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Analysis and modelling of wood pyrolysis

Enrico Grieco*, Giancarlo Baldi

Dept. Material Science and Chemical Engineering, Politecnico of Torino, C.so Duca degli Abruzzi 24, 12129 Torino, Italy

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ABSTRACT

In many industrial processes wood is treated as big fragments or pellets. In such conditions kinetics and yields are different with respect to the case of particles with few mg weight. However most of published kinetic models were based on experimental data obtained with very small samples. In this work pyrolysis of wood pellets was investigated by using a special experimental device which allowed to determine kinetics of total weight loss, gas and tar production. Two different heating rates, 0.05 and 1 K/s, were employed to determine kinetic parameters. Dynamic and isothermal pyrolysis tests were carried out on beech and pine wood previously dried in an oven. A simple but realistic kinetic scheme was proposed able to take into account the phenomena that happen in big wood particles. The numerical parameters were determined from the results of experimentation on beech wood. The proposed kinetic model takes into account the presence of two different stages during pyrolysis: a first one involving only unreacted wood and a second one where the products not yet escaped from the solid matrix react further. This kinetic model allowed to fit the experimental data quite well. The model was successfully validated with tests performed at an elevated heating rate (approximately 60–100 K/s) of the external surface of the pellets. In these conditions, the pellets showed a marked gradient of temperature inside, which was suitably considered.

1. Introduction

Wood is considered as one of the most important renewable energy sources. Feedstock arise both from specific crops, from forest wastes or from separate collection of woodsy Municipal Solid Waste (MSW) (Orfao et al., 1999). Direct energy recovery from wood – either electrical or thermal energy – is obtained by combustion, but other thermal processes like pyrolysis or gasification allow to convert woodsy biomasses in more valuable gaseous or liquid combustibles (Janse et al., 2000).

Pyrolysis is the first stage in any thermal treatment of biomass (Rajeswara Rao and Sharma, 1998) and its kinetics and products have a crucial influence on gasification and incineration. It consists in a decomposition of the wood polymeric chains (cellulose, lignine, etc.); the products of this decomposition can be roughly subdivided into gas, tar and char. Gaseous products are mainly constituted by CO, H_2, CO_2, CH_4 and other light hydrocarbons (Fagbemi et al., 2001; Sharypov et al., 2002; Boroson et al., 1989; Williams and Besler, 1996). Tar is made by hydrocarbons of higher C content and other organic compounds which are volatile at the temperature of pyrolysis and condense at low temperature; generally tar is considered as constituted by compounds with a condensing temperature higher than benzene. Char is the solid residual after pyrolysis; it consists of carbonaceous solid compounds with a high C/H ratio.

Many kinetic models for wood pyrolysis have been reported in the literature; a good review is given by Di Blasi (2008). The simplest models were based on a single decomposition reaction, and they do not allow to predict the influence of pyrolysis conditions on the amount of products (Di Blasi, 1998). Other models assume some parallel reactions to predict the production kinetics of gas tar and char (Thurner and Mann, 1981; Chan et al., 1985; Font et al., 1990). More complex reaction schemes were also adopted, involving a further decomposition of tar in the gas phase (Liden et al., 1988; Di Blasi, 1993) or an intermediate product deriving from primary decomposition of biomass, giving rise to gas, tar char (Koufopanos et al., 1989; Shafizadeh and Bradbury, 1979; Bradbury et al., 1979; Park et al., 2010). Distributed activation energy model (DAEM) approach was also applied to biomass pyrolysis (Rostami et al., 2004; Wojtowicz et al., 2003).

Most of these models were developed on the basis of experimental results obtained by pyrolysis of few mg of biomass in powder, often with a very high increase of temperature.

Actually, the biomass is often treated in the form of pellets or fragment of a certain size. This implies that gradients of temperature exist in the biomass and that the temperature variation is generally slower inside (Babu and Chaurasia, 2004); furthermore, the products generated by decomposition of biomass polymers must diffuse into

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* Corresponding author. Tel.: +39 0115644644; fax: +39 0115644699.
E-mail address: enrico.grieco@polito.it (E. Grieco).

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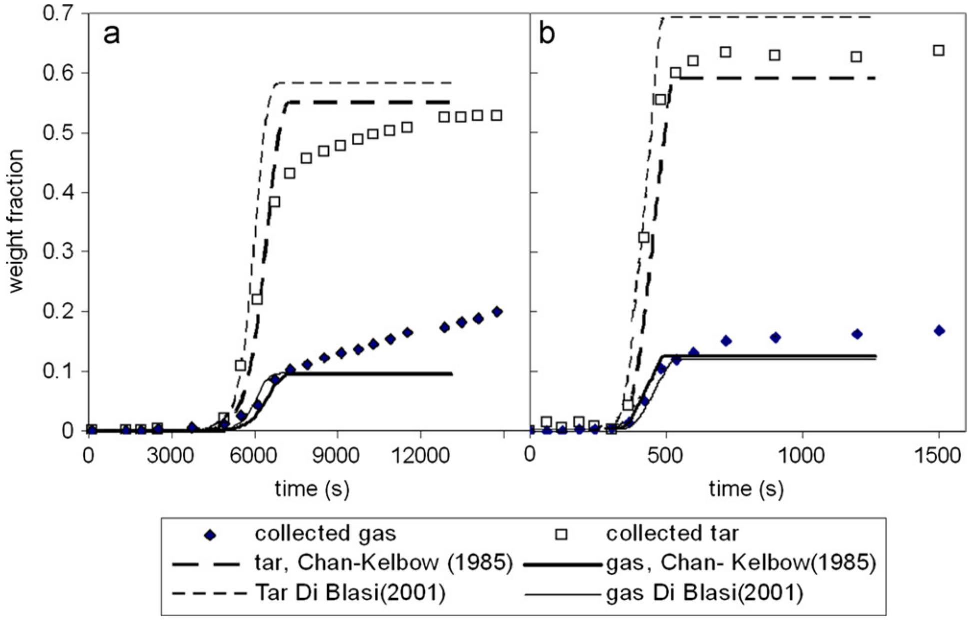


Fig. 1. Gas and tar production, comparison with the results of some well-known literature models; heating rate 0.05 K/s (a) and 1 K/s (b).

the mass of matter. Some literature results have in fact shown an influence of the sample size on the amount of tar and gas yields both for cellulose (Di Blasi and Branca, 2001) and wood (Chan et al., 1985).

However it is quite common to couple kinetic models developed from very small samples to energy, mass and sometimes momentum balances in order to simulate the behaviour of large particles, according to the hypothesis that secondary reactions can be considered negligible or take places only in gas phase (Helsen and Van der Bulck, 2001). Normally very low heating rates are neglected also in complex models for single large particle (Gronli and Melaaen, 2000) and much of the efforts were concentrated on fast heating rates (Di Blasi, 2002). On the other hand, it is well known that characteristic times of heat exchange have often the same order of magnitude of pyrolysis reaction times (Gronli and Melaaen, 2000). As a consequence of this, kinetic phenomena, especially those ones connected with secondary pyrolysis, are often hidden by heat transport effects.

For this reason in this work a kinetic model was developed by using experimental data obtained on large particles at very low heating rate. These tests allowed to highlight the importance of secondary pyrolysis within solid particles. Such reactions with higher heating rates become negligible or simply hidden in the global kinetic of product release.

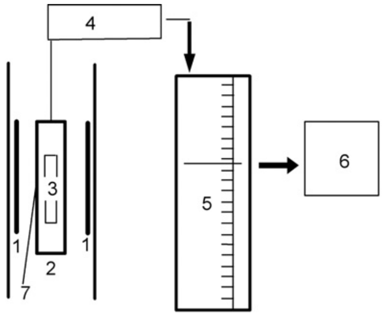
Fig. 1 shows some results of pyrolysis obtained with 12-mm pellets, compared with the results calculated with two kinetic models (Di Blasi and Branca, 2001; Chan et al., 1985): as can be seen, the agreement is initially good, but the models fail in the final part of pyrolysis in particular when temperature rise is very low.

Aim of this work is to analyze pyrolysis of wood in the form of pellet in different conditions of heating and to propose a model to interpret the phenomenon by taking into account the effect of the secondary reaction within solid, heat transfer in the solid was taken into account too.

2. Experimental

2.1. Pyrolysis apparatus and procedures

The experimental setup is schematically drawn in Fig. 2. The wood samples were placed in a stainless steel capsule, previously filled by N_2. The capsule was placed in an oven and heated up. The capsule is 22 mm i.d. and 120 mm length. Through the upper part of the capsule two thermocouples with 1 mm OD were introduced (T1 and T2): the first one was used to measure the temperature at the surface of the sample (T1) and the second one was placed in the centre of the sample (T2). The thermocouple T1 was connected to a temperature programmer in order to impose well-defined rising rates to the sample surface temperature. The heat transfer between biomass and thermocouples could be a critical aspect. In order to reduce this problem, thin thermocouples (1 mm O.D.) were used. The temperature profiles both in the centre and at the surface were highly reproducible, for this reason the errors related to the temperature measurements were considered acceptable. Different procedures were adopted for kinetic analysis and model validation.



1 electric heaters. 2 capsule. 3 sample. 4 tar condenser. 5 gas reservoir. 6 gas cromatograph. 7 thermocouple.

Fig. 2. Organization of the experimental apparatus.

2.1.1. Kinetic analysis

The empty oven can reach a maximum heating rate of 5 K/s but in order to obtain a precise control of temperature the maximum temperature rise velocity was limited to 1 K/s.

Each run consisted of two separate tests:

In the first one, the capsule was suspended to an electronic balance and the pyrolysis kinetics (decrease of mass sample with time) was measured; a simultaneous recording of the weight and