two independent heating zones, one for the bottom bed and one for the freeboard, and is equipped with 4 thermocouples and two controllers, allowing the control of temperature in both zones.

N₂, CO₂, CO and H₂ can be fed to the reactor using mass flow controllers and the flow of air fed is adjusted by a flowmeter. Steam was generated by vaporizing a fixed flow of water. The steam generated was mixed with

the other gases and the mixture was fed to the reactor. The flow of water was adjusted by a peristaltic pump, which was calibrated before each test. At the exit of the reactor there is a cyclone for collecting any particles entrained from the reactor. After the cyclone the gas passes through a series of equipment where steam is condensed and tar is eliminated to protect the gas analyzer. The composition of the exit gas was measured by a Siemens analyzer using a non-dispersed infrared method for CO, CO₂ and CH₄ and thermal conductivity and paramagnetic methods for H₂ and O₂, respectively.

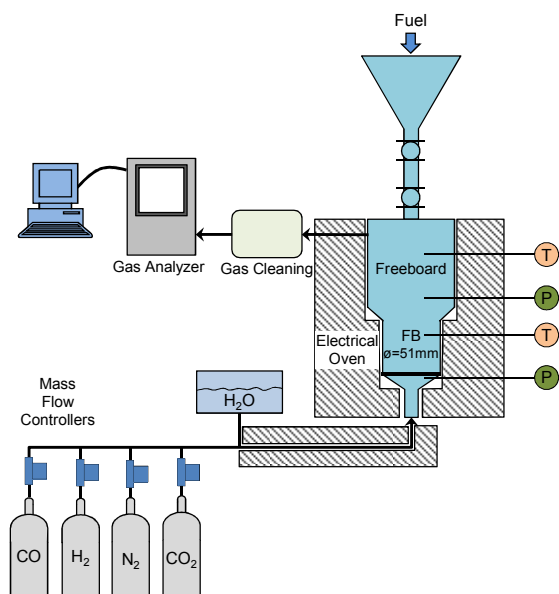


Figure 1: Experimental setup

2.2 Material

The fuel employed was olive tree pruning (OTP), which is a heterogeneous fuel containing both branches and leaves from olive trees. In order to enable small, but homogeneous samples, the received sample of OTP was

ground to particle size below 0.5 mm. Pellets were prepared from the resulting material using a pelletizing machine. The pellets produced had a diameter of 6 mm.

The bed material employed was bauxite with particle size between 250 and 500 μm .

2.3 Operating conditions

Tests were carried out at temperature between 760 and 900 $^{\circ}\text{C}$. The gas velocity employed was approximately 3 times the minimum fluidizing velocity of the bed material. Tests with $\text{CO}_2\text{-N}_2$ mixtures were carried out to study the gasification with CO_2 and tests with $\text{H}_2\text{O-N}_2$ mixtures were employed to study the gasification with H_2O . CO_2 concentrations of 10-40% and H_2O concentrations of 20-40% on a volume basis were studied. Also CO_2 gasification tests with 10% CO and H_2O gasification tests with 10% H_2 were conducted to investigate the inhibition effects of CO and H_2 . The simultaneous gasification with CO_2 and H_2O was studied using $\text{CO}_2\text{-H}_2\text{O-N}_2$ mixture containing 20% CO_2 and 20% H_2O .

2.4 Experimental procedure

First, the reactor was heated by setting the test temperature in the oven. During the heating period a continuous flow of air was fed. Once the desired temperature was reached, the fluidizing gas was switched to N_2 and when no more oxygen was detected by the analyzer, a batch of OTP was fed through a pipe that ends near the bed surface. When the CO , CO_2 , CH_4 and H_2 concentrations measured by the gas analyzer were nearly zero, devolatilization was considered to be complete. Then the flow of the gasification gas started. Gasification conditions were maintained until the concentrations of the product gases (CO , CO_2 and H_2) at the exit were close to zero and too low to allow accurate measurements. After gasification, the gas feed was switched to air in order to burn the remaining char.

When studying the simultaneous gasification with CO_2 and H_2O , the test procedure was slightly modified. The devolatilization of the fuel was carried out in situ using the same method as described above. After the devolatilization was completed the feeding of the gasification gas mixture started, but gasification conditions were not maintained until complete conversion was achieved. Instead, the gasification was interrupted after a certain period of time varying between 4 and 15 minutes. Afterwards the fluidizing gas was switched to air to burn the remaining char. The amount of carbon in char was determined from the CO_2 and CO concentrations in the exit gas during combustion and the value obtained was employed to calculate the char conversion, x . Using this method, the conversion achieved after a certain time of gasification could be determined.

The effect of gas mixing was taken into account to correct the gas concentrations measured during the char tests. Blank tests with CO_2 injection into the fluidized bed were performed to assess the effects of gas mixing in the exit line.

3 RESULTS

3.1 Selection of particle size for measuring the intrinsic kinetics

Since the aim of this work is to measure intrinsic

gasification kinetics, i.e. without mass transfer limitations, tests were carried out with successively lower particle size until no significant variation in the reaction rates measured was observed. This was done for the reaction with H_2O only, since it is faster than the reaction with CO_2 . It was found that to diminish the mass transfer limitations it was necessary to reduce the particle size of the pellets by grinding and use a particle size fraction that passed through a 2.8 mm sieve, but did not pass through a 1 mm sieve. These particles were employed because they were small enough to have negligible mass transfer limitations and they were sufficiently large to avoid entrainment of the char from the FB.

3.2 Gasification in $\text{CO}_2\text{-N}_2$ and $\text{H}_2\text{O-N}_2$ mixtures

The char conversion is defined as:

$$x = \frac{m_{c_0} - m_c}{m_{c_0}} \quad (1)$$

m_{c_0} and m_c being the mass of carbon in the char at initial time and at conversion x , respectively.

Fig. 2 shows the conversion rate, dx/dt , measured with 20% CO_2 and 20% H_2O at 800 $^{\circ}\text{C}$, as a function of conversion.

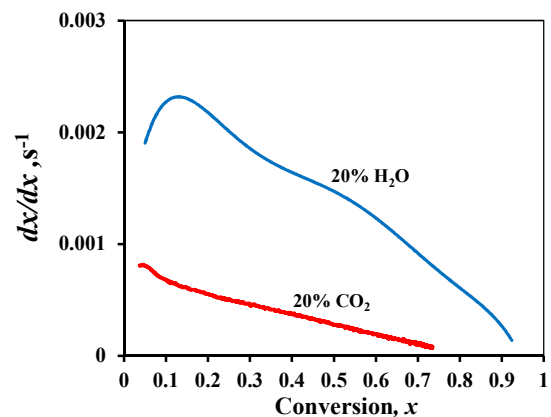


Figure 2: Conversion rate, dx/dt , measured with 20% CO_2 and 20% H_2O at 800 $^{\circ}\text{C}$, as a function of conversion

It can be seen in Fig. 2 that the reaction with H_2O is 3-4 times faster than the reaction with CO_2 . It was found that both for the reaction with CO_2 and H_2O , the shape of the curve dx/dt vs x did not vary with CO_2 or H_2O concentration and the variation of the shape with temperature was small. This means that the gasification kinetics can be expressed using Eq. (2).

$$\frac{dx}{dt} = \left(\frac{dx}{dt} \right)_x (T, p_{\text{CO}_2/\text{H}_2\text{O}}) F(x) \quad (2)$$

$(dx/dt)_x$ being the conversion rate at reference conversion x and $F(x)$ is a function that expresses the variation of the reaction rate with x . Only $(dx/dt)_x$ depends on the temperature and gas concentration. Here the reference state of conversion chosen for expressing the reaction rate was $x=0.20$. Fig. 3 shows, dx/dt at $x=0.20$, measured with CO_2 and H_2O for different temperatures and gas composition.

3.3 Inhibition effect of CO and H₂

To investigate the inhibition effects of CO on the gasification reaction with CO₂, tests were conducted with CO₂-CO-N₂ mixture containing 20% CO₂ and 10% CO. The inhibition effect showed to be very important, especially at low temperature. The reaction rate was reduced with up to 50 % due to the presence of CO. For measuring the effects of H₂ on the gasification reaction with H₂O, tests were conducted with H₂O-H₂-N₂ mixture containing 20% H₂O and 10% H₂. It was found that adding 10% of H₂ reduced the reaction rate around 30%.

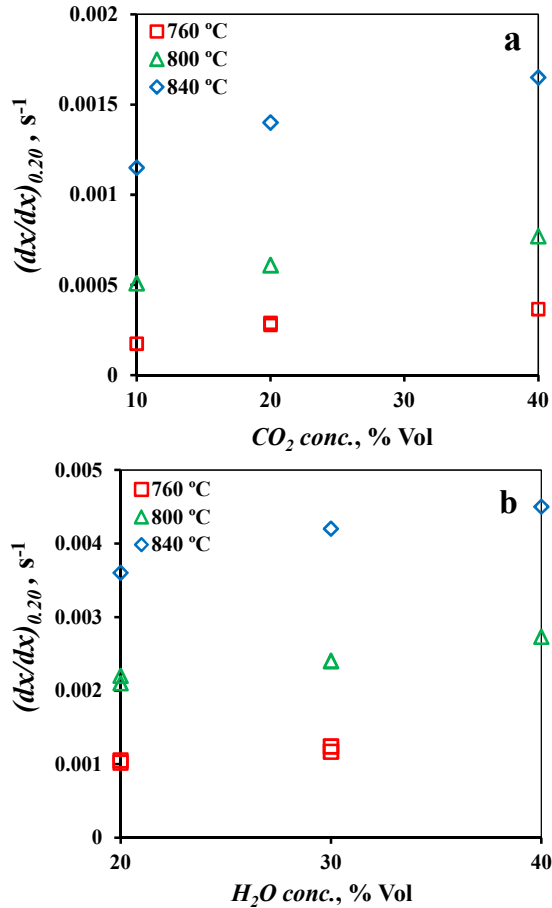


Figure 3: Reaction rate at 20% conversion as a function of gas concentration measured at different temperatures: a) reaction in CO₂-N₂ mixtures; b) reaction in H₂O-N₂ mixtures

3.4 Determination of gasification kinetics

To express the reaction rate with CO₂ as a function of CO₂ and CO concentration and rate of gasification with H₂O as a function of H₂O and H₂ concentration, Langmuir-Hinshelwood kinetics was employed.

Reaction with CO₂:

$$\left(\frac{dx}{dt}\right)_{0.20} = \frac{k_1 P_{CO_2}}{1 + k_2 P_{CO_2} + k_3 P_{CO}} \quad (3)$$

Reaction with H₂O:

$$\left(\frac{dx}{dt}\right)_{0.20} = \frac{k_1 P_{H_2O}}{1 + k_2 P_{H_2O} + k_3 P_{H_2}} \quad (4)$$

The values of the parameters k_1 and k_2 were obtained by linear regression using the results obtained with CO₂-N₂ mixtures (for gasification with CO₂) and H₂O-N₂ mixtures (for the gasification with H₂O) and then the k_3 values were calculated from the results obtained with CO₂-CO-N₂ mixture and H₂O-H₂-N₂ mixture. The values of k_1 , k_2 and k_3 for the gasification reaction with CO₂ are shown in Table I and the values for the reaction with H₂O are given in Table II.

The dependence of the kinetics parameters on temperature can be expressed using the Arrhenius equation:

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

Table I: Kinetics parameters for the gasification of char with CO₂ (Eq. (3)).

Temperature, °C	$k_1, s^{-1}bar^{-1}$	k_2, bar^{-1}	k_3, bar^{-1}
760	0.0025	4.08	36.4
800	0.0098	10.03	30.0
840	0.0268	14.41	15.8

Table II: Kinetics parameters for the gasification of char with H₂O (Eq. (4)).

Temperature, °C	$k_1, s^{-1}bar^{-1}$	k_2, bar^{-1}	k_3, bar^{-1}
760	0.0142	8.89	43.2
800	0.0277	7.95	40.3
840	0.0445	7.35	34.4

The values of k_1 were well represented by the Arrhenius equation, while the k_2 and k_3 showed reasonable correlation. The Arrhenius parameters obtained for k_1 , k_2 and k_3 are shown in Table III and Table IV for the reactions with CO₂ and H₂O, respectively.

Table III: Values of the Arrhenius constants for calculating kinetic parameters k_1 , k_2 and k_3 of the gasification with CO₂

	k_1	k_2	k_3
k_0	$7.1 \cdot 10^{11} s^{-1}bar^{-1}$	$2.0 \cdot 10^8 bar^{-1}$	$3.8 \cdot 10^{-4} bar^{-1}$
$E_a, kJ/mol$	286	152	-99

Table IV: Values of the Arrhenius constants for calculating kinetic parameters k_1 , k_2 and k_3 of the gasification with H₂O

	k_1	k_2	k_3
k_0	$1.2 \cdot 10^7 s^{-1}bar^{-1}$	$0.62 bar^{-1}$	$1.9 bar^{-1}$
$E_a, kJ/mol$	137	-23	-27

3.5 Simultaneous gasification with CO₂ and H₂O

Gasification experiments were carried out using a CO₂-H₂O-N₂ mixture containing 20% CO₂ and 20% H₂O.

The temperatures tested were 760, 800, and 840 °C and the gasification conditions were maintained for 4, 6, 8 or 15 minutes depending on the temperature. In Fig. 4 the conversion achieved after a certain time of gasification in CO₂-H₂O-N₂ mixture is compared to the conversion versus time curves for the gasification with only 20% H₂O. The results show that the reaction rate is slightly increased when substituting part of the N₂ in a H₂O-N₂ mixture with CO₂. Other authors have found that the reaction rate in a CO₂-H₂O-N₂ mixture is equal to the sum of the individual reaction rates measured with only CO₂ or H₂O [9], while others have found that the mixture gasification rate is higher than the rate with only H₂O, but lower than the sum of the two individual reaction rates. [3].

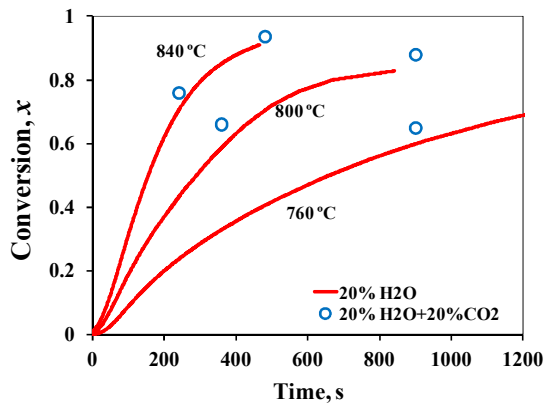


Figure 4: Conversion as a function of time at different gasification temperatures measured with: a mixture containing 20% CO₂+ 20% H₂O (points) and a mixture containing only 20% H₂O and N₂ (lines).

4 CONCLUSIONS

Kinetics of the gasification of char from olive tree pruning with CO₂ and H₂O was measured in fluidized bed in the range of 760-900 °C. The inhibition effects of CO and H₂ were found to be important especially at low temperature and the reaction rates were expressed in terms of Langmuir-Hinshelwood kinetics. The simultaneous gasification with CO₂ and H₂O was investigated, finding that the char was converted slightly faster in a gas mixture containing both CO₂ and H₂O than in a gas with the same H₂O concentration but substituting CO₂ by N₂.

5 NOMENCLATURE

E_a	Activation energy, kJ/mol
$F(x)$	Function that expresses the variation of reactivity with char conversion, -
k_0	Preexponential factor, s ⁻¹ bar ⁻¹ or bar ⁻¹
k_1, k_2, k_3	Kinetic parameters
m_C	Mass of carbon in char at any time, g
m_{CO}	Initial mass of carbon in char produced after devolatilization, g
p_{CO_2}	Partial pressure of CO ₂ in the feed gas, bar
p_{H_2O}	Partial pressure of H ₂ O in the feed gas, bar
p_{CO}	Partial pressure of CO in the feed gas, bar
p_{H_2}	Partial pressure of H ₂ in the feed gas, bar

R	Ideal gas constant, 8.314 J/(molK)
T	Temperature, K
t	Time, s
Abbreviations	
FB	Fluidized bed
OTP	Olive tree pruning

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