Multiplicity in CSTRs

ChE-409 Chemical Engineering Lab & Project

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TP 2.2

2025

This TP aims to study the stability of a CSTR during an exothermic reaction. The kinetic properties of the decomposition of hydrogen peroxide will be measured and used to simulate the behavior of a CSTR at steady state. Depending on reaction conditions, multiple steady states could be observed.

MAIN TARGETS

- Measurement of hydrogen peroxide decomposition parameters
- Simulation of CSTR steady state behavior
- Operation of CSTR and investigation on CSTR hysteresis

TABLE OF CONTENTS

1. INTRODUCTION

1.1 Steady state behavior in CSTRs

Continuous stirred-tank reactors (CSTR) are one of the most common types of reactors used in industrial settings. They offer the advantage of continuous operation when mixing is required, particularly for biphasic reactions. However, due to their large volumes, it is extremely important to properly control the reactor temperature, especially when running exothermic reactions where inadequate heat removal could result in a runaway reaction and explosion.

For a CSTR to operate at steady state, the heat removed must equal the heat generated by the reaction. Assuming a first order, exothermic reaction, no heat loss, at steady state the heat balance looks like the following

$$UA(T_{reactor} - T_{cool}) - F_{in}\rho C_p(T_{feed} - T_{reactor}) = -\Delta H_r V k \frac{C_{feed}}{1 + k\frac{V}{F_{in}}}$$

The left hand side of the equation is the rate of heat removal Q_{rem}, while the right hand side of the equation is the rate of heat generation Q_{gen}. The plot of each curve against $T_{reactor}$ gives the steady state temperature of the reactor at the intersection of both curves (Figure 1).

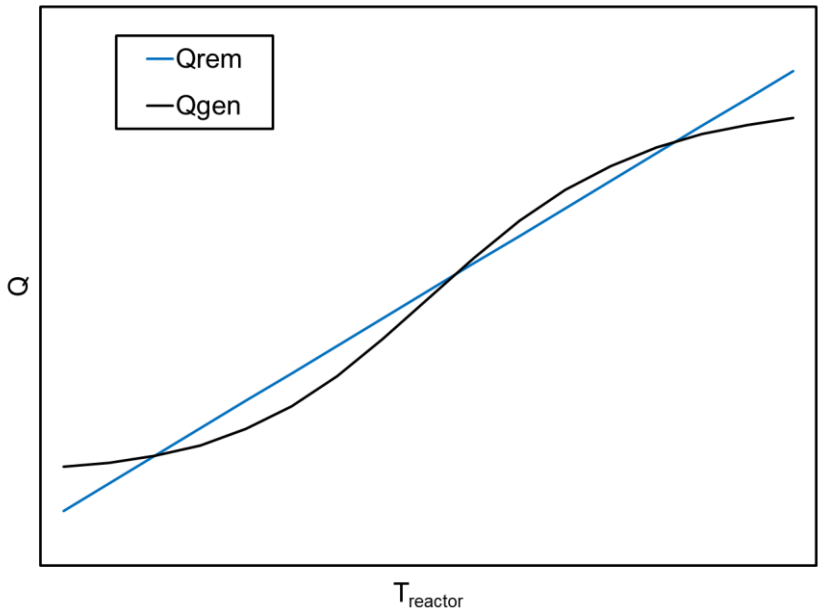

Fig. 1: Heat generation and removal as a function of reactor temperature.

Note that while Q_{rem} is a straight line, Q_{gen} typically has an S shape curve due to the fractional and exponential dependence on $T_{reactor}$. This

means that with careful choice of reaction conditions, multiple steady state reactor temperatures are available at the same conditions.

It is possible to change reaction conditions to shift either curves in order to achieve different operating temperatures and thus conversions. What's interesting now is the behavior of the CSTR at the transition from multiple steady states to a single steady state (Figure 2).

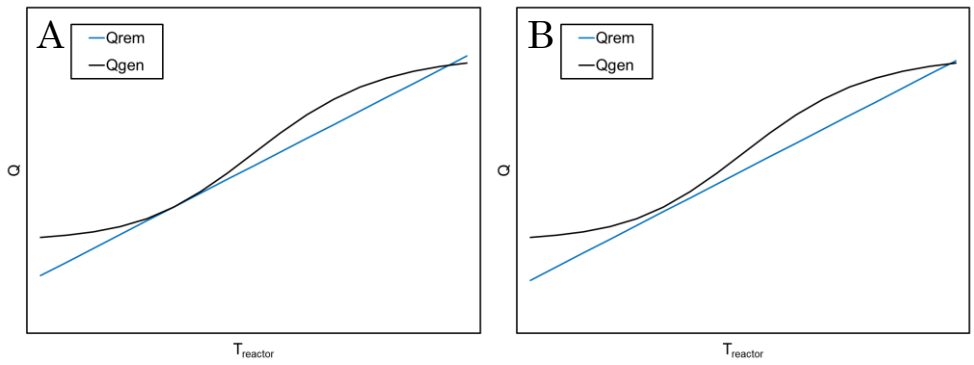

Fig. 2: Heat generation and removal as a function of reactor temperature. A) The heat removal curve is tangent to the heat generation curve at the low temperature steady state. B) Feed temperature increased slightly from A, thus lowering the overall heat removed.

At certain conditions, two steady states are still possible, albeit with the lower steady state at a reactor temperature at the tangent of both curves (Figure 2A). Slightly reducing the amount of heat removed changes the curve such that the only possible steady state is at high temperature. The reactor undergoes what's called ignition, where the temperature rises rapidly to the corresponding steady state. The opposite behavior is called extinction.

Importantly, the behavior in the opposite direction is different. Imagine now that at the high temperature steady state, we increase the heat removal curve back to the point where two steady states are possible. In this case, at the same reaction conditions as before, the temperature of the reactor remains at the high temperature steady state, instead of returning to the lower temperature steady state from before. Extinction of the reactor then occurs at the other tangent of the curves, at different reaction conditions. This direction-dependent behavior of CSTRs is termed hysteresis.

1.2 Decomposition of hydrogen peroxide

The reaction we will use to study the behavior of CSTRs is the decomposition of hydrogen peroxide in an acidic solution, using iron(III) nitrate as the catalyst.

$$H_2O_2 \xrightarrow{Fe^{3+},H^+} H_2O + \frac{1}{2}O_2\ ,\Delta H_r = -94.8\ kJ/mol$$

This reaction is a first-order irreversible reaction in the following concentrations:

$$1M < [H_2O_2] < 2.8M$$

$$0.005M < [Fe^{3+}] < 0.25M$$

$$0.05M < [H^+] < 0.5M$$

The first-order rate law is then given by:

$$r = kC_{H_2O_2}$$

Whereby the rate constant is the Arrhenius equation:

$$k = k_o e^{-\frac{E_a}{RT}}$$

And the pre-exponential factor dependent on both iron (III) and acid concentrations:

$$k_o = k'_o \frac{C_{Fe^{3+}}}{C_{H^+} + K_f}\ , K_f = 10\ mol/m^3$$

2. OBJECTIVES

The objectives of the present work are:

- *Measurements of the physical and kinetic parameters of the reaction.* Reactions in adiabatic batch mode will be carried out at different concentrations to measure the reaction parameters.
- *Simulation of steady state behavior.* The measured parameters are then used to simulate the behavior of a CSTR. This will allow a prediction of the reaction conditions that will lead to multiple steady states
- *CSTR operation and observation.* Operate the CSTR using the predicted reaction conditions and attempt to observe the hysteresis of CSTRs. If no hysteresis is observed, explain why.

3. EXPERIMENTAL

3.1 Safety

Safety goggles and lab coats are mandatory. Gloves are required when handling dangerous chemicals (eg. acidic solution of H_2O_2). Fume hoods are available for the manipulation of dangerous chemicals. A safety tour will be provided by the assistant for each group to identify safety procedures. As the reaction produces oxygen gas as a product, decomposition of large amounts of hydrogen peroxide in a short period of time could expand the volume of the solution and overflow the reactor. As such, the volume and concentration of the reaction should be kept as low as possible. For reference, at 2M hydrogen peroxide and 0.2M iron(III), the volume of the reaction should be no larger than 350 mL. Furthermore, while the vapors that come out of the reactor are hot, as is the outlet of the reaction. If the heater is to be used, take care that the minimum volume of the reaction should be around 500 mL, so that the heater does not overheat and damage itself. During the experimental runs, conversion calculations are required to understand the extent of the reaction: especially when the reaction runs at low conversions, the liquid wastes have to be redirected to a specific container under the fume hood, in which quenching with sodium bicarbonate has to be repeatedly carried out.

3.2 Experimental setup

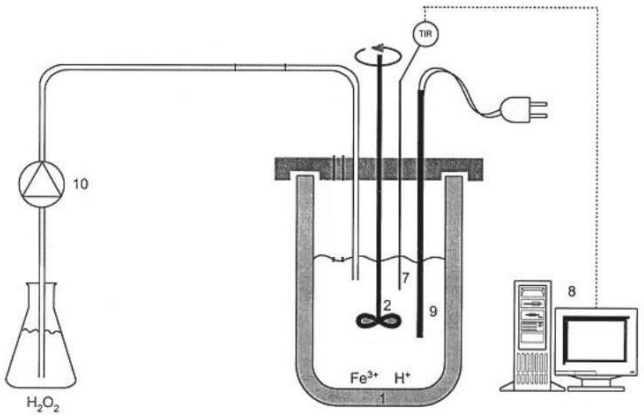

Fig. 3. *Experimental set-up*

The set-up consists of a glass reactor (1) with a bottom discharge valve (V=1.2 l) containing a mechanical agitator (2) with variable speed and a heating element (P=250W) (9). Thermo-probes (7) measure the temperature of the cooling liquid and the reaction mass. The temperatures are recorded on a PC (8). The pump (10) and the tanks for reactants can be used to introduce reactants to the reactor.

3.3. Preparations

At the beginning of each session, the following solutions must be prepared:

- Prepare a 5L solution of 5M H_2O_2 from available commercial H_2O_2 and 0.2 M HNO3 from available commercial HNO3. Subsequently titrate this solution.
- If necessary, prepare 250 ml of 1 M $Fe(NO_3)_3$.

3.4 Heat and mass balance for a batch reactor

As long as the physical and kinetic parameters of the system are known, heat and mass balances can describe the behavior of the reactor.

In this TP, we will consider the case of a first order, irreversible, polytropic reaction:

Mass balance

$$dn_1/dt = n_{1,0}\,dX/dt = -R_1 V = V k_0 exp(-E_a/RT) C_{1,0}(1-X)$$

which, when rearranging, becomes:

$$dX/dt = k_0 exp(-E_a/RT)(1-X)$$

Heat balance

$$(C_w + mC_p)\,dT/dt = V(-\Delta H R)(-R1)$$

3.5. Titrations

Ferric ion titration

This titration is realized by a classical redox dosage. The solution of ferric nitrate prepared has to be about 1M.

Take 2 ml of the solution to be titrated, and dilute with 50 ml of water. Add 25 ml of HCl 1N and 25 ml of KI 60 %. Titrate with $Na_2S_2O_3$ 0.1N. Before the end of the titration, add some drops of starch. The final solution must be clear. The reactions during this titration are:

$$2\ Fe^{3+} + 2\ I^- \rightarrow 2\ Fe^{2+} + I_2$$

$$2\ Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2\ NaI$$

Hydrogen peroxide titration

Take 1 ml of the solution to be titrated and dilute with 25 ml of water and 50 ml of H_2SO_4 25 %. Titrate with $KMnO_4$ 1N up to red-purple persistent tint of the solution. The reaction of the titration is described by:

$$2\ MnO_4^- + 5\ H_2O_2 + 6\ H^+ \rightarrow 2\ Mn^{2+} + 5\ O_2 + 8\ H_2O$$

H+ titration

Titrate the acid with NaOH 0.1N in the presence of phenolphtalein.

3.6. Determination of C_w

Besides the calorific capacity of the reaction mass, it is necessary to consider the calorific capacity of all the equipment surrounding the liquid, CW. This value is determined by plunging a heating element susceptible to supply a power (P, 250 Watts) in the vessel filled with a known mass of water, m_e. The power supplied is completely absorbed by the water, the immersed accessories and the wall of the reactor.

Initially, the temperature is T_0. The temperature is recorded according to time. A simple thermal balance leads to:

$$(m_e C_{p,e} + C_W) dT/dt = P$$

For a broad range of temperatures, the temperature profile is almost linear, which allows integrating as follows:

$$(m_e C_{p,e} + C_W) \Delta T = P \Delta t$$

By knowing m_e, $C_{p,e}$ and P, we can deduce Cw.

4. DETAILED PLAN OF MANIPULATIONS

The experiments that need be performed in order to meet the objectives of this TP are listed below. Any suggestions or modifications to the plan are warmly welcome.

1. Characterization of the thermal properties of the reactor and do all the calibrations for increased accuracy.

2. Kinetics. Determine the kinetics of the hydrogen peroxide decomposition reaction working under adiabatic conditions.

3. Simulating the behavior of the system in CSTR mode and investigate the possibility of hysteresis.

4. Running the reaction in CSTR mode and compare the obtained results with the simulated one.

5. By choosing the suitable concentrations of reactants and other parameters, try to obtain the hysteresis behavior like the following diagram

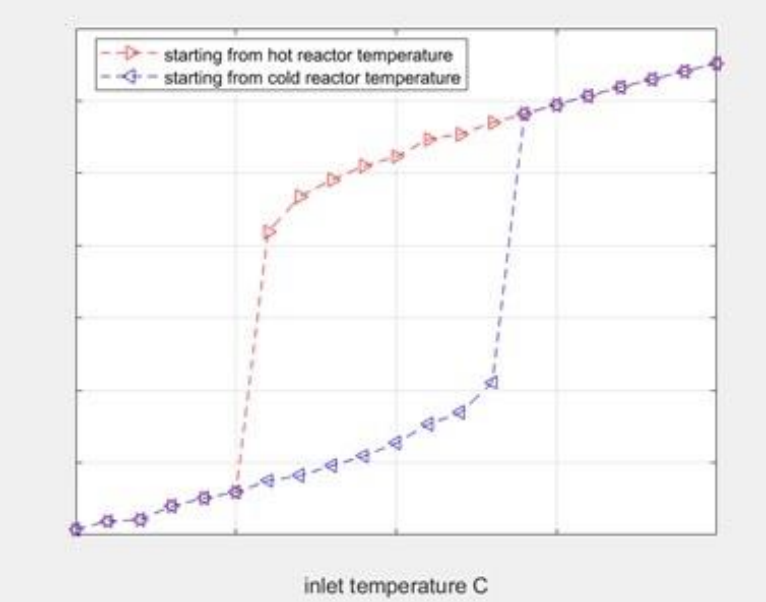

Fig. 4. Observing hysteresis behavior by changing the inlet temperature

Reminder

The lead group is responsible for planning the experiments to be done and must inform the backup groups of their duties and experiment plan in due time.

For the first session, the following schedule is proposed:

- Presentation of the subject by the assistant 60 min
- Individual study of the manipulation by the student 3 h

Work plan

Mass and heat balances applied for the study have to be developed and presented to the assistant

- Discussion with the assistant 30 min

Definitive work plan

- Presentation of the set-up 30 min
- Preparation of solutions, preliminary measurements (Cw), titrations, calibrations 3 h
- Measurements and simulations 2 days

5. REFERENCES

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Appendix I – List of chemicals and safety considerations

Name	Formula	Form	Precautions
Hydrogen peroxide	H_2O_2	solution, 30%	
Hydrochloric acid	HCl	solution, 1mol/l	
Iron (III) nitrate	$Fe(NO_3)_3$	powder	
Nitric Acid	HNO_3	solution, 65%	
Phenolphthalein in methanol		solution	
Potassium iodide	KI	powder	
Potassium permanganate	$KMnO_4$	solution, 0.2mol/l	
Sodium hydroxide	NaOH	solution, 0.1mol/l	
Sodium thiosulfate	$Na_2S_2O_3$	solution 0.1mol/l	
Starch (Amidon)		powder	
Sulfuric Acid	H_2SO_4	solution, 25%	

Appendix II: Nomenclature

U	Heat transfer coefficient (jacket or coil)
A	Area (m^2)
$T_{reactor}$	Temperature of the reactor °C
T_{cool}	Temperature of the cooling system (jacket or coil) °C
T_{feed}	Temperature of the inlet flow °C
ΔH_r	Enthalpy of the reaction (kJ/kmol)
V	Volume of the solution in the reactor
k	Rate constant (1/sec)
C_{feed}	Concentration of reactant in the inlet flow
F_{in}	Molar flow of the reactant
k_0	Arrhenius constant
E_a	Activation energy (kJ/kmol)
C_w	Heat capacity of the reactor
m_e	Mass of water
$C_{p,e}$	Specific heat capacity of water
Q_{rem}	Removed heat from the system by the environment or cooling system
Q_{gen}	Generated heat by the reaction
t	Time (sec)
P	Power of the heater (watt)
X	Reactant conversion
$C_{1,0}$	Initial concentration of H_2O_2

Remarks

The solutions of hydrogen peroxide and iron nitrate acid are very corrosive and require working cleanly by taking into account safety rules (safety goggles, gloves and lab coat!).

The titrations are normally performed twice and the average is used to calculate the conversion.

WARNING

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At the end of the work, the installation must be cleaned and free of products. The report will not be corrected until everything is clean! If necessary, a negative point will be added to the final mark.

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