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MICROWAVE ASSISTED PYROLYSIS OF BIOMASS: A REVIEW

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ABSTRACT

Pyrolysis is a promising bioconversion technique for energy recovery, waste management, and converting biomass into useful energy products which has attracted considerable attention during the past decades. Char/carbonaceous residue, bio-oil, and syngas are the three main products of the pyrolysis process. Various efforts has been made to improve pyrolysis process towards higher yield and quality of liquid biofuels and better energy efficiency The pyrolysis technique is one of the major barriers for large-scale commercialization of this method. This study strives to extensively review the recent work on microwave-assisted technology that is Catalytic microwave torrifaction and pyrolysis applied to the pyrolysis process as a way of cost reduction. The fundamentals of microwave irradiation and a brief background of pyrolysis . It is concluded that microwave-assisted technology is an effectual method to reduce the pyrolysis reaction time and increases the quality of value-added products from different kinds of feedstock. In addition, this technique can overcome the needs of feedstock shredding and improves the quality of heating as well.. Catalytic microwave torrifaction and pyrolysis is one of the promising attempt mainly due to efficient heating of feedstock by microwave heating effect. This review starts with brief overview of key factors and key features of conventional pyrolysis, catalytic microwave torrifaction and pyrolysis and summery of pyrolysis condition that favors' liquid biofuel production. This paper presents state of the art review of microwave torrifaction and pyrolysis.

***Keywords:* Biofuel, Biomass, Catalytic microwave torrifaction and pyrolysis, Microwave pyrolysis, Pyrolysis.**

I INTRODUCTION

Energy is the most important necessity of humans' existence on the earth. It is involved in most economic sectors, such as transportation, agriculture, industry and electricity generation, as well as food. Biomass fuels can provide more environmental advantage s in comparisons with fossil fuel or other type of alternate energy. It is considered to be clean and abundant future energy . During the growth of biomass material, the amount of CO_2 removed from atmospheres via photosynthesis can offset the emission of CO_2 due to combustion of biomass fuels.

Biomass materials can be converted into biomass fuels through physical, thermal, chemical, biological technologies.Bioenergy is the only one kind of alternative energy which can supply the fuels in liquid, gas and solid phases.[1]

II PYROLYSIS

Pyrolysis is the thermal decomposition of biomass occurring in the absence of oxygen. The word is derived from the Greek words “pyro” meaning fire and “lysis” meaning decomposition or breaking down into constituent parts. More than 5500 years ago in Southern Europe and the Middle East, pyrolysis technology was used for charcoal production. Pyrolysis has also been used to produce tar for caulking boats and certain embalming agents in ancient Egyptian Since then; use of pyrolysis processes has been increasing and is widely used for charcoal and coke production. Due to environmental and safety of energy supply concerns and negative implication of 1st-generation biofuels on food resources, production of 2nd-generation biofuels from biomass residues and waste feedstock is attracting a great interest worldwide Pyrolysis technology has the capability to produce bio-fuel with high fuel-to-feed ratios. Therefore, pyrolysis has been receiving more attention as an efficient method in converting biomass into bio-fuel during recent decades. The ultimate goal of this technology is to produce high-value bio-oil for competing with and eventually replacing non-renewable fossil fuels. However, the development of advanced technologies is the next challenge for pyrolysis researchers to achieve this target. It is necessary to convert biomass into liquid fuels for direct use in vehicles, trains, ships and airplanes to replace petrol and diesel. [2]

2.1 Principle

Biomass is one of the first sources of energy used by mankind. It is still the major source of energy in developing countries. In this process; thermal decomposition of organic components in biomass starts at 350°C–550°C and goes up to 700°C–800°C in the absence of air/oxygen The long chains of carbon, hydrogen and oxygen compounds in biomass break down into smaller molecules in the form of gases, condensable vapors (tars and oils) and solid charcoal under pyrolysis conditions. Rate and extent of decomposition of each of these components depends on the process parameters of the reactor (pyrolysis) temperature; biomass heating rate; pressure; reactor configuration; feedstock; *etc.*

Torrefaction process is one of the thermal treatments and can be regarded as pretreatment process before combustion and gasification. Similar to pyrolysis process torrifaction takes place in a inert atmosphere but the temperature requirement is not as high as pyrolysis process (Usually as temperature above 400-500^{0}C) while being suggested to set between 200-300^{0}C and heating rate of torrifaction has to be less than 50 ^{0}C. Untreated biomass material are known for disadvantages such as high water content, low energy density, expensive transportation and thermal instability resulted from high oxygen /carbon ratio. There are some advantages of torrefied biomass which has very lower moisture content and high energy content. The moisture content of torrefied biomass is generally about 1−6wt%. The C/O ratio of torrefied biomass is increased after torrefaction. The high heating value (HHV) of torrefied biomass is increased to 22 to 25MJ/kg which is 20−30% higher than that of fresh biomass. About 90% of energy content in raw biomass is maintained in torrefied biomass which is about 70wt% of raw biomass. The energy density of torrefied biomass is significantly increased. Torrefied biomass also has high grind ability as biomass structure is changed during torrefaction It will reduce the energy consumption for biomass grinding. The power consumption in size reduction is decreased about 80−90%. [3,4]

2.2 Fast Pyrolysis

Pyrolysis is thermal decomposition occurring in the absence of oxygen. Lower process temperatures and longer vapor residence times favors the production of charcoal. High temperatures and longer residence times increase biomass conversion to gas, and moderate temperatures and short vapor residence time are optimum for producing liquids. Three products are always produced, but the proportions can be varied over a wide range by adjustment of the process parameters. Fast pyrolysis for liquids production is currently of particular interest as the liquid can be stored and transported, and used for energy, chemicals or as an energy carrier.

2.2.1. Principles

In fast pyrolysis, biomass decomposes very quickly to generate mostly vapors and aerosols and some charcoal and gas. After cooling and condensation, a dark brown homogenous mobile liquid is formed which has a heating value about half that of conventional fuel oil. A high yield of liquid is obtained with most biomass feeds low in ash. The essential features of a fast pyrolysis process for producing liquids are:

- Very high heating rates and very high heat transfer rates at the biomass particle reaction interface usually require a finely ground biomass feed of typically less than 3 mm as biomass generally has a low thermal conductivity,
- Carefully controlled pyrolysis reaction temperature of around 500^0C to maximise the liquid yield for most biomass
- Short hot vapor residence times of typically less than 2 s to minimize secondary reactions,
- Rapid removal of product char to minimize cracking of vapours,
- Rapid cooling of the pyrolysis vapors to give the bio-oil product

As fast pyrolysis for liquids occurs in a few seconds or less As fast pyrolysis for liquids occurs in a few seconds or less, heat and mass transfer processes and phase transition phenomena, as well as chemical reaction kinetics, play important roles. The critical issue is to bring the reacting biomass particles to the optimum process temperature and minimize their exposure to the lower temperatures that favors formation of charcoal. One way this objective can be achieved is by using small particles, for example in the fluidized bed processes that are described later. Another possibility is to transfer heat very fast only to the particle surface that contacts the heat source which is used in ablative processes that are described later.

The main product, bio-oil, is obtained in yields of up to 75 wt.% on a dry-feed basis, together with by-product char and gas which can be used within the process to provide the process heat requirements so there are no waste streams other than flue gas and ash. Liquid yield depends on biomass type, temperature, hot vapor residence time, char separation, and biomass ash content, the last two having a catalytic effect on vapor cracking [1,5].

III MICROWAVE HEATING TECHNOLOGY

3.1. Fundamentals of Microwave Heating

Von Hippel formulated the basic understanding of macroscopic microwave interactions with matter for the first time. The application of microwave technology in the thermal treatment of biomass has increased from the mid-nineties. This technique not only reduces the energy consumption and processing time, but also enables the use of new chemistry (unique internal heating phenomenon associated with microwave energy).It can also enhance the overall production quality

Microwave irradiations an electromagnetic irradiation in the range of wavelengths from 0.01m to 1m and the corresponding frequency range of 0.3–300GHz. Most microwave reactors for chemical synthesis and all domestic microwave ovens operate at 2.45GHz frequency, which corresponds to a wavelength of 12.25cm. According to the interaction of microwave irradiation(electric component of microwave field) with materials, there are three ways in which a material may be categorized:

1) Insulator or microwave-transparent material where microwaves pass through without any losses (e.g. quartz, teflon, etc.),
2) Conductor where the microwaves cannot penetrate and are reflected (e.g.metals),and
3) Absorber where the microwaves can be absorbed by the material (e.g.water,oils, etc.).Microwave dielectrics are known as a material which absorbs microwave irradiation, thus microwave heating is called dielectric heating.[2]

3.2. Microwave Pyrolysis

Microwave Pyrolysis technology offers a number of advantages over conventional pyrolysis. The main advantage is that microwave pyrolysis can be occurred for large size particle feedstocks as the heating is agitated by the polar molecules which oscillate under the influence of an oscillating electric and magnetic field. Compared to fast pyrolysis like fluidized bed, pre-dried biomass is not required in microwave pyrolysis. The moisture in biomass needs to be removed for obtaining high heating rate in conventional fast pyrolysis. But in microwave pyrolysis the moisture is a good adsorption material for irradiation that induces the pyrolysis. Microwave pyrolysis also produces clean products like bio-oil and syngas because the process does not have to use biomass powder and does not require agitation and fluidization. The syngas produced by microwave pyrolysis has higher heating value since it is not diluted by the carrying gas.). Compared to the fast pyrolysis, microwave pyrolysis of biomass produced low liquid yield. [5,6,7,8]

3.2.1 Variables affecting the microwave-assisted pyrolysis process

The yield and quality of produced value-added products are affected by some critical parameters in the microwave-assisted pyrolysis process. In order to obtain the highest quality and maximum conversion yield, these variables should be optimized. The most important variables in microwave-assisted pyrolysis reaction processes are listed below:

- Type and size of input biomass/materials
- Moisture and water content of input biomass/materials
- Reaction temperature
- Reaction time (residence time)
- Microwave output power
- Microwave type (multimode or single-mode)
- Reactor design/type
- Microwave receptor type, size, and amount/concentration
- Catalyst type and concentration
- Mixing intensity (stirring)
- Type and flow rate of carrier gas

3.2.2Advantages of Microwave-Assisted Pyrolysis Technology

Microwave-assisted pyrolysis technology has the potential for energy and cost reduction. It has been proven as a powerful tool in waste reduction, material recovery, and converting biomass and bio wastes into value-added products. However, this method has not been industrialized yet, although it is an attractive option for further industrialization. In this section, the advantages of microwave-assisted pyrolysis technology are summarized as an efficient alternative method to conventional technology. Fast, selective and uniform heating are the first advantages of this method, which make the treatment and utilization of non-homogeneous wastes and large size biomass possible. Thus, the solid feedstock with high moisture content, including forest and agricultural wastes and residues, municipal solid wastes (MSW), and municipal waste solid sludge, can be treated using this method. It enhances the product quality, chemical reactions, and overall efficiency. Process flexibility and equipment portability are the other advantages of this technique.[7,9]

3.2.3Challenges in Microwave Pyrolysis

Compared to fast pyrolysis , microwave pyrolysis of biomass produced low liquid yield.In biomass fast pyrolysis using conventional heating reactor , the liquid yield is upto 60-70%weight. However in microwave assisted pyrolysis of biomass ,the liquid yield was generally less than 30% .In some reports microwave absorption material or catalyst were added to increase heating rate and liquid yield production .The liquid yield can be increased up to 40% but it is still lower than fast pyrolysis. It indicates that the high liquid yield production is big challenge in microwave pyrolysis. [10]

IV CATALYTIC MICROWAVE TORRIFACTION

Since biomass shows poor MW absorbing characteristics, the introduction of an additional material capable of absorbing MW was required. These are usually referred to as microwave absorbers or susceptors, and the process at a temperature of upto 300^{0}C is known as a catalytic microwave Torrifaction. The role of such materials is to absorb the MW energy and transfer it to a poorly absorbing material such as biomass. The ratio with which the MW absorber is doped with biomass during MW pyrolysis plays an important role in achieving optimum bio-oil yield. It is assumed that an increase in the carbon percentage might increase the temperature of MW pyrolysis in the presence of a stirrer. The research work is carried out to evaluate the effects of catalysts on product selectivity of microwave-assisted pyrolysis of corn stover and aspen wood. Metal oxides, salts, and acids including K_2Cr_2O7, Al_2O_3,H_3BO_3,Na_2HPO_4, $MgCl_2$, $AlCl_3$, $CoCl_2$, and $ZnCl_2$ were pre-mixed with corn stover or aspen wood pellets prior to pyrolysis using microwave heating. These catalysts may function as a microwave absorbent to speed up heating or participate in so-called ‘‘in situ upgrading’’ of pyrolytic vapors during the microwave-assisted pyrolysis of biomass. Microwave torrefaction of biomass could be a competitive technology to employ the least energy and to retain the most bioenergy [11,12].

Integration of Catalytic Microwave Torrefaction And Pyrolysis To Improve Biofuel Quality:

Torrefaction can modify the structure and chemical compo-nents of biomass by removing hemicelluloses and dehydrating and partially reducing cellulose and lignin. The torrefied biomass was rich in cellulose and lignin. These changes may affect the reaction pathways of biomass pyrolysis. The interaction between hemicelluloses and cellulose has negative effect on the formation of sugars and positive effect on the formation of furans. In pyrolysis of torrefied biomass this interaction might be eliminated or reduced as the hemicelluloses were removed during torrefaction. This might explain our findings in analysis of bio-oil that the pyrolysis of torrefied biomass had the selectivity for sugars production the bio-oil analysis also showed that some guaiacols were replaced by phenols in the torrefied biomass pyrolysis. This implied that the torrefaction also affected the mechanism of lignin decomposition. The small amount of phenols in woody bio-mass pyrolysis was produced by the cleavage of methyl from O_CH_3 at the temperature over 471 ^{0}C . But in the pyrolysis of torrefied biomass this cleavage was enhanced resulting in the large amount of phenols. [13, 14]

V CONCLUSION

Due to the unique features of microwave heating (e.g., rapid, volumetric heating, inverted heat transfer, easy control) and the required pyrolysis conditions for liquid biofuels production (e.g., rapid heating rate, fine control of temperature at a moderate level), microwave heating is expected to enhance pyrolysis for bio-oil production. The integrated method of microwave torrifaction and microwave pyrolysis, enhances quality of biofuel , biochar and Syngas. The bio-oil yields were decreased with the severity of torrefaction. The compositional analysis of bio-oils showed that the torrefaction improved the sugars, phenols, and hydrocarbons production and reduced organic acids which might has potential benefits for bio-oil storage and refinery such as less hydrogen consumption. Additionally, the torrefaction enhanced the CH_4 and H_2 in syngas and reduced the CO_2 production, suggesting that the torrefaction significantly improved the syngas quality during pyrolysis of torrefied biomass.

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