

# Kinetic modelling of biomass torrefaction as a pre-treatment for gasification

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## Abstract

Biomass presents some obstacles regarding its usage, such as the moisture content, low bulk density, low calorific value, high volatile and oxygen contents, and its tenacious and fibrous nature can create challenges to store, transport and efficiently convert biomass into fuels and other products. Torrefaction has the potential to improve biomass properties acting as a mild heat treatment in the temperature range of 200-300 C under inert atmosphere inducing partial decomposition of the organic biomass components. The literature, focused on experimental studies, shows that torrefaction reduces the moisture content, confers hydrophobicity, biochemical stability, higher energy density and high grindability of biomass. It is well known that the kinetic modeling of biomass torrefaction is essential to define the progress of the decomposition-reaction paths and to evaluate the dependence of the rate of progression on process parameters, especially in regards to kinetic mechanisms that are able to predict release rate profiles, product yields and the product speciation, focused on the torrefaction uses. Therefore, the developed works consists of adapting a torrefaction kinetic scheme. These adaptations consist on adjusting two tunable parameters, correction of kinetic parameters and molar coefficients of specific species, in order to provide better results for a sample of nut shell, resultant from agricultural residues. It was compared against experimental data the product yields and gas composition. The implemented model, despite having a relative error of 30 %, it is the one with better predictions. The kinetic model, after the adaptations, presented an improvement of 20 % against the pre-modified kinetic scheme.

**Keywords:** Biomass, Torrefaction, Kinetic modelling

## 1. Introduction

For the past few years, fossil fuels have been the main energy source to meet the energy demands across the globe, even though its availability is limited and the use of fossil fuels has proven to cause a negative impact on the environment. As a consequence, renewable energy sources have been rising to eventually replace fossil fuels. However, the current renewable energy sources have to be strategically placed accordingly to the geographic profile of a given region, besides its dependency on weather conditions, which causes intermittency on its availability. The unreliability of renewable energies is seen as a major disadvantage when compared to fossil fuels, which are available regardless of the weather. In this regard, biomass has a great advantage over other renewables, such as solar, hydropower or windpower, since it can be stored and transported, allowing it to be used where and when necessary, regardless of the weather conditions and the geographic profile of the location. This characteristic of biomass resembles the practicality of fossil fuels in terms of availability, without the negative

impacts intrinsic to fossil fuels exploration. There are residues resultant from some activities which might be used in bioenergy production, such as agricultural residues, although, these usually present a lower energy density when compared to other fuels like coal. The difference between the energy content constitutes a challenge, which delays biomass use in the energy market. In order overcome this obstacle, biomass can undergo thermochemical processes to improve its thermodynamic proprieties, increasing its value as a fuel and therefore becoming more competitive. Torrefaction in particular, is a biomass pre-treatment, run under low temperatures, under inert atmosphere [8, 7, 6, 4], which causes the partial decomposition of biomass, improving its proprieties to be used in other thermochemical processes like gasification. Torrefaction also improves biomass capacity to be stored and transported [8], since the resultant biomass becomes hydrophobic and less voluminous as some of the mass is loss due to light devolatilization. Torrefaction of agricultural residues in particular can bring even more challenges due to the higher variability within these

residues. In this context, there is a necessity to better predict the behaviour of this biomass type under the torrefaction processes to spread its use in the bioenergy industry. Anca-Couce et al. [3] suggested a kinetic scheme which was able to predict the mass loss evolution and product yields with the presence of secondary reactions under torrefaction temperatures for woody biomass but does not account for different hemicellulose types, which leads to inaccuracies on non-woody biomass. A study by Debiagi et al. [5] introduced the variability of the different hemicellulose types by adjusting two molar coefficients and its ratios which can lead to better predictions, therefore, the general objective of the present work is to study the kinetic scheme of torrefaction as a pre-treatment for gasification of agricultural residues, adapt it and compare it against experimental data.

## 2. Theoretical Foundation

### 2.1. Biomass composition

Biomass is structured by the cell walls, which are the primary components, extractives and ash. The primary components provide the structural support against mechanical stresses and strength for the plant. These structural components are cellulose, hemicellulose and lignin. However, biomass can fall under different categories accordingly to the its origin and/or composition. Wood and woody biomass; herbaceous and agricultural biomass are two of the several categories. These types of biomass have different hemicellulose compositions, glucuronoxylans is the predominant component in hardwood biomass, which belongs to the woody biomass classification. On the other and, herbaceous and agricultural residues are predominant in arabinoxylans.

### 2.2. Torrefaction

Torrefaction is a biomass pre-treatment [8, 7, 6, 4], that is run at low temperatures, under inert atmosphere, and with a heating rate lower than 50 C/min [4]. This pre-treatment targets, mainly, hemicellulose thermal degradation, although other components might still be affected. This partial decomposition leads to some devolatilization, resulting in loss of mass and chemical energy, where the mass loss is greater than the energy loss [4]. Therefore, the resultant solid has a greater energy content per unit of mass. This implies a higher heating value, which upgrades biomass thermal proprieties and its value as a fuel. What happens during torrefaction can be described as nonreactive drying, reactive drying and destructive drying [8].

## 3. Numerical Model

The purpose of the numerical model is the implementation and adaptation of a kinetic scheme from Anca-Couce et al. [3] which describes torrefaction

of woody biomass. The numerical model aims to solve the species mass conservation ( Eq. 1) and reaction rates ( Eq. 2) using a stiff ordinary differential equation solver in Python [2] using Cantera [1] reaction kinetics library.

$$m_p \frac{dY_{sp}}{dt} = \dot{m}_{sp, gen} \quad (1)$$

Where:

$m_p$  is the mass of the particle [Kg]

$Y_{sp}$  is the mass fraction of a given specie

$\dot{m}_{sp, gen}$  is the mass generated of a given specie [Kg s<sup>-1</sup>]

$$k_i(T) = A_i \cdot \exp\left(\frac{-E_i}{R \cdot T}\right) \quad (2)$$

Where:

$A_i$  is the pre-exponential factor [s<sup>-1</sup>].

$E_i$  is the Activation energy [J mol<sup>-1</sup>].

$R$  is the ideal gas constant of 8.3144 [J mol<sup>-1</sup> K<sup>-1</sup>]

$T$  is the temperature of the species within the reactor [K]

Solving the kinetics allows to explore values of interest such as the product yields and its respective composition, which is extremely important to evaluate the released gases. The product yield is given by Eq. 3 and the composition of a given product yield is given by Eq. 4.

$$Yield_i = \frac{\sum(M_{w, sp, i} \times Y_{sp, i})}{m_{p, 0}} \quad (3)$$

where:

$Yield_i$  is the yield of a product, with i being solid, liquid or gas [%]

$M_{w, sp, i}$  is the molecular weight of a given product yield specie [Kg kmol<sup>-1</sup>]

$Y_{sp, i}$  is the mass fraction of a given product yield specie

$$Yield_{sp, i} = \frac{\sum Y_{sp, i}}{Yield_i} \quad (4)$$

where:

$Yield_{sp, i}$  is the yield of a given product specie [%]

### 3.1. Kinetic scheme

The kinetic scheme is influenced by the imposed temperature profile, biomass composition,  $x_i$ ,  $y_{13}$  and the chosen hemicellulose reaction, which varies accordingly to the biomass type. The imposed temperature profile and biomass composition are fixed parameters for the purpose of this work; the influence of  $y_{13}$  is disregarded;  $x_i$  and the chosen hemicellulose reaction, combined with the introduced adaptation to better represent hemicellulose types

by Debiagi et. al [5], are considered variable parameters of the kinetic scheme which might be adapted to better fit the experimental data. In order to determine the best combination of parameters a tool was developed to account for the relevant points and its deviations, where the deviations are given by Eq5.

$$Error = \sum_i \left| \frac{P_{i, num} - P_{i, exp}}{P_{i, exp}} \right| w_i \quad (5)$$

where:

$P_{i, exp}$  is the experimental value of parameter  $i$ .

$P_{i, num}$  is the numerical value of parameter  $i$ .

$w_i$  is the weight of the given parameter.

The relevant parameters considered were:

- Location and value of mass loss rate peak ; this parameter allows to quantify the extension of the reactions that take place under a given temperature profile.
- Mass, liquid and gas yields; the generated products yields are relevant to quantify the volatile matter that goes to each phase.
- Gas composition; similarly to the yields, permits the quantification of each produced gas.
- Location and value of CO and CO<sub>2</sub> production rates peaks; with the biggest gas contributions coming from CO and CO<sub>2</sub>, the profile of the released gases present great relevance to predict the behaviour of devolatilization under an imposed temperature profile.

#### 4. Results

The parameter combination which provided the smallest error was then further adapted by changing some kinetic parameters and molar coefficients of specific species to fit experimental data. The adapted model in regards to the original model proposed by Anca-Couce et al. [3] provided better results which are shown in Table 1 and 2.

Table 1: Deviation from experimental data.

Yield (%)	Solid	Liquid	Gas
Anca-Couce	5.3	57.2	216.9
Anca-Couce Adapted	6.9	51.9	110.0

Table 2: Deviation from experimental data. (%)

	CO <sub>2</sub>	CO	Avg.
Anca-Couce	44.7	325.4	50.2
Anca-Couce Adapted	25.0	231.3	33.1

Despite some large deviations regarding the characterisation of devolatilization, the adapted model has limited accuracy still provides the best behaviour under torrefaction as a pre-treatment for gasification out of the tested kinetic schemes.

#### 5. Conclusions

It was implemented a torrefaction kinetic scheme with several parameters that could vary accordingly to biomass composition and imposed temperature. Even though the kinetic scheme from Anca-Couce et al. [3] was validated for woody biomass, there were several parameters that could be changed in order to accommodate the use of other biomass types. On an attempt to predict the behaviour of agricultural biomass, a tool was developed in order to account for the relevant points and its deviations. The best points were found and the one which provided the smallest error was further adapted to fit the experimental data. The adaptations consisted on a kinetic parameter adjustment, and the adjustment of specific molar coefficients. After the adjustments, the new kinetic scheme improved significantly on gas composition predictions, which was a major factor for the purpose of this work. Since the devolatilization profile is extremely important in this context, as torrefaction is used as a pre-treatment for gasification, therefore, it is out of interest to preserve the volatile matter to be later released during the thermochemical process. Despite the adapted model having a deviation over 30 %, out of all the previous kinetic schemes available, it provided the best predictions overall. The obtained results are only valid for the biomass in use and the imposed temperature profile.

##### 5.1. Future Work

During the development of the present work, some aspects could not be explored, which are relevant to close the gap in kinetic modelling torrefaction of non-woody biomass. The major aspect that needs to be further explored is the molar coefficients of the released volatile matter, which might have to be optimised individually, instead of having several coefficients multiplied by the same factor ( $x_i$ ). Gathering more experimental data from different non-woody biomass samples for a greater temperature range might be helpful to optimise the proportions at which the products are released.

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