A PROJECT REPORT ON SIMULATION OF CATALYST DECAY EFFECTS IN A BATCH REACTOR USING ANALYTICAL AND NUMERICAL METHODS

Submitted in partial fulfillment of the requirements for the subject: **Chemical Reaction Engineering (CRE)**

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1. INTRODUCTION

Catalysis is an underlying pillar of chemical reaction engineering, being a corner-stone of chemical processes for industry.[1] In nearly every major sector of chemical manufacturing— be it petroleum refining, petrochemicals, pharmaceuticals, or pollution control systems— catalysts are used to speed up rates of reaction, enhance selectivity, and reduce operating costs. Of the numerous reactor configurations, the batch reactor is most commonly used in laboratory-scale research and specialty chemical production because of its flexibility, simplicity, and adaptability for small-scale production or time-sensitive reactions. But in batch reactors, the dynamic time dependence of operation makes it necessary to take into account aspects affecting the temporal evolution of the reaction system. One such factor, frequently ignored in model theory but extremely significant in application, is catalyst decay. [2]

Deactivation of the catalyst refers to the gradual loss of catalytic activity over time due to different physical and chemical processes. Typical mechanisms include thermal degradation, chemical poisoning, sintering of active metal particles, fouling by deposition of products or reactants, and structural change of support materials of the catalyst. These deactivation processes cause a time-dependent decrease in the effective rate constant of the reaction, with important ramifications for conversion efficiency, selectivity, and overall yield. Neglect of catalyst decay in design, batch reactor prediction, and operation can produce erroneous conclusions about reactor performance, leading to inefficient resource utilization, economic loss, or even unsafe operating conditions.[3]

The main aim of this project is to critically explore the influence of catalyst deactivation on the performance of a batch reactor via both analytical and numerical methods. The investigation starts by developing a generalized mathematical model that describes the transient dynamics of a catalytic reaction with declining activity. The reaction kinetics are taken to obey a first-order rate law with the reactant and catalyst deactivation is included through a time-dependent decay function. This gives rise to a system of ordinary differential equations (ODEs) that capture the time evolution of the reactant concentration and activity of the catalyst. Analytical solutions are obtained under certain assumptions to provide closed-form equations for reactant conversion in terms of time and decay rate constant.

Still, the project employs numerical simulation via MATLAB or Python since analytical methods have their limitations when dealing with non-linearities or more sophisticated decay models. The numerical method provides us with more leeway for investigating numerous types

of decay kinetics. These range from exponential and linear to real data-based empirical decay profiles. We divide the time domain into sections and apply numerical integration methods such as the Euler method or the Runge–Kutta method. This enables us to model how concentration alters with time and determine the end conversion for various catalyst decay conditions.

The study moves forward by changing the catalyst decay constant in a step-by-step manner to examine its effect on key reaction metrics. These metrics include the time to hit 90% conversion, the total yield, and the apparent reaction duration. This knowledge proves useful for people who design reactors, engineers working on processes, and those developing catalysts. It allows them to forecast batch reactor performance with greater accuracy and aids in making choices about how much catalyst to load how long each cycle should run, and when to swap out the catalyst.

This research fills an important hole in chemical engineering education at the college and graduate levels. Most reactor design models taught assume catalysts behave over time. By modelling real-world decay, this project shows students more practical approaches that capture the challenges industry faces. What's more, this study paves the way for exploring things like how temperature affects deactivation complex reaction paths, or scaling up production. This makes it a great starting point for future studies or teamwork with companies.

This project achieves dual objectives by advancing theoretical insights into catalyst decay within batch reactors while simultaneously providing engineers with practical simulation tools to analyse its effects. By merging analytical precision with computational simulation techniques, this study underscores the necessity of including realistic degradation phenomena in the design of chemical reactors and process optimization. The simulation framework presented in this work offers adaptability for various reactor types and extension to multiphase systems, establishing it as a multifaceted advancement in chemical reaction engineering.

2. LITERATURE SURVEY

1. **Temperature effect on the kinetic profile of Ziegler–Natta catalyst in propene polymerization**

In this study, propene was polymerized using a diether-based Ziegler–Natta catalyst in a batch reactor. The reaction started with a 10-minute phase at different temperatures (from 10 °C to 70 °C), followed by a 90-minute run at 70 °C. The goal was to see how the initial temperature affects how quickly the catalyst loses its activity. By analysing heat transfer data, the reaction behaviour was modelled using equations that account for catalyst deactivation over time. Both first- and second-order deactivation models gave a good fit, showing that the temperature in the early stage plays a key role in how fast the catalyst slows down later.[1]

2. **Reference Optimal temperature policies for reactors subject to catalyst deactivation— Batch reactor**

This study looked at how to choose the best temperature over time for reaction $A{\rightarrow}R$ is happening in a batch reactor, where the catalyst slowly loses activity. Using a method from calculus of variations, the researchers found an exact solution for the optimal temperature plan. They showed that the best approach depends on how fast the reaction and the catalyst deactivation respond to temperature. If the catalyst deactivates more slowly than the reaction speeds up (ϵ < E), it's best to run at the highest possible temperature. But if the catalyst deactivates faster than the reaction speeds up (ϵ > E), it's better to slowly increase the temperature in a way that keeps the overall reaction rate steady. This finding works for any reaction or deactivation order. They also gave a simple equation to follow the optimal temperature and looked at how temperature limits affect the result.[2]

3. **Catalyst deactivation kinetics: An apparent delay in the decrease in catalyst activity, "inflection point", and data interpretation**

This study focuses on understanding catalyst deactivation and how to test catalyst stability. It investigates the common delay observed before deactivation becomes noticeable and explains how to interpret it. The paper also analyses the inflection points in conversion decay curves— where the rate of deactivation changes—and how these points are influenced by reaction kinetics, deactivation behaviour, and the type of reactor used. It provides practical equations and real-world examples to help with analysis.[3]

3. METHODOLOGY

Catalyst deactivation reduces catalyst efficiency over time and must be considered in reactor design using a time-dependent activity function, a(t). In separable kinetics, the reaction rate and catalyst decay can be analyzed independently. The activity decreases due to mechanisms like sintering or poisoning. The rate of decay is modelled using functions of activity. In first-order decay, the decay rate is directly proportional to activity: p(a) = a. In second-order decay, it increases more rapidly with activity: $p(a) = a^2$. The appropriate model depends on the deactivation mechanism and helps ensure accurate reactor performance prediction.

The second-order decay model applies when deactivation is highly sensitive to activity, such as during bimolecular surface interactions or particle collision-driven sintering. In these cases, decay accelerates with increasing activity, making this model more accurate.[4,5]

Let's take 2nd order for deactivation via sintering

decay laws is second order with respect to the present activity

$$-r_d = k_d a^2 = -\frac{da}{dt}$$

Integrating, with a = 1 at time t = 0, for constant k_d during the time t yields

$$\int_1^a -\frac{da}{a^2} = \int_0^t k_d \, dt$$

$$\left(\frac{1}{a} - 1\right) = k_d t$$

$$\left(\frac{1}{a}\right) = 1 + k_d t$$

$$a(t) = \frac{1}{1 + k_d t}$$

The amount of sintering is usually measured in terms of the active surface area of the catalyst

$$S_a = \frac{S_{a0}}{1 + k_d t}$$

The sintering decay constant, k_d follows the Arrhenius equation

$$k_d = k_d(T_0) exp\left[\frac{E_d}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$
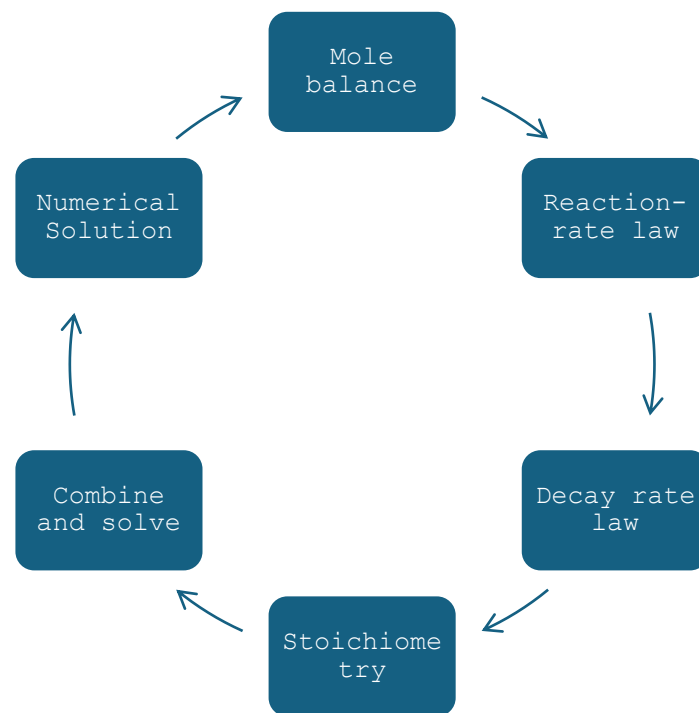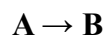
An algorithm to solve:

Fig 1: Algorithm to solve catalyst decay problem

Conversion with catalyst Decay in Batch Reactor for first order isomerization:

A → B

Assumptions

- Isothermal batch reactor

- Catalyst deactivation via sintering (second order)

- No external/internal mass transfer resistance

- Catalyst activity is uniform throughout

- Reaction is kinetically controlled

- No volume changes due to reaction

Analytical approach

1. **Mole Balance:**

For a batch reactor with catalyst decay, the mole balance is:

$$N_{A0} \frac{dX_d}{dt} = -r_A' W$$

Where:

- X_d: Conversion of species A when the catalyst is decaying
- W: Mass of catalyst
- N_{A0}: Initial moles of A
- r_A': Reaction rate per unit mass of catalyst

2. **Reaction-rate law:**

The rate of reaction with decaying catalyst activity is:

$$-r_A' = k' a(t) C_A$$

Where:

- k': Intrinsic rate constant (per unit catalyst mass)
- $a(t)$: Catalyst activity (dimensionless, $a(0) = 1$)
- C_A: Concentration of A

3. **Decay rate law:** For second-order decay by sintering:

Assuming **second-order decay by sintering**, the catalyst activity decays as:

$$a(t) = \frac{1}{1 + k_d t}$$

Where: k_d is Catalyst decay constant (1/time)

4. **Stoichiometry**

$$C_A = C_{A0}(1 - X_d) = \frac{N_{A0}}{V}(1 - X_d)$$

Substitute into the rate equation and define:

$$k = \frac{k' * W}{V}$$

So the conversion rate becomes:

$$\frac{dX_d}{dt} = k(1 - X_d)a = k\frac{(1 - X_d)}{(1 + k_d t)}$$

where X is the conversion when there is decay.

Conversion Without Decay (Reference Case):

Set k_d=0 (no decay):

$$\frac{dX}{dt} = k(1 - X)$$

5. Combine and solve

a) When there is no decay

$$\frac{dX}{dt} = k(1 - X)$$

Integrating:

$$\int_0^X \frac{dX}{(1 - X)} = \int_0^t k dt$$

$$\ln(1 - X) = -kt$$

$$\boxed{X = 1 - e^{-kt}}$$

This serves as the benchmark for comparison.

b) Conversion With Catalyst Decay:

Now include second-order deactivation:

$$\frac{dX_d}{dt} = k\frac{(1 - X_d)}{(1 + k_d t)}$$

Integrating:

$$\int_0^X \frac{dX_d}{(1-X_d)} = \int_0^t k\frac{dt}{(1+k_d t)}$$

$$ln\left(\frac{1}{1-X_d}\right) = \frac{k}{k_d}ln(1+k_d t)$$

$$\frac{1}{1-X_d} = (1+k_d t)^{\frac{k}{k_d}}$$

$$\boxed{X_d = 1 - \frac{1}{(1+k_d t)^{\frac{k}{k_d}}}}$$

6. **Dimensionless formulation:**

To generalize the solution and reduce parameters:

- Dimensionless time: $\Theta = kt$

- Decay parameter: $\alpha = k_d/k$

- Dimensionless conversion

$$\boxed{X_d(\Theta) = 1 - \frac{1}{(1+\alpha\Theta)^{\frac{1}{\alpha}}}}$$

4. PROBLEM STATEMENT:

A first-order irreversible reaction

A→B

is carried out isothermally in a batch reactor using a solid catalyst. The catalyst loses activity over time due to thermal sintering, a process in which active surface area is diminished, leading to decreased reaction rates. The reaction rate follows first-order kinetics in the concentration of A and is directly proportional to the time-dependent catalyst activity, a(t), which decreases according to a second-order decay law.

Given parameters:

Case 1: Plot the graph for the comparison between catalyst decay (a = 1) and no catalyst decay (a = 0)

Initial concentration of A C_{A0} = 2 mol /L

Reaction rate constant K = 0.3 min^{-1}

Catalyst decay constant: a= 0 min^{-1} and a= 1 min^{-1}

time for evaluation t = 3,6,9,12,15 min

calculate the conversion X(t) for both cases:

- Case A: Catalyst does not deactivate (k_d = 0)

- Case B: Catalyst deactivates by second-order decay (k_d = 1)

- Compute and plot conversion vs. time for both cases over the interval t = 0 to 15 mins.

Case 2: Plot a graph for comparison of the effect of catalyst decay on conversion in batch reactor

Dimensionless time, Θ = 0 to 5

Catalyst decay parameters, α = 0,0.2,0.5,1.0

5. RESULTS AND DISCUSSION

Analytical Results Summary:

The conversion-time relationship for a batch reactor undergoing catalyst deactivation was derived using an analytical approach. The catalyst activity was assumed to decay via a second-order sintering mechanism, expressed as:

$$a(t) = \frac{1}{1 + k_d t}$$

Substituting this into the batch reactor mole balance led to an expression for conversion with deactivation:

$$X_d = 1 - \frac{1}{(1 + k_d t)^{\frac{k}{k_d}}}$$

For the case of no decay (k_d), the conversion simplifies to the classical batch reactor equation:

$$X = 1 - e^{-kt}$$

Graphical Comparison:

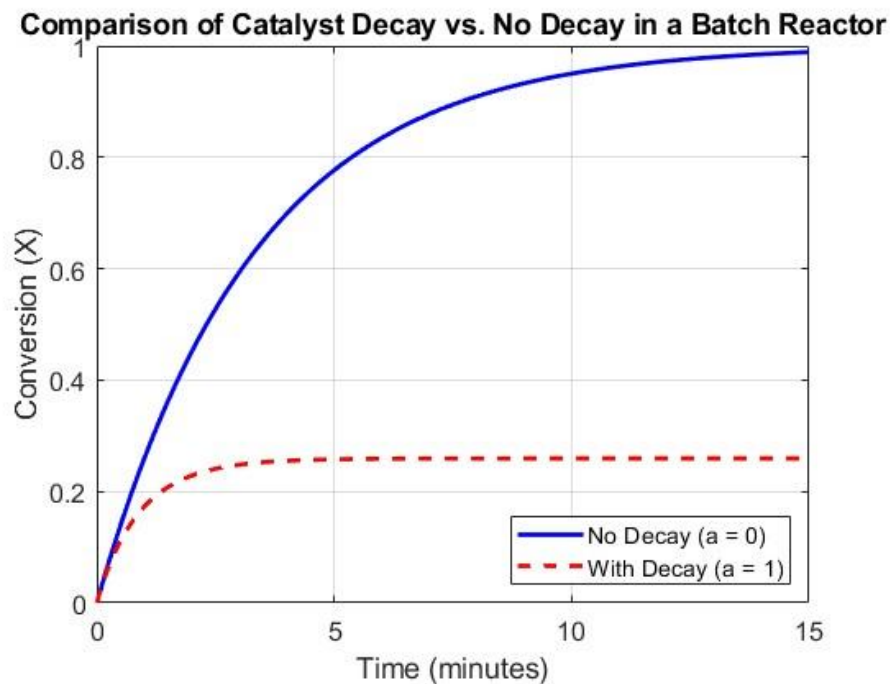Comparison between **catalyst decay (a = 1)** and **no catalyst decay (a = 0)**

Fig 2: Plot of comparison of no decay and with decay catalyst

1. Observation from the Graph:

Parameters	No decay (a=0)	With decay (a=1)
Initial conversion rate	fast	slower
Final conversion (15 min)	Near 90-95 %	~55–65%
Curve shape	Exponential rise	Flattens early (saturation)

No Decay (a = 0): The conversion accelerates sharply with time and asymptotically levels off at a high value (~0.95). This is to be expected for a first-order irreversible reaction with constant catalyst activity.

With Decay (a = 1): The conversion curve rises first and then becomes flat early because of the quick decline in catalyst activity. This indicates that the effective rate constant grows weaker over time, decreasing conversion efficiency.

The graph plotted shows the conversion X as a function of **dimensionless time** $\Theta=kt$, for various values of the **dimensionless decay parameter** $\alpha = k_d/k$

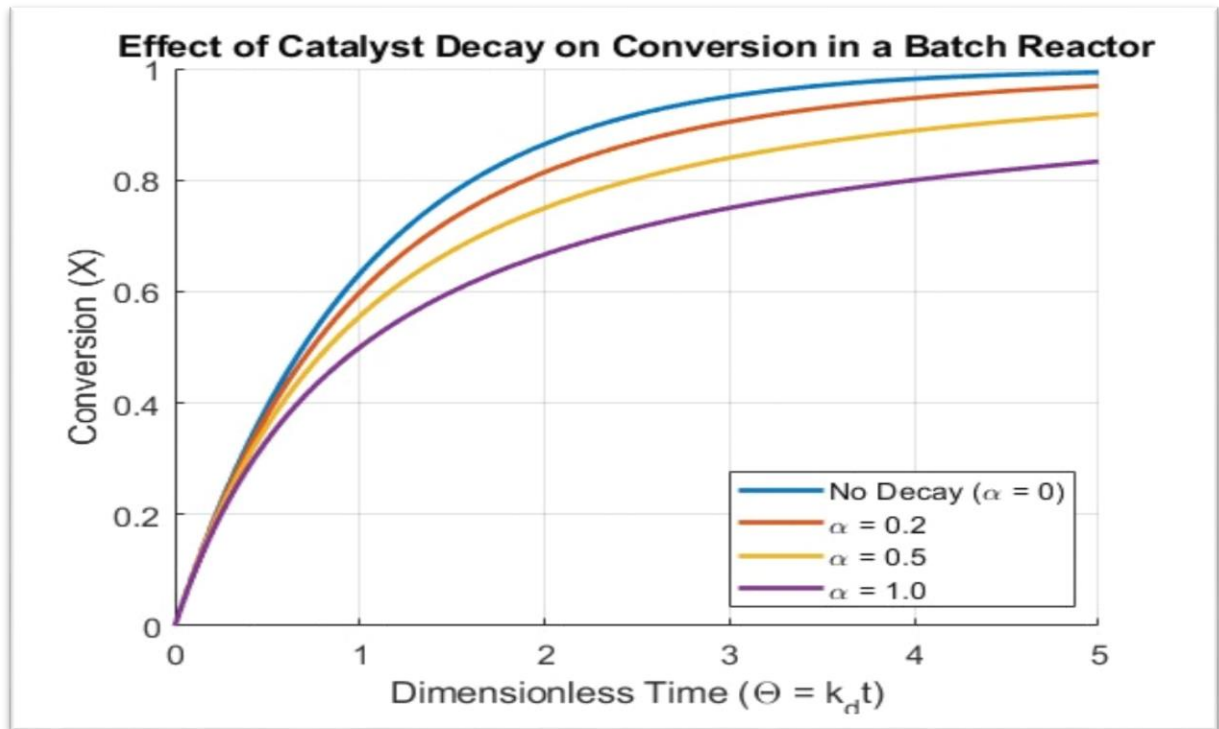| Decay Parameter α	Catalyst Behavior
0.0	No decay (reference case)
0.2	Mild decay
0.5	Moderate decay
1.0	Moderate decay

Fig 2 : Plot the graph for effect of catalyst decay on conversion in a batch reactor

The curves show the following trends:

- For α = 0 (no decay), conversion approaches unity smoothly.

- For increasing values of α, the conversion curve flattens earlier, indicating slower overall reaction progress.

- The deactivation significantly impacts the final conversion, even though the system may still have enough time.

- As α increases, the effective catalytic activity drops faster, reducing the available active sites for reaction.

6. CONCLUSION

In this research, the influence of catalyst deactivation on the performance of a batch reactor was studied through analytical and numerical methods. Catalyst sintering-induced decay was added to the reaction kinetics for an irreversible first-order reaction and was represented as a second-order decay process. Using dimensionless analysis, the time-conversion relationship was obtained and simulated for different deactivation cases through the decay parameter

$\alpha = k_d/k$.

The simulation results showed that:

- In the absence of catalyst decay ($\alpha = 0$), conversion increases exponentially and is almost complete within a very short period. With increasing α, the effective reaction rate falls, resulting in slower conversion and lower final conversion.
- For $\alpha = 1.0$, swift deactivation of the catalyst strongly constrains reactor performance and emphasizes the importance of catalyst stability in design and operation. This calculation emphasizes the need to consider catalyst lifetime in kinetic model development and reactor design. In industrial practice, neglect to include the decay effects of catalysts can cause the conversion to be overestimated and the performance of the reactor system to be underutilized.

Finally, this simulation methodology is a useful predictive tool for evaluating the effect of deactivation mechanisms on reaction conversion and can be used by engineers to optimize the reactor operation, catalyst choice, and regeneration cycle.

7. ACKNOWLEDGMENTS

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