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Experimental study of alkalinisation of cellulose in industrial relevant conditions

Diana Carolina Reyes Forsberg

Akademisk avhandling

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Fakultetsopponent: Professor Ulf Germgård,
Department of Engineering and Chemical Sciences, Karlstad University, Karlstad, Sweden

Department of Chemistry, Umeå University

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Diana Carolina Reyes Forsberg

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Abstract

Mercerisation of cellulose pulp with a solution of NaOH is the first step of manufacturing cellulose-based value-added products, *e.g.* viscose fibres and cellulose ethers. During this process, cellulose transforms into a swollen crystalline structure, alkali cellulose (Na-Cell). This increases the reactivity of the cellulose and makes it more accessible for reagents to penetrate and react with the hydroxyl groups. The mercerisation conditions are known to affect the degree of alkalinisation of cellulose as well as the final products. The main objective of this thesis is to investigate how the alkalinisation of softwood sulphite dissolving cellulose pulp is influenced by the co-variation of process variables in the mercerisation in industrial relevant conditions, for both viscose and cellulose ether production. This objective was achieved by quantitative analysis of the effect of simultaneous variation of a set of key parameters on the degree of alkalinisation (*i.e.* degree of activation, DoA) of the chosen dissolving pulp. Quantitative measurements were performed using Raman spectroscopy data, evaluated by partial least squares (PLS) regression. For mercerisation at viscose production conditions, the effect of studied variables on mass yield was also considered. In the case of mercerisation at ether processing conditions, formation of alkali cellulose at a fixed temperature was included. The knowledge obtained on mercerisation under ether processing conditions was then applied for preparation of the ionic cellulose ether carboxymethylcellulose (CMC).

The overall results show that temperature has a strong effect on DoA and mass yield for mercerised samples under steeping conditions. Measured DoA decreases as the temperature increases from 20 to 70 °C. Mass yield correlates positively with the temperature up to 45-50 °C in the PLS model, after which the relation is negative. The [NaOH] and reaction time show a complex dependence of other variables. At mercerisation conditions for cellulose ether production, the NaOH/AGU stoichiometric ratio, denoted as (r), shows to be very important for DoA, with a positive correlation. At these mercerisation conditions, temperature shows no effect on DoA. The influence of the [NaOH] (which also refers to the concentration of water) shows a complex dependence on (r). As (r) increases and [NaOH] decreases, the measured DoA increases. Prolonged mercerisation time shows no significance in the modelled DoA. However, a gradual increase of the DoA over time was seen when mercerisation was performed with 30% and 40% [NaOH] at (r) = 0.8, suggesting a slow diffusion of NaOH and Na-Cell formation. ^{13}C CP-MAS NMR measurements of samples produced at room temperature show that formation of the Na-Cell allomorph is mainly determined by the [NaOH]. However, in the transition area between Na-Cell I and Na-Cell II, (r) also seems to be of importance. An increase of *DS* in the produced CMC samples also shows to be consistent at such conditions with the increase in the measured DoA and with increased (r) and decreased [NaOH]. However, these conditions also favour the formation of by-products. In the synthesised CMC samples, a *DS* of up to 0.7 was achieved. Measured solubility was lower than expected for any given *DS*. This, along with the non-statistical distribution of monomer units in the polymer chains, indicates high heterogeneity in the synthesised samples. The distribution of substituents within the AGU shows attachment to hydroxyl oxygens in the order O3 < O2 ≈ O6. The relative importance of the substitution at O3 indicates an increase at this position when [NaOH] increases.

The models presented in this thesis will hopefully serve as a basis for predicting the effects of the studied variables on the DoA, as well as on the mass yield of cellulose pulp when mercerisation conditions are adjusted. Moreover, it is believed that the presented studies can give a better understanding of mercerisation at cellulose ether conditions, hence enabling further development of this process step

Keywords
Mercerisation. Alkalinisation. Cellulose I. Cellulose II. Alkali cellulose. Viscose. Cellulose ether. Carboxymethylcellulose. Sodium glycolate. Sodium diglycolate. Raman spectroscopy.

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