Identification of kinetics parameters of wheat straw and sugar beet pulp hydrolysis with sulphurous acid

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Abstract. The mathematical modeling of the conversion of hemicelluloses of wheat straw and sugar beet pulp into monosaccharides using diluted sulphurous acid (0.59 and 1.18% wt) at high temperatures was performed. Kinetic equation, activation energy, pre-exponential factor and reaction order of the acid catalyst were determined. It was shown that agreement between the experimental data and kinetic model is good. It was proved that the process proceeds in the kinetic region and the entire array of measurements of the yield of monosaccharides satisfactorily described by the model with the minimum number of steps. The model predicts a decrease of duration of the process and increase of monosaccharides concentration in hydrolysates of lignocellulosic feedstock with temperature increase.

Key words: dilute acid hydrolysis, hemicelluloses, sulphurous acid, kinetic parameters.

INTRODUCTION

Conversion of plant's polysaccharides to monosaccharides solves important problems of processing and utilization of agricultural wastes and promotes the production of new products for chemical industry and biotechnology. Usually processing of plant biomass into bioethanol includes following stages: pretreatment, enzymatic hydrolysis, fermentation. Due to the fact that plant biomass can vary in composition (lignin amount, composition of hemicelluloses), each stage can be complicated and include diversified conditions (Donkoh et al., 2012). Stages of pretreatment and enzymatic hydrolysis have the greatest commercial cost (Wooley et al., 1999). Fermentable carbohydrates arise as a result of these two stages. In the event that lignocellulosic residuals are subjected to enzymatic hydrolysis without pretreatment obtained complex mixture of carbohydrates will be fermented not effective and hydrolysis will take a long time (Scheper et al., 1999). Pretreatment of plant raw materials, which enables removal of substances hindering the enzymatic hydrolysis, can have various rates of aggressiveness (Alvira et al., 2010). This treatment must be intensified to break chains of cellulose and hemicelluloses (Scheper et al., 1999); however, too much aggressive treatment can lead to formation of non-hydrolyzable products, as well as toxic for yeast products – furfural and hydroxymethylfurfural (Palmqvist & Hahn-Hägerdal, 2000). Acid hydrolysis is one of the most promising pretreatment methods with respect to industrial implementation Jönsson & Martín, 2016; Germec et al., 2016).

In spite of high catalytic efficiency of sulphuric, hydrochloric and phosphorus acid, problems of neutralizing and regeneration of these acids remains unsolved. Higher efficiency of sulphurous acid relative to sulphuric acid during pretreatment of plant raw materials was shown as exemplified by wheat straw (Nurtdinov et al., 2011). Besides, partial regeneration of sulphurous acid after pretreatment completion is possible through absorption of sulphur dioxide distilling stream.

Wheat straw and sugar beet pulp were used as sources of biomass for this study. These agricultural lignocellulosic residuals are renewable, cheap, and abundant wastes in Russia. High content of easily hydrolyzable polysaccharides in these raw materials stipulates expediency of its using for the production of commercially significant products such as furfural and its derivates, feed additives and food.

Predictive modeling of monosaccharides yield during agricultural raw materials acid hydrolysis is attractive for further development of technological processes and equipment.

Several kinetic studies of wheat straw and sugar beet pulp acid hydrolysis with sulphuric, hydrochloric, maleic and phosphorus acids have been reported in the literature (Ranganathan et al., 1985; Gonzalez et al., 1986; Jiménez & Ferrer, 1991; Tsoutsos & Dimitris, 2011;   El-Tayeb et al., 2012;   Katsamas & Sidiras, 2013).   Significant discrepancies in values of the kinetics parameters obtained by various authors can be explained by differences in the applicable form of raw materials, the type and concentration of the hydrolyzing agent pretreatment conditions, hydrolyzing temperature, solid-to-liquid ratio and employed models and reactors.

Since conditions of hydrolysis and variations in composition and structure of biomass affect reaction rates, it is necessary to know the kinetic parameters that determine optimal conditions of treatment. The goal of this study was approximate evaluation of kinetics parameters hydrolysis of abundant wastes products using diluted sulphurous acid.

MATERIALS AND METHODS

Wet sugar beet pulp (*Beta vulgaris)*, produced on LLC 'Buinsk sugar refinery' (Buinsk city, Russian Federation; February, 2013) and wheat straw were used as raw material in this work. Moisture content of sugar beet pulp was $80.3 \pm 0.3\%$, giving solid to liquid ratio close to 1:4. To obtain the lower solid to liquid ratio (1:3), dried sugar beet pulp with moisture content $2.0 \pm 0.3\%$ was added in corresponding amounts. Solid to liquid ratio was calculated as ratio of absolutely dry matter amount (g) of sugar beet pulp to total quantity of water including moisture (g) contained in feedstock. Wet samples were stored in freezing chamber at -6 °C.

Moisture content of heat straw was $2.2 \pm 0.2\%$.

To determine dry-matter content, samples (2.0 g) were weighed into porcelain cups (diameter 50 mm) and dried in an oven at 105 °C for up to 3 days, until the weight was constant.

Composition analysis of easily-hydrolysable polysaccharides and hardly-hydrolysable polysaccharides

For determination of easily-hydrolysable polysaccharides sample of sugar beet pulp was hydrolysed with 2 M trifluoroacetic acid at 120 °C during 1 h. For determining of hardly-hydrolysable polysaccharides the remaining residue was hydrolysed with 72% sulphuric acid during 1 h at 25 °C, then water was added to achieve 3.4% final concentration of sulphuric acid and the sample was kept at 120 °C during 1 h. The obtained solution was neutralized with barium hydroxide (Fry, 1988). Further, the monosaccharide content and composition of the clarified hydrolysates was determined (Kharina et al., 2014; Kharina et al., 2016).

Conditions of pretreatment with sulphurous acid

Hydrolysis of sugar beet pulp was carried out in sealed thermostatically controlled capsules in a laboratory bench unit of proprietary design (Nurtdinov et al., 2011). The parameters of the hydrolysis process are represented in the Table 1.

Table 1. Regimes of the hydrolysis process

Raw material	T (°C)	C_{ac}, (wt %)	S/L*
Wheat straw	180–190	0.59; 1.18	1:5.8
Sugar beet pulp	180–190	0.59; 1.00	1:3

*S/L – solid- to- liquid ratio.

To check the course of hydrolysis process, the sampling was carried out each 5 min from 0 to 50 min of treatment. Experiments were conducted three times.

Analysis of oligosaccharides and monosaccharides

For separation of polysaccharides and low molecular weight carbohydrates (mono- and oligosaccharides) released during hydrolysis of sugar beet pulp, 96% ethanol was added to clarified hydrolysates to reach the final concentration of 80%. High-molecular weight polymers (polysaccharides) precipitated in ethanol, while low molecular weight carbohydrates remained in supernatant. Content of polysaccharides in hydrolysates was determined by the weight of the pellet which was formed upon treatment with ethanol after drying it.

Quantitative and qualitative composition of free monosaccharides in aliquates of supernatant was analyzed by means of high performance anion exchange chromatography on a column CarboPac PA-1 (4 x 250 mm, Dionex, USA) using a pulsed amperometric detector (Dionex). Elution rate was 1 ml min^{-1}, column temperature 30 °C. Buffers: A–100 mM NaOH in 1 M NaOAc, B–15 mM NaOH. Gradient elution was carried out as follows: 0–20 min B–100%; 20–21 min B–90%, A–10%; 22–41 min B–50%, A–50%; 42–55 min A–100%; 56–85 min B–100%. Results were analyzed using PeakNet software (Kharina et al., 2014; Kharina et al., 2016).

In order to determine oligosaccharides, the rest of supernatant obtained after ethanol precipitation of polysaccharides was dried and hydrolyzed with 2 M trifluoroacetic acid during 1 h at 120 °C. Quantitative and qualitative composition of monosaccharides after hydrolysis was estimated as mentioned above. Composition of oligosaccharides was determined according to the difference of individual monosaccharide content before and after hydrolysis with trifluoroacetic acid.

Qualitative and quantitative composition of polysaccharides is presented in (Kharina et al., 2014; Kharina et al., 2016).

The kinetic models for hemicellulose hydrolysis

To describe the mechanism of polysaccharides hydrolysis different simplified formal kinetic models are used. A number of researchers suggest that a simple two-step pseudo-homogeneous model can be applied for this type of reaction (Saeman, 1945; Ranganathan et al., 1985; Gonzalez et al., 1986; Jacobsen & Wyman, 2000; Tellez-Luis et al., 2002; Karimi et al., 2006; Lenihan et al., 2010; Katsamas et al., 2013).

This model use pseudo-homogeneous irreversible first-order reactions

$$P \xrightarrow{\ k_1\ } M \xrightarrow{\ k_2\ } decomposition\ products \qquad (1)$$

where: P, M – polysaccharide and monosaccharide, respectively; k_1, k_2 – the reaction rate constants for generation and decomposition of monosaccharide, respectively (min^{-1}).

Different hemicelluloses of raw material in kinetic calculations were considered as separate polymers whose hydrolysis occurs independently. Based in these two reactions, the differential equations that describe the changes of concentrations of substances are as follows:

$$\frac{d[P]}{dt} = w1, \ \frac{d[M]}{dt} = w2 \qquad (2)$$

where:

$$w1 = -k_1 \cdot [P] \qquad (3)$$

$$w2 = \mu\, k_1 \cdot [P] - k_2 \cdot [M] \qquad (4)$$

The concentration of monosaccharides is determined by the equation:

$$[M] = \mu \cdot \frac{[P_0] \cdot k_1 \cdot}{(k_2 - k_1)} \cdot \left(e^{-k_1 \cdot t} - e^{-k_2 \cdot t} \right) + [M_0] \cdot e^{-k_2 \cdot t} \qquad (5)$$

where: $[P_o]$ – initial concentration of polysaccharide, measured in a process of complete hydrolysis ($mol\ l^{-1}$); $[M_o]$ – initial concentration of monomer; $[M_0] = 0$; t – duration of hydrolysis (min); μ – stoichiometric conversion factor of polysaccharide to monosaccharide.

Reaction rates constants were calculated, using:

$$k = A \cdot e^{-Ea/(R \cdot T)} \cdot [C_a]^{\alpha} \qquad (6)$$

where: A – pre-exponential factor (min^{-1}); E_a – activation energy ($kJ\ mole^{-1}$); T – temperature (K); C_a – acid concentration; R – universal gas constant ($kJ\ mole^{-1}\ K^{-1}$); α – exponential acid parameter.

The chosen values were the ones giving the minimum values of the Sum of Squares of Error (SSE) for run data. The minimization of errors was performed using the ODE Solver function for Mathcad. The SSE was defined as

$$SSE = \sum (C_{calc} - C_{exp})^2 \rightarrow min \qquad (7)$$

Hydrolysis was carried out according to conditions reported in Materials and Methods. Parameters of wheat straw and sugar beet pulp hemicelluloses hydrolysis were determined based on experimental data using pseudo-homogeneous kinetic model.

Experimental data

The main part of the chemical composition of the studied samples of lignocellulosic feedstock is easily hydrolysable polysaccharides (Table 2). They are quite heterogeneous because can contain glucans, pentoses and organic acids e.g. galacturonic acid. So different hemicelluloses were chosen for the study due to the dissimilar biomass.

Table 2. Chemical composition of raw material (% dry matter)

	Easily hydrolysable polysaccharides		Difficult hydrolysable polysaccharides	
	Wheat straw	Sugar beet pulp	Wheat straw	Sugar beet pulp
Total	68.6	69.9	14.7	12.1
Xylose	36.5	4.6	0.4	0.5
Arabinose	10.4	16.6	0.2	0.4
Glucose	13.3	16.4	14.1	10.7
Galactose	3.8	8.3	traces	0.3
Rhamnose	1.8	6.6	0.0	0.1
Galacturonic acid	1.5	16.1	traces	0.1
Glucuronic acid	1.3	1.3	traces	0.0

Monosaccharides of wheat straw hydrolysates obtained during complete hydrolysis were represented mainly by xylose, arabinose and glucose due to the predominance of glucuronic arabinoxylan and glucan with mixed type of molecular bonds in easily hydrolysable polysaccharides. Hydrolysates of sugar beet pulp have high content of arabinose, galactose and low content of xylose due to the predominance of arabinans and arabinogalactans in the easily hydrolysable polysaccharides.
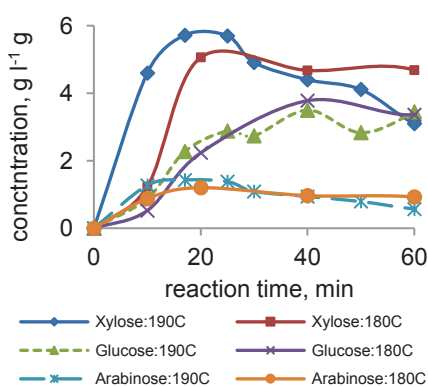

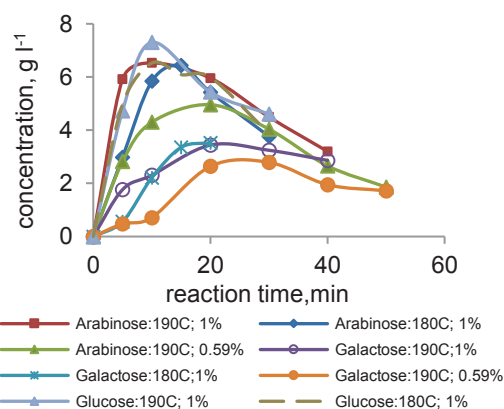**Figure 1.** Kinetics of wheat straw hydrolysis (0.59%).

Figure 2. Kinetics of sugar beet pulp hydrolysis.

Hydrolysis of raw biomass with deluted sulphurous acid was carried out at 180–190 °C, maximum pretreatment time was 90 minutes. Experimental data of monosaccharides concentrations in hemicellulosic hydrolysates are represented in Figs 1 and 2. As known, during low-temperature hydrolysis (<160 °C) parallel firstorder reactions fast and slow fractions easily-hydrolysable polysaccharides hydrolysis can exist (Esteghlalian, 1997). As shown in Fig. 1 some difference in hydrolysis constants takes place for glucans and xylans at 180 °C. With increasing temperature reaction rate of these fractions are practically the same.

Intrinsic factors such as chemical constitution and location of hemicelluloses in the fibers of feedstock influence on hydrolysis rate. The time of achieving of maximum concentrations of glucose and arabinose slightly lower for sugar beet pulp then for wheat straw. Cell wall of sugar beet pulp less strong. Microfibrilles and hemicelluloses of sugar beet pulp submerged in matrix of pectic polysaccharides. Pectic polysaccharides consists of galacturonic acid residues linked α-$(1\rightarrow4)$- bonds, and can include $(1\rightarrow4)$-linked β- galactans with low degree of polymerization (Roberts, 1991; Carpita & Gibeaut, 1993; McCann & Spagnuolo et al., 1997).

Kinetic modeling of hemicelluloses hydrolysis

The effective reaction rate constants of hydrolysis with dilute sulfurous acid was obtained by curve fitting with the least sum of square error. Constants and the statistical coefficient R^2 derived from these study are displayed in Table 3.

Table 3. Rate constants

Process conditions		Constants		R^2
		k_1(min^{-1})	k_2(min^{-1})	
Wheat straw				
Arabinose	C(H$_2$SO$_3$)=0.59 wt %; 190°; S/L=1:5.8	0.0238	0.2207	0.82
Glucose		0.0078	0.0238	0.75
Xylose		0.0167	0.1338	0.83
Sugar beet pulp				
Arabinose	C(H$_2$SO$_3$)=1.00 wt %; 190°; S/L =1:3	0.0333	0.2125	0.82
Galactose		0.0152	0.0958	0.83
Glucose		0.0351	0.2124	0.70

The values of k_1 are higher for arabinose, it will be the first accumulation (Table 3). This trend persists at higher concentration (1.18% H$_2$SO$_3$; T = 190 °C; Arabinose: k_1 = 0.0314 min^{-1}; Xylose: k_1 = 0.0256 min^{-1}). The faster susceptibility of arabinose to acid hydrolysis is in line with literature data. In works (Dudkin & Gromov, 1991) it was noted that under equivalent conditions arabinose appeared in solution at a faster rate than xylose, presumably due the ease of cleaving of the single α1-2 or α1-3 arabinose linkages to the xylan backbone. Later during hydrolysis decomposition of xylans occurs with forming of dextrins and xylobioses.

In consequence of low catalytic activity of sulphurous acid obtained hydrolysis constants (k_1) are lower than hydrolysis constants for hydrolysis of wheat straw with hydrochloric and sulphuric acid. Nevertheless the values are consistent with the evidence for similar lignocellulosic materials (Lenihan et al., 2010). It ought to be noted that the value of monosaccharides decomposition reaction constant (k_2) is higher than hydrolysis

constant. Similar dependence during hemicelluloses hydrolysis was observed in other works (Carvalheiro, et al., 2005; Lenihan et al., 2010). Temperature extrapolation for k_1/k_2 of wheat straw is shown in Fig. 3. The value of constants ratio increases with temperature growth.
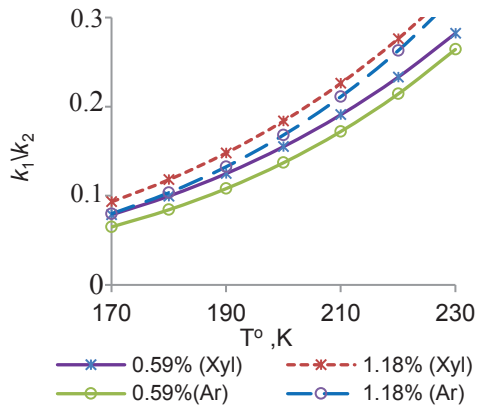

Figure 3. Dependence of k_1/k_2 of Xylose and Arabinose of Wheat straw.

In describing of hydrolysis using pseudohomogeneous kinetic model is necessary to ensure a в behavior of process in kinetic region. Kinetic region of heterogeneous processes are usually characterized by relatively high activation energy ($E_a > 40$ kJ $mole^{-1}$) and a strong dependence of the rate of reaction temperature (changing in 2–4 times for each 10 °C). Based on the values of the activation energy (Table 3) and temperature coefficient of Van't Hoff (Table 4), we can conclude that at least for the wheat straw the process remains in the kinetic region.

Table 4. Temperature coefficients of the Van't Hoff (at 180–190 °C)

Raw material	Arabinose	Galactose	Glucose	Xylose
Wheat straw	2.65	-	1.91	2.60
Sugar beet pulp	1.85	1.60	1.44	-

The Arrhenius parameters and exponential acid parameters for different hemicelluloses represented in Table 5. The value of apparent activation energy hydrolysis (E_1) for Xylan → Xylose coincides with literature value, which obtained for the hydrolysis of wheat straw by using sulfuric treatments: 167.0 kJ $mole^{-1}$ (Ranganathan et al., 1985). As is shown in Table 5, for WS and SBP the E_2 for degradation of monosaccharides is significantly higher than E_1. Values of the Arrhenius parameters of sugar beet pulp is rather lower for sugar beet pulp than for wheat straw.

Table 5. Kinetic parameters of the acid hydrolysis of lignocellulosic feedstock

	A_1 (min^{-1})	E_1 (kJ·mole^{-1})	α_1	A_2 (min^{-1})	E_2 (kJ mole^{-1})	α_2
	Wheat straw					
Arabinose	9.44E + 17	169.7	0.397	5.25E + 13	126.1	0.102
Glucose	2.49E + 12	112.4	1.592	2.77E + 14	129.8	1.243
Xylose	5.26E + 17	166.6	0.617	7.80E + 13	127.1	0.372
	Sugar beet pulp					
Arabinose	4.07E + 11	107.2	1.088	5.25E + 13	64.5	0.896
Galactose	4.64E + 08	81.5	1.407	3.34E + 08	75.4	1.127
Glucose	4.13 E + 06	63.4	1.006	1.77E + 04	37.9	0.802

The Arrhenius parameters allow to predict conversion reactions of wheat straw and sugar beet pulp under any combination of time, temperature and acid concentration. Figs 4, 5 show the comparison between the model predicted values and experimental values. As mentioned earlier, temperature dependence of speed of the process is defined with constants ratio (k_1/k_2), which increases with temperature (Fig. 3). Consequently with increasing temperature, the kinetic model predicts a decrease in the optimal time of the process for all types of feedstock, as well as an increase in the maximum concentration of monosaccharides. The concentration of the acid catalyst has a significant effect for wheat straw monosaccharides, whereas sugar beet pulp characterized by a weak dependence of coefficients of formation and decomposition from the concentration of sulfurous acid.
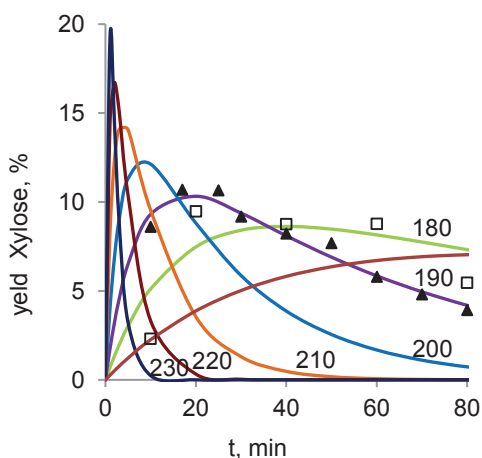

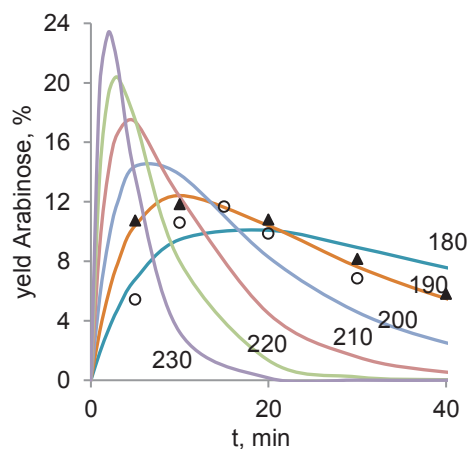**Figure 4.** The yeld of Xylose of WS (0.59%): ○ – 180 °C; ▲ – 190 °C; ━ – model.

Figure 5. The yeld of Arabinose of SBP (1%)○ – 180 °C; ▲ – 190 °C; ━ – model.

As we can see from the Figs 4 and 5, empiric two-stage model, based on consecutive, irreversible reactions quasi-first order, shows good agreement between the experimental data and kinetic model.

CONCLUSIONS

The reaction of wheat straw and sugar beet pulp hemicellulose hydrolysis catalyzed with dilute sulphurous acid, was studied by kinetic modeling analysis. The effect of temperature, acid concentration and duration of hydrolysis on the efficiency of hydrolysis was investigated. Computational experiments were carried out, and kinetic parameters of the process (rate constants of hydrolysis, reaction rate constants for decomposition of monosaccharides, values of apparent activation energy, pre-exponential factor, exponential acid parameters) were determined, coefficients of determination were calculatec. It was shown that the process proceeds in the kinetic space and the entire array of measurements of the yield of monosaccharides satisfactorily described by the model with the minimum number of steps. Sulphurous acid is the less effective catalyst of hemicelluloses hydrolysis than sulphuric and hydrochloric acid. It

finds expression in lower constants of hydrolysis for sulfurous acid. Nevertheless it has advantage over other acids in the context of low cost, capability of regeneration and ecological safety. Maximum yields of xylose and arabinose lie in the range from 10 to 12%, depending on type of raw material. These yields can be obtained for the majority of hemicelluloses at reaction time lower than 20 minutes and more mild conditions (1.18% H_2SO_3, 190 °C). Supposedly, low yield can be explained with fast decomposition of monosaccharides, which can be confirmed with high values of corresponding reaction constants. It was shown that arabanes of wheat straw are more readily hydrolyzed than xylans. The values of apparent hydrolysis constants of wheat straw are sufficiently close to the typical values reported in the literature, but values of reaction rate constants for decomposition of monosaccharides are essentially higher. Values of hemicelluloses activation energy and arrhenius parameters for sugar beet pulp are essentially lower than for wheat straw. Good agreement of experimental and calculated kinetic data obtained using two-stage model of acid hydrolysis to be indicative of availability this approach for quantitative interpretation of experimental results.

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