

The Effect of pyrolysis conditions to produce levoglucosan from rice straw

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Abstract. The industrial sectors that produce synthetic chemicals and polymers rely heavily on fossil resources. Rice straw is very abundant in Indonesia and can be used as a substitute for fossil resources to produce petrochemical precursors. It is known that cellulose component is the main source for LG formation. Due to high contain of cellulose, the potential of rice straw can be transform by pyrolysis to produce bio-oils and derivative products towards levoglucosan (LG) should be developed. Levoglucosan is an important intermediate compound as it can be convert to the precursor of bio-polymer adipic acid, bio-ethanol, etc. Nowadays it's still rarely research focused on this mechanism route producing LG through pyrolysis. LG then can run into a further reaction and produce derivative products. In order to obtain the highest yield of LG in bio-oil, a condition that may inhibit the further reaction of LG during pyrolysis takes place. The factor of biomass source and composition, temperature, and holding time (adjusted by N₂ feed) most likely greatly affect the product composition formed at the end of pyrolysis. In this study, fast-pyrolysis of rice straw was performed in fixed-bed reactor (5 grams of biomass) under different temperature ranges (450 to 600 °C), N₂ flow rate (1200 to 1582 ml/min) to maximize the yield of LG. The content of LG on bio-oil was measured by GC-MS instrument. The maximum yield of LG (67.78% of area) was obtained at an optimal temperature of 500°C with holding time of 1.35 s.

1 Introduction

Production of chemicals and fuels from lignocellulosic biomass has gained attention as conventional resources are dwindling [1]. Pyrolysis is one way that can be done to convert biomass into value-added chemical products as well as a fuel substitute for petroleum derivatives [2]. Fast pyrolysis is a promising one to convert solid biomass into liquid bio-oil. Bio-oil is a complex mixture of hundreds of organic compounds. Many of these are valuable chemicals, whereas the recovery of specific chemicals is difficult due to their low concentrations in conventional bio-oils [3]. To solve this problem, selective pyrolysis has been proposed in recent years to produce the target chemicals predominantly via the selectively controlling the biomass pyrolysis process [4].

Compared to its use as an alternative fuel, bio-oil pyrolysis products for chemical raw materials or precursors are more favorable today because they are more efficient and less expensive. Among the chemical products contained in bio-oil from biomass pyrolysis, levoglucosan (hereafter written as LG) is a major product of great interest to study because of its uniquely broad structure and utility.[2]

LG can be used for the synthesis of adipic acid, which is a petrochemical base material used as a nylon-6,6 precursor [5]. LG can also be used in the synthesis of

pesticides, growth regulators, antibiotics, and bio-ethanol [2].

Although it has many applications as a final product, LG is still not a major product in biomass pyrolysis. The research that has been done so far has focused on pyrolysis of biomass to produce phenol and ketone compounds as the main products in bio-oil. Meanwhile, LG is only an intermediate during pyrolysis and converted into other compounds up to the end of pyrolysis, thus causing only a small amount of LG to be produced as a final product of pyrolysis [6].

The lignocellulosic biomass component that plays a role in levoglucosan formation is cellulose. Levoglucosan forms in the early stages of pyrolysis as an intermediate product and will undergo further reactions resulting in a derivative product. The pyrolysis reaction of the cellulose component passes the route of formation of levoglucosan and other carbonaceous sugar compounds. Theoretically, LG will be formed from cellulose depolymeration in the early stages of fast-pyrolysis in the temperature range 314°C and 400°C and with a very fast residence time of 1.4 to 6.8 seconds [2].

The pyrolysis reaction of the cellulose component passes the route of the formation of levoglucosan and the sugar compound. Considering the previous theories and results of the fast-pyrolysis of lignocellulosic compounds, the present study is to create a condition

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which can inhibit the dehydration reaction in levoglucosan intermediates to produce bio- oil rich in levoglucosan (LG). In terms of reaction conditions, the temperature reaction and residence time (holding time) factor become a variable that is very influential on the expected product composition. Therefore, the residence time effect will be investigated by varying it in the range of 1.35 to 1.8 seconds, which is done by adjusting the flow rate of N₂ gas as a carrier gas. In addition to the influence of residence time, the effect of temperature.

The consideration for biomass selection is that based on the dominant and abundant containing cellulose content available in Indonesia is expected to increase the levels of LG in bio-oil. The type of biomass used as feed is rice straw. With cellulose content up to 37% [7], rice straw is expected to produce the high yield of LG under the optimum temperature and holding time. Cellulose content of 37% showed the predominant number among other constituent in rice straw i.e. hemicellulose (16.5%) and lignin (13.6%) [7]. There is another type of biomass that contains more cellulose components compared to rice straw, for example is cotton straw (45.5%), corn straw (42.7%), and bamboo (39.8%) which is certainly more potential sources as raw material to obtain the higher LG yield through a pyrolysis process [8,9]. However, the stock of rice straw is very abundant in Indonesia because the rice straw production reaches 69 million tons per year [10]. Commonly, the utilization of rice straw is not optimal, it just stacked and burned with the impact causing the air and environmental pollution. Hence, the usage of rice straw as a pyrolysis feedstock is also expected to reduce environmental problem.

2 Experimental

2.1. Materials

The type of biomass used as feed in this research was a rice straw. The samples of rice straw were provided from Pangandaran, Indonesia. Rice straw was shredded and sieved into particle size of 400 µm. Then the samples were dried in an oven at 60° C until reached a constant weight. All the samples were stored in sealed containers.

The amount of samples used for each pyrolysis experiment was 5 g. The solvent (ethanol) was purchased from Merck. The standard LG (with purities > 99 %) was provided by Sigma Chemical Company (Beijing, China).

2.2. Pyrolysis procedure

Fast pyrolysis was conducted in fixed bed reactor. The reactor was made from stainless-steel tube. The fixed bed reactor has the height of 400 mm and a diameter of 72 mm. Detail information of reactor system is shown in Fig.1. The bio-oil product was collected at the bottom of the tube.

Fast-pyrolysis temperatures were varied from 450°C to

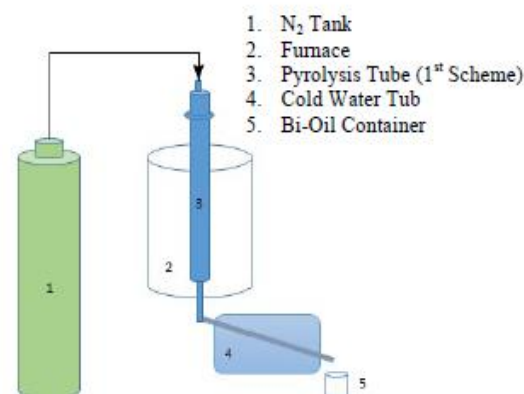


Fig. 1. Schematic diagram of experimental apparatus for biomass pyrolysis

600°C, the gas flow rate varied from 1200-1582 ml/min to investigate the effect of holding time in the atmospheric pressure condition. The N₂ gas was used as an inert pyrolysis gas and to purge the air present in the reactor tube. The function of N₂ carrier gas was also to force the pyrolysis product to move downward and enter the bio-oil tube container.

The gas product from pyrolysis process was captured by a system called cold gas absorption. Cold gas absorption is a system in which there was a tube containing a solution of ethanol pro-analyst and was kept with a cooling jacket to cool the solution. The gas product stream flowed into the cold gas absorption system and directly contacted to the solution so that it underwent the quenching process and cold absorption. The product gas, particularly LG compound, was then dissolved together in the solvent bulk due to high solubility of this compound in ethanol. The chemical compositions of the products were analyzed by GC-MS, and their relative contents were determined. The GC-MS is HP type instrument using capillary column HP-5MS type with specification 30 m length, i.d 0.25 mm coated by 0.25 µm film thickness. The GC-MS analysis was equipped with MSD Chemstation packet software program for compound identification.

3 Result and discussion

The purpose of this study is to investigate the effect of the main parameters of the biomass pyrolysis process on levoglucosan yield. It is known that reaction temperature, holding time, and initial biomass size can significantly affect pyrolysis products [2]. In this rice straw pyrolysis, temperature variations and holding time produce different amount of levoglucosan yields as shown in Fig. 3 and Fig. 4. Figure 2 shows the chromatogram resulting GC-MS analysis for the sample product from the pyrolysis of rice straw at 500°C and retention time of 1.35 s (as the best example condition). It can be seen that the LG peak clearly seems superior at a retention time of around 11.4 seconds. This identification

Table 1. Composition analysis of bio-oil obtained from rice straw pyrolysis

Groups	Area (%)			
	450° C	500° C	550° C	600° C
Saccharides (LG)	63.832	67.645159	57.182804	56.879219
Furans	5.81857	5.5624449	5.4220939	11.551563
Ketones	2.32408	3.7887781	1.5960784	3.2453894
Alcohols	-	-	-	0.9089217
Phenols	2.29332	7.2019177	7.2779809	6.709473
Esters	20.7993	7.9904683	17.064626	7.1726425
Others (benzene, toluene, xylene, alkenes)	4.9327	7.8557026	11.456417	13.532791
Total	100	100	100	100

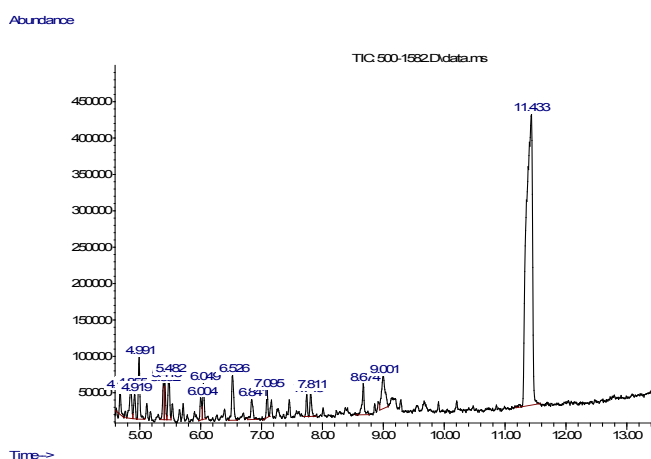


Fig. 2. Typical chromatogram of GC-MS for sample resulting from the pyrolysis of rice straw at 500°C and holding time of 1.35 s.

3.1 The effect of pyrolysis temperature

The effect of temperature on the pyrolysis product (bio-oil and LG) is shown in Figure 3. With increasing temperatures up to 500° C, the bio-oil and LG yields also increase. The increase in the yield of bio-oil with increased temperature could be associated with the degradation of cellulose, hemicellulose, and lignin in rice straw.

Bio-oil from cellulose pyrolysis mainly consisted of saccharides, furans, and ketones. The content of saccharides (mainly LG) significantly raised from pyrolysis temperature of 450°-500° C, then dropped

significantly with increasing the pyrolysis temperature (>500°C). Observed from Figure 3, LG raised from 63.83% to 67.65% then reduced constantly until 57%. It is explained LG is the major product of fast-pyrolysis at the condition of medium temperatures. However, the heat stability is weak, so it is easy to be degraded at higher temperature [8].

LG formed by breakage and rearrangement of chemical bond in cellulose molecule at initial stage of cellulose pyrolysis process. The initial carbon bond cracking of cellulose started between 250° C and 380° C, and the LG is the major product obtained [2, 8, 10-11]. Patwardhan et al. [12] confirmed that the formation of LG and other pyrans was directly correlated with the degree of polymerization (DP) of a sample, and a higher DP favored the formation of pyrans. They proposed that the formation of LG from the cleavage of glycosidic bonds can easily bind to the hydroxyl group at the C6 position of the glucose residue. Furans, such as HMF, were mainly formed from the stepwise dehydration of monosaccharide units such as LG. Similar to LG, the reason why bio-oil yields decreased at pyrolysis temperature of 500–600°C was the reduce of the organic due to secondary cracking of volatiles at temperature above 500°C [11].

Moreover, the Table 1 shows the composition of bio-oils obtained from rice straw pyrolysis at different temperature conditions. It is hard to have a complete characterization of pyrolytic bio-oil since it contains a large number of reactive functional groups. In addition to a review of levoglucosan, it will be explained about the by-products resulting from pyrolysis of cellulose, hemicellulose, and lignin components as well as the possible product of secondary reaction of levoglucosan.

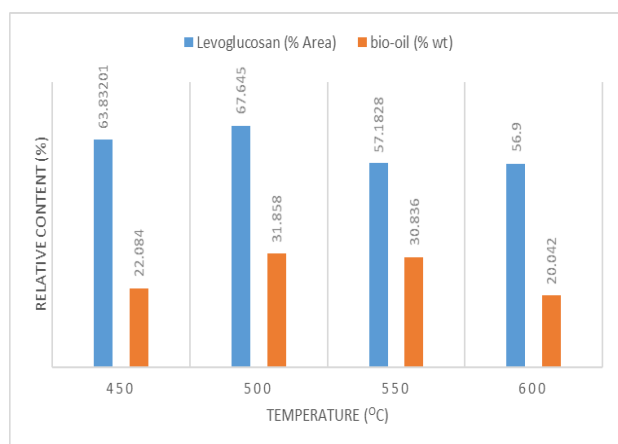


Fig. 3. Effect of temperatures on the yields of bio-oil and LG

Cellulose derived bio-oil mainly consisted of LG, furans and ketones. Lignin derived phenols and esters, and hemicellulose derived ketones. Observed from Table 2, little influence of pyrolysis temperature on the content of ketones. Ketones and phenols were formed at temperature more than 500°C. Phenols relatively stable from temperature range of 500-600 °C and furans (mainly furfural) relatively stable from temperature range of 450-550 °C. The content of furans increased as the effect of secondary reactions of intermediate product (LG). Of phenols, it was due to the deep cracking of lignin and secondary reactions of primary product at temperature pyrolysis of 500°C (such as guaiacol). The content of esters in bio-oil were falling especially at 600°C [8].

3.2 The effect of holding time

To investigate the maximum conversion of cellulose to LG in bio oil, holding time is a primary parameter in the fast pyrolysis process. From most previous research, if holding time in the reactor pyrolysis is too short, the yield of bio-oil will be negatively affected [2]. On the other hand, if the holding time is too long, it results in the formation of a large amount of gas, liquid, or char products and reduces LG's production in bio-oil because it undergoes a secondary reaction.

In this experiment, fast-pyrolysis was studied at different conditions of holding times, between 1.35 s and 1.8 s, which were adjusted by the nitrogen gas flow rate and the result is presented in Fig. 4 as the product yields as a function of holding time. The holding time is the volume of biomass divided by the inlet gas flow rate at reactor conditions. Five different holding times are 1.2 L/min, 1.3 L/min, 1.4 L/min, and 1.582 L/min of nitrogen gas flow rate, respectively.

There was little difference in the yields of bio-oil and LG at the residence times of 1.35 s and 1.5 s. However, when the residence time was prolonging to 1.8 s, the yields of bio-oil and LG were clearly reduced, it means that the bio-char increased. When prolonging the holding time, the primary degradation products (mainly LG) run

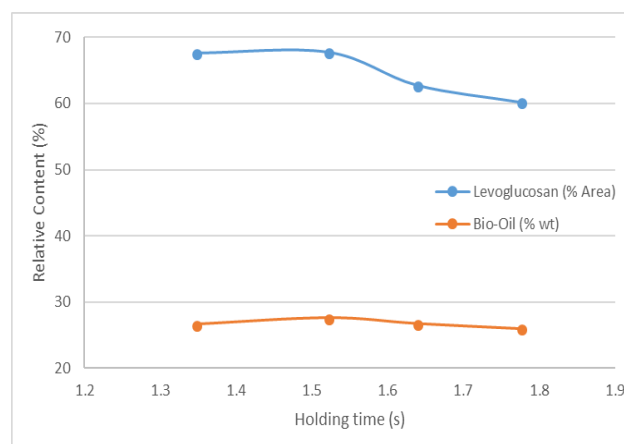


Fig. 4. Effect of holding time on the yields of bio-oil and LG

into secondary cracking reactions, in fact, when residence time is on the order of few seconds, LG has been reported to produce oligomerization sugars [2,3]. In addition, shorter holding time is essential for the economics of industrial operation. Above all, the holding time of 1.35 s showed the suitable pyrolysis parameter of LG. Apparently, the decomposition of Levoglucosan (1,6-anhydro-β-d-glucopyranose) is also an important step during biomass/cellulose pyrolysis and for secondary tar reactions. The mechanism of levoglucosan thermal decomposition included the direct CO bond breaking, direct CC bond breaking, and dehydration [13].

4. Conclusions

We have described novel pyrolysis conditions on LG yield from rice straw and qualitative analysis for LG. In this study, pyrolysis experiments of rice straw were carried out in a fixed bed reactor in order to investigate the effects of pyrolysis temperature and holding time on LG yield. The maximum yield of LG was obtained at an optimal pyrolysis temperature of 500°C, 1.35 s of holding time.

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