

УДК 66.093.6:661.733

Sodium Hydrosulfate as the Catalyst for Carbohydrate Conversion into the Levulinic Acid and 5-Hydroxymethylfurfural Derivatives

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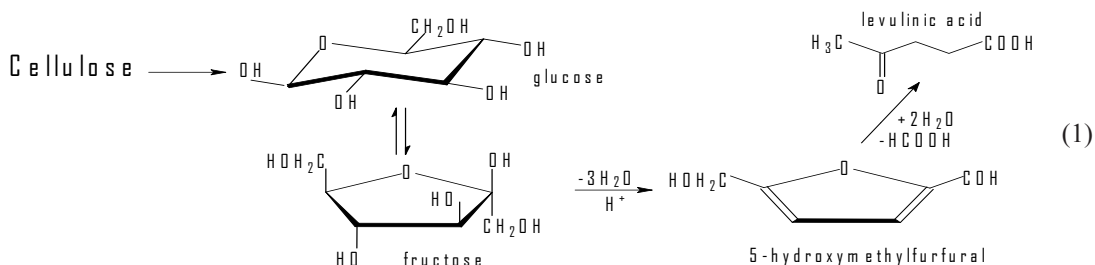
Received 15.01.2008, received in revised form 15.03.2008, accepted 10.04.2008

The new regenerable catalyst $H_2SO_4 + Na_2SO_4$ for the levulinic acid production has been developed. The catalyst provides product extraction from the reaction mass with *n*-butanol during the reaction. The acid-catalyzed dehydration process of fructose and sucrose in three systems (homogeneous water solution, homogeneous butanol solution and two-phase system water-butanol) has been studied and compared. The ester of levulinic acid and ether of 5-hydroxymethyl-2-furaldehyde were found to be the main products in the presence of butanol, and their total yield is of maximum in the two-phase system. It attains 83 – 90 mol. %. The structure of 5-butoxymethyl-2-furaldehyde was identified by PMR, NMR ^{13}C spectroscopy and GC-MS analysis. The results obtained show that to increase the product yields one should separate the products from the catalyst and carbohydrate converted during the acid-catalyzed conversion.

Keywords: levulinic acid, 5-hydroxymethylfurfural, 5-hydroxymethyl-2-furaldehyde, 5-butoxymethylfurfural, 5-butoxymethyl-2-furaldehyde, fructose, sodium hydrosulfate, butanol, catalysis.

Hexose carbohydrates, like cellulose, sucrose and fructose, are known to produce levulinic acid (LA) and 5-hydroxymethylfurfural (HMF, 5-hydroxymethyl-2-furaldehyde) in the acid media. Levulinic acid is applied for the polymer

production and in other fields of chemical industry and research. 5-hydroxymethylfurfural is used as a food flavor and can be used as the initial material for different organic syntheses [1]. LA and 5-HMF are produced from carbohydrates according to the general scheme:



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All these steps comprise acid-catalyzed reactions, and different kinds of catalysts are used for these processes. The conversion of carbohydrates into levulinic acid, as well as cellulose into glucose are known to be carried out in concentrated or diluted solutions of strong mineral acids at moderate ($\approx 100^\circ\text{C}$) or elevated ($> 160^\circ\text{C}$) temperatures, correspondingly [2,3]. Both approaches have their advantages and disadvantages. Hydrolysis with diluted acids is used in industry and does not require high consumption of catalyst. High-temperature hydrolysis of polysaccharides, however, does not allow attaining high yields of monosaccharides and LA [4-6]. The main problem of the levulinic acid production from glucose and cellulose is rather low selectivity of processes (20 - 40 wt. %) [7,8] yields increase can be principally attained at low temperatures.

There are many kinds of catalysts used for these processes at moderate temperatures: ion exchange resins [9,10] zeolites, [11] mineral acids, [12,13] transition metal salts [14,15]. The main disadvantage of solid catalysts is their deactivation by tar, humic substances formed in the quantity at least 5 – 10 wt. % based on the target products. The next problem with resins and zeolites is their insufficient catalytic activity in water media. The activity of metal salts transition is also not enough to catalyze fructose dehydration below 100°C in water media [14].

In water media only strong mineral acids possess the necessarily high acidity and catalytic activity at the moderate temperatures [4,16] The rate of fructose conversion is proportional to Hammett acidity function in the range of HCl concentration 0.5-2.0 M [13]. Maximum yield of LA in HCl-catalyzed glucose conversion is also characterized by liner dependence on Hammett acidity function in the range of HCl concentration 5 - 8 M, [16,17] and the yield increases with decreasing the catalyst concentration. Such

selectivity gain can be explained by raising the water activity and decreasing the contribution of pathways connected with the reactant and intermediate condensation into humic substances [17].

The relative activity of different carbohydrate materials at 98°C decreases in the order: fructose $>$ sucrose $>$ inulin $>$ glucose $>$ cellulose. Glucose is of 20 – 40 times less reactive, than fructose, and cellulose is of 30 times less reactive, than glucose [4,17].

Despite the great difference of the substrate activity (1000 times), the activation energy of the process is almost independent of the carbohydrate nature: these values vary in the region of 140 – 176 kJ/mole [7,16]. Nevertheless, due to the difference in the activation energy the reaction ability of glucose and cellulose becomes equal at the temperature of the process around 200°C . This means that fructose and even glucose could be successfully converted into levulinic acid at moderate temperatures around 100°C , but for treating cellulose the temperatures above 150°C are desirable.

The next aspect of the temperature sensitive process is the ratio of the rates of formation and conversion of 5-hydroxymethylfurfural. The activation energies of 5-HMF formation and consumption are equal to 141 and 64 kJ/mol, correspondingly [7]. Therefore 5-hydroxymethylfurfural can be produced as the main product at temperatures above 200°C even from cellulose, but the process selectivity does not exceed 40 – 50 mol. % [6,18,19].

Another possibility to obtain 5-hydroxymethylfurfural, but not levulinic acid, is the application of non-water solvents. 5-HMF is the product of dehydration and levulinic acid is formed as a result of addition of two water molecules to 5-HMF. This indicates that in an anhydrous media 5-HMF could be produced as the main product, and water should promote the

LA formation. Indeed, at temperatures around 100°C 5-HMF is formed in such solvents as dimethylsulfoxide and dimethylformamide with good yields up to 90 mol. % at the low substrate concentrations 0.1 – 0.2 M [20]. In water media under the similar conditions LA is the main product, and 5-HMF is observed as an intermediate in the low concentration (1). Substituting water by polyethylene glycol-600 accelerates the formation of 5-HMF and retards its hydration in the process of acid-catalyzed fructose conversion, and the total yield of LA and 5-HMF increases by a little value in the interval 60 – 70 mol. % [20].

The last and the main problem of obtaining these two products is selectivity of the processes. The most convincing data on fructose conversion selectivity was published by Kuster [5,13,18,20]. The total selectivity of obtaining 5-hydroxymethylfurfural and levulinic acid from fructose does not exceed 85 mol. % in the temperature range of 80–220°C. Glucose produces 35 – 40 mol. % of levulinic acid in the presence of sulfuric or hydrochloric one at 98°C, [21] and this value is two times less than for fructose. The yield of levulinic acid in the Y-zeolite catalyzed glucose conversion does not exceed 20 mol. % at 110 – 160°C [11]. Glucose conversion at 160 - 240°C by sulfuric acid produces 33 - 55 mol. % of LA, and the best selectivity is attained at the lowest temperature 160°C [11]. The most important side process which decreases the selectivity is the humic substance formation.

In this way, the highest selectivity is attained at low temperatures and requires high acid concentrations. Under these conditions regeneration of the catalysts becomes the main problem. The products of the hexose conversion have too low vapor pressure and can not be removed from the reaction mass by evaporation. Hence, the catalyst should be separated from the products by extraction and the efficient catalytic process should combine the highest possible

distribution coefficient for levulinic acid and the least one – for the catalyst.

However, levulinic acid is rather hydrophilic compound and its distribution coefficients are not high ($k = 0.28$ for diethyl ether and $k = 1.2$ for furfural) [22,23]. One of the most efficient and available extractant for levulinic acid is butanol (the distribution coefficient $k = 4$) [22,23]. Lengthening the carbon chain of alcohols leads to decreasing the distribution coefficient ($k = 0.28$ for pentanol) [22]. Butanol forms the stable two-phase system with water, but concentrated sulfuric (above 5.1 M) and hydrochloric acids are known to give homogeneous solutions with the alcohol [24]. The mixture of sodium sulfate and sulfuric acid as the catalyst (sodium hydrosulfate with or without addition of sulfuric acid) could be applied to prevent homogenization. This approach permits to create stable two-phase system water – butanol with good catalytic activity. Comparison of sulfuric and hydrochloric acids from this viewpoint demonstrates the advantages of the former catalyst: HCl distribution coefficient in the system water – isopentanol is of 5 – 10 times greater than for sulfuric acid, and hydrochloric acid is distributed into organic phase under the effect of calcium chloride additives [24]. The possibility to apply sodium hydrosulfate solution to catalyze the process is described in the only patent [26]. The yield of levulinic acid from wood attains 14 – 20 wt. % based on cellulose at 150 – 200°C. Methyl isobutyl ketone was used as the extractant, and after extracting levulinic acid the catalyst solution was removed into the reactor. The activity, selectivity and the possibilities to apply sodium hydrosulfate for the conversion of carbohydrates in the mild conditions have not been described yet. Potassium and sodium hydrosulfates are known to be used for dehydration of benzyl alcohols [27].

In this paper the catalytic properties of the sodium hydrosulfate in the processes of carbohydrate conversion are studied. The

conversion of fructose, sucrose and glucose is studied and compared in the homogeneous water and butanol solutions and in two-phase systems water – alcohols.

Results and discussion

The catalytic activity of the mineral acids

Fig. 1 shows the influence of the acid nature on the kinetics of glucose conversion at constant $H^{\circ} -2.6$. Hydrochloric acid is twelve times more active, than sulfuric acid, but the selectivities of the LA formation are practically the same in both cases. Such ratio of rates is caused, probably, by greater activity of a proton in the first case. Phosphoric acid is too weak for application as the catalyst of the process: the maximum yield of levulinic acid does not exceed 5 mol. %, and the rate of process is small (Fig. 1, Table 1).

To explain these ratios of the rates and yields one can take the approximate connection between H° and activities of H_2O and H_3O^+ into account [28]:

$$H^{\circ} = a - \lg \frac{X(H_3O^+)}{X(H_2O)} \quad (2)$$

According to equation (2) the necessary H° value can be attained either by increasing $X(H_3O^+)$ for the strong acids or by decreasing $X(H_2O)$, the water activity in the case of weak acids. Weak phosphoric acid does not provide the necessary combination of the high hydroxonium ion activity

(supporting the rate of the reaction) and the high water activity (preventing profound dehydration into humic substances and thus supplying good selectivity of the reaction).

The comparison of the results performed in Fig. 1 and Table 1 shows that the water activity, but not Hammett acidity function, is responsible for the selectivity of the levulinic acid formation. Sulfuric acid like hydrochloric one permits to attain good selectivity of producing levulinic acid.

Thus, despite a relatively high oxidizing potential and low acidity of sulfuric acid, it can be effectively applied to obtain levulinic acid. The next step to develop the catalyst is the estimation of catalytic activity of hydrosulfate ion.

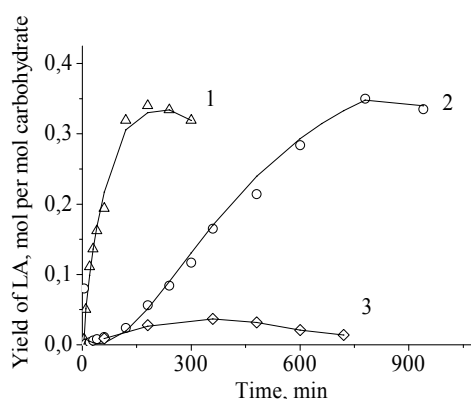


Fig. 1. The influence of the acid nature on the kinetics of levulinic acid formation from glucose (0.35 M) at 98°C and $H^{\circ} = -2.6$: 1 – 7.2 M HCl, 2 – 5.8 M H_2SO_4 , 3 – 10.0 M H_3PO_4

Table 1. The influence of temperature and nature of acid on the kinetics of LA formation in the process of glucose hydrolysis (0.35 M)

Temperature °C	Acid and its concentration, M	Acidity function H°	Initial rate of LA accumulation, M/min * 10 ⁴	Parameters of maximum concentration of LA		
				Concent-rat-ion of LA, g/l	Yield, mol. %	Time, min
98	HCl, 7.2 M	-2.6	21 ± 0.9	19.80	35	180
98	H_2SO_4 , 5.8 M	-2.6	1.8 ± 0.07	21.50	38	720
98	H_3PO_4 , 10.0 M	-2.6	0.52 ± 0.012	2.80	5	360

Sucrose conversion in the water solution of sodium hydrosulfate

Table 2 summarizes the data on the catalytic activity of sodium hydrosulfate and sulfuric acid in the process of levulinic acid formation from sucrose.

It is a well known fact that sulfuric acid is more acidic and active catalyst than sodium hydrosulfate of the same concentration: under the similar conditions the rates of levulinic acid formation differ by a factor 5 – 10 for these two catalysts. Maximum yields of levulinic acid also decrease with increasing the salt concentration, but this negative effect can be completely compensated by the sulfuric acid additives. So, the mixtures of 2.0 M sodium hydrosulfate and 1.2 M sulfuric acid provides practically the same activity and selectivity of the catalytic process as the sulfuric acid solution.

Undoubtedly, the main advantages of the sodium hydrosulfate - sulfuric acid catalyst are the possibility to form stable two-phase systems the water solutions – alcohols and comparatively low degree of sulfuric acid extraction by butanol and other alcohols. Table 2 shows that the extraction of sulfuric acid from the water phase into butanol phase during the levulinic acid separation from the catalyst is of 2 – 4 times less for the hydrosulfate catalysts in comparison with the solution of sulfuric acid. The total losses of sulfuric acid during the levulinic acid extraction do not exceed 2 – 5 % based on the initial quantity, and, hence, the catalyst described can be successfully regenerated

in contrast with hydrochloric acid. It should be noted that the main unsolved problem for the process of wood hydrolysis by the concentrated mineral acids is the catalyst regeneration, and for this reason the process has not been developed on an industrial scale despite its great advantage in the selectivity.

So, the obtained results demonstrate the possibility to create a two-phase catalytic reaction system water – butanol, which permits to separate the products of carbohydrate conversion (in organic phase) from the catalyst (in water phase) during the reaction. This can lead to increase of selectivity of the acid-catalyzed conversion of carbohydrates. Similar method to remove the products from the reaction mass with methylisobutylketone for obtaining levulinic acid and 5-hydroxymethylfurfural was described in, but the process required great quantities of the ketone [30].

The acid-catalyzed conversion of carbohydrates in the two-phase system water solution of hexose and catalyst – butanol

Despite the abundance of water in the two-phase reaction mixture, the main products of the acid-catalyzed sucrose and fructose conversion in the presence of butanol are butyl levulinate and 5-buthoxymethylfurfural. Their structures are confirmed by GC-MS, ¹³C and ¹H NMR spectra.

Butyl levulinate is a well-known compound and its spectra correspond to the published data [30]. The 5-hydroxymethylfurfural ethers were

Table 2. The influence of sulfuric acid and sodium hydrosulfate on the maximum yields of levulinic acid from sucrose (0.29 M) in the water solutions

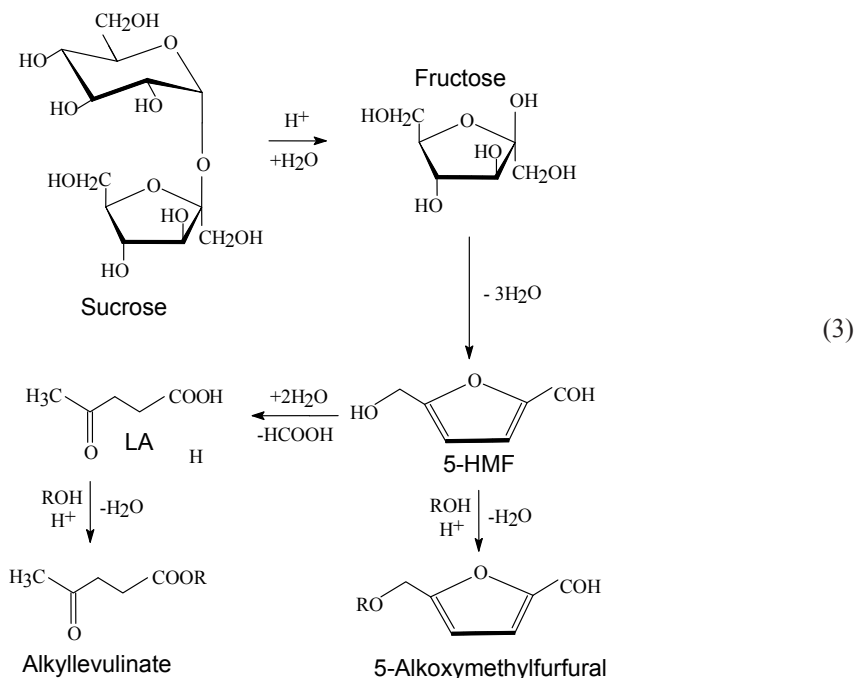
H ₂ SO ₄ , mol/liter	1.84	1.34	0.84	–	–	1.20	1.70
Na ₂ SO ₄ , mol/liter	–	1.0	2.0	4.0	4.0	2.0	2.0
Temperature, °C	98	98	98	98	105	105	105
Time, min	45	180	180	210	150	60	30
Yield of levulinic acid, mol. %	74	59	45	22	55	69	60
Sulfuric acid losses, wt. % *	8.5	5.3	3.5	2.0	2.0	3.5	3.7

*The part of sulfuric acid extracted into butanol phase together with levulinic acid.

synthesized earlier from 5-chloromethylfurfural, but their spectra were not described [31]. The possibility of formation of the 5-hydroxymethylfurfural ethers as byproducts of the fructose conversion was noted in, but neither yields nor isolation procedure were described [20,32]. Mass-spectra of 5-butoxymethylfurfural and 5-hydroxymethylfurfural are very similar,

and it confirms the identification of the former. ^1H and ^{13}C NMR spectra obtained correspond to the structure of 5-butoxymethylfurfural.

The following scheme demonstrates how acid-catalyzed conversion of carbohydrates in the two-phase reaction mixture water – butanol is carried out with this method application.



5-hydroxymethylfurfural obtained from fructose can be consumed in two ways: by rehydration into levulinic acid and etherification into 5-butoxymethylfurfural. Levulinic acid formed from 5-hydroxymethylfurfural is then esterified into butyl levulinate. The equilibrium of the LA and 5-HMF alkylation in the two-phase system is greatly shifted to the side of the ether and ester formation, because according to the chromatographic data the relations of concentrations of ester and ether to the corresponding non-alkylated compounds are of order of 10^2 (Fig. 2).

Fig. 3 shows the dynamics of 5-butoxymethylfurfural and butyl levulinate

formation when converting fructose in the two-phase system at different sodium bisulfate concentrations. All curves are of extreme character, and the best yield of the products (up to 75 – 80 mol %) are obtained in the presence of NaHSO_4 and H_2SO_4 mixture as the catalyst.

The dependences of the product yields and rates of formation versus catalyst concentration have maximums at 4.5 M NaHSO_4 (Fig. 4). This extreme character of the curves could be explained by growing the proton activity when increasing hydrosulfate concentration up to the optimum, followed by decreasing the parameters due to following down the water activity at highest salt concentrations.

The increasing of sucrose concentration greatly decreases the product yields (Table 3). This is a known tendency, [2,13] but it has not been explained before. We assume that selectivity decrease of carbohydrate conversion into levulinic acid when increasing the substrate concentration can be caused by humins formation as a result of the carbohydrate and product interaction.

Fructose gives greater yields of the products, compared to sucrose and glucose (Table 4). Low selectivity of the glucose conversion probably results from its insufficient reactivity.

Comparing the efficiency of carbohydrate conversion in homogeneous and two-phase systems

The most important problem of improving the efficiency of the acid-catalyzed conversion of carbohydrates is to maintain the high selectivity when increasing the substrate concentration. As noted above, the yields of approximately 90 mol. % were obtained in many cases at carbohydrate concentrations around 0.1 M, but increasing the substrate concentration inevitably leads to decrease of the yields of levulinic acid and 5-hydroxymethylfurfural based on the carbohydrate.

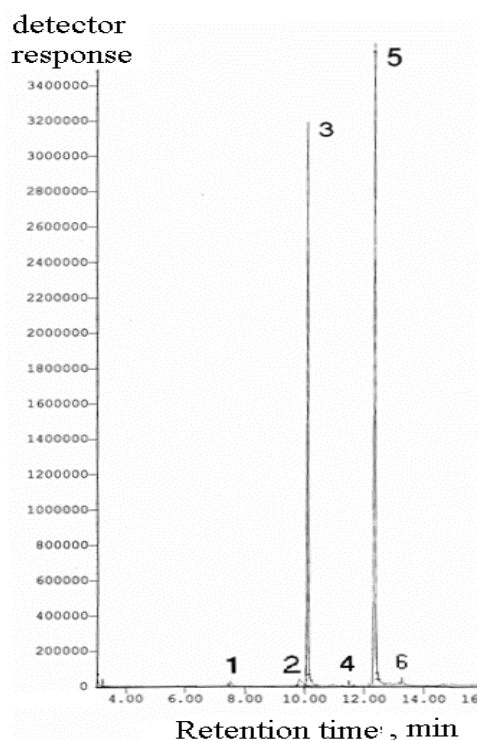


Fig. 2. Chromatogram for conversion products of sucrose in two phase system (static condition): 102°C: 1 – LA, 2 – 5-HMF, 3 – butyl levulinat, 4 – furancarboxylic acid, methyl ether, 5 – 5-butoxymethylfurfural, 6 – 5-acetoxymethyl-2-furaldehyde

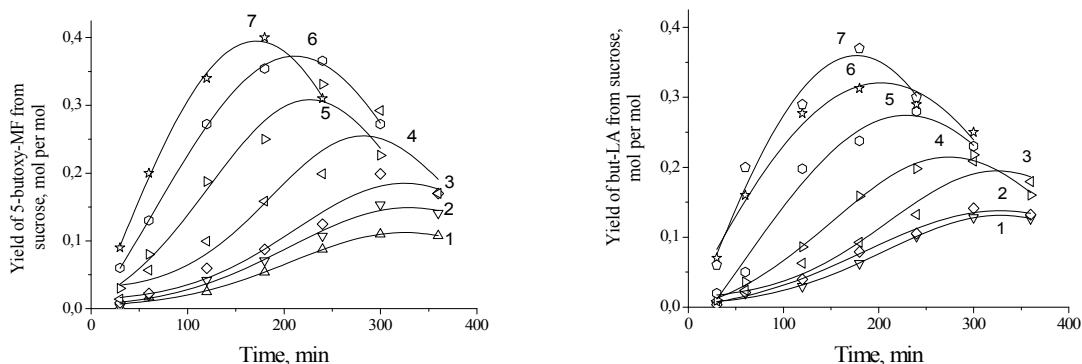


Fig. 3. The influence of sodium bisulfate concentration on the yield of butyl levulinat (right) and 5-butoxymethylfurfural (left) in the water - sucrose (0.438M) – NaHSO₄ – butanol reaction mass. 102°C, organic/water = 2:1 vol. NaHSO₄, M: 1 – 2.5, 2 – 3.0, 3 – 3.4 M, 4 – 3.8 M, 5 – 4.2 M, 6 – 4.6 M. 7 – 4.6 M NaHSO₄ + 0.2 M H₂SO₄

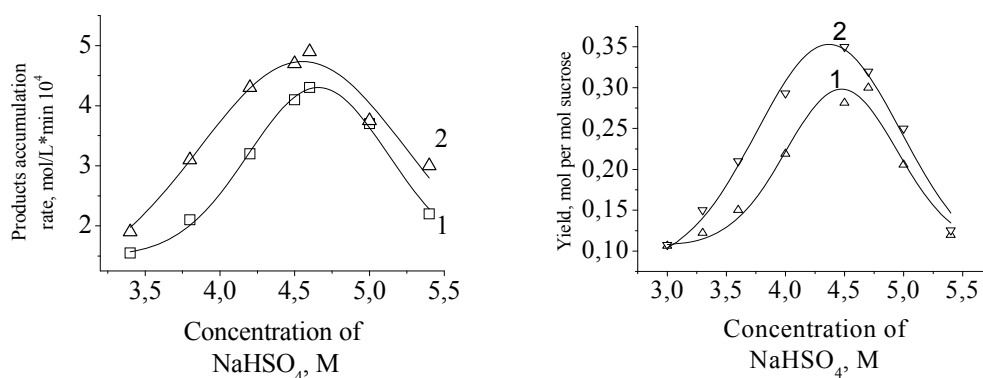


Fig. 4. The influence of sodium bisulfate concentration on the rate of formation (right) of butyl levulinate (1) and 5-butoxymethylfurfural (2) and maximal yield (left) in the water - sucrose – NaHSO₄ – butanol reaction mass. The conditions see Fig. 3

Table 3. The influence of sucrose concentration in water phase on yield and concentration of the products in organic phase. 102°C, 3.6 M NaHSO₄ in water phase, the ratio of organic phase to water 2:1 vol

Sucrose concentration in water phase, M	Products concentration, g/l in organic phase		Total yield, mol per mol of sucrose.
	Butyl levulinate	5-butoxymethylfurfural	
0.146	10.5	13.1	0.91
0.292	12.5	15.2	0.53
0.438	14.7	14.9	0.38
0.584	6.2	8.2	0.14

Table 4. The data for sucrose, fructose and glucose conversion in the system water - butanol - sodium hydrosulfate. 102°C, 4,6 M NaHSO₄ in water phase, the ratio of organic phase to water 2:1 vol

Carbohydrate	Sucrose	Fructose	Glucose
Carbohydrate concentration, M	0,438	0,876	0,438
Time of maximum of the product concentration, min	300	210	330
Maximum concentration of butyl levulinate, g/l	21,2	55,0	2,0
Yield of butyl levulinate, mol per mol of carbohydrate	0,28	0,36	0,026
Initial rate of butyl levulinate accumulation, mol/l · min	4,1·10 ⁻⁴ ±0,13·10 ⁻⁴	6,2·10 ⁻⁴ ±0,22·10 ⁻⁴	0,14·10 ⁻⁴ ±0,004·10 ⁻⁴
Maximum concentration of 5-butoxymethylfurfural, g/l	25,6	75,0	4,09
Yield of 5-butoxymethylfurfural, mol per mol of carbohydrate	0,32	0,47	0,052
Initial accumulation rate of 5-butoxymethylfurfural, mol/l · min	4,7·10 ⁻⁴ ±0,17·10 ⁻⁴	8,6·10 ⁻⁴ ±0,28·10 ⁻⁴	0,3·10 ⁻⁴ ±0,01·10 ⁻⁴
Total products yield, mol per mol of carbohydrate	0,60	0,83	0,078

Table 5 shows the dependencies of maximum total yields of the products of fructose conversion (the sum of LA, 5-HMF and their ester and ether) on the substrate concentration in the different media: homogeneous water solution, homogeneous butanol medium and two-phase system water – butanol. These results are obtained under the rather

close conditions (the same temperature, nature and activity of the catalysts), and therefore they permit to demonstrate convincingly the influence of the phase quantity in the reaction system on the product yields of the catalytic conversion.

Moderate and high product yields (40 – 90 mol. %) in the homogeneous water and butanol

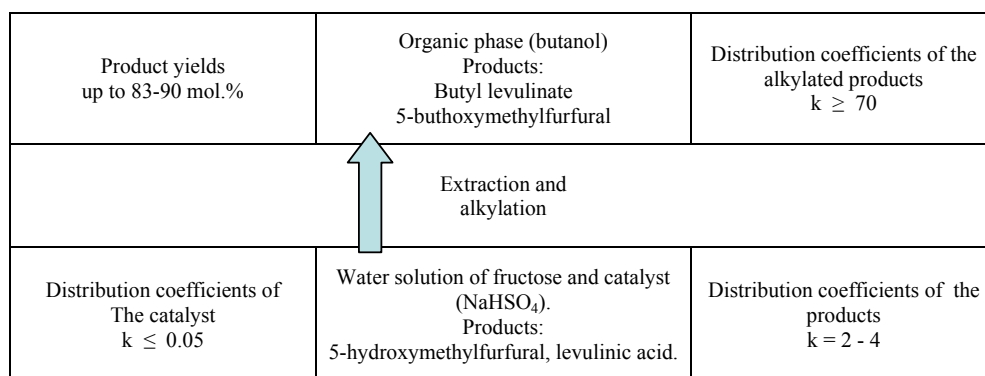
Table 5. Influence of fructose concentration on yields of LA, 5-HMF and its alkylated derivatives in various medium

Fructose concentration, M	0.2	0.5	0.8	1.0
Total product yields (mol. %) in various conditions				
Homogeneous water solution				
Levulinic acid	41	16	10	-
5-HMF	1.3	0.5	0.1	-
Total yield of LA and 5-HMF	42.3	16.5	10.1	-
Homogeneous butanol solution				
LA ester	32	8	16	-
5-HMF ether	60	26	7	-
Total yield of LA ester and 5-HMF ether	92	34	13	-
Two-phase system butanol - water				
LA ester	-	43	40	32
5-HMF ether	-	51	47	44
LA + 5-HMF	-	-	-	-
Total yield of the products	-	94	87	76
Products yields ratio in two-phase and homogeneous systems				
	-	2.8 – 5.7	6.7 – 8.6	-

solutions are observed only at the fructose concentration less than 0.2 M. When increasing the substrate concentration up to 0.8 M the yields of the products reduce by a factor of 4 – 7. In opposite to homogeneous solutions, reducing the yields below 80 mol. % in the two-phase system takes place at fructose concentration over 0.8 M. Thus the yield of the products in the two-phase system is 6 – 8 times greater than in the homogeneous media at high fructose concentrations. These are the greatest known results on the selectivity of

the acid-catalyzed conversion of concentrated solutions of carbohydrates, and they have attained due to applying sodium hydrosulfate as the catalyst.

Such great distinctions between the efficiency of the processes in the two-phase and homogeneous systems are obviously explained by separation of the products from the catalyst and carbohydrate in the two-phase system. The latter process could be described by the scheme:



In opposite to sulfuric acid, sodium hydrosulfate stabilize two-phase system water – butanol, and the distribution coefficient for the catalyst does not exceed 0.03 – 0.05 even for its concentrated solutions in water (Table 2). The distribution coefficients for levulinic acid and 5-hydroxymethylfurfural produced in water solution are equal to 2 – 4 [24], but as a result of the product alkylation with butanol their distribution coefficients increase up to the values of 70 – 100 (scheme above). Such ratio of the distribution coefficients for the catalyst and products provides their efficient separation, and these effects prevent side reactions of the products with the catalyst and substrate.

In such a manner, removing the reaction products from reactive water phase by combining the processes of alkylation and extraction permits to increase the product yields at high fructose concentration, and this is the most efficient approach among described processes.

The acid-catalyzed conversion of carbohydrates in the two-phase water–butanol system in the flow reactor

The next step to develop a two-phase system for the carbohydrate conversion is to remove the products from water phase during the process with the flow of butanol. This approach give an opportunity to separate the products from the reaction mass as well as concentrating and fast cooling thereof. Fig. 5 shows the kinetics of the acid-catalyzed sucrose conversion when continuously removing the products, the 5-buthoxymethylfurfural, 5-hydroxymethylfurfural and butyl levulinate with the flow of butanol. The curves are of extreme character and characterize the product concentrations in the butanol flow removed from the reactor. These data are connected with the rate of the reaction and concentration of the products in water phase in the reactor. Integrating these

concentrations on the volume of flowed butanol gives the total yields of the products in the process. Extreme character of the concentration curves is obviously connected with the rates of formation and removal of the products in the reactor. In opposite to the static two-phase process (Fig. 3, 4), in the flow conditions 5-hydroxymethylfurfural is not completely alkylated into 5-buthoxymethylfurfural and obtained as one of the main products (Fig. 5). This means that contact time of butanol volume in the reactor is not enough to alkylate 5-hydroxymethylfurfural completely, and levulinic acid is alkylated much quicker.

Fig. 6 shows the influence of butanol flow speed on the total product concentration in the butanol solution removed from the reactor. The dependencies are of extreme character, and maximum of the concentration is shifted the little times when increasing the flow speed. Maximum total yield of the products (39 mol %) is less, than the yield in the static two-phase system (60 mol. %, Table 4). Increasing the flow rate of butanol after maximum product yields decreases the product yields and its concentrations in butanol. Physical removing the products from the reactor with butanol flow can not decrease the product yields. This means that together with products of the process the extractant flow removes from the reactor carbohydrates or intermediates, which are not registered by GLC. This conclusion is supported by the direct determining the content of dry matters in the butanol extract: it exceeds concentration of the target products determined by GLC by a factor of 2 – 5. The possible nature of the extracted substances is the goal of further study.

In this way, butanol flow and, hence, butanol phase in the static experiments extract substrate or some intermediates together with the products of the acid-catalyzed carbohydrate conversion. This side process restricts the product yields in the flow experiments and permits to explain the shift

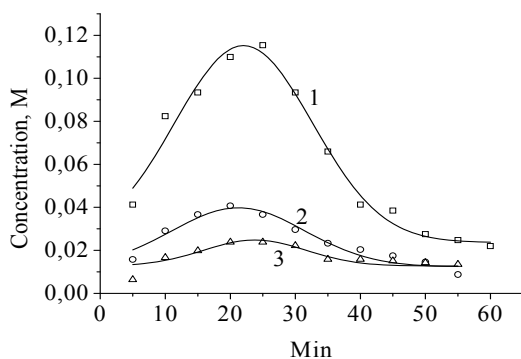


Fig. 5. Kinetic curves of the 5-butoxymethylfurfural (1), butyl levulinate (2) and 5-hydroxymethylfurfural (3) formation in the flow unit. The product concentrations in the removing butanol phase are given. 96°C, 0.584 M sucrose, 2.36 M NaHSO₄, 0.8 M H₂SO₄, butanol flow 600 ml/hour, 200 ml of water phase in the reactor. Total yield of the products is of 0.25 mol/mol of sucrose (5-butoxymethylfurfural - 0.16 mol/mol, butyl levulinate - 0.06 and 5-hydroxymethylfurfural - 0.04)

of the curve maximums in Fig. 6 and decreasing the product yields when increasing the speed of butanol flow. Hence, for the further increasing the selectivity of the two-phase process one should prevent the extraction of intermediates and carbohydrates from water phase.

Conclusion

The acid-catalyzed conversion of carbohydrates into levulinic acid, 5-hydroxymethylfurfural and their derivatives at moderate temperatures (around 100°C) are very promising for the technological development due to their high selectivity. These processes require active acid catalysts like concentrated solutions of strong mineral acids, and the problem of their regeneration should be solved.

The results obtained show that sodium hydrosulfate, sulfuric and hydrochloric acids are the catalysts of close selectivity, but the first could be successfully regenerated in opposite to the others. When applying sodium hydrosulfate as the catalyst in water solution, levulinic acid formed could be extracted from the reaction mass

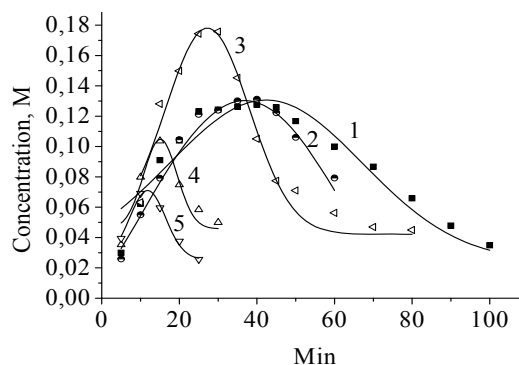


Fig. 6. Kinetic curves of sum of the product concentration (5-butoxymethylfurfural, butyl levulinate and 5-hydroxymethylfurfural) for different flow speed in the flow unit. Conditions see Fig. 6. Flow speed of butanol, cm³/h: 1 – 100, 2 – 300, 3 – 600, 4 – 800, 5 – 1200. Total yield of the products, mol/mol of sucrose: 1 – 0.39, 2 – 0.25, 3 – 0.26, 4 – 0.086, 5 – 0.05

with butanol, and losses of sulfuric acid from water phase do not exceed 3 – 5 %. The sodium hydrosulfate catalyst permits to create a stable two-phase catalytic system for the carbohydrate conversion: water solution of carbohydrate and sodium hydrosulfate – butanol. The main products of the acid-catalyzed carbohydrates conversion under these conditions are 5-butoxymethylfurfural and butyl levulinate, and their total yield attains 83 – 90 mol. % at fructose concentration as much as 1 M. These selectivity exceeds the results in the homogeneous water and butanol solutions by a factor 3 – 5. Moreover, such great selectivity of the acid-catalyzed conversion of carbohydrates at high substrate concentration has not been described before.

Therefore, removing the target products from the active water phase by extraction and alkylation leads to exceeding the selectivity of the process on the new level.

Methods and materials used

Fructose, glucose and sucrose of food quality were used in the experiments. The experiments

were carried out in a 250 ml thermostated magnetically stirred glass flask. The temperature of 98°C, 3 – 7 M acid and 0.33 M of the carbohydrate were used in the main experiments. The necessary amount of catalyst was heated to the required temperature and was added to the aqueous solution or suspension of the carbohydrate. In order to obtain the kinetic curves the reaction mixture was sampled periodically, quickly cooled and analyzed. The humic substances were filtrated and dried to constant weight. Then the humic substances and reaction mixture were extracted with ethyl acetate and the extract was analyzed by G.L.C. The byproducts and intermediates were analyzed by GC-MS with Hewlett – Packard GCD Plus spectrometer. HMF, α - and β -angelicalactones were registered as intermediates or byproducts of fructose degradation. Elemental analysis was carried out using a Fleshe EA™ 1112 Thermo Quest (Italy) instrument.

Hammett acidity function (H^0) was calculated according to the data neglecting the influence of carbohydrates and other components of reaction mixture [35].

^{13}C NMR spectra were recorded at +25°C using a Bruker AM-400 instrument (100.61 MHz) locked to the deuterium resonance of the solvent. The chemical shifts were calculated relative to the solvent signal (CDCl_3) used as the internal standard: δC 76.90 ppm.

Reaction rates were determined by slops of the curves concentration - time.

Carbohydrate conversion in the presence of aliphatic alcohols in static conditions were carried out in a 250 ml thermostated magnetically stirred glass flask. The solutions of sodium hydrosulfate with or without additives of sulfuric acid were used as the catalyst. The heated water solutions of the catalyst and carbohydrates mixed with necessary volume of heated to the same temperature butanol. Water phase aliquots (1 ml) was sampled and analyzed, as described above.

Organic phase aliquots (1 ml) was sampled, neutralized by saturated water solution of sodium sulfate and sodium bicarbonate up to pH 3.0 – 4.0 and analyzed by GLC.

Conversion of carbohydrates with continuous removal of products by extraction with butanol flow was carried out using the installation shown in Fig. 7. The water solutions of sodium hydrosulfate and sulfuric acid were used as the catalyst. Water solution of sucrose and catalyst (200 ml) were loaded into a vertical glass tubular reactor 4. A flow of heated butanol from the preheater 3 was fed into the bottom of the reactor 4. Butanol drops passed through the solution of catalyst and carbohydrate and separated in the top of the reactor. Butanol solution of the products was removed, cooled in the cooler 6 and analyzed.

5-buthoxymethylfurfural

The butanol solution of the products from experiments with two-phase system was separated from water and used for isolating and purifying the 5-HMF esters and LA ethers. The solution was washed with alkaline water solution to hydrolyze butyl ether of levulinic acid and to remove the latter. Butanol solution of 5-buthoxymethylfurfural was dried with sodium sulfate, evaporated, and the product was isolated by vacuum distillation. ^1H NMR (200 MHz, CDCl_3): δ 0.940 (triplet) – CH_3 of butyl group, 1.42 (7 lines), 1.62 (5 lines) and 3.55 (triplet) – CH_2 -groups of butyl radical, 4.56 (singlet) – CH_2 of methoxy group, 6.53 and 7.55 (doublets) – CH -groups of furan ring, 9.64 (singlet) $\text{HC}=\text{O}$ -group; ^{13}C NMR (100 MHz, CDCl_3): δ 14.25 (CH_3 of butyl group), 19.62, 32.04 and 65.41 (CH_2 -groups of butyl radical), 71.50 (CH_2 of oxymethyl group), 111.37 and 122.42 (CH -groups of furan ring), 152.94 and 159.37 (2 and 5-C-atoms of furan ring), 178.17 (C-atom of $\text{HC}=\text{O}$); mass-spectrum (m/z): M^+ 182 (8), 153 (13), 125 (4), 109 (100), 97 (76), 81 (30), 69 (7),

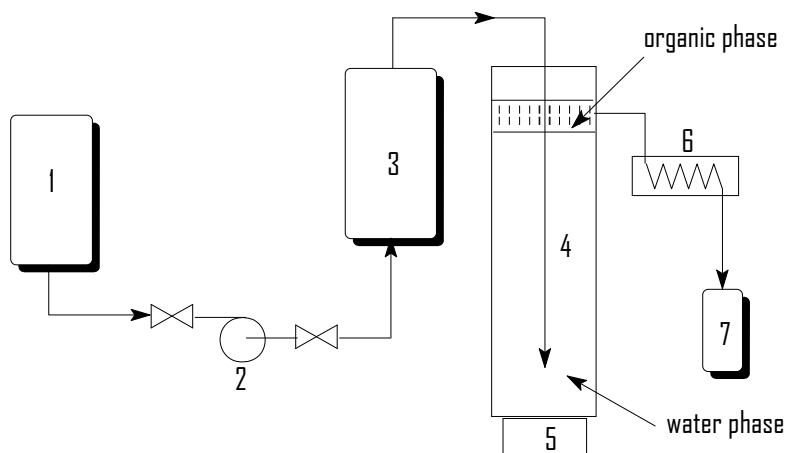


Fig. 7. The unit for the acid-catalyzed conversion of carbohydrates in the flow reactor: 1 – vessel with butanol; 2 - pump; 3 - preheater; 4 - reactor; 5 - magnetic stirrer; 6 - condenser; 7 – extract collector

57 (8), 53 (20). Elemental analysis: C 66.3, H 7.8, O 25.9; calculated: C 65.93, H 7.69, O 26.37.

5-hydroxymethylfurfural was identified in the water solutions of the conversion products and in the butanol solutions removed from the flow reactor by GC-MS. Mass-spectrum (m/z): M^+ 126 (50), 109 (7), 97 (100), 81 (8), 69 (30), 53

(17), 51 (10). ^1H NMR spectrum of the compound isolated was also registered, and it coincides with the known data [30].

Acknowledgement

The financial support from Russian Science Support Foundation is greatly acknowledged.

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