Appl Biochem Biotechnol (2012) 167:250–258
DOI 10.1007/s12010-012-9675-y

# Selective Liquefaction of Wheat Straw in Phenol and Its Fractionation

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Received: 20 December 2011 / Accepted: 9 April 2012 /

**Abstract** For the first time, a method of phenol-selective liquefaction is proposed for the fractionation and multilevel conversion of lignocellulose. Through phenol-selective liquefaction, lignin and hemicellulose are liquefied, with large amounts of cellulose retained in the unliquefied residues. Using a phenol/straw ratio of 3 and a sulfuric acid concentration of 3 %, large amounts of hemicellulose (≥85 %) and lignin (≥70 %) can be liquefied at 100 °C in 30 min, with a high quantity of cellulose (≥80 %) retained. Unliquefied residues from selective liquefaction have higher susceptibility for enzymatic attack. Enzymatic hydrolyzation of residues can be as high as 65 % in 48 h with 40.7 FPU/g of dry materials, which can then be used to prepare sugar platform intermediates. The liquefied products of wheat straw are then resinified with formaldehyde in the presence of NaOH as a catalyst and synthesized into phenol formaldehyde-type resins reaching up to GB/T 14732-2006 standards. Phenol selective liquefaction, a new technology for the fractionation of lignocellulose, achieves effective fractionation and multilevel conversion of straw components. Hence, it is an important tool to achieve full utilization of biomass and high value-added conversion of lignocellulose.

**Keywords** Selective liquefaction · Fractionation · Biomass · Resin adhesive · Enzymatic hydrolysis

## Introduction

Biomass, the most abundant renewable resource in the world, includes forestry residue, agricultural residue, yard waste, wood products, animal and human wastes, and so on [1]. With the depletion of fossil resources and the increased attention to environmental issues, bio-based products are widely used in energy, chemicals, textiles, paper, and herbal medicine due to their environmentally friendly and sustainable features.

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However, because of the structural heterogeneity of biomass materials and the lack of systematic theories on resource utilization, there is still a certain gap before the large-scale application of bio-based products is realized, based on current technologies and economic acceptability. The main reason for this is that only a single technology is generally adopted for producing bio-based products with the utilization of a single component [2], which, in turn, causes pollution and waste of other components.

The lack of technology integration and systems engineering research results in higher costs for the pretreatment of raw materials and other production processes. A variety of conversion technologies should be integrated for directional multilevel conversion based on the characteristics of the materials used in the production of bio-based products to achieve high-value utilization of biomass [3].

Liquefaction with organic solvents [4–10] is an effective means for lignocellulose transformation, by which lignocellulose can be converted into small liquid molecules and used for further synthesis of polymer materials. However, because of lack of concepts on the multilevel utilization of natural solid organic materials, in general, raw materials are liquefied with organic solvents as much as possible to achieve maximum liquefaction yield. This process is called complete liquefaction.

For complete liquefaction of lignocellulose, the conditions adopted are usually acute (high temperature, long reaction time, and large reagent consumption) to obtain the maximum liquefaction yield. Large amounts of unliquefied residues are discarded, which results in resource wastage and pollution. This practice goes against the basic engineering concepts of environment safety, efficiency, and economy.

Currently, phenol plays an important role in the liquefaction of lignocellulose [11–14]. Liquefaction of lignocellulose with phenol is characterized by the easy liquefaction of lignin and hemicellulose. By contrast, cellulose is liquefied with difficultly, retained in the residues, and then discarded. Based on these features, phenol-selective liquefaction of lignocellulose for multilevel conversion is proposed. Hemicellulose and lignin can be liquefied as much as possible, whereas cellulose is retained selectively. Lignin and hemicellulose react with phenol to generate phenolic compounds (those combined with phenol). Liquefied products can also be further synthesized into resin substances [15–18]. Retained high-value cellulose is used in enzymatic hydrolysis to prepare sugar platform intermediates.

Based on the heterogeneity of lignocellulose, the technology of phenol-selective liquefaction of lignocellulose for multilevel conversion is presented for the first time in this paper. The effects of all four variables (liquefaction temperature, time, catalyst concentration, and phenol dosage) on the change in the straw components and enzymatic hydrolysis yield of liquefaction residues are demonstrated. The performance of synthetic resin adhesive from the liquefied products is also assessed. Phenol-selective liquefaction effectively achieves fractionation and biomass full utilization of lignocellulose, thus opening up a new avenue for bio-based product development.

## Materials and Methods

### Materials

The powders of air-dried wheat straw (collected in Hebei Province, China) were grinded into 20–80 mesh, and its chemical composition was determined by a modified sequential gravimetric method [19]. The average main components (percent, by weight) of wheat straw, as determined by three replicate analyses, were as follows: 40.40 % cellulose, 33.13 % hemicelluloses, and 15.4 % lignin. “Guaranteed reagent grade” phenol and acetone (organic solvent), a 37 % formaldehyde (formalin) solution (main component of resol/cross linking agent), 98 % sulfuric acid, and 40 % aqueous NaOH (catalysts for liquefaction and resinification of wheat straw, respectively) were purchased from Beijing Chemical Reagent Corp., China.

### Methods

An appropriate proportion of phenol added in the flask firstly was melted into liquid at 41 °C and then the corresponding proportion of concentrated sulfuric acid was added and mixed evenly. Ten grams of dry wheat straw was added and well stirred and then put into oil bath with the desired temperature.

The resulting reaction mixture was dissolved with acetone and filtrated with a filter paper. The acetone-soluble parts were evaporated at 50 °C under vacuum in order to remove the acetone.

While the acetone-insoluble parts, the so-called “unliquefied residues,” were rinsed to colorless with 1 % NaOH and deionized water, respectively, and then was oven-dried at 103 ±2 °C in an oven and weighed. Finally, percent unliquefied wheat straw residue (UWr) was determined by Eq. 1. Liquefaction yield (LYc) and residual yield (RYc) of main chemical components (hemicellulose, cellulose, or lignin) were calculated by Eq. 2 and Eq. 3:

$$\mathrm{UW}(\%)_{\mathrm{r}} = \frac{W_{\mathrm{r}}}{W_0} \times 100 \tag{1}$$

$$\mathrm{LY}_C(\%) = \frac{W_0 \times C_0 - W_{\mathrm{r}} \times C_{\mathrm{r}}}{W_0 \times C_0} \times 100 \tag{2}$$

$$\mathrm{RY}_C(\%) = 1 - \mathrm{LY}_C \tag{3}$$

where $W_0$ is the oven-dry weight of starting wheat straw material (gram) and $W_{\mathrm{r}}$ is the oven-dry amount of unliquefied wheat straw residues determined after the liquefaction stage (gram). $C_0$ and $C_{\mathrm{r}}$ are the percentage contents of one component (hemicellulose, cellulose, or lignin of starting and unliquefied straw, respectively).

In order to determine the percent combined phenol (i.e., percent phenol reacted, essentially, with various degraded components of the straw along with sulfuric acid and phenol itself), the amounts of free phenol remaining in the acetone-soluble part were first measured by using high-performance liquid chromatography (HPLC) (Agilent 1200) equipped with an RID detector and a XDB-C18 column. Measurements were done at 30 °C and a flow rate of 0.5 mL/min using a methanol/water solution (1/1, v/v) as the mobile phase and a standard phenol solution for calibration. For the measurements, the acetone-soluble part (10 mL) having a concentration of 0.1 % was injected into the HPLC apparatus. Then, the amount of combined phenol, so-called “percent combined phenol”(CPh), was determined as follows [20]:

$$\mathrm{CPh}(\%) = \frac{\omega_{\mathrm{A0}} - \omega_{\mathrm{A}}}{W_0 - W_{\mathrm{r}}} \times 100 \tag{4}$$

where $w_{\mathrm{A0}}$ and $w_{\mathrm{A}}$ are the amounts of starting phenol (gram) and phenol remaining after liquefaction (gram), respectively.

The mixture of *Penicillium* decumbens cellulase and glucosidase, supplied by Ningxia Cellulase Preparation Plant, China was used to detect the enzymatic convertibility of the liquefaction residues to reducing sugar. Filter paper activity (FPA) and β-glucosidase activity were determined to be 101.0 IU/mL and 38.6 IU/mL, respectively, according to the method of Miller [21] and Kubicek [22], respectively. Each individual sample, approximately 0.5 g dry weight of the wet or dried solid fiber fraction from the pretreatment process was put into a 100-mL flask and suspended quickly with acetate buffer (0.2 M, pH 4.8) to acquire 25.5 g slurry with 2 % solids (w/v) to reduce end-product inhibition. The slurry was then supplemented with cellulase enzymes of 40.7 FPU $g^{-1}$ dry basis. Enzymatic hydrolysis was performed at 180 rpm in a rotary shaker at 50 °C for 48 h. Analysis of reducing sugar was carried out by the method in Ref. [21]. The ratio of enzymatic hydrolysis of residues was calculated as:

$$\text{Enzymatic hydrolysis yields}(\%) = \frac{\text{Reducing sugar} \times 0.9}{\text{Carbohydrate}(\text{g})} \times 100 \tag{5}$$

A 37 % aqueous formaldehyde (formalin) was added to the liquefaction mixture obtained as mentioned in the preceding section in the ratio of the formaldehyde-to-phenol (F/Ph) (determined above) molar ratio of 2.2, and the pH of the mixture was adjusted to 11 by dropwise addition of 40 % aqueous NaOH solution. The so-prepared mixture was first heated at 60 °C for 1 h and then at 85 °C for 2 h with constant stirring. The adhesive eventually obtained was pastelike liquid containing a small amount of unliquefied straw particles (in some cases), water, straw components reacting with phenol, reacted or some unreacted phenol, and free formaldehyde [11]. The properties of the resin adhesive synthesized by liquefied straw were determined using the Chinese National Standard GB/T 14732-2006.

## Results and Discussion

### The Effect of Liquefaction Temperature

In complete liquefaction, high temperatures are needed to liquefy all the components of lignocellulosic biomass including cellulose, hemicellulose, and lignin. In the study of Alma [11], 92 % of the grapevine cane dissolved in phenol in the presence of sulfuric acid as catalyst at 150 °C for 2 h. In the study of Lee [20], temperatures above 180 °C were preferred to liquefy corn bran. However, cellulose, which is more difficult to liquefy, is reserved in the residues, so the temperature for selective liquefaction is much lower than that of complete liquefaction.

As shown in Fig. 1, selective liquefaction mainly occurs at low temperatures. High liquefaction yields of hemicellulose (≥80 %) and lignin (≥55 %), along with high residual yield of cellulose (≥95 %), can be achieved at temperatures as low as 50 °C using a catalyst concentration of 3 % (based on the mass ratio of sulfuric acid to the whole system). As temperatures increase from 50 °C to 100 °C, the liquefaction yield of lignin increases from 55 % to 87 %, with the residual yield of cellulose slightly decreasing. However, with temperatures increasing from 100 °C to 150 °C, the residual yield of cellulose decreases sharply as the residual yield of lignin rises a little. At 150 °C, wheat straw is almost liquefied, with a low residual yield of cellulose (≤20 %). Thus, selective liquefactions are more frequent at low temperatures. Furthermore, the increase in the residual yield of lignin at high temperatures (>100 °C) indicates that adverse reactions are accelerated by high temperatures, thereby generating more side products that leach out from the liquefied products.

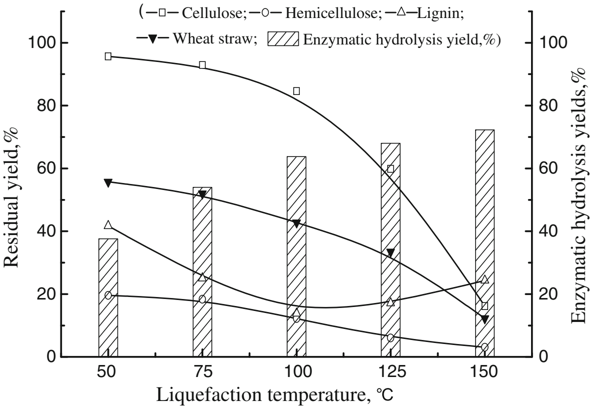

**Fig. 1** Effects of liquefaction temperature on fractionation of straw and enzymatic hydrolysis of unliquefied residues. Liquefaction was carried out with phenol/straw ratio 3, $H_2SO_4$ concentration 3% for 60 min

Unliquefied residues exhibit high susceptibility to enzymatic digestion. In this study, the unliquefied residues were obtained using a phenol/straw ratio of 3 with 3 % $H_2SO_4$ at 100 °C for 60 min, under which conditions selective for liquefaction have better levels of fractionation. The residual yield of cellulose is ≥80 %, and the liquefaction yield of lignin is ≥80 %, with a high enzyme hydrolysis yield (≥65 %). However, residues obtained at low temperatures (50 °C to 100 °C) did not exhibit high enzyme hydrolysis efficiency despite the high liquefaction yield of lignin. This can be attributed to lignin or lignin–carbohydrate complexes, which are both resistant to enzyme attack, in the residues during the oven-drying process [23]. Despite the lower residual yield of cellulose and the increasing residual yield of lignin, residues obtained at high temperatures (100 °C to 150 °C) are more susceptible to enzyme attack. This phenomenon may be due to the breakdown of the lignocellulosic matrix, which supplies cellulose with more surface area of pulp [24]. There is also a tendency for side products that leached out from liquefied products to not interfere with the enzyme hydrolysis of residues. This is shown by residues obtained at 150 °C, which have a high residual yield of lignin as well as high enzymatic hydrolysis yield (≥70 %).

## The Effect of Liquefaction Time

Liquefaction time is closely related to other liquefaction factors. Under appropriate conditions, complete liquefaction can achieve rapid liquefaction. Lee et al. [20] reported that the liquefaction of grapevine cane was complete within 30 min at temperatures higher than 200 °C. Wood was also rapidly liquefied at the supercritical temperature of phenol by over 90 % within 0.5 min [25]. Selective liquefaction can achieve the purpose of rapid liquefaction under mild conditions.

As depicted in Fig. 2, hemicellulose and lignin can be liquefied quickly at 100 °C with a catalyst concentration of 3 %. The maximum liquefaction yield of lignin (≥70 %) and hemicellulose (≥80 %) can be achieved with a high residual yield of cellulose (≥80 %) in 30 min. After that, residual yield of lignin increases slightly from 30 min to 60 min and then continues to increase sharply after another 60 min. This finding illustrates that at the early stage of selective liquefaction, liquefaction of hemicellulose and lignin is dominant; however, during the final stage, cellulose degradation and other side reactions take over.

In addition, Fig. 2 shows the relationship between the enzymatic hydrolysis yield of residues and liquefaction time. From 0 min to 60 min, the enzymatic hydrolysis yield of unliquefied residues gradually increases, obtaining the maximum value at 60 min. This period may possibly be when the removal of lignin and hemicellulose promotes enzymatic hydrolysis of pretreated straw [26]. Besides, the presence of sulfuric acid solubilizes hemicellulose and

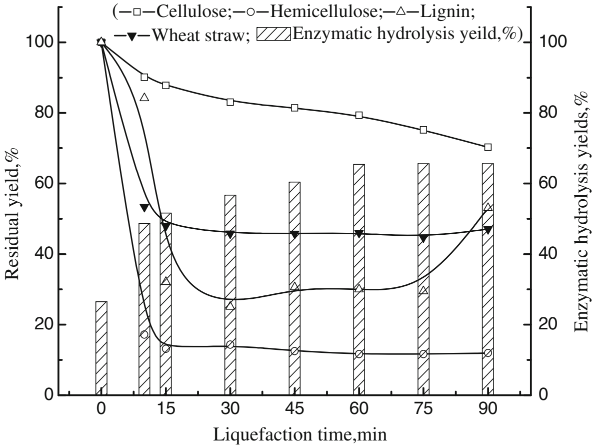

**Fig. 2** Effects of liquefaction time on fractionation of straw and enzymatic hydrolysis of unliquefied residues. Liquefaction was carried out at 100 °C, with phenol/straw ratio 3, $H_2SO_4$ concentration 3%

remains intact in lignin and cellulose so that the enzymatic digestibility of cellulose is enhanced [27]. After 60 min, the residual yield of unliquefied residues increases, but the enzymatic hydrolysis yield remains almost constant, probably because by-products have a little effect on cellulose enzymatic hydrolysis, which is also reflected in Fig. 1.

## The Effect of Sulfuric Acid Concentration on Liquefaction

As a catalyst, sulfuric acid is associated with the residue yield of lignocellulose [11]. A high amount of sulfuric acid is needed to liquefy all the components of lignocellulosic biomass. However, cellulose, which is more resistant to liquefaction, needs to be reserved in selective liquefaction. Thus, the concentration of sulfuric acid for selective liquefaction is lower than that of complete liquefaction. Figure 3 shows that selective liquefaction can be achieved with a catalyst concentration ranging from 3 % to 5 %, whereas complete liquefaction requires a catalyst concentration of more than 6 % under other similar conditions.

As shown in Fig. 3, sulfuric acid plays an important role in selective liquefaction, which has a greater effect on lignin and hemicellulose than on cellulose. With $H_2SO_4$ concentration increasing from 0 % to 4 %, large amounts of lignin (about 80 %) and hemicellulose (about

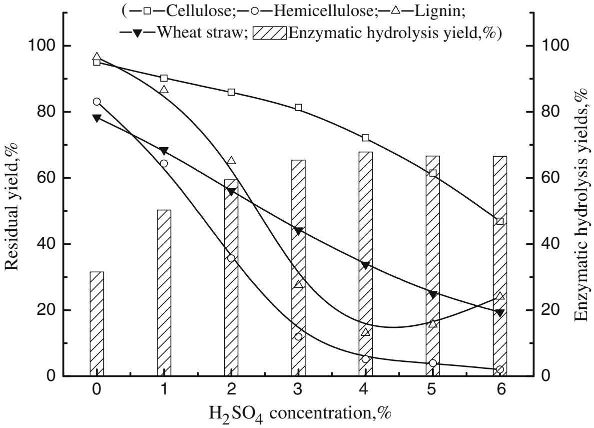

**Fig. 3** Effects of the amount of sulfuric acid on fractionation of straw and enzymatic hydrolysis of unliquefied residues. Liquefaction was carried out at 100 °C for 60 min with phenol/straw ratio 3

78 %) are liquefied, with little cellulose (less than 30 %) being degraded. On the other hand, with $H_2SO_4$ concentrations above 4 %, the liquefaction yield of cellulose is accelerated and side reactions are aggravated. Therefore, a proper concentration of $H_2SO_4$ should be chosen to make liquefaction proceed more selectively.

Besides, Fig. 3 also shows that the enzymatic hydrolysis of unliquefied residues during selective liquefaction is high, which is in accordance with the liquefaction of lignin. The maximum enzymatic hydrolysis yield (≥70 %) is obtained at the $H_2SO_4$ concentration of 4 % where the liquefaction yield of lignin is 80 % with a residual yield of cellulose above 70 %. Although large amounts of lignin leach out from liquefied products when $H_2SO_4$ concentration is above 4 %, they rarely have anything to do with enzymatic hydrolysis.

## The Effect of Phenol Concentration on Liquefaction

Phenol plays an important role in the liquefaction of lignocellulosic biomass, as it is not only a perfect solvent but also a reagent associated with the presence of combined phenol in liquefied products [20]. As demonstrated in Fig. 4, phenol has greater effects on lignin and hemicellulose than on cellulose. With the ratio of phenol/straw increasing from 1 to 5, residual yields of lignin and hemicellulose decrease from 50 % to 40 % and from 70 % to 20 %, respectively, whereas the residual yield of cellulose decreases slightly from 92 % to 80 %. Therefore, it is advisable to increase phenol dosage in selective liquefaction.

With the ratio of phenol to straw increasing from 1 to 3, the enzymatic hydrolysis yield of unliquefied residues increases from 45 % to 65 %, which may be associated with the removal of lignin and hemicellulose. Although it is beneficial to increase phenol dosage for fractionation separation, it does not always have a positive association with the enzymatic digestion of unliquefied residues. When the phenol ratio goes up from 3 to 5, the enzymatic hydrolysis yield of unliquefied residues decreases slightly from 65 % to 61 %, which may be attributed to the increased crystallinity of cellulose with increasing amounts of phenol [28].

## Changes in the Amount of Combined Phenol during Selective Liquefaction

From Fig. 5, the amount of combined phenol is closely related to the liquefaction yield of each component. During the initial 20 min, lignin and hemicellulose are rapidly liquefied, and the concentration of combined phenol increases linearly (from 0 to 100 %). Then, the increment rate of combined phenol slows down with the decreasing liquefaction rate of lignocellulose. In

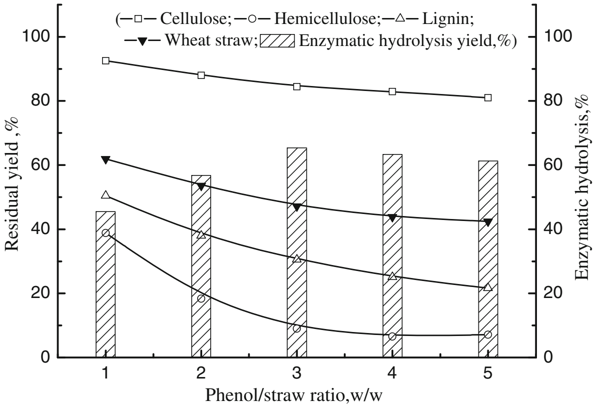

**Fig. 4** Effects of the amount of phenol on fractionation of straw and enzymatic hydrolysis of unliquefied residues. Liquefaction was carried out at 100 °C for 60 min with $H_2SO_4$ concentration 3%

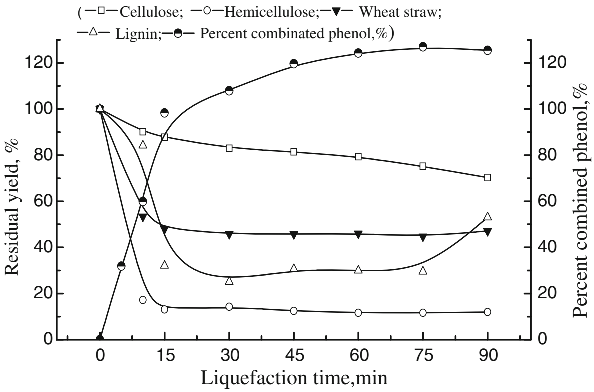

**Fig. 5** Changes in the amount of combined phenol during selective liquefaction. Liquefaction was carried out at 100 °C, with phenol/straw ratio 3, $H_2SO_4$ concentration 3%

selective liquefaction, liquefaction yields of lignin and hemicellulose are positively affected by the concentration of combined phenol, which, in turn, shows that when the best results of fractionation are achieved, the amount of combined phenol reaches the maximum.

### Performance Analysis of Resin Adhesive

The properties of the resin adhesive synthesized by liquefied straw determined using the Chinese National Standard GB/T 14732-2006 are summarized in Table 1. The performance of the resin adhesive meets the national standard, which guarantees the high-value utilization of lignocellulose.

## Conclusions

The following conclusions can be drawn from the study:

1. Using phenol-selective liquefaction, lignin (≥70 %) and hemicellulose (≥85 %) are liquefied, with large amounts of cellulose (≥80 %) retained in the unliquefied residue. In phenol-selective liquefaction, not only can the liquefied products be used for the synthesis of resins, the unliquefied residues with high cellulose content are also useful for enzymatic digestion.

**Table 1** Properties of resin adhesive synthesized by liquefied wheat straw

| Index | Unit | National standard | Self-made resin adhesive |
|---|---|---|---|
| Appearance | – | No impurity, transparent liquid from reddish brown to dark red | Black liquid |
| pH value | – | ≥7.0 | 11.0±0.2 |
| Solid content | % | ≥35.0 | 48.3±0.6 |
| Viscosity | mPa s | ≥60.0 | 59.5±1.2 |
| Free formaldehyde content | % | ≤0.3 | 0.22±0.04 |
| Free phenol content | % | ≤6 | 4.2±0.3 |
| Bonding strength | MPa | ≥0.7 | 0.77±0.12 |

2. Compared with complete liquefaction, selective liquefaction can be carried out under lower temperatures or lower catalyst concentrations, within a shorter period, obtaining high yields of high value-added products with low pollution. Thus, selective liquefaction achieves multilevel conversion for lignocellulose and opens up a new avenue for the development of bio-based products.

**Acknowledgments** This work was financially supported by the National Basic Research Program of China (No. 2011CB707401), the National High Technology Research and Development Program of China (SS2012AA022502), and the National Key Project of Scientific and Technical Supporting Program of China (No. 2011BAD22B02).

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