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The Nature and Mechanism of Selectivity Decrease of the Acid-catalyzed Fructose Conversion with Increasing the Carbohydrate Concentration

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To understand the effect of decreasing the process selectivity with increasing the carbohydrate concentration, the influence of levulinic acid and glucose additions on the fructose acid-catalyzed conversion was studied. Levulinic acid yield significantly decreases by initial addition of levulinic acid and glucose to the reaction mixture. Humins were found to include structural fragments of levulinic acid, carbohydrates, and 5-hydroxymethylfurfural. According to the mechanism suggested, the carbocation formed from fructose interacts with water producing target products (5-HMF and levulinic acid) or with levulinic acid or another carbohydrate molecules giving humins. In these assumptions the levulinic acid formation in the process is a reaction of first order with respect to substrate concentration, and the humic substance formation is a reaction of second order with respect to the initial carbohydrate concentration. These two process characteristics, water to substrate ratio and the reaction orders distinction, are the reasons of decreasing the carbohydrate conversion selectivity with increasing the substrate concentration.

Keywords: carbohydrates, fructose, glucose, homogeneous catalysis, levulinic acid, 5-hydroxymethylfurfural, selectivity.

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Природа и механизм снижения селективности кисотно-каталитической конверсии фруктозы с ростом концентрации углеводов

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Изучено влияние добавок левоулиновой кислоты и глюкозы на селективность кислотно-каталитической конверсии фруктозы. Выход левоулиновой кислоты при дегидратации фруктозы значительно снижается при введении в начальный момент времени в реакцию левоулиновой кислоты и глюкозы. Образующиеся гуминовые вещества содержат фрагменты левоулиновой кислоты, углеводов и 5-гидроксиметилфурфурола. Согласно предложенному механизму образующиеся из фруктозы карбокатионы взаимодействуют либо с водой, либо с конечными продуктами процесса. В первом случае образуются 5-ГМФ и левоулиновая кислота, а в последнем – гумины. В соответствии с этим механизмом левоулиновая кислота образуется по реакции первого порядка по концентрации углевода, а гумины – по реакции второго порядка по начальной концентрации углевода. В результате основными причинами снижения селективности кислотно-каталитической конверсии углеводов с ростом их концентрации являются снижение отношений активности воды и углевода, а также различие порядков реакций образования целевых продуктов и гуминов по концентрации субстрата.

Ключевые слова: углеводы, фруктоза, глюкоза, гомогенный катализ, левоулиновая кислота, 5-гидроксиметилфурфурол, селективность.

A sustainable future for the chemical industry requires the employment of renewable raw materials. Almost 2/3 of renewable biomass consists of carbohydrates, and the catalytic upgrading of these substances is a very actual problem. One of the most common way to process hexose carbohydrates is their acid-catalyzed conversion in water medium to levulinic acid (4-ketopentanoic acid, LA) and 5-hydroxymethylfurfural (5-hydroxymethyl-2-furaldehyde, 5-HMF). Levulinic acid is applied for the polymer production and in other fields of chemical industry and research. 5-hydroxymethylfurfural is used as the food flavor and can be used as the starting material for the different organic syntheses [1–5]. Many kinds of catalysts have been employed for this process: mineral acids [1–3, 6–7] and solid catalysts [8–10]. The main disadvantage of solid catalysts is their deactivation by tar and humic substances which are formed during the process in the quantity at least 5 – 10 wt. % based on the target products. In water medium strong mineral acids possess the highest acidity and catalytic activity at the moderate (~100°C) temperatures [6,11–12]. To produce LA and 5-HMF different organic solvents including ionic liquids are applied [13–21].

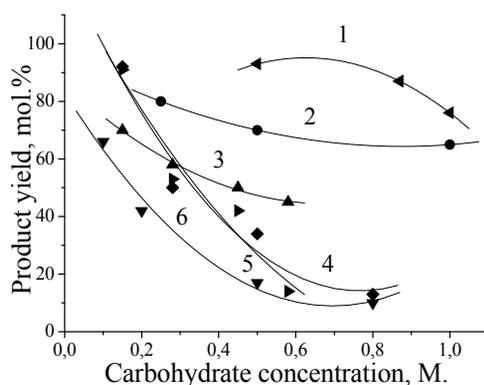


Fig. 1. The influence of carbohydrate concentration on the yields of LA, 5-HMF and their derivatives in different media (1 – fructose – water NaHSO_4 – butanol [13], 2 – fructose – water – HCl [6], 3 – sucrose – water – HCl [5], 4 – fructose – butanol – H_2SO_4 [13], 5 – sucrose – water NaHSO_4 – butanol [13], 6 – fructose – water NaHSO_4 [13 – 14])

The most important problem of the carbohydrate acid-catalyzed conversion to LA and 5-HMF is to maintain the high selectivity with increasing the substrate concentration up to 0.8 – 1 M. High 5-HMF yields (80 – 95 mol. %) are obtained only in solutions of 0.1 – 0.2 M carbohydrate concentrations [5,6,13,14], and they decrease dramatically at higher concentrations (Fig. 1). This problem is extremely important from the theoretical and industrial point of view.

Fig. 1 shows the influence of carbohydrate concentration on the product yields in different reaction media under similar conditions. The highest product yields (80 – 90 mol. %) in homogeneous water solutions are attained for low fructose concentration 0.1 – 0.2 M [5–6, 13–14]. With increasing the substrate concentration up to 0.8 M, the yields of the products decrease from 67 – 92 mol. % down to 10 – 15 mol. % in the presence of NaHSO_4 (lines 6 and 7). In the presence of HCl as a catalyst, similar, but slight decreasing the yield is observed when increasing fructose concentration (line 2). On the other hand, in the two-phase system water-butanol with NaHSO_4 as a catalyst (line 1) decreasing the yields below 80 % take place only at fructose concentrations over 0.8 M. The yield of the target products in this two-phase system (line 1) is 6 – 8 times greater than in the similar homogeneous media at high fructose concentrations (right ends of lines 4 and 6) [13–14]. These results are required to be interpreted in terms of the reaction mechanisms.

The main cause of the low selectivity at high carbohydrate concentration was associated with the instability of 5-HMF and its condensation to humic substances. The previous kinetic models [6, 22–24] for fructose conversion in the presence of strong proton acids take into account the stage of fructose conversion to 5-HMF and parallel reactions of 5-HMF conversion to LA and humic substances. Weingarten described the kinetics of humins formation as a sum of the first order reactions of glucose and 5-HMF [25]. Only Girisuta [26] experimentally estimated the reaction order with respect to 5-HMF concentration for the humins formation by the value of 1.23. For the solid catalysts humins are formed from fructose on Lewis acid sites in opposite to 5-HMF formed on Brønsted acid sites [27]. The mechanism of humins formation via interaction of 5-HMF and carbohydrate molecules was suggested in [28]. However, all these studies did not discuss the role of LA in the process of the humins formation. It should be also remarked that kinetic models [21–25,

27,28] do not explain the principal dependences of decreasing the selectivity with increasing the carbohydrate concentration (Fig. 1).

The goal of this paper is to study the influence of glucose and LA progressive additions on the selectivity of the fructose acid-catalyzed conversion and to propose a mechanism for the described above and discussed below data on the selectivity decrease.

Experimental

Food fructose, glucose, and levulinic acid of ACROS-ORGANICS (USA) were used in the experiments. The experiments were carried out in a 250 ml thermostated magnetically stirred glass flask. The solutions of sodium hydrosulfate with addition of sulfuric acid were used as the catalysts. The necessary amount of catalyst was heated to the required temperature and added to the heated aqueous solution of the carbohydrate. Then the additives were added (LA or glucose solutions). The water phase was sampled periodically, quickly cooled, and analyzed by GLC. The humic substances were filtered, washed with water and dried to constant weight.

The byproducts and intermediates were analyzed by GC-MS with Hewlett – Packard GCD Plus spectrometer. 5-HMF, α - and β -angelicalactones were registered as intermediates or byproducts of fructose degradation. Elemental analysis of humic substances was carried out using a Fleshe EATM 1112 Thermo Quest (Italy) instrument. ¹H NMR spectra of humic substances were recorded at +25 °C using a Bruker Avance III 600 MHz instrument locked to the deuterium resonance of the solvent. The chemical shifts were calculated relative to the solvent signals (D-pyridine, D-DMSO).

Results and discussion

The element content of humins. Table 1 shows the data on elemental analysis of humic substances obtained in the processes of carbohydrate conversion. The data are practically independent of the experimental conditions, and the average values are very close to the published data [26]. The elemental analysis corresponds to C₆H_{4.61}O_{2.21} stoichiometric formula of humins. This formula is chemically close to results of the carbohydrate or 5-HMF dehydration (approximately four and one water molecule, correspondingly). Carbohydrates may produce humins via reversion [29]. The 5-HMF reaction without carbohydrates might form humins by aldol condensation mechanism with following water elimination [30]. Condensation of 5-HMF is assumed to be responsible for humins formation in the acid-catalyzed carbohydrate conversion [31]. Nevertheless, the data shown below

Table 1. The elemental analysis of humic substances formed in the fructose conversion (0.4 M, 108°C, 2 M NaHSO₄, 1.7 M H₂SO₄)

Additives	C, wt. %	H, wt. %	O, wt. %
LA, 0 M	63.3	4.1	32.3
LA, 0.02 M	64.3	3.8	31.5
LA, 0.09 M	64.9	4.2	30.7
Glucose, 0.12 M	63.8	4.1	31.6
Average values	64.1	4.1	31.5

demonstrate the process of humins formation during the carbohydrates conversion may be of another origin.

The effect of LA and glucose addition on fructose conversion. The LA addition at the beginning of the fructose conversion greatly decreases the maximum yield of LA obtained in the process, favoring the increase of the humin mass (Fig. 2 and 3). There is a linear dependence between masses of added levulinic acid and formed humic substances (Fig. 3), and tangent of these straight lines is of 1.5 ± 0.1 . In all the experiments, mass of humic substances increases with increasing fructose concentration. These facts indicate that levulinic acid reacts with fructose producing humic substances.

Combining the data of Table 1 and Fig. 3, one may conclude that the main part of carbon in humins (app. 63 % for upper line of Fig. 3) and, hence, main part of humins are formed from fructose. Therefore the data on elemental content of humins produced with the levulinic acid additives and for usual humins are in close agreement.

The glucose addition similarly affects the fructose conversion (Fig. 4). The influence of the glucose concentration on the humic substance yield shows linear character (Fig. 5), and tangent of the straight line is 1.3 ± 0.1 . These results show that glucose reacts with levulinic acid formed from fructose, and this process forms the humic substances.

The rate ratio of fructose and glucose conversion into levulinic acid is approximately 20 – 30 [7, 12]. Therefore glucose additives into the solution of converted fructose cannot detectably increase the overall LA yield, but purely demonstrate the formation of humic substances from carbohydrates.

The LA formed in the fructose conversion reacts with carbohydrates molecules independently of their nature giving rise to byproducts: this process decreases carbohydrate concentration in solution and, hence, the maximum LA yield.

Comparing the concentration data of Fig. 2 and 4 shows that levulinic acid is approximately 6 times more active than glucose in depressing the maximum LA yield. This means that high final concentration of levulinic acid, but not high initial carbohydrate concentration in the process, principally limited selectivity of the acid catalyzed carbohydrate conversion.

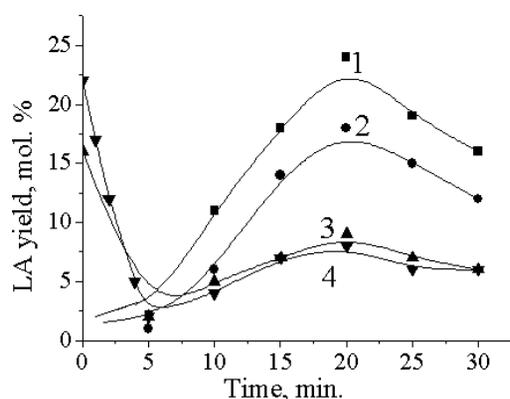


Fig. 2. Influence of LA additions on the LA yield in fructose conversion (0.4 M, 108 °C, 2M NaHSO₄, 1.7 M H₂SO₄. The initial added LA concentration: 1 : without LA addition, 2 : 0.02 M, 3 : 0.07 M, 4:0.09 M

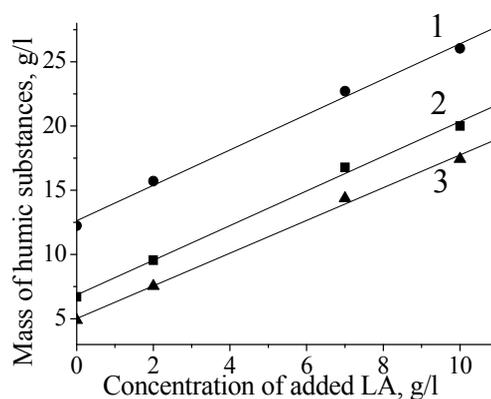


Fig. 3. Influence of added LA concentration on the yield of humic substances in fructose conversion (108 °C, 2 M NaHSO₄, 1.7 M H₂SO₄. The initial fructose concentration: 1 : 0.4 M, 2 : 0.27 M, 3 : 0.14 M)

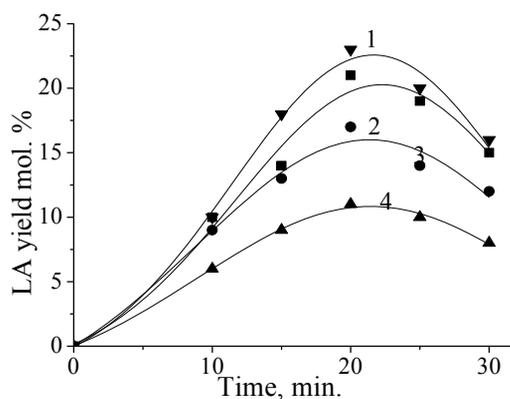


Fig. 4. Influence of glucose additions on the LA yield in the fructose conversion (0.4 M, 108°C, 2 M NaHSO₄, 1.7 M H₂SO₄. Glucose concentration: 1 : without glucose addition, 2 : 0.12 M, 3 : 0.24 M, 4 : 0.4 M

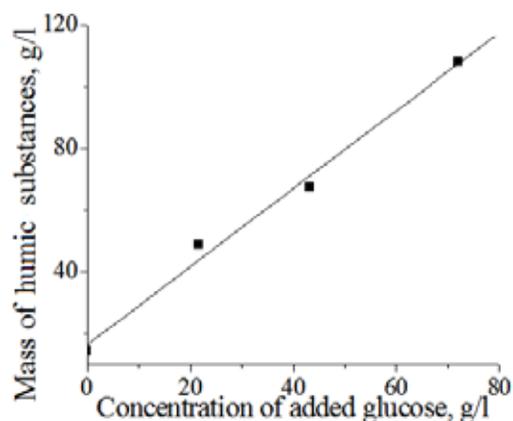


Fig. 5. Influence of added glucose concentration on the humic substance mass in the fructose conversion (0.4 M, 108 °C, 2 M NaHSO₄, 1.7 M H₂SO₄.)

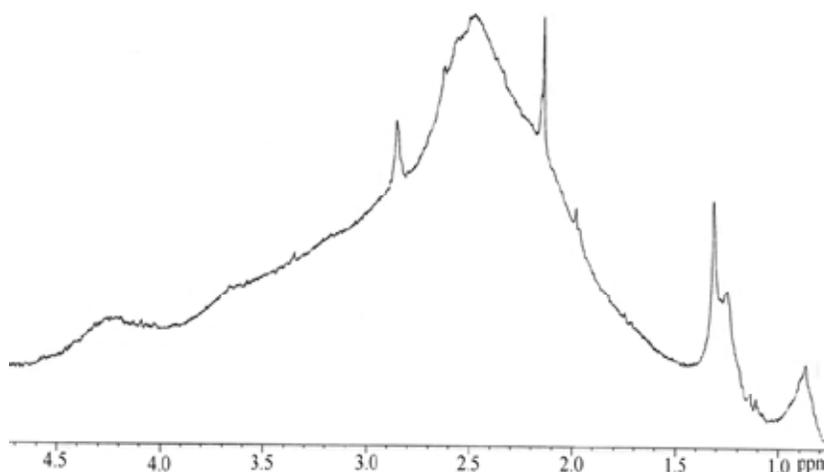


Fig. 6. NMR spectrum (pyridine-d₃) of humic substances produced from glucose (reaction conditions 108 °C, 0.4 M glucose, 2 M NaHSO₄, 1.7 M H₂SO₄)

NMR study of humins. Some information on structure of the humins gives their NMR spectra. Humic substances obtained from glucose show relatively simple spectrum (Fig. 6). The main wide signal belongs probably to alkyl groups connected to carbonyl group (2.5 ppm). This signal decreases to the chemical shift values 4.5 – 4.7 ppm. Protons of carbohydrate alkyl groups are characterized by chemical shifts of 3.2 – 3.9 ppm and up to 4.6 ppm [32]. Hence, a part of the signal in a region of 3 – 4.5 including maximum at 4 – 4.5 ppm (Fig. 6) belongs to hydroxyalkyl- or carbohydrate alkyl groups included into a structure of humins. Any signals in the region of olefin and aromatic protons lack in the spectrum of humins from glucose.

NMR spectra of humic substances produced from fructose in the different solvents (Fig. 7, 8) demonstrate similar signals in a region of 1.0 – 3.7 ppm including maximum at 2.1 – 2.3 ppm, and

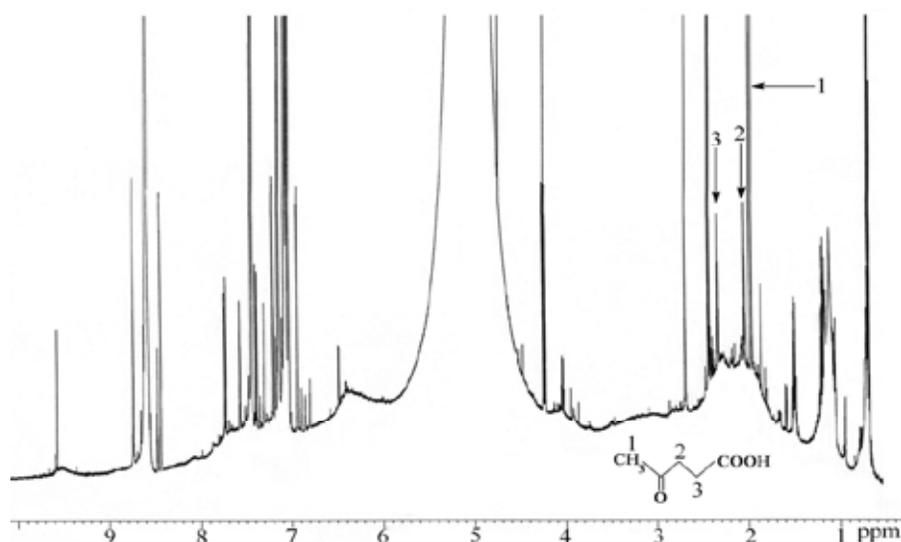


Fig. 7. NMR spectrum (pyridine- d_5) of humic substances produced from fructose (reaction conditions see Fig. 6)

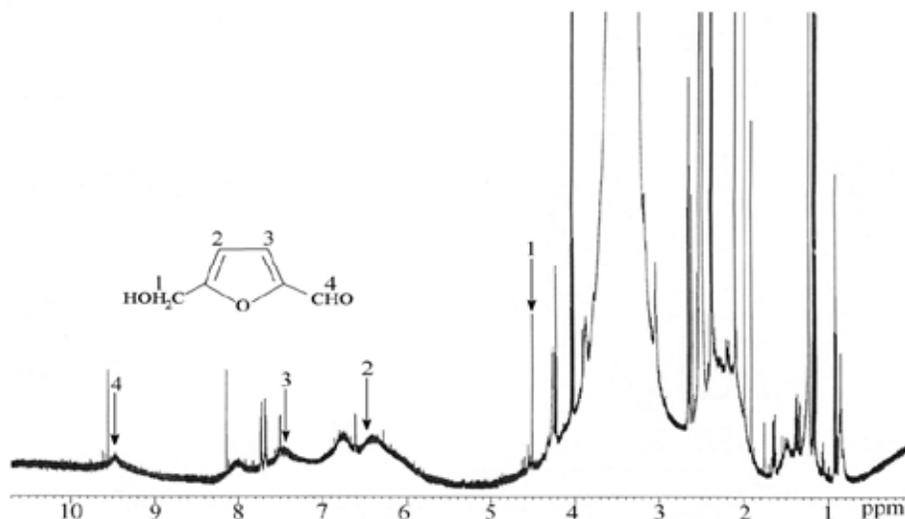


Fig. 8. NMR spectrum (DMSO- d_6) of humic substances produced from fructose (reaction conditions see Fig. 6)

this signals belong probably to methyl and methylen groups bonded to the carbonyl group. Weak wide signal 3.8 – 4.2 ppm belongs probably to hydroxyalkyl protons of carbohydrates. These signals are common for humic substances from fructose and glucose. Besides, the spectra contain four signals at 5.4 – 8.3 ppm (more clearly observed in DMSO, Fig. 8). These signals may correspond to the protons of furan ring and aldehyde group, and they indicate that 5-HMF fragments are included into humin structure.

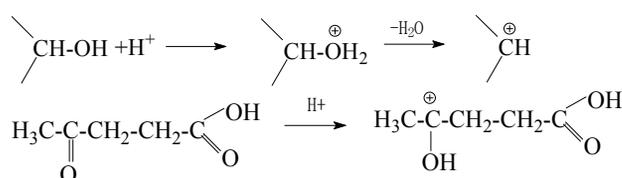
The obtained spectral data may be interpreted as follows. Glucose converts into 5-HMF relatively slow as compared with fructose. 5-hydroxymethylfurfural is of low stationary concentration in this

situation, because it converts into levulinic acid almost completely. Then humins are mainly formed as a result of levulinic acid and glucose condensation.

Fructose converts into 5-HMF faster than glucose, and stationary concentration of the product is higher in the fructose solutions. Higher concentration of 5-hydroxymethylfurfural [7,11] leads to its partial condensation forming humins with furan and aldehyde structural groups together with products of the LA and carbohydrate condensation.

On the mechanism of humin formation. In order to explain the obtained results and the just known data [6, 8, 26] we suggest a novel hypothesis on the mechanism of target products and byproducts formation involving common carbocation species. These species are well-known intermediates of the carbohydrates acid catalyzed conversion [33–34].

The first stage of LA and carbohydrate conversion involves proton accepting and formation of the corresponding carbocations, immediately or after the removal of a water molecule:

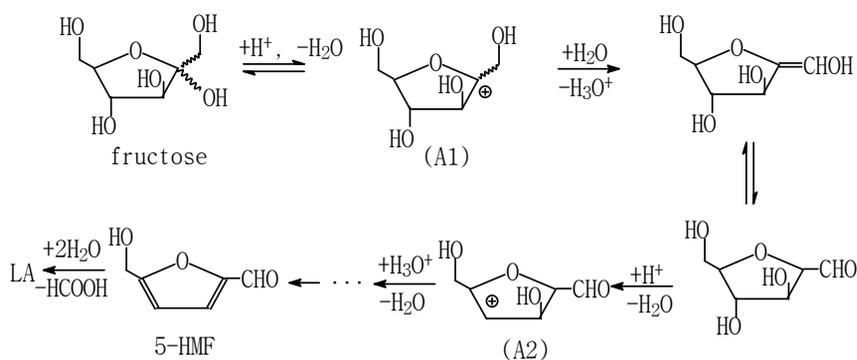


These carbocation species can react then with the different molecules present in solution by electrophilic addition. These interactions can be divided in the two groups and therefore the two possible pathways of carbocations conversion can be discussed:

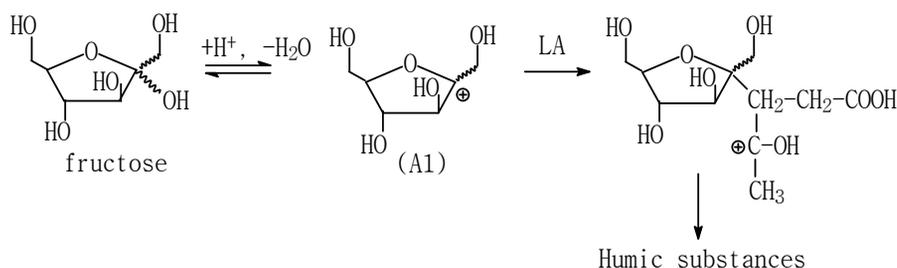
- interaction with water molecule (or solvent molecule);
- interaction with substrate molecule or molecular products of its conversion (5-HMF or LA etc.)

Pathway (A) of interaction of the carbohydrate derived cations with water molecules results finally in levulinic acid formation [33-36]:

Pathway (B) of the carbocation interaction with the reagent or the target product molecules results in increasing the product molecular mass, oligomerization and formation of humic substances. For example, interaction of A1 carbocation formed from fructose with enolic form of LA can give rise to derivatives of higher molecular weight with respect to the starting reagents:



Scheme 1. Pathway A of the fructose conversion



Scheme 2. Pathway B of the fructose conversion

Thus, selectivity of the acid-catalyzed conversion depends on the relative contributions of the (A) and (B) pathways. The relationship between these pathways depends on the ratio of water to substrate activity, and, hence, the levulinic acid yield has to decrease with increasing the carbohydrate concentration in the reaction mixture.

Pathway (A) includes formation of some intermediate carbocations (A1) – (A3). Each of these cations could react with carbohydrate molecules or products of their conversion and any such interaction results in decreasing the process selectivity. The high complexity of this process does not change the general conclusion: the target products yield depends on the ratio of water to carbohydrate reactivity and decreases with increasing the substrate concentration.

It should be pointed out that according to the suggested mechanism in a simplest assumption the levulinic acid formation is a reaction of first order with respect to substrate concentration, and the humic substance formation is a reaction of second order with respect to the initial carbohydrate concentration. Such a kinetic behavior of the systems explains the dependences presented in Fig. 1.

According to this mechanism a selectivity decrease should be observed when water activity decreases as a result of another modification of the aqueous solution, for example, catalyst nature or its concentration. Indeed, selectivity of the glucose conversion decreases when using phosphoric acid as the catalyst instead of hydrochloric acid at the same Hammett acidity function [12]. Similarly, the selectivity decreases moving from hydrochloric acid to sodium hydrosulfate (Fig. 1) and from sulfuric acid to sodium hydrosulfate at higher concentration [37].

The suggested mechanism permits to assume that in order to increase selectivity of the acid-catalyzed conversion of concentrated carbohydrate solutions one should extract levulinic acid from the acid carbohydrate solution. This approach has been implemented many times in two-phase systems consisted of water and butanol (Fig. 1) [13–14], tetrahydrofuran, acetonitril, methylisobutylketon, and others [39–43].

Conclusion

The significant decrease of 5-hydroxymethylfurfural and/or levulinic acid yields with increasing the initial carbohydrate concentration is a very dramatic effect which lowers the economic advantage of the carbohydrate conversion processes.

The obtained results show, for the first time, that levulinic acid yield in the fructose acid catalyzed conversion decreases with the LA or glucose addition to the reaction mixture. NMR data shows

that humins include structural fragments of levulinic acid, carbohydrates, and 5-HMF. In order to explain these effects the scheme of formation of levulinic acid and humic substances from the same carbocations has been suggested. According to this mechanism the carbocation species formed in the process can react with water forming the target products (5-HMF and LA) or with LA or carbohydrate producing the humic substances.

As a result, the process overall selectivity depends on the ratio of water to carbohydrate activity in the reaction solution and therefore it decreases with increasing the carbohydrate concentration. On the other hand, in a simplest assumption, humins formation is a reaction of second order with respect to the initial substrate concentration, as a condensation reaction, and the desired LA and 5-HMF are formed in the first-order reactions with respect to carbohydrate concentration. Such a character of the kinetic system also explains the dependences of products yield *versus* carbohydrate concentration.

In order to increase the LA or 5-HMF yield, the products has to be removed from catalyst and substrate. This approach was realized adopting a two-phase water-butanol system: in this such a process the products yield, 5-butoxymethylfurfural and butyl levulinate, attained 80 – 90 mol. % at a carbohydrate concentration up to 1 M [13–14]. Similar results in other two-phase systems were obtained later [38–43].

Hence, high final concentration of levulinic acid (or 5-hydroxymethylfurfural), but not high initial carbohydrate concentration in the process, principally limits selectivity of the acid catalyzed carbohydrate conversion.

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