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Microwave Pyrolysis of the Spruce Sawdust for Producing High Quality Syngas

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Currently, a demand for alternative energy sources to replace traditional fossil fuels is growing. Although there are still found new reserves or mining techniques – e.g. Shale gas, searching for new substitute solutions is needed. Waste from the wood processing industry could be serving as a potential feedstock for energy production, e.g. hydrogen.
Microwave irradiation is an alternative heating method and has already been successfully applied to biomass pyrolysis. Compared with convectional heating processes where heat is transferred from the surface to the core of the material through conduction driven by temperature gradient, microwaves induce heat at the molecular level by direct conversion of the electromagnetic energy into heat, and therefore, they can provide uniform internal heating for material particles. Microwave pyrolysis promotes the heterogeneous catalytic reaction and produces greater concentration of syngas and hydrogen in the product gas than convectional pyrolysis. In addition, it is easier for a rapid start-up and shut-down.
The biomass is mixed with a suitable material which significantly absorbs microwave radiation for generation of intensive heating in the reactor. In our case, the spruce sawdust was mixed with char from previous pyrolysis of spruce sawdust. Char from the pyrolysis of sawdust also contains small amounts of ash (up to 5 %), which includes alkali metals and alkaline earth metals. The presence of such char has a catalytic effect on the pyrolysis process, the cracking of tars and phenolic compounds to the simple gases (H_2 and CO).
In this work the influence of various parameters of microwave pyrolysis of spruce sawdust (microwave power, particle size, ratio of sawdust and char, pyrolysis duration, etc.) was studied to maximize the yield of hydrogen, or syngas. Experiments were carried out in a conventional microwave oven with power up to 1 kW. The influence of parameters on the quantity of products (gas, liquid and solid), but also the amount of waste water in the liquid condensate were studied.

1. Introduction to microwave pyrolysis

Waste materials are being generated every year around the world. Some of these wastes are effectively collected and recovered for use as an energy source or chemical feedstock, while some are simply discarded or burned in ways that can pollute the environment. The combustion of waste results in the release of greenhouse gas such as CO_2 that contributes to climate change. As a further matter, the cleaning of the flue gases produced is expensive due to strict regulations on atmospheric emissions. For that reason, research has moved towards developing a better solution, from an environmental and economic point of view, by thermally reprocessing the waste materials into more useful energy forms using thermal conversion processes. Thermal conversion involves the use of a wide range of thermal decomposition processes to decompose waste materials into smaller molecules that can be used as energy source or deposits for the synthesis of new applicable substances, e.g., hydrocarbon wastes are decomposed to produce syngas which can be used as a fuel directly, or converted into liquid fuel through the Fischer–Tropsch process (Dry, 2002).
Production of energy from wood biomass is as old as humanity itself. In the recent 20 y there has been enormous progress in research of torrefaction, pyrolysis and mainly in gasification of the biomass. Products from conventional pyrolysis of the biomass are gas known as syngas, liquid condensate known as bio-oil and char termed as bio-char. Pyrolysis techniques have been developed as an alternative to treat and convert

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waste materials to products suitable for use as a potential energy source (Bridgwater, 2012). The main pyrolysis advantage is the potential to recover both the energy and chemical value of the waste by generating potentially valuable products. The oil and gaseous products with a high calorific value are generated, and the produced char can be used as a substitute for carbon black.

Most of the articles dealing with convection pyrolysis of biomass are focused on bio-oil production. Only some works deal with the possibility to produce high-quality syngas (H_2+CO) or hydrogen alone. For this purpose, the most appropriate technology seems to be microwave pyrolysis.

Microwave pyrolysis is a relatively new process and was initially developed by Tech-En Ltd. in Hainault, UK (Holland, 1995). Microwave heating is performed at frequencies of 915 MHz (λ = ~33 cm) and 2.45 GHz (λ = ~12 cm) as specified by international agreement (Meredith, 1998). This thermal treatment in a microwave-heated bed of particulate-carbon has been shown to be an effective method of recovering and recycling chemicals present in wastes. In particular, microwave-heated processes show a distinct advantage in providing rapid and energy-efficient controlled heating compared to conventional technologies, and thus facilitating increased production rates. As a result of microwave heating, the waste material is thermally cracked in the absence of oxygen into smaller molecules. The resulting volatile products are either condensed into an oil product or collected as incondensable gaseous products.

Microwave heating combined with the use of carbon material has been applied, carbon materials are good microwave-absorbents that show high capacity to absorb and convert microwave energy into heat; the dielectric loss tangent (tan δ) of carbon materials such as activated carbon, is either comparable to or higher than the tan δ of distilled water (~0.1), which is commonly known as a very good microwave-absorbent (Menéndez, 2010).

Microwave heating represents a unique way of heating where the heating effect arises from the interaction of electromagnetic wave with the dipoles within the material being heated. Principally, three mechanisms are responsible for the microwave heating. By such heating mechanisms, heat is generated within the material rather than from an external source, thereby giving a more efficient heating process compared to conventional surface heating with respect to even distribution of heat and easier control. In addition, high temperatures and heating rates can be obtained through microwave heating (Lam et al., 2012), and it shows remarkably high conversion efficiency of electrical energy into heat (80 % – 85 %). Microwave heating combined with the use of carbon materials has recently been applied in pyrolysis processes to treat a variety of materials, e.g. biomass. The results of the composition of the products show a similarity with the products after gasification. Due to the high temperatures the process leads to the destruction of tar substances to the basic gases (H_2, CO, CH_4).

2. Materials and methods

The waste spruce sawdust from sawmill was used as a material for syngas production. For the sample proximate and ultimate analysis were carried out (see Table 1). For the determination of moisture content W, ash A and volatiles matter A thermogravimetric analyser TGA - 601 was used according to the standards ČSN 44 1377, ČSN ISO 562 and ČSN ISO 1171. Elemental analysis was performed with the use of the unit LECO CHSN628, working on the principle of gas chromatography.

Table 1: Ultimate and Proximate analysis

Component	wt. %	Component	wt. %
C	51.75	Moisture	0.90
H	6.09	Volatile	80.12
N	0.96	Fixed Carbon	18.38
O	40.60	Ash	0.65

The carbonaceous material from convectional spruce sawdust pyrolysis was used as a microwave absorbent, The carbonaceous material contain more than 90 wt. % of carbon and approximately 3 wt. % of ash. This material was separated with the use of sieves on the size: >1.6, 1.6-0.63, 0.63-0.125 and <0.125 mm.

2.1 Experimental device

Laboratory apparatus assembled for the purpose of experiments is shown in Figure 1. A sample with an appropriate mass was placed into the prepared flask. The flask was gas-tightly closed, inserted into the conventional microwave oven with power up to 1 kW and connected to the rest of the components of the device. For purging the flask nitrogen was used as an inert medium. The pyrolysis gas was cooled with water (the condensate was captured in a condensate flask) and cleaned in five gas washing bottles (water, 3x acetone and water). Prior to the collection of process gas the gasometer was included. The gas samples were taken discontinuously into gas sampling bags. The selected gaseous components were analysed by gas chromatography (methane, ethylene, propane, hydrogen, carbon monoxide and carbon dioxide).

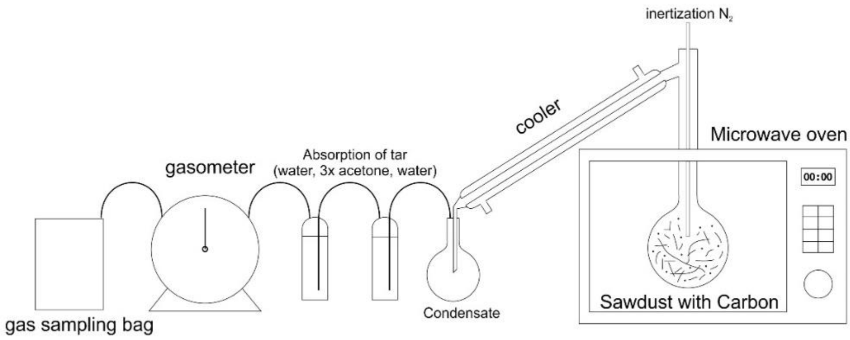

Figure 1: Laboratory microwave apparatus

2.2 Mass balance

The mass balance of the pyrolysis tests was determined by weighing the particular products from the pyrolysis (gas, liquid and solid) and from gas composition. The input material was a mixture of 50 g of spruce sawdust (dried with 1 wt. % of water) with 10 g of carbonaceous material.

2.3 Analysis of gaseous products

Analysis of the pyrolysis gas was performed with the use of the Agilent 7890A gas chromatograph with flame ionization detector (FID) and thermal conductivity detector (TCD). For separation of gaseous components the Micropacked column (2 m x 0.53 mm) was used.

3. Results and discussion

Most authors use for their experiments the ratio of the absorbent material to input material 1:5, which is a 16.67 wt. %. This ratio was used for experiments in our laboratory too. It was found that with increasing content of the absorbent of microwave radiation the quantity of pyrolysis gases increases and the amount of solid residue decreases. The content of liquid condensate remained about the same. These results correspond with work of Wang et al. (2015). The spruce sawdust was dried to the 1 wt. % of water. Process time of microwave pyrolysis was 20 min. for each experiment. The main problem in experiments is measurement of process temperature. The material of thermocouple at the high temperature (probably more than 600 °C) is high absorbed of electromagnetic irradiation, so it is not possible to measure temperature inside of reactor. The temperature measurement by IR cannot be used, because glass flask has a significant different temperature than the material inside. That is the reason why the temperature of experiments in the results is not listed.

3.1 Effect of moisture on the quality and the quantity of gas products

The moisture of material is very important parameter in pyrolysis or gasification process. The dry sawdust has 1 wt. % of water; the wet sawdust has 37 wt. % of water. The power of microwave was 440 W. The carbonaceous particle with size of 0.63 – 1.6 mm was used. The composition of gases is listed in Table 2.

Table 2: Gas content from dry (1 wt. % of water) and wet sawdust (37 wt. % of water)

Dry	vol. %	Wet	vol. %
H_2	25.4	H_2	32.7
CO	37.3	CO	32.5
CO_2	21.8	CO_2	20.7
CH_4	12.8	CH_4	9.8
C_2H_4	2.36	C_2H_4	1.9

The dried sawdust produced gas only 0.4 dm^3(gas)/g, while the wet produced 0.53 dm^3/g. The higher content of hydrogen in the case of wet sawdust is connected with water-gas shift reaction, and decomposition of light hydrocarbons. This result is supported by the fact that water is used as a gasification medium. On the other side, in the several minutes after start was sawdust dried in microwave and when the content of water decrease to some level, the pyrolysis was started. Further, the amount of condensate is relative high and with high content of water.

3.2 Effect of particle size (carbonaceous material) on the quality and the quantity of products

The particle size of carbonaceous material is very important parameter in microwave process and has a significant effect on the pyrolysis process (Ren, 2012). It was measured, that the syngas volume increased with decreasing of particle size (carbonaceous material). Comparison between particle size bigger than 1.6 mm and smaller than 0.125 mm is shown in Figure 2. It can be seen that the main syngas production is only during the first 10 minutes.

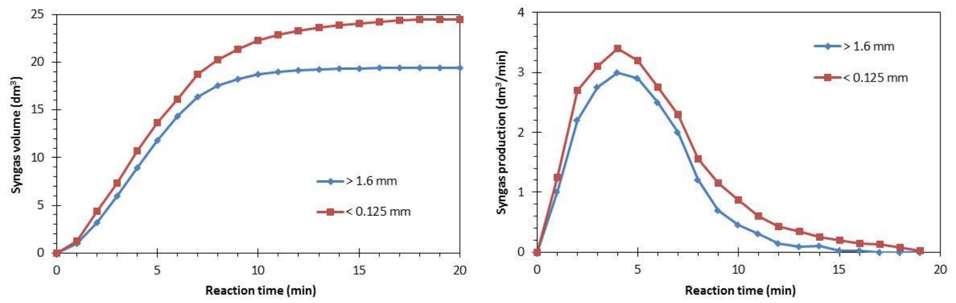

Figure 2: Syngas volume and production per time for carbonaceous particle with size bigger than 1.6 mm and smaller than 0.125 mm

Shang et al. (2015) found that the particles larger than 0.8 mm generate gaseous products mostly, while for the particles in the range from 0.25 to 0.5 mm the solid residue is rather formed. We cannot agree with these published results. The heat from carbonaceous particle (absorbent of electromagnetic irradiation) is transferred by heat conduction to other material (low absorption of electromagnetic irradiation). The high heat conduction is connected with great contact between different material (homogeneous mixture) and it leads to faster heating and higher amount of syngas.

3.3 Effect of microwave power on the quality and the quantity of products

Effect of microwave power on the quantity and the composition of the products have been studied by several authors. With increasing power the amount of produced gas significantly increases and at the same time the amount of solid residue and the liquid condensate decreases. Nevertheless, the above mentioned articles are not focused on the influence of particle size or the type of material on microwave pyrolysis. It should be noted that these parameter have strong influence on microwave pyrolysis, so in some cases the yield of products can be the same and it is case of our experiment. As is shown in Figure 3, the amount of producing syngas was same for both power input.

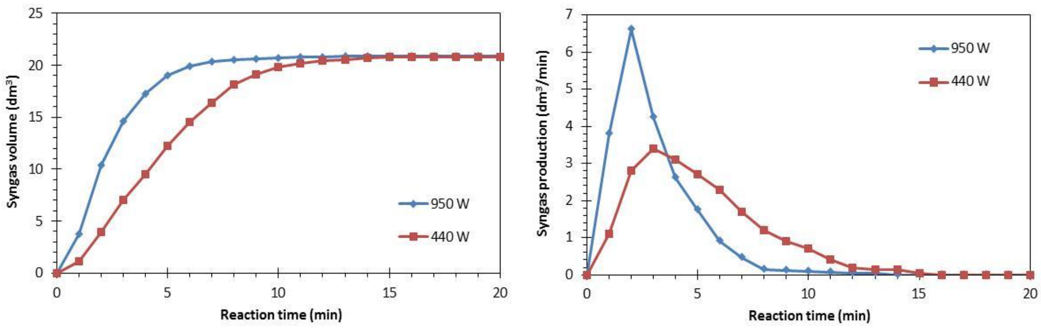

Figure 3: Syngas volume and production per time for various powers with carbonaceous particle size 0.63-1.6 mm

The syngas production was very high at the power 950 W. Production rate (almost 7 dm^3/min) is really high from 50 g of spruce sawdust, and after 5 min. the pyrolysis process is already finished.

The power consumption was measured too. The average power of 1,022 W was measured for set-up 950 W, and average power of 641 W was measured for set-up 440 W. When these values are recalculated on the kWh unit, experiment with 950 W is less energy consumption on the amount of produced syngas.

Effect of microwave power on the composition of gaseous products is already more apparent. The evolution of hydrogen with microwave power rises significantly (Huang, 2015). This trend has not been confirmed by our experiments. Content of the syngas was equal for experiments, 440 and 950 W.

3.4 Effect of additives

Effect of additives can be classified into two levels. The first is the additive in terms of the absorbent of microwave irradiation. Here we can distinguish the type of the absorbent, e.g. SiC, activated carbon, graphite, and solid residue after pyrolysis or even NaOH, K_2CO_3, Fe_3O_4 (), or the related amount of the absorbent in the mixture. The solid residue after pyrolysis appears as the best one of the above mentioned absorbents because it is possible part of product recycle in the process.

The pyrolysis solid residue was used as an absorbent also in our laboratory. The carbonaceous material was analysed by Elementary analysis and content of the carbon and the ash was after microwave pyrolysis same as before process. The second is the additive in term of the catalyst element of pyrolysis processes. These chemical additives play a main role in chemical reactions, such as inorganic element in the ash. In the future work, some type of elements as chemical additives will be tested for better understanding of microwave processes.

4. Conclusion

The pyrolysis experiments of waste spruce sawdust in the microwave oven were done. The syngas, liquid condensate and solid residue were created. Many process parameters were studied. Some trend correspond with publish data, but some not.

The high calorific syngas was a main topic of this study. It was found that moisture has significant effect on the pyrolysis product, especially on the syngas composition. The high calorific value of produced syngas ranged from 40 to 51 MJ/kg, depending on the water content. On the other hand, the power input has not affected composition of the syngas, but it can accelerate the pyrolysis process and reduce the residence time. Many experiments were measured for every parameter, but figures show only marginal values for better understanding of graphs and results.

The solid residue has a significant role in the microwave pyrolysis. It is carbonaceous material and it has 10 times higher absorbance of electromagnetic irradiation than water. The solid residue as a product from one microwave pyrolysis is input material to next microwave pyrolysis. Due to the high content of carbon and inorganic ash this material can be used (pyrolysis product) as substrate for the flora. The amounts of created solid residue were for every experiment the same, 22 wt. % approximately.

The liquid condensate were analysed too, but it is most complicated pyrolysis product. The composition of liquid condensate were analysed by Karl-Fisher titration for prediction of water content in water- and oil-phase and by gas chromatography with mass spectrophotometer for prediction of organic compounds. The liquid condensate from biomass pyrolysis have more than 100 compounds, such as phenols, cresols, organic acids, alcohols or levoglucosan and other product from cracking lignin, hemicellulose and cellulose. The content of water was 63.8 wt. % in the water-phase and 5.6 wt. % in the oil-phase. Many author believe, that bioraffinery is a future way for Europe's independence to oil and oil derivatives, but research of new catalyst and treatment processes is still on the start. For this reason, study of liquid condensate was omitted in this paper.

We conclude that microwave pyrolysis is an interesting process for syngas production from waste biomass, in our case from the spruce sawdust. But there are many processes in electromagnetic field, which are still unknown (such as catalytic activity carbonaceous material - microwave absorbent or generation of electric arc). This should lead to further research activities.

Acknowledgments

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References

Bridgwater A.V., 2012, Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenergy, 38, 68–94.

Dry M.E., 2002, High quality diesel via the Fischer–Tropsch process—A review. J. Chem. Technol. Biotechnol, 77, 43–50.

Holland K.M., 1995, Apparatus for Waste Pyrolysis. U.S. Patent 5,387,321, 7 February 1995.

Huang Y.-F., Chiueh P.T., Kuan W.H., Lo S.L., 2015, Effects of lignocellulosic composition and microwave power level on the gaseous product of microwave pyrolysis. Energy, 89, 974-981.

Kuan, W.H., , Huang Y.F., Chang C.C., Lo S.L., 2013, Catalytic pyrolysis of sugarcane bagasse by using microwave heating. Bioresour Technol, 46, 324-9.

Lam S.S., Chase H.A., 2012, Review on Waste to Energy Processes Using Microwave Pyrolysis, Energies, 5, 4209-4232.

Lei H., Ren S., Julson J., 2009, The Effects of Reaction Temperature and Time and Particle Size of Corn Stover on Microwave Pyrolysis. Energy & Fuels, 23, 3254-3261.

Menéndez J.A., Arenillas A., Fidalgo B., Fernández Y., Zubizarreta L., Calvo E.G., Bermúdez J.M., 2010, Microwave heating processes involving carbon materials. Fuel Process. Technol., 91, 1–8.

Meredith R., 1998, Engineers' Handbook of Industrial Microwave Heating; The Institution of Electrical Engineers: London, UK.

Ren S., , Lei H., Wang L., Bu Q., Chen S:, Wu J., Julson J., Ruan R., 2012, Biofuel production and kinetics analysis for microwave pyrolysis of Douglas fir sawdust pellet. Journal of Analytical and Applied Pyrolysis, 94, 163-169.

Shang H., Lu R.R., Shang L., Zhang W.H., 2015, Effect of additives on the microwave-assisted pyrolysis of sawdust. Fuel Processing Technology, 131, 167-174.

Wang N., , Tahmasebi A., Yu J., Xu J., Huang F., Mamaeva A., 2015, A Comparative study of microwave-induced pyrolysis of lignocellulosic and algal biomass. Bioresour Technol, 190, 89-96.