

Development of a Variable Energy model for Biomass devolatilization

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Devolatilization is a crucial step in all thermochemical processes (pyrolysis, gasification and co-combustion) for conversion of biomass into energy, fuels and/or chemicals. A thermogravimetric (TG) balance is used in this work to characterise different types of biomass, including residues (rice husks, olive cake, cacao shells), woods (poplar, beech, pellets), and grasses (mischantus) to achieve a fundamental insight into devolatilization kinetics. The effect of the heating rate is evaluated in the range 10-80 K/min providing significant parameters for the fingerprinting of the fuels. Kinetic parameters are obtained by applying traditional isoconversional methods. The activation energy as a function of the conversion reveals the multi-step nature of the biomass devolatilization. Although average values allow the comparison of the reactivity of different fuels, a first order reaction model can hardly predict the biomass devolatilization over the whole range of conversion, suggesting the need for more refined tools of kinetic analysis. A VEB (Variable activation Energy model for Biomass devolatilization) model is developed, based on the results of the kinetic analysis. A good agreement is obtained for all biomasses in all runs in the entire range of temperatures.

1. Introduction

Biomass fuels represent a renewable energy source, may be abundant in specific local areas and cause disposal problems. Thermochemical processes (co-combustion, gasification and pyrolysis) constitute interesting options for biomass utilization (Abbas 1996, Spliethoff 1998, Sami 2001, Bridgwater 2003, Wall 2007). Devolatilization is the first step of all these processes. It consists in the release of volatile matter (condensable and light gases) during the continuous heating of the solid fuel due to the thermal scission of chemical bonds in the natural polymers (cellulose and lignin). Therefore, the process is a complex mechanism because consecutive and parallel paths act in a very narrow range of temperatures.

The thermogravimetric (TG) technique is the basis for a fundamental investigation and gives the fingerprinting of the fuel. It provides important characteristics (temperature of devolatilization, volatile matter released), reaction kinetics and significant parameters for preliminary modelling. When biomass devolatilization is studied in a thermogravimetric balance, a composite profile in the devolatilization curve (derivative dtg) can be observed, which make the single first order reaction (SFOR) models

unsuitable for kinetic modelling. This is commonly ascribed to the decomposition of different chemical components (cellulose, hemicellulose and lignin) and is the basis of summative models (Caballero 1997, Varhegyi 1997, Orfao 1999, Manya 2003, Hu 2007), based on the hypothesis that the devolatilization proceeds independently from each others (Koufopoulos 1989, Raveendran 1996). The number of parameters in this approach is actually very high.

The aim of this work is to perform a kinetic study on the devolatilization of biomass fuels of different origin and characteristics and develop an innovative model, which starts from the results of the fundamental study. The simplicity of the SFOR model is preserved. The Variable activation Energy model for Biomass devolatilization (VEB) is validated in the range 10-80 K/min for agricultural residues, woods and grass. It allows an accurate simulation of biomass devolatilization and can be included in comprehensive codes for combustion and gasification.

2. Experimental section

2.1 Materials

Six biomass fuels of different origin are studied: grass (miscanthus), wood (beech, poplar, pellets), residues (rice husks, exhausted olive cake). They were crushed and sieved and the fraction 90-125 μm used for the experimental runs.

2.2. Equipment

A thermogravimetric balance (TG Q500 V6.1 of TA Instruments) is used for all tests. Pure nitrogen is used for the devolatilization tests (100 ml/min STP). The sample (5-6 mg) is loaded and dried at 380 K directly in the TG balance before each run. Then, a constant heating rate (HR) is programmed to 1220 K. After cooling down the sample to 1070 K, the gas flow is switched to air and the carbonaceous residue is burnt. Five heating rate programs are studied: 10, 20, 40, 60 and 80 K/min.

2.3. Kinetic analysis

The kinetic analysis of solid state decompositions is usually based on a single-step kinetic equation:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \quad (1)$$

where α is the extent of conversion, A and E the Arrhenius parameters, pre-exponential factor and activation energy, respectively, $f(\alpha)$ the reaction model, that is a function of α . Generally, the triplet A, E and $f(\alpha)$ are needed to define the kinetics of a reaction. Model-free methods allow for evaluating the Arrhenius parameters without choosing the reaction model. In particular, the isoconversional methods (Friedman 1965, Flynn 1966, Kissinger 1957) yield the effective activation energy as a function of the extent of conversion. In the case of non-isothermal runs, they require a set of experimental tests at constant heating rate. The Friedman method has been selected as the starting point for the VEB model development: E/R can be obtained for a given value of α by plotting $\ln(d\alpha/dt)$ against $1/T$. In his original analysis, Friedman considered the possibility of a single nth-order reaction. If the value of E varies with the extent of conversion, the

results should be interpreted in terms of multi-step reaction mechanisms. Let define $E_{isoc}(\alpha)$ the function obtained from the isoconversional method.

3. Experimental results

The conversion curves of all materials are compared in Figure 1 in the case of 20 K/min. In the case of beech wood, curves obtained under all heating rates are compared in Figure 2. The composite nature of these materials can be observed in the subpeaks of the dtg curves. In general, the devolatilization profile exhibits a complex peak with a well-defined main peak, a shoulder at earlier temperatures and a long tail zone. The analysis of sub-peaks is generally performed by using deconvolution procedures and each peak ascribed to the decomposition of chemical components or pseudo-components (extractives, cellulose, hemicellulose and lignin).

The temperature-conversion data are elaborated according to the Friedman method for the kinetic analysis. The results of the activation energy $E_{isoc}(\alpha)$ are reported in Figure 1 for all materials as function of the conversion and three ranges can be observed:

- at low conversions (up to 10%) E increases, to become practically constant;
- a plateau can be observed in a wide range of conversions;
- for conversions higher than 70% an irregular trend can be observed.

As a matter of fact, the linearization of isoconversional points is good only in the first two ranges of conversion, while it is not acceptable at high conversion. This can be due to uncertainties in the experimental data as well as steep variations in the activation energy, which invalidate the hypothesis of the Friedman method, making it not applicable. The characteristic equations of the isoconversional methods are indeed derived assuming a constant activation energy. This assumption introduces some systematic error in estimating $E_{isoc}(\alpha)$, when this latter varies significantly.

Average values of E in the plateau range are compared in Table 1 for all materials. These data can represent the reactivity of devolatilization and be used to compare different fuels. Although they may be sufficient for a preliminary approximation of biomass devolatilization, a SFOR model with constant activation energy can hardly describe the composite nature of biomass fuels. Therefore, a further step in the kinetic model should be done to give a better simulation of biomass devolatilization.

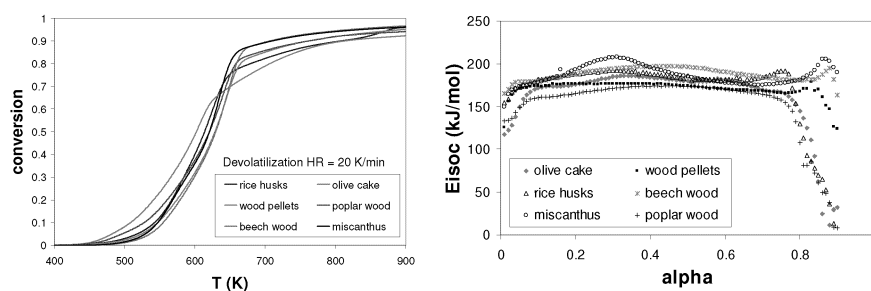


Figure 1. Comparison of conversions and activation energies obtained by using the Friedman method for the devolatilization of all biomasses

Table 1. Comparison of kinetic parameters and deviation obtained by different approaches for all biomasses.

	SFOR model –constant E		VEB model –variable E	
	mean E plateau [kJ/mol]	lnA	lnA	dev
olive cake	180.2	31.8	33.10	5.38
rice husks	187.0	32.5	33.12	8.35
wood pellets	173.2	28.6	29.39	4.23
beech wood	190.3	31.9	32.50	7.42
miscanthus	185.7	31.6	33.33	4.21
poplar wood	168.9	28.1	28.72	9.70

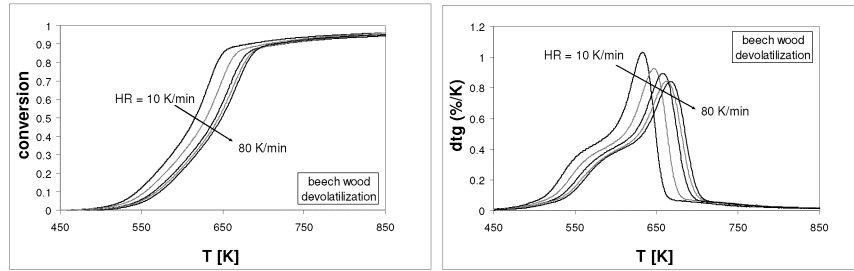


Figure 2. Comparison of conversion and dtg curves for beech wood under different HR.

4. Development of the VEB model and discussion

A SFOR model (assuming the average value the activation energy) can give only a representation of the main devolatilization, but hardly can give a description of the earlier devolatilization and the long final tail. The agreement (not reported here) was proved to be not accurate. However, the SFOR model is the simplest approach, easy to be included in comprehensive codes for combustion and gasification, and therefore some modifications may improve the approach to benefit these features.

Preliminarily, some trials were done introducing in equation 1 the activation energy $E_{isoc}(\alpha)$ directly obtained by the isoconversional method. The results (not reported here) were not satisfying. Observing the curves of Figure 1, the value of $E_{isoc}(\alpha)$ in the earlier steps is very low giving unrealistic low onset temperatures. Vice versa, in the tail zone, the trend of $E_{isoc}(\alpha)$ is irregular, causing an unrealistic behaviour in the final zone of conversion made of unlikely subpeaks. As a matter of fact, only at the intermediate values of the conversion the agreement could be considered good.

This was the basic observation to develop a Variable activation Energy model for Biomass devolatilization (VEB). The function $E_{isoc}(\alpha)$ can be modified to give a more satisfying fit of the experimental results. The following points describe the VEB model.

1. The intermediate values of $E_{isoc}(\alpha)$ are preserved, selecting an interval $[\alpha_1, \alpha_2]$ of the main devolatilization where the experimental noise is low and the activation energy is a weak function of the conversion (see the plateau in Figure 1). Let say this function $E_{plat}(\alpha)$. A preliminary value of the pre-exponential factor A_p is calculated from the minimization of the deviation of

equation 2, limiting the comparison to this interval of α .

$$dev(\%) = \sum_{hr} \frac{\sum_N |\alpha_{VEB} - \alpha_{exp}|}{N} * 100 \quad (2)$$

where α_{VEB} and α_{exp} are the model and experimental conversions, respectively, N is the number of results considered for each curve obtained under a certain heating rate and the sum is extended to all runs under different heating rates (10-80 K/min).

2. Two values of E are fixed for $\alpha=0$ (Eon) and $\alpha=0.9$ (Eoff) and, correspondingly, two cubic functions are defined (Ecub1(α) in the range [0, α_1] and Ecub2(α) in the range [α_2 ,1]) to interpolate the points (0,Eon) and Eplat and the points of Eplat and (0.9,Eoff), respectively.
3. EVEB(α) is defined in three intervals: Ecub1(α) in the range [0, α_1], Eplat(α) in [α_1 , α_2] and Ecub2(α) in [α_2 ,1]. The constant E in equation 1 is then substituted with EVEB(α). The procedure is optimized by varying Eon and Eoff and considering the widest interval [α_1 , α_2] for each material that minimizes the deviation of equation 2.
4. Finally, the value of A can be further optimized to minimize the deviation in the entire range of α for all runs.

The difference of EVEB(α) with respect to Eisoc(α) are remarkable at the earlier conversions and in the tail zone, EVEB(α) exhibiting milder variations (Figure 3). For all materials, Eon results between Eisoc(0) and Eisoc(α_1), while Eoff results higher than Eisoc(α_2). The correspondent values of A and the deviations are compared in Table 1. Finally, the comparison of the experimental results and the results of the VEB model is shown in Figure 4 for some materials. The agreement is good for all runs and all materials. It is worth noting that the specific behaviour of the material in the devolatilization curves is guaranteed by adopting Eisoc(α) in the main devolatilization interval [α_1 , α_2], which is a result of the fundamental study reported in the results section. This is not really constant, but varies weakly with the conversion allowing the composite shape of the main devolatilization to be well-predicted.

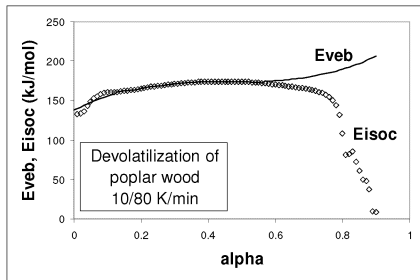


Figure 3. Comparison of the activation energy functions.

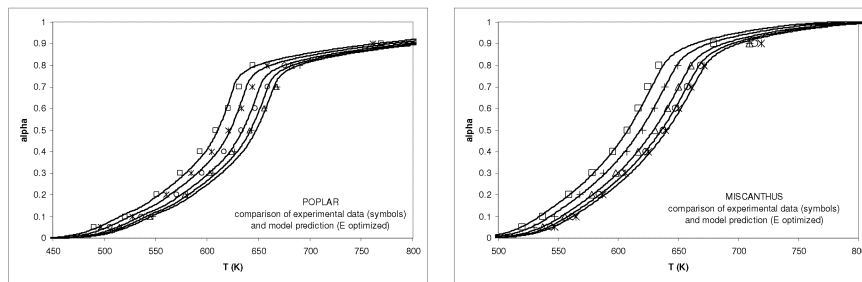


Figure 4. Comparison of the experimental and VEB model conversions.

Conclusions

An innovative approach in the kinetic model of biomass devolatilization has been developed and validated on the basis of the experimental results obtained on biomasses of different origin and characteristics. The results of the VEB model are very good for the specific approach (with E_{VEB} optimized for each biomass) and derive mainly from a fundamental study. A simple kinetic scheme is adopted without assuming any chemical or pseudo components, even though the multistep mechanism can be studied. A generalized approach (with E_{overall} obtained for all materials) will be pursued on groups of biomasses, once a significant number of runs and materials are studied.

Acknowledgement

This work collects part of the results of the FISR Italian Project on “Integrated Systems for Hydrogen Production and Use in Distributed Generation”.

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