On-Line Estimation of Heat Capacity of Process Fluids Using Dynamic Excitation of Temperature

by

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USING DYNAMIC EXCITATION OF TEMPERATURE

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ABSTRACT

In process control involving energy balances the heat capacity of the process fluid is needed. Although many methods for accurate heat capacity measurements are available for the laboratory, an instrument for online heat capacity measurement has yet to be successfully developed.

This paper presents such a method of online heat capacity measurement. The method is optimized with respect to the design, and a preliminary statistical analysis shows measurement accuracy is within several percent.

INTRODUCTION

Online estimation of thermodynamic properties of process fluids is a growing need in modern process industry. Those properties are needed for computer models of process operation for control and monitoring purposes. In process control involving energy balances the specific enthalpy or heat capacity is needed. Although in the past 30 years or so, heat-capacity measurements have developed from the simple ice calorimeter to advanced, high precision laboratory instruments; a reliable online instrument for process fluids has not yet been developed.

Table 1 is a list of the known methods of heat capacity measurement [6,9,13].

<table>
<thead>
<tr>
<th>Method</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothermal Shield Calorimeter</td>
<td>liquids, solids</td>
</tr>
<tr>
<td>Adiabatic Calorimeter</td>
<td>liquids, solids</td>
</tr>
<tr>
<td>Isothermal Drop Calorimeter</td>
<td>liquid, solids</td>
</tr>
<tr>
<td>Steady-Flow Calorimeter</td>
<td>gases, liquids</td>
</tr>
<tr>
<td>Temperature Pulsation Method</td>
<td>gases, liquids</td>
</tr>
<tr>
<td>Isentropic Expansion Method</td>
<td>gases</td>
</tr>
<tr>
<td>Velocity of Sound Method</td>
<td>gases, liquids</td>
</tr>
<tr>
<td>Joule-Thompson Effect Method</td>
<td>gases</td>
</tr>
<tr>
<td>Conduction Calorimeter</td>
<td>liquids, solids</td>
</tr>
<tr>
<td>Mixing Method Calorimeter</td>
<td>gases, liquids</td>
</tr>
<tr>
<td>Heat-Exchanger Calorimeter</td>
<td>gases, liquids</td>
</tr>
</tbody>
</table>

Tab. 1. Physical principles behind specific heat capacity measurements.

Of all these possible methods, four have been developed extensively to be used as precision laboratory instruments: the isothermal shield calorimeter, the adiabatic calorimeter, the drop calorimeter and the steady-flow calorimeter [6]. Of these four only the steady-flow calorimeter is applicable for the estimation of gas heat capacities, and has also been used with liquids. The heat capacity of the calorimeter is not involved in measuring heat capacities of flowing fluids since ideally under steady-state conditions the calorimeter does not change temperature during the experiment. However, the method requires a great deal of time to assure steady-state for accurate estimation. Also, the measurement of fluid flowrate is required as a separate experiment for proper accuracy.

The temperature pulsation method is an intriguing new method to measure heat capacity of gases or liquids by measuring its effect on the resistance of a tungsten wire heated by an alternating current [4.6.7.10.12]. This method uses the dynamics of heat diffusion through a tungsten wire to estimate the heat conductivity and the heat capacity of the fluid. However, use of a stagnant fluid limits the accuracy of heat-capacity estimation of gases due to the low overall heat capacity of a stagnant gas sample.

Indirect determination of specific heat has also been attempted. Three such methods are the isentropic expansion method, the velocity of sound method, and the Joule-Thompson effect method. Unfortunately, none of these has proven to be of significant use in accurate heat-capacity measurements. One of the major drawbacks of these indirect methods is that they rely on accurate P-V-T information [9,13].

Of all the general methods above, the temperature pulsation method is the only method that takes advantage of heat dynamics. Only two of these general methods are advantageously used for gases; the steady-flow calorimeter and the temperature pulsation method. For the purposes of laboratory experimentation the methods are extremely accurate; thus the experimenters have been very successful. Unfortunately, none of these methods has been successfully developed for use as an online heat-capacity measurement instrument. Also, none of the techniques uses any statistical analysis of the data beyond the fit of a straight line using least squares, and no analytic optimization of design or experimentation is attempted.

The method proposed here is a straightforward technique of dynamically exciting the process fluid temperature by oscillating the heat input. From the resulting temperature oscillations the fluid heat capacity is theoretically available for online estimation, along with the fluid flowrate, the axial dispersion coefficient, and the heat transfer coefficients. Proper design of the apparatus and choice of excitation frequencies is imperative for accurate estimation and decoupling of the parameters. Statistical analysis of the final design will prove the usefulness of the concepts proposed, i.e. the feasibility of online estimation of heat capacity and other properties of a process fluid stream.

DESCRIPTION OF A SYSTEM AND ITS GOVERNING EQUATIONS

Figure 1 shows the basic concept proposed. The process fluid is flowing past a heating coil and two thermocouples, one before and one after the heater. The temperature response observed in the fluid is a function of a whole series of
parameters and properties among which the specific heat capacity is one important one. The energy input to the heating element is changed as a predetermined cyclic function of time with fundamental frequencies chosen to best decouple the estimation of the parameters of interest.

\[ \frac{dT}{dt} = (F/p) \frac{\partial T}{\partial x} + D \frac{\partial^2 T}{\partial x^2} + (h_w \rho C_p \rho A C_p) (T_w - T) + (h_H \rho A_H \rho C_p L) (T_H - T) \]  

(1)

A second-order linear partial differential equation in time and space. The following dimensionless variables are defined:

\[ \Theta = \frac{T - T_e}{T_e} \quad \Psi = \frac{(T_w - T_e)}{T_e} \quad \Phi = \frac{(T_H - T_e)}{T_e} \quad \zeta = \frac{x}{L} \quad \tau = \frac{t}{\tau_0} \]

which leads to the following dimensionless constants:

\[ \alpha_1 = \frac{(F_o \tau_o \rho A L)}{1} \quad \alpha_2 = \frac{(D_o \rho \rho F_o L)}{4 L / d_0} \quad \alpha_3 = \frac{(h_w / F_o C_p)}{4 L / d_0} \]

where, \( \alpha_2 \) is the ratio of the mass flux transported via dispersion to the mass flux transported via the overall fluid flow, and \( \alpha_3 \) is the ratio of the power flux per degree Celsius transported through the pipe wall to the power flux per degree Celsius transported via the flow. Of specific interest are the following dimensionless parameters:

\[ P_1 = \frac{C_p}{C_p} \quad P_2 = \frac{F}{F_o} \quad P_3 = \frac{h_H}{h_H} \quad P_4 = \frac{D}{D_o} \quad P_5 = \frac{h_w}{h_w} \]

This leads to the dimensionless form of eqn (1):

\[ \frac{\partial \Theta}{\partial \tau} = - P_2 \Theta \frac{\partial \Theta}{\partial \zeta} + \alpha_2 P_4 \frac{\partial^2 \Theta}{\partial \zeta^2} + (\alpha_3 P_5 / P_1) (\Psi_1 - \Theta) + (\alpha_4 P_3 / P_1) (\Phi - \Theta) \]  

(1a)

Now, the inside wall temperature, \( \Psi_1 \), and the heating coil temperature, \( \Phi \), must be modeled.

The heating coil is a thin wire with oscillating power input, \( E \). The wire resistance is assumed to be constant (although in reality it is a weak function of temperature), and thus the wire is a single temperature at any instant in time, which is described by an ordinary differential equation:

\[ \frac{d\Phi}{d\tau} = \Omega(\tau) + \beta_1 P_3 (\Theta - \Phi) \]  

(2)

where:

\[ \beta_1 = \left( \frac{h_H}{F_o C_p} \right) \left( 4L / d_H \right) \left( \rho / \rho_H \right) \left( C_p / C_p \right) \]

and

\[ \Omega(\tau) = \left( \frac{E}{A_H} \right) \left( F_o C_p T_e \right) \left( \rho / \rho_H \right) \left( 4L / d_H \right) \left( C_p / C_p \right) \]

is a normalized power input. \( \beta_1 \) is the ratio of the energy transferred to the heating coil per degree Celsius to the energy needed to change the coil temperature a degree Celsius. \( E \) is the power input to the heating coil.

The solution to eqn (2) in the frequency domain is given by:

\[ \Phi(\omega, \tau) = H_2(\omega P_3) \Theta(\omega, \tau) + H_3(\omega P_3) \Omega(\omega) \]  

(2a)

where:

\[ H_2 = (\beta_1 P_3 + 1)^{-1} \quad H_3 = H_2(\omega P_3) / \beta_1 \]

are transfer functions, and \( \beta_1 \) is a constant.

The inside wall temperature is found by modeling the radial diffusion of heat through the wall. The energy balance on a thin element of the wall gives the following second-order linear partial differential equation:

\[ \frac{\partial \Psi}{\partial \tau} = (1/r) \left( \frac{\partial \Psi}{\partial r} \right) + \frac{\partial^2 \Psi}{\partial r^2} \quad r \equiv \left( rR / \sqrt{k} \right) \]  

(3)

Taking the Fourier transform of eqn (3) gives:

\[ \hat{r}^2 \hat{\partial} \hat{\Psi}(j \omega, r) / \hat{dr}^2 + \hat{r} \hat{\partial} \hat{\Psi}(j \omega, r) / \hat{dr} - j \omega \hat{\Psi}(j \omega, r) = 0 \]  

(3a)

The general solution of eqn (3a) is given by:

\[ \Psi(\omega, r) = c_1 \left\{ \text{ber} \left( \sqrt{\omega} r \right) + j \text{bei} \left( \sqrt{\omega} r \right) \right\} + \left( c_2 \text{ker} \left( \sqrt{\omega} r \right) + j c_2 \text{kei} \left( \sqrt{\omega} r \right) \right) \]

where ber, bei, ker, and kei, are tabulated Kelvin functions [1]. The constants \( c_1 \) and \( c_2 \) are determined by the boundary conditions. Assuming the exterior surroundings to be of constant temperature \( T_e \) and solving for \( c_1 \) and \( c_2 \) simultaneously from convective boundary conditions at \( r = r_1 \) and \( r = r_e \) the resulting transfer function between the gas temperature and the outside wall temperature is a function of the frequency \( \omega \), and of the gas-wall heat-transfer coefficient, \( P_2 \) and given by:

\[ \Psi(\omega P_3) / \Theta(\omega) = H_1(\omega P_3) \]  

(4)

Returning to the energy balance equation (1) for the gas dynamics, performing the Fourier transformation, and substi-
tuting eqns (2a) and (4) into eqn (1a) gives:

\[
d^2\Theta/d\xi^2 - (\alpha_1/\alpha_2) (P_2/P_3) \ d\Theta/d\xi - \Psi(\omega,P)\Theta
= - (\alpha_1/\alpha_2) (P_3/P_4 P_4) H_3(\omega,P_3) \Omega(\omega)
\]

(5)

The general solution of eqn (5) is given by:

\[
\Theta(\omega,\xi) = c_1(\omega) \exp(\lambda_1(\omega) \xi) + c_2(\omega) \exp(\lambda_2(\omega) \xi) + \Theta_p(\omega)
\]

(6)

where the eigenvalues \(\lambda_1\) and \(\lambda_2\) are given by:

\[
\lambda_{1,2} = (\alpha_1/2\alpha_2)(P_2/P_4) \\
\pm (1/2)[(\alpha_1 P_2/\alpha_2 P_4)^2 + 4\Psi(\omega,P)]^{1/2}
\]

(6a)

and the particular solution, \(\Theta_p\), is given by:

\[
\Theta_p = (\alpha_1/\alpha_2) (P_3/P_4 P_4) (H_3(\omega,P_3) \Omega(\omega) / \Psi(\omega,P))
\]

(6b)

The constants \(c_1(\omega)\) and \(c_2(\omega)\) are found from the inlet and exit boundary conditions as a function of frequency. To properly define these boundary conditions, the characteristic portion of eqn (6) was assumed to apply to an infinite section of pipe before and after the heating coil [15]. The boundary conditions are then given by the two compatibility conditions and the two flux balances between the three sections:

These boundary conditions are:

\[
\Theta_B = \Theta at \xi = 0 \hspace{1cm} (7a) \\
\Theta = \Theta_A at \xi = 1 \hspace{1cm} (7b)
\]

\[
(1/Peb) d\Theta_B/d\xi = (1/Pc) \ d\Theta/d\xi at \xi = 0 \hspace{1cm} (7c)
\]

\[
(1/Pc) d\Theta/d\xi = (1/PcA) \ d\Theta_A/d\xi at \xi = 1 \hspace{1cm} (7d)
\]

where \(\Theta_B\) is the gas temperature before the heating coil, and \(\Theta_A\) is the temperature after. Assuming the axial dispersion and flowrate are constant in the three sections (\(Peb = Pc = PcA\)) allows for the solution of \(c_1\) and \(c_2\). The gas temperature in the section before the heating coil is thus given by:

\[
\Theta_B = a_1 \exp(\lambda_2 \xi)
\]

(8a)

The gas temperature in the section after the heating coil is:

\[
\Theta_A = d_1 \exp(\lambda_1 \xi)
\]

(8b)

After some algebra, the transfer function between the outlet gas temperature and the power input to the heating coil may be found as a function of frequency and the parameters \(P_1\) to \(P_5\) and the design variables \(\beta\):

\[
\Theta(\omega)/\Omega(\omega) = H(\omega,P,\beta)
\]

(9)

where \(\Theta(\omega) = \Theta(\omega,\xi=1), P\) is the parameter set, \(\beta\) is the design variable set and \(\omega\) is the frequency.

**FREQUENCY RESPONSE INFORMATION**

For a given set of parameters \(P\) and design variables \(\beta\) the transfer function in eqn (9) is shown as a function of frequency, \(\omega\), in figure 3 which contains information on the order of magnitude of the various time constants of the system. The largest time constant is on the order of 1,000+ seconds which corresponds to the dynamics of the pipe wall. This demonstrates the need to wait on the order of 2-3 hours for steady-state to be assured.

The plateau between 0.001 and 0.1 hertz corresponds to the point where the wall time constant is no longer of consequence and the heater and gas time constants have not yet been predominant. The separation of these effects proves to be good design since the estimation will thus be unaffected by wall dynamics.

The second major time constant is on the order of 1 second. This time constant corresponds to the gas heat capacity, and the heating-coil dynamics. The small hump at the end of the frequency range provides information about the axial dispersion. For on-line estimation purposes only a reasonable frequency range is chosen; that is between 0.05 and 6 hertz.

The sensitivity of the frequency response curve to the parameters of interest is shown in figures 4-6. In figure 4, curve 1 is the reference, curve 2 shows a 50% increase in the flowrate from the reference, and curve 3 shows a 50% increase in the fluid heat capacity from the reference. As expected, curve 3 is simply a proportional shift of curve 1 corresponding to the proportional shift in heat capacity, i.e. dynamics provide no qualitatively new information about the heat capacity over a steady-state measurement. However, the change in the frequency response curve due to flowrate changes is a strong function of frequency. Figure 2 demonstrates that since these two effects are qualitatively different, with proper choice of excitation frequencies, the flowrate and heat-capacity estimations can be exactly decoupled.

Figure 5 shows the sensitivity of the frequency response curve to the dispersion. As expected, only at the higher end of the frequency range is dispersion significant, but in this frequency range the amount of information is heavily reduced. This is expected to cause difficulty in the estimation of the dispersion.

Figure 6 shows the sensitivity of the frequency response curve to the convection heat-transfer coefficients between the gas and pipe wall, \(h_w\), and between the gas and heating coil, \(h_h\). The latter proves to have little significance in the frequency range used since the heating-coil time constant used is 1/3 the highest frequency used. The pipe-wall heat transfer coefficient shows a strong sensitivity in the lower end of the frequency range used.

**DISCUSSION ON DESIGN VARIABLES AND PRIMARY TIME CONSTANTS**

The design variables of interest are the pipe diameter, the pipe length, the fluid flowrate, and the heating-coil design. The design constraints include a minimum Reynolds number to assure turbulent flow, and a proper ordering of the time constants to assure reasonable estimation.

The pipe length, diameter, and the gas flowrate are chosen such that the Reynolds number is greater than 5000, and the
dispersion coefficient are quite large over a wide range of the Peclet number. It is expected because axial dispersion affects the frequency response only at the high end of the frequencies used and the amplitudes are highly attenuated at such frequencies.

CASE 2: Simultaneous online estimation of flowrate and fluid heat capacity

Simultaneous online estimation of F and $C_p$ is found to be possible with relatively high accuracy. The final accuracy of such an estimation of course depends on $\sigma_T$, and the systematic errors in the a priori given parameter values: $(P_0 - P_0^T)$. Here $P_0^T = (h_w h_{H1} D)$. Since these are a priori given values, $\varphi (F)^{1/2}$ and $\varphi (C_p)^{1/2}$ are shown in Table 2 for various values of $\sigma_T$ and % errors in the a priori given parameters.

<table>
<thead>
<tr>
<th>% Error in $C_p$</th>
<th>% Error in F</th>
<th>% Error in h_w</th>
<th>% Error in $h_{H1}$</th>
<th>% Error in D</th>
<th>% Error in $\sigma_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
</tr>
<tr>
<td>9.4</td>
<td>7.5</td>
<td>-0.03</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>6.8</td>
<td>4.2</td>
<td>0.32</td>
<td>5</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>4.7</td>
<td>3.7</td>
<td>-0.03</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>3.0</td>
<td>1.8</td>
<td>0.40</td>
<td>2</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

Tab. 2. Results for case 2.

As is clearly seen in Table 2, if the $2\sigma$ error band for the random noise in the temperature amplitude measurements is reasonable, and a priori estimates for $h_w$, $h_{H1}$, and D could be calculated, then the flowrate F, and the heat capacity $C_p$ could be simultaneously estimated online with excellent accuracy.

CASE 3: Estimation of flowrate, fluid heat capacity, and heating-coil heat transfer coefficient

Table 3 is analogous to Table 2 with $h_H$ added to the regressed set. As expected the estimation of the convective heat-transfer coefficient between the gas and the heater coil is quite poor.

<table>
<thead>
<tr>
<th>% Error in $C_p$</th>
<th>% Error in F</th>
<th>% Error in $h_H$</th>
<th>% Error in $h_{H1}$</th>
<th>% Error in $\sigma_T$</th>
<th>% Error in $\rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
</tr>
<tr>
<td>12.7</td>
<td>8.6</td>
<td>95.8</td>
<td>-0.35</td>
<td>0.72</td>
<td>-0.45</td>
</tr>
<tr>
<td>6.3</td>
<td>4.3</td>
<td>47.9</td>
<td>-0.35</td>
<td>0.72</td>
<td>-0.45</td>
</tr>
<tr>
<td>4.5</td>
<td>1.8</td>
<td>24.1</td>
<td>-0.09</td>
<td>0.83</td>
<td>-0.14</td>
</tr>
</tbody>
</table>

Tab. 3. Results for case 3.

This is explained by the fact that the heating coil time constant used is quite small, thus $h_H$ doesn't affect the frequency response curve significantly in the frequency range used, 0.05 to 6 hertz.

CASE 4: Online estimation of flowrate, fluid heat capacity, and pipe-wall convective heat-transfer coefficient

Table 4 shows the estimation results for simultaneous estimation of flowrate F, fluid heat capacity $C_p$, and the convective heat-transfer coefficient between the gas and the pipe wall, $h_H$. Accurate estimation of these three parameters is a reasonable assumption of Table 4. The correlation found between F and $h_H$ is quite high. This may be reduced by more careful selection of excitation frequencies.

<table>
<thead>
<tr>
<th>Error in $C_p$</th>
<th>Error in F</th>
<th>Error in $h_H$</th>
<th>Error in $\rho$</th>
<th>Error in $\sigma_T$</th>
<th>Error in $h_H$</th>
<th>Error in $h_H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>in $C_p$</td>
<td>in F</td>
<td>in $h_H$</td>
<td>in $h_{H1}$</td>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
</tr>
<tr>
<td>11.8</td>
<td>9.4</td>
<td>15.1</td>
<td>0.36</td>
<td>-0.88</td>
<td>-0.68</td>
<td>10</td>
</tr>
<tr>
<td>6.3</td>
<td>4.7</td>
<td>7.8</td>
<td>0.35</td>
<td>-0.88</td>
<td>-0.67</td>
<td>5</td>
</tr>
<tr>
<td>5.9</td>
<td>4.7</td>
<td>7.5</td>
<td>0.36</td>
<td>-0.88</td>
<td>-0.68</td>
<td>5</td>
</tr>
<tr>
<td>2.6</td>
<td>1.8</td>
<td>3.2</td>
<td>0.34</td>
<td>-0.88</td>
<td>-0.66</td>
<td>2</td>
</tr>
</tbody>
</table>

Tab. 4. Results from case 4.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>°C</td>
<td>Fluid temperature</td>
</tr>
<tr>
<td>$T_e$</td>
<td>°C</td>
<td>Exterior surroundings temperature</td>
</tr>
<tr>
<td>$T_w$</td>
<td>°C</td>
<td>Pipe wall temperature</td>
</tr>
<tr>
<td>$T_{H1}$</td>
<td>°C</td>
<td>Heating-coil temperature</td>
</tr>
<tr>
<td>$\chi$</td>
<td>m</td>
<td>Axial coordinate</td>
</tr>
<tr>
<td>L</td>
<td>m</td>
<td>Length of pipe section containing heating coil</td>
</tr>
<tr>
<td>t</td>
<td>sec</td>
<td>Heating-coil time coordinate</td>
</tr>
<tr>
<td>F</td>
<td>kg/m²·sec</td>
<td>Mass flux of fluid</td>
</tr>
<tr>
<td>$\rho$</td>
<td>kg/m³</td>
<td>Fluid density</td>
</tr>
<tr>
<td>$\rho_H$</td>
<td>kg/m³</td>
<td>Heating-coil density</td>
</tr>
<tr>
<td>A</td>
<td>m²</td>
<td>Cross-sectional area of pipe</td>
</tr>
<tr>
<td>D</td>
<td>m²·sec</td>
<td>Axial dispersion coefficient</td>
</tr>
<tr>
<td>$h_w$</td>
<td>W/m²·K</td>
<td>Convective heat-transfer coefficient between fluid and pipe wall</td>
</tr>
<tr>
<td>$h_H$</td>
<td>W/m²·K</td>
<td>Convective heat-transfer coefficient between fluid and heating coil</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>m</td>
<td>Inside diameter of pipe</td>
</tr>
<tr>
<td>$C_p$</td>
<td>J/kg·K</td>
<td>Heat capacity of fluid</td>
</tr>
<tr>
<td>$C_pH$</td>
<td>J/kg·K</td>
<td>Heat capacity of heating coil</td>
</tr>
<tr>
<td>$V_{H1}$</td>
<td>m³</td>
<td>Volume of heating coil</td>
</tr>
<tr>
<td>$A_{H1}$</td>
<td>m²</td>
<td>Surface area of heating coil</td>
</tr>
<tr>
<td>$\omega$</td>
<td>sec⁻¹</td>
<td>Frequency</td>
</tr>
<tr>
<td>R</td>
<td>m</td>
<td>Radial coordinate used for pipe wall</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>m²·sec</td>
<td>Thermal diffusion coefficient for pipe wall</td>
</tr>
</tbody>
</table>
References:


