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Simulation Model for Urea-Formaldehyde Reactor

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Summary: A comprehensive simulation model for urea/formaldehyde (UF)-resins has been developed. The model utilizes kinetic results reported in the literature for low molecular weight systems and extends these to higher molecular weight systems by using a functional group approach. The model consists of

- 9 functional groups, 5 urea groups and 4 formaldehyde groups.
- 9 reactions, 5 methylolation reactions and 4 condensation reactions. In all these reactions both the formation and the decomposition reactions are included.

All the kinetic constants are pH and temperature dependent.

Two batch runs with different U/F ratios were used to adjust a couple of model parameters. Samples from these batch runs were analyzed with HPLC for low molecular weight compounds, and GPC for the average molecular weight. A run with continuous IR measurement showed excellent fit for the formaldehyde concentration. The model also estimates the viscosity from the functional groups.

Keywords: Kinetics; modeling; Urea-Formaldehyde; resins; step-growth polymerization

Introduction

Urea-Formaldehyde (UF) resins are the most important and most used class of amino-resin adhesives. These condensation products are produced all over the world, and it is important for the producers to establish good models for continuous optimisation and development.

The literature concerning the reactions between urea and formaldehyde is comprehensive, and substantial experimental work has been performed, especially in the years 1950-1980. One of the most important contributions is the work of De Jong and De Jonge[1-8] from 1952 and 1953. They performed a detailed study of the formation of low molecular weight species (mono- and di-urea)

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by measuring the amount of free formaldehyde and methylol groups by titration. To a large extent publications afterwards have confirmed their kinetic results. However, more sophisticated analytical tools has become available, like HPLC, NMR and GPC. These have revealed new insight into the UF system, e.g. that a substantial amount of dimethylene ether linkages are present in the condensate mixture, and that there exist two different dimethylol species. In the present model both the basic work of De Jong and De Jonge and these later results has been included.

Main reactions

Methylolation (addition) reactions

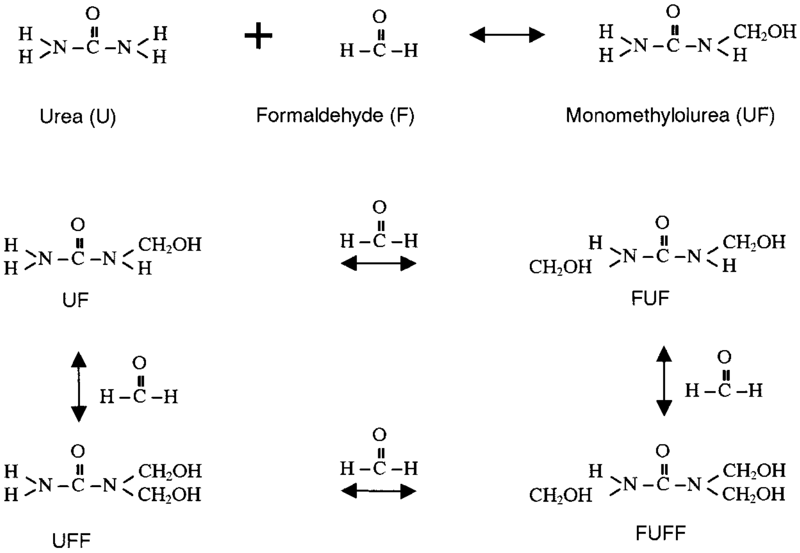

Figure 1 Methylolation reaction network. (UFF and FUF are NN and NN' dimethylolureas)

The first reaction that occurs between urea and formaldehyde is the formation of monomethylolurea (see Figure 1). De Jong and De Jonge[1] found that the formation is of second order and the decomposition is of first order:

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$$\frac{d[UF]}{dt} = k_f[U][F] - k_r[UF] \qquad (1)$$

The reaction shows general acid and base catalysis

$$k_{f,Tr} = k_{H^+}[H^+] + k_{OH^-}[OH^-] + k_{H_2O}[H_2O] + \sum_i k_{A_iH}[A_iH] + \sum_i k_{A_i^-}[A_i^-] \qquad (2)$$

Here $k_{f,Tr}$ is the forward reaction constant at a reference temperature T_r. The A_iH and A_i^- terms in eq 2 may represent any acid-base pair present, for instance in terms of buffer solutions. Glutz and Zollinger[9] have determined the specific constants for a lot of different acids and bases for this reaction. The reverse reaction rate constant k_r may be calculated from the equilibrium constant K, i.e. $k_r = k_f/K$. In order to calculate the constants k_f and K at temperatures different from the reference temperature T_r, the following Arrhenius expression is used:

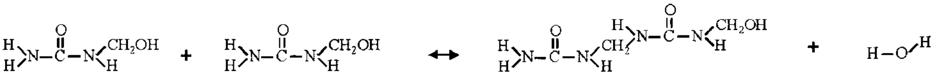
$$k_{f,T} = k_{f,Tr} \cdot e^{-\frac{E_f}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)} \qquad K_T = K_{Tr} \cdot e^{-\frac{H_{reac}}{R \cdot}\left(\frac{1}{T} - \frac{1}{T_r}\right)} \qquad (3)$$

Values for the activation energies are also given by De Jong and De Jonge[1] Formaldehyde reacts further with other hydrogen atoms in urea and form di- and tri- methylolureas. In Figure 1 all these methyloation reactions are shown. Each reaction is equilibrium based, and pH dependent. The formation of tetramethylolurea is disregarded because the literature has found only negligible amounts of this compound. De Jong and De Jonge[1,2,4] have provided kinetic constants for most of these reactions. However, their analytical methods could not distinguish between the two dimethylolureas (FUF and UFF), and in order to do so we have used the results of Timota and Hirose[10] and Kumlin and Simonsen [11-15].

Condensation reactions

There are two different types of condensation reactions that form larger UF-molecules.

1) Mehylene linkages (>N-CH_2-N<). These are reactions between a methylol group and an amino hydrogen, e.g. between two monometylolurea molecules



De Jong and De Jonge [5-8] investigated these reactions with different low molecular species and

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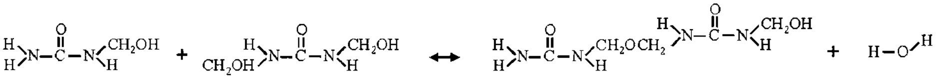
found that these reactions show specific acid catalysis, i.e.

$$k_{f,Tr} = k_{H^+}[H^+] \qquad (4)$$

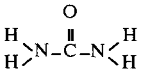
2) Dimethylene ether linkages (>N-CH_2-O-CH_2-N<). These are reactions between two methylol groups, e.g. between monometylolurea and dimethylolurea.



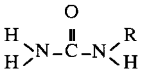
These reactions show general acid and base catalysis like the methylolation reactions. It is difficult to find exact values for kinetic constants in the literature, but one may estimate them from figures in Kumlin and Simonsen[13]. The equilibrium constant is given by Slonim et al. [16]

Kinetics based on functional groups

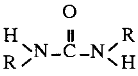
The condensation reactions give an increasingly number of compounds during the batch, and it is preferably to do some simplifications in order to make the reaction scheme manageable. One popular simplification is to employ the functional group approach, in which one assumes a chain length independent reactivity. The reaction groups in the UF system are the amino groups in urea, pure formaldehyde, and the methylol groups. The reactivity of a hydrogen atom in an amino group depends, however, on the number and position of all the other hydrogen atoms in urea. We therefore use an approach proposed by Kumar and Sood[17], in which the urea is considered as separate functional groups depending on how many of the hydrogen atoms that has reacted. In the case of urea we have five different groups:



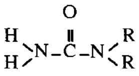
U



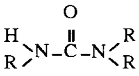
U_1



U_2



U_{2b}



U_3

Here R is a substitute for hydrogen, e.g. methylol or a polymer branch, U is urea, U_n is a group where *n* of the four urea hydrogen atoms have reacted. In U_2 the two substitutions are in NN' positions, while in U_{2b} the substituions are in NN positions. In a similar way we may define four

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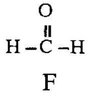
different formaldehyde groups



$H-\overset{O}{\overset{\|}{C}}-H$

$H-C(=O)-H$	$-CH_2OH$	$-CH_2-$	$-CH_2OCH_2-$
F	F_1	F_2	F_{2b}

i.e formaldehyde, methylolgroup, methylene linkage and dimethyl ether linkage. Every macromolecule will then consists of alternating sequences of F_i and U_i. At the ends it will be either U_1 or F_1. U_3 represents a branch point. The sum of urea groups will always equal the total amount of urea fed to the reactor. In Figure 2 an illustration of a macromolecule is shown.

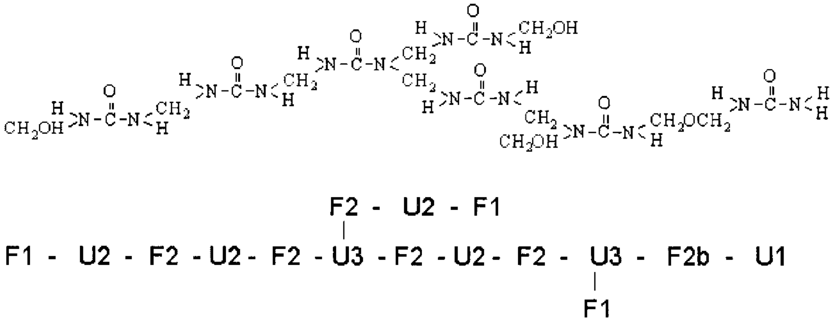


Figure 2 Illustration of a macromolecule described by functional groups.

Methylolation reactions

$$U + F \underset{k_1/K_1}{\overset{k_1}{\longleftrightarrow}} U_1 + F_1$$
$$U_1 + F \underset{k_2/K_2}{\overset{k_2}{\longleftrightarrow}} U_2 + F_1$$
$$U_1 + F \underset{k_3/K_3}{\overset{k_3}{\longleftrightarrow}} U_{2b} + F_1$$
$$U_2 + F \underset{k_4/K_4}{\overset{k_4}{\longleftrightarrow}} U_3 + F_1$$
$$U_{2b} + F \underset{k_5/K_5}{\overset{k_5}{\longleftrightarrow}} U_3 + F_1$$

Condensation reactions

$$U + F_1 \underset{k_6/K_6}{\overset{k_6}{\longleftrightarrow}} U_1 + F_2 + H_2O$$
$$U_1 + F_1 \underset{k_7/K_7}{\overset{k_7}{\longleftrightarrow}} U_2 + F_2 + H_2O$$
$$U_1 + F_1 \underset{k_8/K_8}{\overset{k_8}{\longleftrightarrow}} U_{2b} + F_2 + H_2O$$
$$U_2 + F_1 \underset{k_9/K_9}{\overset{k_9}{\longleftrightarrow}} U_3 + F_2 + H_2O$$
$$U_{2b} + F_1 \underset{k_{10}/K_{10}}{\overset{k_{10}}{\longleftrightarrow}} U_3 + F_2 + H_2O$$
$$F_1 + F_1 \underset{k_{11}/K_{11}}{\overset{k_{11}}{\longleftrightarrow}} F_{2b} + H_2O$$

Figure 3 The reaction scheme based on functional groups

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The reaction scheme in terms of functional groups is shown in Figure 3. The kinetic constants are found from the literature as discussed above. According to De Jong and De Jonge[5] the reactions 8 and 9 might be eliminated from the reaction scheme. In the present model they are included with very small values.

In all the reactions we assume that the forward reaction is of second order and the reverse decomposition reaction is of first order, i.e.

$$r_{Un,decomp} = -\frac{k_{f,i}}{K_i} U_n$$

However, we do not know whether, for example U_2 decomposes to U_1 and F (reaction 2) or to U_1 and F_1 (reaction 7). Kumar et al.[17] assumed that methylolation reactions dominates in the first period of the batch, and methylene linkage reactions in the last period after pH has been lowered. We rather assume that the probability of U_2 to decompose and produce F or F_1 is proportional to the ratio concentrations of F_1 and F_2 in the reaction. This is implemented by multiplying the fractions $\frac{F_1}{F_1+F_2}$ and $\frac{F_2}{F_1+F_2}$ to the concentration of the functional groups in the decomposition reactions. For instance, the reaction rate expression for reaction 2 then becomes

$$r_2 = k_2 U_1 F - \frac{k_2}{K_2} U_2 \frac{F_1}{F_1+F_2} \qquad (5)$$

The kinetic scheme has been implemented in the programming system Matlab. The program integrates the functional groups with time assuming the reactor is perfectly mixed. In addition to the feed specification, the measured temperature and pH during the batch is used as inputs.

Experimental verification of the model

Two laboratory batch runs with different F/U ratios were performed in order to evaluate the model and possibly adjust some of the model parameters.

The lab reactor consists of a 6 litres large glass bulb with an impeller and a condenser at the top. It is equipped with a system for continuous monitoring of temperature and pH. Samples were taken at certain intervals for off-line analysis of free formaldehyde by titration, urea, monourea, and diurea with HPLC, and molecular weight with GPC.

At start standard aqueous formaldehyde solution was put into the vessel. After 10 min urea was added to the vessel. The temperature dropped temporarily (the solution energy of urea is endothermic) and was then raised to about 90°C. In this period the pH also dropped. After a while the pH was lowered to about 5 by supplying acid catalyst. More urea was added in the end of the batch.

After comparing the simulation results with the measurements from the two test runs, two parameters were adjusted (10-20%) from their original values. In addition, the kinetic constant for the dimethyl ether linkage, the most uncertain parameter from the literature, had to be changed significantly.

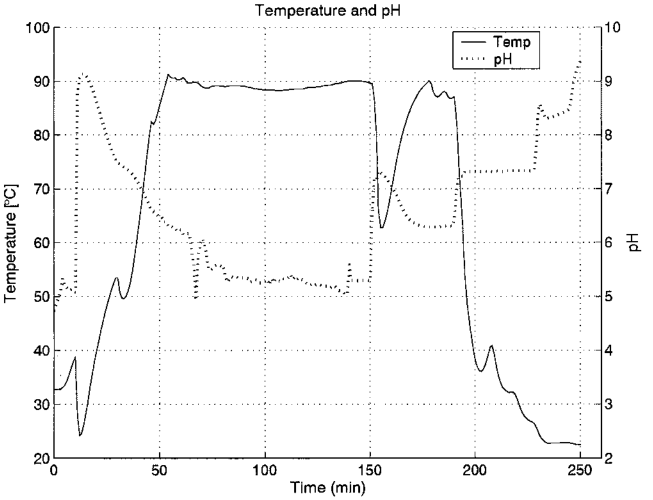

Figure 4 Temperature and pH profiles during test run

In the first test run additional amount of urea was fed at 152 and 195 minutes. The measured pH and temperature profiles are shown in Figure 4. These values were used as input to the

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simulation model to calculate all the functional groups shown in Figure 5. Note that the adjusted kinetic constants are used in this and subsequent figures.

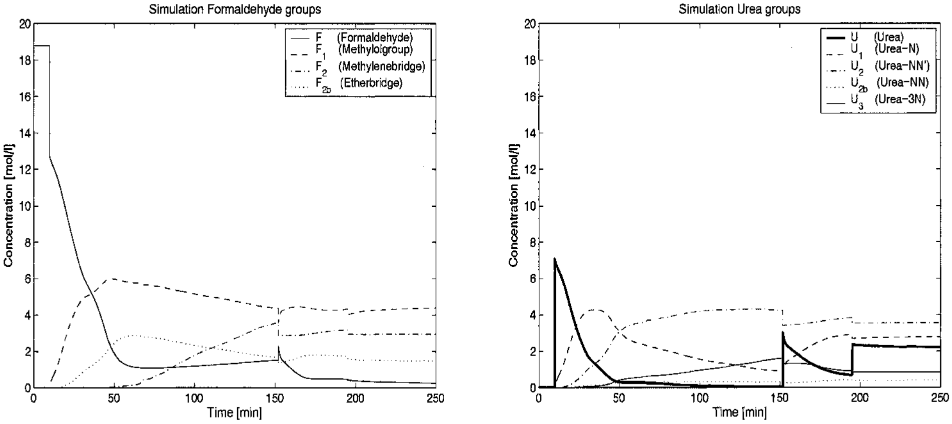

Figure 5 Simulation results from the experimental run

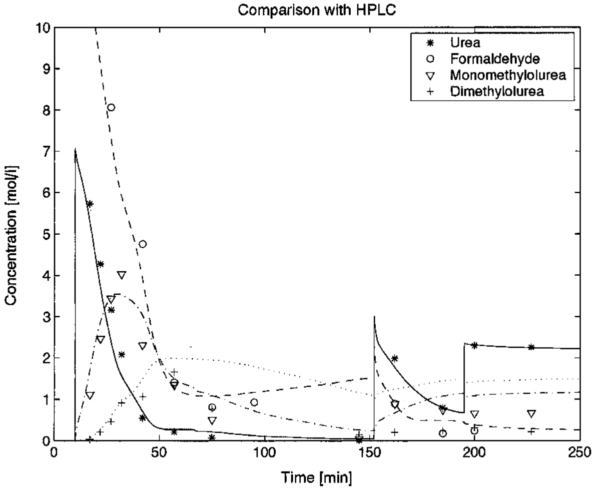

Figure 6 Comparison with HPLC and titration of free formaldehyde. Lines are simulation values

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A comparison between the model and the measured samples is shown in Figure 6. The development of formaldehyde and urea seems to be very close. In the case of monomethylolurea and the NN'-dimethylolurea we had to estimate the values from the simulated U1 and U2. This estimation becomes uncertain late in the batch when the composition mixture is complex. But at least in the beginning of the batch the accordance is good.

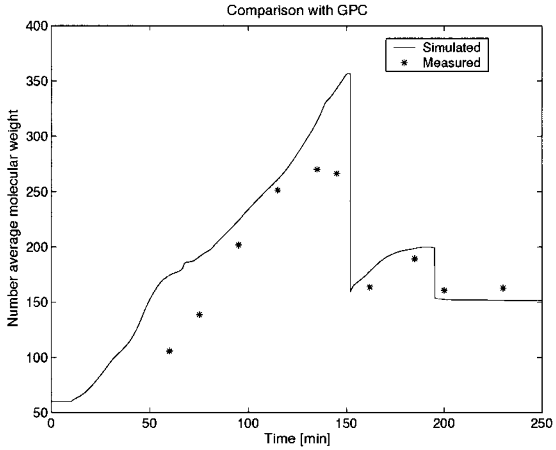

Figure 7 Number average molecular weight

In Figure 7 the mean molecular weight from the simulations are compared with the molecular weight measured from GPC. Although there are some differences they both show similar trends.

A corresponding comparison of the second test run with a higher F/U ratio is shown in Figure 8. The figure shows that the model fits equally well for different formaldehyde urea ratios.

Comparison with continuous FTIR.

There was also available a test run with a continuous IR measurements. This run was a demonstration provided by the company Mettler Toledo. The signals from the instrument

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ReactIR1000 were not calibrated for the UF system, but the spectrum for formaldehyde could be

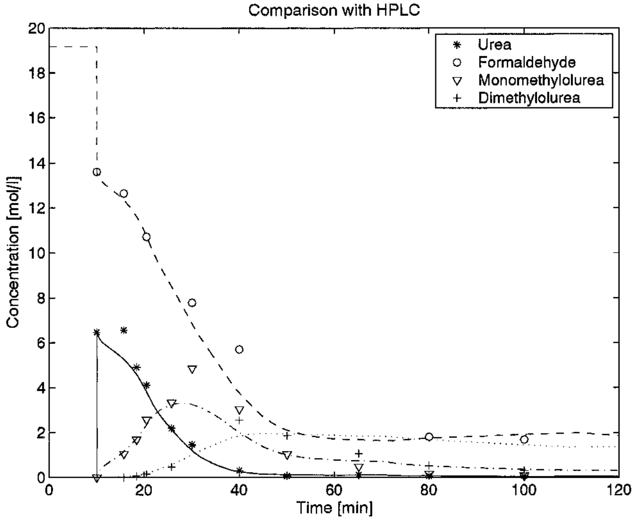

Figure 8 Comparison simulation values (lines) with measurements in the second test run

obtained in the beginning of batch before urea was added (see Figure 9). Consequently the software for this instrument could use the signals for this compound. From the same batch run pH and temperatures profiles were available such that a simulation could be performed and tested against the signals. In Figure 10 the IR-signal, corrected only with a constant gain and bias, is compared with the simulations. As can be seen, the two curves coincide very well.

Viscosity model

Viscosity is presently one of the main quality parameters and it is of great importance to have a model that could predict its value during the batch. Mehdiabadi et al.[18] showed that good prediction could be obtained by correlating the logarithm of the viscosity to the batch time and pH. We wanted to correlate the viscosity to the concentration values from the simulation so that it could be a part of the simulation program.

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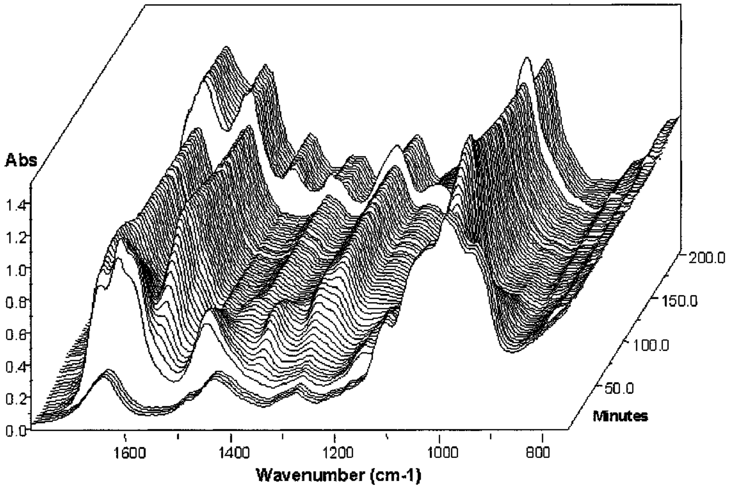

Figure 9 Continuous FTIR measurements spectra

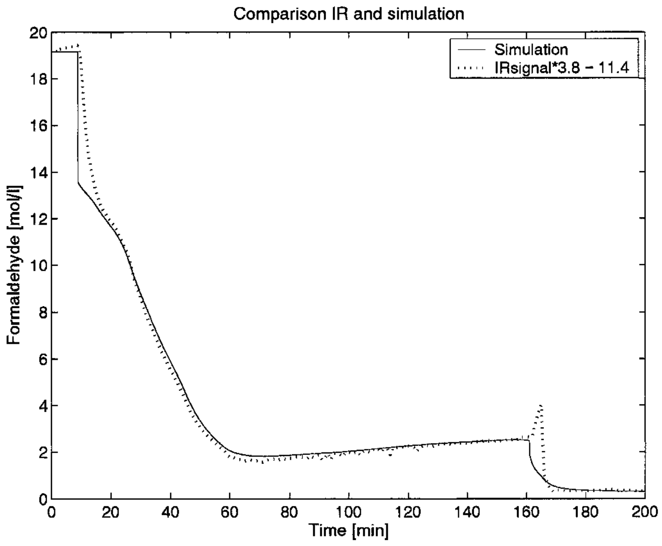

Figure 10 Comparison between the simulation model and the IR signal for formaldehyde

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After testing different viscosity model alternatives we found the best fit for the following model structure

$$\ln(\eta - b_0) = b_1 C_{F_2} + b_2 C_{F_{2b}} + b_3 C_{U_3} \qquad (6)$$

Equation 6 shows that the viscosity depends on the amount of methylene linkages, ether linkages and U_3, i.e. amount of branching. Terms with other functional groups were not statistically significant.

In Figure 11 the best fit of 4 different runs is shown. These runs have F/U rations from 1.8 to 2.5.

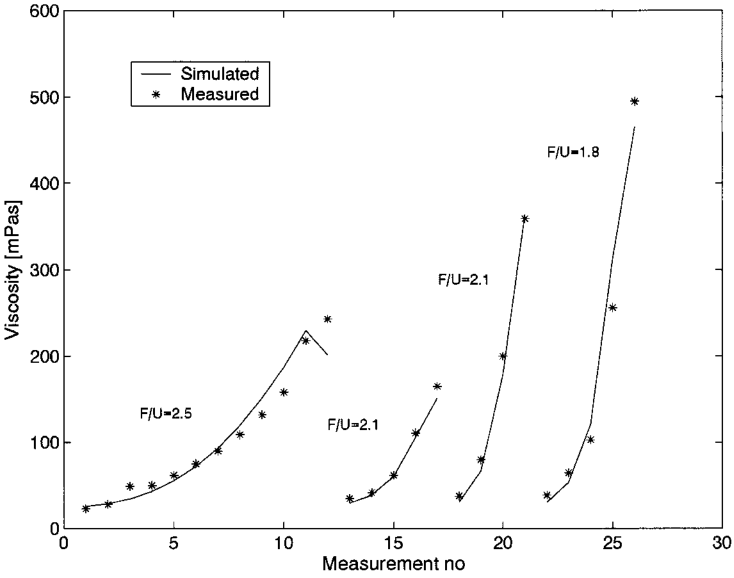

Figure 11 Comparison between measured and predicted viscosity

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Discussion

The kinetic parameters in the model were far too many to be identified within our project, and we had to rely, at least partly, on literature sources. The resulting model is therefore a mix of thoroughly evaluated literature data combined with two laboratory batch runs used for a final adjustment. It is actually surprising that only small adjustments were necessary in order to fit our test runs to the kinetics found in the literature.

The deviations actually found may have different causes. For example, De Jong and De Jonge conducted most of their measurements in diluted solutions while our reaction conditions are quite concentrated. Although they could not find any effect of concentration when increasing from dilute to 3 mol/l[3], our concentrations are about 3 times higher.

The formation of methylene linkages is specific acid catalysed and this makes the model predictions inherently sensitive to incorrect pH measurements. For example, a deviation of 0.1 pH will give an increase/decrease of 26% in this rate constant.

The comparison with the IR-measurements for formaldehyde was very promising since the fit was excellent also dynamically, e.g. the formaldehyde minimum point matched exactly. This technique, combined with proper calibration, can be a very powerful tool for kinetic modelling of this system.

The viscosity model seems to be reliable for a wide range of F/U ratios, and can be useful for online prediction and control. The viscosity model also gives confidence to the kinetic model itself, because it shows that the simulated functional groups are well correlated with a physical quantity like viscosity. It is also reasonable and sound that the statistics showed the highest correlation with viscosity for the methylene linkages, the ether linkages, and number of the triple points.

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Conclusion

The comparison of simulation results with different types of measurements (HPLC, GPC, FTIR, viscosity) shows that the kinetic model is basically sound and describes the urea formaldehyde reaction system well.

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