Effects of Process Factors on Slow Pyrolysis of Sorghum Waste

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Slow pyrolysis of sorghum stalk and leaves was conducted in a fixed bed reactor using carbon dioxide as a carrier gas. Pyrolysis products consisted of a char, a pyrolytic oil and incondensable gases. Effects of process factors, i.e., power density (0.145 and 0.248 W/cm^3), carbon dioxide superficial velocity (1.7 and 3.4 cm/min) and sorghum particle volume (0.05 and 0.20 cm^3), on process responses (bed temperature, char and oil specific masses) were established. Under conditions studied, the power density and particle volume had significant influence on the pyrolysis dynamics and yield of pyrolysis products. Correlations between characteristic factors and final responses of pyrolysis process were determined by 2 ^{3} factorial design. A one-stage global reaction kinetic model was selected to describe the process dynamics and its parameters were fitted based on experimental data. The experimental and predicted data may provide useful data for the design, scale-up and operation of fixed bed pyrolysis reactors.

Keywords: factorial experiment, kinetic model, pyrolysis, sorghum

Currently, in the context of an increasing demand for energy as well as of environmental degradation and fossil fuel depletion, the replacement of conventional fuels with biomass-based ones is an attractive option. Vegetal materials, especially wastes and by-products, are abundant, inexpensive, renewable and carbon neutral resources, that can be converted into energy using various thermo-chemical technologies, *e.g.*, combustion, pyrolysis, gasification. Among them, pyrolysis is the only technique leading to solid, liquid and gas products which are valuable sources of energy and chemicals [1-6].

Biomass pyrolysis consists in thermal decomposition of organic matrix in an oxygen depleted atmosphere, obtaining a porous carbonaceous solid (char) and volatiles. The volatiles, consisting of non-condensable light gases, condensable gases (tar) and water vapour, are further condensed resulting in a non-condensable fraction (pyrolytic gas) and a pyrolytic liquid (oil) containing *cca.* 15-35% water. Pyrolysis tar usually contains hundreds of organic compounds, *e.g.*, alcohols, aldehydes, ketones, carboxylic acids, sugars, furans, alkenes, nitrogen compounds, phenolics, BTX (benzene, toluene, xylene), PAH (polyaromatic hydrocarbons), whereas pyrolytic gas mainly consists of CO_2, CO, H_2, CH_4, C_2H_6, C_2H_4 and small amounts of C_3H_8, NH_3, NO_x and SO_x [6]. The pyrolysis process is usually conducted in the presence of a carrier gas which can be inert (N_2, Ar) or oxidant (CO_2, steam). Pyrolysis products result from both primary reactions of solid material devolatilization and secondary reactions of primary products degradation, *e.g.*, tar thermal cracking, tar and char carbon gasification (reforming with CO_2, H_2 and H_2O) [1,5,6].

The pyrolysis rate as well as the distribution, composition and properties of the pyrolysis products mainly depend on heating rate, process temperature, residence time of volatiles, raw material properties (type, size, shape, pretreatment), type and flow rate of carrier gas. A decrease in char yield and an enlargement of volatiles yield with an increase in *heating rate* have been reported [6-8]. Higher levels of process *temperature* produce the same effect. At temperatures lower than 500 °C, non-condensable gases and oil amounts increase with temperature, whereas at temperatures higher than 500 °C, gas yield increases and oil production decreases with an increase in temperature due to an enhancement of tar thermal cracking [6-17]. The *size of vegetal material particles* may have an important effect on the yield of pyrolysis products. An increase in grain size determines larger temperature gradients in the particle leading to an increase in char yield and a decrease in oil amount [6,18]. The presence of an *oxidizing carrier gas* (*e.g.*, steam, CO_2) and increased *residence times* enhance the production of pyrolytic gas due to gasification and cracking reactions [6].

This paper has aimed at studying the fixed bed pyrolysis of sorghum waste, *i.e.*, stalk and leaves, under carbon dioxide atmosphere. The effect of process independent variables, *i.e.*, heat flow rate, carbon dioxide superficial velocity and sorghum waste size, on the process dynamics and yield of pyrolysis products was measured and predicted.

Experimental part

Materials

Crushed sorghum stalk and leaves were employed as a vegetal material. Two fractions of sorghum waste particle size, *i.e.*, about 1 x 5 x 10 mm (fine) and 1 x 10 x 20 mm (coarse), corresponding to a mean volume of 50 mm^3 and 200 mm^3, respectively, were selected for subsequent studies.

Equipment and procedure

Laboratory set-up and experimental procedure referring to the slow pyrolysis of vegetal materials were detailed in our previous studies [19-21]. Sorghum waste was packed in a 5 cm internal diameter and 50 cm height quartz column. Column external wall was heated by an electric resistance fed by an autotransformer, leading to the heating and thermal decomposition of vegetal material.

Carbon dioxide from a cylinder up-flowed through the fixed bed sorghum waste and left the column along with the volatiles obtained during the pyrolysis. The mixture of gases and vapour was cooled in a condenser, resulting in a

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Table 1
EXPERIMENTATION MATRIX OF 2^3 FACTORIAL EXPERIMENT

Exp.	P (W/cm³)	w (cm/min)	V (cm³)	x_1	x_2	x_3	y_1	y_2	y_3
1	0.145	1.7	0.05	-1	-1	-1	0.27	0.31	0.42
2	0.145	3.4	0.05	-1	1	-1	0.25	0.28	0.48
3	0.248	1.7	0.05	1	-1	-1	0.22	0.31	0.47
4	0.248	3.4	0.05	1	1	-1	0.22	0.38	0.40
5	0.145	1.7	0.20	-1	-1	1	0.37	0.32	0.31
6	0.145	3.4	0.20	-1	1	1	0.26	0.26	0.48
7	0.248	1.7	0.20	1	-1	1	0.26	0.30	0.44
8	0.248	3.4	0.20	1	1	1	0.27	0.29	0.44

pyrolytic oil and incondensable gases. The masses of vegetal material and pyrolytic oil were recorded on-line by the electronic balances whereas the temperatures of bed centre and column internal wall were measured by the thermocouples. All experimental data were collected by an acquisition system.

Experimental variables

The experimental study was conducted at two levels of process factors, *i.e.*, power density, P (W/cm^3), expressed as heat flow rate divided by bed volume, carbon dioxide superficial velocity, w (cm/min), and mean volume of sorghum waste particle, V (cm^3), according to a 2^3 factorial experiment (table 1). Vegetal material mass, m (g), oil mass, m_{oil} (g), bed centre temperature, t_c (°C), and internal wall temperature, t_w (°C), were continuously recorded as a function of heating time, τ (min).

Results and discussions

Pyrolysis experimental curves

Experimental data referring to the pyrolysis dynamics, i.e., m/m_0, m_{oil}/m_0 and t_b vs. time (τ), where m_0 (g) represents the initial mass of sorghum waste and t_b (°C) is the bed temperature estimated as a logarithmic mean between t_c and t_w, are illustrated in figures 1-3. Depicted data highlight an enlargement of bed temperature (t_b) and specific mass of pyrolytic oil (m_{oil}/m_0) as well as a decrease in specific mass of sorghum waste (m/m_0) at the higher level of heating rate (P=0.248 W/cm^3). Moreover, an increase in t_b and m/m_0 as well as a decrease in m_{oil}/m_0 is observed for coarse particles (V=0.20 cm^3).

Statistical model

Specific mass of sorghum waste, m/m_0, specific mass of pyrolytic oil, m_{oil}/m_0, and mean temperature of fixed bed sorghum waste, t_b, were selected as process

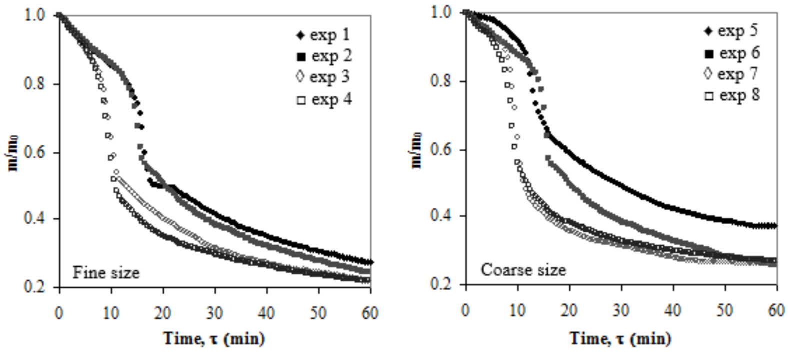

Fig. 1. Specific mass of sorghum waste *vs.* time

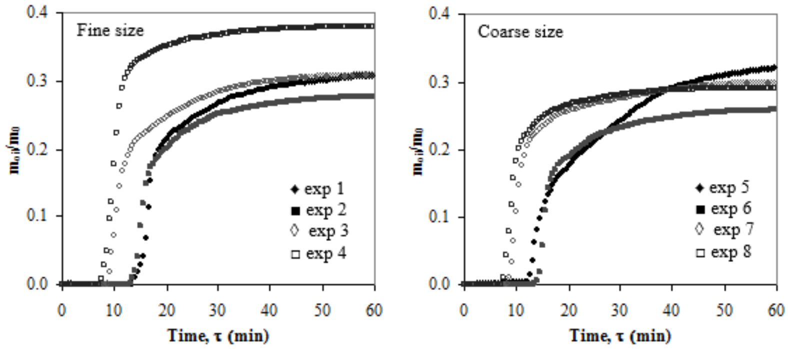

Fig. 2. Specific mass of pyrolytic oil *vs.* time

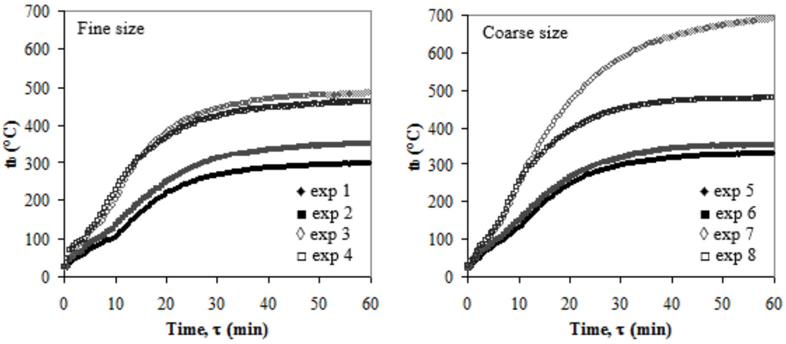

Fig. 3. Mean temperature of fixed bed sorghum waste *vs.* time

Table 2
PRE-EXPONENTIAL FACTOR (A/β) AND ACTIVATION ENERGY (E) REGRESSED FROM EXPERIMENTAL DATA

Exp.	α	β (K/min)	E (kJ/mol)	A/β (min^{-1})
1	0.18-0.73	9.68	103.86	427
2	0.13-0.66	11.11	55.31	324
3	0.100.62	18.75	39.18	118
4	0.09-0.66	21.43	44.70	204
5	0.07-0.80	8.89	55.25	945
6	0.10-0.77	10.53	45.41	892
7	0.07-0.70	26.67	39.98	863
8	0.08-0.72	23.53	34.70	812

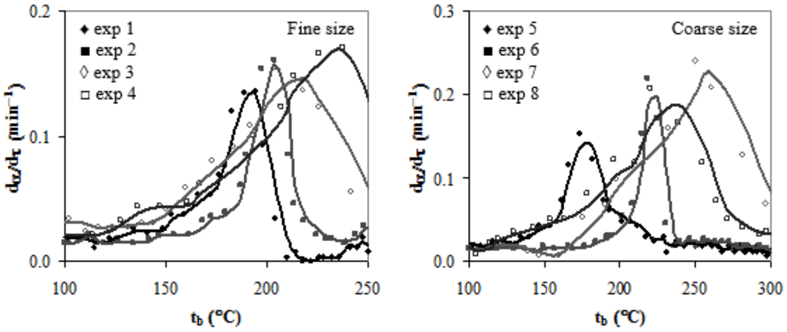

Fig. 4. Comparison between experimental (symbols) and simulated (solid lines) differential conversion curves

dependent variables (responses). Their final values, i.e., $y_1=m_f/m_0$, $y_2=m_{oil,f}/m_0$ and $y_3=t_{b,f}$, as well as the dimensionless values of process factors, calculated with eqs. (1)-(3), are given in table 1. Tabulated data were processed using the procedure recommended for a factorial experiment with 2 levels [22] and eqs. (4)-(6) were obtained.

$$x_1 = \frac{P-0.197}{0.052} \tag{1}$$

$$x_2 = \frac{w-2.55}{0.85} \tag{2}$$

$$x_3 = \frac{V-0.125}{0.075} \tag{3}$$

$$\begin{aligned} y_1 &= 0.265-0.023x_1-0.015x_2+0.025x_3+0.018x_1x_2- \\ &-0.003x_1x_3-0.010x_2x_3+0.013x_1x_2x_3 \end{aligned} \tag{4}$$

$$\begin{aligned} y_2 &= 0.306+0.014x_1-0.004x_2-0.014x_3+0.019x_1x_2- \\ &-0.011x_1x_3-0.014x_2x_3-0.006x_1x_2x_3 \end{aligned} \tag{5}$$

$$\begin{aligned} y_3 &= 432.19+97.39x_1-20.39x_2+31.89x_3-38.96x_1x_2+ \\ &+23.88x_1x_3-27.57x_2x_3-19.47x_1x_2x_3 \end{aligned} \tag{6}$$

Conforming to figures 1-3, eqs. (4)-(6) emphasize that:

-high levels of power density (x_1) result in low char production (y_1) as well as in high values of oil yield (y_2) and mean bed temperature (y_3);

-high levels of particle volume (x_3) lead to large values of y_1 and y_3 as well as low values of y_2.

Kinetic model

A one-stage global reaction model was adopted to describe the conversion process from raw material to char and volatiles [8, 23-26]. For dynamic data obtained at a constant heating rate, $\beta = \frac{dT_b}{d\tau}$, the decomposition rate was described by eq. (7), where the conversion of volatiles was expressed by eq. (8).

$$\frac{d\alpha}{d\tau} = (1-\alpha)\frac{A}{\beta}\exp\left(-\frac{E}{RT_b}\right) \tag{7}$$

$$\alpha = \frac{m_0-m}{m_0-m_f} \tag{8}$$

Taking natural logarithms on both sides of eq. (7) yields:

$$\ln\left(\frac{1}{1-\alpha}\frac{d\alpha}{d\tau}\right) = \ln\frac{A}{\beta} - \frac{E}{RT_b} \tag{9}$$

The values of pre-exponential factor, A/β, and activation energy, E, which are summarized in table 2, were obtained from the intercept and the slope of the straight line given by a plot of $\ln\left(\frac{1}{1-\alpha}\frac{d\alpha}{d\tau}\right)$ versus $\frac{1}{T_b}$. Table 2 contains also the values of the mean heating rate, β, as well as the ranges of conversion, α, wherein these mean values were estimated. As can be seen, the activation energy decreases with heat flux increasing, according to other researches [21,27].

Figure 4 compares the experimental results with the differential conversion curves predicted based on the kinetic parameters. A good agreement between experimental and simulated data was obtained (root mean square errors less than 0.01 min^{-1}).

Conclusions

Fixed bed pyrolysis of sorghum stalk and leaves was studied in a bench scale set-up. Carbon dioxide was employed as a carrier agent in the pyrolysis process. A char, a pyrolytic oil and a gaseous fraction were produced.

Experimental results referring to the yield of pyrolysis products were statistically analized by 2^3 factorial programming. Power density, carbon dioxide superficial velocity and sorghum waste particle volume were selected as process factors, whereas mean bed temperature, specific masses of sorghum waste and pyrolytic oil were considered as process responses. Correlations between dimensionless factors and final values of process responses were established. Higher level of power density led to lower char yield as well as higher oil yield and bed temperature, while higher char yield and bed temperature as well as lower oil yield were obtained for coarse particle size.

It was experimentally found that the pyrolysis develops intensely in a main stage. A one-stage global reaction kinetic model, whose parameters were estimated based on experimental data, was selected to simulate the process dynamics.

Under conditions studied, power density and particle volume had a significant effect on the pyrolysis dynamics and final values of process responses. Statistical and kinetic models predicted well the real conditions and could facilitate the design, scale-up and operation of fixed bed pyrolysis reactors.

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Nomenclature

A/β - pre-exponential factor, 1/min
E - activation energy, kJ/mol
m - sorghum waste mass, g
m_{oil} - pyrolytic oil mass, g
P - power density, W/cm^3
R - gas universal constant, R=8.314 J/mol K
t - temperature, °C
T - absolute temperature, K
V - mean volume of sorghum waste particle, cm^3
w - carbon dioxide superficial velocity, cm/min
x_i - process dimensionless factor, i=1…3
y_j - process final response, j=1…3

Greek letters

α - volatiles conversion
β - heating rate, $\beta = dT_b/d\tau$, K/min
τ - time, min

Subscripts

b - bed
c - bed centre
f - final
w - column internal wall
0 - initial

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