Optimization and Control of a Semi-Batch Polymerization reactor

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Abstract— **The research work presented in this paper considers the polymerization plant in MITOL chemical factory in Sežana, Slovenia. This is the leading glue manufacturer in the country with production rate more than 90% of its capacity. One of the challenges now is to increase the production rate, while keeping the quality parameters at the desired values. A possible approach to reach this goal is by applying better control strategies that will decrease the batch time. The underlying research is aimed at the design of the process model and its application in the search for more optimal plant operation.**

Model simulation results based on real plant data, derived in gPROMS model environment, are presented.

I. INTRODUCTION

The research work in this paper considers the polymerization process in MITOL, a chemical factory in Sezana, Slocenia. This is the leading glue manufacturer in the country with the production rate more than 90% of its capacity. The challenge we are facing now, is to design optimal control strategies in order to increase the production rate and decrease the batch time by keeping the quality parameters in the desired levels. The production process is semi-batch polymerization process with initiator and monomer added during the batch. The large quantities of raw materials and equipment resources prevent us from performing experiments for batch optimization directly on the plant. Therefore we need a good predictive model for controlling the input variables (initiator and monomer) and also to control the temperature during the batch. For that purpose a model consisting of differential and algebraic equations (DAE) have been constructed. The model predicts four outputs, i.e. conversion, particle size diameter, solid content and viscosity. That model as not able to predict the changes in the temperature profile. In order to improve the predictive capabilities, the model was extended by adding additional differential equations, that estimate the reactor temperature profile as a function of the concentrations of the reacting chemicals. This paper presents the extended model using first principle modeling (energy balance).

II. PLANT PROCESS DESCRIPTION IN MITOL

The process presented hereby is a polymerization of vinyl acetate by using potassium persulfate (KPS) as initiator and polyvinyl alcohol as protective colloid. The production process is semi-batch polymerization. In the beginning initial amounts of monomer and initiator are added into the reactor as well as the whole amount of polyvinyl alcohol and water. The reactor is closed and the heating starts. The heating of the reactor is done by pumping hot water in the heating jacket around the reactor. The hot water is pumped with a temperature of 90°C. When the temperature in the reactor reaches approximately 65-70°C, the operator stops the hot water. The exothermic reaction and the heat of the remaining water filling the heating coat, continue to rise the temperature. After the reactor temperature reaches a certain level, the remaining monomer starts to be pumped into the reactor with a continuous flow of 370 kg/h. The monomer flow rate is controlled by a PID controller acting on the pump. The temperature of the added monomer is with outdoors temperature, fig. 1.
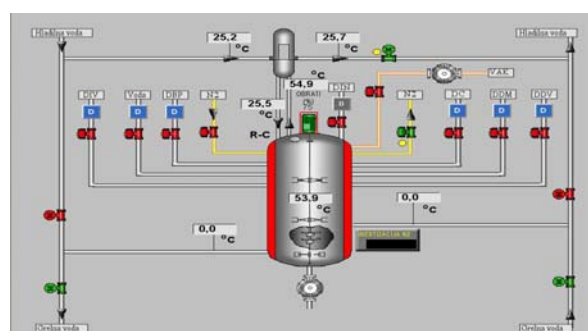

Fig. 1 Scheme of the polymerization reactor in MITOL

In the beginning of the reaction, the temperature can reach 82°C, but afterwards, for the product quality reasons, it is necessary to keep the temperature between 75°-80°C. Temperature control is performed by manually adding a small amount of initiator every time when the temperature decreases. When all the monomer is added into the reactor, a larger amount of initiator is added in order to terminate the reaction. The temperature is then allow to reach 90°C. The reaction is consider as finished when the temperature starts

to decrease again.

The main variables affecting the duration of the reaction and possibly used in the batch optimization are: reactor temperature, flow rate of the monomer and the addition of the initiator.

The quality of the product is defined by the following parameters: conversion into polymer, particle size distribution, viscosity and solid content.

III. ENERGY BALANCE

The current model is based on a more complex one described in previous papers [1][2][3]. In the first model the monomer flow rate, the initiator addition and the temperature in the reactor were taken as inputs into the systems. The data for them were provided from the real plant in MITOL. In that case the temperature in the reactor was not estimated by the model. In order to observe the changes in the temperature as a result of monomer and initiator addition, we took out the temperature as input and rather estimate it from the energy balance model. The model is applied within a model predictive optimization scheme aimed to search for an optimal policy of manipulating initiator and monomer feed rates.

The polyvinyl alcohol covers the particles, providing steric stabilization. The partition of the PVOH between the water phase, the droplets and the particles is modelled with the Langmuir model [16], based on adsorption isotherms.

$$V_w[G_w] + K_{gd}[G_w]V_d + \frac{A_{c\infty}K_{ad}[G_w]A_{ps}}{1+K_{ad}[G_w]} = \frac{G_0}{MW_{PVOH}} \quad (1)$$

Where $[G_w]$ is the concentration of PVOH in the water phase, K_{gd} is the partition coefficient on the droplets, $A_{c\infty}$ is the equilibrium coverage of the particles and G_0 is the total mass oPVOH

The mass of the initiator in the reactor (I) is increased by the flow addition of initiator (I_e) and decreased by its thermal decomposition [9][10]. To obtain the concentration of the initiator (I_w) in the aqueous phase we divide by the volume of water (V_w).

$$\frac{dI}{dt} = I_e - k_d[I_w]V_w \quad (2)$$

$$[I_w] = \frac{I}{V_w} \quad (3)$$

To account for higher rate of decomposition of KPS at higher temperature we use the following function:

$$K_d = 8.4 \cdot \left(\frac{T-Tstart}{40}\right)^2 + 1.6 \cdot \left(\frac{T-Tstart}{40}\right) \quad (4)$$

where K_d is the initiator decomposition rate constant, T is the reactor temperature and Tstart is the temperature when an appreciable decomposition is observed.

The addition of the initiator is calculated from the weight change of the initiator dozing tank (fig. 1)
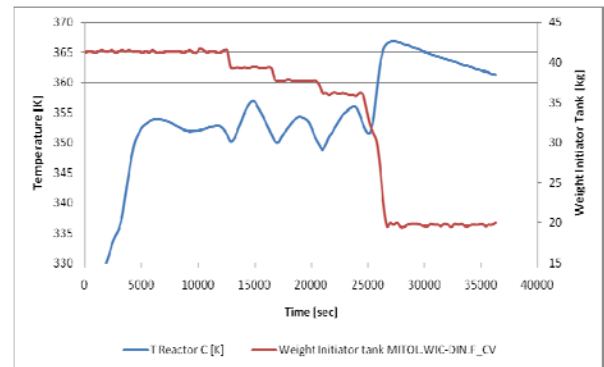

Fig. 2. Estimating the initiator profile from the weight of the initiator tank

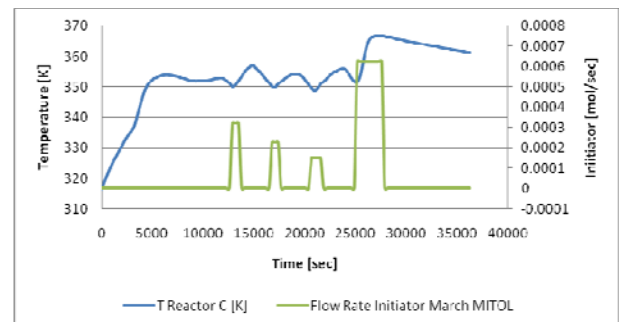Having this profile we are able to estimate the initiator profile and it is:

Fig 3 Estimated temperature profile

The feed rate of the monomer (Q_m) is an input to the model; its values are read from a database containing real data from the plant. The monomer in the reactor (M) is consumed in the water phase due to the initiation, propagation and chain transfer reactions, and, above all, in the particle phase, the main locus of polymerization. The equation for the monomer is given by:

$$\frac{dM}{dt} = Q_m - \left(M_w\begin{pmatrix} k_{iwm}R\cdot + k_{pw}(R_w\cdot - M_1\cdot) + \\ k'_{iwm}M_1\cdot + k_{trm}(R_w\cdot - M_1\cdot) \end{pmatrix}\right) + $$
$$k_{pp}[M_p]\bar{n}\sum_{i=1}^{NoC}(PSD_i)V_w) \quad (5)$$

The energy balance model is based on reaction heat capacity and the energy produced and consumed during the reaction. The latter include the following:
- Heating of the reactor through the heating jacket
- Producing heat in the exothermic reaction

- Heating the incoming monomer
- Cooling the reactor by the reflux in the condenser
- Heat losses to the surroundings

The reaction heat capacity is calculated by the monomer in the reactor, the converted into polymer monomer, initial amounts of water and polyvinyl alcohol and their heat capacities as follow:

$$K_R = MMW_m Cp_{mon} + M_{conv} MW_m Cp_{pol} + V_w Cp_{water} + PVOHCp_{pol} \quad (6)$$

The heating of the reactor through the heating jacket is given by:

$$\Delta H_{jacket} = 0.00018 (T - T_{jacket}) K_R \quad (7)$$

where T is the temperature in the reactor and T_{jacket} is the temperature in the reactor jacket. The changes in the latter are modeled as follow:

$$dT_{jacket} / dt = (0.00018 K_R / 4.18 \cdot 1000)(T - T_{jacket}) \quad (8)$$

The energy needed to heat the incoming monomer is represented by the flow rate of the monomer, its molecular weight, heat capacity and temperature:

$$Q_m MW_m Cp_{mon} T_{mon} \quad (9)$$

The losses due to the reflux from the condenser are also taken into account. It is estimated by the flow coming in the condenser and out of the condenser, the heat capacity of the condenser and the temperature of the reflux going through the condenser.

$$Q_{cond} = Q_{FC} Cp_{Cout} (T_{Cout} - T_{Cin}) - Q_{FC} \lambda \quad (10)$$

where λ is the vaporization heat and it is calculated by the following equation:

$$\lambda = -0.00281 T_{Cout}^2 - 0.32738 T_{Cout} + 408.178 \quad (11)$$

The heat losses through the surroundings are also modeled and are:

$$Q_{loss} = C3 (T - T_{ext}) \quad (12)$$

The energy balance model is divided into three parts depending on the stage of the process and the reaction (fig. 3)
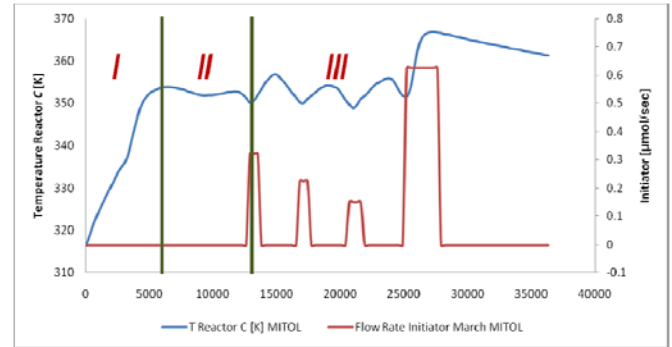

Fig. 4 Three phases model separation

The first part of the model starts when we close the reactor and start heating it up with hot water through the heating jacket. This first part of the modeled reaction ends when the hot water stops to be pumped in the jacket and wait till the temperature reaches around 80°C. In that first part the heat losses are negligible and also there is no flow through the condenser. Therefore the energy balance model in that first part is given by:

$$K_R \frac{dT_R}{dt} + T_R \frac{dK_R}{dt} = Q_m MW_m Cp_{mon} T_{mon} - \quad (13)$$
$$\Delta H_r r_{pol} - C_3 \Delta H_{jacket}$$

The left side of the equation account for the changes in the internal energy of the reactor, which is due to the changes of the reactor temperature (first term) and the change of its heat capacity (second term)

The second part of the modeled temperature profile starts at the end of the first part and ends at the first initiator addition during the batch. In that part the reactor is no more heated through the heating jacket, the losses are negligible, as well as the flow through the condenser because the reaction has just been started. The energy balance model includes only monomer enthalpy and the reaction heat. The equation is the following:

$$K_R \frac{dT_R}{dt} + T_R \frac{dK_R}{dt} = Q_m MW_m Cp_{mon} T_{mon} - C_4 \Delta H_r r_{pol} \quad (14)$$

The energy balance for the third and last part of the modeled reaction takes into account the reflux though the condenser and the heat losses through the surroundings. The equation has the following form:

$$K_R \frac{dT_R}{dt} + T_R \frac{dK_R}{dt} = Q_m MW_m Cp_{mon} T_{mon} - \quad (15)$$
$$C_5 \Delta H_r r_{pol} - Q_{cond} - C_6 Q_{loss}$$

Model parameters in the equations (3-13) are taken from the literature [4] or estimated based on real plant data (C_3, C_4, C_5, C_6), so that a satisfactory agreement between the process

and the model was obtained. The values of the model parameter are given in Table I

Table I

Parameter	Value
k_{iwm}	3.70E+05
MW_m [gmol^{-1}]	86.09
ρ_p [g l^{-1}]	1170
k'_{iwm} [l mol^{-1} s^{-1}]	3.70E+04
K_{trm}[l mol^{-1} s^{-1}]	1.75E-04
K_{pp}[l mol^{-1} s^{-1}]	3700
Cp_{pol} [kJ kg^{-1} K^{-1}]	1.77×10^{-2}
Cp_{mon} [kJ kg^{-1} K^{-1}]	1.77×10^{-2}
Cp_{out} [kJ kg K^{-1}]	1.17
Cp_{water} [kJ kg K^{-1}]	4.18×10^{-2}
T_{ext} [K]	283.15
ΔH_r [kJ mol^{-1}]	-87.5
C_3 (dimensionless)	0.50
C_4 (dimensionless)	0.35
C_5 (dimensionless)	0.60
C_6 (dimensionless)	Depending on the batch

The output quality parameters are also modeled. The conversion is given by:

$$x = 100 \cdot \frac{M_c}{M_t} \qquad (16)$$

Mathematically express the particle size diameter is:

$$D_{pu} = \left(\frac{6000 M_c MW_m}{\pi \rho_p N_P} \right)^{1/3} \qquad (17)$$

Solid content:

$$SC = \frac{M_c MW_m + G_0}{M_t MW_m + G_0 + V_w} \qquad (18)$$

The viscosity is calculated by:

$$\upsilon = \frac{\upsilon_0}{\left(1 - \dfrac{sc}{sc_{ref}} \right)^2} \qquad (19)$$

IV. RESULTS

The presented model was simulated using gPROMS [5][6] modeling tool. Model simulations were performed based on real plant data. The flow of the added monomer during the batch was measured, while the addition of initiator was calculated from the weight change of the initiator dozing tank. The reactor temperature and initiator flow rate during the batch are shown in Figure 2.

With the presented model we are able to get relatively good estimates of the reactor temperature. From Figure 3 it can be seen that the estimated profile follows the dynamics of the real one. Not so good estimates are obtained at the beginning and at the end of the batch. At the beginning of the batch, the most influential part of the model is the heating of the reactor through the heating jacket. So most probably, the corresponding model parameters still need to be estimated more precisely. The agreement of the model is also not good in the last part of the estimated profile. This is when the whole amount of monomer has been already added in the reactor and a larger amount of initiator is put to finish the reaction. There are two possible reasons that the performance of the model in this part is not so good, i.e., (i) the actual heat losses are higher than estimated, (ii) the final addition of initiator was smaller than calculated. For the latter we have to take into account that the amount of initiator is obtained from the weight change of the dozing tank, so there might be some disparity of the final addition because of its larger amount. The obtained model still needs fine tuning of parameter values and close inspection of the initiator addition
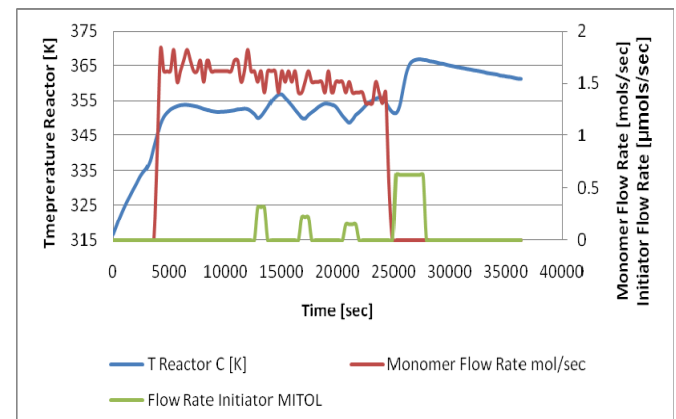

Fig. 5 Initiator addition, monomer flow rate and the temperature prfile during the batch
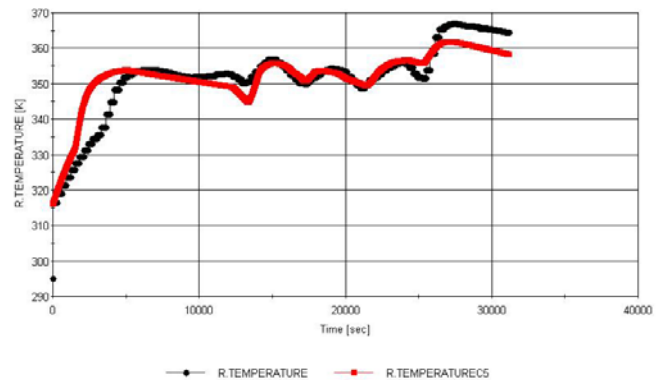

Fig. 6 Modeled temperature profile vs. real plant temperature profile

The overall model was also used to calculate the product quality parameters. Table II shows the validation of the model for one batch for simulation time of 31000 seconds.

The ranges for the outputs are the following: the conversion for all the batches is over 99%, the solid content is between 44-46%, the range of the viscosity is 27000 – 34000. For the viscosity and the solids content, laboratory analyses were performed at the end of the reaction. These measurements are normally performed after mixing several batches and therefore no individual data is available.

Table II Output variables – real plant data and estimated data

Batch No.	Conversion (%)		Solids Content (%)		Viscosity (Brookfield 200C, 50rpm), (mPas)	
	Real Data	Modelled Data	Real Data	Modelled Data	Real Data	Modelled data
1192	99.95	99.79	46.4	45.84	37520	33723
1203	99.90	99.74	45.9	45.86	31200	36324
1214	99.89	96.17	45.4	43.88	25040	32697
1253	99.13	99.36	46.9	45.97	34000	35486
1256	99.37	99.45	46.4	45.61	30160	33343

From the table we can see that the model output variables are in good agreement with real plant data. To obtain these results it was necessary to adjust the C_6 parameter for each batch. This could be attributed to the variable and increased fouling of the reactor walls between cleaning periods. The average model error for conversion and solids content is around 2% and for the viscosity around 15%. Some bigger deviations can be noticed for batch 1214 for all output variables.

V. CONCLUSION

A model for polymerization of vinyl acetate has been developed. The model has two inputs – flow rate of monomer and flow rate of initiator addition. The outputs of the presented model are four – conversion, particle size diameter, solid content and viscosity. The overall model has thirteen differential equations, sixty-three algebraic equations and nine adjustable parameters. In this model we are able to observe temperature profile and based on it apply the control of the initiator addition and estimate more precisely the sufficient amount of initiator which needs to be added during the batch. The model has been validated on data of five batches taken from the real plant. The presented temperature profile is quite satisfactory and also the model output variables are in the range. The work continues with the design and testing of initiator and monomer control strategies.

ACKNOWLEDGMENT

NOMENCLATURE

I	Moles if initiator in the aqueous phase	mol
I_e	Flow Rate Initiator	mol/ sec
I_w	Concentration of the initiator in the aqueous phase	mol l-aq^{-1}
k_d	Initiator decomposition rate constant	sec^{-1}
V_w	Volume of the water	L
T_{start}	Starting temperature	[K]
Q_m	Flow Rate Monomer	mol/ sec
M_w	Moles of monomer dissolved in the aqueous phase	mol
$R\cdot$	Total concentration of primary radicals from initiator	mol l-aq^{-1}
$R_w\cdot$	Overall concentration of oligomeric radicals (RM· and M·)	mol l-aq^{-1}
$M_i\cdot$	Monomeric radicals of chain length i	mol l-aq^{-1}
$[M_p]$	Concentration of monomer in the polymer phase	mol l^{-1}
PSD(i)	Moles of particles of group i	mol
T_R	Temperature in the reactor	[K]
K_R	Reaction heat capacity	kJ kg K^{-1}
Q_m	Flow rate of monomer	mol s^{-1}
MW_m	Molecular weight of monomer	gmol^{-1}
Cp_{mon}	Specific heat capacity of monomer	kJ kg K^{-1}
Cp_{pol}	Specific heat capacity of polymer	kJ kg K^{-1}
Cp_{out}	Specific heat capacity of the monomer going in and out of the reactor	kJ kg K^{-1}
T_{mon}	Temperature monomer	[K]
ΔH_r	Heat of polymerization	kJ mol^{-1}
r_{pol}	Polymerization reaction rate	-
ΔH_{jacket}	Heating through the heating jacket	kJ mol^{-1}
Q_{cond}	Reflux through the condenser	kJ kg K^{-1}
Q_{loss}	Heat losses to the surroundings	[K]
T_R	Temperature in the reactor	[K]
k'_{iwm}	Rate constant for propagation of monomeric radicals	l mol^{-1} s^{-1}
K_{pp}	Rate constant for propagation in the polymer phase	l mol^{-1} s^{-1}
k_{iwm}	Rate constant for propagation of initiator radicals	l mol^{-1} s^{-1}
K_{trm}	Rate constant for chain transfer to monomer	l mol^{-1} s^{-1}
D_{pu}	Diameter of an unswollen polymer particle	cm
M_c	Total moles of monomer charged in the reactor	mol
M_t	Total amount of monomer added to the reactor	mol
N_P	Number of particles	Adim.
G_0	Total mas of polyvinyl alcohol	mol
ν	Viscosity of the latex	Poise
ν_o	Viscosity of the water	Poise
sc	Solids content	Adim.
ρ_p	Polymer density	Polymer Handbook

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