International Journal of Environmental Engineering – IJEE
Volume 1: Issue 2 [ISSN 2374-1724]
Publication Date : 25 June 2014

Thermochemical conversion behavior of dried black liquor under microwave induced heating

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***Abstract*— Pyrolysis of dried pulverized BL was carried out using a microwave. Microwave method offers several advantages such as volumetric heating, rapid turnover as well as efficient energy conversion. The objectives this works were to study microwave heating pyrolysis technique and resulting products as well as conversion efficiency. Weak BL used in this experiment was taken from soda and kraft pulping process from local pulp mill which was then dried and sieved. Pyrolysis was performed in quartz reactor heated in microwave using silicon carbide as microwave receptor. It was found that the reaction temperature may reach 545-1120°C within 10 min by employing microwave heating depending on the amount of dried BL used. The obtained gas products were quantified by gas analyzer. Char and tar were collectively analyzed by weight measuring. Results indicated that optimum operating conditions were pyrolysis of BL achieved at microwave power of 625 W (1120ºC), BL 10 g., silicon carbide ratio 1:1 and residence time 6 min where high fuel gases (H_2, CO, CH_4, and CO_2) were 25.9, 20.0, 1.6 and 0.4 vol.%, respectively. The syngas (H_2 and CO) increased from 17.62 %vol and 12.20 %vol to 25.90 %vol and 20.00 %vol, respectively when increasing of temperature from 830°C to 1120°C. It was observed that yields of gas product increased, while the yield of solid char decreased. Comparison of the results suggested that microwave heating had obvious advantages over conversional heating in terms of more valuable products and energy efficiency.**

I. Introduction

There is increasing interest in the use of new and renewable energy sources due to climate change, limited fossil fuel and international regulations on CO2 emissions, which are the driving forces for increased biomass energy utilization. A variety of initiatives are under development and low carbon sources and reducing oil dependency. Forest-based biomass plays an important role as a raw material for wood products. In the pulp and paper industry, large quantities of forestry biomass have been used resulting in large amount of BL which is spent pulping chemical waste. BL is one of the major biomass resources that can be further used to produce electricity, heat and biofuels [1]. At kraft and soda pulp mills, spent cooking liquor, referred to as "weak BL," from the brown stock washers is routed to the chemical recovery. The recovery process involves concentrating weak BL, combusting organic compounds, reducing inorganic compounds, and reconstituting the cooking liquor. Currently recovery boilers are used to generate heat from the organic in the BL for energy purpose and to recover the cooking chemical.

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Nevertheless, the recovery boiler has several disadvantages in terms of low electricity generation efficiency, smelt-water explosions and reduced-sulfur gas emissions [2]. There has been major interest in developing new technologies.

The use of microwaves for heating is well established in society. However, there is potential for this technology to be introduced and applied to many other industrial heating processes, which offers unique advantages not attained with conventional heating. Microwave pyrolysis not only overcomes the disadvantages of conventional pyrolysis methods such as slow heating and necessity of feedstock shredding, but also improves the quality of final pyrolysis products. At the same time it significantly saves processing time and energy. However, there are several major limitations which are preventing this technology from being widely employed in the waste manufacturing industry. These include the absence of sufficient data to quantify the dielectric properties of the treated waste streams, the need of a multi-disciplinary approach to design and develop the related conversion units, and the uncertainty about the actual costs.

Microwaves are electromagnetic waves with frequencies between 300 MHz and 300 GHz, and thus the corresponding wavelengths are between 1 mm and 1 m. Microwave heating includes two mechanisms: one is the dipole rotation, and the other is the ion migration. Both of them are able to heat materials quickly and uniformly. Microwave heating is also a selective and energy saving technology without direct contacts with the heated materials [3].

The microwave pyrolysis is one of the most promising methods of increasing and speeding of chemical reactions. This conversion technique can proceed more efficiently in comparison with other conventional methods due to effective heat transfer profiles. It is regarded as one of the most promising technologies for the pyrolysis process. Microwave pyrolysis technique has been reviewed and tested by many researchers. Zhao et al. reported the effect of temperature on the microwave-induced pyrolysis of wheat straw. It was observed that the temperature is an effectual parameter in the performance of microwave pyrolysis process. Yield of gas products increase with the temperature [4]. Fernandez and Menéndez studied the effect of initial characteristics of raw materials for syngas production under microwave and conventional heating, as well as their related time and energy savings. The microwave-assisted technique produced a higher gas yield with greater syngas content in comparison with the conventional heating method [5]. Menendez et al. investigated the microwave-assisted pyrolysis of four different types of wet sewage sludge from urban waste water treatment plants and

milk-derivative factories. A lab- scale multimode microwave reactor was used for drying and pyrolysis of these waste materials [6]. The results were compared with those from conventional pyrolysis methods and it was found that microwave pyrolysis required a much shorter time in comparison with an electrical furnace. Besides, microwave pyrolysis increased the syngas. As a result, microwave induced pyrolysis was applied to test the conversion of BLs to fuel products. Currently there is no report on microwave pyrolysis of BL. In this study, the thermochemical conversion behavior of dried BL under microwave heating pyrolysis using a quartz reactor under 375-625 W microwave power generator was investigated for studying its product distribution and conversion efficiency.

II. Materials and methods

Material

The weak BLs (BL) used in this work was kraft and soda pulping of eucalyptus from local pulp mill. BL was dried in oven at 100ºC for 2 weeks, grinded and sieved to 425 µm. Before the experiment was carried out, dried BL samples were analyzed to investigate their chemical compositions.

Instrument and experiment

Pyrolysis was performed in a quartz reactor heated by using silicon carbide as microwave receptor. A diagram of the apparatus was shown in Fig. 1. Reactor was made from quartz with 18 cm in length and 10 cm outer diameter. For each run, 2.5-10.0 g of dried BL and SiC was mixed in a quartz reactor and placed in a microwave chamber. The carrier gas (N_2) was purged into the reactor at a constant flow rate of 1 L/min which was controlled by rotameter. When the purging was sufficient to produce an anoxic state, the microwave power was set to desired wattage of 375 – 625 W. For temperature measurement, type-K thermocouple was used. However, microwave would create an electric arc with any metal or conductive material, so temperature measurement can only be done at the end of each run by rapidly inserting thermocouple to the reactor. Produced gas flowed through outlet to condensate unit for collection of liquid fractions .

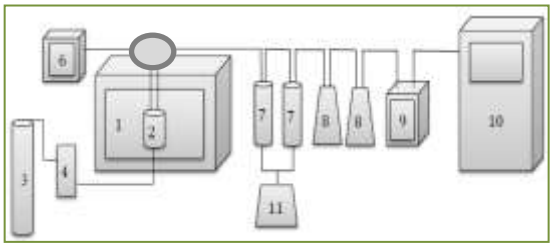

Figure 1. Diagram of the microwave pyrolysis experiment.

The rest gaseous product further passed to gas washer for cleaning and continued through gas flow metering unit for gas production rate measurement. The composition of gas yield would be detected by online-gas analyzer and showed on monitor as CO, CO_2, H_2, and C_xH_y. Liquid and solid fractions were weighted and kept in desiccator for further analysis.

III. Results and discussion

Elemental analysis of dried BL samples

The BL used in this research comes from kraft and soda pulping of eucalyptus. It contains organics from wood and inorganics from pulping chemicals around 55 and 45 wt.%, respectively. The elemental analysis of dried BL used in this study was listed in Table 1. In the general, BL contains organic compounds (mainly from lignin) and inorganic salts from pulping chemicals mostly sodium and water). The combustible characteristics are the lower heating value (LHV) of 12.32 MJ/kg for kraft liquor and 11.35 MJ/kg for soda liquor. Comparing to other biomass, BL has relatively high LHV. Therefore, BL is qualify as appropriate biomass to produce quality synthesis gas. Not only high LHV, BL also has an advantage over some biomass due to its low nitrogen and sulfur (for soda liquor) contents. Whenever BL was used as raw material for fuel production, high quality product with low pollutant may be achievable.

Table 1. Elemental analysis of BL (dry solids)

BL process	Element (wt.%)					LHV (MJ/kg)
	Carbon	*Hydrogen*	*Nitrogen*	*Sulfur*	*Oxygen*	
Kraft	32.95	3.35	0.12	5.12	35.29	12.32
Soda	32.80	2.97	0.04	0.25	38.73	11.35

Temperature profile of BL with and without silicon carbide bed

Measurement of BL temperature under microwave power with and without silicon carbide (SiC) was carried out to study the effect of SiC addition. It was found that the temperature of BL mixed with SiC increased rapidly as the microwave radiation was effectively absorbed by SiC. On the other hand, temperatures of BL without SiC were slowly increased with insignificant variation under different power levels (Fig. 2). At 250 W, temperatures of BL with SiC and without SiC were quite similar, 100 and 65ºC respectively. Because at that low wattages, there is not enough power to stimulate SiC to generate heat and hence, the power level of 250 was not considered to further study in this research. This work was carried out at the initial power level of 375 W due to distinct temperature increment from heat generated from SiC induced by microwave. From Fig. 2, the power level at 375 W resulted

in temperature of the experiment with and without SiC of around 500ºC and 90ºC respectively. Highest temperature of more than 1200ºC can be achieved at microwave wattages of 1000 while the run without SiC only yields temperature of around 200ºC. Reasons for this difference are apparent because a material will be heated under microwave according to its dielectric constant [7]. SiC has a much higher dielectric constant than that of BL. Consequently, the temperature of BL mixed with SiC would significantly higher than the temperature of BL without SiC under similar microwave irradiation. Obviously at power level of 375 W, SiC would produce enough heat to initiate the pyrolysis experiment which was targeted at about 500-900ºC in this work.

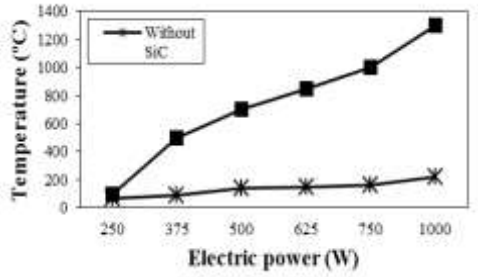

Figure 2. Temperature profile of BL mixed with and without SiC during the microwave radiation heating.

Effects of silicon carbide loading to the reaction temperature

The relation between amounts of SiC to achievable temperature at different microwave power levels was studied to find the optimum experimental condition. BL was mixed with SiC at the ratio of 1:1 and 1:2 and subjected to microwave irradiation at the power of 375, 500, and 625 W for 10 min. The results showed that the higher loading of SiC may cause temperature dropping. From Fig. 3, at the power level of 375 W, an experiment with 1:1 ratio generates higher temperature than the ratio of 1:2 which is similar to the case of 625 W. Appropriate dispersion of SiC at 1:1 ratio might be the reason for higher temperature. For the case of 1:2 ratio, agglomerated silicon carbide may encourage hot spot and led to lower heating efficiency and temperature.

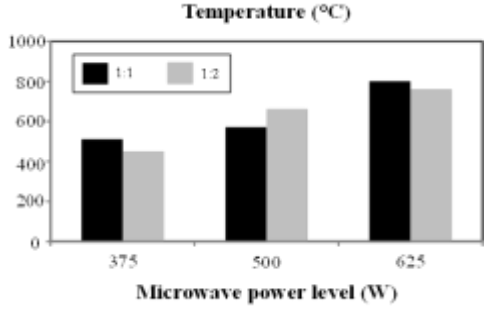

Figure 3. Silicon carbide loading and resulting temperature at various microwave power levels.

Microwave and conventional heating

For comparing between different heating methods, dried BL of 5 g was heated under both conventional furnace and microwave oven. The resident time was 5 and 10 minute at targeted temperature of 800ºC. Weight loss was used as an indicator of the efficiency for the heating process. It was found that at the resident time of 10 min, weight loss of BL in microwave was higher than conventional heating at around 2.5 times (Table 2). Even when double the resident time in conventional heating, weight loss of BL in microwave at 5 min was still higher than conventional heating at 10 min for about 1.2 times. Therefore, the efficiency of microwave heating was far greater than conventional method. As a result, rapid and efficient heating as well as uniform internal temperature distribution could be obtained. However, several parameters also have an effect to microwave pyrolysis process, such material properties, heat and mass transport mechanisms, and chemical reactions. The significant effect on the reaction by those variations determined the temperature profiles and products distribution [8].

Table 2. Comparing weight loss of black liquor in conventional and microwave heating

Type of furnace	Time (min)	BL (g)	Temperature (ºC)	Weight loss (%)
Conventional	10	5	800	18.60
Microwave	5	5	500	22.68
	10	5	860	47.22

Gas product

Sources of gas product formation were tar cracking, the decomposition of char at high temperature and the reactions between the various chemical species formed during pyrolysis. To study gas product distribution, the experiments were set at microwave power of 375, 500 and 625 W with targeted temperature of 700°C, 830°C, and 1120°C, respectively. Carrier gas was set at 1 L/min and 10 min of residence time. Gas product was measured and recorded for CO, CO_2, H_2, C_xH_y at 1 min interval by online-gas analyzer. Difference of gas product depended on BL loading, temperature and time to absorb microwave.

A. Effect of black liquor loading

Gases yield

For investigating in the relation between gases yield and BL loading, the experiments were carried out by varying the amount of BL loading as 2.5, 5.0 and 10.0 g. From Fig. 4, when increase BL quantity, producer gas would increase accordingly due to ample initial feedstock for thermal cracking at the higher temperature. The highest yield was at 625 W which obtained as 14.35%, 9.26%, 0.84, and 0.21% for H_2, CO, CH_4, and CO_2, respectively.

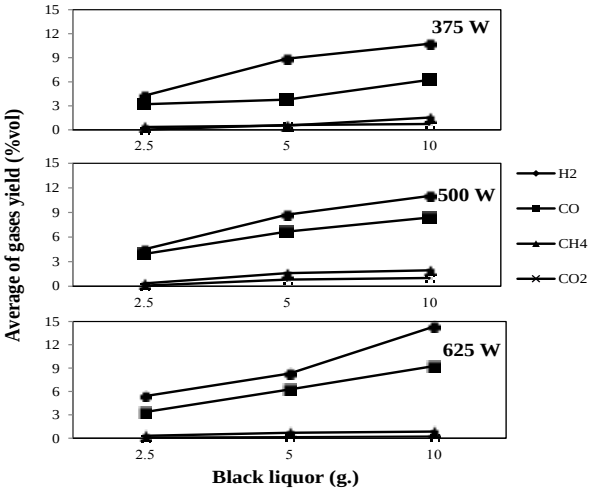

Figure 4. Gas yields at various Black liquor loadings.

B. *Effect of temperature*

Gases yield

For investigating in the relation between gas yield and temperature, the experiments were carried out at various power levels with 10.0 g of dried BL, heating for 10 min (Fig. 5). Gas yields which were H_2, CO, CH_4, and CO_2 were reported in percentage by volume. At temperature of 700ºC, gas productions were 10.8, 6.2, 1.6 and 0.7 %vol, while 11.0, 8.4, 1.9 and 1.0 %vol were obtained at 830ºC and 14.3, 9.3, 0.8 and 0.2 %vol for 1120ºC, respectively. Producer gas, especially for H_2 and CO would increase slightly with temperature. While H_2 and CO increased, lesser CO_2 and CH_4 could be related to carbon gasification reaction In addition, temperature has direct effect to decompose CH_4 and to dry reforming reaction of CH_4 [9].

Although this research was focus on pyrolysis reaction, actual experimental temperatures were quite high which could encourage the mechanism of thermal cracking due large amount of gas yield. Nevertheless, these combustible gases can be used as the direct firing in boilers for heat production, turbine and engines for electricity production.

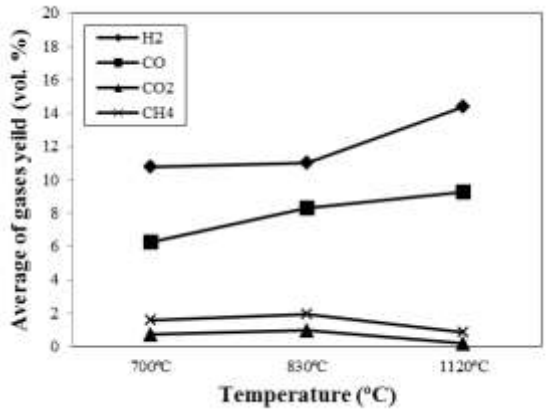

Figure 5. Average gas yields at various temperatures

Conversion of gas product

For study of the relation between conversion percentage of gas product and reaction temperature, the experiments were carried out at power level 375W (700ºC), 500W (830ºC) and 625W (1120ºC), respectively with 10.0g dried BL for 10 min (Fig. 6). The results revealed that temperature could be the key factor for carbon conversion. Because of thermal cracking reaction, higher temperature was cause of higher decomposition. Therefore, carbon conversion of CO had trend to rising by higher temperature which were 11.5% at 700ºC and increased to 17.8% at 1120 ºC. In the contrast, carbon conversion in CH_4 had a trend toward decreasing since less amount of yield at higher temperature. Carbon conversion in CH_4 was 2.90%, 3.20%, and 1.60% at 700ºC, 830ºC, and 1120ºC, respectively. Moreover, hydrogen conversion was similar to carbon conversion. The percentage of hydrogen conversion would be raised due to higher temperature. Hydrogen conversion was insignificantly decreased from 700ºC to 830ºC. However, the conversion percentage of hydrogen was quite big increased from 32.30% to 44.10% at temperature 700ºC to 1120ºC.

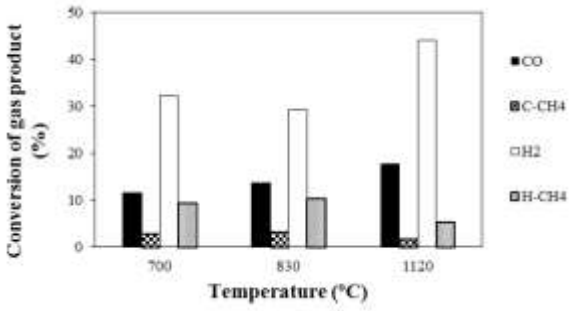

Figure 6. The conversion of carbon and hydrogen at different temperatures.

Effect of reaction time

The effect of heating time on gas production was investigated by determining the accumulated produced gas achieved for 10 g BL and 10 minutes. It was found that at the highest gas production rate occurred during 5-8 minutes, (Fig. 7). The profile of gas production changed over time and temperature. The highest gas production rate were slightly different with temperature. All of experiment had the same pattern of produced gas especially in CH_4, CO and H_2. After the maximum point of CH_4 was achieved for one minute, both of CO and H_2 were reached the highest level while CH_4 slightly decreased. Decreasing of CH_4 and increasing of CO and H_2 might cause by thermal cracking. Therefore, higher temperature resulted greater gas production rate. However, the highest percentage by volume of producer gas was at five minutes. For CO and H_2, the greatest yield was at 1120ºC which were 20.0 %vol and 25.9 %vol, respectively, whereas CH_4 was 4.3 %vol at 830ºC.

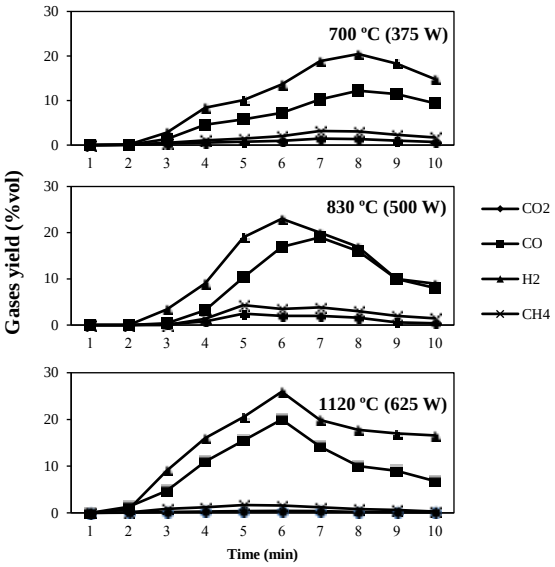

Figure 7. Gas yield vs reaction time.

From Table 3, H_2 content in produced gas at 500 W increased 12.52% from 375 W level. Similarly, H_2 was increased 12.60% from 500 W to 625 W. However, the electricity charge at 375 and 500 W was similar at 0.05 KWh but at 600 W, the electric city charge was increased 25% from 500 W level. The same conclusion may be drawn for the case of CO and CH_4 production. By comparing of gas yields and electricity charge at different power level, one may suggest that, economically, 500 W may be the optimum power level for the case reported here.

Table 3. Comparison of time, electricity charge and gas yield at different power levels.

Gas yield	375 W			500 W			625 W		
	T.[a]	E.C.[b]	G.Y.[c]	T.[a]	E.C.[b]	G.Y.[c]	T.[a]	E.C.[b]	G.Y.[c]
H_2	8	0.050	20.44	6	0.050	23.00	6	0.062	25.90
CO	8	0.050	12.24	7	0.058	19.00	6	0.062	20.00
CH_4	7	0.044	3.16	5	0.041	4.30	5	0.052	1.70

[a]Time (min), [b]electricity charge(KWh.), [c] Gases yield(%vol)

IV. Conclusion

From the results of this paper, it was showed that microwave induced pyrolysis process has several advantages over conventional heating method. The study revealed that SiC plays an important role as a microwave absorber in the microwave heating process which helps initiate and maintain the pyrolysis process. The temperature and the maximum heating rate were both increased when increasing the microwave power levels. The yield of syngas (H_2 and CO) in gaseous products were appreciably high indicating applicability of microwave pyrolysis to BL conversion process. Moreover, the gas contained a lower concentration of CO_2 and CH_4 with the increasing in the temperature suggesting robust efficiency of the process. Economically, the optimum power level was achieved at 500 W.

Acknowledgement

This research was funded by the Ratchadaphiseksomphot Endowment Fund of Chulalongkorn University (RES560530188-EN). Authors also thank the National Metal and Materials Technology Center and Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University for their support.

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