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Kinetic Modelling of Sawdust and Beech Wood Pyrolysis in Drop Tube Reactors Using Advanced Predictive Models

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Two detailed pyrolysis models are used to predict pyrolysis products of the conversion of two biomass fuels in a drop tube reactor. In both models, biomass is considered as a combination of the reference components cellulose, hemicellulose and lignin, but their mathematical modelling approaches are different. Two distinct methods are used to estimate the composition of the biomass fuels based on their ultimate and proximate analysis. A heat balance is applied to the particle, considering convective and radiative heat transfer along with drying effects. A tar cracking model was used in a post-processing step. The results obtained using different combinations of pyrolysis models and methods to estimate the composition were compared to experimental results. All combinations used under-estimated the total volatile yield, and the tar cracking model is necessary to capture the final yields of gas and tar. Finally, the predicted pyrolysis products very sensitive to the composition of the biomass.

1. Introduction

Experimental studies of biomass pyrolysis have been mainly restricted to the kinetic controlled regimes to minimize the effect of transport processes. To achieve these conditions, thermogravimetry analysis (TGA) is used, but heating rates and final temperatures are limited in such technique, falling considerably outside the typical conditions of practical applications (Di Blasi 2008; Oyedun 2012). Studies undertaken in drop tubes are also reported in the literature, but temperatures were typically low (Babu 2008). A few studies on pyrolysis have been emerging at high heating rates and high temperatures using a drop tube reactor (Septien et al. 2012; Sun et al. 2010). Giving the complexity of the conversion process, it is difficult to characterize it based solely on the experimental data; therefore state of the art network based models can give a better understanding the conversion process. Pyrolysis prediction capabilities are of direct use for computational fluid dynamics (CFD) modelers, and biomass combustion and gasification plant designers.
A number of phenomenological network models have been developed to describe the complex process of coal pyrolysis that were extended for biomass pyrolysis. The most widely used are the Chemical Percolation Devolatilization (CPD) model (Grant et al. 1989), the Functional-Group, Depolymerization, Vaporization, Cross-linking (FG-DVC) model (Solomon et al. 1988), and the FLASHCHAIN (Niksa and Kerstein 1991). All of them include network modelling, coal structure characterization, depolymerization reactions, cross-linking reactions, and non-condensable gas, tar, and char formation. Adding to this family of network models, a purely mechanistic model was developed by Sommariva et al. (2010), referred here as PoliMi. In this model, the devolatilization of the actual coal is obtained as a linear combination of the thermal degradation of the reference coals and no structural parameters are required directly as input, but are indirectly considered through the differences in the reference coals. These models were extended and adapted to biomass pyrolysis, specifically, the Bio-CPD (Fletcher et al. 2012), the FG-Bio (Chen et al. 1998), the Bio-FLASHCHAIN (Bio-FC) (Niksa 2000), and the Bio-PoliMi (Ranzi et al. 2008). The most notable adaptation consists in the description of the biomass as being a mixture of three reference components, cellulose, hemicellulose, and lignin. It is assumed that no interactions occur during the

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conversion of the biomass; therefore the final products are a weighted sum of the individual reference component products. In this work, both the Bio-CPD model and the Bio-PoliMi model are used.
The Bio-CPD model inherited the phenomenological network characteristics from its parent coal model and extension to biomass consisted in the adaptation of structural parameters and kinetic parameters of each reference component (Fletcher et al. 2012; Lewis and Fletcher 2013). The evolution of rates and yields of gases, tar and chars is governed by the conversion of the chemical bridges that connect structural units. Percolation lattice statistics are used to predict the population of bridges broken and detached clusters. The Bio-PoliMi model has a mechanist approach based on conventional multistep devolatilization models of the three reference components of biomass and predicts the yields and lumped composition of gas, tar and solid residue.
The pyrolysis of two biomass fuels – sawdust and beech wood - in a drop tube reactor is studied here using the advanced models Bio-CPD and Bio-PoliMi. The objectives of this work are (1) to evaluate the predictions of the advanced pyrolysis models comparing them to experimental results, and (2) to assess the sensitivity of the pyrolysis predictions to the composition of the biomass.

2. Numerical approach

The pyrolysis kinetic preprocessor (PKP), originally developed for coal studies (Vascellari et al. 2013), is used here. The code has been developed to calibrate simple empirical models using results either from experiments or advanced models such as CPD, FLASHCHAIN or FG-DVC. In this work, the model library was extended to include both the Bio-CPD model and the Bio-PoliMi model.
Eq. (1) describes the heat balance for the spherical, thermally thin biomass particles in an inert laminar flow. Both the convective and radiative heat transfer are considered along with the effect of drying. The global heat of reaction during devolatilization is neglected. The convection term is correct for high rates of mass transfer with a blowing parameter θ described in Eqs. (2) and (3) (Fletcher 1989).

$$m_p c_p \frac{dT_p}{dt} = hA_p \left(T_g - T_p\right) \theta + \sigma \epsilon_p A_p \left(T_g^4 - T_p^4\right) + h_{dry} \frac{dm_{moist}}{dt} \tag{1}$$

$$\theta = B/(e^B - 1) \tag{2}$$

$$B = c_{p,g} \frac{dm_p}{dt} / 2\pi d_p k_g \tag{3}$$

Following the work of Lewis and Fletcher (2013), Vizzini's first-order tar cracking model was used in a post-processing step (Vizzini et al. 2008). The model can be applied to any biomass as it follows the same premise of biomass composition defined by a combination of reference composition. The model was applied to the primary pyrolysis yields of cellulose, hemicellulose and lignin of the Bio-CPD predictions.
Both the Bio-CPD model and Bio-PoliMi model require the knowledge of the reference components composition of the biomass of interest. However, this information is not always available. Typically, biomass fuels are characterized in terms of proximate and ultimate analysis as it has been done for coal, although specific standards were developed for biomass. Since the pyrolysis methods require the knowledge of the reference components, a few strategies were developed to retrieve the composition of cellulose, hemicellulose, and lignin from the data obtained with the proximate and ultimate analysis. Sheng and Azevedo (2002) developed a correlation based on literature data to express the mass fraction of the reference component as a function of the oxygen to carbon ratio, the hydrogen to carbon ratio and the volatile matter. The hemicellulose content is calculated by difference. This method referred here as the correlation method. Cuoci et al. (2007) considered five different reference components: cellulose, hemicellulose, lignin-H, lignin-C, and lignin-O specifically for the Bio-PoliMi model. The representation of lignin as a combination of three different components is justified by the complexity of its composition. The suffixes -H, -C, and -O denote a lignin rich in hydrogen, carbon and oxygen, respectively. Three reference biomass fuels, with specific oxygen to carbon ratio and hydrogen to carbon ratio, are defined as a linear combination of the five former components, defining a triangle. In this way, any biomass contained in the range of hydrogen and carbon enclosed by the triangle vertices can be described as a linear combination of the reference biomass fuels. This method is referred here as the triangulation method.

3. Experimental data

Two experimental studies with fast pyrolysis were selected to compare their results with model predictions (Septien et al. 2012; Sun et al. 2010). In both cases, the tests were conducted in a drop tube reactor using nitrogen as the carrier gas. The biomass fuels are fed from the top of the reactor. The reactor walls are heated by an external electrical heater. In both studies, solid samples were collected at the outlet of the reactor and characterized. The ash tracer method was used to determine the char yield. Sun et al. (2010) measured the concentrations of the following gases: CO, CO_2, H_2, CH_4 and C_2H_4, while Septien et al. (2012) additionally measured H_2O, C_2H_2, C_2H_6, C_3H_8 and C_6H_6. Sun et al. (2010) collected tar and water through condensation in an ice-cooled condenser. The tar and water were not measured separately and the total weight was taken as the yield of liquid. Septien et al. (2012) defined tar as all the organic compounds with a molecular weight higher than C_6H_6 excluding soot and char. The tar yield was estimated through a mass balance considering the char and gas yields.
Table 1 shows the proximate and ultimate analysis of the studied biomass fuels as well the fractions of hemicellulose, cellulose and lignin, respectively, based on the two different methods. Table 2 shows the respective operating conditions considered in this study. The gas temperature is considered to be equal to the wall temperature and constant along the reactor axis for calculation purposes.

Table 1: Biomass composition

Biomass	Sawdust (Sun et al. 2010)	Beech wood (Septien et al. 2012)
Ultimate analysis (%wt daf)		
Carbon	43.02	49.2
Hydrogen	5.42	6.0
Oxygen	51.19	44.1
Nitrogen	0.17	0.5
Sulphur	0.02	0.02
Proximate analysis	*(% ar)*	*(% db)*
Volatile matter	75.46	85.3
Fixed carbon	13.8	14.3
Moisture	9.2	0
Ash	1.54	0.4
Correlation method		
Cellulose	41.7	40.9
Hemicellulose	34.1	34.3
Lignin	24.2	24.8
Triangulation method		
Cellulose	34.6	41.5
Hemicellulose	23.1	27.6
Lignin	42.3	30.9

Table 2: Operating conditions for the drop tube experiments

Particle size [µm]	Temperature [K]	Residence time [s]
Sawdust (Sun et al. 2010)		
400	973	2.5
	1,073	
	1,173	
	1,273	
Beech wood (Septien et al. 2012)		
350	1,073	3.8
	1,273	
	1,473	
	1,673	

4. Results

4.1 Pyrolysis product yields

Figure 1 shows the total volatile yield over time for the sawdust at 1,073 K and 1,273 K. All combinations of models and methods to estimate the composition under-predict the total amount of final volatile yields and the operating temperature marginally affects the final predicted yields. The operating temperature influences how early pyrolysis starts due to the corresponding heating rates. At the early stages of the predicted devolatilization the difference between the combinations of models and methods are noticeable. The Bio-CPD predictions present a change in slope corresponding to the release of hemicellulose. Such behavior is typically seen in TGA experiments (Di Blasi 2008). The Bio-PoliMi predictions present a smoother curve. When using different estimation methods in the Bio-CPD model, the change of the slope occurs at different volatile yields due to the different amounts of estimated hemicellulose (see Table 1). Nonetheless, the final yield is not affected by the different estimated composition, neither it is by the temperature. The Bio-PoliMi predictions are affect by temperature, as observed by a higher final total volatile yield for 1273 K.

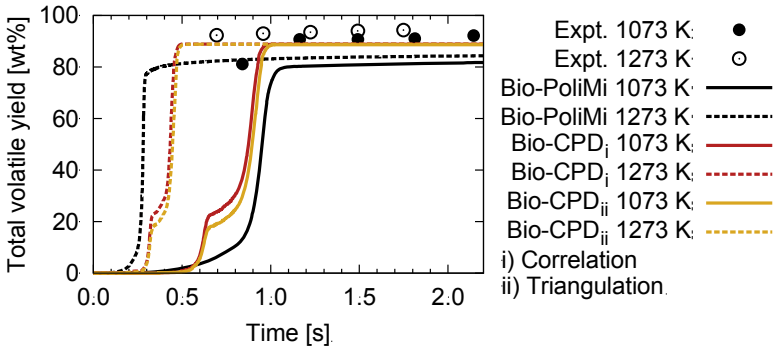

Figure 1: Total volatile yield of sawdust at 1073 and 1273 K

Figure 2 shows the pyrolysis main products obtained using several pyrolysis models and the different methods to estimate the reference components. All combinations of model and methods overestimate the char yield, as seen in Figures 2(a) and 2(d). The predictions using the Bio-PoliMi model reproduce the same decrease of char yield with temperature trend as in the experiments, although it produces the highest char yield of all combinations. On the other hand, the Bio-CPD model produces the same yields regardless of the temperature. Figures 2(b), 2(c), 2(e), and 2(f) show clearly that within the operating conditions typical of drop tube experiments it is necessary to consider tar cracking. The use of the Vizzini's tar cracking model improved slightly the gas and tar predictions of Bio-CPD, with improvements more noticeable at higher temperatures. It is interesting to note that the Bio-PoliMi and Bio-CPD predictions with Vizzini's tar-cracking model are similar, even though no secondary reactions were considered in the later. It is expect that the inclusion of secondary reactions in the Bio-PoliMi model may lead to the improvement of its predictions.

4.2 Influence of composition on the pyrolysis prediction

Figure 3 shows the sensitivity analysis of the pyrolysis yields to the biomass composition. To evaluate the influence of the composition of the biomass on the pyrolysis predictions, a sensitivity analysis was performed considering the full spectra of possible compositions. A total of 68 predictions were performed covering any possible combination of the cellulose-hemicellulose-lignin ternary system considering a step of 10%. Figure 3(a) shows the total volatile yield obtained in the reference components ternary system for the test case using sawdust at 973 K. The same runs were performed for the beech wood case at 1,673 K, but no significant differences in terms of yield variations were observed. Figure 3(a) shows that for the heating conditions and final temperature, when varying the whole spectra of possible combinations of cellulose-hemicellulose-lignin, a modest variation of 20% of total volatile yield is obtained. Figure 3(a) also shows the composition of sawdust calculated using the correlation method represented by the black dot, surround by three polygons. The vertices of the polygons correspond to a variation of 5%, 10% and 20% of each component in the ternary system. For a variation of 20% in the composition of the biomass the total volatile yield does not vary more than 10%. Figure 3(b) shows the sensitivity of product yields predictions to the biomass composition for the same case as Figure 3(a) with a 20% variation in composition. In the

horizontal axis, the plus symbol represent 20% more of a component and the minus symbol represent 20% less, *e.g.*, C + HL- has 20% more cellulose and 20% less lignin than the composition in Table 1. As expected the char yields did not vary significantly (less than 10%). Tar and gas yields on the other hand varied significantly. Varying hemicellulose and lignin, while keeping cellulose constant (CH + L- and CH - L+), did not produce significant changes, evidencing that both hemicellulose and lignin have the same effect on the production of tar and light gas. When keeping the hemicellulose and the lignin constant it is possible to observe that cellulose governs the production of gas, whereas hemicellulose and lignin govern the production of char and tar.

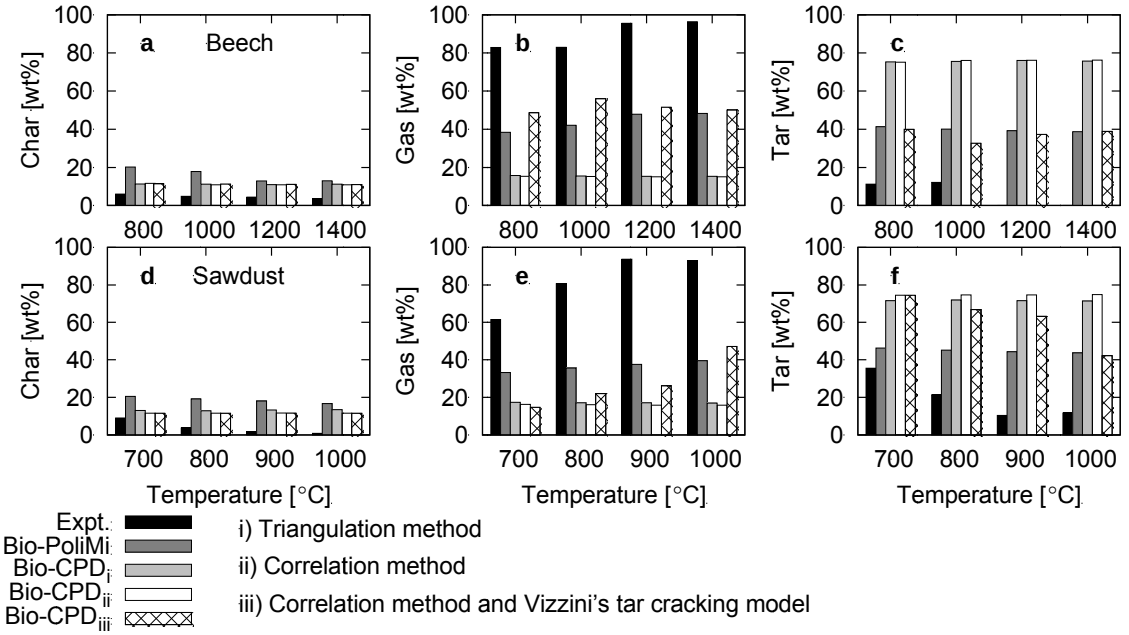

Figure 2: Products of pyrolysis (char, gas, tar) when using different models and methods to calculate reference components at different operating temperatures

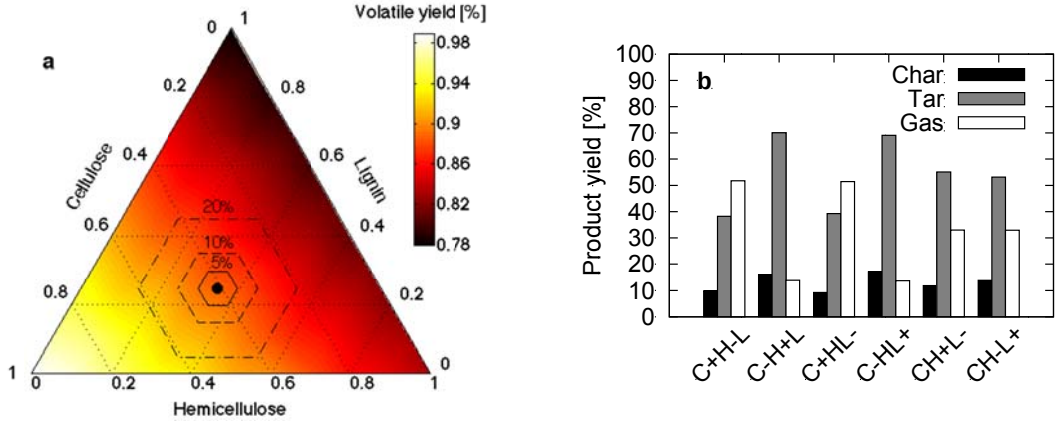

Figure 3 Sensitivity analysis of the pyrolysis yield to the biomass composition. a) Total volatile yield versus composition; b) Product yield versus composition

5. Conclusions

The pyrolysis of two different biomass fuels in a drop tube reactor was studied numerically using two advanced pyrolysis models. A tar cracking model was included in a post-process step. The composition of the biomass fuels was estimated using two different methods. Results of different combinations of pyrolysis models and method for estimating the composition were compared with experimental results from drop tube reactors. Both the network-based model Bio-CPD and the mechanistic model Bio-PoliMi under-estimated the total volatile yield, although the latter captures the trend of increasing yield with

increasing temperature observed in experiments. Using different methods to estimate the fractions of hemicellulose, lignin and cellulose of the biomass did not produce a significant difference in the investigated cases when using the Bio-CPD model. A sensitivity analysis showed that the total volatile yield predictions using the Bio-CPD did not vary significantly within the whole spectra of the composition. However, gas and tar predictions are sensitive to the estimated composition as cellulose governs the production of light gas, whereas hemicellulose and lignin govern the production of char and tar.

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