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OPTIMAL DATA AQUISITION FOR HEAT FLOW CALORIMETER

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ABSTRACT

A number of parameters must be identified before a reaction calorimeter can be used to determine kinetic data. These parameters can be divided into calorimeter specific constants and parameters which depend on the reaction system. Within the last group some are independent of reaction extent while others vary with time. A general procedure for sequential identification of the parameters is proposed. As examples the jacket side heat transfer coefficient, the heat loss to the surroundings, and a possibly time varying heat capacity of reaction fluid are determined for a BSC-81 heat flow calorimeter controlled by a microprocessor. The recursive on-line estimation of the heat capacity is fast, accurate and requires very little core storage in the microprocessor.

INTRODUCTION

Certain problems concerning thermal hazards during the production process and in storage of either raw materials or products have lately become a major concern of the chemical companies. For this reason considerable efforts are spent in thermokinetic studies. Typical topics are,

1) Estimation of kinetic parameters in processes for which direct measurement of conversion is impractical.
2) Determination of temperature dependent process and equipment related parameter groups which must be known to ensure an economic or even a safe scale up of the process.
3) Determination of optimal temperature-time profiles for batch reactions.

All the above information is often conveniently obtained in a calorimetric study of the chemical reaction, and for this reason a number of reactor calorimeters have been developed.

Our group is investigating semibatch organic reactions with at least one fluid phase. The experiments are carried out in a microprocessor controlled isothermal calorimeter. Several bench scale instruments of this type are described in the literature (refs. 1-5) with reactor volumes between 0.1 and 2.5 liters. Ours is a 2.5 liter glass reactor design BSC-81 (ref. 15), developed by Ciba-Geigy and documented for a number of applications in references 5-15. The set-up of BSC-81 is shown schematically in Figs. 1 and 2.

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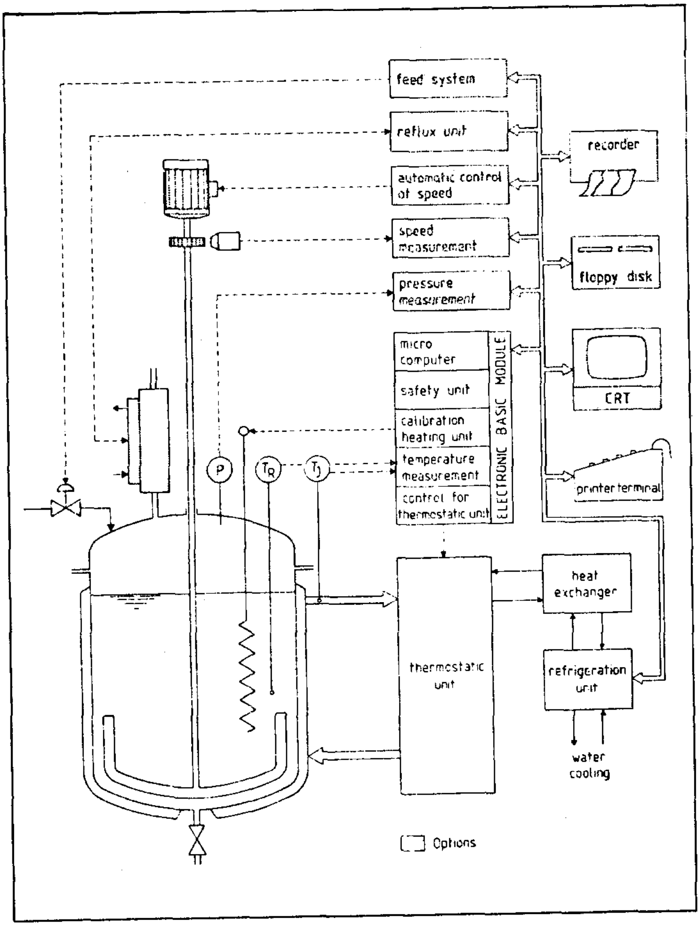

Fig. 1: Schematic representation of BSC-81

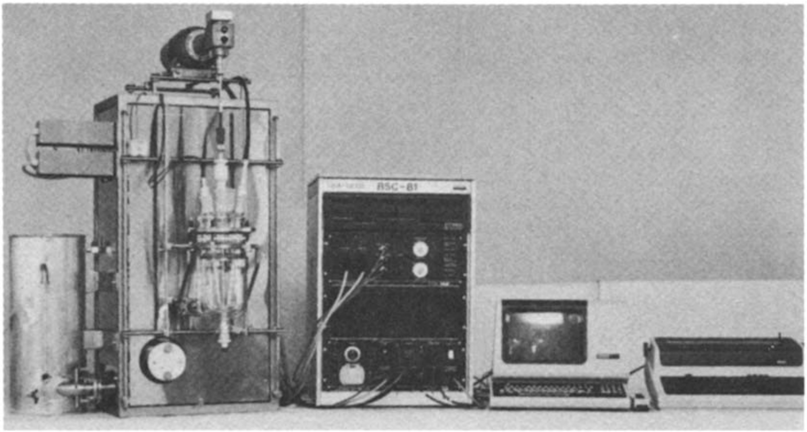

Fig. 2: Units of BSC-81

The 2.5 liter reactor is surrounded by a glass jacket (0.3 l) in which silicone oil is rapidly circulated (1 kg/s). Reactor temperature T_R and jacket temperature T_J are measured by Pt-100 resistance thermometers, and every 2 seconds digitally represented values of T_R and T_J with variances of respectively $5 \cdot 10^{-6}$ K^2 and $1 \cdot 10^{-4} K^2$ are available in the microcomputer. The response time of the thermometers is about 2.5 s.

During the reaction T_R is kept constant by manipulation of T_J, using a thermostat unit with a time constant of about 50 s. The calorimeter can operate in the range $0 < T_R < 200°C$. A resistance immersed in the reactor allows dissipation of a known amount of heat into the reactor fluid, and hence a calibration of the unit.

The control is achieved by an LSI 11/02, 30 K words fast memory microprocessor, equipped with a CRT-screen and a typewriter for communication, and with two floppy discs for storage of experimental data and process control programs. For security reasons a hardware shut-off system is superimposed on the software control system.

The processor has the following tasks:

1) On-line data acquisition and control of measurements
2) Control of T_R by calculation of a setpoint for T_J
3) Control of thermostat unit
4) Control of the user communication facilities
5) Control of the off-line calibration procedures.

Our main research goal is to develop software routines for accurate measurements, also on fast chemical reactions under non-ideal process conditions where the reactor heat capacity, the heat transfer between reactor and jacket, or the heat loss to the surroundings may be functions of reaction extent.

MATHEMATICAL MODELING

The following is demanded of the reactor model:

1) Dynamically correct estimation of the heat evolution $q_R(t)$. The estimation is to be based on the measured reactor and jacket temperature profiles $T_R(t)$ and $T_J(t)$.
2) A simple calibration procedure which should only infrequently be activated.
3) To give a fast estimation of $q_R(t)$ the model should be as simple as possible.

These requirements are satisfied by the model described below:

We adopt the very reasonable assumptions of homogeneous reactor and jacket temperatures, and of negligible response time for all temperature measurements, and obtain the following heat balances:

Reactor: $$m_R\, C_{PR} \frac{\partial T_R}{\partial t} = q_F + q_C + q_{sec} + q_R \tag{1}$$

Wall: $$\frac{\rho_W\, C_{PW}}{\lambda_W} \frac{\partial T_W}{\partial t} = \frac{\partial^2 T_W}{\partial \ell^2} \tag{2}$$

with boundary conditions: $$- \lambda_W \left.\frac{\partial T_W}{\partial \ell}\right|_{\ell=0} = h_J(T_J - T_W|_{\ell=0}) \tag{2a}$$

and $$\lambda_W \left.\frac{\partial T_W}{\partial \ell}\right|_{\ell=L} = h_R(T_R - T_W|_{\ell=L}) \tag{2b}$$

The heat flux q_F into the reactor from the glass wall separating jacket and reactor is:

$$q_F = - A\, \lambda_W \left.\frac{\partial T_W}{\partial \ell}\right|_{\ell=L} \tag{3}$$

and the heat flux q_C from the calibration heater is:

$$q_C = A_C\, h_C\, (T_C - T_R) \tag{4}$$

where the right hand side is given by a heat balance for the calibration unit:

$$A_C h_C (T_C - T_R) = ui - m_C C_{PC} \frac{\partial T_C}{\partial t} \tag{5}$$

The secondary heat effects q_{sec} are mainly connected with heat loss to the surroundings, or perhaps also with heat input from the impeller.

At steady state equation (1) simplifies to

$$UA(T_J^{\,s} - T_R^{\,s}) + ui + q_{sec}^s + q_R^s = 0 \tag{6}$$

where

$$U^{-1} = (h_R^{-1} + \frac{\lambda_W}{L} + h_J^{-1}) \tag{7}$$

The dynamic model (1)-(5) is solved by standard methods for partial differential equations (ref. 16) to give the following state space model consisting of coupled linear differential equations.

$$\frac{dx}{dt} = F\,x + G\,u \tag{8}$$

The state vector $\mathbf{x} = (T_C, T_R, T_{W1}, T_{W2}, \ldots, T_{WN})$ where T_{Wi} is the temperature at one of N selected positions in the reactor wall.

The input vector $\mathbf{u} = (T_J, ui, q_R, q_{sec})$ while the system matrix F and the input matrix G are derived from the parameters in equations (1)-(5). We may collect all parameters that enter into F and G as vector **a**:

$$\mathbf{a} = (m_C C_{PC},\ A_C,\ \frac{\rho_W C_{PW}}{\lambda_W},\ \lambda_W,\ L,\ h_J,\ A,\ h_R,\ h_C,\ m_R C_{PR}) \tag{9}$$

Finally the measurable variables are collected into vector **z**:

$$\mathbf{z} = (T_R,\ T_J,\ ui) \tag{10}$$

Discretization of the original model in the state-space formulation (8) to (10) enables us to utilize the powerful control and estimation methods attached to this representation (refs. 17, 18).

CALIBRATION PROCEDURES

On-line estimation of $q_R(t)$ requires that the parameter vector **a** is known. If **a** is time independent it can be found off-line, but in important applications of the reactor-calorimeter several components of **a** (such as the heat transfer coefficients) vary with time and have to be estimated on-line during the experiment.

We can divide the parameters into the following groups

a) Reaction independent parameters a_c which are calibrated once and for all.
b) Reaction dependent parameters a_s which are calibrated once for each experiment.
c) Time varying parameters $a_t(t)$ which are either modeled or estimated on-line.

The reaction independent parameters are

$$\mathbf{a}_c = (m_C\ C_{PC},\ A_C,\ \frac{\rho_W C_{PW}}{\lambda_W},\ \lambda_W,\ L,\ h_J) \tag{11}$$

- i.e. $\mathbf{a}_c$ is given for a given reactor construction while $\mathbf{a}_s$ depends on the investigated reaction system and on the operating conditions:

$$\mathbf{a}_s = (A,\ h_R,\ h_C,\ q_{sec},\ m_R C_{PR}) \tag{12}$$

where in principle any of the parameters in $\mathbf{a}_s$ may have to be reallocated to $\mathbf{a}_t(t)$.

The first five parameters in $\mathbf{a}_c$ are easily obtained by independent methods (physical properties of glass and a measurement of A_C and of L). To determine h_J we make an experiment under non-reacting, stationary conditions ($q_R^s = 0$, q_{sec}^s = constant) using either ui = 0 or ui $\neq$ 0. Now from (6):

$$UA = \frac{ui}{(T_J^s - T_R^s)_{ui=0} - (T_J^s - T_R^s)_{ui\neq 0}} \tag{13}$$

If A is measured out we may determine U from (13). In a wide Reynolds-number range ($500 < N_{Re} < 500000$) the reactor side heat transfer coefficient h_R depends only on the impeller speed N_{imp} (ref. 19):

$$h_R = k\, N_{imp}^{2/3} \tag{14}$$

When (14) is inserted with U into (7) we see that h_J can be estimated by linear regression of U^{-1} vs. $N_{imp}^{-2/3}$.

For any given reactor fluid we can now estimate a constant reactor side heat transfer coefficient h_R if we know A and a_c - formulas (13) and (7) are again used, and h_C can be taken to equal h_R.

Once U has been found from (13) we can obtain the secondary heat effects q_{sec} from (6). The non-jacketed part of the reactor is not insulated, and q_{sec} must vary strongly with T_R through processes which are difficult to model (condensation and reflux of reactor fluid). Consequently q_{sec} is incorporated in the model as an experimentally (reactor fluid dependent) function of T_R. We have, however, obtained entirely satisfactory results by piecewise linearization of q_{sec} over 40°C ranges in T_R.

An off-line estimation of $m_R\, C_{PR}$ can be carried out either in the time or in the frequency domain using standard methods (ref. 20), but these methods are time and storage consuming and therefore not well suited for microprocessor operation. Hence we have preferred an on-line approach by a recursive scheme:

Given an estimate $(m_R \hat{C}_{PR})_k$ for $m_R\, C_{PR}$ at time k, equation (8) predicts the temperature $\hat{T}_{R,k+1}$ at time k+1, using the measurement z_k, the constant parameters $\mathbf{a}_c$ and the remainder of the parameters in a_s.

Let $T_{R,k+1}$ deviate from $\hat{T}_{R,k+1}$:

$$\varepsilon_{k+1} = T_{R,k+1} - \hat{T}_{R,k+1} \tag{15}$$

then

$$(m_R \hat{C}_{PR})_{k+1} = (m_R \hat{C}_{PR})_k + K_C \varepsilon_k \tag{16}$$

where we use a Wiener-filter to estimate the states of the system (8).

This method is a very simple version of a family of recursive identification methods (ref. 21). Inherent in the procedure is, of course, that the predicted reactor temperature $\hat{T}_R$ should be sensitive to variations in $m_R C_{PR}$, e.g. that the difference $|\Delta T| = |T_R - T_J|$ is reasonably large.

ON-LINE ESTIMATION OF $q_R(t)$

Once we have determined $\mathbf{a}_c$ and $\mathbf{a}_s$ we can use the above procedure for estimation of $m_R C_{PR}$ to find $q_R(t)$.

Instead of (16) we use

$$\hat{q}_{R,k+1} = \hat{q}_{R,k} + K_q \varepsilon_k \qquad (17)$$

This becomes very complicated when some of the elements in a_s are time dependent. The most likely elements to change with time are

$$a_t(t) = (A,\ h_R,\ m_R C_{PR}) \qquad (18)$$

Normally A and $m_R C_{PR}$ are constant and if they change with time - as in semi-batch operation - it is best to model these changes by measurement of the feed rate. This leaves h_R as a parameter which may have to be estimated along with $q_R(t)$, and a means to do this is provided by the calibration heater which may be switched on and off during the reaction experiment.

RESULTS

We shall here report on the determination of h_J, q_{sec} and of $m_R C_{PR}$ for the BSC-81, using the above described methods with a parabolic approximation for the wall temperature T_W.

First, in Figs. 3a and 3b we show the results for $h_J(T_J)$.

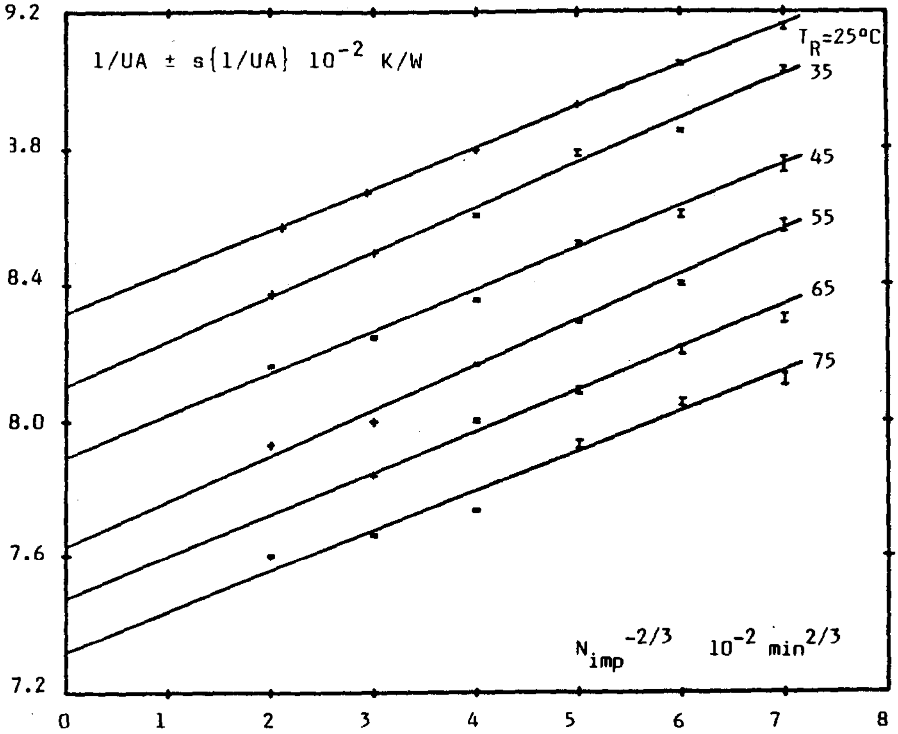

Fig. 3a: 1/UA vs. $N_{imp}^{-2/3}$. The external heat transfer resistance is given by the intersection of the straight lines with the line $N_{imp} \to \infty$

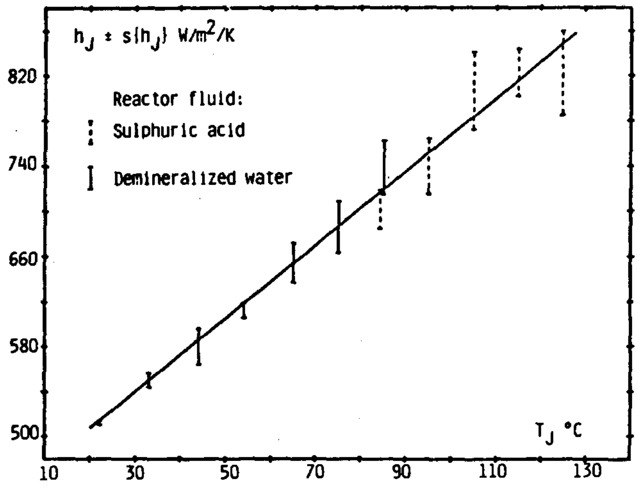

Fig. 3b: Jacket side heat transfer coefficient h_J as a function of T_J

The linearity of the log h_R vs. log N_{imp} plots in Fig. 3a strongly supports the relation (14). The intercepts which are plotted in Fig. 3b are accurate enough to give an error of less than 1% in h_J at T_J = 25°C. h_J increases with T_J since the viscosity of the jacket silicone oil decreases.

Figure 4 shows $q_{sec}(T_R)$, and it is seen that the linear approximation is satisfactory for temperature ranges less than 40°C.

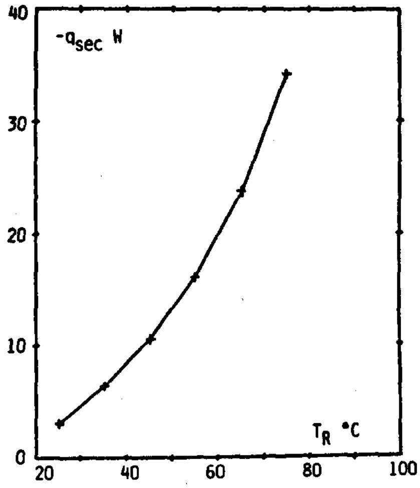

Fig. 4: Secondary heat effects in BSC-81 for 2.0 l reactor fluid (demineralized water) and impeller speed N_{imp} 200 min^{-1}

An example of a recursive $m_R C_{PR}$ estimation is shown in Fig. 5. The reactor contains 2.0 kg demineralized water and a glass impeller (immersed part: 65 g) which gives a heat capacity of $m_R C_{PR}$ = 8410 J/K. The estimation is started during the transient response of a step-change of 40°C in the setpoint for T_R. From the figure we can see that the response time for the estimation procedure is about 90 s, and that the final estimate is accurate to within 1%, and (for practical purposes) free of bias.

The theoretical standard deviation of the estimate as obtained from the variance of the measurements is

$$s_{theory} \{\hat{m_R C_{PR}}\} = 40 \text{ J/K}$$

which is in agreement with the $\hat{m_R C_{PR}}$ response of Fig. 5 where a $4 \cdot s_{theory}$-window is shown.

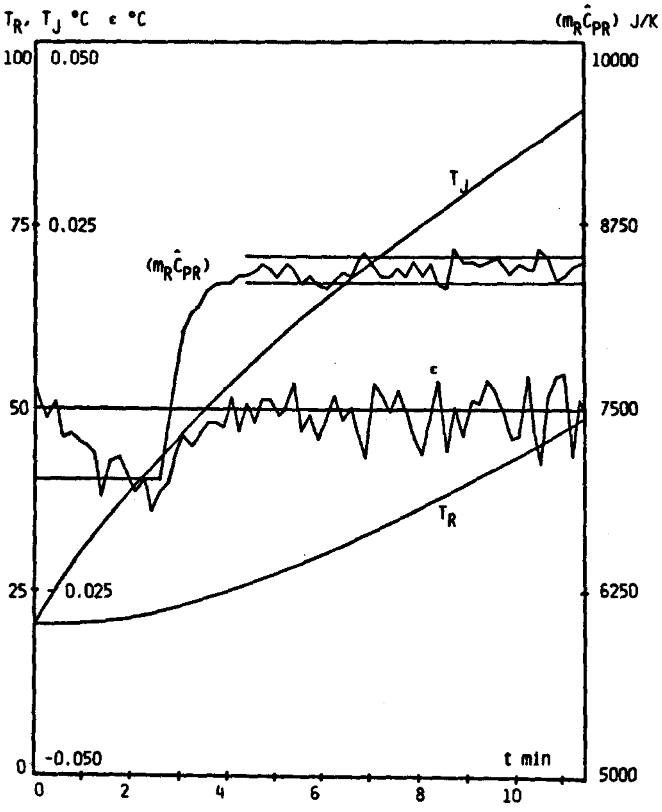

Fig. 5: Estimation of $m_R C_{PR}$

The software occupies 4K words fast memory and takes 100 ms CPU time for each estimation cyclus. The sampling period of BSC-81 is 2.0 s which leaves ample time for the estimation.

Finally, it should be noticed that the software developed to estimate $m_R C_{PR}$ is quite general and can be used also for estimation of $h_R(t)$ or $q_R(t)$.

CONCLUSIONS

1. The acceptable $m_R C_{PR}$ estimation suggests that a simple parabolic approximation for the reactor wall temperature is adequate for the dynamic reactor model.
2. Simple off-line calibration methods combined with recursive routines for time varying parameters will yield an accurate reactor model within a short estimation time period.
3. On-line estimation software requires only a small fraction of the storage and CPU capacity of the medium sized microcomputer.
4. With no extra requirement on core storage and CPU-time the estimation software can be extended to include on-line estimation of reactor heat evolution $q_R(t)$ and to track a time varying reactor side heat transfer coefficient $h_R(t)$.

This leaves the definite impression that a combination of effective mathematical modeling and modern estimation theory will be very fruitful in extending the versatility of bench scale calorimetry.

NOMENCLATURE

q_R	Reaction heat evolution
T_R	Reactor temperature
T_J	Jacket temperature
$m_R C_{PR}$	Reactor heat capacity
q_F	Heat flux from reactor wall to reactor fluid
q_C	Heat flux from calibration heater to reactor fluid
q_{sec}	Secondary heat effects
$\frac{\rho_W C_{PW}}{\lambda_W}$	Reactor wall time constant
$T_W(\ell)$	Reactor wall temperature
t	time
ℓ	Coordinate in glass wall, separating reactor and jacket. $\ell=0$ on the jacket side
L	Reactor wall thickness
h_J	Jacket side heat transfer coefficient

h_R	Reactor side heat transfer coefficient
A	Heat transfer area reactor - jacket
A_C	Heat transfer area calibration heater - reactor
h_C	Heat transfer coefficient calibration heater to reactor fluid
$m_C C_{PC}$	Heat capacity of calibration heater
ui	Energy input to calibration resistance
U	Overall heat transfer number
$\mathbf{x}$	State vector
$\mathbf{F}$	System matrix
$\mathbf{G}$	Input matrix
$\mathbf{u}$	Input vector
$\mathbf{a}$	Parameter vector
$\mathbf{z}$	Vector of measured variables
$\mathbf{a}_c$	System independent parameter vector
$\mathbf{a}_s$	System dependent parameter vector
$\mathbf{a}_t$	Time varying components of $\mathbf{a}_s$
N_{Re}	$D_{imp}\ N_{imp}\ \rho_R/\mu_R$ Reynolds number
N_{imp}	Impeller speed
D_{imp}	Impeller diameter
ρ_R	Density
μ_R	Viscosity
ε	Prediction error
K	Estimation gains
$\hat{\mathbf{x}}$	Estimated value of $\mathbf{x}$

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