

Devolatilisation and Pyrolysis of Biomasses: Development and Validation of Structural Models

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1. Introduction

This work involved modifying the currently available Chemical Percolation Devolatilization (CPD) model [1], and making it suitable for modeling pyrolysis of biomass feedstocks. The assessed version of CPD simulates coal as a macromolecular network and includes a statistical processes of depolymerization, from which derives the release of non-condensable gases evolving from the bond rupture and the vaporization of the lighter n-mers, competing with cross-linking, for tar and char formation. Recent development in the modelling of biomass devolatilisation involves the use of other network models such as the bio-FG DVC [2] and bio-FLASHCHAIN [3]. This suggest that also the CPD may be extended to biomass pyrolysis. Some partial efforts in that direction have already been accomplished, focusing mainly on lignin [4, 9], which is similar to coal in being a cross-linked aromatic. Nevertheless, at now, unlike the cases of coal and lignin, no general CPD model of whole biomass pyrolysis (including cellulose and hemicellulose components) has yet been proposed. Achieving the bio-version of CPD is a goal of primary importance, because, owing to its computational efficiency, it can be included in comprehensive 3D combustion codes. For example, a modified coal version of the CPD model has been incorporated already into a mechanistic combustion code, and applied for process studies of combustion devices [5].

The pyrolysis of biomass fuels has been the subject of numerous studies, as summarized in several reviews and collected papers (see references in [6]). One of the principal differences between coal and biomass is the fact that coal is predominantly an aromatic material, whereas the aromatic component of biomass (lignin) is a relatively minor constituent (~20%) for many biomass materials. Biomass also has a much higher oxygen content as compared with coal, that is present as ether, hydroxyl, carboxyl, aldehyde, and ketone functionalities, which decompose during pyrolysis to produce oxygenated gases (CO, CO₂, H₂O). The yields of these species are similar to those produced by pyrolysis of low-rank coals (5-10 dry wt.% for CO₂ and H₂O, 5-15 dry wt.% for CO). Biomass pyrolysis, however, gives much higher tar (liquid) yields than low-rank coals (40-50% versus 10-20% on a dry basis). The increased tar yield comes primarily at the expense of char, the yield of which is much lower for biomass than for low-rank coals (<10% versus 40-50%). The depolymerization of biomass is the predominant pyrolytic reaction [7], whereas, in the case of coal, depolymerization reactions compete with cross-linking events, which enhance the char formation [8]. Most of the char formed from biomass is derived from the lignin component, which is close to low-rank coal in its chemical composition. As in the case of coal, the yield and distribution of products from pyrolysis of biomass depend on other variables in addition to the final temperature and holding time. These include heating rate, total pressure, ambient gas composition, and the presence of mineral catalysts [7]. One approach to the quantitative modeling of biomass

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pyrolysis is based on the approximation that the three main components of biomass (cellulose, hemicellulose, and lignin) behave independently during pyrolysis (see, e.g., Nunn et al. in ref. [6]). Consequently, yields can be predicted based on a knowledge of the behaviour of pure components. The shortcoming of this technique is that it cannot account for possible interactions between the biomass components. Following the behaviour of each component (cellulose, hemicellulose and lignin) a complex model, called CHL, was recently developed and validated over a wide range of experimental conditions [6]. As schematised in fig. 1, CHL, compared to other approaches, is closer to be a complete tool for simulating the pyrolysis behaviour of a large number of lignin-cellulosic materials in different conditions. It encompasses the material balance, the energy balance and the description of physical and chemical phenomena occurring during the process, and it was validated with experimental data from both “fast pyrolysis” and “slow pyrolysis” conditions (see references in [6]).

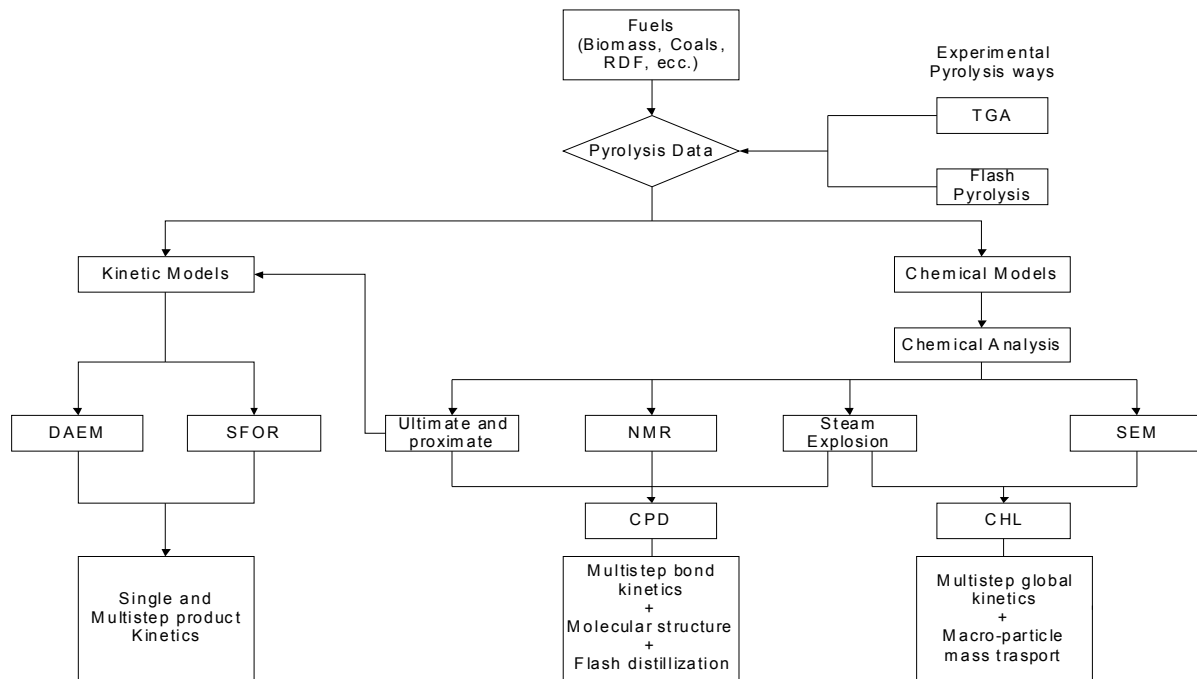


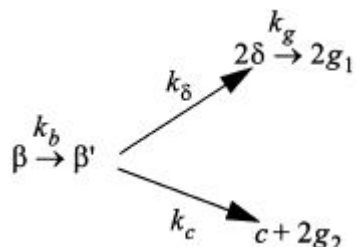
Fig. 1 Methodological approaches to the modelling of biomass pyrolysis.

Even if some important phenomena are neglected (as the vaporisation of condensable products), the complexity, the high number of parameters and the high computational cost of CHL model make it suitable to describe most of phenomena of practical interest for a single particle. Nevertheless, it cannot be included straight in comprehensive combustion codes, but it can be used as simulator to provide a set of data for assisting the development of structural models. The scheme of the work still in progress and some preliminary results are described in the following.

2. Overview of the structural model

According to the CPD model for coal pyrolysis [1], the labile bonds (i.e. linking movable or breakable bridging bonds) between the clusters in the molecular structure lattice are cleaved, resulting in two general classes of fragments. One set of fragments has a molecular weight low enough (and correspondingly a vapour pressure high enough) to escape from the biomass particle as light gases. The other set of fragments are tar vapour precursors that have a relatively higher molecular weight (and correspondingly a lower vapour pressure), and tend to remain for longer periods of time in the particle during typical devolatilization conditions.

During this time, reattachment with the biomass lattice can occur, which is referred to as crosslinking. The high molecular weight compounds plus the residual lattice are referred to as metaplast. The portion of the lattice structure that remains after devolatilization comprises metaplast, char and mineral matter. The CPD model characterizes the chemical and physical processes by considering the molecular structure as a simplified lattice or network of chemical bridges linking the polymeric clusters. The description of the cleaving of the bridges and the generation of light gases, char and tar precursors is then considered to be analogous to the following chemical reaction scheme.



The previous kinetic scheme was firstly introduced by Bradbury et al. (1979) (see references in [6]) for the decomposition of cellulose and adopted also in the CHL for all constituents. According to the novel perspective of CPD model, that kinetic scheme doesn't refer to the global component anymore, but to the bounds. The variable β represents the original population of labile bridges in the biomass lattice. Upon heating, these bridges become the set of reactive bridges, β' . For the reactive bridges, two competing paths are available. In one path, the bridges react to form side chains, δ . The side chains may detach from the aromatic clusters to form gases, g_1 . As bridges between neighbouring aromatic clusters are cleaved, a certain fraction of the biomass matter becomes detached from the lattice. These detached polymeric clusters are the heavier molecular weight tar precursors that form the metaplast. The metaplast vaporizes as tar. The metaplast can also reattach to the lattice matrix (crosslinking). In the second path, the bridges react and become a char bridge, c , with the release of an associated light gas product, g_2 . The related set of reaction rate expressions describe this reaction scheme assuming that the reactive bridges are destroyed at the same rate that they are created [1]. Given the set of reaction equations for the lattice structure parameters, it is necessary to relate these quantities to changes in mass and the related release of volatile products. The fractional change in the mass as a function of time is divided into three parts: light gas, tar precursor fragments, and char. Algebraic expressions are obtained for each part using percolation lattice statistics. In accounting for mass in the metaplast (tar precursor fragments), the part that vaporizes is treated in a manner similar to flash vaporization, where it is assumed that the finite fragments undergo vapor/liquid phase equilibration on a time-scale that is rapid with respect to the bridge reactions. As an estimate of the vapor/liquid that is present at any time, a vapor pressure correlation based on a simple form of Raoult's law is used. For the part of the metaplast that reattaches to the coal lattice, a crosslinking rate expression is used. In the present work, the mathematical formulation of the mass balances was substantially revised introducing a population balance for the liquid numbers, and the ability to differentiate the fate of the tar yields in the vapour phase and the liquid metaplast remaining in the particle.

3. Setting model parameters

For the development of bio-CPD, the basic assumption of CHL is maintained: each biomass fuel consists of cellulose, lignin and hemicellulose (hard- and softwood), so the problem is to assess kinetic, structural parameters and vapour pressure correlation for each component.

The structure of the cellulose molecule is well known, its representative formula is $(C_6H_{10}O_5)_n$ and its molecular weight varies from 250.000 to 1.000.000. Cellulose is a linear polymer:

unlike starch, no coiling occurs, and the molecule adopts an extended rod-like conformation. In microfibrils, the multiple hydroxyl groups on the glucose residues hydrogen bond with each other, holding the chains firmly together and contributing to their high tensile strength. As a consequence of the previous considerations, the structural parameters required by CPD for the initial cellulose network schematisation may be assigned with less uncertainty: the number of attachments per cluster ($\sigma + 1$) are very close to 2, the fraction that are stable bridges (p_0) is near to 1, the molecular weight per cluster (M_{CL}) is near to the molecular weight of the monomer 166 a.m.u.. The molecular weight per side chain (M_s) is supposed to be small, because it has to be considered a mean value expressed on a per monomer basis of the mass of the terminal chains and of the lattice amorphous defects. Finally, cellulose pyrolysis produces much lower char yields, when compared with hemicellulose and lignin, so the initial value for the population of char bridges (c_0) may be set to 0. The exact values of all the structural parameters, together with kinetic parameters need to be fitted to data on light gases, tar and char yields over a meaningful range of temperatures. To that purpose CPD model was used together with an optimization program to find the best parameter values.

The hemicellulose is a hetero-poly-saccharide: its molecular structure is not so well defined as that of cellulose. It is formed by C6 (glucose, mannose, galactose) and C5 (xylose, arabinose) units. The molecular weight of the monomers is usually lower than that of cellulose and they have a weak undifferentiated structure compared to crystalline cellulose. Its degree of polymerisation is very much lower than that of cellulose: this could explain the higher reactivity and the lower thermal stability of hemicellulose. Practically, the decomposition of the hemicellulose can be assumed to follow the same pathways of the cellulose decomposition, and it may be described with appropriate modifications of structural and kinetics parameters. Respect to the cellulose, the more branched but still linear structure of the hemicellulose may be represented with a value of ($\sigma + 1$) between 2 and 3; the value of p_0 will be lesser because to account for the higher initial fragmentation; c_0 is greater than 0 to explain the increased char yield; the molecular weight per cluster (M_{CL}) may be assumed something more than the xylan one, with side chains contribution (M_s) more substantial than for the cellulose network.

Lignin is similar to low rank coal with a three-dimensional lattice structure of phenolic compounds. Its structure is not well defined and depends on the biomass type. One of the main problems when studying lignin is the impossibility of extracting it from the biomass without chemically modifying it. Using ^{13}C NMR analysis and theory research, previous investigations [9] proposed that for the CPD model coniferyl, sinapyl and p-coumaryl acids are the base clusters. The set of values for the structural parameters recently proposed in the above citation was adopted in the present work as initial “guess” for a further optimization.

4. Results

The primary step of the work consisted in tuning the CPD model parameters. The data sets for the optimisation was generated with CHL model, used as generator of equivalent ‘numerical’ experiments. For each component (cellulose, hemicellulose and lignin) CHL produced temporal profiles of gas, tar and char yields for an “ideal” particle small enough in order to neglect internal transport phenomena. The temporal profiles of the yields and for three final temperatures (773, 873, 973 K) and the respective temperature profiles calculated for fast heating rate conditions (HR 14000 K/s) have been used to fit the model parameters. The numerical fit was formulated as a nonlinear least squares problem subject to bounds on the variables and it was solved using a modified Levenberg-Marquardt algorithm and a finite-difference Jacobian. As example, the fitting curves for the cellulose yields are showed in fig. 2 and 3. Once produced the best fit parameters for each component, then keeping them fixed the assessment of the scheme was started by comparing model predictions with experimental results of effective biomasses, showing encouraging preliminary agreement.

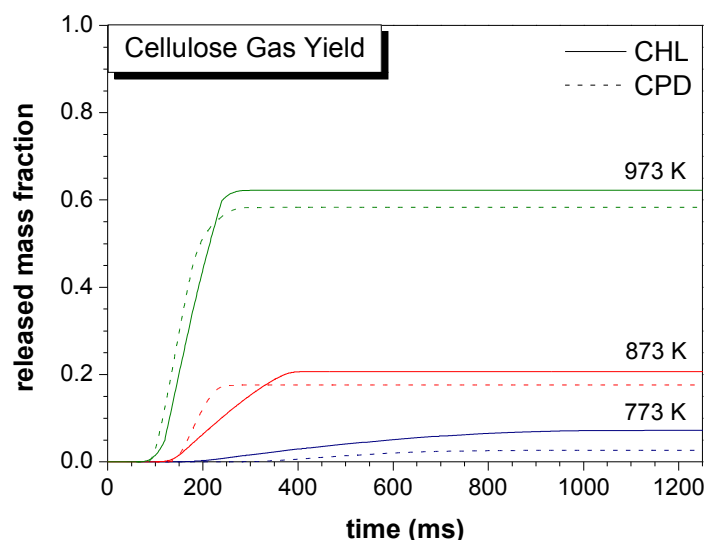


Fig. 2 Curve fitting of CPD model for gas yield from cellulose.

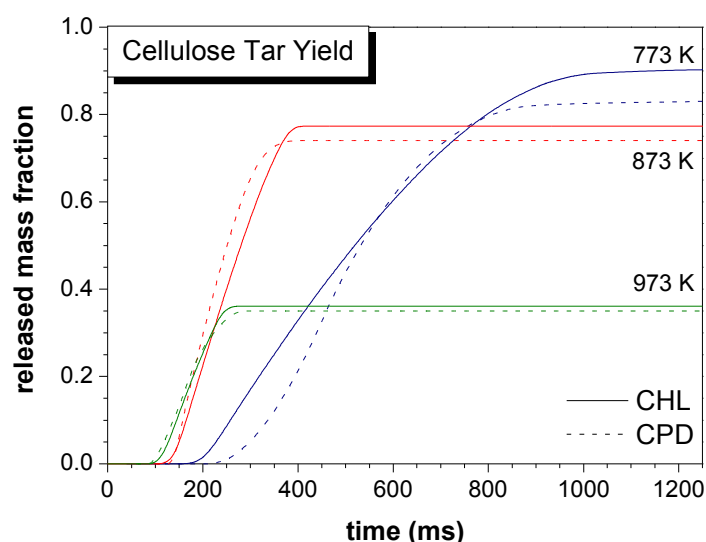


Fig. 3 Curve fitting of CPD model for tar yield from cellulose.

5. Final remarks and future work

The CPD model has been modified to describe biomass pyrolysis products as a mass weighted distribution of predictions for individual components. The framework of the bond kinetic scheme was maintained, but the formulation of the mass balances was substantially revised introducing a population balance for the liquid n-mers, and the ability to differentiate the fate of the tar yields in the vapour phase and the liquid metaplast remaining in the particle. In this way also the role of the secondary reactions of tar cracking in the gas phase has become apparent. The chemical structural and kinetic parameters for each component (cellulose, hemicellulose, lignin) have been developed based on theory, literature review and curve-fitting. The predictions have been compared with experimental data with encouraging but still preliminary results, some refinement are needed to better include secondary reactions and the interactions among each component. Future work will devoted to integration of a program calculating component composition from elemental analysis, and the development of predictive methods for the speciation of volatile yields and the reactivity of char yields.

6. References

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