Complex processing of plant raw materials for furfural and glucose production

I V Loginova¹, M V Kharina²,₄, Z A Kanarskaya², M N Meshcheryakova³ and N Z Dubkova³

¹ Chemical Cybernetics department, Kazan National Research Technological University, 68 Karl Marx street, Kazan, 420015, Russia
² Food biotechnology department, Kazan National Research Technological University, 68 Karl Marx street, Kazan, 420015, Russia
³ Food production equipment department, Kazan National Research Technological University, 68 Karl Marx street, Kazan, 420015, Russia

₄ E-mail: somariya@mail.ru

Abstract. Data on the dynamics of furfural yield from wheat straw, corn cobs, birch sawdust, oat husk and sugar beet pulp in a narrow temperature range (180 – 190 °C) were obtained. Low-concentrated solutions of sulfuric and phosphoric acids were used. Enzymatic hydrolysis of cellulosic residues was conducted. It was shown that the maximum yield of glucose in birch sawdust was 21.8%, in the corn cobs 18.6%, in wheat straw 19.4%, in sugar beet pulp 15.8 % of absolutely dry substance respectively.

Every year, a huge quantity of cheap biomass accumulates in the world, such as agricultural waste (straw, cereal husks, peeling, empty glume, bagasse), food (sugar beet pulp, corn cobs) and wood-processing (sawdust, wood chips) industry. The low cost and renewability of plant by-products make it very profitable to process these plant raw materials into various valuable products.

Furfural is one of the biomass conversion products that is desirable on the world market - the only monomer for industrial organic synthesis obtained not from oil, but capable of almost completely replacing petrochemical products [1, 2].

Furfural synthesis mainly originates during the boiling treatment of biomass with mineral acids, as well as in the presence of salt catalysts [3, 4].

\[
\begin{align*}
(C_6H_5O_3)_n + nH_2O &\rightarrow nC_4H_10O_5 \\
C_5H_{10}O_5 &\xrightarrow{2H_2O} C_5H_4O_2 \\
C_6H_{12}O_6 &\xrightarrow{3H_2O} C_6H_4O_3 \rightarrow CH_2O + C_5H_4O_2
\end{align*}
\]

The main primary product for the furfural derivation is xylose, which contains in plants as a polysaccharide – xylan. Furfural can be produced from almost any pentosan-containing plant material. Promising sources of xylose are corn cobs, wheat straw, sugar beet pulp, oat husk and birch sawdust in connection with the high content of pentosans [5-11].
Sugar beet pulp can also be a promising source of furfural, as it is rich in pentosans, mainly arabinans (the second most abundant pentosan in hemicellulose). However, earlier, researchers paid little attention to it, although the topic of the conversion of arabinose to furfural has been studied enough.

The cellulose-containing residue obtained after the conversion of pentosans to furfural is an environmental problem, but at the same time, it can serve as a promising substrate for further enzymatic hydrolysis to obtain simple sugars. The solid residue extracted after hydrolysis and distillation of furfural, the so-called lignocellulose, can be processed into glucose by subsequent enzymatic hydrolysis. Studying this issue will reduce the burden on the environment and increase the efficiency of integrated waste-free processing of cellulose-containing material. The furfural yield during hydrolysis depends on many factors, including the chemical composition of plant biomass, temperature, distillation time, the catalyst used, the reactor design (batch or continuous), solid to liquid ratio, etc. [3]. There is no single generally accepted mechanism for the formation of furfural. In this regard, modeling the kinetics of furfural yield is of particular interest, which allows us to predict the preparation of the target product at different temperature conditions and, based on the results obtained, select the optimal values of the process parameters. Non-isothermal conditions typical for the stage of heating of raw materials should be taken into account. This leads to difficulties in determining the process temperature and the uncertainty of the kinetic experiment.

The goal of the work was to study the processes of complex processing of plant materials with low-concentrated acid solutions pretreatment to derive furfural and conversion of cellulosic residues.

The following types of plant raw materials were investigated in the work: wheat straw (Triticum sphaerococcum); corn cob (Zea mays); oat husk (Avenae stramentum); birch sawdust (Betula); sugar beet pulp (Beta vulgaris).

With the exception of beet pulp, all native raw materials were subjected to drying, grinding and fractionation (1-3 mm).

Furfural obtaining was carried out in a batch reactor ChemRe Sys R-201 Series (Republic of Korea) with a frame type stirrer (figure 1, 2) in the presence of various catalysts.

![Figure 1](image1.jpg)

**Figure 1.** Laboratory setup with a batch reactor ChemRe Sys R-201 Series.

The technological scheme of the laboratory setup is shown in figure 2.
Figure 2. The technological scheme of the laboratory setup: 1 - tank with distilled water, 2 - high pressure pump, 3 - water heater, 4 - steam generator, 5 - pressure gauge, 6 - threaded valve, 7 - ball valve, 8 - batch reactor, 9 - needle valve, 10 - refrigerator, 11 - thermostat, 12 - collection of furfural, 13 - collection of volatiles, 14, 15 - PID controller OWEN TRM-210, 16 - PID high-precision controller TS4 Series, 17 - computer, 18 - tap water.

The conditions for furfural obtaining in a series of experiments are presented in table 1. The mass of a sample of raw materials was 100 g. Solid to liquid ratio of loading the mixture into the reactor for all experiments was 1: 8. All samples were taken in flasks with thin sections, in which 1 ml of triethanolamine C₆H₁₅NO₃ (a stabilizer) was previously added.

| Raw material            | Hydrolyzing agent | Treatment duration (min) | T °C | Enzymatic hydrolysis of residues |
|-------------------------|-------------------|--------------------------|------|----------------------------------|
| Wheat straw             | 0.5% H₂SO₄        | 240                      | 180  | -                                |
| Wheat straw             | 1% H₂SO₄          | 120                      | 180; 190 | +                              |
| Wheat straw             | 1% H₂SO₄          | 240                      | 180; 190 | +                              |
| Wheat straw             | 0.5% H₃PO₄        | 240                      | 180  | -                                |
| Wheat straw             | 1% H₃PO₄          | 150                      | 180  | +                                |
| Wheat straw             | autohydrolysis    | 180                      | 180  | +                                |
| Corn cobs               | 1% H₂SO₄          | 180                      | 180; 190 | +                              |
| Sugar beet pulp         | 1% H₂SO₄          | 140                      | 180; 190 | +                              |
| Birch sawdust           | 1% H₂SO₄          | 130                      | 180; 190 | +                              |
| Oat husk                | 1% H₂SO₄          | 130                      | 180; 190 | -                              |

* - Target temperature

The furfural content was determined on Flexar liquid chromatography (Perkin Elmer, USA). Condensates containing furfural were diluted with bidistilled water and passed through membrane filters with a pore diameter of 0.45 μm. Chromatography was performed through a Brownlee Analytical C18 reverse-phase column. Column dimensions 4.6 x 150 mm, sorbent size 5 microns. Detection was conducted on a UV detector tuned to a wavelength of 274 nm.

The enzymatic agent CelliCTec2 (Novozymes) was used: components - cellulase CAS 9012-54-8 and xylanase CAS 37278-89-0; density - 1.15 g / ml; optimal temperature is 45–50 °C; optimal pH is 5.0–5.5; activity - 115.6 FPU / ml [12].
The concentration of the enzyme complex was 0.05 g of the enzyme per 1 g of absolutely dry raw material. The process proceeded in a sodium citrate buffer with pH varying from 3.0 to 6.0, solid to liquid ratio 1:30, and a temperature 35.0 - 60.0 ± 2 °C. To prevent the growth of microorganisms, 40 μl of a 1% solution of tetracycline in 70% ethanol was added to each flask. The sampling interval for determining glucose ranged from 4 to 12 hours, and the duration of each process was 72 hours. The glucose content in the hydrolysates was determined in accordance with the glucose oxidase method.

The purpose of studying the kinetics of furfural formation is to compare the reactivity of hemicelluloses of five types of plant materials depending on the process conditions.

The results of the quantitative analysis by HPLC are shown in figure 3-7. The data in figure 3 were obtained for identical experimental conditions. They show that the chemical composition of biomass has a significant effect on the concentration and overall yield of furfural. The amount of product in the condensate after 2 hours of treatment at 180 °C (figure 4) corresponds to the xylose content in the series: corn cobs > wheat straw > birch sawdust > sugar beet pulp.

The lowest furfural content in distillates is observed for sugar beet pulp, in which the composition of the cell wall hemicelluloses is predominantly represented by arabinans.

In the furfural derivation, the process variables should ensure the hemicelluloses hydrolysis and the dehydration of monosaccharides forming pentoses. In current work, the temperatures used are optimal for producing monosaccharides [13], including xylose. However, at high temperatures, the decomposition of furfural to formic acid and humic substances is accelerated [6], which leads to efficiency decrease in the of the process at 190° C (figure 5).

![Figure 3. Furfural concentration at 1% H₂SO₄, 180°C (WS - wheat straw; BS - birch sawdust; FSO - oat husk; CC – corn cobs; SBP - sugar beet pulp).](image)

![Figure 4. Furfural yields (% of dry matter) at 1% H₂SO₄ for 120 min at 180°C](image)

![Figure 5. Effect of temperature on furfural yield during treatment of raw materials with 1% H₂SO₄ for 120 min](image)
The influence of the acids on the process is investigated using wheat straw. It is a promising biomass material for the derivation of furfural and allows us to get it in an amount comparable to the commercial run. The results of HPLC samples obtained by the distillation of furfural from wheat straw hydrolysates in various conditions are presented in figure 6-8. The maximum concentration of furfural in hydrolysates was observed after 120 minutes of wheat straw treatment (figure 6a). The lowest reaction rate and the degree of conversion of the raw material are characteristic for the autocatalytic method (autohydrolysis). In this case furfural yield after 3 hours of distillation is less than 15% of the potential (figure 6b), but with acid-free treatment, the environmental impact is minimized.

![Figure 6. Concentration (a) and yield (b) of furfural during treatment of wheat straw at 180 °C.](image)

For the conditions of this study, the most significant process control parameter is the concentration of the acid catalyst. The ratio of furfural yield $Y(1\% \text{ w/w})/Y(0.5\% \text{ w/w})$ at 120 min is on average 1.8 for sulfuric acid and reaches 2.7 for orthophosphoric acid.

The next most influential parameter is the duration of the process. The ratio $Y(240\text{ min})/Y(120\text{ min})$ is 1.5 and 1.3 for sulfuric acid and 1.6 for phosphoric acid. The influence of temperature in a narrow diapason of $10^\circ \text{C}$ is insignificant - the ratio $Y(180^\circ)/Y(190^\circ)$ is about 1.13.

![Figure 7. Furfural yield (%) from Wheat Straw for 120 min at 180°C.](image)

![Figure 8. Furfural yield from Wheat Straw depending on time and processing temperature.](image)
The yield using phosphoric acid is slightly lower compared to sulfuric acid (figure 7-8). However, with an increase in the concentration of both acid catalysts from 0.5% to 1% w/w the difference in furfural yield is reduced by almost 60% at 120 min, and with an increase in hydrolysis time from 120 to 240 min, by 20%. This is important since phosphoric acid has advantages in a number of characteristics - it is less corrosive, and also has a lesser effect on cellolignin, which can be used to obtain additional products.

For wheat straw, the best result was obtained by hydrolysis for 4 hours using 1% sulfuric acid at 180 °C. The yield of furfural was about 60% of the potential yield, the result can be considered as enough acceptable.

The solid residue extracted after hydrolysis and distillation of furfural, the so-called lignocellulose, can be processed into glucose by subsequent enzymatic hydrolysis. In the study, cellulose-containing fractions of biomass were studied using the CellicCTec2 enzyme complex at a temperature of 45 °C, pH 5.0 in order to determine the possibility of their further processing. The solid fraction (figure 9, b) remaining after distilling furfural was washed with distilled water in order to remove acid in order to create optimal pH concentrations for enzymes and increase the efficiency of enzymatic hydrolysis.

Figure 9. Wheat straw before (a) and after distillation of furfural (b).

Figure 10. Glucose yield from Corn cobs: 1 – 180 °C; 2 – 190 °C; 3 – without pretreatment.

Figure 11. Glucose yield from birch sawdust and sugar beet pulp: 1 – birch sawdust at 180 °C; 2 – Birch sawdust at 190 °C; 3 – Sugar beet pulp at 180 °C; 4 – Sugar beet pulp without pretreatment.
The glucose yield depends on the furfural derivation conditions (table 1). The more stringent the conditions for the biomass pretreatment (temperature, pH, process time), the lower the glucose yield (figures 10 - 12).

So, with an increase in pretreatment temperature, the amount of glucose decreases. And the greatest sugar yield from wheat straw is obtained after acid-free treatment (figure 12). Without raw material pretreatment, the structure of the cell wall makes it difficult for enzymes to access lignocellulose fibers and, accordingly, glucose output increases.

Enzymatic hydrolysis allows you to additionally extract glucose in an amount of from 14% of absolutely dry substance (sugar beet pulp) up to 22% of absolutely dry substance (birch sawdust). This indicator for wheat straw and corn cob has an intermediate value. The result correlates with the cellulose content in the source plant material [5-11].

An experimental study of the kinetics of the processes of one-stage production of furfural from Wheat straw, Corn cobs, Birch sawdust, Beet pulp, and Oat husks was carried out. It has been shown that in the case of low-acid hydrolysis of biomass, the key factor in increasing the furfural yield is the concentration of the acid catalyst. The influence of temperature was studied in a narrow range, and according to the data obtained, with an increase in temperature from 180°C to 190°C, a decrease in the amount of the obtained product is observed, which is explained by the intensification of the process of furfural decomposition. The quality of solids after receiving furfural was evaluated in order to study the possibility of their further processing. It was shown that the maximum yield of glucose in Birch sawdust was 21.8%, in the Corn cobs 18.6%, in Wheat straw 19.4%, in Sugar beet pulp 15.8% of absolutely dry substance respectively.

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