MODELLING OF BIOMASS PYROLYSIS
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ABSTRACT

Pyrolysis is an essential preliminary step in a gasifier. The first step in modelling the pyrolysis process of biomass is creating a model for the chemical processes taking place. This model should describe the used fuel, the reactions taking place and the products created in the process. The numerous different polymers present in the organic fraction of the fuel are generally divided in three main groups. So, the multistep kinetic model of biomass pyrolysis is based on conventional multistep devolatilization models of the three main biomass components - cellulose, hemicelluloses, and lignin. Numerical simulations have been conducted in order to estimate the influence of the heating rate and the temperature of pyrolysis on the content of the virgin biomass, active biomass, liquid, solid and gaseous phases at any moment.

Keywords: kinetic models, pyrolysis, biomass pyrolysis.

INTRODUCTION

A study of pyrolysis kinetics provides important information for the engineering design of a pyrolyzer or a gasifier. It also helps to explain how the different processes in a pyrolyzer affect product yields and composition. The three major processes that influence the pyrolysis rates are the chemical kinetics, the heat transfer, and the mass transfer. This paper describes the kinetic aspects that govern the process.

Pyrolysis is a fundamental thermochemical conversion process that can be used to transform biomass directly into gaseous and liquid fuels. In this regard, a thorough understanding of pyrolysis kinetics is vital to the assessment of items including feasibility, design, and scaling of industrial biomass conversion applications [1, 2].

Pyrolysis is an essential preliminary step in gasification, involving thermal decomposition of the long chain molecules of the biomass into smaller molecules in the gas (condensable and noncondensable).

Pyrolysis of biomass is typically carried out in a relatively low temperature range of 300 to 650°C. The initial products are condensable gases and solid char. The condensable gas may break down further into noncondensable gases (CO, CO₂, H₂, and CH₄), liquid tar, and char. This decomposition occurs partly through gas-phase homogeneous reactions and partly through gas-solid phase heterogeneous thermal reactions. In gas-phase reactions, the condensable vapor is cracked into smaller molecules of noncondensable permanent gases, such as CO and CO₂ [3].

Condensable and non-condensable vapor are separated from the biomass, leaving the pyrolysis zone, while the particles of the solid carbon residue is distributed as follows: partially in the chamber or partially in the gas.

The detailed examination of a large number of kinetic models of biomass pyrolysis, presented in [4, 5], allows to be classified into three groups:

One-stage global single reaction. The pyrolysis is modeled by a one-step reaction using experimentally measured mass loss rates.

One-stage multiple reactions. Several parallel reac-
tions are used to describe the degradation of biomass into char and several gases. A one-stage simplified kinetic model is used for these parallel reactions. It is useful for determination of product distribution.

Multistep kinetic model. This model includes both primary and secondary reactions, occurring in series.

The first step in the modelling of the biomass pyrolysis is creating a model for the chemical processes taking place. This model should describe the used fuel, the reactions taking place and the products, created in the process.

The numerous different polymers, presenting in the organic fraction of the fuel, are generally divided in three main groups: cellulose, hemicellulose and lignin. The proportions of these groups depend on the type of wood, but normally the mass fractions range from 40 to 50 % for cellulose, from 15 to 25 % for hemicellulose and between 20 and 30 % for lignin. Together these three groups form 90 – 95 % of wood. The other 5 – 10 % consist of mineral matter and some organic compounds. The three groups are described in more detail in [5, 6].

The multistep kinetic model of biomass pyrolysis is based on conventional multistep devolatilization models of the three main biomass components (cellulose, hemicelluloses, and lignin) and gives detailed information on the composition of the yields of gas, tar, and solid residue. Successive gas phase reactions of the released volatile species are then described by a general kinetic scheme of pyrolysis [11].

Fig. 1 illustrates schematically the model according to which the process involves a pyrolysis reaction with an intermediate (I), followed by several reactions of first order [6 - 11]:

Reactions III include dehydration and decarbonation, carbonation with a sequence of steps to obtain a carbon residue, and non-condensable gases, such as water vapor, carbon dioxide and carbon monoxide. Reaction II includes depolymerization and liberation of fumes forming tar and condensable gases. If the condensable gases leave the reactor, they condense as tar. On the other hand, if they remain in contact with the biomass in the reactor, secondary reactions (IV), such as cracking of the non-condensable gases to a secondary carbon residue, tar and gas, can occur (see Fig.1). Reactions II, III and IV are preceded by a reaction (I), which forms a very transient intermediate called active fiber [12 - 14]. There are different views on the existence of reaction I, because such unstable phase is not detectable in the final product in most processes of pyrolysis.

Each of the virgin components undergoes the same generic competitive reaction scheme:

\[
\begin{align*}
\text{virgin(s)} & \rightarrow \text{active(s)} \\
\text{active(s)} & \rightarrow \text{tar(g)} \\
\text{active(s)} & \rightarrow X.\text{char(s)} + (1 - X).\text{gas(g)} \\
\text{tar(g)} & \rightarrow \text{gas(g)}
\end{align*}
\]

where i is: c (cellulose), h (hemicelluloses), and l (lignin).

As indicated in the kinetic scheme, the initial components, the active intermediates and the char, are solid phase species, while the tar and the gas, representing groups of compounds, are fume products. All reactions are modelled with the first order Arrhenius kinetic model:

\[
K_i = A_i \exp(-E_i/RT),
\]

where \( A_i \) - the rate constants, \( E_i \) - activation energies for reactions \( K_1, K_2, K_3 \) and the mass ratio \( X \) are dependent on the particular component, whereas all heats of reaction and secondary tar decomposition parameters \( K_4 \) are independent of the source component. The char

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Fig. 1. Scheme of biomass pyrolysis.
formation ratio for reaction $K_3$ are: $X_c = 0.35$, $X_h = 0.60$, and $X_l = 0.75$ [11].

All of the pre-exponential constants $A$, and the reactions activation energy, $E$, are shown in Table 1 and are dependent on the source component [11].

A model of the kinetics of biomass pyrolysis is chosen. An algorithm of the process for determination the quantities of the final products of the process depending on the model parameters (heating rate and temperature of the pyrolysis) is composed. The algorithm is implemented using software.

**EXPERIMENTAL**

The algorithm of the pyrolysis process involves solving a system of ten differential equations. The types of these equations are determined based on the equations 1, 2, 3 and 4 and Table 1, for the three components of the biomass. To determine the total mass of each of the final products of the process it is assumed that they are the sum of the results for cellulose, hemicellulose and lignin. The system of equations is solved using a manifest stable finite difference scheme. Collaborative decision of the above equations makes it possible to determine the composition and quantity of the gas phase and the solid residue. The software algorithm is implemented and series of calculations were carried out under the following conditions:

- composition of the biomass: cellulose - 42 %, hemicelluloses - 31.5 %, lignin - 6.5 %;
- pyrolysis temperature of 650 K, 700 K and 750 K;
- residence time of the biomass in the reactor 20 s.

Figs. 2, 3 and 4 illustrate some of the numerical experiments.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A$ (1/s)</th>
<th>$E$ (J/kmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{1,C}$</td>
<td>$2.8 \times 10^{19}$</td>
<td>$242.4 \times 10^6$</td>
</tr>
<tr>
<td>$K_{2,C}$</td>
<td>$3.28 \times 10^{14}$</td>
<td>$196.5 \times 10^6$</td>
</tr>
<tr>
<td>$K_{3,C}$</td>
<td>$1.30 \times 10^{10}$</td>
<td>$150.5 \times 10^6$</td>
</tr>
<tr>
<td>$K_{1,h}$</td>
<td>$2.10 \times 10^{16}$</td>
<td>$186.7 \times 10^6$</td>
</tr>
<tr>
<td>$K_{2,h}$</td>
<td>$8.75 \times 10^{15}$</td>
<td>$202.4 \times 10^6$</td>
</tr>
<tr>
<td>$K_{3,h}$</td>
<td>$2.60 \times 10^{11}$</td>
<td>$145.7 \times 10^6$</td>
</tr>
<tr>
<td>$K_{1,l}$</td>
<td>$9.60 \times 10^8$</td>
<td>$107.6 \times 10^6$</td>
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</tr>
<tr>
<td>$K_{3,l}$</td>
<td>$7.70 \times 10^6$</td>
<td>$111.4 \times 10^6$</td>
</tr>
<tr>
<td>$K_4$</td>
<td>$4.28 \times 10^6$</td>
<td>$108 \times 10^6$</td>
</tr>
</tbody>
</table>

Table 1. Rate constants and activation energies for the biomass pyrolysis kinetics scheme.

Fig. 2. Kinetics of the pyrolysis (temperature 650 K and time of heating 20 s).

Fig. 3. Kinetics of the pyrolysis (temperature 700 K and time of heating 20 s).

Fig. 4. Kinetics of the pyrolysis (temperature 750 K and time of heating 20 s).

**RESULTS AND DISCUSSION**

The results of calculations for the mass fractions of virgin biomass ($M_v$), active biomass ($M_{act}$), char ($M_{ch}$), tar ($M_{t}$) and gas ($M_{g}$) are presented on Figs. 2 - 4.

The first graph in Fig. 2 presents the kinetics of the process at a temperature of 650 K and pyrolysis residence time of biomass in the reactor 20 s. It is clearly seen how the initial biomass is converted...
into active biomass, after which, over time, the active biomass decreases and the amount of tar increases, while the amount of the gas and the solid carbon increases insignificantly.

The second graph (Fig. 3) presents the kinetics of the process at a temperature of 700 K and pyrolysis residence time of biomass in the heated area 20 seconds. At higher temperature and same heating time the initial biomass is transformed completely into an active one. With decreasing the amount of the biomass, the amount of the gas is increasing. The amount of tar reaches its peak around the fourth second, then starts to decrease because of gas formation. The formation of solid carbon increases up to about the 4th second and then remains constant.

The third graph (Fig. 4) shows the kinetics of the process at a temperature of 750 K and pyrolysis residence time of the biomass in the area of heat 20 seconds. It is seen that the active biomass is fully transformed at about the 1st second of the process. The formation of tar is decreasing with the formation of gas. The amount of solid waste remains constant.

CONCLUSIONS

After analysis of the existing models for kinetics of biomass pyrolysis a kinetic model of biomass pyrolysis, based on conventional multistep devolatilization models of the three main biomass components - cellulose, hemicelluloses, and lignin, is proposed. Software implementation of a composite algorithm allows determining the quantities of the end products of the process depending on heating rate and temperature of pyrolysis. Simulation calculations have been conducted on the influence of the heating rate and the temperature of pyrolysis on the quantities of the virgin biomass, the active biomass, the liquid, solid and gaseous phases, at any time.

REFERENCES