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Automatic Lab scale equipment for continuous HMF production in biphasic systems

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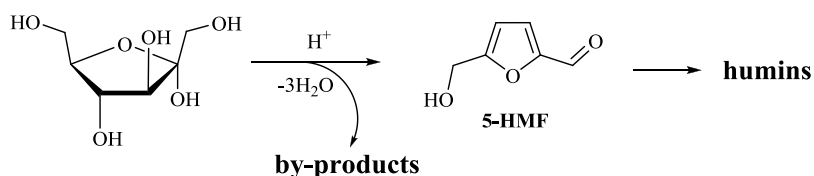
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Abstract. An automatic lab scale equipment for continuous HMF production by the dehydration of fructose with homogeneous catalysis in biphasic systems (water solution - MIBK) was designed, manufactured and tested. The dependencies of the HMF yield on the process parameters were studied. The feed rate of fructose varied from 50 to 100 g·h⁻¹, the extractant (MIBK) flow rate from 0.5 to 1.4 L·h⁻¹ and the process temperature was maintained in the range from 50 to 87 °C. The maximum productivity of the automatic lab scale equipment 33.6 g·h⁻¹ with a high HMF yield 48 % is achieved with the following process parameters - 87 °C, the fructose feed rate 100 g·h⁻¹ and the extractant flow rate 1 L·h⁻¹. This automatic lab scale equipment may be prospectively used for the kilogram scale HMF synthesis.

1. Introduction

Interest in the use of bio-renewable raw materials for the production of fuels and valuable chemicals in the last decade has increased significantly [1]. Unlike fossil analogs (oil, gas, coal), biomass contains an excess of oxygen. This complicates its direct use as an energy source or source of raw materials in chemical technology. To reduce the amount of oxygen, the biomass must be dehydrated and hydrogenated [2-4]. One of the most important intermediates of biomass dehydration is 5-hydroxymethylfurfural (HMF). The products of its further oxidation / reduction (2,5-diformylfuran, 2,5-furandicarboxylic acid, dimethylfuran, etc.) in the near future will be a substitute for the raw materials currently used for the production of polymers, drugs and fuels.

Currently, the most efficient and rational pathways for the synthesis of HMF are based on the use of fructose as a raw material [4-6]. To date, many options have been proposed for synthesis of HMF from a carbohydrate-containing raw material: homogeneous (acidic dehydration in an aqueous or anhydrous medium, in ionic liquids) and heterogeneous that used solid acids as catalysts. When ionic liquids or aprotic solvents are used as a reaction medium, high yields of HMF (more than 90%) are achieved. However, the high cost of reagents and the difficulty of isolation of HMF from the reaction mixtures lead to a high product cost [3-7]. The introduction of a heterogeneous catalyst makes it possible to increase the yield of HMF in aqueous solutions, but the synthesis proceeds at high temperatures (up to 200 °C) and pressure [3].



(1)

Regardless of the synthesis approach used, the isolation of HMF is carried out by its extraction with low-boiling water-immiscible organic solvents. Entering the extractant into the reaction zone during the synthesis in aqueous medium allows to increase the yield of HMF by times due to its removal from the reaction zone, thereby partially preventing the occurrence of side reactions. The most effective



extractant is methyl isobutyl ketone (MIBK) [2, 9]. The production of HMF in two-phase aqueous-organic systems is commercially more justified compared to the synthesis in ionic liquids [6,7].

Most of the published studies on the production of HMF from monomeric sugars (fructose) or from other raw materials were carried out using laboratory equipment (autoclaves, test tubes) under periodic conditions. Even a few studies on the production of HMF in kilogram scales were also focused on the periodic action reactors [10]. Continuous synthesis methods are investigated only for systems with a heterogeneous catalyst [11].

Earlier, we have proved the prospects of $\text{Na}_2\text{SO}_4 \times 10\text{H}_2\text{O}$ and concentrated H_2SO_4 system as catalyst for the HMF synthesis in a two-phase aqueous solution - MIBK system [6, 12]. $\text{Na}_2\text{SO}_4 \times 10\text{H}_2\text{O}$, reacting with H_2SO_4 , with formation of NaHSO_4 , that is a selective catalyst for the dehydration of fructose and fructose carbohydrates (sucrose, inulin) to HMF [2]. We optimized the process of fructose dehydration in this two-phase system in a batch reactor. We determined: (i) the duration of the process, (ii) the influence of the sulfuric acid content, (iii) temperature and (iv) the amount of extractant in terms of the maximum of HMF yield.

In this work, we are present a developed automatic lab scale equipment for continuous HMF production in biphasic systems and results of the optimization process of the dehydration of fructose during continuous synthesis to create a technologically, environmentally and economically efficient method for producing HMF.

2. Methods

The process of dehydration of fructose proceeds relatively slowly. For carrying out of the process under periodic conditions, the optimal synthesis parameters are: fructose concentration of 15%; the volume ratio of an aqueous solution of NaHSO_4 / MIBK equal to 3: 1; the temperature is 85 °C during 2 hours [12].

To implement the process in continuous conditions, automatic lab scale equipment was designed and manufactured, the general scheme and photo of which are presented in Figure 1. The reactor is made of chemically resistant stainless steel because of the reaction medium contains both sodium hydrosulfate and free sulfuric acid and are very corrosive. In addition formic acid and other by-products are also formed.

To separate the water-organic emulsion formed in the reactor 4, it is necessary to provide a side branch in the form of a collector 11. Due to the absence of mixing in the collector, conditions for the separation of two liquid phases are provided. Collector is equipped with a transparent part made of glass to fix the liquid level by the operator and prevent extractant overflow in emergency cases.

Heating of the reactor is carried out using electric heating elements. The temperature is controlled by an electronic TIR controller with accuracy maintain temperature 1 °C. To prevent heat from dispersing into the environment and to prevent the operator from contacting the heated surface, the reactor is wrapped in a heat insulating material and covered with a protective cover.

$\text{Na}_2\text{SO}_4 \times 10\text{H}_2\text{O}$ and concentrated H_2SO_4 are loaded into reactor 4 (Figure 1). After stirring the mixture for 15 minutes using a stirrer 3, MIBK is poured into the reactor. After heating of the reactor to a predetermined temperature from the hopper 5 using a dispenser for bulk materials 6, raw materials (fructose) are continuously fed into the reactor. MIBK also flows continuously from tank 1 using a peristaltic pump 2. Vapors formed in the reactor are condensed in refrigerator 7 and returned back. The finished product in the form of the HMF solution in MIBK continuously removed from the reactor using a peristaltic pump 8. To remove free acids the exit solution is passed through an absorber 9 mixture of calcium carbonate and sodium bicarbonate. The freed from acids HMF solution is collected in the tank 10, then it is sent for evaporation on a laboratory rotary vaporizer. The isolation of HMF requires removal of MIBK by distillation and re-extraction of the product with methyl tert-butyl ether to remove the main part of tars. As a result, the product has a purity of 95-96%.

The concentration of HMF in the reaction mixtures was determined by HPLC on an Agilent 1260. Infinity chromatograph equipped with a diode array detector and an Eclipse PAH reversed phase column (250×4.6 mm); eluent acetonitrile– water (70 : 30 by volume), flow rate 0.5 mL min⁻¹; column temperature 30 °C; detection wavelength λ 284 nm; retention time of HMF 4.5 min.

The yield of HMF (wt. %) was determined using the equation given below.

$$Y(\text{HMF}) = \frac{C(\text{HMF}) \cdot V \cdot M(\text{Fructose}) \cdot 100}{W(\text{Fructose}) \cdot M(\text{HMF})}$$

Here, C refers to concentration (g·L⁻¹), M is the molecular weight (g·mol⁻¹), V extractant consumption (L·h⁻¹) and W fructose mass flow (g·h⁻¹).

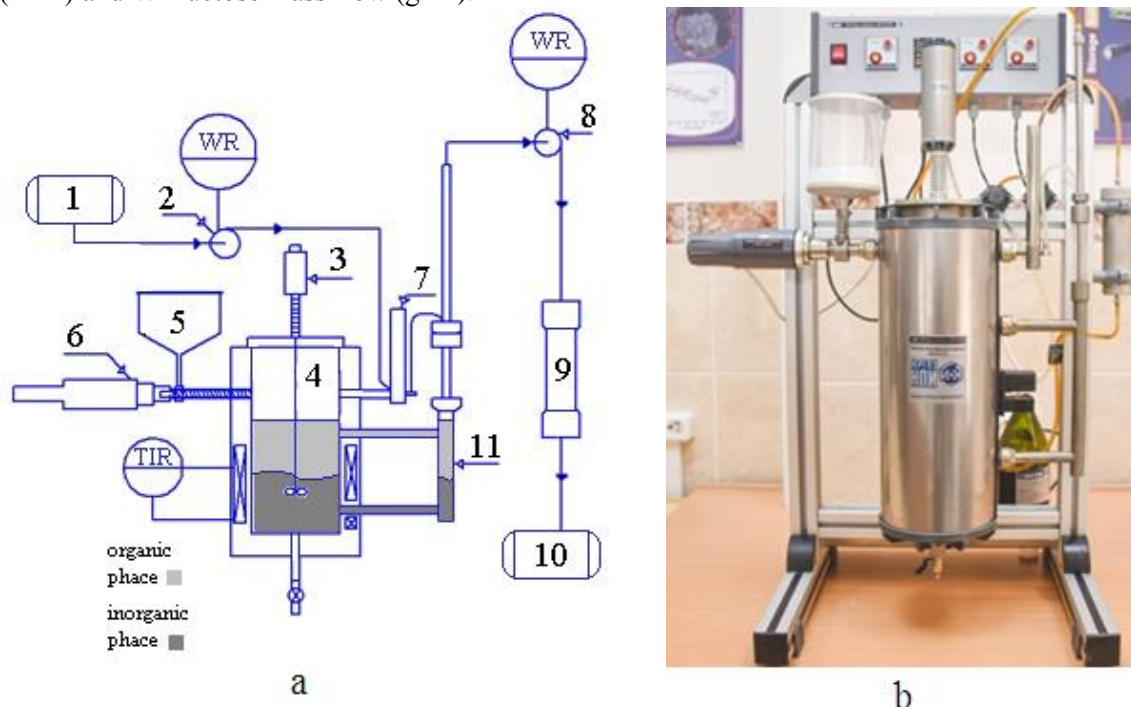


Figure 1 - Scheme (a) and photo (b) of the automatic lab scale equipment for continuous HMF production

1- tank with MIBK; 2,8 - pumps; 3 - mixing device; 4 - reactor; 5 - tank with raw materials; 6 - dispenser; 7 - refrigerator; 9 - acid absorber; 10 - tank for the HMF solution in MIBK; 11 - collector. WR - peristaltic pump; TIR - temperature TIR-controller.

3. Optimization of synthesis conditions

When carrying out the process in laboratory conditions according to the method described in our previous article [11], in this was found that the presence of an extractant has a great effect. HMF accumulates in the reaction medium. Reaching the maximum concentration, it begins to react with fructose, which leads to the formation of by-products (humins) [13] (Scheme 1). To avoid such an outcome, it is necessary to organize the continuous removal of products from the reaction zone. This is achieved by carrying out the process in a two-phase system. HMF has a greater solubility in MIBK than in water; as a result it is extracted into the organic phase. Therefore, it can be expected that the continuous removal of the extractant, saturated with HMF, from the reaction system will contribute to an increase in the yield of the target product as compared with the process carried. It is very important to establish the optimal ratio of the feed rates of the reagent and flow rate of the extractant. These parameters were determined by calculation; however, they needed experimental verification and possibly refinement.

We studied the effect on the HMF yield and humins accumulation under following process parameters: the feed rate of fructose, the flow rate of the extractant and the temperature (Table 1).

With an increase in the fructose feed rate, the yield of HMF is decreases, and the HMF productivity of automatic lab scale equipment has extreme character. At low feed rates ($50\text{--}70\text{ g}\cdot\text{h}^{-1}$) the concentration of fructose in the reaction medium does not reach the optimum, and at high feed rates, fructose does not have time to be converted and accumulates in the reactor. This leads to an increase in the rate of accumulation of insoluble humins in the aqueous phase (Table 1, lines 1-5).

When the flow rate of the extractant into the reactor is increase up to $1\text{ L}\cdot\text{h}^{-1}$, the yield of HMF increases too, and then almost does not change (Table 1, lines 6-10). Apparently, with an increase in the MIBK flow rate, the HMF concentration in the organic phase decreases that lead to increasing of the HMF extraction from water phase to organic phase rate. The optimal flow rate of the extractant $1.0\text{ L}\cdot\text{h}^{-1}$ provides to get the highest yield of HMF 48% (Table 1, line 3).

With increasing of temperature from 50 to $87\text{ }^{\circ}\text{C}$, the yield of HMF increases from 3 to 48%. The largest yields of HMF was obtained at temperatures of $85\text{--}87\text{ }^{\circ}\text{C}$ for 8 hours with MIBK flow rate $1\text{ L}\cdot\text{h}^{-1}$, and fructose mass flow $100\text{ g}\cdot\text{h}^{-1}$ (Table 1 line 3).

Table 1. Optimization of conditions of HMF synthesis in two phase system of aqueous solution of NaHSO_4 / MIBK (1: 3 volumes ratio) using automatic lab scale equipment

№	Fructose feed rate ($\text{g}\cdot\text{h}^{-1}$)	MBIK flow rate ($\text{L}\cdot\text{h}^{-1}$)	Temperature ($^{\circ}\text{C}$)	HMF yield (%)	HMF productivity ($\text{g}\cdot\text{h}^{-1}$)	Humins accumulation rate ($\text{g}\cdot\text{h}^{-1}$)	MIBK volume needs for extraction of 1 g HMF (mL)
1	50	1.0	87	63	22	0.5	-
2	70	1.0	87	58	28	2.1	-
3	100	1.0	87	48	34	5.0	29.3
4	120	1.0	87	37	31	13.2	-
5	140	1.0	87	28	27	25.2	-
6	100	0.5	87	27	-	-	32.5
7	100	0.7	87	33	-	-	30.3
8	100	1.0	87	48	-	-	29.8
9	100	1.2	87	50	-	-	34.3
10	100	1.4	87	53	-	-	37.7
11	100	1.0	50	3	-	-	-
12	100	1.0	60	7	-	-	-
13	100	1.0	70	14	-	-	-
14	100	1.0	80	45	-	-	-

4. Conclusion

The automatic lab scale equipment for continuous 5- HMF production in biphasic systems was developed, manufactured and tested for dehydrating fructose in a homogeneous catalytic system. It was established that the maximum productivity of the equipment is $33.6\text{ g}\cdot\text{h}^{-1}$ with a high HMF yield of 48 % is achieved with the following process parameters - $87\text{ }^{\circ}\text{C}$, the fed rate of fructose $100\text{ g}\cdot\text{h}^{-1}$ and the flow rate of the extractant $1\text{ L}\cdot\text{h}^{-1}$. This automatic lab scale equipment may be prospectively used for the kilogram scale HMF synthesis .

Acknowledgement

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