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The Role of Pressure in the Heat of Pyrolysis of a Lignocellulosic Biomass

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The present study investigates the influence of the operative conditions on the heat of pyrolysis of four energy crops. Focus is mainly on the role of system pressure in defining heat of pyrolysis and the residual char yield. An experimental investigation has been carried out to measure these parameters by the integrated use of thermogravimetric analysis and differential scanning calorimetry. The results evidence that an increase in the operating pressure reduces the heat requirements of the pyrolysis process and the thermal effect of pyrolysis reactions may shift from endothermic to exothermic.

These findings can be interpreted considering that the experimental conditions limiting mass transfer provide a higher residence time of the volatiles products from primary thermal degradation reactions. These primary volatiles react with the pyrolysis products, resulting in exothermic reactions with the formation of secondary char. The heterogeneous secondary reactions lead to carbon enrichment of the final residue and reduce the overall thermal effect of the conversion. Moreover, the heat of reaction as a function of pressure was shown to fit a Langmuir adsorption curve. The results suggest that the role of exothermic secondary reactions and the inhibition of the evaporation of high molecular weight compounds formed in the primary pyrolysis process may be among the main factors affecting the heat demand of the overall pyrolysis process.

1. Introduction

Energy crises and environmental problems have led to an increasing focus on renewable energy sources, alternative to traditional fossil fuels. Biomass has been recognised as a promising feedstock for producing liquid biofuels in the future. Pyrolysis conversion processes are an important technological option for biofuels or bio-based intermediates production (Bridgwater, 2003). Pyrolysis is also a first step in gasification and in other thermochemical conversion processes for the exploitation of energy from biomass (McKendry, 2002). Thus, the investigation of the influence of operating conditions on the outcomes of the thermal conversion of biomass feedstock in pyrolysis processes is an important element to enhance the design and the optimization of new biomass to energy processes.

High pressure reactors for biomass conversion may have several potential advantages, as higher yields of valuable products, higher throughput, lower compression costs of product gases, increased reaction rates. However, the design of high pressure gasification and pyrolysis processes needs to gather detailed data on the effects of operating pressure on the product yields and on the thermal effects during biomass conversion.

Limited experimental data are available on the influence of pressure on the thermal effects of the pyrolysis process. Mok and Antal (1983) report that during the pyrolysis of cellulose the increase of the operating pressure reduces the required heat of reaction, increases the yield of char and of CO_2, and reduces the yields of CO and of all hydrocarbons formed in the process.

The present study is focused on the influence of pressure on the heat of pyrolysis of four lignocellulosic biomass. Experimental runs were carried out using a high-pressure differential scanning calorimetry (DSC).

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2. Experimental

2.1 Materials

Four biomass samples were analyzed: corn stalks, poplar, switchgrass “Alamo” and switchgrass “Trailblazer”. The biomass feedstock was provided by the Department of Agro-Environmental Science and Technology of the University of Bologna (Italy). The material was farmed and harvested in Ozzano and Cadriano (Bologna, Italy), dried overnight (15 h at 105°C) and ground up to a particle size lower than 1mm. Table 1 reports the proximate analysis of the biomass samples on dry basis.

Samples for TG and DSC runs were obtained pressing and punching the biomass particles to compact discs (about 5mm diameter and 0.4 to 0.7 mm height depending on the desired sample weight) that fitted the crucibles used in DSC analysis. Typical sample weights of about 8 mg in aluminum crucibles (d=5.1mm) were used. The crucibles were used without lid to maximize mass transfer and ease the separation of volatiles from the solid substrate.

Table 1: Proximate analysis on dry basis of the biomass samples

Biomass	Volatile matter wt%	Fixed carbon wt%	Ash wt%
Corn stalks	77.7	16.0	6.3
Poplar	81.8	14.8	3.4
Switchgrass “Alamo”	79.3	12.1	6.7
Switchgrass “Trailblazer”	64.1	8.6	27.3

2.2 Experimental techniques and procedures

The thermal degradation of the four biomass were analysed by the integrated use of thermogravimetric analyser and differential scanning calorimeter.

The thermogravimetric analysis (TG) at atmospheric pressure were obtained using a TA Instruments-Waters (USA) TGA-Q500 device. Samples used in TG runs were previously dried at 105 °C under a nitrogen flux of 60 mL/min for 10 min. Constant heating rate runs were carried out on the dry samples using a pure nitrogen purge gas flow rate of 60 mL/min, a heating rate of 10 °C/min and a final temperature of 950 °C. The purge gas was then switched to air (60 mL/min for 10 min) in order to allow detecting the ash content of the sample (Gomez-Mares et al., 2012).

Differential Scanning Calorimetry (DSC) data were obtained using a DSC-Q2000 for atmospheric runs and a DSC Q20P for runs under pressure. Both DSC devices were supplied by TA Instruments (USA). Calibration procedure, as described in the literature (Mok and Antal,1983), were performed to calculate the slope and offset values needed to calculate the baseline and the zero of the heat flow signal. Heat flow and temperature calibration were obtained by constant heating rate runs carried out on known standards (indium and lead) for both DSC. An additional set of calibration was performed only on DSC Q20P in order to calibrate the pressure, comparing pressure values from the instrument with those from an external pressure gauge.

In the DSC-Q2000 atmospheric tests, the sample cell was conditioned by a constant nitrogen purge flow (50 mL/min) at atmospheric pressure. In the DSC-Q20P device a specific gas circuit was built to allow DSC runs under pressure in the presence of a constant purge gas flow. A control loop was realized to pressurize the test cell up to the selected operating pressure and to keep a constant pressure and a constant purge gas flow during the test (Basile et al., 2014). An EL-PRESS P-702CV pressure controller and an EL-FLOW F-201CV mass flow controller, both by Bronkhorst (The Netherlands) were used for pressure and gas flow control. In all experimental runs, the inlet nitrogen flow rate was fixed to 0.050 NL/min, corresponding to an outlet flow rate of 50 mL/min, in order to obtain a constant heat capacity of the gas flow during experimental runs. Runs were carried out at the following operating pressures: 0.1, 0.5, 1, 2, and 4 MPa. Gas residence time in the DSC is affected by temperature and pressure, but was always comprised between about 0.1 and 0.9s, well below the time scale of DSC measurements.

Samples used in DSC runs were previously dried at 105 °C under a nitrogen flux of 60 mL/min for 10 min. All DSC runs were started at 105 °C. A constant heating rate of 10 °C/min, was used up to the final temperature, set at 550 °C. At the end of each run, the furnace was cooled down to 30 °C under nitrogen purge gas flow and a second run was performed on the char sample using the same temperature-time program. At the end of the DSC runs the char residue was weighed, and the yields in char and volatile products were estimated. The set-up of the DSC devices used for experimental runs do not allow the separate determination of the yields in gaseous and liquid products among volatile species (Barontini et al, 2013). It should also be remarked that the heating rates allowable in TG and DSC devices, used in the present study, only allow the reproduction of slow pyrolysis conditions.

3. Results and discussions

The influence of pressure on the thermal effects of the pyrolysis process was analyzed, carrying out experimental runs at 0.5, 1, 2 and 4 MPa. Actually the experimental curves obtained in a DSC analysis result from several contributes, some depending on the thermal behavior of the sample (heat capacity of the sample, latent heat of evaporation of volatile components, heat of primary pyrolysis, heat of secondary reactions) and some due to the experimental setup - asymmetric radiative heat exchange between the sample and the DSC cell due to the change in the surface emissivity of the biomass (Wolfinger et al., 2001). In order to obtain quantitative data for the heat of pyrolysis from the raw DSC curves, the approach of Rath et al. (2002) was used to separate the contribution of the pyrolysis reaction process from other thermal effects recorded by the DSC device.

Figure 1 compares the curves obtained for the reaction heat (Q_r) at different operating pressures. As evident from the figure, pressure has a strong influence on the thermal effects of the pyrolysis process for all the four biomass samples considered.

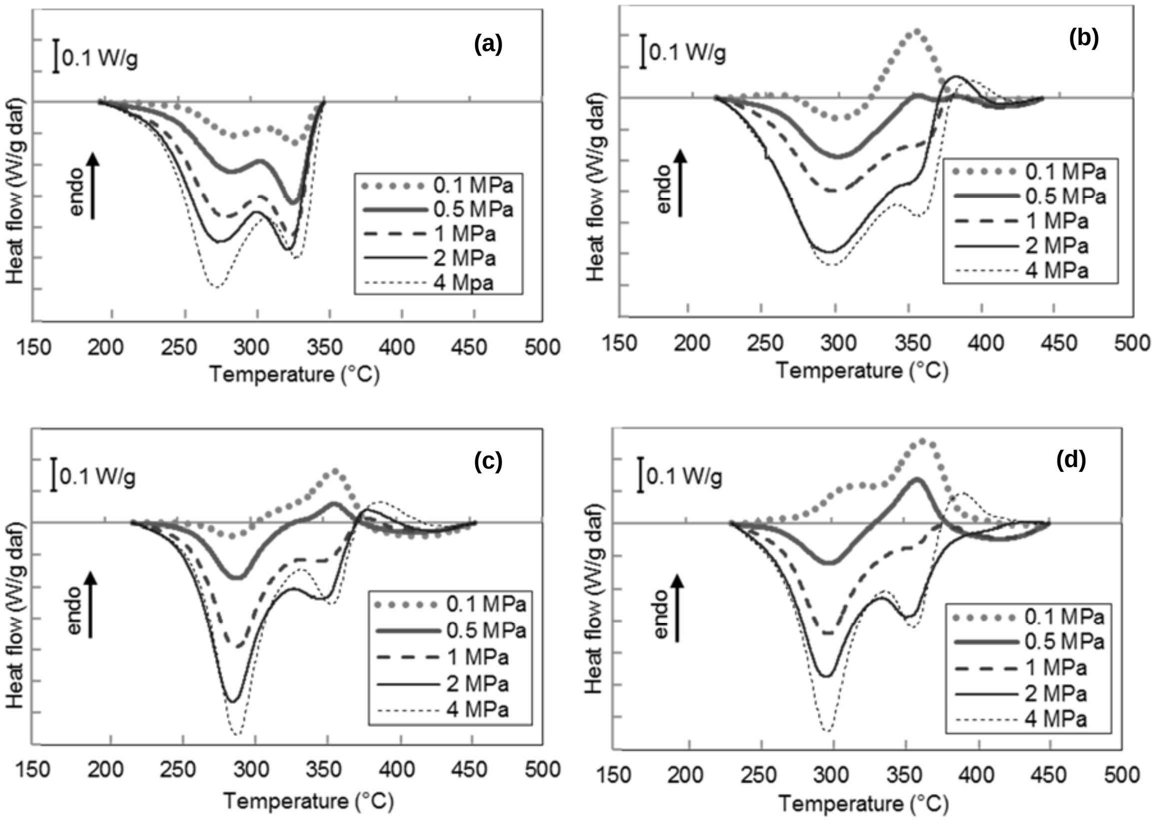

Figure 1: Heat flow at different pressure for corn stalks (a), poplar (b), switchgrass Alamo (c) and switchgrass Trailblazer (d). Conditions: Pure nitrogen, 10°C/min, crucibles without lids.

Increasing the pressure a clear decrease in the heat demand of the pyrolysis process can be observed for all the materials. In the case of switchgrass Trailblazer, the change is so significant that a shift from an overall endothermic to an overall exothermic process takes place. As shown in Table 2, when increasing the pressure from 0.1 MPa to 4 MPa, the total heat of pyrolysis shifts from -50 J/g to -272 J/g for corn stalks, from 29 J/g to -283 J/g for poplar, from 37 J/g to -199 J/g for switchgrass Alamo, and from 92 J/g to -210 J/g for switchgrass trailblazer (negative values are used for exothermic processes).

Table 2: Heat of pyrolysis for the four biomass samples at different operating pressures. Initial sample weight of about 8 mg. Negative values of the heat correspond to an exothermic behaviour.

Biomass	Pressure (bar)	Char yield (% daf)	Heat of pyrolysis (J/g daf)
Corn stalks	40	28.4	-272
Corn stalks	20	28.5	-229
Corn stalks	10	27.5	-171
Corn stalks	5	26.3	-118
Corn stalks	1	23.8	-50
Poplar	40	30.7	-283
Poplar	20	28.2	-272
Poplar	10	26.0	-191
Poplar	5	22.1	-71
Poplar	1	17.3	29
Switchgrass “Alamo”	40	27.3	-199
Switchgrass “Alamo”	20	26.4	-203
Switchgrass “Alamo”	10	23.2	-134
Switchgrass “Alamo”	5	21.4	-40
Switchgrass “Alamo”	1	15.1	37
Switchgrass “Trailblazer”	40	28.5	-210
Switchgrass “Trailblazer”	20	29.2	-212
Switchgrass “Trailblazer”	10	26.3	-123
Switchgrass “Trailblazer”	5	21.8	-21
Switchgrass “Trailblazer”	1	19.1	92

As evident from the data in Table 3, the pressure has a strong influence also on the yields of char: when increasing the pressure from 0.1 MPa to 4 MPa, the char yield increases from 24 % to 28 % for corn stalks, from 17 % to 31 % for poplar, from 15 % to 27 % for switchgrass Alamo and from 19 % to 29 % for switchgrass trailblazer. These results confirm the findings of Mok and Antal (1983), that report that increasing the pressure from 0.1 to 2.5 MPa causes the pyrolysis process of cellulose to shift from endothermic (heat requirement of about 230 J/g) to exothermic (heat generation of about -130 J/g), with char yield increasing from 12 to 22 %.

The influence of pressure on the heat requirement of the pyrolysis process can be explained by the inhibition of the evaporation processes of high molecular weight products formed in the primary pyrolysis process, and, as a consequence, by the promotion of exothermic secondary reactions of the primary pyrolysis products. As reported by the comprehensive studies of Ranzi et al. (2008), Di Blasi et al. (2002, 2008), and Ahuja et al. (1996). Exothermic secondary reactions of tar vapors, both homogeneous and heterogeneous, include processes such as cracking, partial oxidation, re-polymerization and condensation.

As evidenced by Antal (2003), higher pressures limit mass transfer, thus providing a higher residence time in the porous solid substrate of the volatile products from primary thermal degradation reactions. The highly reactive tarry vapors at high pressure have lower specific volumes. Consequently, their intra-particle residence time is prolonged. Thus, the partial pressure of the tarry vapor is higher, increasing the rate of the secondary exothermic decomposition reactions.

In Figure 2 the values calculated for the total heat of pyrolysis were plotted as a function of the operating pressure. Although a number of factors may justify the results obtained, it is interesting to notice that such behaviour may be in accordance with a Langmuir adsorption model of the volatiles, suggesting that adsorption equilibria may play a role in the immobilization of the volatile compounds responsible of the secondary reactions. Assuming for the sake of simplicity that volatiles generated in the primary pyrolysis process may be considered as a single pseudocomponent, a phenomenological description of the immobilization of the volatiles in the solid can be most simply obtained by a Langmuir adsorption model. The Langmuir isotherm relates the adsorption of molecules on a solid surface to the pressure of the absorbed gas at a fixed temperature:

$$\vartheta_v = \frac{\alpha p_v}{1 + \alpha p_v} \tag{1}$$

where θ_v is the fraction of volatile products adsorbed on the surface of the solid, p_v is the partial pressure of the adsorbate (the volatile pseudocomponent) in the gas phase and α is the Langmuir adsorption constant.

Several literature (Rath et al. 2002, Gomez et al. 2009, Haseli et al. 2011) results allow assuming that the measured heat of reaction can be considered as the sum of two contribution, one due to the heat required for the primary degradation of the biomass (endothermic) and a second due to the secondary (exothermic) decomposition of volatiles. If volatile decomposition is assumed to be dependent on the fraction of volatile matter in the solid, the total heat of reaction can be expressed as:

$$H_P = H_1 + H_2 \frac{\alpha y_v P}{1 + \alpha y_v P} \tag{2}$$

where H_1 is the heat due to the primary degradation of biomass and H_2 is the heat due to the volatile decomposition, both assumed as independent on pressure; the fraction term multiplied by H_2 represents the dynamic adsorption-desorption equilibrium between the vapor-phase and the surface of the solid, and y_v is the molar fraction of the volatile pseudocomponent, and P is the total pressure of the system. The values of H_1, H_2 and the product αy_v are averaged values for the overall degradation, which were calculated by experimental data fitting. The best-fit parameters calculated from experimental runs are reported in Table 3, and in Figure 2 are reported the heat of pyrolysis obtained applying Eq(2) using the best-fit parameters of Table 3.

Table 3: Best-fit parameters for Eq. (2) calculated from experimental runs

Biomass	H_1 *(J/g daf)*	H_2 *(J/g daf)*	αy_i *(-)*
Corn stalks	-23	-338	0.777
Poplar	68	-442	0.976
Switchgrass “Alamo”	89	-352	1.70
Switchgrass “Trailblazer”	147	-482	1.27

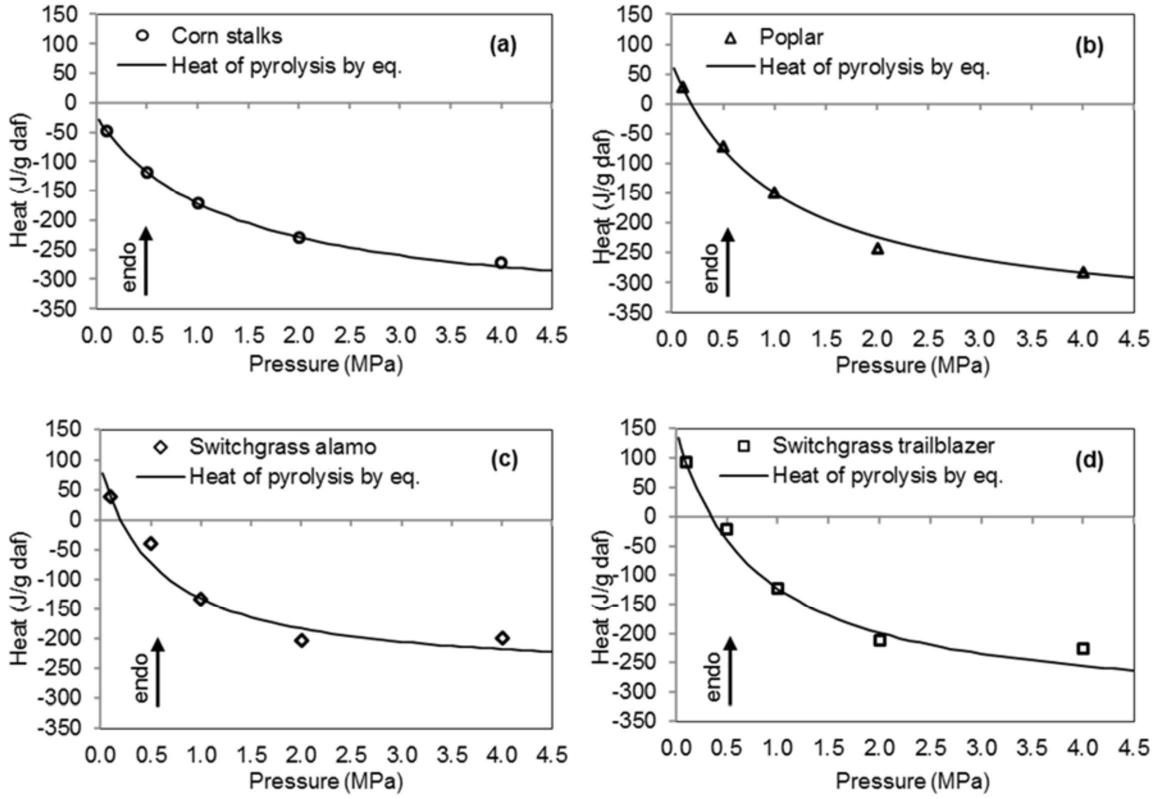

Figure 2: Heat of pyrolysis as a function of pressure for corn stalks (a), poplar (b), switchgrass Alamo (c) and switchgrass Trailblazer (d). Conditions: Pure nitrogen, 10 °C/min, crucibles without lids. Heat of pyrolysis curves by equation (3) using the best-fit parameters reported in Table 3.

The figure shows that Eq(2) provides a reasonable fitting of the trend recorded for the heat of pyrolysis with respect to operating pressure. Clearly enough, the simplified model presented here supports only a phenomenological interpretation of the effect of pressure on the material degradation, and is not introduced to provide a detailed description of the complex mechanism underlying secondary char formation. Nevertheless, the important role of secondary gas-solid interactions on the overall heat demand of the pyrolysis process seems to be confirmed by the above findings. The total heat of reaction changes with the pressure as described by the adsorption model. This supports the hypothesis that total heat of pyrolysis is influenced by the secondary reactions occurring between the volatiles adsorbed and the primary char.

4. Conclusions

The thermal effects of the pyrolysis process were investigated for four energy crops. The results evidence that an increase in the operating pressure increases the char yields and reduces the heat requirements of the pyrolysis process, shifting from endothermic to exothermic. These results confirm the presence of a competitive mechanism between the endothermic reactions of the primary decomposition, leading to volatile formation and the exothermic vapor-solid interactions, leading to secondary char formation.

The heat of reaction as a function of pressure was shown to fit a Langmuir adsorption curve. The results suggest that the role of exothermic secondary reactions and the inhibition of the evaporation of high molecular weight compounds formed in the primary pyrolysis process may be among the main factors affecting the heat demand of the overall pyrolysis process.

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