Lignin depolymerization using spent catalyst in a batch reactor

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Abstract: This study used spent catalyst to degrade lignin using slow and fast pyrolysis. The operation factors such as kind of catalyst, heating rate, reaction temperature, catalyst life time, kind of lignin and weight ratio of catalyst to lignin were investigated to achieve an optimal condition. The kinetic and thermal behavior of lignin degradaton were investigated using thermogravimetric analysis and derivative thermogravimetry. The dehydration of alkaline and dealkaline lignin with or without catalyst were conducted in the temperature range 210-400 °C. The apparent activation energies of alkaline lignin degradation with and without catalyst were 128 kJ/mol and 143 kJ/mol, respectively. The activation energies of dealkaline lignin with and without catalyst were 124 kJ/mol and 133 kJ/mol, respectively. The degradation of lignin was conducted in 3L-batch reactor. The yield of liquid, gas and solid of product of depolymerization lignin using fast catalytic pyrolysis were 25.4%, 25.2 % and 49.3 % respectively, with ratio of lignin to spent catalyst (1:4).

Keywords: Depolymerization, Catalytic pyrolysis, Lignin .

1. Introduction

Lignin is one of the three major components of lignocellulosic biomass, the other two components being cellulose and hemicellulose. Lignin is a three dimensional amorphous polymer consisting of methoxylated phenylpropane structures. Pyrolysis is thermal decomposition of the biomass or lignin in the absence of oxygen with or without catalyst was usually operated in the temperature range between 300 and 600 ◦C. Lignin depolymerization is very promising process which can generate value added products from lignin raw materials. The primary purpose of lignin depolymerization is to convert the complex lignin compound into small molecules for fuels and basic chemicals or oligomers for further application. Kinetic analysis of thermal decomposition processes has been the subject interest for many investigators all along the modern history of thermal decomposition[1]. In reviewing recent studies report, there wasn't researcher focuses on depolymerization alkaline & dealkaline lignin using spent catalyst. This study aims to investigate the thermal degradation of lignin, depolymerization kinetics of alkaline and dealkaline lignin.

2. Experimental

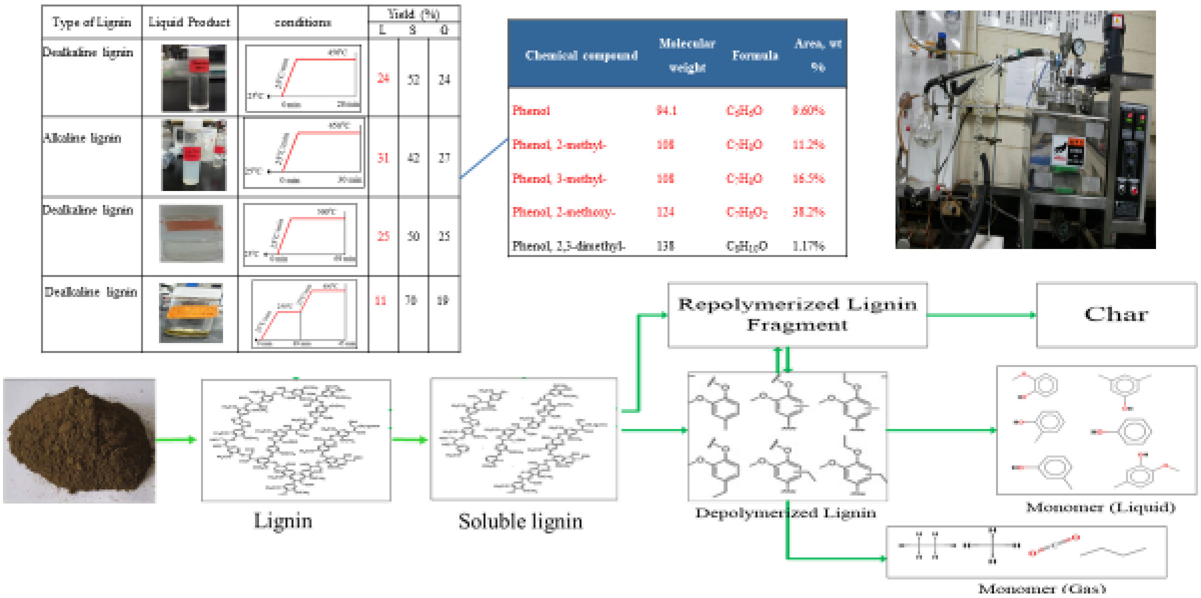
Depolymerization of alkaline and dealkaline lignin were conducted in a 3 L-stainless steel batch reactor with two condensers to condense substance, the liquid product was collected in liquid storage flasks. The laboratory batch reactor of depolymerization lignin is shown in Fig 1. The lignin and spent catalyst were introduced to the reactor. The sample was heated from room temperature up to 450 °C with agitation of 150 rpm, the flow rate of nitrogen gas is 50 mL/min and temperature of cooling water is down 2 oC.

There were two kind of pyrolysis used in this experiment, (i) fast pyrolysis with short residence time pyrolysis of lignin started at temperature 25 °C until 450 °C was used to obtain high yield of liquid products, and (ii) slow pyrolysis was studied with initial temperature 25 °C then increased to 250 °C and hold up until there was not liquid product at the condenser than the temperature increased started at 250 °C up to 400 °C.

3. Results and discussion

During catalytic fast pyrolysis process, initially small amount of condensate come out at the temperature below 200 °C then, the thick cloudy vapor or gas was observed, it still was continuously heating when the temperature reaction increased to 450 °C liquid was condensed with colorless. After completion of depolymerization and cooling process, the liquid product was collected. The yields of gas, liquid and solid residue for alkaline and dealkaline lignin with ratio of catalyst is 1:4 under inert atmosphere of nitrogen were

24%, 52% and 24% respectively for reaction time 28 min. On the other hand, the fast pyrolysis for alkaline lignin has higher yield liquid product than dealkaline lignin. The total yield of liquid, solid and gas were 31%, 42% and 27% respectively. Further studies on gas chromatography the derived products, the major distribution liquid product was phenolic compound such as phenol, phenol 2-methyl, phenol 3-methyl, phenol 2-methoxy, phenol 3,5-dimethyl and phenol 2,4-dimethyl



Type of Lignin	Liquid Product	conditions	Yield (%)		
			L	S	G
Dealkaline lignin			24	52	24
Alkaline lignin			31	42	27
Dealkaline lignin			25	50	25
Dealkaline lignin			11	70	19

Chemical compound	Molecular weight	Formula	Area, wt %
Phenol	94.1	C_6H_6O	9.60%
Phenol, 2-methyl-	108	C_7H_8O	11.2%
Phenol, 3-methyl-	108	C_7H_8O	16.5%
Phenol, 2-methoxy-	124	$C_7H_8O_2$	38.2%
Phenol, 2,3-dimethyl-	138	$C_8H_{10}O$	1.17%

Figure 1. Possible routes during depolymerized lignin using catalyst.

4. Conclusions

The spent catalyst be able to degrade alkaline and dealkaline lignin. The TGA curves presented that alkaline and dealkaline without catalyst had higher tail of percentage weight loss curve. On the other hand, alkaline and dealkaline lignin with spent catalyst on ratio 1:4, the weight loss curve had lower than without catalyst. Spent catalyst can be decreased activation energy, the total amount activation energy alkaline and dealkaline lignin with ratio catalyst 1:4 were 133.2 kJ/mol and 123.8 kJ/mol respectively. The yield and characteristics of liquid product from lignin were dependent on the pyrolysis conditions.

References

1. Damayanti, Ho Shing Wu, 2017, Pyrolysis kinetic of alkaline and dealkaline lignin using catalyst, Journal of Polymer Research, 25(1) 7:1-11