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APPENDICES

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APPENDIX

A.1 Description of the RC1 Reaction Calorimeter

The Mettler RC1 reactor is a bench scale calorimeter, the development of which was based on the work of Regenss. With this reactor, it is possible to run experiments in any of three operating modes, namely: (i) adiabatic mode, in which the jacket temperature (T_j) is adjusted in such a manner that the heat of reaction is conserved, i.e., there is no heat transfer through the wall of the reactor, thus operating as an isolated vessel; (ii) isoperibolic mode, where the jacket temperature is kept at a specified constant value and the reaction temperature (T_r) follows the reaction profile; and (iii) isothermal mode, in which the desired reaction temperature is set at a constant value and T_j changes automatically to maintain T_r at the specified value. There are advantages of using the RC1 reaction calorimeter to perform kinetic studies in emulsion polymerization: (i) the rate of polymerization is obtained directly, with the conversion being calculated from the integral of the heat of reaction curve; and (ii) nearly continuous information for the process is obtained (every 2 s). With this information, a detailed examination of the polymerization kinetics can be made, allowing the observation of important features which cannot be seen using any other techniques.

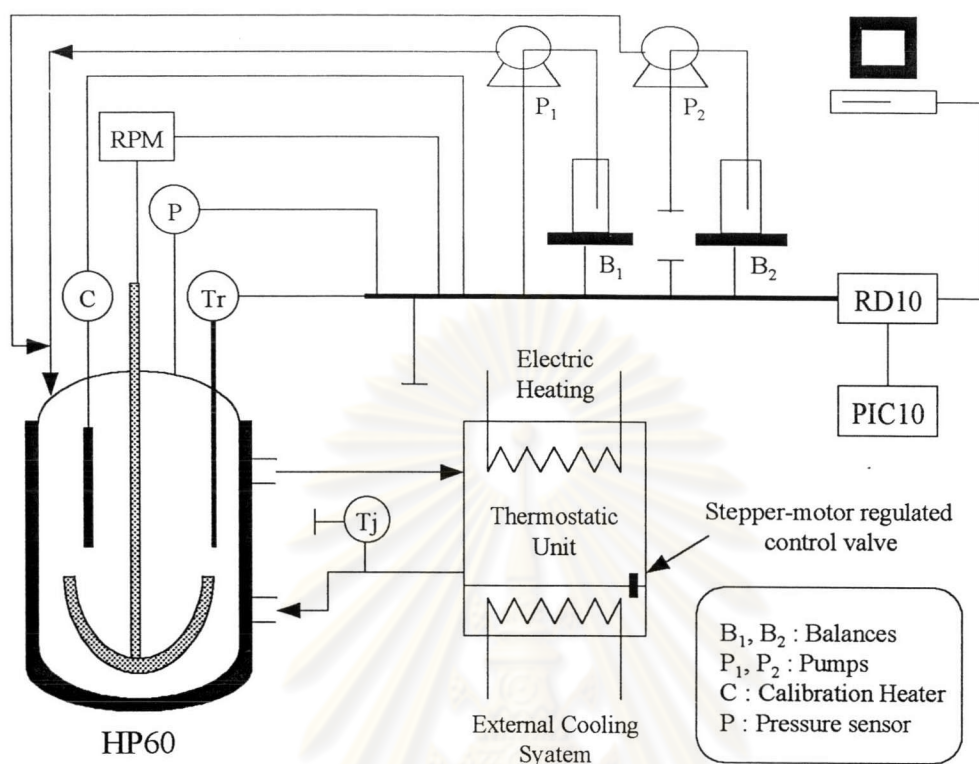


Figure A-1 Schematic skeleton of the Mettler RC1 reaction calorimeter.

A schematic representation of the RC1 reactor is shown in Figure A-1. The reactor is surrounded by a jacket, through which silicone oil flows at a high flow rate ($2 \text{ dm}^{-3} \text{ s}^{-1}$). A baffle and different types of impellers can be used. The complete RC1 system is comprised of: (i) a reactor/thermostat unit (HP60); (ii) a dosing controller (RD10); (iii) a computer; and (iv) a pressure indicating controller (PIC10). The reactor/ thermostat unit used to carry out all of the experiments reported here is a 1.5-dm^{-3} high-pressure glass reactor rated at 60 bars (HP60). The metallic cover of the reactor can be thermostated to minimize heat losses due to condensation. A magnetic drive allows operation of the impellers at speeds ranging from 50 to

2,000 rpm. A safety rupture disc located on the reactor cover prevents any damage to the reactor due to excessive pressure. The computer displays and stores data measured during the experiments by the RC1/RD10. Also, it transfers the set points and safety related parameters to the RC1/RD10. It serves as the interface between the user and the reactor. The thermostat unit controls the reactor temperature at the set point, pumping the heat transfer fluid (silicone oil) through the jacket of the reactor in a closed system. This circulation system is divided into two separate parts: the heating circulation system with electrical heating and the cooling circulation system provided by an external cooling system. Control of the reactor temperature profile is carried out by adjusting the jacket temperature, which is accomplished by activation of the electric resistances in the heating system and by supplying a cold stream of silicone oil to the heated circulation system. The coolant flow is controlled by a stepper-motor regulated control valve.

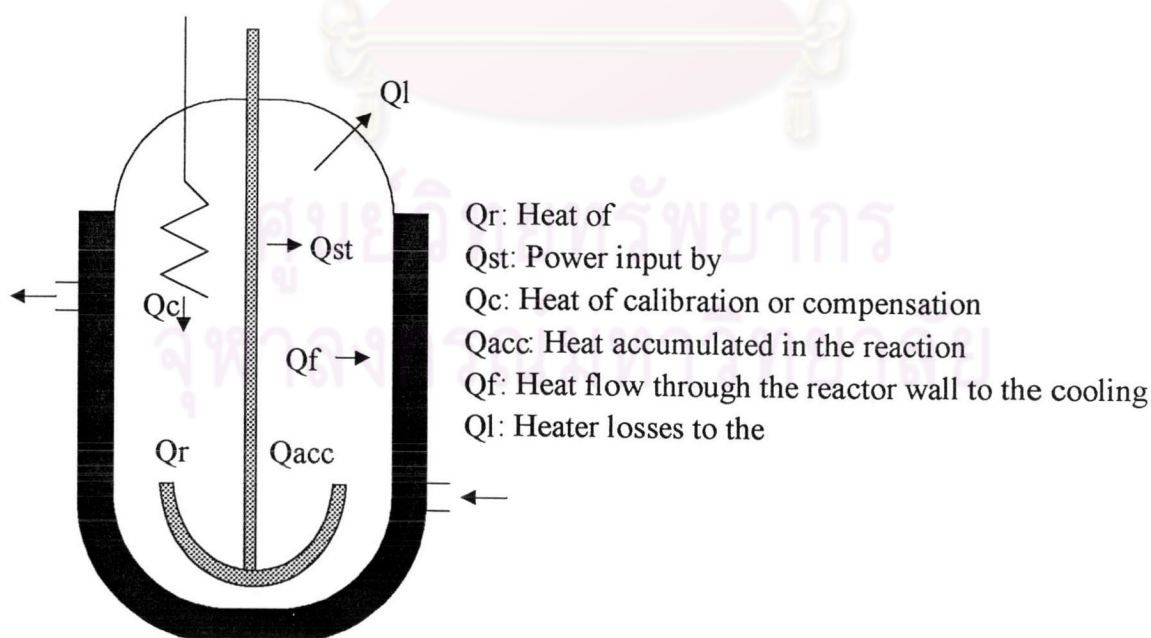


Figure A-2 Energy balance for a batch reactor without condensers.

The heating system and the control value are activated automatically by the computer. The experimental values of the variables or parameters studied (T_r , T_j , rpm, pressure, etc.) are sent to the computer at a minimum of every two seconds and are used to calculate other parameters (Q_r , Q_{flow} , dT_r/dt , etc.). All of these can be displayed on the monitor, recorded on the printer, and stored on the data diskette.

A.2 Energy Balance

The basis for calorimetry is an energy balance around the reactor. The energy terms involved in the equation are presented in Figure A-2. In this case, kinetic and potential energy terms are neglected, the reactor and jacket temperatures are considered homogeneous, and the reaction system is regarded as perfectly mixed. The energy balance for a batch process is then given by eq. (A-1):

$$Q_r + Q_{\text{st}} + Q_c = Q_{\text{acc}} + Q_f + Q_i \quad (\text{A-1})$$

where the heat of reaction is calculated by eq. (A-2):

$$Q_r = V_{\text{aq}} \Delta H_p R_p \quad (\text{A-2})$$

where V_{aq} is the volume of water in the system (dm^{-3}); ΔH_p is the heat of polymerization of the monomer (J mol^{-1}) used; and R_p is the rate of polymerization ($\text{mol dm}^{-3} \text{s}^{-1}$).

The heat input by the stirrer is given by:

$$Q_{\text{st}} = P_o N^3 d^5 \rho \quad (\text{A.3})$$

where P_o is the power number; N is the stirrer speed; d is the diameter of the impeller; and ρ is the density of the system. The accumulated heat of reaction is calculated by:

$$Q_{\text{acc}} = [(mC_p)_R + (mC_p)_i] dT_r/dt \quad (\text{A-4})$$

where $(mC_p)_R$ and $(mC_p)_i$ are the masses and the heat capacities of the reaction mixture and inserts, respectively, whereas dT_r/dt is the derivative of the reaction temperature. The heat flow through the reactor wall to the cooling system is given by:

$$Q_f = UA\Delta T \quad (\text{A-5})$$

where U is the overall heat transfer coefficient ($\text{W m}^{-2} \text{ }^\circ\text{C}^{-1}$), A is the wet area (m^2), and ΔT is the difference between the reaction and jacket temperatures.

From eq. (A-2), it is seen that the rate of reaction is directly proportional to the measured heat evolved. This is valid only for single reaction or when one of the reactions in a scheme dominates the other ones, which is the case for a free radical or chain polymerization process.

Heat losses to the surroundings, Q_l , and Q_{st} are considered in the baseline, Q_b , which is the initial Q_r signal under no reaction and calibration conditions, U is measured by performing calibrations in which a known and constant amount of energy (approximately 24 J s^{-1}) is applied to the system for a period of 10 min. During this period, T_r is constant and no reaction occurs, thus U is simply a function of ΔT and the heat of calibration, Q_c ; $(mC_p)_R$ is calculated by performing temperature ramps. Q_r is then calculated using the following equation:

$$Q_r = UA (T_r - T_j) + (mC_p)_T dT_r/dt + Q_b \quad (\text{A-6})$$

Thus, the rate of polymerization can be calculated directly by measuring the parameters in eq. (A-6) and combining the result with eq. (A-2). The extent of conversion in the RC1 reaction calorimeter at any time is calculated using the expression in eq. (A-7):

$$X_r = \frac{\int_0^t Q_r dt}{t_f \int_0^{t_f} Q_r dt} \quad (\text{A-7})$$

where X_r is a relative calorimetric conversion. The integral in the numerator is the partial heat of reaction evolved at time t , and the integral in the denominator is the total heat of reaction at the end of the polymerization or at t_f . As one can see, for $t = t_f$, X_r will be always equal to one, which is not likely to be the true final conversion (X_f)

in an emulsion polymerization. Thus, it is necessary to introduce a correction factor to obtain the actual calorimetric conversion (X_c). The latter is defined as:

$$X_c = \frac{\int_0^t Q_r dt}{M_{A_0} \Delta H_p} \quad (\text{A-8})$$

where M_{A_0} is the initial moles of component A , and ΔH_p is the heat of polymerization whose value can be obtained from the literature or be determined by:

$$\Delta H_p = \frac{\int_0^{t_f} Q_r dt}{M_{A_0} X_{gf}} \quad (\text{A-9})$$

where X_{gf} is the final conversion determined by an independent measurement (e.g., gravimetry). Substituting eq. (A-9) in eq. (A-8), and combining the result with eq. (A-7), the corrected or real calorimetric conversion (X_{rc}) is obtained, which is given by:

$$X_{rc} = \frac{\int_0^t Q_r dt}{\int_0^{t_f} Q_r dt} X_{gf} = X_r \times X_{gf} \quad (\text{A-10})$$

Then, to obtain the calorimetric fractional conversion, it is simply necessary to multiply the relative conversion values given by the RC1 reaction calorimeter by the final gravimetric conversion.

VITA

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