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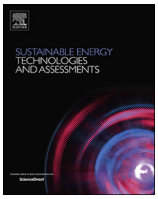

Original article

# Effectiveness of thermodynamic adaptative equilibrium models for modeling the pyrolysis process

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ABSTRACT

The pyrolysis process of biomass is one of the innovative actions for delivering sustainable energies. The research carried out introduces two thermodynamic equilibrium models (TEMs), called PyRO_2 and PyRO_3, developed for simulating pyrolysis process of biomass. This study typology constitutes tricky task since it involves a large number of physical and chemical transformations and produces several species. Particularly, it is difficult to obtain the simultaneous and trustworthy estimation of the bio-oil yield and combustible gases (CO, $H_2$ and $CH_4$) through TEM, on considering the presence of elementary hydrogen and carbon in the bio-oil chemical formula. Thereby, the mathematical models need to be preliminarily "tuned" for the specific pyrolysis process in order to achieve reliable results. In this study two pyrolysis processes, low and intermediate, were carried out on different biomasses, to test the effectiveness of the models. The comparison among simulations and experimental data indicates that the yields of released volatiles, the lower heating value (LHV), as well the bio-oil yield can be predicted with a reasonable accuracy under various operating conditions. In particular, a decrease of the bio-oil yield has been detected with the rise of the process temperature, in agreement with the thermal cracking of gases and vapors.

## Introduction

Thermochemical conversion of solid biomass may contribute to reduce the dependence by conventional fossil fuels and the greenhouse effect due to the $CO_2$ emissions [1,2], and thereby increasing the sustainability of the energy supply. Among the various thermochemical conversion of biomass, the pyrolysis process produces the lowest emissions of carbon respect to gasification [3,4], likewise the $NO_x$ emissions are reduced since the water content in the pyrolysis bio-oil diminishes the flam temperature. Therefore, the pyrolysis process may provide a significative contribute to the gradual phase-out of conventional biofuels as indicated in the Renewable Energy Directive for the post 2020 period (See Table 1).

The pyrolysis of biomass is induced by the heat supplied to the organic substrate, causing its thermal decomposition into a huge number of products, which can be used as combustibles: solid (char), liquid (bio-oil) and gaseous (pyrogas). The percent distribution and the chemical composition of the pyrolysis products depend by the biomass characteristics (composition, moisture, size and metal/mineral content [5–9]) as well as by the operational conditions (heating rate, temperature, pressure, residence time in the reactor [10–12]). Literature studies highlighted that:

- the yield of bio-oil is improved operating with temperatures of 500–550 °C, high reactor heating rates and short vapor residence times;
- the yield of char increases operating with low temperatures and low heating rate;
- the yield of non-condensable gases (NCGs) increases operating with high temperatures, low heating rates and extended residence times [13,14].

Secondary reactions, like vapors cracking, which are responsible of the reduction of the bio-oil yield and of the consequent grow of the not condensable gases (NCGs) yield [15], can be minimize by limiting the process temperatures beneath 500–550 °C, quickly removing the char and quenching the vapors produced.

The pyrolysis process is classified in slow, intermediate, fast and flash pyrolysis. Each kind of pyrolysis has a typical distribution of the three products of the process, even if the bio-oil yield is higher than char and gas ones in each case. Despite the variety of biomasses, methodologies, operative conditions and reactors, the pyrolysis

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Table 1
Classification of the pyrolysis process and products yields [17].

| Typology of Pyrolysis | Reactor Residence Time | Yield (weight percentages on biomass, dry basis) | | |
|---|---|---|---|---|
| | | Bio-oil | Char | Gas |
| Flash | 0.5 s | 66 | 24 | 10 |
| Fast | 1–2 s | 75 | 12 | 13 |
| Intermediate | 10 s–5 min | 50 | 30 | 20 |
| Slow | 20–45 min | 30 | 35 | 35 |

experiments shows a general trends for both products distribution and their properties as a function of temperature [16].

Several studies have described the pyrolysis process through kinetic models, which determine the biomass weight loss (versus time or process temperature) [18–20]. Grieco and Baldi [21] supposed the total biomass degradation and simultaneous reactions to produce bio-oil, NCGs and char. Other studies described the pyrolysis as a two-stage process, in which the products obtained in the first stage provide further chemical reactions that generate the secondary pyrolysis products [22,23]. Lam et al. [24] developed a model that describe the pyrolysis kinetic, particle heat transfer, particle shrinking and reactor operation. Wang et al. [25] proposed a kinetic model with one-step for cellulose degradation, three and two steps respectively for hemicellulose and lignin degradation. Thunman et al. [26] proposed a particle model, where the energy, mass balances and two additional empirical relationships were used to calculate the yields of six volatile species.

The main limit of the kinetic models is the possibility to evaluate only the yield of char, bio-oil and gases, instead the thermo-dynamic equilibrium models (TEMs) determine both the yields of the products and the chemical composition of the producer gas as a function of process parameters and biomass composition [27,28]. TEMs may be usable for simulating the pyrolysis process since its kinetics is very fast compared to the residence time [29,30]. However, as the global equilibrium is applied, gradient of temperature and species are not taken into account [31], as well the design and the size of the reactor [32].

In literature, to the best of our knowledge, there is a scarceness of mathematical models able to describe the pyrolysis process, due to the complexity of the process. In particular, the appraisal of the bio-oil yield, through a thermodynamic equilibrium model, is a difficult task since it is fundamentally a non-equilibrium product. On considering that Life Cycle Analysis (LCA) on biomass use showed an impact, in term of $CO_2$, of at least one order of magnitude lower than that generated by fossil fuels (coal and gas) for the same energy produced [33], it is worth of interest to provide reliable simulations models that can enrich the awareness on the pyrolysis process.

The novelty of this study is the developing of two thermodynamic stoichiometric equilibrium models, named PyRO_2 and PyRO_3, which allow calculating the chemical composition, the lower heating value (LHV) of the pyrogas as well as the bio-oil yield produced by the pyrolysis process. In the first part of this study, the main features and the system of the equilibrium equations that constitute the mathematical models are presented. Subsequently, the phase of models calibration and validation is described. In particular, the results of the models have been compared with two different set of experimental data, which are representative of two kinds of pyrolysis: intermediate and slow pyrolysis process.

The procedure followed is here summarized:

a) the predictions of each model have been compared with a first set of experimental data;
b) the two models have been calibrated introducing specific calibration coefficients that allow to “tune” the predictions of the model on the specific features of the pyrolysis process (i.e. residence time in the reactor, temperature of the process);
c) the predictions of the “calibrated models” have compared with the experimental data for evaluating their affordability.

The above mentioned steps have been retraced using a second set of experimental data. At the end of the study, a summary of the performances of the two models is proposed. Considering that for obtaining affordable results the proposed models need to be calibrated on each specific pyrolysis process, we have titled them as “adaptative” models.

## Pyrolysis products

### *Pyrogas*

Pyrogas is mainly composed by $H_2$, CO, $CO_2$, $CH_4$, $H_2O$ and, in less quantity, by $C_2H_4$ and $C_2H_6$. Its yield is enhanced especially in process of slow and intermediate pyrolysis. Pyrogas contains condensable organics (tar) and dusts that have to be removed, for avoiding fouling and obstruction as well as corrosion, by means of quenching, filtering and wet electrostatic precipitators. The gas cleaning is essential for using pyrogas as combustible in gas-fired boilers, gas turbines, spark ignition engines (SI). Hossain and Davis [34] presented the state of the art and the future prospects for the use of pyrolysis liquids and gases as alternative combustibles in internal combustion engines (IC), for combined heat and power generation (CHP) or combined cooling heat and power generation (CCHP).

The LHV of pyrogas is influenced by:

- biomass characteristics: the moisture content lowers the LHV;
- process temperature: the increase of temperature increases the LHV as a consequence of the growth of the all combustible gases to the detriment of the $CO_2$;
- residence time: e.g. high residence times favor the production of CO and $CH_4$ in spite of $CO_2$ production.

### *Bio-oil*

In literature, condensable organics are a complex mixture constituted by hydrocarbons with a molecular weight higher than benzene [35]. In this study, the condensable organics are, conveniently, lumped into a group and referred to as “Bio-oil”.

The yield of bio-oil increases under the below reported circumstances:

- small size of the biomass: biomass size not higher than 3 mm, since the biomass has low thermal conductivity which prevents the heat transfer [36];
- fast heating rates lead to higher yields of liquids and lower yields of char [37];
- water content of about 10%: higher moisture content implies the production of a bio-oil with too high water content, that must be removed before using it as combustible; nevertheless, a moisture content lower than 10% it isn’t appropriate, since water favors the biomass thermochemical conversion;
- low ashes content: the catalytic effect of ashes on the vapor cracking reaction causes the decrease of bio-oil yield and the increase of the char and NCGs yields;
- high content of cellulose [5].

The bio-oil, that must be cleaned to obtain suitable characteristics for its utilization [23], is reputed to be used as an alternative combustible, despite there are some constrains that limit its exploitation in the field of transports [34].

### *Char*

The char can be used in heating, co-firing in coal plants, as soil