

# Biorefinery cascade processing for converting corncob to xylooligosaccharides and glucose by maleic acid pretreatment

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## Research Article

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# Abstract

Corn cob as an abundant and low-cost waste resource has received increasing attention to produce value-added chemicals, it is rich in xylan and regarded as the most preferable feedstock for preparing xylooligosaccharides. The use of xylooligosaccharides as core products can cut costs and improve the economic efficiency in biorefinery. In this study, maleic acid, as a non-toxic and edible acidic catalyst, was employed to pretreat corn cob and produce xylooligosaccharides. A response surface methodology experimental procedure yielded 52.9% xylooligosaccharides using 0.5% maleic acid at 155 °C for 26 min. Maleic acid prehydrolysis generated a positive effect for enhancing the enzymatic hydrolysis efficiency, resulting in an enzymatic glucose yield of 87.5% with a total of 10% solids loading. A cascade processing for converting corn cob to xylooligosaccharides and glucose by sequential maleic acid pretreatment and enzymatic hydrolysis was designed for the corn cob wastes utilization.

## Introduction

Biorefinery technologies provide a route to improve the use of lignocellulosic biomass, especially in the agricultural and forestry waste processing industries, which could be used as raw materials for producing energy, chemicals, and fuels (Boonchuay et al., 2018; Chen et al., 2021; Li et al., 2020). Corn cob, as the main byproduct of corn processing, is a suitable candidate for biorefinery because it is inexpensive and available in abundance (Cai et al., 2021). In 2020, the world corn production was 885.3 million tons and China holds the second position with 260.7 million tons (Arumugam et al., 2021). That means about 41.5 - 46.1 million tons of corn cob could be obtained from corn production in China. However, due to lack of policy support and poor management, a large amount of corn cob was burned or discarded, resulting in serious environmental pollution and waste of resources. Therefore, it is urgent to develop an efficient approach for the efficient utilization of this renewable feedstock. The contents of corn cob mainly include cellulose (39-45%), hemicellulose (25-35%), and lignin (17-21%), and its ash and extractives content are very low (Liao et al., 2021). Hence, the efficient utilization and conversion of polysaccharide components from cellulose and hemicellulose plays a crucial role to develop an economically feasible biorefinery process of lignocellulosic biomass.

Cellulose can be transformed into glucose by pretreatment and enzymatic hydrolysis, and then glucose can be further converted to various fuels and organic acids via fermentation (Himmel et al., 2007; Ríos-González et al., 2021; Wei et al., 2021). Hemicellulose, which is mainly composed of xylan, can be transformed to xylose, furfural, xylonic acid, xylitol, xylooligosaccharides (XOS) (Jayapal et al., 2013; Scopel and Rezende, 2021). Among others, XOS are acting as emerging functional oligosaccharides, which show favorable effects on human intestinal flora by selectively promoting the growth of probiotic bacteria (Lian et al., 2020; Mhetras et al., 2019). The worldwide market for XOS is increasing yearly, and it is estimated to reach \$ 130 million by 2023, which makes XOS become one of the most competitive products all over the world (Santibáez et al., 2020; Singh et al., 2019). Overall, the corn cob biorefinery focused on XOS production can effectively boost the agricultural waste processing industries' economy (Huang et al., 2019).

Pretreatment of lignocellulosic biomass is the first and crucial step of a biorefinery, and pretreatment methods mainly include enzymatic, alkaline, and acidic treatment (Lin et al., 2020; Wei et al., 2021; Zhang et al., 2018; Zheng et al., 2021). Enzymatic pretreatment is not associated with a pollution problem apart from its high cost, while alkaline is environmentally problematic despite its low cost. Thus, the prospect of industrialization is still some way off for both methods. In contrast, acid pretreatment is preferable due to its dual functions, XOS production and pretreatment for improving enzymatic hydrolysis (Cesaro et al., 2020; Ling et al., 2020; Yang et al., 2016). Acid pretreatment could be either mineral acid or organic acid hydrolysis, which both of them have been reported to be capable of hydrolyzing xylan to produce XOS (Zhou and Xu, 2019). However, the use of strong mineral acids always leads to an excessive xylan degradation to undesired by-products such as xylose and furfural, leading to a decrease in the yield of XOS. Comparatively, organic acids tend to be more favorable for XOS generation because of their considerable benefits, such as high yields of oligomeric sugars and lower amounts of degradation by-products.

Regardless of the type of acids used, their separation and recovery are inevitable steps to the production of XOS. However, using edible organic acids like acetic acid and gluconic acid, which could be co-prepared with XOS as feed additives, could reduce the production cost and water treatment cost (Guo et al., 2021; Moure et al., 2006). Although edible gluconic acid and acetic acid have been reported to achieve high XOS yields of over 50%, the usage of acid concentration over 10% resulted in a low XOS product purity when acid and XOS were simultaneously co-prepared (Han et al., 2020; Zhang et al., 2017). Maleic acid (MA) is also a type of edible organic acid that has been mainly used in pharmaceutical and resin synthesis (Bian et al., 2019). Relatively, MA, as a dicarboxylic and tiny molecule acid, shows a low pKa value with a low dosage, which can depolymerize hemicelluloses more efficiently compared with monocarboxylic acids. In this study, MA was used as an acid catalyst for the pretreatment of the corncob. To get the highest yield of XOS, the optimum values of the reaction temperature, MA concentration, and hydrolysis time were evaluated using response surface methodology (RSM) experimental design (Bian et al., 2014). The interactive effects of the variables were also studied. Subsequently, the enzymatic hydrolysis of MA pretreated corncob solids was evaluated. We have designed a new and cascade biorefinery process for the co-production of XOS and glucose using MA as an acid catalyst.

## **Materials And Methods**

### ***2.1 Materials***

Corn cob was harvested in October 2020 in Shandong, China. It was ground to 60-80 mesh and naturally air-dried to a constant moisture content of less than 10%. The air-dried corn cob powder was used as feedstock to conduct the subsequent experiments. The chemical composition of corn cob was determined by National Renewable Energy Laboratory's standard method, and it mainly contained 33.1% glucan, 31.8% xylan, 19.0% lignin, and 4.2% ash (Sluiter et al., 2010).

### ***2.2 Maleic acid pre-hydrolysis***

The reaction temperature ( $x_1$ ), hydrolysis time ( $x_2$ ), and MA concentration ( $x_3$ ), as the key factors for corncob hydrolysis, were investigated and optimized by the response surface method (RSM). As shown in Table 1, a total of 13 experimental runs were performed at the reaction temperature of between 130 and 170°C with 0.25 to 0.75 % (w/v) MA concentration and hydrolysis time of 15 to 45 mins.

The acidic hydrolysis of corncob was conducted in a 50 mL screw-top pressure-resistant steel reactor. 3 g of corncob powder and 30 mL of MA solution were mixed and stirred uniformly, and then the reactor tube was sealed with caps and immersed in the oil bath while it reached the preset temperatures, and held varying durations accordingly. Once the reaction was finished, the reactor tube was immediately taken out and immersed into the cold water bath. The solution was centrifuged, the supernatant was collected for XOS determination, and the residues were used for component analysis and enzymatic hydrolysis process.

### **2.3 Enzymatic hydrolysis**

The corncob residue pretreated with MA was first washed to neutrality by deionized water and then air-dried to a constant weight. The enzymatic hydrolysis assay was performed using a screw-capped 150 mL flask shaken at 50 °C. The cellulase loading was 20 FPIU/g glucan (Cellic CTec2, Novozymes, Sigma, Shanghai, China). Sodium citrate buffer was used for maintaining the pH at 4.8 (0.1 mol/L). After 72 h of the enzymatic hydrolysis process, the slurry was then centrifuged at 6,000×g, and the supernatant was collected.

### **2.4 Response surface method analysis**

The yield of XOS was used as the evaluation index of the response surface method (RSM). A quadratic polynomial stepwise regression fitting was performed on the response values of the indexes through a quadratic polynomial model (Eq. 1) to obtain the functional relationship between the respective variables and the response values of XOS yield. Analysis of variance was employed to test the significance of the RSM experiment.

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \quad (1)$$

In the above model (Eq. 1),  $\beta_0$  was a constant term, while  $\beta_i$ ,  $\beta_{ii}$ , and  $\beta_{ij}$  were the coefficients of the first and quadratic terms, respectively.  $Y$  represented the response value of xylooligosaccharides yield.

## **Results And Discussion**

### 3.1 Hydrolysis of corncob by maleic acid

The degradation rate of hemicelluloses strongly depends on the reaction temperature, reaction time, and acid concentration. Therefore, in this study, the effects of these three factors on the degradation of corncob to produce XOS were first investigated by RSM design, using the minimum set of runs. In this study, the MA concentrations of 0.25 to 0.75% (w/v), hydrolysis time of 15 to 45 min, and reaction temperatures of 130 to 170 °C were selected for optimizing XOS yield. The experimental designs with 13 runs and the XOS yield are presented in Table.

Fig. 1 shows the yields of xylose, X2, X3, X4, X5, X6, and furfural from the RSM designed conditions. The highest XOS yield obtained was 52.4% at a temperature of 150 °C, 0.5% MA solution, and duration of 30 min. As depicted in Fig. 1a, when the reaction was conducted at 130 °C, the XOS yield (the sum of the yields of X2, X3, X4, X5, and X6) increased from 0.8% (0.25% MA, 30 min) to 18.7% (0.75% MA, 30 min) and 1.5% (0.5% MA, 15 min) to 14.1% (0.5% MA, 45 min). Although increased MA concentration and hydrolysis time could slightly increase the reaction rates at the low reaction temperature, the yields of xylose and XOS are still very low. This is because low temperatures decelerated the hemicelluloses being hydrolyzed into oligosaccharides and a high yield of XOS needs a higher reaction temperature. However, when the reaction temperature was raised to 150 °C, the XOS yield decreased sharply with the increase of MA concentration and hydrolysis time. As shown in Fig. 1c, the XOS yield decreased from 28.1% (0.25% MA, 30 min) to 11.6% (0.75% MA, 30 min) and 42.5% (0.5% MA, 15 min) to 8.7% (0.5% MA, 45 min) while the furfural and xylose yields were drastically increased. On the other hand, lower amounts of X5 and X6 but relatively higher amounts of X2 and X3 were obtained. This could suggest that the higher levels of reaction temperature, MA concentration, and hydrolysis time lead to further degradation of XOS into smaller oligosaccharides (X2 and X3) and xylose, even furfural.

The results indicated that reaction temperature, hydrolysis time, and MA concentration significantly influenced the XOS yields. For higher XOS yields, reactions at low temperatures require prolonged hydrolysis time and more acid dosage, which is economically unfavorable, but the excessive temperatures would result in XOS degradation and a large amount of xylose accumulation.

### 3.2 Fitting models

Design Expert software was employed to fit all polynomial models based on the experimental results, which were summarized in Table 1. The data obtained were fitted to a second order polynomial equation. The response values (yields of XOS) were calculated according to the following Equation:

$$Y=17.04x_1+11.01x_2+630.38x_3-0.0387x_1x_2-1.716x_1x_3-2.386x_2x_3-0.0489x_1^2-0.0715x_2^2-288.44x_3^2-1573.46$$

The coefficient of determination ( $R^2 = 0.9644$ ) and adjusted coefficient of determination (Adj.  $R^2 = 0.8574$ ) indicated the feasibility of the fitted model for experimental results and predicted values. Values of Adj.  $R^2$  and Adj.  $R^2$  greater than 0.80 shows the goodness of fit of the regression equation (Nath and

Chattopadhyay, 2007). In addition, the Adeq Precision value of 10.634 (>4) also suggested that the obtained model by RSM analysis was reasonable. Fig. 2 depicts the linear relationship between the predicted and actual value and feasibility of the model. Overall, all data indicated that the model has a good correlation.

The results of the analysis of variance (ANOVA) of the model are given in Table 2. The  $F$ -value of 9.02 and the  $P$ -value of 0.0484 (<0.05) suggest the model is significant. And it can be seen that the  $P$ -values of  $x_1$ ,  $x_1x_2$ ,  $x_1^2$ ,  $x_2^2$ , and  $x_3^2$  were all less than 0.05, indicating all significantly affected the XOS yield. Smaller  $P$ -values represent higher significance. Therefore, the order of significance of each factor on XOS yields was: MA concentration < hydrolysis time < reaction temperature.

The 3D response surface and contour plots, graphical representations of a regression equation, can reveal the interactive effects of two factors on XOS yields. Fig. 3 represents the interaction effect between two independent variables. The results indicated that slight changes in the reaction temperature, hydrolysis time, and MA concentration significantly affected the XOS yield. Furthermore, a higher amount of each independent variable led to accelerated degradation of the corncob. As depicted in Fig. 3a, a maximal contour (XOS yield 50%) could be determined under certain conditions (reaction temperature ranging from 150~160 °C and hydrolysis time ranging from 21~33 min), but further increase in the reaction temperature or hydrolysis time would not improve the XOS yield. Additionally, similar phenomena were observed in Fig. 3b and 3c, indicating the interaction effects of reaction temperature vs MA concentration and hydrolysis time vs MA concentration on XOS yield, respectively.

In the case of lower temperature, higher MA concentration or hydrolysis time is required to improve the XOS yield; however, a consistent increase in the MA concentration or hydrolysis time did not continuously improve the XOS yield. On the other hand, excessive temperature and hydrolysis time lead to XOS degradation and increased xylose yield. These results indicated that these parameters should be controlled to achieve the expected XOS yield. Overall, the values of  $x_1$ ,  $x_2$ , and  $x_3$  were in the ranges of 150~160 °C, 21~33 min, and 0.45~0.55%, respectively, where the yields of XOS increased at least by 50%.

The 3D response surface plots with convex shapes can suggest the optimum condition for the highest response. In the fitted model, the optimal conditions for obtaining the highest XOS yield were 155 °C reaction temperature, 26 min hydrolysis time, and 0.5% MA concentration. The experiment was conducted in triplicate based on the predicted optimal condition. The mean value of the highest XOS yield was 52.9%, with a total amount of 22.27 g/L, which was in agreement with the predicted value (53.8%). Additionally, the X2, X3, X4, X5, and X6 contents in hydrolysate from xylan hydrolysis at optimized conditions were 5.34, 3.59, 3.36, 2.4, and 2.24 g/L, respectively. The experimental result of XOS yield was consistent with the predicted result from the fitted model, suggesting the accuracy of the established regression equation.

### ***3.3 Evaluation of enzymatic hydrolysis efficiency for pretreated corncob***

According to previous reports, acid pretreatment can effectively improve the efficiency of the enzymatic hydrolysis by increasing cellulose accessibility to cellulases (Wei et al., 2021; Yang and Wyman, 2010). Using the optimum conditions (0.5% MA at 155 °C for 26 min) that yielded the maximum XOS, the pretreated residue of corncob was found to contain 56.1% cellulose, 14.7% hemicellulose, and 24.8% lignin. MA pre-hydrolysis process for XOS production also simultaneously changed the composition of the corncob. Most of the cellulose and lignin were preserved in the solid residues after MA pretreatment. Generally, solid loading is a crucial factor for enzymatic hydrolysis, and an increase in solid loading can decrease water/energy consumption and the cost of downstream processing (Martins et al., 2015). Thus, to study the influence of solids loading on enzymatic hydrolysis, 5, 10, and 15% (w/v) of solid loadings were subjected to enzymatic hydrolysis process.

The results of enzymatic hydrolysis with different solids loading indicated that solid loading significantly influenced the efficiency of enzymatic hydrolysis (Fig. 4). Although, the final glucose content increased with increasing solid loading, a final content of 73.1 g/L glucose could only be achieved with 15% solid loading and the yield was only 79.1%. Relatively higher enzymatic hydrolysis yields of 85.4% and 87.5% were obtained from that of 5% and 10% solid loadings, respectively. The decrease in enzymatic hydrolysis yield may be caused by the lack of free water in the high solids loading enzymatic system, which also resulted in difficulties in mass transfer (Cheng et al., 2020). In summary, 10% solid loading is suitable for enzymatic hydrolysis of MA pretreated corncob solids to obtain glucose with a high yield. In addition, the mass balances were systematically calculated for the production data of XOS and glucose, approximately 160 g of XOS (mainly X2, X3, and X4) and 275 g glucose could be obtained by MA pretreatment and subsequently enzymatic hydrolysis process from 1 kg corncob. These results clearly indicated that pretreatment of corncob with MA for co-production of glucose and XOS was a profitable option, which can maximize the economic value of corncob.

## Conclusions

A response surface methodology of pretreating corncob using edible MA to co-produce XOS and glucose as high value products was successfully implemented to determine optimal values of MA concentration, temperature, time. The maximum yield of XOS (52.9%) was achieved with 0.5% MA at 155 °C for 26 min, meanwhile the enzymatic hydrolysis yield of the retained solids residue was 87.5%. MA pretreatment provides an economical and environmentally friendly method for processing the available lignocellulosic biomass.

## Declarations

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### CRediT authorship contribution statement

**Qibo Zhang:** Methodology, Formal analysis, Investigation, Writing-original draft. **Kankan Jiang:** Data curation, Formal analysis, Writing - review & editing. **Xin Zhou:** Conceptualization, Data Curation, Writing - review & editing.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Tables

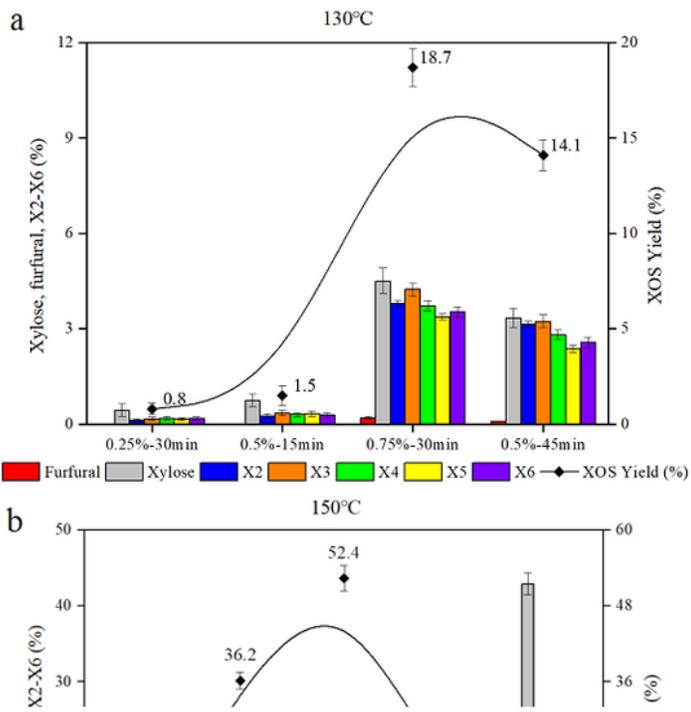
**Table 1.** The experimental design and response value

| Run | Factor                    |                       |                      | Furfural (%) | Xylose (%) | Response |           |
|-----|---------------------------|-----------------------|----------------------|--------------|------------|----------|-----------|
|     | $x_1$                     | $x_2$                 | $x_3$                |              |            | Y        | yield (%) |
|     | Reaction temperature (°C) | Hydrolysis time (min) | MA concentration (%) |              |            |          |           |
| 1   | 130                       | 15                    | 0.5                  | 0            | 0.75       | 1.52     |           |
| 2   | 130                       | 30                    | 0.25                 | 0            | 0.44       | 0.83     |           |
| 3   | 130                       | 30                    | 0.75                 | 0.2          | 4.5        | 18.67    |           |
| 4   | 130                       | 45                    | 0.5                  | 0.1          | 3.34       | 14.12    |           |
| 5   | 150                       | 15                    | 0.25                 | 0.3          | 7.41       | 6.11     |           |
| 6   | 150                       | 15                    | 0.75                 | 0.88         | 16.73      | 36.24    |           |
| 7   | 150                       | 30                    | 0.5                  | 1.2          | 24.3       | 52.39    |           |
| 8   | 150                       | 45                    | 0.25                 | 0.42         | 11.33      | 18.14    |           |
| 9   | 150                       | 45                    | 0.75                 | 4.75         | 42.93      | 12.61    |           |
| 10  | 170                       | 15                    | 0.5                  | 2.44         | 28.5       | 42.52    |           |
| 11  | 170                       | 30                    | 0.25                 | 2.6          | 30.27      | 28.05    |           |
| 12  | 170                       | 30                    | 0.75                 | 9.79         | 57.93      | 11.58    |           |
| 13  | 170                       | 45                    | 0.5                  | 12.06        | 62.69      | 8.71     |           |

**Table 2.** Analysis of variance in RSM model

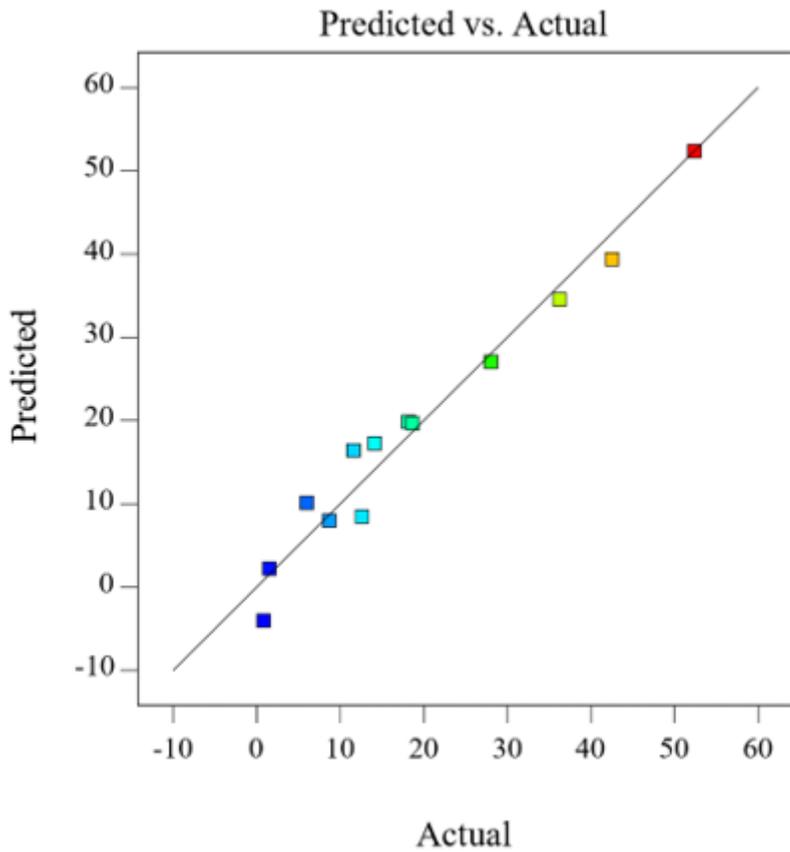
| Source         | Sum of squares | DF | Mean square | F-value | P-value |             |
|----------------|----------------|----|-------------|---------|---------|-------------|
| Model          | 2966.21        | 9  | 329.58      | 9.02    | 0.0484  | Significant |
| -Temperature   | 387.95         | 1  | 387.95      | 10.61   | 0.0472  |             |
| -Time          | 133.74         | 1  | 133.74      | 3.66    | 0.1517  |             |
| -Concentration | 84.89          | 1  | 84.89       | 2.32    | 0.2249  |             |
|                | 538.70         | 1  | 538.70      | 14.74   | 0.0312  |             |
|                | 294.29         | 1  | 294.29      | 8.05    | 0.0658  |             |
|                | 320.23         | 1  | 320.23      | 8.76    | 0.0595  |             |
|                | 874.50         | 1  | 874.50      | 23.93   | 0.0163  |             |
|                | 592.11         | 1  | 592.11      | 16.20   | 0.0276  |             |
|                | 742.84         | 1  | 742.84      | 20.32   | 0.0204  |             |
| Residual       | 109.65         | 3  | 36.55       |         |         |             |
| Cor Total      | 3075.86        | 12 |             |         |         |             |
| R <sup>2</sup> |                |    | 0.9644      |         |         |             |

## Figures



**Figure 1**

Yields of furfural, xylose, X2, X3, X4, X5, and X6 in hydrolysate produced from corncob with different MA concentrations and times at **(a)** 130 °C, **(b)** 150 °C, and **(c)** 170 °C

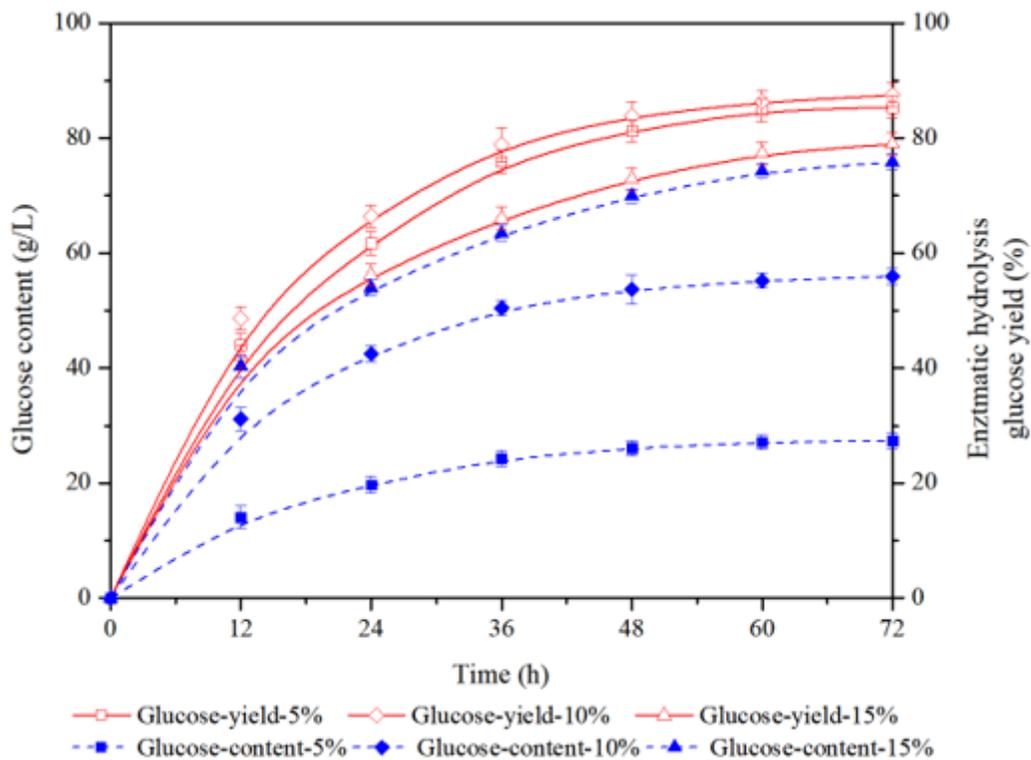


**Figure 2**

Correlation between predicted value and actual value

**Figure 3**

Response surface plots showing interaction effects of reaction temperature and hydrolysis time **(a)**; reaction temperature and MA concentration **(b)**; hydrolysis time and MA concentration **(c)** on XOS production.



**Figure 4**

Performance of enzymatic hydrolysis of solid residue from MA-pretreated corncob using 5, 10 and 15% solid loadings

## Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Graphicabstract.docx](#)