# OPTIMIZATION FOR THE LIQUEFACTION OF MOSO BAMBOO IN PHENOL USING RESPONSE SURFACE METHODOLOGY

*Rongrong Li*

Lecturer
Beijing Key Laboratory of Wood Science and Engineering
Beijing Forestry University
Beijing, China 100083
College of Furnishings and Industrial Design
Nanjing Forestry University
Nanjing, China 210037
E-mail: lirr722@hotmail.com

*Wei Xu*

Associate Professor
College of Furnishings and Industrial Design
Nanjing Forestry University
Nanjing, China 210037
E-mail: xuwei@njfu.edu.cn

*Chuangui Wang*

Professor
School of Forestry and Landscape Architecture
Anhui Agriculture University
Hefei, China 230036
E-mail: 15055196968@163.com

*Shuangbao Zhang**

Professor
Beijing Key Laboratory of Wood Science and Engineering
Beijing Forestry University
Beijing, China 100083
E-mail: shuangbaozhang@163.com

*Wei Song**

PhD Student
Beijing Key Laboratory of Wood Science and Engineering
Beijing Forestry University
Beijing, China 100083
E-mail: j5international@163.com

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**Abstract.** Bamboo liquefaction is a key process during bamboo high-value utilization, such as bamboo-based nano-carbon fiber manufacturing. Liquefaction parameters have direct effects on the performance of final products. The impact of mass ratio of phenol/bamboo (P/B) powder, temperature, and liquefaction time during moso bamboo liquefaction was studied. All these parameters were studied to perform experiments based on response surface methodology (RSM). Residue content was calculated to evaluate the efficiency of moso bamboo liquefaction. Mathematical models were developed to establish the relationship between the liquefaction parameters and residue content. The results showed that within certain limits the residue content

* Corresponding author

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decreased with the increase of P/B and temperature; however, a further increase of P/B and temperature caused the residue content to increase. In the selected range of liquefaction time in this study, the residue content decreased with the increase of liquefaction time. The optimized combination of liquefaction parameters was 4.5, 163°C, and 46 min for P/B, temperature, and liquefaction time, respectively. The optimized result of residue content from RSM was 7.41934E-008 (%), which meant the bamboo almost completely liquefied. Because of the reasonable error of experiment, the optimized result of residue content from the confirmation experiment was 0.06%.

***Keywords:*** Liquefaction, moso bamboo, response surface methodology, residue content.

## INTRODUCTION

Moso bamboo as an important nontimber forest product is widely distributed in China. Owing to its rapid growth rate and short maturity cycle, it is a good substitute for other wood resources. At present, moso bamboo is usually applied for manufacturing panels, furniture, and structural composites (Xie et al 2016). However, the efficiency and added-value of bamboo use are badly in need of improvement. Researchers have carried out many methods for bamboo-based high-value-added products, such as bamboo-based nano-carbon fiber (Ma and Zhao 2008, 2011; Ma et al 2014). It has a positive effect on reducing usage of petroleum products, and nano-carbon fiber is also a good carrier for photocatalytic material, which has higher value-added than traditional bamboo based products.

Liquefaction, as an important process in bamboo-based nano-carbon fiber manufacturing, has significant effects on the performance of the final product.

Catalytic liquefaction is a promising technology for converting biomass materials to produce sustainable liquid biofuels and chemicals. The published works have revealed that liquefaction parameters have significant influence on residue content during biomass material liquefaction process (Zhang et al 2015; Chu et al 2016; Wu et al 2016; Ye et al 2017). Barnes et al (2017) studied the effect of solvent on wood liquefaction by processing pinewood at 310°C. The results showed that the perfect solvent should have a good interaction with the biomass materials and its initial decay products to minimize char formation. Li et al (2015a) liquefied wood with phenol by microwave heating. The effect of phenol on liquefaction and liquefied residue was evaluated. Results showed that a low phenol to wood ratio tended to result in carbonization of liquefied wood because of an insufficient amount of phenol. Janiszewska et al (2016) presented the characteristics of wood liquefied using different types of solvents in terms of its application for binding particleboards. A slight decrease in the bending strength was observed when a mixture of glycerine and dipropylene glycol was used as the liquefying agent, but this parameter still fulfilled the demands of the European quality standard. The previous published papers revealed that phenol/bamboo (P/B), temperature, liquefaction time, and type of catalyst had significant influence on biomass material liquefaction (Fu et al 2008; Jiao et al 2008; Zhang et al 2009).

However, large amounts of solvents and a long reaction time are required during biomass material liquefaction, bringing with it a considerable increase in the cost of the liquefaction. Therefore, it is urgent to develop an optimized combination of liquefaction parameters. Response surface methodology (RSM) is a collection of mathematical and statistical techniques that are useful for modeling and analyzing the effects of several variables on the response, to optimize this response. In this study, mass ratio of P/B powder, temperature, and liquefaction time were selected as input parameters. The effects of these parameters were analyzed by using RSM, and a specific residue content model for moso bamboo liquefaction process was also established by using RSM. The model considers the specific residue content in terms of the liquefaction parameters which were selected in this research. This model was found helpful in determining liquefaction parameters for moso bamboo.

## MATERIALS AND METHODS

### Materials

The age of moso bamboo used in these experiments was 5 yr, and the material was harvested in Jinzhai, Anhui, China. The composition of moso bamboo was determined according to Chinese standards (GB/T 2677.8 1994; GB/T 2677.10 1995; GB/T 742 2008) as shown in Table 1. Moso bamboo sections were shattered into bamboo powder with particle size of 60-80 mesh, oven-dried at 105°C for 24 h, and then stored in a desiccator to prevent the water exchange between bamboo powder and the environment. The 98 wt% sulfuric acid and phenol used in this experiment were bought from Shanghai Runjie Chemical Reagent Co. Ltd (Shanghai, China).

### Experimental Setup and Procedure

The liquefaction experiments were performed in a 250-mL flask equipped with a mechanical stirrer and a mercurial thermometer to record temperature. The flask was fixed in numerical show constant temperature oil-bathing to acquire the certain temperature for bamboo liquefaction. A total of 5 g of bamboo powder and a certain amount of phenol were introduced into the flask. The reaction was catalyzed by 98 wt% sulfuric acid with an amount of 6% of phenol mass. The time of liquefaction experiment was recorded when the temperature in the flask reached a set point, then the mechanical stirrer was started with a spindle speed of 1000 rpm.

When the reaction was completed, the flask was immersed in a cold water bath (with a temperature of 20°C) to stop the reactions. Then, the material was dissolved in absolute ethyl alcohol under constant stirring for 3 h. The liquefied solutions were vacuum-filtered by using a G4 glass pot. The solid residue retained in the glass pot was oven-dried to a constant weight at 105°C, and the residue content (R/%) was calculated as Eq 1 as follows:

$$R(\%) = \frac{W_r}{W_{BP}} \times 100, \quad (1)$$

where $W_r$ is the weight of residue during moso bamboo liquefaction and $W_{BP}$ is the weight of moso bamboo powder.

Table 1. Composition of moso bamboo.

| Composition | Holocellulose | Acid-insoluble lignin | Ash |
|---|---|---|---|
| Content (%) | 74.81 | 26.54 | 0.74 |

### Plan of Experiment

The analyses and modeling techniques of RSM by using Box-Behnken design (BBD) were applied. The Design-Expert Software was used in the organization of the experimental plan for RSM. It was also used to analyze the data obtained from the experiment (Li et al 2015b, 2015c, 2015d, 2016).

In the analysis, procedure for the approximation of the response was achieved by developing a BBD-based RSM model. Eq (2) presents a model of bamboo liquefaction process.

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i,j}^{k} b_{ij} X_i X_j + \sum_{i=1}^{k} b_{ii} X_i^2, \quad (2)$$

where $b_0$ is the free term of the regression equation. The coefficients, $b_1$, $b_2$, … $b_k$ and $b_{11}$, $b_{22}$, … $b_{kk}$ are the linear and quadratic terms, respectively, whereas $b_{12}$, $b_{13}$, … $b_{kk-1}$ are the interacting terms. The experimental plan was developed to assess the effects of P/B, temperature, and liquefaction time on residue content during the bamboo liquefaction process (Aouici et al 2013).

In this study, the liquefaction experiments are conducted at three levels. The parameters applied and their levels are shown in Table 2.

## RESULTS AND DISCUSSION

The results of residue content are shown in Table 3. All these experiments were conducted in a random order.

Table 2. Liquefaction parameters and levels.

| Parameters | Code | Level | | |
|---|---|---|---|---|
| | | −1 | 0 | 1 |
| Mass ratio of phenol to bamboo powder, P/B | A | 3 | 4 | 5 |
| Temperature, $T$ (°C) | B | 140 | 160 | 180 |
| Liquefaction time, $t$ (min) | C | 30 | 45 | 60 |

## Analysis of Variance (ANOVA)

ANOVA was carried out to ascertain the BBD model adequacy of this experimental design and know the factors having significant influence on the bamboo liquefaction process. The results of the ANOVA for residue content are shown in Table 4. The model $R$ was significant with a probability of $<0.0001$. $p$ value less than 0.05 indicated that the model terms were significant. In this case, the model terms A, B, and C are significant for residue content because of significant contribution to residue content during moso bamboo liquefaction. These results will be important for optimizing liquefaction parameters and selecting reaction parameters for moso bamboo liquefaction.

## Regression Equations

The Design Expert software was applied to develop response surface equations for residue content during moso bamboo liquefaction. The summary statistics of the suggested models are listed in Table 5. The values of $R^2$ are very close to 1, which means that the model achieved a high degree of fit and can provide a satisfying prediction for the experimental results in moso bamboo liquefaction. A quadratic model was selected to obtain the relationship between residue content and liquefaction variable because of the high value of $R^2$. The model equation for residue content during moso bamboo liquefaction is stated in Eq 3 as:

$$\begin{aligned} R/\% = {} & 0.16 - 0.70 \times A - 0.70 \times B - 0.43 \times C \\ & + 0.14 \times A \times B + 0.50 \times A \times C \\ & + 0.39 \times B \times C + 1.03 \times A^2 \\ & + 0.95 \times B^2 - 0.38 \times C^2, \end{aligned} \tag{3}$$

where $A$ is the mass ratio of P/B powder, $B$ is the temperature in °C, and $C$ is the liquefaction time in min.

Table 3. Design matrix and experimentally recorded data.

| Order | Factors | | | Residue content, $R$ (%) |
|---|---|---|---|---|
| | Mass ratio of phenol to bamboo powder, P/B | Temperature, $T$ (°C) | Liquefaction time, $t$ (min) | |
| 1 | 3 | 140 | 45 | 3.86 |
| 2 | 5 | 140 | 45 | 1.84 |
| 3 | 3 | 180 | 45 | 2.17 |
| 4 | 5 | 180 | 45 | 0.73 |
| 5 | 3 | 160 | 30 | 2.36 |
| 6 | 5 | 160 | 30 | 0.26 |
| 7 | 3 | 160 | 60 | 0.37 |
| 8 | 5 | 160 | 60 | 0.29 |
| 9 | 4 | 140 | 30 | 2.18 |
| 10 | 4 | 180 | 30 | 0.03 |
| 11 | 4 | 140 | 60 | 0.68 |
| 12 | 4 | 180 | 60 | 0.07 |
| 13 | 4 | 160 | 45 | 0.16 |
| 14 | 4 | 160 | 45 | 0.17 |
| 15 | 4 | 160 | 45 | 0.16 |
| 16 | 4 | 160 | 45 | 0.17 |
| 17 | 4 | 160 | 45 | 0.16 |

Table 4. Results of the analysis of variance for residue content.

| Source | Sum of squares | df | Mean square | $F$ value | $P$ value prob > $F$ |
|---|---|---|---|---|---|
| Model | 20.07 | 9 | 2.23 | 65.55 | <0.0001 |
| A—mass ratio of phenol to bamboo powder | 3.97 | 1 | 3.97 | 116.71 | <0.0001 |
| B—temperature | 3.86 | 1 | 3.86 | 113.58 | <0.0001 |
| C—liquefaction time | 1.47 | 1 | 1.47 | 43.07 | 0.0003 |
| AB | 0.084 | 1 | 0.084 | 2.47 | 0.1599 |
| AC | 1.02 | 1 | 1.02 | 29.86 | 0.0009 |
| BC | 0.59 | 1 | 0.59 | 17.43 | 0.0042 |
| $A^2$ | 4.50 | 1 | 4.50 | 132.19 | <0.0001 |
| $B^2$ | 3.82 | 1 | 3.82 | 112.28 | <0.0001 |
| $C^2$ | 0.60 | 1 | 0.60 | 17.54 | 0.0041 |
| Cor total | 20.31 | 16 | — | — | — |

Cor., total is sum of squares for total; df, degree of freedom.

The results of predicted and actual residue content for this study are shown in Fig 1. The predicted values from the quadratic model are very close to the actual values of residue content; in other words, the established model is effective to predict the residue content of bamboo liquefaction in phenol.

## Effects of Input Parameters on Residue Content during Moso Bamboo Liquefaction

The results of this study revealed the effects of P/B, temperature, and liquefaction time on residue content during moso bamboo liquefaction. The residue content during liquefaction has a direct influence on bamboo usage, such as bamboo liquefaction spinning processing (Ma and Zhao 2011). A lower value of residue content is preferable during bamboo liquefaction. From previous research, it can be asserted that research and modeling of residue content during bamboo liquefaction are important; the models and effects can be carried out using RSM.

The effect graph for liquefying parameters (P/B, temperature, and liquefaction time) is shown in Fig 2, where it is obvious that P/B and temperature have significant effects on residue content. Within certain limits, the residue content decreased with the increasing P/B and temperature, however, a further increase of P/B caused the residue content to increase. A similar tendency has been observed in some other biomass liquefaction processes (Lu et al 2016). Higher temperature would be in favor of speeding up moso bamboo liquefaction because when moso bamboo is heated, attacks would be initiated on the glycosidic linkages, leading to dehydration, decarbonylation, and cleavage of the molecules into smaller fragments (Zhou et al 2016). But excessive temperature has a negative effect on moso bamboo liquefaction owing to low molecular compounds condensed into an insoluble substance in excessive high temperature. The result has a good agreement to giant reed liquefaction (Jiao et al 2008). For P/B, the residue content decreased with the increasing P/B, but when the P/B increases to a high value, it will have a negative effect on bamboo liquefaction. The value of P/B has a direct influence on the viscosity of the liquefied products (Li et al 2015a). A better fluidity of liquefied products will be acquired in enough phenol. These results indicate that a low value of P/B tends to result in recondensation of low molecular compounds to insoluble residue, possibly because of an insufficient amount of phenol in the reaction system. In Fig 2, when the liquefaction time

Table 5. Summary of results of analysis of variance for different models.

| Responses | Source | Standard deviation | $R^2$ | Adjusted $R^2$ | Predicted $R^2$ | Press |
|---|---|---|---|---|---|---|
| Residue content (%) | Quadratic | 0.18 | 0.9883 | 0.9732 | 0.8125 | 3.81 |

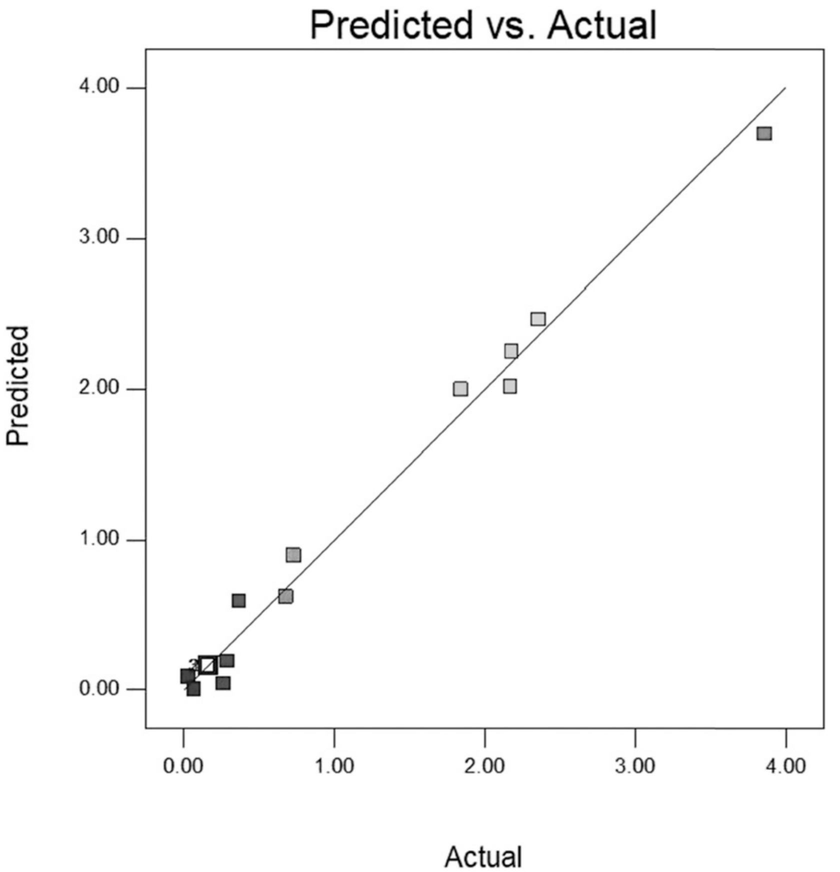


Figure 1. Correlation graph of predicted and actual values for *R*.

increased, the residue content decreased. It can be concluded that the degradation reaction dominated the initial liquefaction to result in the increase of the liquefaction yield. Then, the degradation reaction and polycondensation reaction reached a balance. In the later stage of liquefaction, the polycondensation reaction would bring about an increase in the residue content.

From the result of ANOVA, the interaction effect of liquefaction parameters had a significant effect on residue content (as shown in Fig 3). From Fig 3, it is easy to find the optimized liquefaction parameters for moso bamboo. With the target of residue content at zero, the optimized combination of liquefaction parameters was 4.5, 163°C, and 46 min for P/B, temperature, and liquefaction time, respectively. The optimized result of residue content from RSM was 7.41934E-008 (%), which meant that moso bamboo almost completely liquefied. The optimized result was confirmed by the experiment. Because of the reasonable error of experiment, the optimized result of residue content from the confirmation experiment was 0.06%.

## CONCLUSIONS

The effects of liquefaction parameters on residue content during the moso bamboo liquefaction process were researched and the main conclusions are as follows:

1. In the moso bamboo liquefaction process, the considered parameters (P/B, temperature, and liquefaction time) in this study have significant

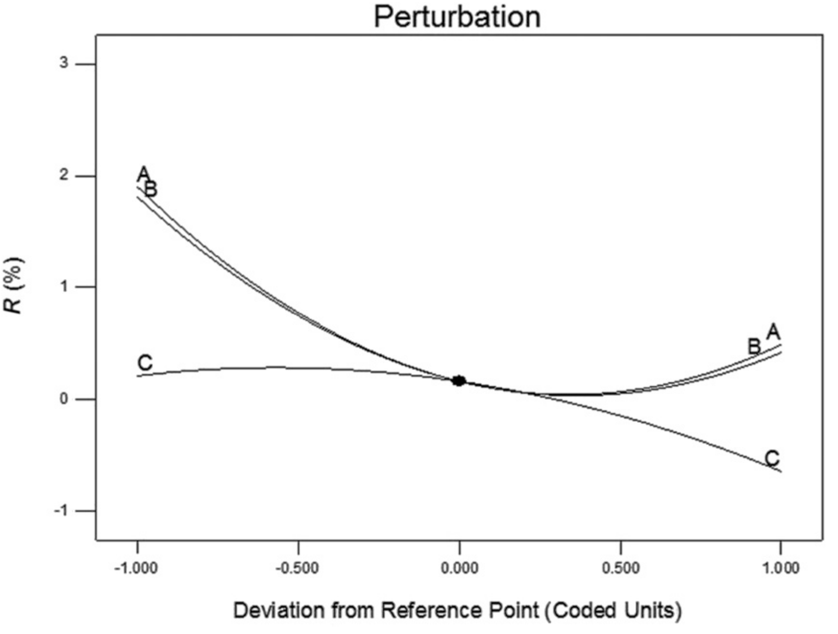


Figure 2. The effect of liquefaction parameters on residue content.

effects on residue content with $p$ value less than 0.05.

2. Within certain limits, the residue content decreased with the increasing P/B and temperature; however, a further increase of P/B and temperature caused the residue content to increase. The residue content decreased with increasing liquefaction time.
3. The optimized combination of liquefaction parameters were 4.5, 163°C, and 46 min for P/B, temperature, and liquefaction time, respectively. The optimized result of residue content from RSM was 7.41934E-008 (%), which meant moso bamboo almost completely liquefied. Because of the reasonable error of experiment, the optimized result of

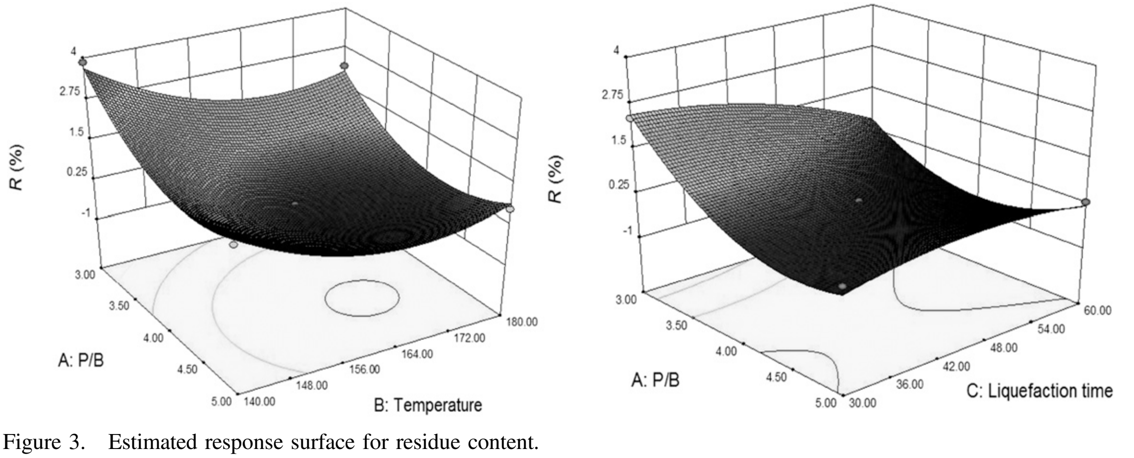


Figure 3. Estimated response surface for residue content.

residue content from the confirmation experiment was 0.06%.

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