

A novel approach to the biomass pyrolysis step and product lumping

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Abstract

The initial pyrolysis/de-volatilization step is common to all high-temperature gas-phase conversion processes (combustion, gasification and pyrolysis) of carbonaceous solids, because condensed phases do not react directly with the gas phase.

The aim of the present work is to introduce a systematic, generic stoichiometric approach to represent a biomass starting material and the repartition of pyrolysis products. The approach transforms the conventional representation of the starting material, into a set of well-defined chemical species while respecting the atom balances.

The starting points are the elemental composition of the dry and ash free matter of the biomass and the list of possible chemical species deriving from devolatilization.

The algorithm is flexible and can accommodate a different selection of possible products. In the current implementation three product groups with 13 species are taken into account. Since there are infinite ways of splitting the starting material over the 13 components, at least 3 repartition coefficients and 8 atom relevance weights must be specified. The algorithm has been implemented using LIBPF (LIBrary for Process Flowsheeting), a process flow-sheeting and modeling tool arranged as a C++ library.

Keywords: stoichiometric, biomass, pyrolysis model, lumping.

1. Introduction

High-temperature processes for the conversion of biomass to energy are widely discussed in the chemical engineering literature (T. Abbasi et al. 2010, A. Evans et al. 2010, L. Zhang and C. Xu et al. 2010, M. Balat et al. 2009 part 1, M. Balat et al. 2009 part 2, H.B. Goyal et al. 2008). This interest is due because biomasses are good renewable energy and sources are quite abundant.

Since biomass is not composed of well defined chemical species, standard stoichiometric approaches are not applicable. More over biomass characterization is usually expressed only as proximate (moisture, ash, fixed carbon and volatile matter) and ultimate analysis (C, H, N, O ...) of the dry and free ash matter. Sometimes cellulose, hemicelluloses and lignin mass fractions are available.

All high temperature processes of biomasses, like pyrolysis, gasification and combustion, develop hundreds of chemical species, and the stoichiometric relation between products and biomass composition is complex to represent. Moreover the solid does not react directly with the gas phase except for solid carbon (char or coke). The solid biomass always undergoes a first step of pyrolysis or devolatilization.

2. Biomass pyrolysis models

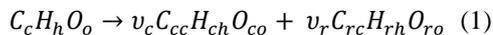
The complexity of the devolatilization behavior is due to the wide number of possible product of the pyrolysis. By a general point of view, devolatilization generates gaseous (non condensable) products (CO, CO₂, CH₄, H₂, etc.), light partly condensable-hydrocarbons (C₂H₄, C₂H₆, C₃H₆, methanol, etc.), inorganic components (NH₃, H₂O, HCN, etc.), and condensable and heavy hydrocarbons. A few hundreds of chemicals have been detected in the products of high temperature conversion processes of biomasses (Milne et al., 1998).

There are three major models of devolatilization behaviors (M. L. Souza-Santos, 2004): isolated kinetic models (global or single step and combination of series and parallel reactions), distributed activation models (series and parallel reactions are related to a distribution of activation energy) and structural models (solid structure and detailed composition define the proper devolatilization path). No information about stoichiometric release, type and composition of products are given by the first two models. The latter, instead, are quite complex and computational expensive and require a lot of experimental parameter. For these reasons, the present work aims to present a simple model that can evaluate product composition.

The FG models (one of the structural models) introduce an important concept that is the *potential tar-forming fraction* of the fuel. It represent the most important starting point for the present lumping approach and is defined as to the maximum yield of a tar component coming out from a particular fuel in a particular process. To evaluate it, all that component formation is taken in account without considering the eventual consumption.

3. Stoichiometric approach

A generic biomass contains a lot of atom types. Most of them are in a very little amount. In order of decreasing common mass fractions, biomass contains carbon, oxygen, hydrogen, nitrogen, sulfur and chlorine (and/or other halogens). In this work, only the first four atoms (C, H, N and O) have been considered. Since nitrogen is present in a very little amount, it is considered to produce N₂ or NH₃ if there is enough hydrogen at the end of all the biomass lumping. So the biomass can be referred as a CHO component. The generic chemical decomposition (1)



re-maps a biomass molar composition as v_c moles of a chemical species desired and v_r moles of a residue and the “reaction” can be represented on a CHO ternary diagram (see Figure 1). The generic chemical product can be either a well defined chemical species or a group of chemicals. A group of chemical species can be represented as one point considering a *weighted barycenter*. The weights are the first important input parameter that the user should define. They are referred to the importance or predominance of atoms in real product deriving from a biomass processing. For example, these weights can be expressed as ratios between oxygenated and non-oxygenated chemicals or

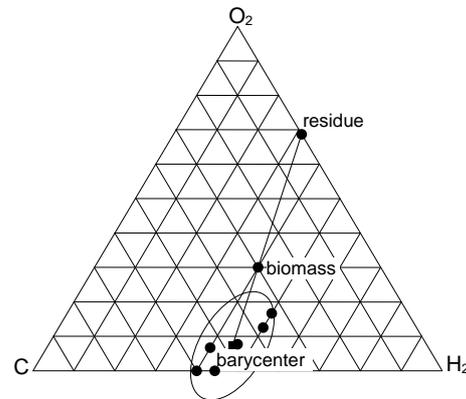


Figure 1: CHO ternary diagram of a sample biomass decomposition in a cloud of chemical species with its barycenter

between hydrogen-rich over hydrogen-poor species. However, in the present work uniform weights have been assumed for the C, H, and O atoms.

Using these basically concepts some C++ routines were written to calculate the amount of *potential chemical forming fractions*.

4. Product

Research (D. K. Seo, 2010; Y. Zhang, 2010) suggests that the pyrolysis of biomass is strongly dependent on the process conditions rather than on the biomass composition. Moreover, a single group of chemical species is not sufficient to describe devolatilization phenomena. In the current implementation three product groups are taken into account, with 13 species.

4.1. Primary products

The first group considered is referred as *primary products*. The chemical species and the nature of this group are directly related to small molecules usually present in the pyrogas or syngas also in thermodynamic equilibrium conditions. The primary products considered are: H₂, O₂, N₂, CO, CO₂, H₂O, CH₄, NH₃, and C.

The algorithm that re-maps biomass into primary products is different from that used in secondary and tertiary ones, because this calculus must exhaust all atoms present in the original matter. Looking to Figure 2, depending on the triangle in which the biomass is localized, the biomass is re-mapped into:

- Triangle 1: Only C, CO, CO₂, CH₄;
- Triangle 2: Only H₂, CH₄, H₂O;
- Triangle 3: Only O₂, H₂O, CO, CO₂;
- Triangle 4: Only CH₄, H₂O, CO, CO₂;

4.2. Secondary products

The second group is referred as *secondary products*. It is representative of light tars with a condensing temperature quite lower than that of water. Chemical species here included in the secondary products are: ethylene (C₂H₄) and methanol (CH₃OH).

4.3. Tertiary products

The third group is referred as *tertiary products*. It is representative of heavy tars with a condensing temperature higher than water. Chemical species here included in the tertiary products are: phenol (C₆H₅OH) and naphthalene (C₁₀H₈).

4.4. Model parameters

The choice of components in the latter two groups is arbitrary and represents a lumping procedure which must be based on a physical understanding the process under study.

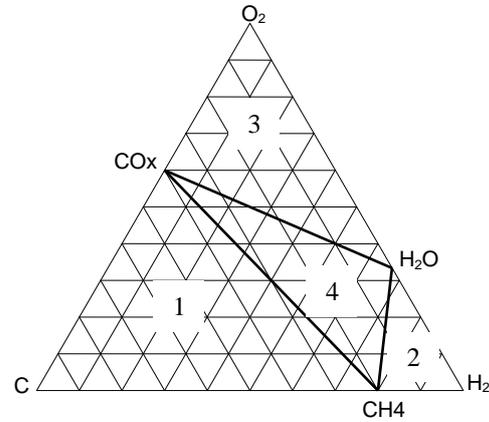


Figure 2: Primary product repartition on a CHO ternary diagram

Table 1: Reference biomass composition (Y. Zhang et al., 2010)

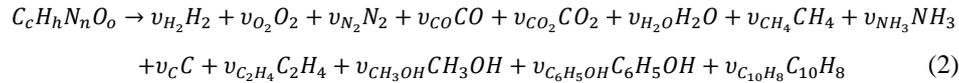
Proximate analysis	
wt% dry	
Ash	0.2
Volatile matter	89.3
Fixed carbon	10.5
Ultimate analysis	
wt% dry and free ash	
C	49.20
H	6.49
N	0.10
O	44.20

To describe all the devolatilization behavior of and the repartition of the biomass into primary, secondary and tertiary products, two *desired repartition coefficients* from each of the three groups were introduced. The specification of “desired” is due to the stoichiometric approach. The algorithm, in fact, tries to accomplish the desired repartition coefficients, but in general a residue always exists. This residue, coming from secondary and tertiary product re-mapping of the biomass, is added to the primary products to respect the amount of atoms present in the biomass. This artificial assumption involves the definition of two *actual repartition coefficients* into the calculus.

These repartition coefficients are defined as the mass of secondary or tertiary products over the total biomass mass, both in dry and free ash basis.

Primary products need another important parameter that is the *carbon oxide ratio*, (CO/CO_2) as a function of temperature (J. R. Arthur, 1951).

The expression (2) resume the biomass lumping calculation of model of pyrolysis described in this paper.



The algorithm proceeds sequentially for each group and calculates one by one the maximum amount of a stoichiometrically defined product that can be obtained respecting the atom balance based on the composition of the residual biomass, until one or two elements are exhausted.

5. Application

There are four cases, representative of a wide scenario, to which the stoichiometric pyrolysis step algorithm could be applied. These cases are pyrolysis (at two different temperatures), steam gasification and partial oxidation. The reference work where the experimental data are kept is that of Y. Zhang et al., 2010.

Table 2: Results of the model of stoichiometric pyrolysis step (PY: pyrolysis, ST: steam gasification, PO: partial oxidation)

	Cases			
	PY 600°C	PY 800°C	SG 800°C	PO 800°C
Desired repartition coefficients (kg of biomass converted / kg of biomass)				
Secondary	0.055	0.042	0.039	0.032
Tertiary	0.080	0.055	0.060	0.020
Actual repartition coefficients (kg of biomass converted / kg of biomass)				
Secondary	0.107	0.082	0.076	0.062
Tertiary	0.146	0.101	0.110	0.038
Mass of product (kg of obtained component / kg of daf volatile matter of biomass)				
Primary products				
C	0.000	0.011	0.008	0.033
CH4	0.220	0.237	0.237	0.251
CO	0.154	0.158	0.158	0.160
CO2	0.483	0.496	0.497	0.503
H2	0.000	0.000	0.000	0.000
H2O	0.007	0.000	0.000	0.000
N2	0.001	0.001	0.001	0.001
NH3	0.000	0.000	0.000	0.000
O2	0.000	0.000	0.000	0.000
Secondary products				
C2H4	0.025	0.020	0.018	0.015
CH3OH	0.029	0.022	0.021	0.017
Tertiary product				
C10H8	0.039	0.027	0.030	0.010
C6H5OH	0.040	0.028	0.030	0.010

The composition and amount of tars obtained by Y. Zang et al., 2010, is converted in the parameters required in the model. These are obtained by summing amounts of chemicals with a boiling temperature criterion. The application of the model to the four cases had generated the results reported in Table 2.

6. Conclusion and further work

The approach proposed in the present work, can be the starting point for the interpretation of experimental data or of kinetic studies on molar basis. In particular, kinetic studies, based on the lumping scheme presented, could be one milestone in the modeling of gasifier, combustors and pyrolyzers.

The biomass lumping (5) does not alter the biomass atomic fractions even in the case of partial conversion of the reactant, because the biomass amount in the system is reduced but its composition does not change. This makes it simple to calculate the energy balances and other properties, because only the initial biomass characteristics (density, enthalpy) are required in a process computation.

In a real process on the other hand in the case of a partial reaction, it is more realistic to assume that a partial pyrolysis will proceed with the lighter components first, leaving a biomass residue enriched in carbon. But this causes difficulties because of the lack of correlations to calculate the density and enthalpy as a function of the biomass atomic fractions. These correlations should be the focus of the further works.

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