THE USE OF MICROWAVE PYROLYSIS FOR BIOMASS PROCESSING

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Summary

The method of processing biomass of various kinds by microwave-assisted pyrolysis has been presented. The fast pyrolysis process, characterized by rapid heating of the feedstock in the absence of oxygen and rapid cooling of the volatile intermediate reaction products, is one of attractive liquid biofuel production methods. However, the pyrolysis still requires improvements as regards the process yield, quality of liquid biofuel products, and energy efficiency of the process as a whole. The microwave pyrolysis is a promising attempt to solve these problems thanks to the fast and efficient feedstock heating through the effect of "microwave dielectric heating". Before proceeding to the main topic of this paper, the conventional pyrolysis has been characterized. At such a technology, the thermal energy necessary to heat the feedstock is transmitted from the surface into the depth, which is rather a slow process. This has been followed by a presentation of the microwave pyrolysis, where the microwave radiation causes fast and productive bulk heating of the material having been finely ground (the material should be susceptible to the action of microwaves). Moreover, a review of materials used as microwave radiation absorbers, biomass types, and methods of biomass preparation for the process, as well as qualitative and quantitative characteristics of the pyrolysis products obtained, i.e. raw bio-oil, which should be subjected to further processing, and synthesis gas ("syngas") have been provided.

Keywords: pyrolysis, microwave pyrolysis, biomass, bio-oil, syngas

Introduction

Pyrolysis, gasification, and direct combustion are the three major thermochemical methods of biomass processing into fuels, chemicals, and electric energy, with pyrolysis playing a predominating role among them. The pyrolysis finds application not only as a separate biofuel production process but also as an initial stage of the combustion and gasification processes.

Pyrolysis is a process of thermal degradation of selected feedstock in an oxygen-free environment. In result of the pyrolysis, the feedstock is transformed into liquid, gaseous, and solid products. The pyrolysis is considered to consist of two basic stages. The first one includes the processes of feedstock degassing (carbonization) and thermal

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decomposition of main feedstock components (dewatering, dehydrogenation, and decarboxylation). At the second stage, secondary reactions between solid and volatile products (e.g. polymerization or condensation) take place.

The course of the pyrolysis process is determined by many factors, which include the composition and fineness of grinding of the feedstock, feedstock heating rate, and residence time (i.e. the time of the feedstock being held in the reactor). Depending on the process temperature, heating rate, and reaction time, pyrolysis can be classified into three main categories: slow, fast and flash pyrolysis. It is difficult to characterize unequivocally individual pyrolysis categories and to assign specific classification criteria to each of them. Actually, two basic parameters, i.e. temperature and time, are chiefly used for this purpose. In most cases, the pyrolysis process is run at temperatures ranging from 400 °C to 1000 °C and the residence time is short, from several minutes for slow pyrolysis to less than 0.5 s for flash pyrolysis. The process parameters are selected depending on the types of the feedstock to be processed and of the product to be obtained. Low process temperatures and low heating rates conduce to the generation of large quantities of solid product, the fast pyrolysis at higher temperatures gives a lot of liquid product, and the flash pyrolysis at temperatures of about 900 °C is conducive to the generation of pyrolytic gases. The process efficiency is also affected by the catalysts used and the feedstock diversification often determines the specific pyrolysis method adopted.

The materials used as feedstock for the pyrolysis process are chiefly process wastes generated by the food-processing industry, agriculture, and forestry. This means that wood biomass (woodchips, tree branches, bark, wood shavings, and lignified plant stalks), agricultural biomass (lucerne, miscanthus giganteus, millet, cereal straw, fruit remains, seed shells, pomace, food wastes), waterborne biomass (e.g. algae), animal biomass (e.g. poultry-processing offal), sewage sludge, and paper industry wastes may be a source of the feedstock.

As mentioned previously, there are three final products of the pyrolysis process:

a) Solid carbon-containing residue (carbonization product), chiefly consisting of elemental carbon, unreacted organic compounds, and solid particles. The carbonization product may be utilized as a solid fuel granulated with another biomass type, as a raw material for the production of activated carbon, as a raw material for the generation of hydrogen-rich gas by gasification, or as a raw material for the production of catalysts with high specific surface area.

b) Pyrolytic oil (bio-oil), which is a mixture of organic and inorganic compounds and consists of a water fraction and an oil fraction. Pyrolytic oils contain carboxylic acids, alcohols, phenols, esters, aldehydes, ketones, and heterocyclic oxygen compounds. The water contained in the bio-oil chiefly comes from moisture content of the material, but may also be a product of the dehydration reaction that takes place during the pyrolysis process; therefore, the water content may vary within a wide range depending on the feedstock material and process conditions. The water fraction may contain acetic acid and phenols.

c) Pyrolytic gas, chiefly consisting of inflammable gases such as H_2, CO, CH_4, C_2H_2, or C_2H_4. It also contains smaller quantities of CO_2, SO_2, and NO_x. The pyrolytic gas may be directly burnt, used for the fuelling of gas turbines, and used for the production of synthesis gas ("syngas").

1. Microwave pyrolysis process

The biomass pyrolysis process consists of the following stages: feedstock receiving and storage; feedstock pre-treatment (e.g. drying or grinding); pyrolysis proper in an appropriate reactor; separation of solid residue (carbonization product and ash); vapour cooling and condensation; and bio-oil collection. Before the condensation, the pyrolytic vapours may be subjected to catalytic reforming in order to obtain adequate process selectivity in respect of the product preferred. A part of the carbonization product may be recovered and returned to the microwave reactor, where it would be used as a microwave radiation absorber and it would make it possible to recuperate a part of the heat. A part of the gaseous product may be burnt to provide thermal energy for the feedstock pre-treatment (e.g. drying).

The process of pyrolysis with a reactor heated by microwave radiation has been schematically shown in Fig. 1.

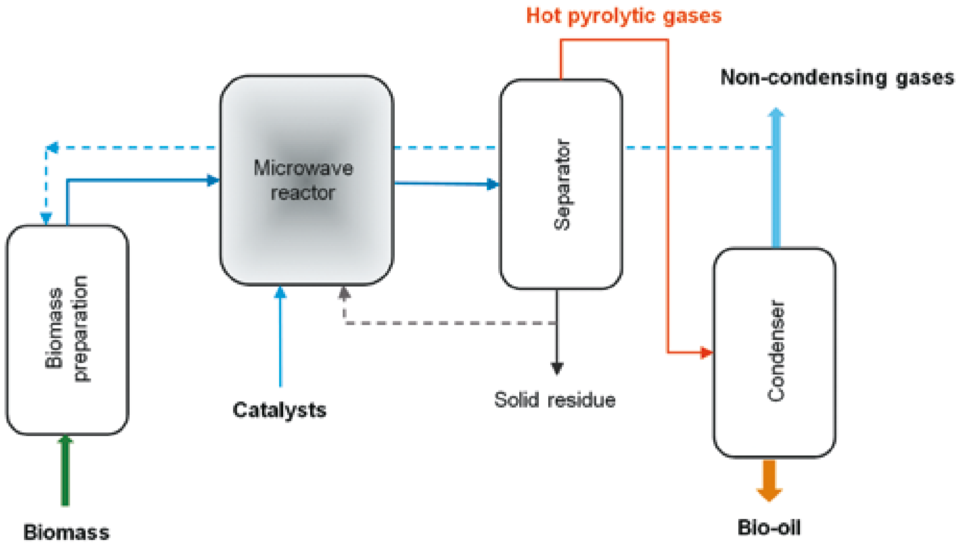

Fig. 1. Schematic diagram of the process of microwave-assisted pyrolysis of biomass

The basic difference between the processes of conventional pyrolysis and microwave pyrolysis lies in the feedstock heating method. At the conventional heating, thermal energy is transmitted from the surface into the depth of the feedstock by convection, radiation, and conduction. Such a process is relatively slow and requires the feedstock material to be finely ground. Instead, the microwave heating is a process of conversion of electromagnetic energy into thermal energy. The microwave energy induces molecular motion by dipole rotation and ion migration [1]. The microwave heating is a contactless and fast process, which takes place throughout the entire material volume; hence, the heat is generated throughout the entire volume of each material particle. The microwave heating is a selective process, i.e. the feedstock behaviour in a microwave field will not be identical for every feedstock material. The materials that are most susceptible to microwave radiation are dielectrics, such as e.g. water or methanol. Materials of this type are referred to as microwave radiation absorbers. The materials that have not dielectric properties will reflect or transmit microwave radiation without being heated. Therefore, the microwave pyrolysis may only be applied to the materials that fully or partly absorb microwave radiation, thanks to which the heating of such materials is possible.

An important process parameter is the residence time. The fast internal heating causes fast release of moisture from the feedstock and, in consequence, a growth in the volatile substances release area during the pyrolysis process. In a microwave reactor, volatile vapours (including small dipolar molecules) loaded with solid particles (chiefly fine particles of the carbonization product) can be easily heated by microwaves to a higher temperature. Therefore, the pyrolytic vapours must be carried away from the reactor very quickly for the secondary cracking of the vapours within the reactor space to be reduced and for water vapour to be removed.

The efficient microwave energy transfer to the feedstock in the bed is another important issue related to the microwave reactor. The reactor vessel, made of materials transparent to microwaves (e.g. quartz), must be carefully and appropriately cleaned, especially at continuous operation mode. The presence of solid particles in the vapours and fine carbon particles on the vessel walls will cause significant difficulties in introducing microwaves into the reaction environment or even local burns of the reaction vessel. It is also important that the feedstock mixture should be homogenous for the microwave field action in the reactor to be uniform and for the forming of ignition points ("hotspots") to be thus avoided. The hotspots may easily cause the loss of control of local pyrolysis temperature and, thus, of the entire reaction process.

When the pyrolysis reaction is completed, the solid residues, chiefly the carbonization product capable of catalysing the secondary cracking in the gaseous phase, must be efficiently separated. Even if the liquid reaction product has been cooled, the carbonization product conduces to the creation of stability problems because it speeds up the polymerization process and raises the viscosity of the liquid reaction product. For this reason, the carbonization product must be separated quickly and completely from the volatile vapours. This process may be carried out by means of solid substance separators such as those used for conventional pyrolysis. A liquid collector used at conventional pyrolysis may be used as well. The collector is necessary to condense the vapours and to collect the liquid phase. The liquid biofuel obtained from this process usually consists of two fractions, i.e. a water fraction and an insoluble oil fraction. The former one consists of water and water-soluble organic compounds, e.g. furfural, and the latter contains a mixture of the hydrocarbons that occur in oils and require further refining.

Optionally, the pyrolysis process may include catalytic reforming, which is employed to improve the process selectivity in respect of the product type preferred (liquid or gas) [2]. In this case, attention should also be paid to the vapour temperature and residence time in order to reduce the secondary vapour cracking.

2. The use of microwave pyrolysis to process various biomass types

The field of lignocellulosic biomass pyrolysis has already been quite well explored. It is generally known that each of the lignocellulose components decomposes with forming other substances, where cellulose and hemicellulose are volatile products and lignins make the solid residue. As mentioned at the beginning, however, other biomass types are now increasingly often used to obtain chemicals or fuel components. Growing importance has been recently attached to microalgae because of their numerous good points in comparison with lignocellulosic raw materials: they are characterized by higher process yield, they do not compete with traditional agricultural products as they can be grown on idle land or in wastewater treatment facilities, and they are extremely rich in oil, which sometimes makes more than 60 % of dry mass in some algae species [3]. Moreover, such materials are now used for this purpose as wheat, maize, and rice straw; coffee hulls; by-product of the distillation of alcohol from grain [4]; oil palm shells [5]; or sewage sludge produced at municipal sewage treatment plants.

2.1. Biomass from algae

Research on the microwave pyrolysis process, where fresh-water algae *Chlorella* sp. were used as the raw material, was carried out by Du Zhenyi *et al*. [6]. The algae were grown on a piloting basis in special photo-reactors. Before the pyrolysis process was started, the algal paste with about 85 % water content was dried. Since the algal paste insufficiently absorbs the microwave radiation, it was mixed with the carbonization product obtained from the first experiment with the pyrolysis process. The biomass thus prepared was subjected to pyrolysis at various values of the microwave heating power, i.e. 500 W, 750 W, 1000 W, and 1250 W, which corresponded to process temperatures of 460 °C, 570 °C, 600 °C, and 625 °C, respectively. The volatile substances involved in the reaction were cooled in five condensers by means of cooling water and the non-condensing gases were accumulated in special gasbags. The pyrolysis time was 20 min.

Table 1. Percentage yield of individual fractions, by mass, depending on the microwave heating power

Fraction **[% (m/m)]**	**Heating power [W]**			
	500	**750**	**1 000**	**1 250**
Oil fraction	26	**28.5**	25	17
Water fraction	21	20	20	22
Carbonization product	**28**	24	25	25
Gaseous phase	24	26.5	29	**35**

The percentage yield, by mass, of individual products of the pyrolysis process at various values of the heating power has been presented in Table 1. For the bio-oil fraction, the highest yield (28.5 %) was recorded for a microwave power of the order of 750 W. The highest and the lowest percentage of the gaseous phase (35 %) were obtained at a power of 1250 W and 500 W, respectively, while the latter power value simultaneously yielded the highest percentage of the carbonization product.

The yield of the water fraction remained on an approximately constant level of about 21 % in the power range examined. The bio-oil was found to contain aliphatic and aromatic hydrocarbons, phenols, indoles, and other nitrogen-containing compounds, polycyclic aromatic hydrocarbons, as well as oleic acid and its derivatives. The gaseous phase consisted of hydrogen, carbon monoxide, carbon dioxide, and light hydrocarbons, i.e. methane and ethane. With growing microwave power, the percentage of carbon dioxide decreased and the hydrogen and carbon monoxide contents increased. The highest concentration of the synthesis gas, also referred to as "syngas" (H_2 + CO) was 49.8 %.

Similar research on biomass obtained from algae *Chlorella vulgaris* was carried out by Hu Zhifeng *et al.* [7]. This research work included a number of microwave pyrolysis experiments with various substances being used as microwave absorption improvers. Apart from the carbonization product mentioned above, the researchers used activated carbon, calcium oxide CaO, and silicon carbide SiC. The catalysts were dried and ground so that the catalyst particles were identical in size to those of the algal biomass prepared for the process. The pyrolysis experiments were carried out at three values of the heating power, i.e. about 200°C, 600°, and 800°C, and the process time was 1200 s. All the catalysts used caused a significant increase in the pyrolysis temperature in comparison with that recorded for the pure algae feedstock, which resulted in an increase in the yield of the gaseous phase and a drop in the bio-oil percentage. Besides, it was noticed during the experiments that the activated carbon reduced the forming of solid pyrolytic residue.

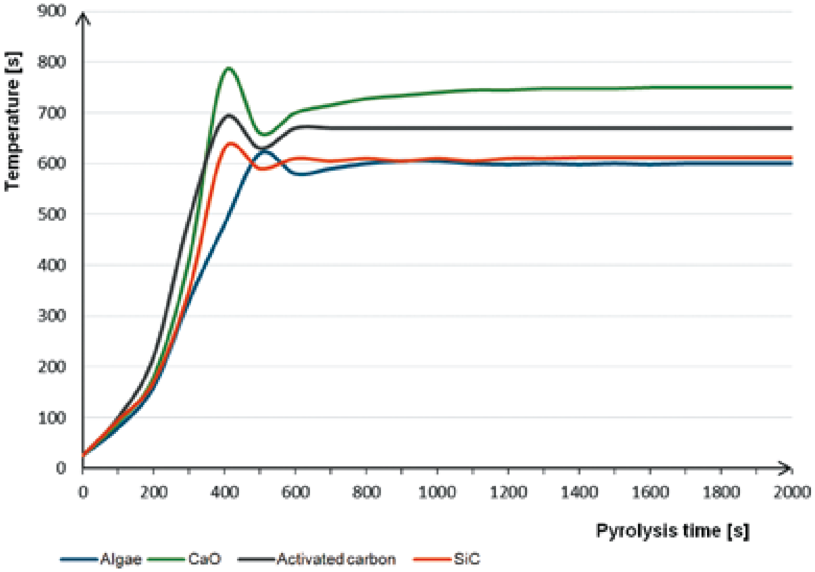

Fig. 2. The course of the microwave pyrolysis process depending on the absorber used

The time histories of the pyrolysis temperature show that the process may be divided into four stages. At the first stage, the process temperature grew with a relatively slow rate, the specimen was dried, and volatile components vaporized. The second stage was characterized by rapid growth in the process temperature. This is explained by the fact that the dry solid residue formed during the first stage conduced to the absorption of microwave radiation. At this stage, the bio-oil and gaseous fractions were also formed. At the third stage, a drop was observed in the process temperature because the formation of bio-oil and gas was an endoergic process. At the fourth stage, the temperature initially slightly rose and then it became stabilized, because the pyrolysis process was completed and heat was no longer taken over by the pyrolytic gases. A small amount of heat was still generated by the solid residue, which caused a slight temperature growth to a constant value resulting from the equilibrium achieved between the heat losses and the residual heat supply.

The experiments carried out by D. Beneroso *et al.* [8] have shown that a properly run process of microwave pyrolysis of algal biomass yields much more syngas ($CO + H_2$) than the conventional pyrolysis does. At a reaction temperature of the order of 800°C, a syngas yield of 87.7% (by volume) was achieved, as against 53.5% (by volume) of syngas obtained from a conventional pyrolysis process run in identical conditions. Conversely, the amount of carbon dioxide produced at the microwave pyrolysis was far less than that observed at the conventional pyrolysis.

2.2. Coffee hulls

Comparative examinations of the conventional pyrolysis and microwave pyrolysis of biomass consisting of coffee bean processing wastes have been presented in a publication by A. Dominguez *et al*. [9]. As the biomass, granulated coffee hulls obtained from the coffee bean treatment process were used. The experiments were carried out at temperatures of 500°C, 800°C, and 1000°C. The reaction time was 25 min. at the conventional pyrolysis and 20 min. at the microwave pyrolysis. The first pyrolysis experiment was performed to obtain a carbonization product that was then used at the next experiments as a microwave radiation absorber. As it is at every pyrolysis process, three product phases, i.e. solid, liquid, and gaseous phase, were obtained. The conventional pyrolysis yielded a larger amount of the bio-oil fraction than the microwave pyrolysis did; for the gaseous phase, an opposite dependence was observed. The quantities of the solid phase were comparable for both the process types.

The gaseous fractions obtained from the conventional and microwave-assisted pyrolysis processes comprised such components as hydrogen, carbon monoxide, carbon dioxide, methane, ethane, and ethene. The largest amounts of CO_2 were produced at the conventional pyrolysis; at the microwave pyrolysis, the main product was hydrogen, with carbon monoxide being ranked second. A comparison between the amounts of individual components of the gaseous phase obtained from the microwave and conventional pyrolysis processes run at temperatures of 500°C and 1 000°C has been presented in Fig. 3.

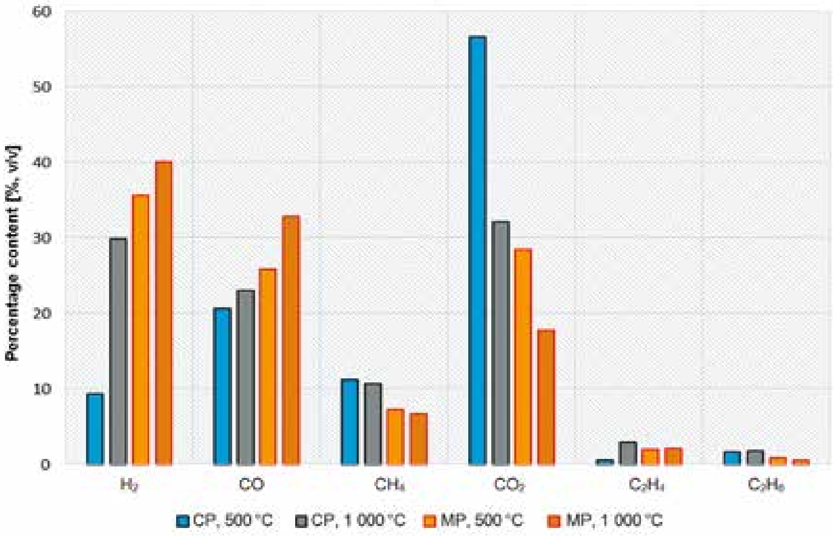

Fig. 3. Comparison between the volumes of gases yielded by the pyrolysis processes of both types at temperatures of 500°C and 1 000°C:
CP – conventional pyrolysis; MP – microwave pyrolysis

The amounts of the hydrogen and carbon monoxide yielded by the process increased with the process temperature. This finding did not depend on the pyrolysis type. In consequence, the syngas obtained from the conventional pyrolysis and microwave pyrolysis processes, in both cases carried out at a temperature of 1000°C, made 52.9 % (v/v) and 72.8 % (v/v) of the total pyrolytic gases, respectively. On the other hand, the amounts of CH_4 and C_2H_6 slightly decreased and the amount of C_2H_4 insignificantly increased with the process temperature. Presumably, this was caused by dehydrogenation of ethane to ethene and liberation of molecular hydrogen, which contributed to the growth in the syngas amount. The high concentrations of CO_2 and CO in the pyrolytic gases resulted from the deoxidation process that took place due to decarbonylation and decarboxylation reactions. It is presumed that the decrease in the CO_2 amount with rising temperature of the pyrolysis process may be related to the carbon gasification reaction, which in turn led to a growth in the production of CO. The research carried out by Raveendran et al. [10] has shown that the processing of potassium-reach biomass is conducive to the carbon gasification reaction and, thus, to a growth in the quantity of the carbon monoxide produced. The calorific value of the oil and gaseous fractions obtained from microwave pyrolysis is higher than that of these substances produced during the conventional pyrolysis process; only the calorific values of the solid residues are comparable with each other. For the microwave pyrolysis process run at a temperature of 1000°C, the calorific values of the gaseous phase, solid residue, and bio-oil are about 15 MJ/kg, about 24 MJ/kg, and about 34 MJ/kg, respectively.

The microwave pyrolysis process yields much more gaseous fraction than the conventional pyrolysis process does, regardless of the process temperature. The decline in the yield of the bio-oil fraction with rising process temperatures suggests that the microwave heating is conducive to the secondary cracking reaction, which leads to the obtaining of lighter products with shorter chains.

2.3. Wood biomass: Douglas-fir

The microwave pyrolysis of lignocellulosic biomass leads, as mentioned before, to the obtaining of liquid and gaseous fractions and a carbonization product (solid residue). Depending on the pyrolysis process conditions, biomass type used, and catalyst applied, a product having different quantitative and qualitative composition of individual fractions may be obtained.

Douglas-fir pellets were subjected to microwave pyrolysis at different temperatures (300–450 °C) and at different process duration time (4–12 min.), with activated carbon being added as a catalyst. The bio-oil obtained from the process contained aliphatic and aromatic hydrocarbons, phenols, furan derivatives, guaiacols, esters, and phenolic acids [11]. The maximum amount of phenolic compounds in bio-oil, of the order of 67%, was obtained when the pyrolysis process was run at a temperature of 315°C for 8 min., at an activated carbon-to-biomass ratio of 3:1. When the pyrolysis process was run without participation of activated carbon and at a process temperature of 400°C, considerable amounts of guaiacols (2 methoxyphenol and its derivatives), even of up to about 52%, were obtained. The phenols obtained may be used in the chemical industry for the synthesis of phenol-formaldehyde resins and the guaiacols may find application in the pharmaceutical industry.

By further processing of the bio-oil, esters may be obtained. The bio-oil upgrading process was carried out in a closed-type reactor, at a temperature of about 230°C, with powdered zinc being used as a catalyst. The reaction medium consisted of ethanol and formic acid. The formic acid-to-ethanol and catalyst-to-bio-oil ratios were 1:1 and 5:1, respectively. When the reaction was completed, the reactor was cooled to the room temperature. The ethanol was vaporized from the reaction mixture in a rotary evaporator at a temperature of 60 °C. After the evaporation, the upgraded bio-oil was separated by decantation.

An identification procedure indicated that the upgraded bio-oil contained about 83 % of long-chain esters of fatty acids (with more than 10 carbon atoms in a molecule). This seems to be a good method for the obtaining of a valuable fuel biocomponent in the form of esters of fatty acids from non-oily raw materials.

3. Recapitulation

The examples presented to illustrate the use of microwave-assisted pyrolysis show that the pyrolysis of biomass may be an effective method for the obtaining of substrates for chemical and fuel industry applications. Regardless of the type of the biomass processed, a several common features of the pyrolysis processes may be distinguished, i.e. fast heating to high temperatures, short process time, and use of activated carbon or another substance as a microwave energy absorber. By appropriate setting of process conditions and selection of an appropriate type of the biomass to be processed, two major utility products, i.e. synthesis gas (syngas) and bio-oil, may be obtained. The raw bio-oil should be subjected to further processing, e.g. hydrogenation or esterification, and only then it may find application as a usable fuel component. The syngas obtained from the pyrolysis may be used as a substrate for chemical synthesis reactions. The microwave pyrolysis is a more productive syngas production method than the conventional pyrolysis. Thanks to the fact that microwaves can heat materials throughout the entire material volume, the course of the pyrolysis process can be modified and the composition of the process products can be controlled.

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