Thermocatalytic Cellulose Transformation with Forming of Levulinic Acid

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It has been studied in this work the composition and yield of forming liquid products of thermocatalytic cellulose transformation on the temperature of 150 to 250 $^{\circ}$ C with used catalyst - HCl and H₂SO₄, the quantity of introduced catalyst into raw material, temperature, duration and process hydro module.

It is established by physical-chemical methods of analysis (GLC, NMR ¹H, ¹³C, chromato-massspectrometry), that the main liquid products of thermocatalytic cellulose transformations in the presence of above indicated catalysts are furfural, levulinic acid, mono- and oligosugars. It is showed that the intensive decomposition of cellulose hexosans is observed on the temperature of 200°C, and in these conditions hexosans are completely transformed into liquid, gaseous and solid products of thermolysis. Levulinic acid yield from cellulose is essentially increased on raising the process temperature from 150 to 200°C, and also it is observed the decreasing of sugar yield. The highest levulinic acid yield was recorded in the presence of 3% HCl and 5% H_2SO_4 , and it was 28,8% and 24,8% accordingly. The further temperature raising of the process increased the levulinic acid yield from cellulose, containing 1% and 3% of catalyst. However, the levulinic acid yield remains practically unaffected with temperature raising on cellulose thermolysis, involving 5% of catalyst. When introducing into cellulose a great number of HCl and H_2SO_4 , the levulinic acid yield does not increase on the thermolysis temperature of 200-240°C. It is experimentally established that the additions of sulphuric acid can play the agent role in the conditions of high temperature thermolysis.

It is showed, that the levulinic acid yield from cellulose in the presence of 5% catalyst practically does not depend on process hydromodel in the interval 1:5-1:10.

For the purpose of selection of regime parameters of the process, providing for the maximum levulinic acid yield it has been studied the temperature influence and the process duration of cellulose thermolysis in the presence of 5% catalyst. The process temperature was ranged from 200 to 240°C, its duration from 2 to 10 hours. The use of lower temperature is inefficient because of low levulinic acid yield. The selection of high limit is restricted by the boiling point of levulinic acid (246°C), it the temperature will be higher, and it is subjected to partial decomposition with forming of humic substances.

The maximum yield of the final product (41,3% from primary cellulose weight) was obtained in the case of use the sulphuric acid as catalyst on the temperature of 240°C and process duration for 4 hours. The further temperature raising and process duration leads to the decreasing of levulinic acid yield.

When using the hydrochloric acid as catalyst the maximum influence of levulinic acid yield resembles the following process parameters: temperature is 230°C and process duration is 10 hours and amounts 21,3% from the weight of primary raw materials.

So, the levulinic acid yield is mostly defined by the temperature, reaction duration, quantity and nature of used catalyst and practically does not depend on the process hydro module.