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Kinetics of solid-phase carboxymethyllation of cotton and microcrystalline cellulose

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ABSTRACT

This article discusses comparative investigation of etherification reaction kinetics of cotton and microcrystalline cellulose, in heterogeneous conditions by solid-phase method in the special adiabatic reactor. On the basis of the received results, activation energy, constant of reaction rate, pre-exponential factors and specific thermal effects of carboxymethyllation reactions of cotton and microcrystalline cellulose were determined.

KEYWORDS

Carboxymethyl cellulose;
Microcrystalline cellulose;
Etherification;
Activation energy;
Kinetics;
Thermal effect.

INTRODUCTION

Carboxymethyl cellulose (CMC) is one of the most spread and industrially large-tonnage madding ethers of celluloses which technical marks are widely applied in various branches, such as in oil, gas, hydrometallurgical, ore dressing, textile, building industries. Purified marks are applied in food, cosmetic, pharmaceutical, medical industries and in production of synthetic washing-up liquids[1-5].

Synthesis process of CMC from cellulose and cellulose containing raw materials consists to two stages – mercerization and etherification of cellulose[6].

Alkaline treatment and etherification reaction of cellulose can be providing with or without using of organic solvents, to be more precise in suspension (pseudohomogenous) or heterogeneous (solid-phase) conditions[7].

One of the advantages of heterogeneous solid-phase method of CMC synthesis is simplicity, absence of production wastes, fire safety. One of problem at realization solid-phase method is difficulty of forecasting of products quality. The reason could be the absence of quality control sufficient possibility in etherification process, difficulty of managing temperature of reaction and so on. Consequently, those factors directly influence to degree of polymerization and distribution of carboxymethyl group along a chain of cellulose macromolecules.

They also depend on high thermal effects, the high rate of carboxymethyllation process, side reactions and complexity of heat removing.

Comparative investigation of etherification reaction kinetics of cotton and microcrystalline cellulose in the special reactor, in adiabatic condition by solid-phase method will be investigated in this article

MATERIALS AND METHODS

Experiments were carried out in identical conditions that used as the initial raw materials of microcrystalline

and cotton cellulose in the process of CMC synthesis.

In order to study of microcrystalline cellulose (MCC) carboximethyllation a special adiabatic reactor which is heat-insulated from external heat exchange was used[8].

The reactor consisted from heat-insulated reaction chamber head-insulated by polystyrene, densely which supplied with thermometer. They were used as the reaction components:

- cotton cellulose (4-6mm);
- microcrystalline cellulose (160 μm);
- 20% of alkaline solution;
- sodium monoclorine acetate.

Solid-state carboxymethyllation microcrystalline cellulose in adiabatic condition

Alkaline MCC was prepared with adding required amount of 20% of alkaline solution at pilot installation by combination of mixing and grinding stages. The period of alkaline treatment was continued 60 minutes at 16^0 sodium monochlorine acetate acid was added and mixed at 16^0 . It is experimentally established that possibility of alkaline hydrolysis of sodium monochlorine acetate the beginning of etherification reaction was practically excluded.

The received mixture was fastly loaded into the adiabatic reactor. Registration of temperature change was measured until completing of reaction temperature increasing of exothermic reaction during 2,0-2,5 hours with determining of DS obtained CMC.

On the basis of the obtained results, activation energy, reaction rate, constant of reaction rate, pre-exponential factor and specific heat effects of carboxymethyllation of cotton and microcrystalline cellulose were determined by using MathCAD software package.

RESULTS AND DISCUSSION

Conduction of the process of carboxymethyllation in adiabatic conditions allowing compare the rate of temperature change with the rate of changing degree of reaction product substitution is take as a base of this experiment.

Investigation of carboxymethyllation reaction of alkaline MCC and cotton cellulose in adiabatic condition showed that the maximum temperature of etherification reaction reached for MCC and cotton cellulose, after 150 and 240 minutes, respectively, taking into account heat exchange to surrounding was excluded (Figure 1).

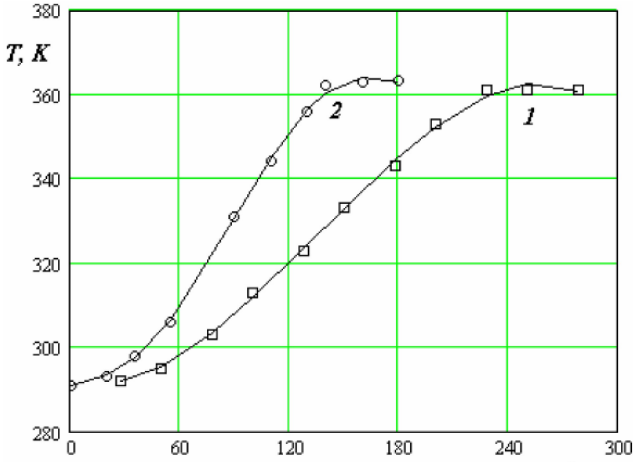

Figure 1 : Dependence of etherification temperatures of cotton cellulose (1) and MCC (2) on time

The maximum temperature of reaction during the etherification of alkaline cotton cellulose and MCC is directly depends on surface area of raw materials. And the average length of cotton cellulose fibers are 4-6 mm, the size of MCC particles are 100-160 mkm. The specific surface area of MCC is significantly larger, than alkaline cellulose in mass unit. Probably, because of this reason exothermic reaction temperature is higher at the process of carboxymethyllation of MCC.

Carboxymethyllation of alkaline cotton cellulose and MCC in this condition also gave information about dependence of DS values with duration of the reaction

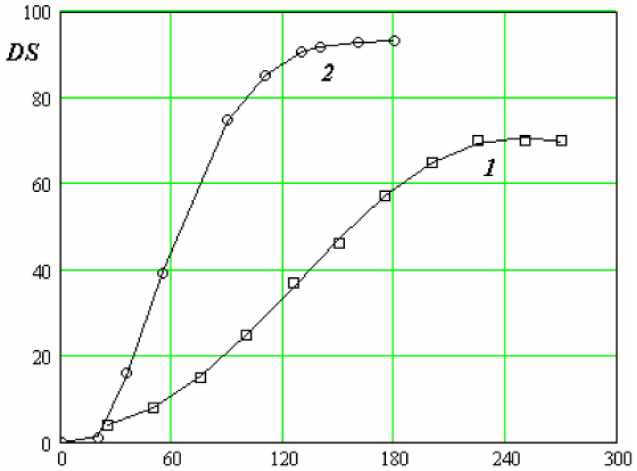

Figure 2 : Dependence of CMC degree of substitution on duration of etherification, obtained from cotton cellulose (1) and MCC (2)

(Figure 2).

As shown in Figure 2, the temperature is directly proportional to DS for cotton and MCC. Increasing duration of etherification process DS of MCC is dramatically grows to DS 0,86 during 130 minutes and than insignificantly changes. At the same condition, DS of cotton cellulose is moderately increases to 0,65 during 240 minutes.

On the basis of obtained datum, speeds of etherification reactions of cotton cellulose and MCC were determined (Figure 3).

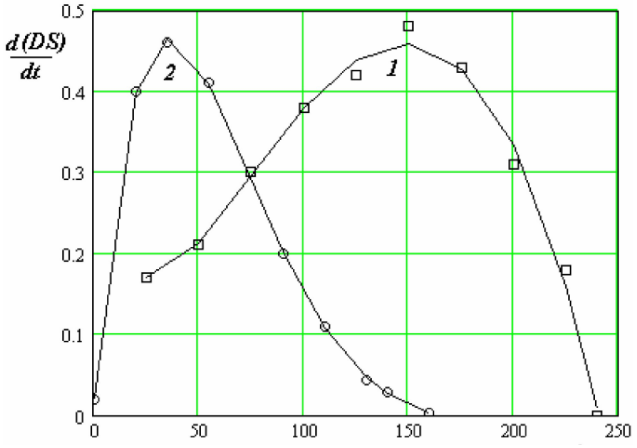

Figure 3 : Dependence of the rate of etherification reaction of cotton cellulose (1) and MCC (2) on experiment time

It is seen in Figure 3, etherification reaction rate significantly higher in comparison with cotton cellulose and MCC in the process of etherification of alkaline MCC by sodium of monochlorine acetatic acid, reaction speed is rapidly grows and reaches to maximum value at 40 minutes. After that, reaction speed of MCC etherification dramatically falls to 160 minutes.

At the same condition, increasing of etherification reaction speed of alkaline cotton cellulose begins after 30 minutes and then sharply rises to maximum value of reaction speed during 150 minutes. Further, reaction speed rapidly increases and after 240 minutes it reaches to 0. Reduction of reaction speed can be explained thatdecreasing of monochlorine acetatic acid sodium concentration.

By the results of dependence of $\frac{\partial DS}{\partial \tau} = f(\tau)$

correspondingly equation of $\frac{\partial DS}{\partial \tau} = K(DS_{\lim} - DS)$

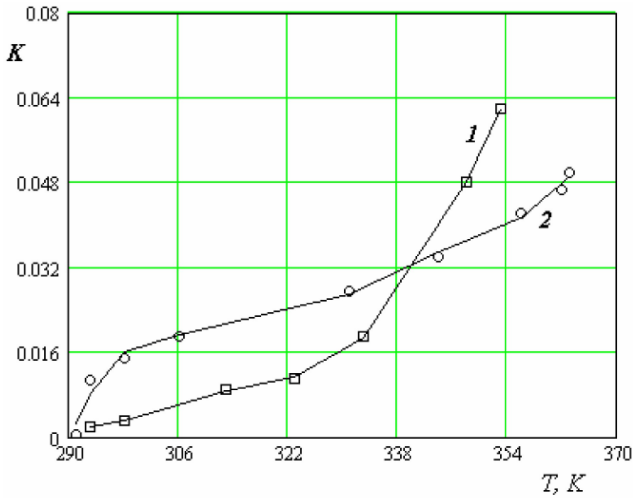

Figure 4 : Dependence of the constant of reaction speed on temperature

and datum of in Figure 1 were defined constant of etherification reaction speed at $K = f(\tau)$ (Figure 4).

Where K - constant of reaction speed; DS_{lim} – limit of DS.

'Corresponding to the value of described by the equation of Arrhenius, determined activation energy $E=3,088\cdot10^4$ J/mol, pre-exponential factor $A=1,641\cdot10^3$ 1/sec and specific thermal effect $Q_p=1789$ kJ/kg for etherification of MCC.

And also, those values in the process of etherification of cotton cellulose equal to: activation energy $E=4,757\cdot10^4$ J/mol, pre-exponential factor $A=6,413\cdot10^5$ 1/sec and specific thermal effect $Q_p=1079$ kJ/kg.

CONCLUSIONS

1 Comparative researches of etherification kinetics of cotton cellulose and MCC in adiabatic condition by the solid-phase method have been carried out. It was established, that etherification reaction is described by the equation of the pseudo-first order.

2 The etherification reaction speed of MCC in adiabatic condition significantly higher than etherification of cotton cellulose which can be explain that the surface of MCC as larger than surface of cotton cellulose.

3 Moreover, experimentally determined and compared activation energy, pre-exponential multiplier

and specific thermal effects of etherification reaction of cotton cellulose and MCC.

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