Biomass pyrolysis for liquid fuels and chemicals: A review

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Biomass pyrolysis produces fuels and chemicals. Pyrolysis (conventional, fast and flash) can produce solid (charcoal), liquid (tar and other organics), and gaseous products (H₂, CO₂, CO) between 625 and 775 K. Charcoal yield decreases as temperature increases. Production of liquid products is maximum between 625-725 K.

Keywords: Biomass, Kinetics of pyrolysis, Pyrolysis, Liquid fuels, Thermal degradation

Introduction

Biomass energy, a clean renewable energy, has gained momentum with depletion of fossil fuels¹⁻⁵. Consumption of biomass as energy⁴,⁶⁻¹¹ has been increasing: developing countries, 35; and world 14%. Average majority of biomass energy¹²,¹³ is produced from: wood and wood wastes, 64; municipal solid waste, 24; agricultural wastes, 5; and landfill gases, 5%. Biomass mainly consists of carbon, hydrogen, oxygen and nitrogen¹⁴. Analysis of dry wood yields: carbon, 52; oxygen, 40.5; hydrogen, 6.3; and nitrogen, 0.4%. Proximate analysis¹,⁶,¹² of wood and bark respectively is as follows: volatile matter, 80.0, 74.7; fixed carbon, 19.4, 24.0; and ash, 0.65%, 1.3%. Woody biomass consists of cellulose (C₆H₁₀O₅)ₙ, hemicelluloses such as xylan (C₅H₈O₄)ₘ, and lignin [C₉H₈O₃(OCH₃)₀.₉₋₁₇]₀.₉₋₁₇ in trunk, foliage, and bark. Cellulose + hemicellulose contents¹⁵,¹⁶ are more in hardwoods (78.8%) than softwoods (70.3%), but lignin is more in softwoods (29.2%) than hardwoods (21.7%).

Biomass can be converted to energy by physical, biological and thermochemical processes. Physical processes are grinding, drying, filtration, pressing, extraction, and briquetting¹⁷. Biological processes (anaerobic digestion and fermentation) are most suitable for high moisture herbaceous plants (vegetables, sugar cane, sugar beet, corn, sorghum, and cotton), marine crops and manure¹⁸.

Pyrolysis

Pyrolysis is a thermochemical change of organic matter in a heated enclosure, usually in an oxygen-absent or very low oxygen level environment. Such processes had been studied using primarily coal, peat, and lignocellulosic materials (wood sludge) as feedstock during 1970’s¹⁹. Thermochemical conversion of biomass using catalytic and non-catalytic pyrolysis as well as gasification aims at maximization of the production of energetically exploitable liquid and gaseous products²⁰. It can be utilized for energy conversion of low moisture herbaceous (small grain field residues) biomass and woody (wood industry wastes and standing vegetation not suitable for lumber) matter¹,⁶,²¹. Thermal conversion of biomass leads to useful products and simultaneously contributes in solving pollution problems arising from biomass accumulation²².

Principles and Technical Assessment of Biomass Pyrolysis

Pyrolysis of biomass is the production of solid (charcoal), liquid (tar and other organics), and gaseous products (H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆) as sources of chemicals and energy¹²,²³,²⁴ (Fig. 1). Pyrolysis liquids are complex mixtures of oxygenated aliphatic and aromatic compounds²⁵ (Table 1). Tars contain resins, intermediate carbohydrates, phenols, aromatics, aldehydes, their condensation products and other derivatives. Pyrolyigneous acids contain methanol (CH₃OH, 50%), acetone (C₃H₆O), phenols and water. Pyrolysis of biomass can yield methanol, which arises from methoxyl
groups of uronic acid and from the breakdown of methyl esters and/or ethers from decomposition of pectin-like plant materials. Acetic acid comes from acetyl groups of hemicelluloses.

Yield of products resulting from biomass pyrolysis can be maximized as follows: i) Charcoal — a low temperature, low heating rate process; ii) Liquid products — a low temperature, high heating rate, short gas
Table 2 — Results of pyrolysis of solid waste and analysis of gas content

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>Char wt%</th>
<th>Liquid wt%</th>
<th>Gas wt%</th>
<th>CO₂ vol%</th>
<th>O₂ vol%</th>
<th>HC vol%</th>
<th>CO vol%</th>
<th>Others vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>507</td>
<td>97.0</td>
<td>0.0</td>
<td>3.0</td>
<td>22.1</td>
<td>0.6</td>
<td>32.5</td>
<td>13.8</td>
<td>31.0</td>
</tr>
<tr>
<td>584</td>
<td>76.2</td>
<td>15.9</td>
<td>7.9</td>
<td>18.9</td>
<td>3.9</td>
<td>32.9</td>
<td>18.2</td>
<td>26.1</td>
</tr>
<tr>
<td>655</td>
<td>62.9</td>
<td>25.4</td>
<td>11.7</td>
<td>34.5</td>
<td>0.4</td>
<td>21.4</td>
<td>10.6</td>
<td>33.1</td>
</tr>
<tr>
<td>683</td>
<td>49.0</td>
<td>35.0</td>
<td>16.0</td>
<td>45.1</td>
<td>4.6</td>
<td>20.9</td>
<td>9.4</td>
<td>19.7</td>
</tr>
</tbody>
</table>

residence time process; and iii) Fuel gas — a high temperature, low heating rate, long gas residence time process. Production of liquid products is maximum between 625 - 725 K. Charcoal yield decreases as the temperature increases. At higher temperatures (Table 2), the rather large molecules present in liquid and residual solid are broken down to produce smaller molecules, which enrich gaseous fraction. At higher temperatures (>575 K), cellulose depolymerizes and produces mainly levoglucosan. High heating rates provide shorter time for the dehydration to take place, which results in a more unstable material left for depolymerization to primary volatiles and therefore lower final char yields. Catalytic pyrolysis (773 K) is the most attractive way of reducing the problems (polymerization, high viscosity, corrosivity) of liquid pyrolysis products. It produces mainly bio-oil, which can be used as fuel or as a source of valuable chemicals.

Initial degradation reactions include depolymerization, hydrolysis, oxidation, dehydration, and decarboxylation. Destructive reaction of cellulose starts at below 325 K and is characterized by a decreasing polymerization degree. The glucose chains in cellulose are first cleaved to glucose and, in a second stage, glucosan is formed by the splitting off of one molecule of water. If wood is completely pyrolyzed, hemicelluloses breaking down first at 470-530 K, followed by cellulose at 510-620 K, with lignin being the last component to pyrolyse at 550-770 K.

Dehydration reactions around 473 K are primarily responsible for thermal degradation of lignin. Cleavage of α- and β- aryl-alkyl-ether linkages occurs between 423 - 573 K. Around 573 K, aliphatic side chains start splitting off from aromatic ring. Finally, carbon-carbon linkage between lignin structural units is cleaved at 643–673 K. Degradation reaction of lignin is an exothermic reaction, with peaks occurring between 498 and 723 K; the temperatures and amplitudes of these peaks depend on whether samples were pyrolyzed under nitrogen or air. Hwang & Obst gave a detailed study on the reaction mechanism of β-O-4 lignins pyrolysis (Fig. 2).

Pyrolysis Methods for Fuels and Chemicals

Pyrolysis can be divided into three subclasses: i) conventional (carbonization); ii) fast; and iii) flash. Conventional pyrolysis consists of slow, irreversible, thermal decomposition of organic components in biomass resulting in high charcoal continent. Fast pyrolysis is associated with tar, at low temperature (675-775 K), and/or gas, at high temperature. At present, the preferred technology is fast or flash pyrolysis at high temperatures with very short residence times.

Fast Pyrolysis

Main goal of fast pyrolysis (thermolysis) is to convert solid biomass (40-75%, dry basis) into a liquid bio-oil. Of remaining biomass, 10-20% is converted into char and 10-30% into an uncondensable gas. In fast pyrolysis, biomass is rapidly heated to high temperature in the absence of oxygen to yield: char, 10-15; bio-oil, 70-80; and light gas, 10-15%. Bio-oil is a liquid mixture of oxygenated compounds containing carbonyl, carboxyl and phenolic functional groups. Bio-oil consists of: water, 20-25; water insoluble pyrolytic lignin, 25-30; organic acids, 5-12; non-polar hydrocarbons, 5-10; anhydrosugars, 5-10; and other oxygenated compounds, 10-25% (Table 4).

There are three main methods of achieving fast pyrolysis: i) Ablative pyrolysis, in which biomass is pressed against a heated surface rapidly moves and melts at the heated surface and leaves oil film that evaporates; ii) Fluid-bed and circulating fluid-bed pyrolysis, which transfers heat to biomass by a mixture of conversion and conduction; and iii) Vacuum pyrolysis, which has slow heating rates but removes pyrolysis products as rapidly as in the pre-liquid product. Commercial
Table 3 — Range of the main operating parameters for pyrolysis processes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Conventional pyrolysis</th>
<th>Fast pyrolysis</th>
<th>Flash pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis temperature, K</td>
<td>550-950</td>
<td>850-1250</td>
<td>1050-1300</td>
</tr>
<tr>
<td>Heating rate, K/s</td>
<td>0.1-1</td>
<td>10-200</td>
<td>&gt; 1000</td>
</tr>
<tr>
<td>Particle size, mm</td>
<td>5-50</td>
<td>&lt; 1</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>Solid residence time, s</td>
<td>450-550</td>
<td>0.5-10</td>
<td>&lt; 0.2</td>
</tr>
</tbody>
</table>

Table 4 — DynaMotive bio-oil properties

<table>
<thead>
<tr>
<th>Biomass feedstock</th>
<th>Pine/spruce 100% wood</th>
<th>Pine/spruce 53% wood, 47% bark</th>
<th>Bagasse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture, wt%</td>
<td>2.4</td>
<td>3.5</td>
<td>2.1</td>
</tr>
<tr>
<td>Ash, wt%</td>
<td>0.42</td>
<td>2.6</td>
<td>2.9</td>
</tr>
<tr>
<td>Bio-oil (solids, &lt; 0.10; ash, &lt; 0.02)</td>
<td>2.3</td>
<td>2.4</td>
<td>2.6</td>
</tr>
<tr>
<td>pH</td>
<td>23.3</td>
<td>23.4</td>
<td>20.8</td>
</tr>
<tr>
<td>Water, wt%</td>
<td>24.7</td>
<td>24.9</td>
<td>23.5</td>
</tr>
<tr>
<td>Lignin, wt%</td>
<td>1.20</td>
<td>1.19</td>
<td>1.20</td>
</tr>
<tr>
<td>Density, kg/l</td>
<td>16.6</td>
<td>16.4</td>
<td>15.4</td>
</tr>
<tr>
<td>Calorific value, MJ/kg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- 20°C</td>
<td>73</td>
<td>78</td>
<td>57</td>
</tr>
<tr>
<td>- 80°C</td>
<td>4.3</td>
<td>4.4</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Fig 2 — Pyrolysis products of β-O-4 lignins

\[
\text{R} = \text{H, V-G} \\
\text{R} = \text{OCH}_3, V-S
\]

\[
\text{R} = \text{H, G} \\
\text{R} = \text{OCH}_3, \text{DMP}
\]

\[
\text{R} = \text{H, T-G} \\
\text{R} = \text{OCH}_3, \text{T-S}
\]

\[
\text{R} = \text{H, C} \\
\text{R} = \text{OCH}_3, \text{DMP}
\]
operation of fast pyrolysis has been achieved from a transport or circulating fluid-bed system, and for food and flavoring products. Fast pyrolysis in combination with an engine produces up to 15 MWe energy with low capital and electricity costs as compared to other thermal conversion processes.

Flash Pyrolysis

Flash pyrolysis can be used for the production of bio-oil. Conversion of biomass to crude oil (efficiency, up to 70%) under flash pyrolysis processes can be used in engines and turbines. Some problems such as poor thermal stability and corrosivity of the oil need to be overcome. Upgrading by lowering the oxygen content and removing alkalis by hydrogenation and catalytic cracking of the oil may be required for certain applications. Liquid fraction of pyrolysis products consists of an aqueous phase containing a wide variety of organo-oxygen compounds of low molecular weight and a non-aqueous phase containing insoluble organics (mainly aromatics) of high molecular weight. This phase is called as bio-oil or tar. Ratios of acetic acid, methanol, and acetone of aqueous phase were higher than those of non-aqueous phase.

In reactors using flash pyrolysis, quality and stability of the produced oil are strongly affected by char/ash content of bio-oil. Besides, known problems concerning solid particles in the bio-oil, char fines will catalyze repolymerization reactions inside the oil resulting in a higher viscosity. Char can be removed by filtering the oil, which is disadvantageous because alkali, concentrated in the char, will dissolve in bio-oil due to high acidity (pH 2-3). Another option is hot gas cleaning of the oil vapor.

Pyrolysis Kinetics

Actual reaction scheme of biomass pyrolysis is extremely complex because formation of over 100 intermediate products. Thermogravimetric analysis (TGA) is the general approach applied to determine the weight loss of pyrolyzed samples at various reaction temperatures. Quantitative methods can be applied to TGA curves (Fig. 3) to obtain kinetic parameters of thermal degradation, which govern reaction rates. Kinetic parameters usually include activation energy, preexponential factor and order of reaction, which describe the rate of mass loss and heat of combustion of volatiles. However, these kinetic parameters are highly dependent on heating rates, sample size and atmosphere and thus
should only be considered as effective kinetic parameters having no physical significance. A wide range of values have been reported for both activation energy and preexponential factor, assuming a simple first order reaction following Arrhenius equation

$$m = A\exp(-E/RT)$$

...(1)

where $m$, mass loss rate; $A$, preexponential factor; $E$, activation energy; $R$, universal gas constant; and $T$, temperature (K).

Kinetic modeling of pyrolysis has been reviewed by several authors (Fig. 4). In global one-step model, decomposition of the fuel into volatiles (no distinction made between gases and tar) is described in one first-order reaction. This approach does not provide any information about the product yield distribution. Often, a constant distribution between products is assumed by introducing stoichiometric coefficients. In this case, the mass balance for tar is given by

$$\frac{d}{dt} m_T = a k_1 (m_S - m_{C_\infty})$$

...(2)

where $m_T$, mass of total tar; $m_S$, mass of solid fuel; $m_{C_\infty}$, mass of final char yield; $a$, stoichiometric coefficient for tar and the reaction constant $k_1$, whose temperature dependence is usually described by the Arrhenius equation

$$k_1 = k_0 e^{-(E_A/RT)}$$

...(3)

where $k_0$, frequency factor; $E_A$, activation energy; $R$, general gas constant; $T$, temperature.

With the assumption of parameters $m_{C_\infty}$ and $a$, final yield of tar is preset and does not depend on the operating conditions. Models with parallel reactions account for different proportions of the main components of woody fuels by assuming independent reactions of cellulose, hemicellulose and lignin. However, these models have the same disadvantage as the one step models, that is, the product distribution has to be preset by stoichiometric coefficients.

**Conclusions**

Pyrolysis has been used for commercial production of a wide range of fuels, solvents, chemicals and other products from biomass feedstocks. Yield of products resulting from biomass pyrolysis can be maximized as follows: i) Charcoal — a low temperature, low heating rate process; ii) Liquid products — a low...
temperature, high heating rate, short gas residence time process; and iii) Fuel gas — a high temperature, low heating rate, long gas residence time process.

References

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