A Chemical Engineering Approach to Cellulose Substitution Kinetics

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A general kinetic model for the substitution of cellulose was developed. The model assesses the differences in the reactivity of the cellulose hydroxyl groups and a decrease in the reactivity as the substitution proceeds. The model predicts the detailed distribution of the different mono (2, 3, 6)-, di (23, 26, 36) – and trisubstituted (236) units as a function of the reaction time. The classical Spurlin distribution is obtained as a special case of the general model. Numerical strategies were developed for the solution and computer simulation of the model. Simulation results were shown to be valid for various reactivity ratios of the hydroxyl groups. The modelling concept was verified with experimental data obtained for carboxymethylation of cellulose in a slurry reactor. The detailed data, which revealed the non-uniform reactivities of the different hydroxyl groups and the decline of the substitution rate with time, were successfully described by the mathematical model.

1. Introduction

The research of chemical components originating from renewable sources is obtaining a growing interest throughout the world. A very important macromolecule originating from biomass is cellulose, which is the main component in wood. Cellulose is a rich source of chemicals, particularly cellulose derivatives are manufactured in large quantities, and all their potentials have not been discovered yet. A lot of research on cellulose derivatives has been carried out, but mainly qualitative work by chemists. In this work, we present the chemical engineering approach to the preparation of cellulose derivatives: detailed kinetic modelling based on the chemical analysis of the substituted hydroxyl groups in cellulose.

The most common cellulose derivatives are cellulose esters and cellulose ethers. Cellulose ethers are prepared by letting alkyl halogenides or allyl halogenides or alkene oxides to react with alkali cellulose. The cellulose fibres are pretreated by alkali to promote swelling of the fibres and ionization of the hydroxyl groups. With alkyl halogenides, the reaction proceeds as follows,

$M^+Cell\text{-}O^- + RX \rightarrow Cell\text{-}OR + M^+X^-$

where cell-O- represents the ionized cellulose and RX is the alkyl halogenide. M^+ denotes an alkali metal ion, typically Na^+. Depending on the halogenide, various products are obtained: with methyl ($RX = CH_3Cl$) and ethyl chloride ($R = CH_3CH_2Cl$), methyl and ethyl cellulose are obtained as main reaction products, whereas with α-monochlorocarboxylic acids, carboxyalkylcelluloses are obtained, such as carboxymethyl and carboxyethyl celluloses. The most important of them is carboxymethylcellulose (CMC), which is obtained by letting alkalicellulose to react with monochloroacetic acid: $M^+Cell\text{-}O^- + CH_2ClCOOH \rightarrow Cell\text{-}OCH_2COOH + M^+Cl^-$. The sodium salt of CMC is widely used, for instance, in detergents, alimentary products, textiles, glues as well as emulgators in various products such as dyes, ceramic products and cosmetics.

Pioneering models for the substitution kinetics of cellulose have been proposed by Spurlin (1939), who derived the classical distribution between mono-, di- and trisubstituted anhydroglucose units for the case that all of the hydroxyl groups (OH-2, OH-3, OH-6) have equal reactivities. Timell (1952) presented differential equations for the substitution reactions for cases that first order kinetics is obeyed and Salmi et al. (1994) have developed kinetic models for carboxyalkylation of cellulose with α-chlorocarboxylic acids. Diffusion phenomena inside the fibers was treated (Salmi et al. 1994, Salmi et al. 2003) with an empirical model and with a reaction-diffusion model. A detailed study, including a comparison of three analytical methods, on the carboxymethylation of starch was carried out by Lazik et al. (2002), who concluded that the reactivities of the different hydroxyl groups in starch are different, but their ratio is constant; thus the classical model of Spurlin (1939) was applicable.

The aim of the present paper is to develop a generalized simulation model for the substitution of cellulose, including both the reactivity differences and concentrations of the individual hydroxyl groups as well as the prediction of the product distribution of the substituted anhydroglucose units.

2. Experimental Section

The commercial cellulose from birch hardwood was obtained from Metsä-Serla chemicals; the cellulose obtained was screened to a size of 0.35 mm. In the heterogeneous carboxymethylation experiments were performed in a glass laboratory-scale autoclave (500 ml) with fixed molar ratios of cellulose-to-monochloroacetic acid-to-NaOH 1:4:8. 2-propanol was used as the solvent and the reaction temperatures during carboxymethylation experiments were 30, 40 and 60°C. The reaction time was 120 min and samples were withdrawn from the reaction mixture at pre-defined intervals (10 min, 20min, 40 min etc). High-pH anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) was applied for the chemical analysis. Before the analysis, the CMC samples were subjected to acid hydrolysis with trifluoroacetic acid (TFA). The hydrolysis products were analyzed by HPAEC with PAD on a Hewlett Packard 1100 Series LC system with a Dionex ED50 electrochemical detector, a Dionex

CarboPac PA1 anion-exchange column (semi-preparative 9 × 250 mm and analytical 4 × 250 mm combined with guard 4 × 50 mm, column temperature 30°C). The detection was performed by the PAD with a gold working electrode and triple pulse amperometry. The details of the analysis method are reported by Damlin et al. (2010).

3. Mathematical Modelling Principles

The anhydroglucose unit of cellulose has three functional hydroxyl groups (OH) adjacent to carbon atoms 2, 3 and 6 (OH-2, OH-3, OH-6). The reactivity of the hydroxyl group varies, depending on the substitution reaction and the conditions. The most acidic hydroxyl group is OH-2, which implies that it is claimed to be the most reactive one, for instance, in hydroxymethylation. On the other hand, as the size of the substituent increases, steric factors become important, thus preferring the reactivity of OH-6.

The overall reaction scheme is displayed in Fig. 1.

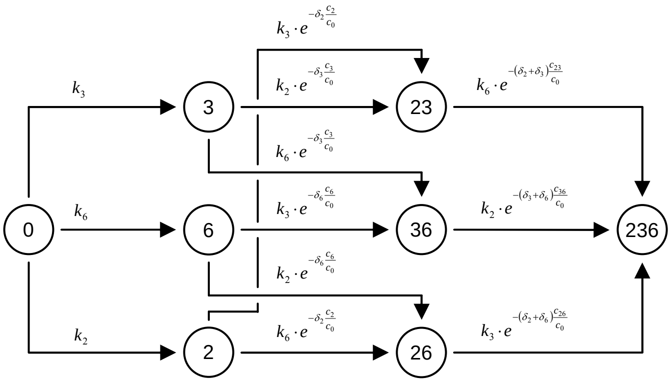

Figure 1. Reaction scheme for the formation of substituted anhydroglucose units. Notation: 0, unsubstituted glucose unit; 2, 3, 6, monosubstituted glucose units (substituted at hydroxyl groups 2, 3 and 6); 23, 36, 26, disubstituted glucose units (substituted at hydroxyl groups 2 and 3, 3 and 6 and 2 and 6); 236, trisubstituted glucose units.

The detailed product distribution in the time scale can be simulated by using the mass balance (1) and the reaction scheme. In the actual case, the balance equations of the components in a constant-volume batch reactor are written as

$$dc'_i / dt = r_i \tag{1}$$

where i = 0, 2,3, 6, 23,…236, R. The generation rates of different anhydroglucose units are listed below:

$$r_0 = -(k_2 + k_3 + k_6)c'_0\, c_R{}^{\alpha} \tag{2}$$

$$r_2 = -(k_2 c'_0 - (k_3 + k_6)c'_2\,)c_R{}^{\alpha} \tag{3}$$

$$r_3 = -(k_3 c'_0 - (k_2 + k_6)c'_3\,)c_R{}^{\alpha} \tag{4}$$

$$r_6 = -(k_6 c'_0 - (k_2 + k_3) c'_6)\, c_R{}^{\alpha} \tag{5}$$

$$r_{23} = (k_2 c'_3 + k_3 c'_2 - k_6 c'_{23})\, c_R{}^{\alpha} \tag{6}$$

$$r_{26} = (k_2 c'_6 + k_6 c'_2 - k_3 c'_{26})\, c_R{}^{\alpha} \tag{7}$$

$$r_{36} = (k_3 c'_6 + k_6 c'_3 - k_2 c'_{36})\, c_R{}^{\alpha} \tag{8}$$

$$r_{236} = (k_2 c'_{36} + k_3 c'_{26} + k_6 c'_{23})\, c_R{}^{\alpha} \tag{9}$$

The consumption rate of the substitution reagent is obtained from

$$r_R = -((k_2 + k_3 + k_6) c'_0 + (k_3 + k_6) c'_2 + (k_2 + k_6) c'_3 + (k_2 + k_3) c'_6 + k_2 c'_{36} + k_3 c'_{26} + k_6 c'_{23})\, c_R{}^{\alpha} \tag{10}$$

If the substitution reagent (R) undergoes side reactions, their effects are added to the expression of r_R. Typical side reactions are substitution of hydroxyl groups and elimination reactions in an alkaline environment, as discussed by Salmi et al (2003). Furthermore, the reactivity of a hydroxyl group diminishes due to the substitution to another group in the same anhydroglucose unit, the effect can be taken into account in the rate constant. The following semi-empirical function was used:

$$k_j = k_{j,ref}\, e^{-E_{a,j}/(R\theta')}\, e^{-\delta_0 \cdot DS}\, e^{-\sum \delta_k \cdot c_{Pk}/c0} \tag{11}$$

which predicts the decline of the reactivity as the substitution progresses.

The concentrations of mono (I)-, di (II)- and trisubstituted (III) units are defined as (Fig. 2):

$$c_I = c'_2 + c'_3 + c'_6 \tag{12}$$

$$c_{II} = c'_{23} + c'_{26} + c'_{36} \tag{13}$$

$$c_{III} = c'_{236} \tag{14}$$

The degree of substitution is expressed as the weighted sum of the mono-, di- and tri-substituted units (n=I, II, III),

$$DS = c_I / c_0 + 2 c_{II} / c_0 + 3 c_{III} / c_0 \tag{15}$$

The differences between the observed anhydroglucose units (c'_0, c'_2,…c'_{236}) and those predicted by the model (eqs 1-11) were minimized by nonlinear regression, after which the total concentrations and DS were simulated (eqs 12-15).

4. Modeling Results and Discussion

The carboxymethylation kinetics of cellulose in 2-propanol was recorded at 30, 40 and 60°C in the batch reactor. The overall degree of substitution (DS) and the substitution rate increased as the temperature was augmented. The concentrations of native (unsubstituted), mono-substituted (I), di-substituted (II) and tri-substituted (III) cellulose units at 60°C are displayed in Fig. 2. At 30°C and 40°C, the reaction rate was rather slow, and the concentrations of all of the substituted units (DS) still increased. At 60°C, however, the rates were clearly higher, and a maximum in the concentration of the mono-substituted units becomes visible. The concentration of the tri-substituted units was very low at 30°C and 40°C, while it becomes clearly visible at 60°C (Fig. 2, left). Hydroxyl group OH-6 is the most reactive one: the mono-substituted unit (‘6’) is formed more rapidly, but declining more slowly than the other mono-substituted units (‘2’ and ‘3’). A characteristic feature obtained throughout the experimental domain was that the reaction rate stagnates and a complete substitution seems to be in practice impossible.

Preliminary parameter estimation efforts revealed that the reactivities of the hydroxyl groups OH-2 and OH-3 are rather similar and the retardation process is complicated, depending both on the overall DS and the specific effect according to eq (11) (see Fig. 2). It was in practice impossible to distinguish between the relative reactivities of the groups OH-2 and OH-3; therefore the pre-exponential factors and activation energies for the reactivities of these groups were set equal. The regression analysis revealed that the hydroxyl group OH-6 has the highest retardation effect: evidently the substituted group in position 6 can by rotation shield the substitution to the OH-groups 2 and 3. Once the substituted OH-6 has been formed, it reacts further rather slowly to the di-substituted units (‘26’ and ‘36’); the disubstituted unit (‘23’) is formed most rapidly of the di-substituted units, because the shielding effect of substituted OH-6 is not present. To describe the overall retardation effect, the approach given by eq. (11) is necessary.

A summary of the parameter estimation statistics is provided here. The rate constants obtained the following values: . $k_{2,ref} = k_{3,ref}$=0.24 L/(mol min), $k_{6,ref}$ =0.33 L/(mol min), δ_2=2.0, δ_3=4.4, δ_6=6.5, δ_0=4.8; $E_{a,2}= E_{a,3}$=140 kJ/mol, $E_{a,6}$=127 kJ/mol. The reference temperature (T_{ref}) is the average temperature of the experiments (in K). The transformed temperature (θ’) is defined as $1/\theta' = 1/T - 1/T_{ref}$, in K). The overall estimation statistics was fairly good, taking into consideration the complexity of the system. The estimated activation energies of the kinetic constants are reasonable, around 130 kJ/mol for OH-6 and around 140 kJ/mol for OH-2 and OH-3. The parameters listed in Table 1 represent the minimum set of parameters, which is able to describe the behavior of the system. It can be concluded that the modeling approach was successful, taking the complexity of the system into account.

5. Conclusions

An analytical method was developed which enables the detailed determination of the carboxymethylation kinetics of cellulose. A mathematical model was developed for the substitution of the anhydroglucose units of cellulose and the kinetic parameters incorporated in the model– including the shielding effect – were estimated with regression analysis. The model gave a reasonably good description of the formation of carboxymethylcellulose and has thus a perspective for process scale-up purposes.

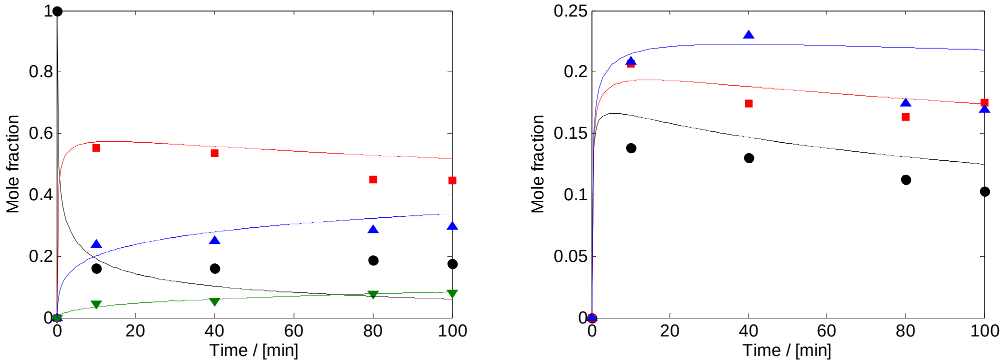

Figure 2. Measured (symbols) and modeled (lines) mole fractions (x) in carboxymethylation of cellulose; left figure: ●, *unsubstituted glucose units;* ■, *mono-substituted;* ▲, *di-substituted;* ▼, *tri-substituted; right figure:* ●, x_2; ▲, x_6; ■, x_3;. *Temperature: 60°C*

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