

INVESTIGATION OF CONDENSATION REACTION DURING PHENOL LIQUEFACTION OF WASTE WOODY MATERIALS

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ABSTRACT

The liquefaction of waste woody materials in the presence of phenol and acid catalyst is a promising method for converting waste woody materials into phenolic resin. The condensation reaction during the liquefaction process is a major problem for its practical application. The effects of various reaction conditions on the extent of the condensation reaction were investigated. The residue content, molecular weight distributions and phenol concentration were measured to investigate the condensation reaction. As a result, it was observed that the intense reaction conditions caused fast liquefaction and led to a remarkable condensation reaction. It was also found that the residue content began to increase at an earlier reaction time when a more remarkable condensation reaction occurred. These results indicated that the condensation reaction was one of the causes for too much degradation of liquefied wood molecules under intense liquefaction. The phenol concentrations in the liquefaction products were measured to investigate their effect on the condensation reaction. It was shown that the phenol concentration was 8% lower at the end of the reaction when the condensation reaction was high. It was indicated that the drop in phenol concentration suppressed the liquefaction and promoted the condensation reaction. The addition of methanol during the liquefaction process suppressed the condensation reaction. The residue content was 11% when 50% methanol was added, while it reached 66% when methanol was not added. This can be because methanol reduced the bound phenol, which could be a reaction site of condensation reaction.

Keywords: Condensation mechanism, high performance liquid chromatography, liquefaction, phenol, waste woody materials.

1 INTRODUCTION

Waste woody materials are one of the most abundant biomass resources around the world. A lot of techniques have been developed to utilize waste woody materials for recovery of energy or materials. However, it is not easy to use waste woody materials because the structure of their components such as cellulose and lignin is very complex. In the most cases, more energy or some pretreatments are needed.

Based on that background, more attention has been paid on wood liquefaction technique. This is a solvolysis method to convert all the woody constituents into a liquid matter (so-called ‘liquefied wood’) through a reaction procedure with the phenol and acid catalysts such as sulfuric acid under the suitable temperature. Waste woody materials can be used under relatively low temperature (100°C–200°C) and without any chemical pretreatments in this method. During the liquefaction process, the woody constituents are degraded to small molecules that have similar reactivity as phenol. The liquefied wood can be used as raw materials producing phenolic resins, which are one of the most popular plastic today. Some researches on making various kinds of phenolic resins such as moldings [1], foams [2] and fibers [3] have been conducted previously. In our previous studies, the effects of the species of woody components and different acid catalysts on liquefaction products were investigated [4, 5].

However, the condensation reaction that occurs during the liquefaction process is a big problem for the practical application of the liquefaction technique. It is a spontaneously occurring reaction that causes polymerizations of the molecules of the liquefied wood [6]. In other words, the condensation reaction can be regarded as an opposite reaction of the liquefaction that degrades the molecules of the liquefied wood. This reaction does not occur always but occurs in specific reaction

conditions [6]. Due to this reaction, the quality of the phenolic resin can be deteriorated. Therefore, the condensation reaction should be suppressed. Up to now, the causes and mechanisms of condensation reaction have not been studied enough. But it is very important to understand the characteristics of the condensation reaction. So, the effects of various reaction conditions, such as reaction temperatures, catalyst contents, sizes of woody meal and addition of other chemicals, during the condensation reaction were investigated in this study. In this paper, more results are newly reported and deepened the debate on the contents of a conference paper published in the 4th International Conference on Energy and Sustainability [7].

2 MATERIALS AND METHODS

2.1 Materials

Waste woody meals (or sawdust) of Japanese cedar (*Cryptomeria japonica*) were used as raw waste woody materials for the liquefaction. These waste woody materials were collected from the waste disposal plant of Saitama, Japan, and then sieved into given particle sizes (<0.25 mm, 0.25–0.50 mm and 0.50–1.0 mm). Sulfuric acid was used as the acid catalyst.

2.2 Methods

2.2.1 Liquefaction of woody meal

The liquefaction was carried out using a 500 mL three necked flask equipped with a mechanical stirrer and a reflux cooler. All reaction conditions are shown in Table 1. In this study, three reaction

Table 1: All reaction conditions of liquefaction carried out in this study.

Run No.	Phenol and woody meal ratio ¹	Sulfuric acid (%) ²	Reaction temperature (°C)	Woody meal particle sizes (mm)
1	3:1	50	180	0.25–0.50
2	2:1	50	180	0.25–0.50
3	2:1	50	160	0.25–0.50
4	2:1	50	120	0.25–0.50
5	2:1	30	180	0.50–1.0
5	2:1	30	180	0.25–0.50
7	2:1	30	180	<0.25
8	2:1	40	180	0.25–0.50
9	2:1	10	180	0.25–0.50
10	3:1	10	120	0.50–1.0
11	2:1	30	180	0.25–0.50
12	2:1	30	180	<0.25
13	2:1	40	180	<0.25
14 ³	2:1	40	180	<0.25

¹Total amount of phenol and woody meal is 50 g.

²Weight percentage of initial addition of woody meal.

³Methanol (amount is 50% mol/mol phenol) was added.

conditions for every parameter (e.g. reaction temperature) were performed. These conditions could be divided into 'intense', 'medium' and 'mild'. For example, high reaction temperature, high catalyst content and small woody meal particle size were defined as intense. To start the liquefaction, the given amounts of woody meal samples and phenol (shown in Table 1) were charged into the three-necked flask and immersed in a preheated oil bath. Then, sulfuric acid was added. The charging time of sulfuric acid was regarded as the start time of the liquefaction. The reactions were run up to 300 min. The samples were taken from the flask several times during the process and put into vials. Then, they were immersed in cold water to stop the reaction.

2.2.2 Measurement of residue content

The extent of the reactions including the condensation reaction was evaluated by measuring the residue contents. The residue was a solid mixed matter of the woody meals and the condensed matters that polymerized to some extent. It is known that the residue amount decreases due to the liquefaction at the earlier stage of the reaction, while it increases at the later stage due to the condensation reaction [8]. The increasing rate of the residue amount reflects the extent of the condensation reaction. In order to measure the residue content, the samples were diluted with excess amount of methanol and filtrated using the glass fiber filters (GA-100, Toyo Roshi Kaisha, Co. Ltd., Japan) under reduced pressure. The residues were dried in an oven at 105°C for 24 hours and then weighed. The residue content was defined as the percentage of the weight ratio of the residue in the sample to the weight ratio of charged woody meals in the raw material.

2.2.3 Measurement of phenol concentrations

The concentration of phenol in the samples were measured by using a high-performance liquid chromatography equipped with a detector of SPD-10A (Shimadzu Co. Ltd., Japan) and a column of Wakosil-PAHs (Wako Pure chemicals, Co. Ltd., Japan). The flow rate, the oven temperature and detection wavelength were 2 mL/min, 40°C, 272 nm, respectively. Methanol/H₂O (1:2, v/v) mixed solvent was used as the mobile phase. Samples were diluted to 0.1 wt% by methanol/water (4:1, v/v) mixed solvent for the measurement. Syringe filters (0.45 mm; Toyo Roshi Kaisha Co. Ltd., Japan) were used to remove the residues in the samples when the samples were injected. The phenol concentration was calculated as the weight percentage ratio of phenol in the sample to the weight ratio of phenol in the raw material.

2.2.4 Measurement of molecular weight distribution

The molecular weight distribution of samples was measured by a gel permeation chromatography equipped with a differential refractive index detector (Shimadzu Co., Ltd., Japan). The columns used were KF-802 and KF-806L (Showa Denko Co., Ltd., Japan). Tetrahydrofuran was used as the mobile phase, and the samples were diluted with tetrahydrofuran. The flow rate was 1 mL/min. The other methods were similar to the methods used for the measurement of phenol concentration.

3 RESULTS AND DISCUSSIONS

3.1 Effects of reaction conditions on condensation reaction

3.1.1 Effect of additive amount of phenol on condensation reaction

The relationship between the residue content and reaction time for different amounts of additive phenol is shown in Fig. 1. As a result, the increase of residue content was observed when less phenol was charged, indicating that the strong condensation reaction has occurred. On the other hand, it was

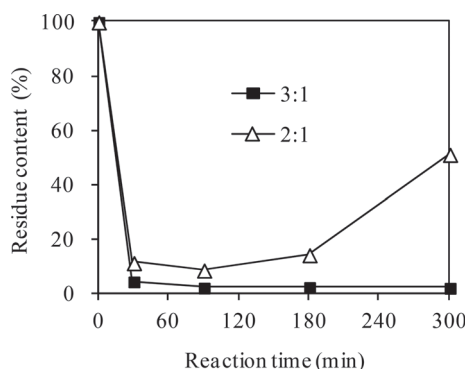


Figure 1: The reaction time of residue content for different phenol and woody meal ratio. Other reaction conditions – catalyst contents: 50%; reaction temperature: 180°C and woody meal particle sizes: 0.25–0.50 mm.

suppressed when more phenol was charged. These results can be explained by following the liquefaction mechanism of cellulose and lignin in the presence of phenol and acid catalyst [9, 10]. First, the most reactive bond against acids in the structure of cellulose and lignin was cleaved and ionized. Subsequently, carbocation has occurred. For example, in the case of liquefaction of cellulose, the glucosidic bonds of cellulose are cleaved.

The carbocation reacts with phenol through nucleophilic substitution to produce phenolic compounds. This process is called phenolysis [11]. After phenolysis, other reactions such as dehydration condensation were carried out repeatedly. Finally, low-molecular-weight substances that have multiple hydroxyl phenyl groups (so-called 'bound phenol') were formed [9, 10, 12, 13]. Here, we consider that the phenolysis is a process that hardly proceeds when the concentration of phenol is at low level because it needs higher concentration of phenol. In that case, the carbocation might react with other compounds compared with phenol, which are considered nucleophilic compounds similar to phenol. For example, the products from phenolysis could be them because they have bound phenol. Actually, it was shown that the condensed matters produced from the liquefaction of cellulose had multi-substituted bound phenol in their structure [8]. Phenolic compounds derived from the degradation of lignin were also considered to play a major role in the condensation reaction [14]. The above reactions between the carbocation and substances other than phenol are inferred to be the condensation reaction. In other words, the phenol concentration suppresses the phenolysis (liquefaction) and promotes the condensation reaction.

3.1.2 Effect of reaction temperatures on the condensation reaction

The reaction time of residue content at different reaction temperatures is shown in Fig. 2. The residue contents were increased in the case of 180°C and 160°C. Meanwhile, the residue contents became almost constant in the case of 120°C after 90 min. It was found that the higher reaction temperatures promoted the condensation reaction because of much carbocation, and phenol was consumed quickly at higher reaction temperature, which degraded the woody constituents severely. When the reaction temperature was 120°C, the residue content was remaining about 20%, indicating that the waste woody meal was not degraded compared with the cases of other temperatures. Accordingly, the condensation reaction seems to be hard to occur unless the woody constituents are intensively degraded.

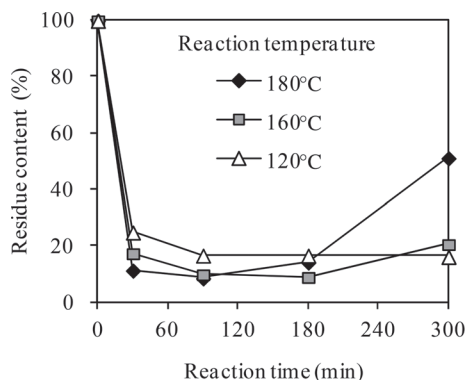


Figure 2: The reaction time of residue content at different reaction temperatures. Other reaction conditions – charge ratio of phenol to wood: 2:1; catalyst contents: 50% and woody meal particle sizes: 0.25–0.50 mm.

3.1.3 Effect of catalyst contents on the condensation reaction

The reaction time of residue content for different catalyst contents is shown in Fig. 3. More catalyst content led to significant increases of residue content. The reason for this was considered as high production of the carbocation and high consumption of phenol, similar to the experiment at different reaction temperatures. The increase of residue content was not observed when 10% sulfuric acid was added. In this case, most of the woody meal was liquefied when the residue content decreased to less than 5% at 300 min. Therefore, it was indicated that the condensation reaction did not occur necessarily even though most of the woody meals were liquefied. This was considered because the molecules of liquefied woody meal were large. If the molecules were degraded to small, the condensation reaction would occur easily because of its less steric hindrance against the reaction site of the condensation reaction. However, even in that case, the high concentration of remaining phenol could cover the sites.

3.1.4 Effect of woody meal particle sizes on the condensation reaction

The reaction time of residue content for different woody meal particle sizes is shown in Fig. 4. It was found that the condensation reaction occurred significantly with smaller woody meal particle. This was considered because phenol was consumed quickly in the phenolysis, accelerated with smaller woody meal particle. Actually, in the cases of woody meal particle size of 0.50–1.0 mm, the time at which the residue content began to increase was later than the cases of other particle sizes. The similar tendency was also determined as presented in Fig. 3.

In general, the condensation reaction is estimated by the residue content [6, 8, 14] because the method is easy to perform. However, only the solid condensed matter can be estimated by this method. The condensation reaction occurred in the liquid phase and after that, the solid condensed matter was produced. Therefore, the condensation reaction could occur in the liquid phase even if the increase of residue content was not observed. In order to confirm it, the molecular weight distributions were measured for the reaction condition of Run 4 where the increase of residue content was not observed (Fig. 2). The molecular weight distribution is shown in Fig. 5. A peak appearing after 20 min was derived from low-molecular-weight substance including unreacted phenol. On the other hand, a peak appearing around 15 min was derived from the substance of molecular weight higher than exclusion limit of the columns, which was mainly due to the presence of condensed matter.

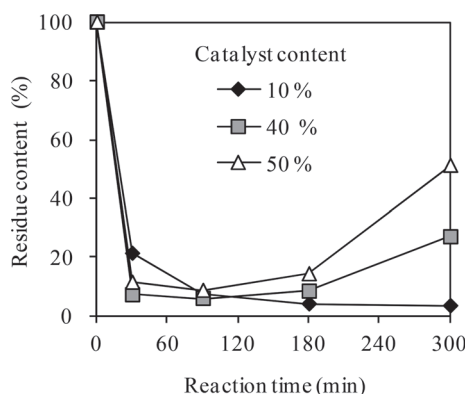


Figure 3: The reaction time of residue content for different catalyst contents. Other reaction conditions – reaction temperature 180°C; charge ratio of phenol to wood: 2:1 and woody meal particle sizes: 0.25–0.50 mm.

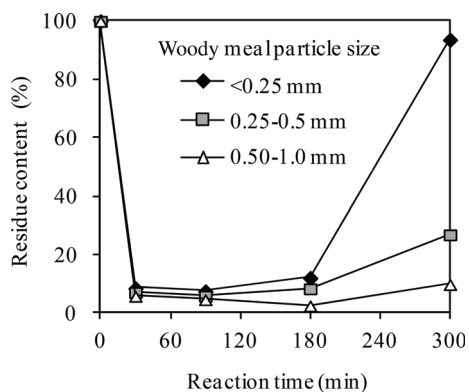


Figure 4: The reaction time of residue content for different woody meal particle sizes. Other reaction conditions – reaction time: 180°C; charge ratio of phenol to wood: 2:1 and catalyst content: 30%.

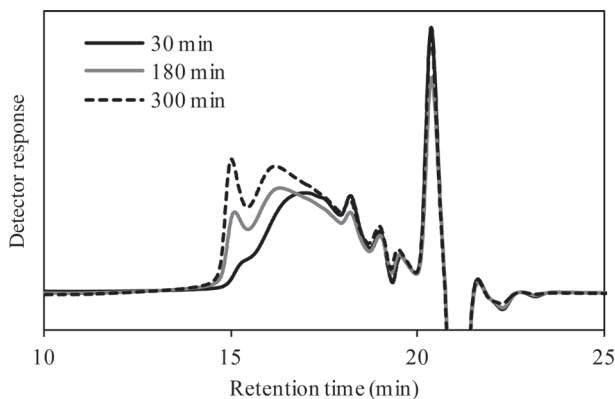


Figure 5: The change in GPC chromatogram. Other reaction conditions: charge ratio of phenol to wood: 2:1; reaction temperature: 120°C; catalyst contents: 50% and woody meal particle sizes: 0.25–0.50 mm.

It was clearly observed that the peak of high-molecular-weight substance increased with the reaction time, which is a typical tendency of the condensation reaction. After that, the peak of high-molecular-weight substance diminished because the solid condensed matter was formed [6]. Therefore, it can be said that the increase of the residue content cannot be the only reason to decide whether the condensation reaction has occurred. However, the measurement of residue content was helpful to estimate the extent of the condensation reaction comparatively, as discussed above.

As observed above, the condensation reaction tends to become more significant under the reaction condition where reaction temperature and catalyst content were higher and woody meal particle sizes were smaller. On the other hand, it was already found that the liquefaction also became fast under higher temperature and concentration of catalyst content [15]. Additionally, the same tendency was considered true for the reaction condition with the smaller woody meal particle sizes. Therefore, it can be concluded that the intense liquefaction conditions lead to the intense condensation reaction.

3.2 Relationship between the condensation reaction and phenol concentrations

If the condensation reaction occurs, the consumption of phenol is thought to be inhibited because the condensation reaction might occur before the phenolysis. Moreover, the phenol concentration should be lower than the case without the condensation reaction. In order to confirm these speculations, the experiments in Section 3.2 were carried out. The reaction time of residue content and phenol concentration under mild reaction condition is shown in Fig. 6. The residue content decreased gradually from the start of reaction time, indicating that the liquefaction proceeded slowly. Similarly, the phenol concentration also decreased gradually, indicating that the phenol continued to be consumed due to phenolysis. Therefore, it was clearly shown that the phenol concentration continued to decrease in the absence of the condensation reaction.

The effects of the phenol concentration on the condensation reaction were investigated. The reaction time of residue content and phenol concentration for different woody meal particle sizes is shown in Fig. 7. According to the result, in the case of particle <0.25 mm, the residue content increased significantly from 90 min, indicating that the condensation reaction has occurred significantly. On the other hand, the increase in residue content was not observed in the case of particle size

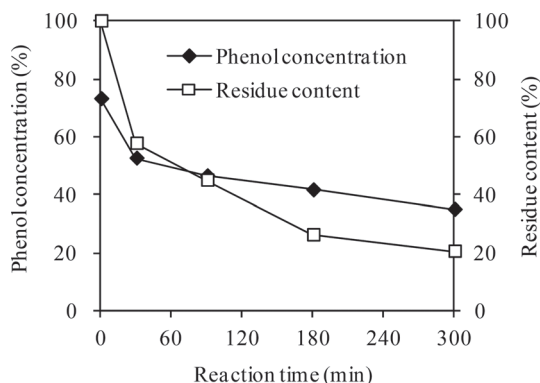


Figure 6: The reaction time of residue content and phenol concentrations. Other reaction conditions – reaction temperature: 120°C; charge ratio of phenol to wood: 3:1; catalyst contents: 10% and woody meal particle sizes: 0.50–1.0 mm.

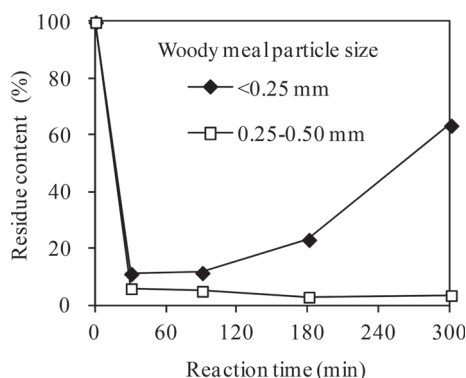


Figure 7: The reaction time of residue content for different woody meal particle sizes. Other reaction conditions – charge ratio of phenol to wood: 2:1; reaction temperature: 180°C and catalyst contents: 50%.

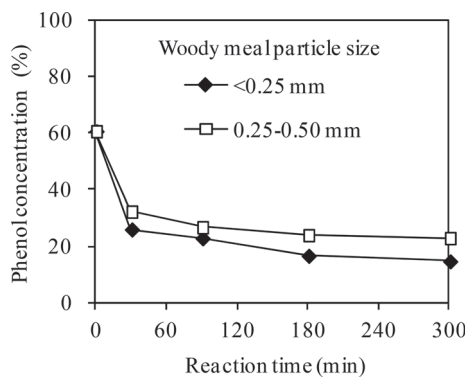


Figure 8: The reaction time of phenol concentrations for two different woody meal particle sizes. Other reaction conditions – charge ratio of phenol to wood: 2:1; reaction temperature: 180°C and catalyst contents: 50%.

0.25–0.50 mm. The phenol concentration was measured for these two conditions (Fig. 8). It was shown that the phenol concentration was lower from the beginning to the end when the increase of residue content was observed. The difference was 8% at the end. Furthermore, the phenol concentration became almost stable after 180 min. These results indicated that the phenolysis was suppressed and the condensation reaction was promoted due to the drop in the phenol concentration. However, in the case of particle size 0.25–0.50 mm, the phenol concentration also became stable. The considerable reason for this was the condensation reaction occurred, although the increase of the residue content was not observed.

3.3 Effect of methanol addition to liquefaction system on condensation reaction

The effect of methanol addition to liquefaction system on the condensation reaction was investigated. The additional amount of methanol was set as 50% to phenol (mol/mol). As shown in Fig. 9, the condensation reaction was suppressed when methanol was added to the liquefaction system.

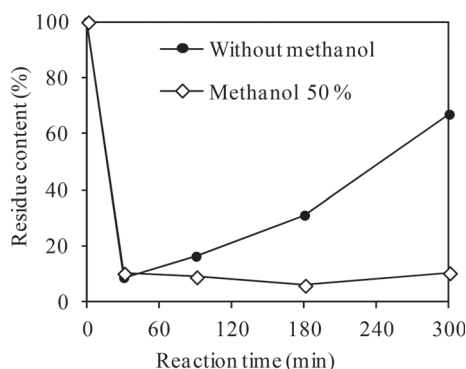


Figure 9: The reaction time of residue content with methanol and without methanol. Other reaction conditions – reaction temperature: 180°C; charge ratio of phenol to wood: 2:1; catalyst contents: 40% and woody meal particle sizes: <0.25 mm.

It was reported that methanol reacted with cellulose and became bound methanol like phenol (so-called ‘methanolysis’) [16]. Therefore, it was considered that the methanolysis and the phenolysis proceeded at the same time in the liquefaction. As a result, the bound phenol that could be the reaction site of the condensation reaction [8] would be decreased in the presence of methanol. That could be the reason why methanol suppressed the condensation reaction.

This methanol addition method can be applicable to the suppression method of the condensation reaction. However, too much additional amount of methanol is not desirable in the synthesis of phenol resin. Much addition of methanol could reduce the amount of the bound phenol, which is also the reaction site of the synthesis reaction of phenol resin. Additionally, methanol itself is not required for the resin synthesis reaction. The addition of 50% methanol seemed to be high but it can be reduced further in the more applicable reaction condition with mild condensation reaction.

4 CONCLUSIONS

This paper was concerned with the effect of the various reaction conditions on the condensation reaction during the liquefaction process of waste woody materials. According to the results, it was found that the intense reaction conditions promoted the condensation reaction. It was observed that the residue content began to increase at earlier reaction time when the stronger condensation reaction occurred. From these observations, it was indicated that the condensation reaction was likely to occur when the woody meal was decomposed strongly. From the measurement of the molecular weight distributions, it was showed that the condensation reaction occurred even if the increase of the residue content was not observed. Therefore, it can be concluded that the presence of the condensation reaction cannot be decided only from the measurement of residue content.

The phenol concentration in the reactant showed a gradual decreasing trend even after 300 min of reaction time when the increase of the residue content was not observed under the mild reaction condition. This result indicated that the phenol continued to be consumed if the condensation reaction did not occur. On the other hand, the phenol concentration became almost stable when the condensation reaction significantly occurred. Therefore, it was considered that the liquefaction reaction (phenolysis) becomes difficult to proceed after the remarkable condensation reaction. Moreover, it was shown that the phenol concentration was lower when the residue content highly increased.

Therefore, it was concluded that the drop in the phenol concentration will cause the condensation reaction during the liquefaction process.

The condensation reaction was suppressed with the addition of 50% methanol. For the future studies, this methanol addition method can be applied as an effective method for suppression of the condensation reaction.

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