BIOMASS PYROLYSIS – THE PREDICTION OF THE PROCESS BEHAVIOUR BASED ON THE CHEMICAL STRUCTURE OF FUEL

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Abstract

Fossil fuel consumption has increase in last few decades. This leads to many environmental problems, like global warming, the deplete ozone layer etc. The use the low-emission fuels like biomass is of growing importance. Biomass is widely available in nature. The International Energy Agency assume that heat, cold and electricity production based on biomass has the potential to provide 10% of the world's primary energy supply by the 2035. Additionally, biofuels can replace up to 27% of world transportation fuel by 2050.

Biomass can be converted into fuels via biochemical and thermochemical routes. The main thermochemical process are combustion (and co-combustion), gasification and pyrolysis. Among it, the pyrolysis has been developed as a promising method to produce liquid and gaseous fuels and char. Due to complexity of biomass structure, pyrolysis process is correlated with the chemical composition of it.

Paper presents the prediction of the influence of the chemical composition of straw and wood on process pyrolysis behaviour. Cellulose, hemicellulose and lignin content of analysed biomass on possible yield of pyrolysis products was investigated.

Keywords: *straw, wood, sewage sludge, pyrolysis, chemical composition*

1. INTRODUCTION

In December 2018 during the UNFCCC COP24 in Katowice, Poland the Governments have adopted a robust set of guidelines for implementing the landmark 2015 Paris Climate Change Agreement. This landmark was defined as a limitation of the global temperature increase "well below 2 °C above pre-industrial levels" [1]. The most important issue in that context is the CO_2 emission reduction on a global scale. Nevertheless, the dominant role of fossil fuels (oil, gas and coal) in energy system does not help this solution. In Figure 1 shares of the primary energy is presented [2] with the perspective to year 2040.

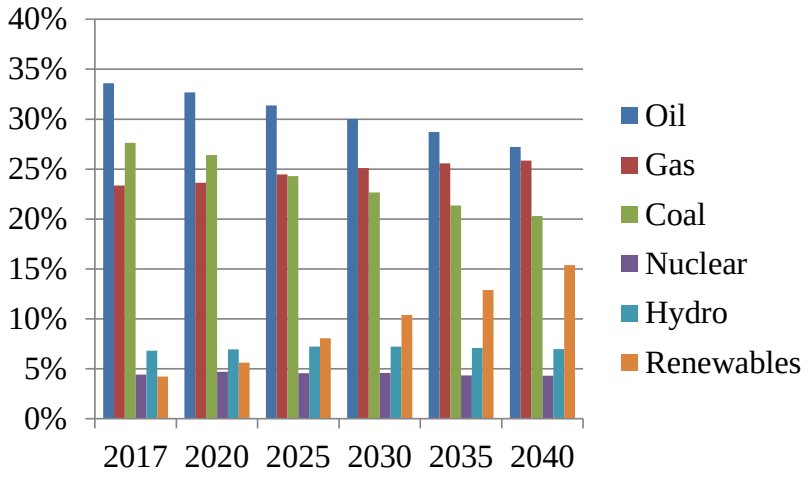


Fig. 1. Shares of primary energy [2]

Analysing data presented in this Figure, it can be concluded that the transition to a lower-carbon energy system continues, with renewable energy and natural gas gaining in importance relative to oil and coal.

Of all sources identified as "renewables", the potential of bioenergy is widely recognized and bioenergy offers opportunities to address questions other than energy. Thus, bioenergy can be a solution for matters relating to economic, national, environmental and political security [3].

1.1. Biomass potential

Biomass for energy purposes comes from various sources such as agriculture, forest and waste. Figure 2 gives an overview about the source of biomass usable for energy production.

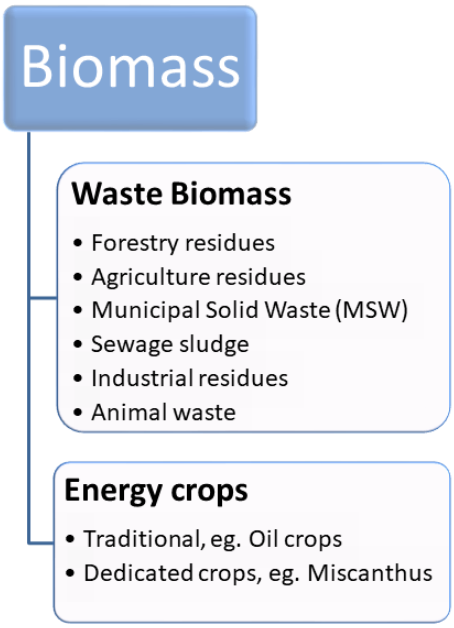


Fig. 2. The types of biomass

Analysing information presented in Figure 2, it can be concluded that the biomass for energy is divided into two main parts: (1) waste biomass and (2) energy crops. In the group of waste biomass, it stands out: (1) forestry residues of forest harvest (branches, tops, stumps etc.) and residues of wood industry (bark, sawdust etc.), (2) agriculture residues (straw from cereals, cultivation waste etc.), (3) municipal solid waste, (4) sewage sludge, (5) industrial residues (black liquor from paper manufacturing etc.) and (6) animal waste (poultry chicken etc.). Three sources of it are characterizing the highest potential: Agricultural, Forestry and Waste [4].

The European Union (EU) provides the potential of these biomass sources in perspective for the year 2050. In Table 1 this potential is presented.

Agriculture	6452
Forestry	4856
Waste	975
Sum	**12283**

Table 1. Bioenergy potentials for the EU28 in 2050, PJ [5]

1.2. Waste-to-Energy concept

This potential can be utilize applying various technologies. The biochemical and thermochemical routes can be possible. In Figure 3 the possible routes of Waste-to-Energy (WtE) idea are presented.

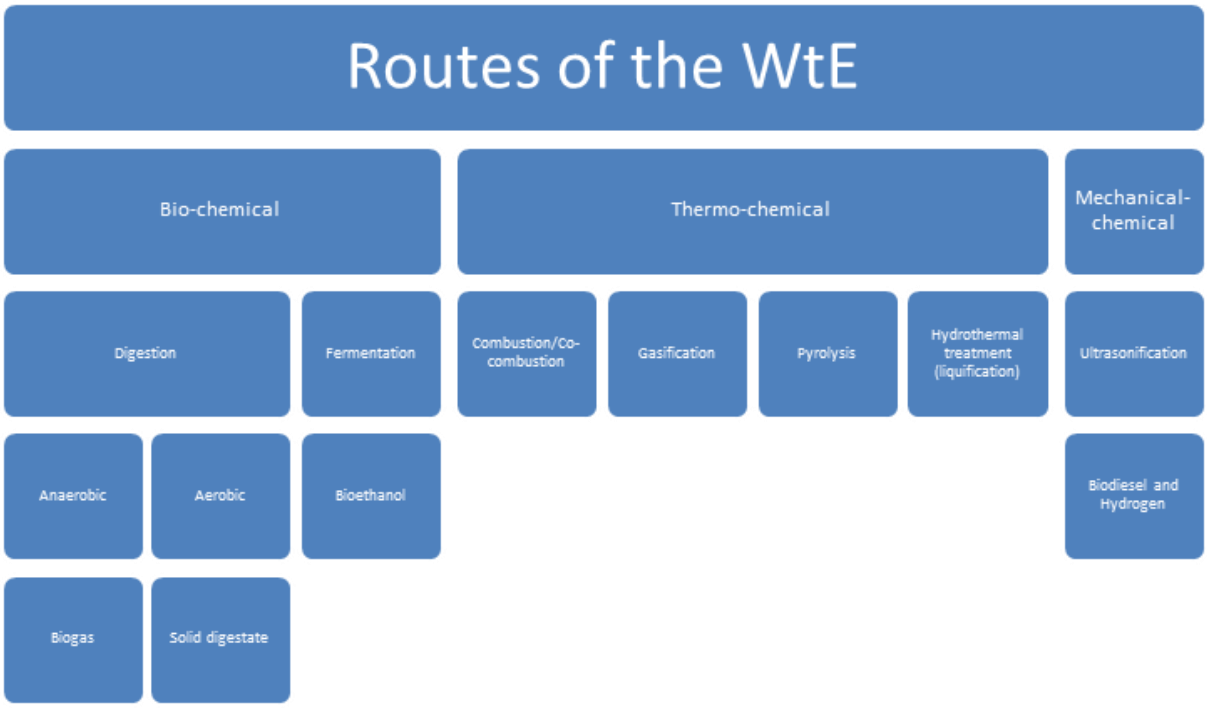


Fig. 3. WtE conversion routes [6]

Biochemical technologies are suitable for materials with the carbon/nitrogen ratio lower than 30 and moisture higher than 30%. It means that it is a group of methods for materials such as organic fraction of municipal solid waste and aquatic crops [7]. Rest of the biomass types can be proceeded via thermochemical routes.

1.3. Thermochemical processes

There are 3 main thermochemical methods: combustion (and co-combustion), gasification and pyrolysis. These methods are presented in Figure 4.

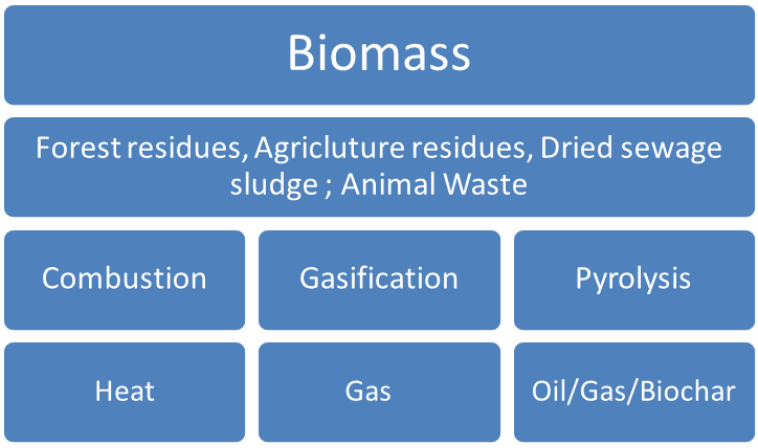


Fig. 4. The main thermochemical method of biomass utilization

Combustion process is just the oxidation of the combustible components of waste biomass feedstock. This process is the most conventional WtE in the heat and electricity production. There are three main combustion technologies: grate, fluidized bed and rotary kilns [8]. The combustion of waste biomass has to meet many challenges. One of the biggest challenges is the GHGs emission. Other pollutants (VOCs – volatile organic compounds, CO, fly ash and others) are also problematic. The heat generated by this method must be exploited immediately for heating or power generation. Other than the obvious problem of low efficiency, this approach also leads to ash emission.

Gasification and pyrolysis are two of the most researched processes for thermochemical biomass conversion.

Gasification is the process of converting a solid fuel into a gas by treating the solid fuel in a generator with oxygen, air, or steam, or by other gasification factors [9]. The process uses a smaller amount of gasification agent, resulting in higher in energy recovery efficiency and limited formation of pollutants.

Unlike combustion, pyrolysis takes place in the total absence of oxygen. Pyrolysis has gained practical attentions due to the advantages including short processing time, lower energy requirement, effective heat transfer and selective heating [10]. It is a thermal decomposition of the organic material into gas, liquid and solid. The yield of the individual fractions depends on the speed of the process. Generally, it should be stated that slow pyrolysis (heating rate 0.1-1°C·s^{-1}) leads to the maximization of the solid fraction and the fast (heating rate 1-100°C·s^{-1}) – maximization of the liquid fraction [11]. Some authors indicate the flash pyrolysis (heating rate 500-900°C·s^{-1}) but it is not obvious, however, which fraction in this case is dominant [12].

The complexity of biomass structure is correlated with the yield of fraction produced during the process.

Paper presents the prediction of the influence of the chemical composition of straw and wood on process pyrolysis behaviour. Cellulose, hemicellulose and lignin content of analysed biomass on possible yield of pyrolysis products was investigated.

2. MATERIALS AND METHODS

2.1. Biomass composition

Biomass consists of many different components. Therefore, it is very difficult to understand their influence on biomass pyrolysis. The most important material of the majority biomass material which was mentioned in Figure 2 is lignocellulose. Lignocellulosic biomass is composed of three major components: cellulose, hemicellulose, lignin. Schematically it is presented in Figure 5.

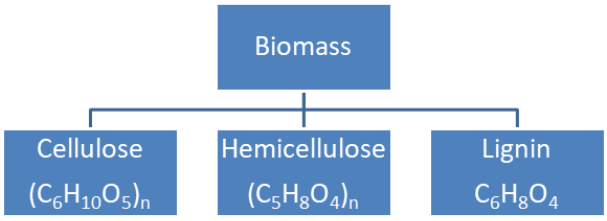


Fig. 5. Three main components of biomass

Cellulose is a linear macromolecular polysaccharide. It consist a long chain of glucose units. Cellulose is the most abundant organic polysaccharide in the Earth. The degree of polymerization n is up to 15,000. Hemicellulose is composed of short-chain heteropolysaccharides. The degree of polymerization “n” is much lower in comparison to cellulose and is up to 200. In contrast to the

carbohydrates structure of cellulose and hemicellulose, lignin has an aromatic matrix. Lignin is mainly an amorphous tridimensional polymer composed of p-coumaryl, coniferyl and sinapyl alcohols [13].

2.2. Analysed fuels properties

The chemical composition of the analysed fuel is presented in Table 2.

Fuel	Cellulose, %mass	Hemicellulose, %mass	Lignin, %mass	Ash + Extractives, %mass
Cereal Straw Pellets	49.7	31.6	6.0	12.7
Wood residue Pellets	54.8	11.8	25.5	7.9

Table 2. The chemical composition of the analysed fuel

The cellulose content was determined using Seifert method. It involves the removal of lignin and hemicelluloses from the wood under the influence of acetylacetone, hydrochloric acid and dioxane mixture. The lignin content was determined using Tappi method. It involves oxidizing the lignin in a measured amount of material with a known quantity of standard permanganate under acidic conditions. The unused permanganate is then determined by titration with sodium thiosulfate solution, and the lignin content is calculated. The hemicellulose content was provided based on the sodium chlorite method.

The cellulose dominate in the chemical structure of the analysed samples. Correa and Kruse [14] said that the simplified average composition of lignocellulosic biomass consist of 40-55 %mass cellulose fibres. The results presented in Table 1 confirm this information. Additionally, it should be concluded that cellulose content in wood is higher in comparison to straw.

This results are also confirmed by Wang et al. [15] because it was confirmed that corn straw cellulose content is equal to 42.2 %mass and poplar wood cellulose content was equal 49.0 %mass.

The hemicellulose content in cereal straw is almost three times higher in comparison to wood. This element content in straw is equal to 31.8 %mass. This value is confirmed by other authors [14] who confirmed that the hemicellulose content in straw is the range of 15.0 %mass for wheat straw up to 39.0 %mass for oat straw. Nevertheless, the achieved hemicellulose content for wood is much lower (11.8 %mass) in comparison to literature results. For example Basu said [12] that hemicellulose content in the lignocellulosic wood is in the range of 15 to 35 %mass. In the other hand, there are examples of wood based biomass, like Albizia, which is characterized much lower content of hemicellulose – 6.7 %mass [14]. Summarizing, the hemicellulose content of analysed wood is similar to other examples of this type of biomass.

The lignin content in analysed feedstock is equal to 6.0 %mass for straw and 25.5 %mass for wood. This element content is wood is comparable with the values taken from the literature. Dhyani and Bhaskar reported that the average lignin content in hardwood is equal to 21.7 %mass and average lignin content in softwood is equal to 28.0 %mass [7]. The lignin content of analysed straw is much lower in comparison to date reported in literature. This value suggest that analysed pellets are a mixture of cereal straw with additives like grass. This hypothesis can be proved by the results achieved by [7]. The lignin content for Orchard grass is equal to 4.7 %mass, for Reed canary grass – 7.6 %mass, for Switchgrass – 6.0 %mass.

The analysed feedstock character can be summarized using the simplified formulas (1)-(3).

$$Cellulose_{wood} > Cellulose_{straw} \quad (1)$$

$$Hemicellulose_{wood} < Hemicellulose_{straw} \quad (2)$$

$$Lignin_{wood} > Lignin_{straw} \quad (3)$$

3. RESULTS

3.1. Influence of individual components on pyrolysis behaviour

The glucose units in cellulose are not very strong and are characterizing by high tendency to cleave under high-temperature conditions. Therefore, the cellulose structure degrades sharply during the pyrolysis. It was confirmed in [15], who found that the temperature correspond to the maximum loss on TG analysis of cellulose samples. Taking into consideration analysed feedstock it can be assumed that wood will be more effective degrade in pyrolysis conditions in comparison to straw. This observation was confirmed by the Greenhalf et al. but in the terms of lignin content [16]. He found that higher lignin content causes higher temperatures during the thermal decomposition. Additionally, other authors discussed the role of hemicellulose in pyrolysis [17]. It was concluded that the hemicellulose is much more stable than others components in biomass. Moreover, the depolymerisation steps can be completely blocked during the pyrolysis due to specific products formation from hemicellulose like acetic acid. The analysed straw is characterizing by much higher content of hemicellulose in comparison to wood. This feature confirm the higher tendency to thermal decomposition of wood. The influence of individual components of biomass on pyrolysis process can be summarized on diagrams presented in Figure 6.

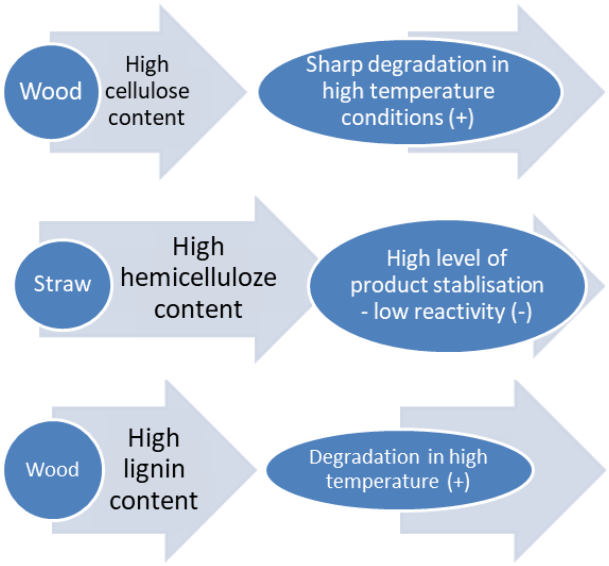


Fig. 6. The influence of individual components of biomass on pyrolysis process

3.2. Interaction between components

The interaction between cellulose, lignin and hemicellulose and its influence on pyrolysis process is a very complex issue. The presence of lignin influence on carbonization of pyrolysis product of cellulose [18]. It was conclude that lignin promote the degradation of cellulose into lighter fractions.

The cellulose block the char formation from lignin but – on the other hand – promote the phenol formation from lignin. Additionally, the presence of lignin decrease the amount of fraction from hemicellulose pyrolysis (negative influence lignin on hemicellulose) and the hemicellulose decrease the amount of fraction from cellulose pyrolysis (negative influence of hemicellulose on cellulose) [19]. This tendency is very positive taking into consideration the wood features as a feedstock for pyrolysis. It is characterized by high content of lignin and cellulose. Thanks to it, the lignin can effectively block the formation of stable product of hemicellulose pyrolysis and finally the formation of products which can incidentally block the cellulose pyrolysis is prevented. As a results, the prediction is very positive – the effective decomposition of biomass into valuable chemicals (gas and liquid) is achieved.

CONCLUSIONS

1. Pyrolysis of lignocellulosic biomass has a potential to provide environmental friendly future fuels.
2. The potential of lignocellulosic biomass, including wood biomass and agricultural residues are promise taking into consideration an alternative fuel production
3. Thermochemical characteristic of three major components of biomass, namely cellulose, hemicellulose and lignin has strong influence on the pyrolysis process.
4. The high content of cellulose and lignin in wood can promote effectiveness of the pyrolysis process.
5. The interactions of biomass components during pyrolysis are significant, especially the influences of lignin to hemicellulose and hemicellulose to cellulose; the negative influence of lignin on hemicellulose and hemicellulose on cellulose is presented.

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