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Regeneration of Hydrochloric Acid in the Catalytic Fructose Conversion to Levulinic Acid

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The extraction method to regenerate hydrochloric acid as the catalyst of the fructose conversion to levulinic acid (LA) is developed. The influence of potassium chloride additions on the conversion and extraction processes is studied. Using HCl and KCl solution as a catalyst and butanol as an extractant permits to regenerate the catalyst, to decrease catalyst and extractant consumptions in comparison with usual LA extraction from neutralized water solutions. The extraction degree of 94 % for obtained butyl levulinate is attained by using 2:1 volume ratio of water and butanol phases in one stage.

Keywords: levulinic acid, butyl levulinate, fructose, acid-catalyzed conversion, hydrochloric acid, catalyst regeneration.

Introduction

In recent years biomass is known to gain high potential as renewable feedstock for chemical production. The major components of biomass are hexose carbohydrates, and their transformation into chemicals is the main direction of sustainable development and “Green Chemistry”. The main product of the acid-catalyzed hexose transformation is levulinic acid (4-oxopentanoic acid, LA) [1-4]. This versatile chemical is applied to produce polymer materials [5-6], pharmaceuticals [7], and biofuels [8]. In industrial scales wood, agricultural wastes, and hexoses are the raw materials for LA production [7, 8-12]. Their acid-catalyzed conversion to 5-hydroxymethylfurfural (5-HMF) with its consequent rehydration produces LA (Fig. 1). The humic substances are formed as a by-product in the conversion.

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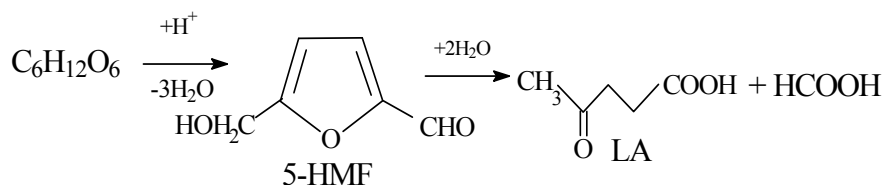


Fig. 1

There are many kinds of catalysts for the processes: mineral acids [7, 11], ion-exchange resins [13], zeolites [14]. The main disadvantages of solid catalysts are their deactivation by tar and low catalytic activity in water media. Using these catalysts, the high LA yields are attained at low carbohydrate concentration (0.2 – 0.3 M). In opposite to solid catalysts, mineral acids have great activity and high acidity in water media [15-16]. On these reasons the regeneration of homogeneous and heterogeneous catalysts becomes the main problem in the conversion processes.

Usually mineral acids are neutralized before extracting the goal product from reaction medium. To prevent neutralization and lost the catalyst one must extract LA from acid solution and separate the catalyst and the product in this step. Hence, the effective homogeneous catalytic conversion has to combine the highest possible LA distribution ratio and minimum HCl distribution ratio for extractant. A lot of extractants of levulinic acid are reviewed: ketones [17], ethers [18], alcohols [19]. Nevertheless, the possibilities of catalyst regeneration when using these extractants are not studied.

We have recently demonstrated the possibility of catalyst regeneration in hexose conversion in water-butanol system [19]. Butanol forms the stable two-phase system with water, but concentrated (5 M) sulphuric and hydrochloric acids are known to give homogeneous solutions with the alcohol. To prevent homogenization the mixture of sodium sulphate and sulphuric acid as the catalyst (sodium hydrosulphate with or without addition of sulphuric acid) can be applied. This approach permits to create stable two-phase system water-butanol with good catalytic activity. Hydrochloric acid is more active than sulphuric acid and sodium hydrosulphate [20]. Its distribution ratio in the system water-isopentanol is 5 – 10 times greater than that of sulfuric acid, and HCl is distributed into organic phase when adding calcium chloride in the water phase [21]. But this catalyst is usually neutralized before the LA extraction after carbohydrate conversion [22], and the literature data on the hydrochloric acid regeneration in the process lack.

In this paper the HCl regeneration in the fructose acid-catalyzed conversion to LA and its derivatives is studied.

Experimental

Fructose of food quality was used in the experiments. Carbohydrate (1 M) conversion in water solution was carried out in a 250 ml thermostated magnetically stirred glass flask with water condenser at 95 °C. Hydrochloric acid of 1 M concentration was used as catalyst and 200 g/l potassium chloride was added into the reaction mass (Fig. 2) [23].

Then the salt concentration was increased to 450 g/l and butanol extraction of LA as butyl levulinate was carried out at 50 °C. Water and butanol phase aliquots (1 ml) was sampled and analyzed

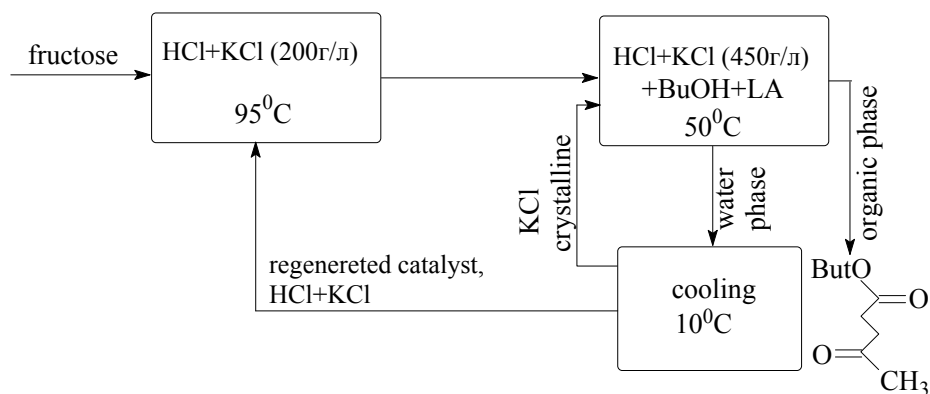


Fig. 2

by G.L.C. Then the water phase of reaction mixture was cooled to 10 °C and crystalline potassium chloride was separated. The water solution containing HCl and KCl was used in a new cycle of the carbohydrate conversion. The catalyst wastes were estimated by the potentiometric titration of butanol and water phases.

Results and discussion

The potassium chloride addition into the system consisted of HCl, fructose, water, and butanol lead to the phase separation, but salt additives decreases yield of levulinic acid in the process. To overcome this contradiction we carried out the catalytic conversion in the solution with low salt concentration, and then the extraction of LA in a form of butyl ester was carried out at high KCl content.

LA is completely alkylated in the process, and butyl levulinate is extracted into the butanol phase, whereas 93-95 % of hydrochloric acid remains in water phase. To convert butyl levulinate into levulinic acid the acid or alkaline hydrolysis may be applied. Adding KCl slightly decreases the conversion selectivity (27 mol. %) in comparison with HCl-catalyzed process without salt additions (30 mol. %) [11]. The experimental results are shown in Table 1.

Extraction with a little volume of butanol (1 : 10 butanol to water ratio) is insufficient, and even repeated extraction permits to removed only a half of the product. The extraction is more efficient at higher butanol to water ratio 1 : 2. Under these conditions butyl levulinate is formed in the extraction system and removed efficiently from water to the organic phase. HCl wastes (a part extracted into organic phase) in all experiments are of 5 – 7 %.

Cooling the water phase after extraction precipitates potassium chloride and recycles the catalyst water solution. This approach allows reducing catalyst consumption by a factor of 10 – 20 in comparison with the usual LA extraction after the acid neutralization [24]. Moreover, in this case the butyl levulinate distribution ratio ($k = 34$) is almost 10 times greater than for the LA extraction from neutral water solutions ($k = 4$) [24-25]. In these conditions the extraction degree of 94 % is attained by using 1 : 2 volume ratio of butanol and water phases in one stage. To attain such extraction degree from neutralized solution one should apply six times greater volume ratio of butanol and water phases of 3 : 1.

Table 1. Influence of KCl additives and butanol volume to the butyl levulinate (But-LA) distribution ratio (D) and extraction degree (α) in fructose conversion and extraction

KCl concentration, g/l in the steps of conversion/ext-raction	Vorg.Vaq.	LA concentration before extraction, g/l in water phase	But-LA concentration, g/l in butanol phase	But-LA yield, mol. %	D	α , %	HCl waste, %
0	-	40	-	-	-	-	-
200 / 450	1 : 10	36	100	28	4.36	32	5.1
450 in a second extraction	1 : 10	31	105	34	2.54	20	4.5
200 / 450	1 : 2	35	60	86	34.00	94	7.5
200 recycled conversion, 450 extraction	1 : 2	34	50	89	20.25	89	5.3

Conclusion

The obtained results demonstrate the efficiency of new method to produce levulinic acid and to separate it from the solution of HCl catalyst. Butanol as extractant and a water solution of hydrochloric acid and potassium chloride as the catalyst are used in this method. Levulinic acid is recovered from the catalyst solution in the form of butyl levulinate. This approach allows increasing the extraction efficiency, decreasing the catalyst and extractant consumption in comparison with traditional LA extraction from the neutralized product solution.

Acknowledgements

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Регенерация солянокислотного катализатора конверсии фруктозы в левулиновую кислоту

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Разработан экстракционный метод регенерации солянокислотного катализатора кислотно-каталитической конверсии фруктозы в левулиновую кислоту (ЛК). Использование добавок хлорида калия на стадиях конверсии и экстракции позволяет регенерировать соляную кислоту, сократив ее расход в 10 раз, и выделить 94 % ЛК в виде бутилового эфира в 6 раз меньшим объемом экстрагента по сравнению с традиционным выделением целевого продукта из нейтрализованного раствора.

Ключевые слова: левулиновая кислота, бутиллевулинат, фруктоза, кислотно-каталитическая конверсия, регенерация катализатора.
