

Investigation of adiabatic batch reactor

Introduction

The theory of chemical reactors is summarized in instructions to „Investigation of chemical reactors”. If a reactor operates adiabatically then no heat is transferred to or from the reactor. The temperature of the reaction mixture will rise (exothermic reaction) or fall (endothermic reaction) as the reaction proceeds. If it is feasible, adiabatic operation is to be preferred for simplicity of design.

Adiabatic batch reactor

Batch reactors are stirred vessels or autoclaves. The reaction mixture is perfectly mixed. Because of the uniformity of concentration and temperature the balance equations may be written for the entire reactor volume.

The material balance equation for a constant volume batch reactor becomes:

$$v_j r = \frac{dc_j}{dt} \quad (9.3-1)$$

The heat balance taken over the whole reactor is:

$$rV(-\Delta H_R) = (V\rho c_{pf} + mc_{pr}) \frac{dT}{dt}, \quad (9.3-2)$$

where v_j stoichiometric coefficient of component j,
 r rate of reaction ($\text{mol/m}^3\text{s}$),
 c_j concentration (mol/m^3),
 t reaction time (s),
 V volume of the reacting mixture (m^3),
 ΔH_R heat of reaction (J/mol),
 ρ density of reacting mixture (kg/m^3),
 c_{pf} specific heat capacity of reacting mixture (J/kgK),
 m mass of reaction vessel (kg),
 c_{pr} specific heat capacity of vessel (structural material) (J/kgK),
 T temperature of the reaction mixture (K).

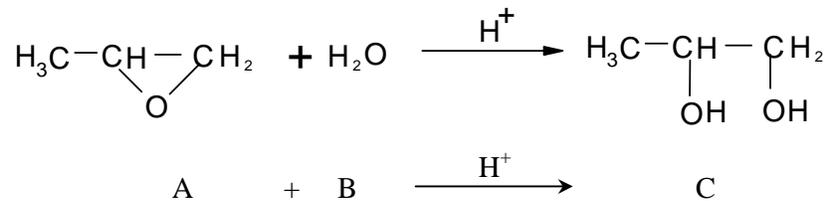
If the reaction is carried out adiabatically the heat released by the reaction is retained as sensible heat in the reactor. The temperature at any time is determined by the heat balance. Since rate of reaction increases exponentially by increasing temperature (the Arrhenius equation represents the temperature dependency of the reaction rate), the reaction rate and the release of heat becomes very fast at the beginning of reaction. Finally, as the reactants are consumed by reaction the rate slows down and the temperature approaches its final value. The heat balance shows that the temperature at any stage in the reaction can be expressed in terms of the conversion only. Substituting of the reaction rate into the heat balance equation and integrating it we have:

$$T - T_0 = \frac{(-\Delta H_R) V c_{j0}}{|v_j| (V\rho c_{pf} + mc_{pr})} X \quad (9.3-3)$$

where T_0 and c_{j0} are the initial temperature and initial concentration, respectively.

The reaction investigated

For investigation of the adiabatic operation the hydrolysis of propylene oxide was selected. The conversion of propylene oxide to propylene glycol is catalyzed by mineral acids. This reaction is exothermic. At low reactant concentrations of the reactant ($c_{\text{propylene oxide}} < 3 \text{ mol/dm}^3$) the only product is propylene glycol.



The reaction was investigated experimentally and it was found that the reaction rate can be expressed as:

$$r = k c_A c_B c_{\text{H}^+}, \quad (9.3-4)$$

ahol k rate coefficient,
 c_A concentration of propylene oxide (mol/m^3),
 c_B concentration of water (mol/m^3),
 c_{H^+} composition of hydrogen ion (mol/m^3).

In a dilute aqueous solution, where a large excess of water is present the reaction is irreversible and pseudo-first order with respect to propylene oxide, since the catalyst concentration remains constant. According to previous experiments carried out at our Department the variation of the reaction rate with temperature and composition can be expressed as :

$$r = 6.351 \cdot 10^{11} \exp\left(-\frac{75150}{RT}\right) \cdot c_{\text{H}^+} \cdot c_A \quad (\text{kmol/m}^3\text{s}), \quad (9.3-5)$$

where R is the gas constant ($R = 8.314 \text{ (J/mol K)}$). The heat of reaction is: $\Delta H_r = -78400 \text{ (J/mol)}$.

Equipment

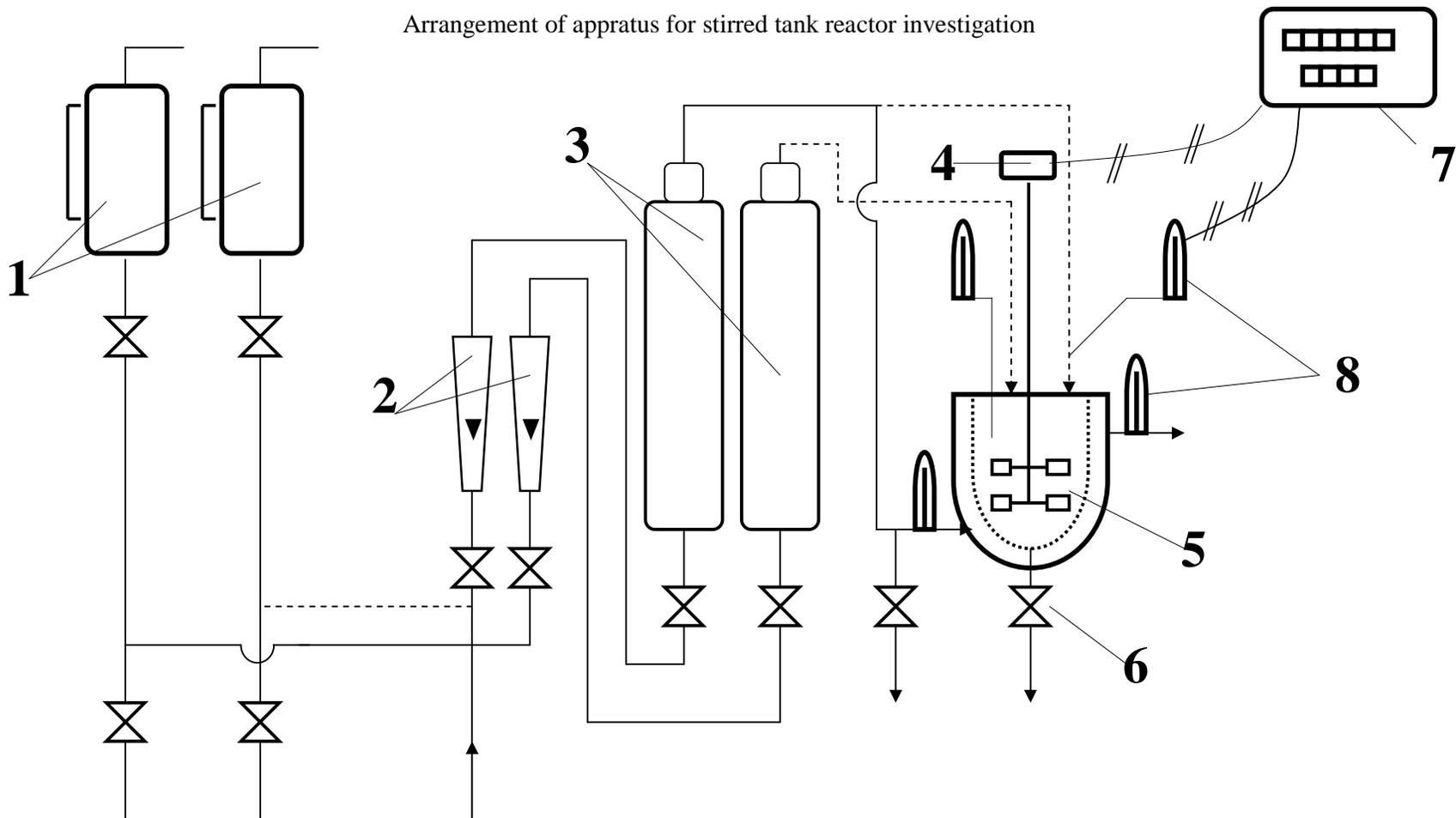
The experimental set-up is shown in Figure 1.

The geometry of the stirred tank reactor:

- reactor I.D.: 150 mm
- volume of reaction mixture: 3 dm^3
- height of the liquid: 200 mm

The stainless steel stirred tank reactor is jacketed for heating or cooling. For prevention of any heat losses the vessel is insulated in glass-wool and aluminum foil. Two impellers (six bladed standard turbine type, diameter 70.6 mm) are mounted on a common shaft. The shaft should be cooled in operation. The stirring speed is variable in a wide range. The unit can be operated batchwise or continuously. In continuous operation the reactants are fed from overhead storage tanks through rotameters. The streams are heated in heat exchangers to the desired temperature. The temperatures are measured at the inlet and inside the tank and are controlled by a PID controller. The outlet line is an overflow near the top of the tank. The vessel can be emptied and the samples are taken at the bottom through the sampling valve.

Arrangement of apparatus for stirred tank reactor investigation



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| 1. Storage tanks | 5. Reactor | — batch |
| 2. Rotameters | 6. Sampling valve | - - - continuous |
| 3. Heat exchangers | 7. Controller | |
| 4. Agitator motor | 8. Thermometers | |

Procedure

Approximately $1.5 - 2.5 \text{ mol/dm}^3$ propylene oxide solution is prepared. The total volume of the reaction mixture in the tank should be 3.05 dm^3 . The amount of sulfuric acid should be calculated so that the composition of hydrogen ion in the mixture should be 0.01 mol/dm^3 . The propylene oxide solution is charged into the tank. A sample is taken for determination of the initial concentration (c_{A0}). The stirrer speed is adjusted. The cooling of the shaft and the reaction mixture is started. For convenience the initial temperature (T_0) should be about 10°C . Once the desired temperature has been achieved the calculated amount of H_2SO_4 solution is added and the reaction time is measured. About 3 – 4 g samples are taken at 5 minute intervals from the reaction mixture and the propylene oxide composition is determined by titration. At every sampling the temperature is registered too.

Determination of propylene oxide:

For determination propylene oxide 25 cm^3 of standardized 0.2 mol/dm^3 HCl solution saturated with CaCl_2 is added into a flask and weighed. The sample taken from the reaction mixture is added to the flask and weighed again. The reaction mixture sample should always kept small enough so that the HCl will be in excess. The flask is allowed to stand at room temperature for 15 – 20 minutes necessary to ensure complete reaction of propylene oxide with HCl. Finally, the excess of HCl is determined by titration with standardized 0.1 mol/dm^3 NaOH solution using 2 – 3 drops of phenolphthalein indicator. Parallel to every third sample a blind titration should be carried out.

Treatment of data

Calculate the fractional conversion of propylene oxide

$$X = \frac{c_{A0} - c_A}{c_{A0}}$$

By the calculation of the actual concentration of propylene oxide please note that the sulfuric acid consumes some NaOH solution.

The material balance (9.3-1) and heat balance (9.3-2) equations can be solved simultaneously by using a 4th order Runge-Kutta method. The following input data should be added for calculation of the concentration and temperature values at different times:

- initial temperature (K),
- initial propylene oxide concentration (mol/dm^3),
- density of mixture (kg/m^3),
- specific heat of mixture (kJ/kgK),
- volume of mixture (m^3),
- activation energy, $E = 75150 \text{ (J/mol)}$,
- heat capacity of the tank, $m \cdot c_{pr} = 1.652 \text{ (kJ/K)}$,
- heat of reaction, $\Delta H_R = -78400 \text{ (J/mol)}$,
- preexponential factor, $\text{preexp} = 6.35 \cdot 10^9 \text{ (1/s)}$,
- reaction time, $t_{\text{max}} \text{ (s)}$,
- time interval (sampling), $L \text{ (s)}$.

Compare the measured values with the predicted ones by construction the following graphs:

- Plot the propylene oxide concentration versus time,
- Plot the conversion versus time,
- Plot the temperature versus time,
- Plot the temperature against propylene oxide concentration.

Reporting

Set up a table with the measured data!

Date:

Amount of propylene oxide = ml, g,

Amount of H₂SO₄ = ml, g,

c_{H2SO4} =

Volume of the reaction mixture = dm³

T_{before cooling} = °C; T₀ = °C

Stirrer speed = Hz = 1/min

Initial concentration of propylene oxide = mol/dm³

sample	time (min)	T (°C)	HCl (ml) c= f=	flask + HCl (g)	flask + HCl + sample (g) or net sample (g)	NaOH (ml) c= f=	Blind sample titration			
							sample	flask (g)	sample (g)	NaOH (ml)