Polymerization Technology – Laboratory

Reaction Calorimetry

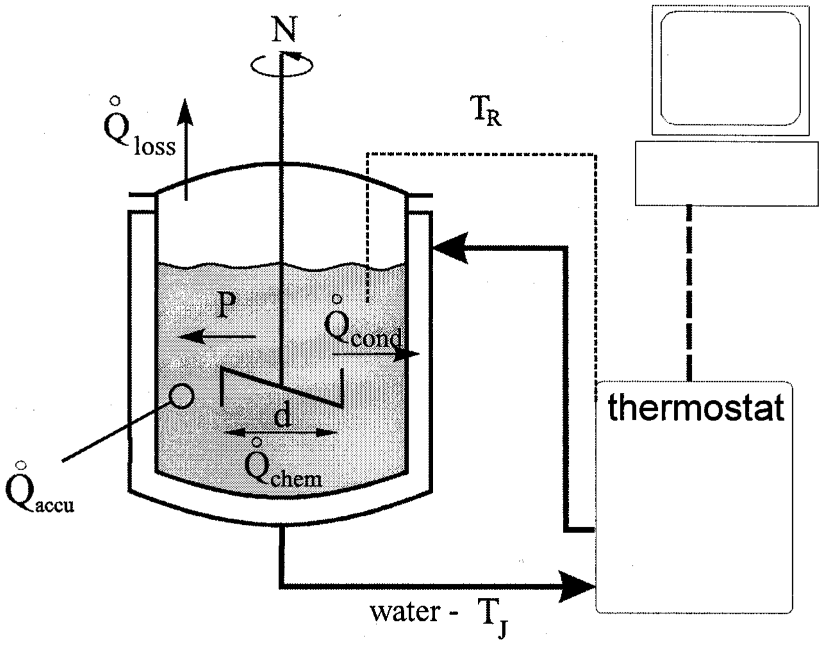
1. Subject

Isothermal and adiabatic emulsion polymerization of methyl methacrylate in a batch reactor.

2. Theory

2.1 Isothermal and adiabatic calorimetry

The most important information needed for the reactor design for polymerization reactions is the heat emission of the reaction over the time. A good heat dissipation to the cooling system is necessary to avoid accidents. In many cases, literature data are not available for the desired reaction, so that own measurements have to be done. For measurements in the laboratory scale, reaction calorimetry is a practical method. This method measures the chemical heat flow of a reaction which is proportional to the reaction rate.
In general, the measurements are done in a stirred tank reactor with a thermostat and a computer. Temperature sensors are placed in the reactor (in the reaction mass) and in the outer cooling jacket. The thermostat measures the inner temperature and regulates the jacket temperature in the desired way.



The general heat flow balance of the calorimeter is given as follows

$$\boxed{\dot{Q}_{chem}[W] = \dot{Q}_{accu} + \dot{Q}_{cond} + \dot{Q}_{loss} - \dot{Q}_{el} - P}$$

$\dot{Q}_{chem} = V_R(-\Delta H_R)r$	reaction heat flow

V_R = reaction volume,
ΔH_R = reaction enthalpy,
r = reaction rate

$\dot{Q}_{accu} = C_p \frac{dT_R}{dt}$	heat storage in the reaction mass

$C_p[J/K] = \sum_i c_{p,i} m_i$ = heat capacity of the reaction micture

$\dot{Q}_{cond} = U \cdot A(T_R - T_J)$	conuctive heat flow through the wall to the cooling jacket

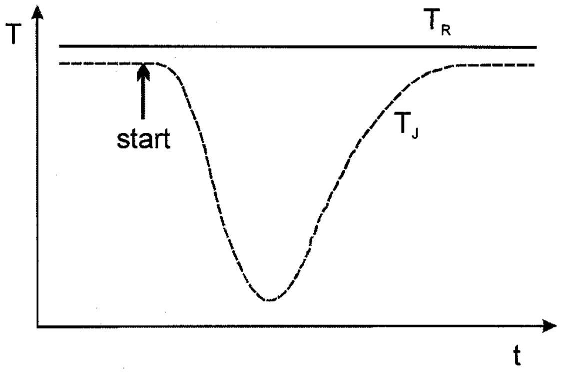
U = overall heat transfer coefficient [$W/(K \cdot m^2)$],
T_R = temperature of the reactor,
T_J = temperature of the jacket,
A = area of the jacket

$\dot{Q}_{loss}$	loss heat flow to the environment
$\dot{Q}_{el}$	heat flow given in the reactor with an electric heater for calibration
P	heat flow produced by stirring

Now we look at two special cases to control a polymerization reaction

a) isothermal

In the isothermal case the reaction mass is kept at contant temperature obver the whole reaction time. For that reason an occurring heat flow, produced by chemical reaction, must be absorbed to the cooling jacket. Thus the jacket will immediately be cooled down by the thermostat, when the reaction starts.



In the isothermal case the general heat flow balance can be reduced to

$$\dot{Q}_{chem} = \dot{Q}_{cond} - P = U \cdot A(T_R - T_J) - P$$

Heat storage in the reaction mass does not occur, because it is kept at constant temperature. The loss heat flow is neglected and if the viscosity of the reaction mass remains low (as it is the case in an emulsion polymerization), the heat flow produced by the stirrer can be neglected, too. In practice, a strictly constant temperature in the reaction mass cannot be reached. Therefore, the storage or accumulation term cannot be neglected.
Before an experiment is started, the product of the overall heat transfer coefficient with the jacket area $U{\cdot}A$ has to be determined. The calibration is done by providing a defined heat flow to the reactor by means of an electric heater:

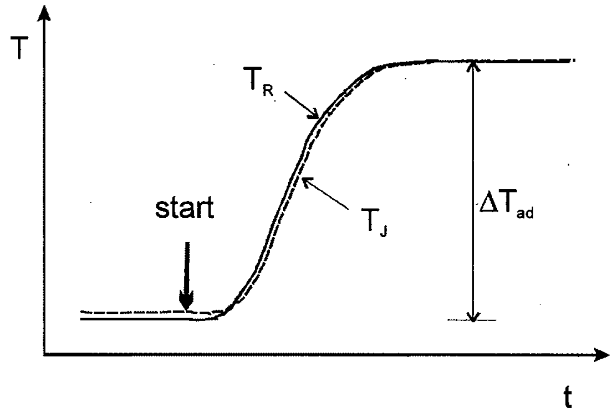
$$U \cdot A = \frac{\dot{Q}_{el}}{(T_{R,heating} - T_{J,heating}) - (T_R - T_J)}$$

$T_{R,heating}, T_{J,heating}$ = reactor, jacket temperature when electric heater is on

The calibration is done one time before and one time after the reaction in order to see if any alterations occur during the reaction. The heat transfer coefficient might change due to precipitated polymer covering the reactor wall.

b) adiabatic

In this case the jacket temperature is set to the same temperature as the reaction mass. If the temperature in the reaction mass increases by chemical reaction the jacket temperature does also! In an ideal case no heat flow from the reactor to the jacket occurs because both of them have the same temperature.



The heat balance is

$$\dot{Q}_{chem} = \dot{Q}_{accu} - P = C_p \frac{dT_R}{dt} - P$$

The detected temperature is proportional to the conversion of the reaction if only one reaction occurs. In general, an isothermal control of the polymerization reaction is desired in the industrial

scale because no temperature rise in the reactor influences the reaction. The function of adiabatic calorimetry is the simulation of the worst case scenario in a small laboratory scale, i.e., failure of the cooling system and uncontrolled increase of temperature in the reactor.
The adiabatic temperature difference ΔT_{ad} is the maximum heating of the reactor by its own reaction.

2.2 Determination of kinetic data

By determination of the heat flow of the reaction, the reaction enthalpy ΔH, the conversion X and rate of conversion dX/dt can be calculated:

$$\frac{dX}{dt} = \frac{\dot{Q}_{chem}}{\int_{t_0}^{t_{end}} \dot{Q}_{chem}\,dt} \qquad X(t) = \frac{\Delta H(t)}{\Delta H} = \frac{\int_{t_0}^{t} \dot{Q}_{chem}\,dt}{\int_{t_0}^{t_{end}} \dot{Q}_{chem}\,dt}$$

t_0 and t_{end} are the times of the beginning and of the end of the measured heat flow peak (integration limits). $\Delta H(t)$ is the reaction enthalpy at time t (partial peak area) and ΔH is the complete enthalpy of the reaction (complete peak area).
The ideal case is simple: only one kind of reaction and 100% conversion. In practice, however, simultaneous reactions occur and 100% conversion is not reached! Therefore, the measured heat flow is the sum of the heat flows of all occurring reactions.

2.3 Wilson plot

The Wilson plot is a method for determining heat transfer data and geometric data of a given reactor. The product of overall heat transfer coefficient and jacket surface is measured in dependence on the stirrer speed N

$$U \cdot A = \frac{\dot{Q}_{el}}{(T_{R,heating} - T_{J,heating}) - (T_R - T_J)} = f(N)$$

Please, become familiar with this method by reading the attached literature.

3. Experimental

1st Day: Isothermal reaction

The recipe for the MMA emulsion is given to you by the assistant.

MMA (methyl methacrylate): __________________ g

H_2O: __________________ g

SDS (sodium dodecylsulfate): __________________ g

AIBA: __________________ g

The emulgator SDS is dissolved in water. Then MMA is added and the mixture is filled to the reactor and degassed by nitrogen for 30 *min*. The reactor is heated at 50°*C* and the calibration is done with the electric heater. When the thermical equilibrium is reached again after switching off the heater, the dissoluted initiator can be injected into the reactor by using a syringe. The temperatures of reactor and jacket are displayed on the computer screen. If the reaction has ended the electric heater is switched on again for the second calibration.

2nd Day: Wilson plot and adiabatic reaction

a) Wilson plot

The Wilson plot is done with water. A defined heat flow is applied to the reactor by the electric heater. Five different $U \cdot A$-values should be measured by varying the stirrer speed between 150 and 500 rpm.

b) Adiabatic reaction

Recipe for the MMA emulsion:

MMA (methyl methacrylate): ________________ g

H_2O: ________________ g

SDS (sodium dodecylsulfate): ________________ g

AIBA: ________________ g

The preparation is done in the same way as in the isothermal case. Calibration is not necessary.

4. Analysis and report

Please give a short theoretical summary of the method and the used equations and a description of the experiments.
Calculate the conversion rate and the conversion over the time for the isothermal and the adiabatic case. Determine the reaction enthalpy from the isothermal experiment and compare with literature data.
What are the advantages and the disadvantages of this method? What simplifications were made? Please discuss possible errors!
Evaluate the Wilson plot as shown in the attached literature.

Data: $\Delta_R H$ = - 55.1 kJ/mol; $c_{p,MMA}$ = 1.5 J/(g · K); $c_{p,water}$ = 4.18 J/(g · K),
M_{MMA} = 100.12 g/mol

Attachment:

~~case estimate of the temperature rise~~ which will occur when heat removal fails.

From *Fig. 4, b*, we see that (not surprisingly) for a second-order reaction, the feed duration must be increased by a factor 4 to halve accumulation.

Fig. 5, a shows calculated runaway scenarios, where the heat of the desired reaction causes the total temperature rise (cooling failure and stop of feed after 0.5 and 1.0 equiv. of B are fed). *Fig. 5, b* shows the case, where the temperature rise caused by near adiabatic conversion of accumulated reactants of the desired reaction triggers an exothermic decomposition. Here, the heat from the desired reaction drives the temperature of the mass into a range where the decomposition reaction is fast enough to become dangerous. The main heat comes from the decomposition reaction.

For simulation, the following parameters were assumed (SR = synthesis reaction, D = decomposition):

- rate constants [h^{-1}] at 100° (process temperature): SR: $k\cdot c_{A0}$ = 1; D: k = $2.5\cdot 10^{-4}$.
- Temperature rise for adiabatic conversion: SR: 200 K (80 K for *Fig. 5, b*); D: 500 K.
- Activation energy [kJ/mole]: SR: 60; D: 100.

When we detect unacceptable accumulation, we have to modify the process procedure, be it by elongation of the feed duration or by increasing the reaction temperature, or both. This often affects selectivity and, worse, product quality. This may lead to a whole new development effort. It is therefore advisable to consider the safety aspect mentioned above early in a process development project.

It has become a (questionable) custom to request a run in a heat flow calorimeter at the end of laboratory work before a new ~~process procedure is introduced on industrial scale. This is a feasible way to avoid~~ the worst. Early consideration of thermal effects ~~and~~ appropriate analysis of the ~~situation would be more effective.~~

3.2. *Heat Transfer Issues*

Heat transfer is obviously an important function in chemical processes. We need data and understanding for

- safety analysis,
- optimization of process procedures,
- design of new equipment and assessment of existing equipment.

There is excellent literature on heat transfer mechanisms and heat transfer data. In most cases, no measurements are needed for solving heat transfer problems in process development. The fact is that we often ignore or neglect heat transfer issues. Thus, the main virtue of applying heat flow calorimetry is the fact that it creates awareness of heat transfer problems.

3.2.1. *Film Heat Transfer Coefficients of Process Fluids*

The film heat transfer coefficient at the boundary of a turbulent liquid is correlated by the *Nusselt* relation:

$$Nu\ (= h\cdot d_v/\lambda) = \text{const.}\cdot Re^{2/3}\cdot Pr^{1/3} \tag{1}$$

Nu = *Nusselt* number
Re = *Reynolds* number = $N\cdot d_s^2\cdot \rho/\eta$
Pr = *Prandtl* number = $\eta\cdot c_p/\lambda$
h = film heat transfer coefficient [W/(m^2 · K)]
η = dynamic viscosity [Pa · s]
λ = thermal conductivity [W/(m · K)]
ρ = density [kg/m^3]
N = stirrer speed [s^{-1}]
d_v = diameter of vessel [m]
d_s = diameter of stirrer [m]
c_p = specific heat [J/(kg · K)]

For pure liquids, reliable estimates of the film heat transfer coefficient are possible, based on data obtained from physical property estimation packages. For viscous slurries, this is not the case. Here, an experimental determination based on *Eqn. 1* is advisable. By rearranging it, we obtain

$$h = \underbrace{\text{const.}\bullet\frac{N^{2/3}\bullet d_s^{4/3}}{d_v\bullet g^{1/3}}}_{\text{engineering data of the reactor}}\bullet\underbrace{\sqrt[3]{\frac{\rho^2\bullet\lambda^2\bullet c_p\bullet g}{\eta}}}_{\text{physical properties of reactor contents}} = z\bullet\gamma \tag{2}$$

with g = gravitational acceleration [m/s^2]

Here, h is the product of two factors, one of the depending only on equipment geometry and operation (the stirrer speed), the other only on physical properties of the sample.

In a stirred-tank heat flow calorimeter with heat flow control by wall-temperature adjustment (see *Sect. 4.1*), we determine the overall heat transfer coefficient (or its inverse, the overall heat transfer resistance) by measuring the temperature difference required to remove a known imposed heat release (electric heating) (*Fig. 6*). Since the heat transfer resistance of inner film, wall and outer film add

$$\frac{1}{U} = \underbrace{\frac{1}{h_s}}_{\text{depends on reaction mass}} + \underbrace{\frac{d_w}{\lambda} + \frac{1}{h_j}}_{\text{depends on reactor}} = \frac{1}{h_s} + \frac{1}{\varphi} \tag{3}$$

we can easily determine the sample film coefficient. This is preferably done by means of the *Wilson* plot [5][6] (*Fig. 7*): We vary the stirrer speed N and plot the inverse of the overall heat transfer coefficient U over $N^{-2/3}$, first with a liquid of known γ to determine the heat transfer data of wall and outer film, $1/\varphi$, and the geometric factor z of the calorimeter vessel, then with the sample to determine its γ-value. The same procedure can be applied to determine φ and z of industrial vessels, if they are equipped with a variable speed stirrer drive.

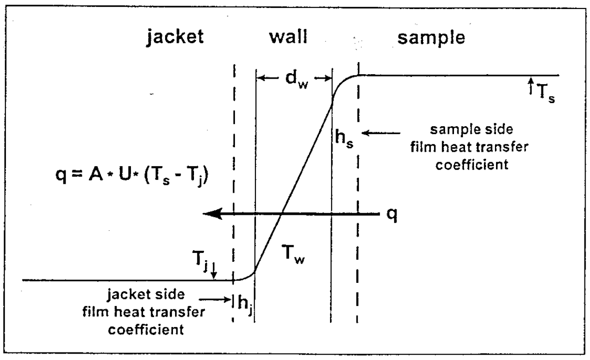


Fig. 6. *Heat transfer through wall of stirred vessel*

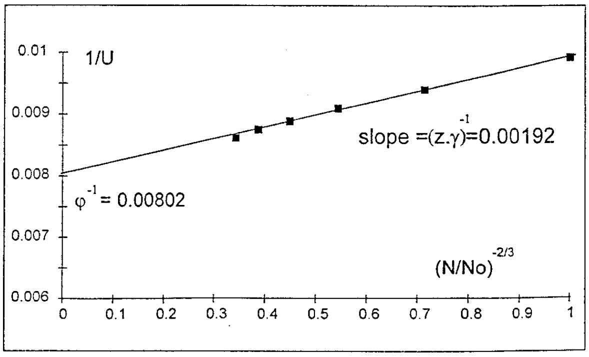


Fig. 7. Wilson *plot* (Courtesy of *F. Stoessel*)