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POTENTIAL FOR IMPROVED CONTROL OF AN ACID SULFITE BATCH DIGESTER USING A FUNDAMENTAL MODEL

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Synopsis

Effective control of pulp digesters has always been hampered by the difficulty of measuring the controlled variable, namely the degree of polymerization. Use of a model in the control strategy can contribute substantially towards effective control. Because of the complex nature of the pulping process, it is however difficult to construct an accurate model. In this study a modeling strategy is proposed which combines the techniques of fundamental and empirical modeling. The basic structure of the model was chosen from first principles and the parameters in the model were then adjusted by fitting simulation results to actual plant data. Excellent results were obtained using this technique. A correlation coefficient of 0,77 was obtained when the simulated final degree of polymerization of 35 cooks was compared with the actual pulp quality obtained on the plant for these cooks.

Keywords: fundamental model, empirical modeling, acid sulfite pulping, batch process, degree of polymerization, process control.

Introduction

During the manufacture of dissolving pulps, the controlled variable is the degree of polymerization (DP) of the cellulose, which gives an indication of the average length of the polymer chains. One of the uses of dissolving pulps is in the textile industry for the manufacture of viscose fiber that is used for woven and non-woven fabrics. Quality of the pulp is of prime importance in this application. The biggest problem in the control of pulp digesters is the difficulty of in-line measurement of the controlled variable. This is especially true when batch digesters are used. In a batch process, no flow of the pulp occurs during pulping where measurements or samples could be taken, and since the digester is operated under very high pressure, no measurements of the pulp quality can be made during pulping. The progress of the reactions can therefore not be monitored and feedback control of the digester is not possible. A model-based control strategy on

the other hand is able to predict the value of the degree of polymerization throughout the cook and can be used for accurate control.

Constructing an accurate model suitable for use in a control strategy is a major problem in the pulping industry. The main reason for this is the complexity of the process and the multitude of reactions taking place. The complexity of the reactions is caused by the complex nature of the wood constituents. Although the components of the wood have been grouped into only three types of polymers, namely lignin, hemicellulose and cellulose, these terms describe a whole range of different molecules, each displaying unique characteristics and reacting differently during pulping. The second problem is caused by the necessity to model three phases present during pulping as well as the equilibria and mass transfer that occur between these phases.

The challenge when modeling the pulping process for control purposes is to have a model that will be accurate enough to give satisfactory control results, yet is simple enough to be implemented in a control strategy without excessive requirements to the control hardware. The most popular type of model used for control purposes is an empirical model fitted to experimental data. These models are simple to obtain and are generally representative of the process over the range of conditions considered. The problem with empirical models however, is that they cannot be extrapolated to conditions that haven't been considered during construction of the model. The applicability of the model is therefore very limited. A fundamental model can solve this problem, since it is based on the principles of the process itself and the model can be used to simulate the process over a wide range of conditions. The disadvantage of a fundamental model on the other hand, is the complexity of a really accurate model. It can be seen that the advantage of the one type of model is the disadvantage of the other type of model.

In this study, these two modeling techniques were combined to create a model for a batch pulp digester where the acid sulfite process is used to produce dissolving pulps. This was done by building a model structure from first principles and then to adjust the parameters in the model by fitting the simulation results of the model to experimental data, as well as actual data from an acid sulfite plant. In this manner a model is obtained which is fundamentally acceptable, and which can be adapted to conform to historical data. A software package was written to assist in the process of finding an accurate model.

Building the model structure from first principles

Since DP is the controlled variable of the process, the primary purpose of the model should be to model the cellulose degradation process. For this, the reactions of the wood constituents during pulping should be considered. These reactions will however depend on the cooking liquor composition and the conditions inside the digester. These factors should all be considered in the construction of the model.

Kinetic rate equations for the reactions of the pulp are necessary to model the wood degradation process. Kinetic studies are very expensive and time consuming and it

was decided to use the results of previous authors. The kinetic rate equations developed by Hagberg and Schöön (1) were used for the modeling of the lignin and hemicellulose degradation reactions taking place in the pulp. They found the delignification rate to be dependent on the residual lignin in the pulp as well as the hydrogen and bisulfite ion concentrations. The rate of hemicellulose degradation is a function of the hemicellulose content of the pulp, as well as the hydrogen ion concentration. The concentrations of lignin and hemicellulose in these rate equations are measured as a mass percentage of the pulp. Sloan (2) proved that the degradation increase of the cellulose in the pulp is a function of only the hydrogen ion concentration of the liquor. He defined the degradation increase (DI) as the number of polymer linkages that haven been broken. The authors all found that the reactions have an Arrhenius dependency on temperature. The reactions of the wood constituents can be summarized as follows:

Lignin:
$$-\frac{d[L]}{dt} = k_L{}^0 e^{-E_L/T}[L]^a \cdot \left[HSO_3^-\right]^\alpha \cdot \left[H^+\right]^\beta \quad (1)$$

Hemicellulose:
$$-\frac{d[HC]}{dt} = k_{HC}{}^0 e^{-E_{HC}/T}[HC]^d \cdot \left[H^+\right]^\gamma \quad (2)$$

Cellulose:
$$-\frac{dDI}{dt} = k_C{}^0 e^{-E_C/T}\left[H^+\right]^\delta \quad (3)$$

The concentrations of lignin and hemicellulose are measured as a percentage of the pulp.

In order to calculate DP from the degradation increase, Sloan (2) proposed the concept of the degree of degradation (DD) which allows the DP decrease to be directly related to the number of cleavages and thus to the extent of the reaction. The degree of degradation is defined as the reciprocal of the DP. This can be expressed as follows:

$$DI = \frac{1}{DP_f} - \frac{1}{DP_0} = DD_f - DD_0 \quad (4)$$

During the pulping process, the lignin monomers that form from the delignification reactions will react with the hydrogen and bisulfite ions to form the so-called strong acids. These strong acids will influence the pH of the cooking liquor and have to be modeled as well. The reaction rate equation proposed by Hagberg and Schöön (3) to calculate the strong acids concentration was used and looks as follows:

Strong Acids: $$\frac{d[SA^-]}{dt} = \left\{\left(\frac{g}{\nu}\right) + \left(\frac{2h}{\nu}\right)([L]_0 - [L])\right\} \cdot r_L + \frac{k_{SA}(T)}{\nu}([L]_0 - [L])^q [HSO_3^-]^b [H^+]^c \quad (5)$$

The parameters *g* and *h* are empirically determined constant parameters, while ν is the liquor-to-wood ratio. This reaction also has an Arrhenius dependency on temperature

The reactions considered involving the degradation of lignin, hemicellulose and cellulose take place in the solid phase. Two important assumptions were necessary in order to simplify the model. The first assumption was that the wood constituents mentioned above react in a homogeneous manner, meaning that the different molecules known as lignin all react in the same way and at the same rate. The same assumption was made for cellulose and hemicellulose. The second assumption was that the concentrations of the hydrogen and bisulfite ions were the same at the reaction site and in the bulk liquor. This assumption was based on the finding of Smook (4) that the diffusion path is very short once complete liquor penetration has occurred. Consequently, the reactions themselves will be the rate determining step.

From the rate equations shown above, the necessity of modeling the liquor composition should be clear. The model equations for the liquor composition were mostly based on the equilibria that exist between the sulfur dioxide in the gas phase and the dissolved sulfur dioxide, as well as the equilibria of the different dissociation reactions taking place inside the liquor. In the preparation of the cooking liquor for the sulfite process, sulfur is burned to yield sulfur dioxide. After cooling, the gas is absorbed in the desired base. The following reactions take place when calcium is used as base and calcium hydroxide is added to the aqueous sulfur dioxide:

$$H_2O + SO_2 \Leftrightarrow H_2SO_4$$
$$H_2SO_4 + Ca(OH)_2 \Leftrightarrow Ca(HSO_3)_2 + H_2O$$
$$Ca(HSO_3)_2 + Ca(OH)_2 \Leftrightarrow CaSO_3 + H_2O$$

First bisulfite (HSO_3^-) and then sulfite (SO_3^{2-}) is formed. The following equilibria exist in the liquor:

$$SO_2(gas)$$
$$\Updownarrow$$
$$SO_2(solution)(+H_2O)$$
$$\Updownarrow$$
$$H_2SO_3$$
$$\Updownarrow$$
$$H^+ + HSO_3^-$$
$$\Updownarrow$$
$$H^+ + SO_3^{2-}$$

The concentration of the various ions will depend on the values of the dissociation constants at the relevant temperatures. The dissociation constant for the equilibria shown above can be defined as follows:

$$k = \frac{[H^+][HSO_3^-]}{[H_2SO_3]+[SO_2]} = \frac{[H^+][HSO_3^-]}{[\text{total } SO_2]-[HSO_3^-]} \qquad (6)$$

It was shown by Rydholm (5) that the dissociation constant for sulphurous acid, H_2SO_3, is very high and that the concentration of sulphurous acid will be very low, especially at high temperatures. The following definition for the dissociation constant can then be used:

$$K_{SO_2} = \frac{[H^+][HSO_3^-]}{[SO_2]} \qquad (7)$$

The benefit of using this definition is that values for this equilibrium constant are more readily available. The values are expressed as a mathematical correlation in a form similar to the Antoine equation to incorporate the temperature dependence of the constant. The general form of these equations is shown in equation (8).

$$\log_{10} A = B + \frac{C}{T} \qquad (8)$$

Values for the parameters B and C that were found in this study are given in **Table 3**.

It was shown earlier that when a base is added to the sulfur dioxide – water system, first bisulphite and then monosulphite will be formed. This will then represent the reactions

in the cooking liquor at the start of the cook. These reactions were used in the construction of equation (9), where the two possible products of bisulphite at the start of the cook are used in the electroneutrality condition.

$$[M^+] + [H^+] = [HSO_3^-] \tag{9}$$

However, as soon as the delignification starts, the lignin monosaccharides will start forming strong acid by reaction with the bisulphite, as shown in equation (10).

$$HSO_3^- \rightarrow RSO_3^- \tag{10}$$

These two equations can be combined to form the electroneutrality equation during the cook, that is, after the formation of strong acids has started. The electroneutrality equation can be stated as follows:

$$[M^+] + [H^+] = [HSO_3^-] + [SA^-] \tag{11}$$

The one property that distinguishes the acid sulfite process from other sulfite cooking processes, is the large excess sulfur dioxide present in the gas phase. This means that an equilibrium will be established between the dissolved sulfur dioxide and the excess sulfur dioxide in the gas phase. The following equilibrium equation can be used to give the distribution of sulfur dioxide between the gas and the liquor phase.

$$K_P = \frac{[H^+][HSO_3^-]}{p_{SO_2}} \tag{12}$$

The equilibrium constant can also be calculated from an Antoine type equation similar to the calculation of the sulfur dioxide protolysis constant.

One more equation will be necessary to completely specify the liquor system. It was assumed that the partial pressure of gases other than sulfur dioxide and water was negligible. Therefore, the total pressure will be equal to the sum of these two partial pressures.

$$P = p_{SO_2} + p_{H_2O} \tag{13}$$

The vapor pressures of both water vapor and sulfur dioxide above water can easily be calculated and data are freely available. Once again, an Antoine type equation can be used to incorporate the temperature dependency into an easily useable model.

Concentration of the metal ions can be calculated from the initial combined SO_2 concentration by assuming that all the base ions will react with bisulfite ions, as was shown in the reactions during preparation of the cooking liquor.

$$[M^+] = 2 \cdot [\text{combined } SO_2] \qquad (14)$$

These additional equations are sufficient to calculate the hydrogen and bisulphite concentrations in the liquor phase during any stage of the cook.

The temperature and pressure profiles are both controlled on the plant using feedback control. Temperature in the batch digester is controlled with an external heat exchanger by circulating liquor from the bottom of the digester through the heat exchanger and returning it at the top of the digester. The assumption was made that the control of the temperature and pressure is effective. This assumption was confirmed to be valid. Temperature and pressure during the cook were therefore modeled according to the control strategy used on the plant by assuming the actual pressure and temperature at the top of the digester to be equal to the setpoint values. The average temperature in the digester was obtained by dividing the digester into ten continuously stirred tank reactor sections and doing a heat balance over each of the section. The average temperature in the digester was taken to be the average of the temperatures in each of the ten sections.

Sixteen variables were identified in the model. Nine model equations were given earlier. Three of the equilibrium variables, P_{H_2O}, K_{SO_2} and K_P, can be calculated from the temperature dependent equations as represented by equation (8). Twelve of the sixteen variables can be calculated from the model equations. Temperature and pressure were taken to be equal to the setpoint values in the control system as was discussed earlier. If the liquor-to-wood ratio and the combined and the free SO_2 are specified as the starting conditions of a cook, the system is completely specified, with sixteen equations and sixteen variables.

Adjustment of the parameters and verification of the model

The lack of measurements during the pulping process was mentioned earlier. In order to be able to verify the correctness of the model, at least a few measurements of each of the variables should be available during a cook. This will be necessary to ensure that the variables that were coincidentally predicted correctly by the model at the end of a cook, are not incorrectly used as proof of the correctness of the model. During the normal operation of the digester, only the final DP value of the product is measured, as

well as the combined and free SO_2 concentrations one hour after the start of the cook. The pH is rarely measured on a batch plant, because of the cost of installing and maintaining pH probes on all of the individual digesters. The DP of pulp is related to the intrinsic viscosity and can be determined by measuring the viscosity of a pulp sample. This method is simple and relatively quick and is most commonly used for the estimation of the DP value of the cellulose. The correlation between the DP value and the measured viscosity was determined by Watson (6) and were found to be:

$$DP = 285{,}4\mu^{0{,}345} \qquad (15)$$

This correlation is valid over a range of $20<\mu<150$.

Experimental studies done by Watson on a mini satellite digester plant provided data to verify the model. Various liquor samples were taken for each cook and the combined as well as free SO_2 concentration was determined. These measurements were used to calculate the bisulfite ion concentration. Six pulp samples were taken over the last hour of the experimental cooks, and from these samples, the DP values as well as the residual lignin concentrations were determined. Temperature, pressure and pH were measured continuously during the cooks.

Experimental data obtained by Watson were used to verify the parameters of the proposed liquor composition and reaction kinetics model. The measured temperature and pressure vectors of the experimental cooks were inserted into the model as such. This was done to ensure that the same conditions were used for the modeling of the reaction kinetics as was present during the experiments. The experimental and verification results could then be compared and the model parameters adjusted to fit the experimental data.

It was also necessary to verify the ability of the model to simulate an actual digester. For this purpose, the conditions inside the digester had to be modeled. Data was available from a dissolving pulp production plant that uses the acid sulfite process. However, only the final DP values were available for comparison with the model results. Since this is the most important variable in the pulping process, it was regarded as sufficient to confirm the ability of the model to predict this final DP value. The loading conditions of the actual cooks were used as the starting values for the simulations, and the final DP values were calculated and compared to the actual values.

A software package was developed in the Matlab/Simulink environment to assist in attaining an accurate model, as well as to verify the correctness of the model. Tools were written in the package to compare the results of the simulations with the model using both sets of verification data. Data was read into spreadsheets and extracted automatically by the package for comparison with the simulation results. Provision was made for the easy adjustment of all the parameters through user-friendly screens.

Data from nine experimental cooks were available for the verification. The simulation and comparison were done with the software package, and the adjustment of the parameters done according to the results of the comparison. The values that were obtained for the parameters in the model were very similar to the values obtained by the authors mentioned earlier. The values that were obtained in this study are given in **Tables 1 and 2**. An example of one of the screens showing the results of the comparison after adjustment of the parameters is shown in **Figure 1**. The values for the simulated variables are shown as solid lines, while the experimental data are shown as crosses. The correlation coefficient for each of the variables that were compared are shown in the bottom right-hand corner of the screen. The average values for the correlation coefficients for all nine cooks used for the verification are shown in Table 3. It should be noted that the DP was expressed as the viscosity of the pulp samples.

Lignin reaction kinetics (mass % of wood /s)		
	[L] > 12,4 %	**[L] < 12,4 %**
K_L^0 (%)	$1{,}346 \times 10^{12}$	$0{,}407 \times 10^{12}$
E_L (K)	12 500	12 500
a	0,646	1,621
α	0,819	0,765
β	0,705	0,779
Hemicellulose reaction kinetics (mass % of wood /s)		
K_{HC}^0 (%)	$1{,}261 \times 10^{11}$	
E_{HC} (K)	14 030	
d	2,542	
γ	0,707	
Cellulose reaction kinetics (DI/s)		
K_C^0	$7{,}68 \times 10^{12}$	
E_C (K)	17 100	
δ	1	
Strong Acids reaction kinetics (kmol/m^3.s)		
k_{SA}^0 (kmol/m^3)	$1{,}887 \times 10^{16}$	
E_{SA} (K)	19 860	
q	2,2231	
b	1,681	
c	0,653	
g	$6{,}87 \times 10^{-3}$	
h	$-1{,}310 \times 10^{-4}$	

Table 1. Parameters in kinetic equations obtained in this study.

A	Temperature range (°C)	B	C
K_{SO_2}	20 – 80	-5,077	1 045
	80 – 120	-6,916	1 700
	120 - 150	-7,971	2 133
K_P	20 – 80	-10,2212	2 392
	80 – 120	-10,5125	2 665
	120 - 150	-11,0348	2 960
P_{H_2O}	20 - 150	5,9648	-2 198

Table 2. Values for parameters B and C in equation (8) obtained in this study.

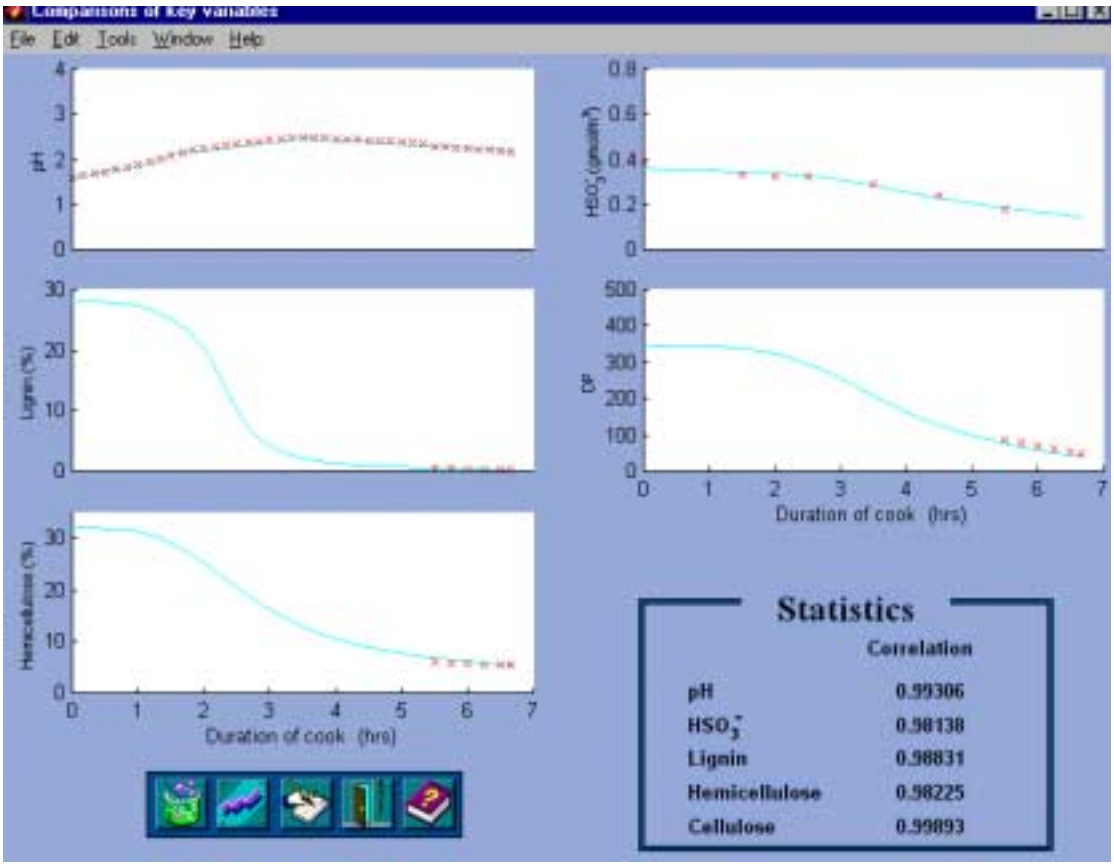

Figure 1. Comparison of the variables in the model with experimental data.

From the figures, as well as the values in **Table 3**, it can be seen that excellent results were obtained for modeling of the experimental cooks. The model should however still be verified against the actual digester values. For this purpose, 35 actual cooks were simulated with the software package and the predicted final DP values compared with the actual measurements. The measure of the accuracy of the model currently used for the control of the digester, is the coefficient of variance (COV). This coefficient is defined as the ratio of the standard deviation of the viscosities obtained over a certain time period to the mean of the viscosity values. This ratio is multiplied by 100 to obtain the standard deviation as a percentage of the mean value. Typical COV values that were obtained with the current model in use on the plant were well above 20. A modification of the S-factor model developed by Yorston and Liebergott (7) is currently used for the control of the DP.

Variable	Correlation coefficient
pH	0,9491
$[HSO_3^-]$	0,9397
Lignin	0,9621
Hemicellulose	0,8808
Viscosity	0,9730

Table 3. Average correlation coefficients for comparison of simulation results with experimental data.

Results of the simulations and the actual values obtained on the plant were plotted on the same set of axes for a visual comparison. The COV was then calculated to allow a comparison of the newly developed model with the model currently in use. The results of the comparison are shown in **Figure 2**. In the graph at the top, the predicted values are indicated as crosses, and the actual values as dots. The calculated COV value is shown in the bottom right-hand corner of the figure. The value of 10,7 that was obtained shows a significant improvement over the model currently in use. The COV obtained over the same period using the S-factor model was 18,9. The correlation coefficient between the sets of measured and predicted data was also calculated and a value of 0,77 was obtained. The value of 0,77 indicates that the good coefficient of variance that was obtained is not incidental. This could easily have been if little variance of the measured values occurred for the cooks that were tested. However, the correlation coefficient indicates that the model can also predict the changes that occurred in the final product quality. The graph at the bottom of Figure 2 was enlarged in **Figure 3** to give a more accurate representation of the results.

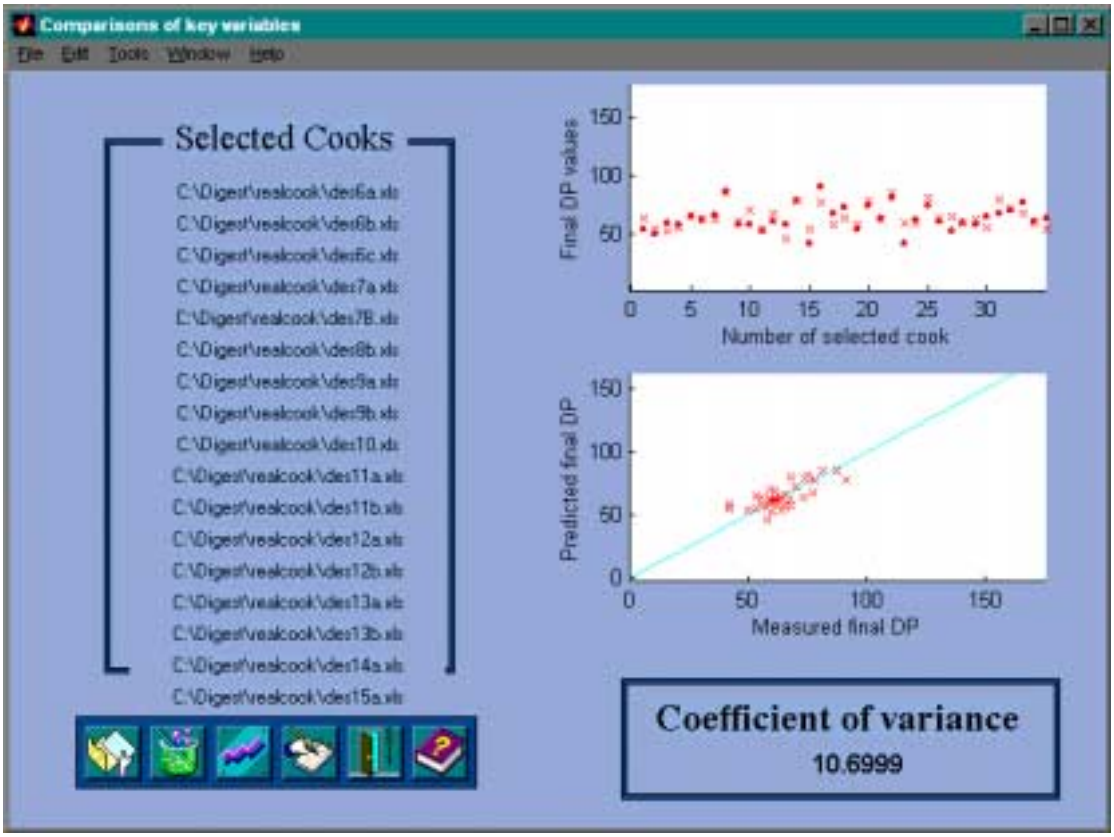

Figure 2. Comparison of model prediction with actual DP values obtained on the plant.

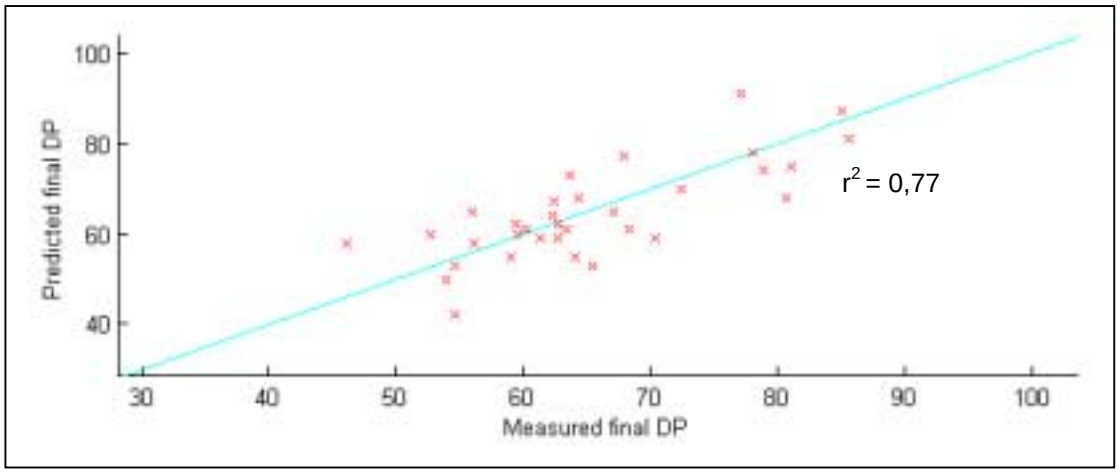

Figure 3. A comparison between values predicted by the model and actual values obtained from the plant.

Conclusion

Very good results were obtained when results of the simulation ware compared with experimental data and actual plant data. The modeling technique used was very simple to use and the resulting model seems to be valid for application to a real situation. The advantages of using both empirical and fundamental modeling techniques were clearly shown by the excellent correlation obtained when compared with plant data.

The results obtained in this study indicate that control of the product quality can be improved by using a fundamental model. The development and implementation of a control strategy based on the model developed in this study is currently under investigation.

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