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High Temperature 5-Hydroxymethylfurfural Synthesis in a Flow Reactor

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Abstract

A flow reactor was used to study the kinetics of 5-hydroxymethylfurfural synthesis from fructose and sucrose at 240 °C in water solutions containing acetic and phosphoric acid as catalysts. The maximum yield of 5-hydroxymethylfurfural was found to be practically independent of the chosen catalyst and carbohydrate. It attained 40 mol. % at 240–250 °C, fructose and phosphoric acid concentrations being 0.25 and 0.01–0.05 M, respectively. The rate of corrosion of steel 12Kh18N10T under these conditions is 1–2 mm/year is by an order of magnitude lower than that observed at carbohydrates conversion at 100–180 °C in other catalytic media.

INTRODUCTION

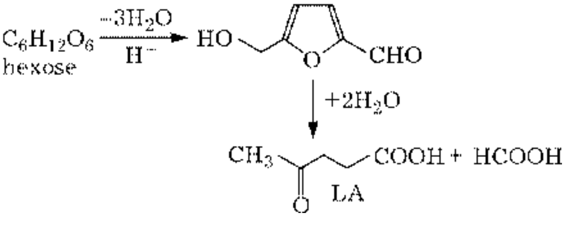
At present carbohydrates chemistry attracts a lot of research attention in spite of various data accumulated in the field, since renewable sources of plant raw for chemical industry are one of the main aspects of sustainable development.

Among other products of the acid catalyzed conversion of hexose monocarbohydrates and hexose-containing materials 5-hydroxymethylfurfural (5-HMF) is used for the synthesis of various pharmaceuticals [1], thermally stable polymers, and food additives [2, 3]. It is produced from hexoses *via* three water molecules removal. It is highly reactive, and easily converts into levulinic acid (LA), and condenses yielding humic compounds [4] (Scheme 1).

A quantitative synthesis of 5-HMF from glucose and cellulose at relatively high temperatures (180 °C) was first studied at the beginning of the last century [5]. However, the obtained 5-HMF yields were insignificant due to its decomposition into levulinic and formic acids. However, some by-products of cellulose conversion were identified during these experiments.

All basic methods for the 5-HMF synthesis may be classified into 5 groups.

1. Homogeneous processes in water solutions at temperatures below 200 °C.
2. Heterogeneous catalytic processes.
3. Processes performed in non-water media.
4. Processes performed in two-phase systems assisted by homogeneous catalysts.
5. Processes in homogeneous water solutions at temperatures above 200 °C.



Scheme 1.

Each of these approaches has its advantages and disadvantages. For example, hexose dehydration in water at temperatures up to 170 °C gives 5-HMF with an yield not higher than 30 % [6, 7].

Heterogeneous catalytic methods have two serious disadvantages: ion-exchange resins and oxide catalysts show a relatively low activity in water [8–11], heterogeneous catalyst surface is quickly covered by tars. Process selectivity never exceeds 90 %, *i.e.* humic substance yield exceeds 10 mass % of the target product. Heterogeneous catalysts regeneration is not discussed in the literature, but this obstacle seems to be quite serious with regard to the practical implementation of heterogeneous catalytic systems.

Process realization in non-water media with aproton solvents and heterogeneous catalysts also has serious limitations. The high yields of 5-HMF (up to 95 %) are attained only in diluted the solutions of carbohydrates (0.1–0.2 M) [12]. Moreover, 5-HMF evolution from thermally unstable solvents, dimethylsulphoxide and dimethylformamide in particular, is not yet optimized. High 5-HMF yields from fructose (up to 65–70 %) were obtained in polyethyleneglycol at 90–180 °C [12–14].

Process performance in the two-phase water-organic media using homogeneous catalysts allows one to avoid the above-mentioned disadvantages. However, in the present of aliphatic alcohols, *i.e.* the most efficient extraction reagents, LA esters and 5-HMF ethers form as main products [15, 16]. Higher product yields (in comparison to homogeneous water solutions) are obtained by combining the extraction and alkylation processes. The forming products are more stable, and their extraction into organic phase protects them from the acidic catalyst.

When the temperature of acid catalyzed conversion increases to 200–250 °C, 5-HMF yield increases, and reaction accelerates [6]. It is in accordance with the well-known data related to the process activation parameters. The activation energy for 5-HMF formation from glucose essentially exceeds the activation energy for its decomposition (141 and 64 kJ/mol, respectively) [17]. High temperatures were applied to study the conversion of cellulose and glucose [7], pine cellolignin [18] and fructose in two-phase system water–methylisobutylketone [4]. Up to 20–30 % of 5-HMF were obtained from cellolignin [7], and up to 75% of 5-HMF were obtained from fructose in the presence of extracting reagent [4].

Therefore, the main problem of acid catalyzed carbohydrates conversion into 5-HMF is the low reaction selectivity. With this regard high temperature processes seem to be more promising, since they are characterized by a comparatively low rate of 5-HMF conversion into LA. Fructose is a more advantageous substrate than glucose, since the rate of fructose conversion into 5-HMF is higher by 20–40-fold [19–21]. There are quite a few papers related to the carbohydrates conversion in water-organic media, as well as to the wood, cellulose and glucose conversion at temperatures above 200 °C [18, 4, 7]. However, most simple and promising systems for the 5-HMF synthesis, such as acid catalyzed homogeneous conversion of fructose and sucrose in water at high temperatures, remain unstudied yet.

The principle problem of process realization in practice is the corrosion activity of the medium under discussed conditions. Corrosion resistance of steels under above-mentioned conditions is not investigated as well.

This study focuses on the possible selective conversion of fructose and sucrose into 5-HMF at temperatures above 200 °C, and on the estimation of corrosion resistance of stainless steel 12Kh18N10T under the process conditions.

EXPERIMENTAL

A flow set-up (Fig. 1) was used for acid-catalyzed conversion of carbohydrates into 5-HMF.

Sucrose or fructose was fed into heater *3* and then reactor *5* with plunger pump *2* with a rate of 5 l/h. Catalyst solution was supplied into reactor *5* from vessel *6*. Temperature in reactor *5* was raised from 210 to 260 °C during the process at a continuous feed of reaction solution. Reaction mass accumulated in separator *7* was continuously removed to receptacle *9* and divided into 1 l samples. Water solutions of orthophosphoric and acetic acid were used as catalysts.

Reaction mass was neutralized by sodium carbonate to pH 6–7 and exposed to extraction

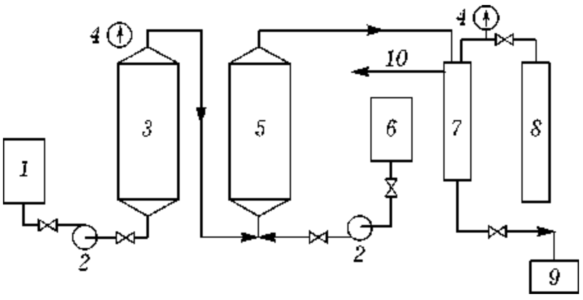


Fig. 1. Schematic view of a slow set-up for the acid catalyzed conversion of carbohydrates at high temperatures: *1* – carbohydrate containing vessel, *2* – plunger pumps, *3* – carbohydrate solution heater, *4* – pressure meters, *5* – reactor (volume 0.25 l), *6* – catalyst-containing vessel, *7* – separator, *8* – gas cylinder (argon of carbon dioxide), *9* – extracted mass receptacle, *10* – gas discharge line.

by ethylacetate. Extracted mixture was then analyzed by liquid gas chromatography. After that reaction product was concentrated in a rotor dryer, and then target product was separated by vacuum distillation (1–2 Hg mm).

Liquid gas chromatography was performed with chromatograph 3700, column 2.6 m, 3 mass % Carbowax-15000 and 1 mass % phosphoric acid on INERTON-AW-DMCS 0.25–0.30 mm, flame ionization detector, gas carrier: helium. Starting temperature was 100 °C (3 min), final – 160 °C, heating rate being 15 °C/min.

Evolved 5-HMF was identified using chromatography mass spectrometry Hewlett Packard GCD Plus (Collective Analysis Centre at Krasnoyarsk Research Centre, SB RAS), and PMR spectroscopy (Brucker DPX-200). The mass spectrum (M^+ 126 (50), 109 (7), 97 (100), 81 (8), 69 (30), 53 (17), 51 (10)) and PMR spectrum (δ 4.45 pm (singlet) – methoxy group CH_2, 6.41 and 7.25 pm (doublets) – furan ring group CH, 9.18 (singlet) – aldehyde group HC=O) of the obtained 5-HMF well agree with the reference data bases [22].

In order to follow the corrosion of setup metal parts, reaction mass (100 ml) was boiled with 10 ml of concentrated nitric acid for 1 h for dissolving organic admixtures and solution homogenization. Thus obtained solutions were alkalized to pH 3–4, and analysed with atomic absorption spectrophotometer ASS-30.

In order to estimate the rate of corrosion of steel 12Kh18N10T weight loss factor *K* was measured, showing the quantitative loss of mass from a unit surface with time [23]: $K = \Delta m/(S\tau)$, where Δm is metal mass loss, g; S is sample surface, m^2; τ is experiment duration, year.

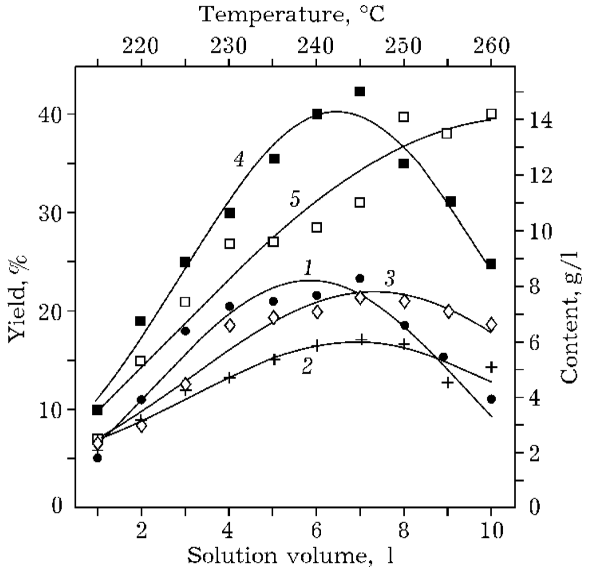


Fig. 2. Yield of 5-HMF from fructose (0.25 M) *versus* temperature and phosphoric acid concentration, M: 0 (*1*), 0.25 (*2*), 0.12 (*3*), 0.04 (*4*), 0.01 (*5*).

Corrosion degree (showing corrosion depth Π, mm/year) was calculated as: $\Pi = 8.76K/d$, where K is mass loss factor, g/(m^2 year); d is metal density, g/cm^3.

RESULTS AND DISCUSSION

Figure 2 shows the 5-HMF accumulation at the acid catalyzed conversion of fructose depending on phosphoric acid concentration and reaction temperature. At a constant residence time each catalyst concentration provides particular optimum process temperature, which increases as phosphoric acid concentration decreases. For a residence time of 3 min maximum 5-HMF yields are obtained at 240–260 °C, catalyst concentration being 0.01–0.05 M. This signifies that reactor productivity with respect to the target product is about 0.25 kg/(l h).

At the further increase of catalyst concentration, products yield decreases due to the growing rate of 5-HMF conversion into LA and humic substances. Relatively low catalyst concentrations allow process performance in the stainless steel reactor (12Kh18N10T); steel cor-

TABLE 1

Reaction mass analysis results with regard to metal content, and calculated steel corrosion rate in the phosphoric acid containing solutions at 240 °C

Reaction mass	Metal content, mg/l		Corrosion rate, mm/year	
	Iron	Nickel	Iron	Nickel
Starting*	1.0	0.2		
No catalyst	1.57	0.3	0.23	0.3
Catalyst 0.01 M phosphoric acid	4.7	0.8	1.5	1.7

*According to the data of atomic absorption analysis of initial solution of fructose and phosphoric acid.

rosion being insignificant (less than 2 mm/year, see Table 1).

Sucrose converts to 5-HMF in the presence of acetic acid with a yield of up to 40 % with respect to stoichiometry, though at a relatively high catalyst concentration (0.6 M, Fig. 3). Figures 2 and 3 demonstrate that maximum 5-HMF yields from sucrose and fructose are practically the same. Therefore, sucrose conversion to fructose most likely goes with a high selectivity, and does not limit the acid catalyzed sucrose conversion.

Catalyst activity decreases in a row: phosphoric acid > acetic acid, which well agrees with the strength of acids, while the maximum selectivity of carbohydrates conversion is practically independent of the catalyst type.

Figure 4 shows the yield of levulinic acid (which is the product of 5-HMF conversion) *versus* reaction temperature and phosphoric acid concentration. Apparently, LA yield grows with increasing catalyst concentration, and the 5-HMF yield is maximum at a relatively low concentration H_3PO_4 (0.01–0.05 M, see Fig. 2). Comparing these results one may see that 5-HMF yield to LA yield ratio may attain 20–30. In water media such a ratio is attained at high temperatures only, owing to the difference of activation energies for the formation of 5-HMF and its conversion to LA [7, 17].

CONCLUSION

Therefore, phosphoric acid catalyzed sucrose and fructose conversions into 5-HMF may be realized in a flow reactor at 240–250 °C with a high productivity (up to 0.25 kg/(l h) and a moderate corrosion activity (1–2 mm/year for steel 12Kh18N10T). Let us note when the same processes are catalyzed by sulphuric acid at 100–180 °C, acid concentration should be 20–50 and

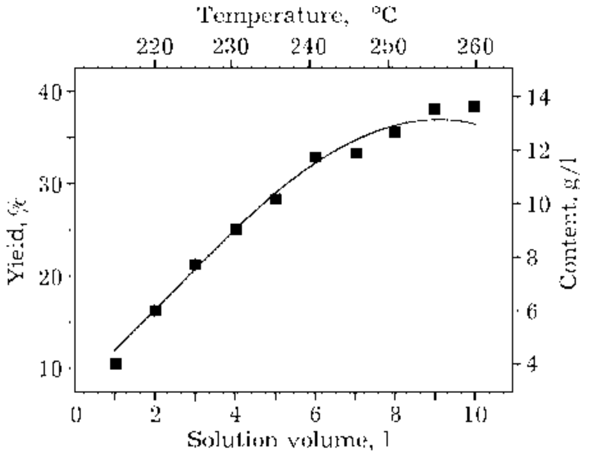


Fig. 3. Accumulation of 5-HMF from sucrose (0.2 M) catalyzed by acetic acid (0.6 M).

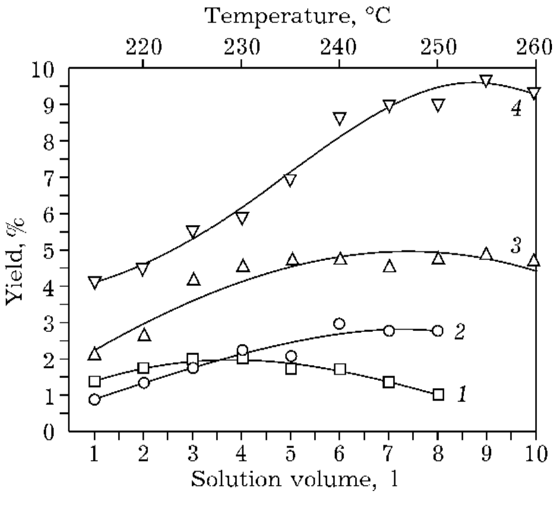


Fig. 4. Levulinic acid accumulation depending on phosphoric acid concentration, M: 0.01 (*1*), 0.04 (*2*), 0.12 (*3*), 0.25 (*4*). Fructose concentration is 0.25 M, process temperature is 220–240 °C.

1–5%, respectively [15, 19]. However, under these conditions steel 12Kh18N10T shows a rather low resistance to corrosion.

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