Thermochemical Conversion of Biomass -
Kinetics, Gasifier, Modeling and Design

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ASBTRACT: For the purpose of this research, there were studied the kinetics of the thermochemical transformation of wooden chips (alder) sample provided by Institute of Coal Chemical Processing in Poland. To obtain the results, methods of Thermogravimetry, Differential Thermogravimetry were used along with Differential Scanning Calorimetry (TG, DTG, and DSC respectively). Firstly, it was studied the reactivity during combustion of the char obtained through pyrolysis up to different temperatures 200°C, 300°C, 400°C. After this, there were carried out experiments of sample's pyrolysis, partial oxidation and complete combustion with different heating rates. As an inert gas nitrogen was used. Partial oxidation was performed with the following partial pressures of oxygen in the gasifying agent PO₂: 0.21, 0.18, 0.15, 0.10, 0.05, 0.025 atm. In the model, reactions were assumed to be first order reactions. After performing kinetic modeling of the given material, simulation of its gasification process was performed with application of Chemcad software. To perform the simulation, a Gibbs reactor was used with parameters for the process and the material's properties along with its proximate and ultimate analysis, as provided by Institute of Coal Chemical Processing in Zabrze (Poland). Prior to the simulation, there was performed thermal analysis to assess the possible products arising from the different material's transformation modes. The results obtained from the simulation were compared to ones given by Institute of Coal Chemical Processing.

Keywords: Biomass gasification, Kinetic modeling, TG, DTG, DSC, Chemcad
1. Introduction

Today's world must face a number of issues related to energy production by means which are harmful to the environment and to humanity. Application of fossil fuels in energy generation processes is still ongoing due to high availability of the sources and relatively low cost. However, nowadays the trend is changing. Thanks to European Union’s commitments made in 2007 through ‘Climate and Energy Package’ program member countries committed to reduce greenhouse gases emissions by 20% below 1990 levels and to increase the renewable energy target up to 20% by 2020. These drivers have caused the need of seeking for alternative ways of energy production, which are less harmful not only in terms of pollution but also in terms of obtaining the sources like mining or transportation threats. One of the methods of clean energy generation is the gasification process. As a feedstock for gasification power plants, biomass is widely used. It is a source which does not contribute to CO₂ emissions accounted for greenhouse gases release and allows to obtain even more clean energy than from coal gasification plants, when just greenhouse gases emission is accounted for. The objective of this work is to study alder chips gasification process through modeling of the kinetics of their thermochemical conversion and simulation of a gasification process with Chemcad software. The aim is to increase interest in biomass gasification in regions which have no application of that process so far. Besides that, the aim is also to show its advantages over other energy generation processes what would help to meet the challenges imposed by the targets established by the European Union and member states.

2. Research methodology

To study the thermochemical conversion of sample, thermogravimetric analysis, and differential scanning calorimetry (TGA-DSC) method was used. TGA method gives information about the mass evolution (gain or loss) in time or temperature, and its rate under controlled conditions and atmosphere. [1] Differential scanning calorimetry, in turn, measures heat effects involved with material’s transition in time or temperature. It is measured based on heat evolved or absorbed during experiments with respect to the temperature difference between studied material and the reference material. [2]

3.1 Sample description

The sample that has been examined was alder wood chips provided by Institute of Coal Chemical Processing. The results of proximate and ultimate analysis on mass basis are as follow:

Proximate analysis (analytical state and total moisture content)

- Total moisture 11,7%
- Moisture (analytical state) 8,9%
- Volatile 76,66 %
- Fixed carbon 11,14 %
- Ash 0,5 %

Ultimate analysis (analytical state)

- Total carbon 47,6 %
- Total hydrogen 5,29 %
- Nitrogen 0,15 %
- Total sulfur 0,04 %
- Oxygen 46,873 %
- Chlorine 0,08 %
- Fluorine 0.003 %

Heating values (analytical state)

- HHV 18536 J/g
- LHV 17164 J/g

2.2 Sample preparation

Before the study was carried out, the sample had been grounded in one's of Institute of Coal Chemical Processing laboratory. It had to be done to make a sample, which originally was in the form of wooden chips, to be homogenized and fit the crucible that was used in the TG/DSC experiments.

2.3 Procedure

At the very beginning of each set of experiments, a blank probe was carried out. That means, both crucibles were empty and placed in the TGA holder. In this condition, the experiment run in the specific atmosphere (either under air or nitrogen condition). Every experiment's data was then corrected with blank probe results. In each set of experiments first the apparatus was tared with both empty pans to get the mass difference to zero value. After it was tared roughly 10 mg of sample were weighted and placed in an alumina crucible.

There were different sets of experiments carried out. There will be presented below:

- Pyrolysis and then combustion of obtained char (carried out up to 200°C, 300°C, 400°C)
- Pyrolysis with heating rates of 10°C/min, 20°C/min or 50°C/min
- Partial oxidation with heating rates of 10°C/min, 20°C/min or 50°C/min
- Combustion with heating rates of 10°C/min, 20°C/min or 50°C/min

The flow of gases was set to be in total around 50 ml/min. In the case of pyrolysis, it was a flow of nitrogen, in the case of combustion it was a flow of air and in the case of partial oxidation a mixture of both gases in total giving flow at the level of 50 ml/min.

The experiments were performed with both temperature conditions: non-isothermal and isothermal, since when temperature which was desired was reached it was carried on for some time at constant temperature.

2.4 Calculations

Calculations regarding kinetics and thermal analysis were carried out in Excel software. After this part of thesis, simulation of biomass gasification with application of Gibbs reactor has been carried out in Chemcad software.

2.4.1 Curve fitting

To study kinetic parameters of given feedstock method of curve fitting has been used. There were 3 pseudo components distinguished: water, hemicellulose (cellulose) and lignin. The kinetic parameters corresponding to the thermochemical conversion of these three components were estimated separately, as follow:

1. As first, masses of three pseudo components were estimated according to TGA graphs of mass at given time vs. time or temperature
2. The rates of components’ decomposition were estimated using Arrhenius equation written using a
The reference temperature, as in equation (1):

\[ \frac{d m_i}{dt} = ri = k_{ref}(T) \exp \left(-\frac{E_a}{R T_{ref}}\right) \times m_i \]

Symbol \( k_{ref}(T) \) stands for rate constant at reference temperature, while \( E_a \) means activation energy [cal/mol], \( R \) gas constant [cal/mol*K]. \( T_t \) stands for temperature at given time [K] and \( T_{ref} \) was set to be 298 K. Symbol \( m_i \) means mass of the sample at given time.

3. The change in mass was computed by integrating equation (1) using the Euler’s method.

\[ m_i \Delta t = m_i + \frac{d m_i}{dt} \times \Delta t \quad (2) \]

Symbol of \( m_i \) is a mass of sample at given time and \( \Delta t \) time step equals to 0.001.

4. The fourth step referred to calculating total modeled weight, which was performed as follow:

\[ m_{\text{total modeled weight}} = m_{\text{water}} + m_{\text{hemicellulose+cellulose}} + m_{\text{lignin}} \]

5. The objective function for the fitting was calculated using the error arising from the difference between experimental material’s weight and total modeled weight. The error was used as an objective function for Solver application to obtain the best fitting curve via changing values of \( k \), \( m_i \) and \( E_a \) parameters for all pseudo components. The optimization was carried-out using a non-linear least square fitting method.

\[ \text{Error} = \sum_{j=1}^{N} (m(\text{experimental}) - m(\text{total modeled weight}))^2 \quad (4) \]

6. Finally, curve’s fitting quality was estimated. To do so, the following formula was applied [54]:

\[ \text{Fit} \% = 1 - \left( \frac{\sigma}{\left(\frac{d m_i}{dt}\exp\right)_{\text{max}}} \right) \times 100\% \quad (5) \]

Symbol of \( \sigma \) is standard deviation of error values.

### 2.4.2 Modeling of kinetic for pyrolysis, partial oxidation and combustion

A kinetic model for pyrolysis mode is developed in this thesis using the curve fitting methodology described in sub-chapter 2.4.1. Kinetic parameters within this zone were modeled using formula (1).

In the case of combustion mode, the influence of oxygen partial pressure had to be taken under consideration.

\[ \frac{d m_i}{dt} = ri = k_{ref}(T) \times m_i \times P_{O_2} \quad (6) \]

Partial pressure is set at the level of \( P_{O_2}=0.2 \) atm.

In general, kinetic parameters of material’s partial oxidation were modeled with equation (6). To minimize error, in some cases of low oxygen partial pressure, the kinetics were modeled with following formula:

\[ \frac{d m_i}{dt} = ri = k_{ref}(T) \times m_i \times P_{O_2} + k_{ref}(T)_{p} \times m_i \]

Symbol of \( k_{ref}(T)p \) stands for rate constant obtained in pyrolysis mode.
Partial oxidation is in these cases treated as a combination of pyrolysis and combustion modes, where partial pressure of oxygen used in the model was equal to the one set in the experiment. As mentioned before used partial pressures of oxygen were 18%, 15%, 10%, 5%, 2.5%

2.5 Thermal analysis of experiments

Thermal analysis was carried out to estimate what kind of reactions may occur within experiments and consequently what may be the products. The pattern of estimation is as follow,

1. Identifying exo- and endothermal peaks (at what time or temperature they occur)
2. The amount of heat evolved at given time was calculated by dividing heat flow (mW) by derivative weight (mg/min)
3. The heat at peak point was taken as one to compare with heats of assumed reactions

Sucrose was chosen as representative of cellulosic components, because when compared reactions occurring with sucrose to the reactions running with xylose and glucose, it seemed heats of sucrose reactions are the most compatible with heats evolved during experiments. Next step was to estimate how far the oxidation/decomposition goes, by comparison to the closest heats of certain reactions to the heat noted in the experiment.

2.6 Gasifier modeling

Modeling is performed based on a design provided by Institute for Chemical Processing of Coal (Poland). The gasifier is an updraft moving bed reactor that has 400 mm of internal diameter and 900 mm of height. [4] The thermal power that may be obtained is around 60 kWt. In the design, there are three air inlets: at the top, to prevent upcoming gases from becoming stagnant, in oxidation zone in the middle and at the bottom to provide additional combustion of remaining char. When performing gasifier mathematical modeling, reactions were assumed to run according certain patterns based on thermal analysis resulting in products predictions and ultimate analysis of material.

It also has to be assumed as the authors of [5] did, that the char is presented as graphitic carbon, the process of gasification is isobaric. Based on sample’s ultimate analysis the formula of modeled biomass at as received state basis could be obtained. Despite the fact, there was a content of sulfur, nitrogen and other species, they were omitted to simplify representative formula. So, the basic biomass pattern was as follow: CxHyOz, where x, y and z stands for molar ratio of these three species within sample. Next step of the model was performing the simulation of the process. This was carried out by means of Chemcad CC: STEADY STATE software.

3. Results and discussion

In this chapter, results of experiments and modeling are presented. In the first part, the results of pyrolysis mode experiments with different upper temperatures are discussed along with an analysis of arising char’s reactivity. Then, the modeling of the kinetics of different gasifier’s zones is discussed to provide the whole description of sample’s behavior when pyrolyzed, oxidized and partially oxidized.
In the second part the simulation of an actual gasifier in Chemcad software is presented.

4.1 Biomass char reactivity

The char’s reactivity results are as follow:

Fig. 1 Char’s reactivity versus temperature for char obtained through pyrolysis at 300°C.

Graph placed above is so called burning profile of char. [6] The peaks have two characteristic temperatures: ignition temperature and peak temperature. Ignition temperature is associated with changes in burning profile after negative deflection from organic matter combustion to positive deflection. [6] Whereas, peak temperature is related to the maximum combustion rate and means the completion of event occurring in the whole process. [6]. First peak occurring presented on the Fig. 1 can be associated with charring process, since char obtained through former pyrolysis might have some remaining volatile matter. Its ignition temperature and peak temperature are respectively 243°C and 322°C, with peak mass loss rate being 0,14 mg/min.

Second peak is associated with char’s combustion showing ignition temperature being 376°C and peak temperature 443°C. Peak rate accounts for 0,43 mg/min.

3.2 Kinetic parameters

For graphic representation of curve fitting quality, graph of experimental mass and modelled mass evolution curve with time will be presented.

Fig. 2 Weight evolution of experimental mass of sample and modelled mass of sample for 20% of oxygen in the gasifying agent with heating rate 10°C/min

The graph shows good curve fitting quality, as the gray curve (modeled weight) coincides with orange one (experimental). The k and Ea kinetic parameters were fitted to the global equation with application of excel add-in, Solver, in the way it allowed to obtain the lowest possible error. Thereafter, the results of curve fittings and obtained kinetic parameters are going to be presented in the form of tables.
Tab: 1 Rate constants at reference temperature k_{ref} [1/min] an activation energies E_a [cal/mol] for three pseudo components (moisture, hemicellulose and lignin):

<table>
<thead>
<tr>
<th>Component</th>
<th>k_{ref} [1/min]</th>
<th>E_a [cal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>moisture</td>
<td></td>
<td></td>
</tr>
<tr>
<td>hemicellulose</td>
<td></td>
<td></td>
</tr>
<tr>
<td>lignin</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From the tables placed above it may be observed, that for water and hemicellulose values of kinetic parameters increase with increasing heating rate. This may happen due to endothermic nature of these components evaporation and decomposition respectively. When it comes to lignin we can notice, that values of activation energy drops when heating rate changes from 20°C/min to 50°C/min. That may mean when performing decomposition of lignin, mostly exothermic reactions occur, such as dewatering. It can be also noticed, that values of kinetic parameters change drastically for pyrolysis, which nature of reaction is different than under oxidizing conditions. The rate of reaction is higher for pyrolysis. Fitting quality averages are 97.8 %; 98.5 % and 98.8 % for 10°C/min, 20°C/min and 50°C/min.

It can be noticed, that the higher heating rate, the higher fitting quality. Overall, it can be deduced, that curve fitting quality is at proper level.

It was also examined, how the rate constants change with the applied partial pressures of oxygen during the experiments. The scale of rate constant axis was changed to logarithmic scale to provide more meaningful data. Reaction rate constant depends on reaction pattern according to which material runs. Due to that, they are expected to be independent on partial pressure of oxygen applied.

![Fig. 3 Relation between modeled rate constant and applied partial pressure of oxygen for lignin](image)

The reaction rate constants stay the same within all oxygen’s contents in the gas flowing apart from pyrolysis mode. It is expected to be changed, because of pyrolysis’ reaction different from oxidation pattern.
3.3 Mass evolution of sample and thermal analysis

Graphs of mass evolution versus time or temperature allow to see material’s behavior when different operating conditions are applied. In the research, based on sample’s mass loss there were distinguished three pseudo components: moisture, hemicellulose, lignin. Three components refer to curve inflections, where the change in curve’s slope is observed. First, component undergoing transformation is moisture, that evaporates up to 160°C [7]. As second component, that undergoes decomposition is hemicellulose and cellulose. It decomposes within range of temperature 220°C-400°C [7]. Third and last constituent decomposes within temperature range 400°C- 900°C [7]. Chart placed below presents change in mass evolutions with different oxygen partial pressures applied. It can be noted, that higher share of oxygen in gasifying agent causes higher decomposition line slope. That means transformation of biomass components goes faster with higher oxygen content in the gas phase. That refers to oxygen adsorption on biomass surface, that speeds up its decomposition.

Fig. 4 Sample’s mass evolution with time for heating rate 20°C/min for different oxygen partial pressures

To get to know more deeply in which direction reactions, that occur within the process go, there are going to be compared DSC results (specific heat evolved in the process) with heats of the reactions, that are assumed to run. This allows, to understand how far process goes and what might be possible products. Because of lignin’s more complex nature to evaluate its possible reaction routes could be burdened with high error. This is why the focus is on first peak of specific heat evolved in the process, so on cellulosic component. It has to be set, what kind of reactions may occur, which heats are to compare with an actual heat evolved. This going to be presented in the form of table.

Tab: 2 Possible routes, that reaction of sucrose may run in the process

<table>
<thead>
<tr>
<th>No.</th>
<th>Formula</th>
<th>Compound</th>
<th>kJ/kg mass lost</th>
<th>Reaction's formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C6H12O6</td>
<td>sucrose</td>
<td>51.4451</td>
<td>C6H12O6-&gt;6CO+6H2O</td>
</tr>
<tr>
<td>2</td>
<td>C6H12O6</td>
<td>sucrose</td>
<td>1588.01</td>
<td>C6H12O6-&gt;12CO3+12H2O</td>
</tr>
<tr>
<td>3</td>
<td>C6H12O6</td>
<td>sucrose</td>
<td>7590.2</td>
<td>C6H12O6+13CO+12H2O</td>
</tr>
<tr>
<td>4</td>
<td>C6H12O6</td>
<td>sucrose</td>
<td>2515.94</td>
<td>C6H12O6+14CO+11H2O</td>
</tr>
<tr>
<td>5</td>
<td>C6H12O6</td>
<td>sucrose</td>
<td>2187.7</td>
<td>C6H12O6+8CO+11H2O</td>
</tr>
</tbody>
</table>

Heats of reactions per mass lost were calculated based on heats of formation and heats of combustion of present compounds. Mass lost was taken as experimental one. Assumed products are carbon monoxide, carbon dioxide, water, hydrogen and carbon. It must be clarified before presenting the result, that evolved heat is contributed by different reactions heats release, with certain ratio. To see, what it looks like when compared to an actual specific heat, the graph will be presented below.
Fig. 5 Specific heat curve presented for heating rate 10°C/min combustion mode with lowered Y axis scale and series of reactions' heats

Thanks to these results it may be assumed what are possible reactions occurring and with what ratios. Although, this assumption will be burdened with error, since occurring products were not confirmed by appropriate experiment, but it gives an initial picture of an actual state and allows for further application in simulation process for the purpose of this thesis.

The closest to the actual specific heat evolved is reaction giving carbon monoxide and water as products. This suggests, that the highest share in the evolved heat has release of CO$_2$ and H$_2$O from cellulosic component of given biomass. However, it is likely to happen, that there is release of CO and H$_2$ occurring during the process. As it can be noticed in the part of gasification simulation, some amounts of methane are assumed too, based on the results of gasification process in Institute of Coal Chemical Processing in Zabrze. [8]

3.4 Simulation of gasification process

In case of biomass sample used in the research there were given stoichiometrics obtained through weight % basis for each biomass species. Primarily, components of the process had to be selected. As the product streams, knowing composition of sample and taking into consideration the DTG curves presented before, as well as knowing the reactions which occur in the biomass gasification process, the product species had been assumed, as follow: CO, CO$_2$, CH$_4$, H$_2$O, H$_2$, C, C$_6$H$_6$ and C$_{10}$H$_8$ as tar representation. Feed stream has been separated into two streams: oxygen and nitrogen joint stream calculated from air flow, the same as used in case of running experiment by Institute of Coal Chemical Processing in Poland, i.e. 21 Nm$^3$/h, taking oxygen content in the air as 21 vol.% and nitrogen content as 78%, and examined biomass material, also with flow being the same as while running experiment in the Institute of Coal Chemical Processing in Poland, i.e. ca. 15 kg/h. Oxygen and nitrogen joint flow stream was set to be at the room temperature, i.e. 298 K and 101325 Pa pressure at the beginning. Before reaching mixer by oxygen flow, it passed through compressor to increase pressure of gas flow and simultaneously its temperature. Compression was done according to adiabatic (isentropic) model. Pressure at the outlet has been set 10 bar with efficiency of the device being 90%. Stream temperature increased to 596,9 K and enthalpy carried with it was 8,3 MJ/h. Biomass feed was at the room temperature, i.e. 298 K and carried enthalpy - 87,7 MJ/h. Both streams were directed to mixer with output pressure 10 bar. After mixing, joint stream had 596,9 K and enthalpy - 79,4 MJ/h. Next step was to set data for Gibbs reactor itself. It required thermal mode specification, where specified heat duty has been chosen. Calculated by software heat duty was 9.2 MJ/h. Reaction phase was chosen as vapor or mixed phase. Moving to optional
specifications pressure in the reactor was chosen 10 bar. Lambda factor for air flow specified as 0.4. In the case of convergence parameters temperature of the process range was specified, being 800-1400 K. The software calculated overall heat of reaction, being -33.4 MJ/h. Char is a residue in gasification process, but as its representative in this simulation carbon was chosen, in its graphite form as modification of carbon. Below is going to be presented chart of simulation flowsheet in Chemcad software.

![Diagram of gasification process](image)

**Fig. 6** Scheme of gasification process taking place in Gibbs reactor. Downstream processes were not considered. Respective streams are signed in squares: 1. Oxygen feed stream before compression, 2. Product stream, 4. Oxygen feed stream after compression, 5. Biomass feed stream, 6. Mixed feed stream. Respective units are signed in circles: 1. Gibbs reactor, 3. Mixer, 4. Compressor.

<table>
<thead>
<tr>
<th>Institute’s results</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂, vol.%</td>
<td>CO₂, vol.%</td>
</tr>
<tr>
<td>H₂, vol.%</td>
<td>H₂, vol.%</td>
</tr>
<tr>
<td>CO₂, vol.%</td>
<td>CO₂, vol.%</td>
</tr>
<tr>
<td>CH₄, vol.%</td>
<td>CH₄, vol.%</td>
</tr>
<tr>
<td>H₂O, vol.%</td>
<td>H₂O, vol.%</td>
</tr>
<tr>
<td>N₂, vol.%</td>
<td>N₂, vol.%</td>
</tr>
</tbody>
</table>

As a default set, the program takes conversion as 100 %, what may be observed in outlet stream composition, since the software assumed no carbon and oxygen in the output. When compared these results to the ones obtained in the Institute of Coal Chemical Processing, it is to be noted, that there are differences in the composition. This table shows, that assumption of species being present in the outlet gas was appropriate. However, the results to not match each other entirely. It may be noticed, that obtained through software yield of water is way lesser than one retrieved in the Institute. The same situation is in case of methane and carbon dioxide. Hydrogen, in turn, was obtained through software in amount much higher than presented in the column referred to yields obtained in the Institute.

4. Conclusions

When it comes to char’s reactivity graph, there can be noticed two peaks: one probably referring to charring process, since some volatile matter left after pyrolysis and the second one referring to char combustion. Temperature when first peak starts to arise is 243°C and its peak temperature is 322°C with peak rate being 0,14 mg/ml. Temperature of
combustion peak are 376°C and 443°C respectively with peak rate 0.43 mg/ml.

Moving to kinetic parameters and the results for rate constants at reference temperature (298 K), it can be observed, that in case of hemicellulose and lignin these parameters do not differ much among each species. However, when it comes to water there might be seen some slight differences due to its fitting sensitivity caused by relatively small amount of water as one of three pseudo-components.

Differences are also observed in case of pyrolysis mode, what is reasonable, since lack of oxygen in the environment changes rates of reaction. In this experiment mode activation energy has tendency to fall, but kinetic constant to rise when compared to modes with oxygen presence in the gas.

When it comes to discussion about weight evolution, the common thing for all conditions applied in the experiment is that, there can be distinguished three pseudo components: moisture, hemicellulose (cellulose) and lignin, based on changes in slopes of curves. Depending what conditions are applied, if it is pyrolysis, partial oxidation or oxidation mode, various slopes of curves are obtained.

Kinetic parameters were obtained through the method based on curve fitting. To the experimental weight of sample curve, by changing values of kinetic parameters, modeled sample’s weight curve was fitted. The quality of that model was checked. According to its results, the method of curve fitting appears to give reasonable results. Average of fitting quality is roughly 98 %, what shows that method may be applied as reasonable tool for kinetic parameters studies. When it comes to performed simulation the results obtained through Chemcad do not coincide as it should with results obtained in the Institute of Coal Chemical Processing in Poland. This happens due to many reasons. In this simulation, using just one reactor it was not possible to perform calculations with regard to three air streams inlets, like it is in actual GazEla gasifier. Due to certain limitations, the simulation has been performed in the way presented in this report. However, in case of Gazela gasifier the last air inlet placed at the bottom of the reactor was added to provide complete combustion of remaining char.

5. References


