Continuous process design for the PAC plant at Grasim (Vilayat) which is currently operating as a batch process

Contents

**PAC plant operating at Grasim industries (Vilayat):**

The PAC (Poly Aluminium Chloride) plant at the Chemical division of the Grasim industries at Vilayat (Gujrat, India) is presently operating as a batch process. There are total ▮▮▮▮▮▮ each operating independently from the other. The industry produces ▮▮▮▮▮▮ grades of PAC (four in powder and three in liquid). However, only two out of these are produced directly from the plant (PAC-18 and RMA). Rest of the five grades are produced by mixing the two in varying proportions.

Rate law of the reaction:

The chemical equation of the reaction can be empirically written as-

$$[Al(OH)_3]_2 + 3.HCl \rightarrow Al2Cl3(OH)_3 + 3.H_2O$$
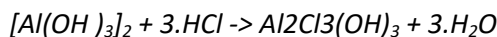
So the most intuitive rate law expression would be -

$$r_a = k_f \; c_{ATH} c_{HCl} - k_b \; c_{PAC} c_{water}$$

However, from the experiments performed on PAC formation, it was established that ATH (Alumina tri-hydrate) is insoluble in HCl at least up to ▮▮▮▮▮▮ pressure. The temperature in the reactor varies from ▮▮▮▮▮▮ while the pressure varies from 1 atm to around 12 atm. If we assume that ATH is soluble in HCl only after it gets converted to PAC, it would imply that the reactants are at different phases (ATH in solid phase and HCl in liquid), which means it is the net area offered by polymeric surface of ATH that affects the reaction and not its volumetric concentration. Also, the kinetics of reverse reaction is too slow to be considered. Based on this, the rate law should be written as

$$r_a = k_f \; .N.a.c_{HCl}$$

Where 'N' denotes the no. suspension particles in a batch and 'a' denotes the average area per suspension particle. In this case there are two extremities are possible, i) In a batch the no. particles remains constant and any change in average concentration* of ATH is adjusted by suspension particle size (and hence the particle's surface area) or ii) The surface are of particles remains constant and any change in average conc. of ATH is adjusted by changing no. of suspension particles.

Assuming the first case, the rate law should be written as

$$r_a = k_f \; .c_{ATH}^{2/3}.c_{HCl}$$

On the other hand, assumption of second case, the rate law becomes

$$r_a = k_f \cdot c_{ATH} c_{HCl}$$

*(since ATH in the reaction mixture exists as suspension, there shouldn't be any quantity as molar conc. for PAC. Instead it is quantified by average concentration, which is total moles of PAC added to the batch divided by the reactor's nominal volume)

The actual situation lies between the above extremities and we at best we can say that the rate law should be written as

$$r_a = k_f \cdot c_{ATH}^m c_{HCl}$$

Where 'm' lies between 2/3 and 1.

Writing equations for mass balance and energy balance in differential form

Taking a batch reactor as our system, the mass-energy balance equation in the simplest form can be written as-
$$in - out + generation - consumption = \ accumulation$$

Based on above relation, the following equations were written for a batch system:

$$S = T_{rd}T_r V_r \ (a_a Cp_a c_a + a_h Cp_h c_h - a_p Cp_p c_p - a_w Cp_w c_w)$$

$$\frac{dT_r}{dt} = \frac{T_r}{Q_r}\left(-\Delta H.V_0 \ c_{a0}\frac{dx}{dt} - hA\left(T_r - \frac{T_w T_{wd}}{T_{rd}}\right) - S\frac{dx}{dt}\right)$$

$$\frac{dT_w}{dt} = \frac{\frac{\left(\frac{T_r}{T_{wd}} - T_w\right)m_f}{m} + h\left(T_r\frac{T_{rd}}{T_{wd}} - T_w\right)\frac{A}{Cp_w m}}{T_{wd}}$$

$$\frac{dx}{dt} = \frac{(kfc_{a0}^m c_{h0}(1 - 3a_h x)(1 - x)_{a0}^{2/3}}{c_{a0}}$$

Here, we have
$$T_r = non-dimensional \ temrature \ of \ the \ reactor \ (\frac{temperature \ of \ reactor \ inKelvins}{desired \ temperature \ in \ Kelvins})$$
$$T_w = non-dimensional \ temperature \ of \ water/steam \ jacket(\frac{temperature \ of \ jacket \ inKelvins}{desired \ temperature \ in \ Kelvins})$$

$$Q_r = total \ amount \ of \ heat \ inside \ the \ reactor \ given \ by$$
$$Q_r = T_{rd}T_r V_0 \ (Cp_a c_{a0}(1 - x) + Cp_h c_{h0}(1 - 3a_h x) + Cp_p c_{p0}(1 + a_p \ x) + Cp_w c_{w0}(1 + 2a_w x))$$

$$V_0 = volume \ of \ the \ reactor$$
$$c_{a0} = initial \ concentration \ of \ ATH$$
$$x = conversion \ of \ the \ ATH(\frac{moles \ of \ ATH \ reacted}{moles \ of \ ATH \ initially \ present})$$
$$h = heat \ transfer \ coefficient \ between \ reactor \ and \ the \ jacket$$
$$A = aread \ of \ heat \ transfer$$
$$T_{wd} = desired \ value \ (at \ t = \infty) \ of \ T_w \ in \ Kelvins$$
$$T_{rd} = desired \ value \ of \ reactor \ temperature \ in \ Kelvin$$
$$m_f = mass \ flow \ rate \ of \ the \ steam \ or \ water$$
$$m = mass \ capacity \ of \ the \ jacket$$
$$Cp_w = Heat \ capacity \ o \ water$$

Approximation of reaction enthalpy (heat of the reaction)

Heat of the reaction at room temperature is calculated by utilizing the thermal data of the plant and implementing simple energy balance:

*Heat supplied to the plant - Heat taken away from the plant = additional energy absorbed by the reaction system = **Heat of the reaction***

Heat supplied to the plant will be given by

$$\int m^*.Cp.\Delta T.dt$$

Above integral is valid for all the four thermal cycles of the plant (i) Low pressure steam heating, ii) High pressure steam heating, iii) 1st therm cooling, iv) 2nd therm cooling)

Here, Cp is the heat capacity of the steam/water; ΔT is Jacket Inlet temperature –Jacket outlet temperature; m^* is the mass flow rate of the steam/water; t is the time

Several assumptions were made while performing the above calculation which includes i) Heat capacity of the steam /water is assumed to be constant (variations with the temperature were ignored) , ii) Disturbances occurring in mass flow rate were also ignored and hence m^* term was also assumed to be constant.

Using above assumptions, the simplified integral looks like:

$$m^\circ.Cp.\int \Delta T.dt$$

The final equation which indicates us the value of heat of the reaction is given by:

$$Q_r = m_{lp}^*.Cp_{lp}.\int_0^{t1} \Delta T.dt + m_{lp}^*.Cp_{lp}.\int_{t1}^{t2} \Delta T.dt + m_{1T}^*.Cp_{1T}.\int_{t2}^{t3} \Delta T.dt + m_{2T}^*.Cp_{2T}.\int_{t3}^{t4} \Delta T.dt$$

The integral was calculated using trapezoid rule (since we had a discrete data):

$$Q_r = \sum_{i=1}^{4} m_i^*.Cp_i .\Delta T_{in-out}.\Delta t_i$$

Approximation of heat transfer coefficient

Net thermal conductance of the interface between the reaction jacket and heating/cooling system will be given by

$$K = \frac{k_1 \, k_2 \, A}{k_1 \, t_2 + k_2 \, t_1}$$

Where

$$t_i = average \ thickness \ of \ \ 'i' material$$
$$k_i = average \ thermal \ conductivity \ of \ 'i' material$$
$$A = area \ of \ heat \ transfer \ between \ the \ jacket \ and \ the \ reaction \ mixture$$

Here 1 and 2 denotes the two materials that make the interface between the jacket and the reaction system, industrial grade steel and glass respectively. Substituting values of ks and ts, we get h ~ 1000 W/m². This value will be valid only if there is 100% efficient heat transfer. However, the above value is still useful as a initial guess value for our optimisation problem that we will discuss later.

Heat transfer coefficient of this system will be given by diving conductivity with the area of heat transfer as-

$$h = \frac{k_1 \, k_2}{k_1 \, t_2 + k_2 \, t_1}$$

Writing MATLAB code to optimise the difference between our model and the plant

We will now discuss the methodology which was developed to optimise the objective function that aimed to retrieve the values of heat of the reaction and the heat transfer coefficient. Other than this, we also had to get values of Arrhenius factor and the activation energy of the reaction. Initially, Newton's gradient descent method was implemented owing to the intuitive approach it serves. However on plotting the objective function, it was found that the function has too many hills and valleys, which makes it impossible to find the global optimal point only by implementing gradient descent method. Another method was to use differential evolution, a method which is applicable to for any type of function and converges at global minima/maxima, unlike the Newton's method which applies for well behaved functions and converges at local optimal point. But the convergence of differential evolution is highly dependent on 'F' and 'CR' parameters we choose and hence can be slow. Therefore, an algorithm hybrid of gradient descent and differential evolution was written. The algorithm is describes as follows:

- Objective variable is a vector having heat of reaction, heat transfer coefficient as its elements (other parameters like Activation energy can also be added in this vector)
- Objective function is a vector having its elements as the temperature of the reactor and conversion at the end of a certain time limit███████taken in our case, which is the time taken by heating cycle)
- CR is a real number between 0 and 1
- F is a real number between 0 and 2
- difference is second order norm of (present objective function – objective function with desired values of parameters)

- ➤ While difference>desired accuracy
  - ○ Choose random integer between 1 to N (N is the size of objv (objective variable))
  - ○ Choose three vectors A,B,C randomly from the domain of objv such that each are different from each other as well as the present objv
  - ○ For j in range (1: length of objv)
    - ▪ Choose random integer between 0 and 1
    - ▪ If the random integer >=CR
      - • Assign jth element of updated objv as A(j) + F * (B(j) − C (j))
    - ▪ Else retain the values of jth element of previous objv
  - ○ Ensure the element of the updated objv have correct sign (heat of reaction should be negative and heat transfer coefficient should be positive. If not, then flip the sign of the element(s)
  - ○ Calculate the value of new objf (objective function) and calculate updated difference
  - ○ If updated difference<previous difference
    - ▪ Apply gradient descent starting from the updated value of objv
    - ▪ Re-update objv based on the precision chosen for descent method and re-update difference
    - ▪ Repeat the iteration
  - ○ Else repeat the iteration

The above algorithm was implemented by varying only two variables, the heat of reaction and the heat transfer coefficient. The other two variables (activation energy and Arrhenius factor) were estimated differently as the objective function was highly sensitive of these two variables, implementing an algorithm which randomly jumps on four dimensional domain and calculate gradient over a small region was not computationally feasible in the software being used. Instead, the values of the remaining two parameters were estimated by running numerous simulations. It was found that the best stability of the objective function was found at ka(Arrhenius factor) =███████and Ea(activation energy) =███████urther, the values stated tend the rate law constant to 1 at T=██████C, which satisfies the observed fact that the reaction demonstrates significant progress at███████ The optimisation algorithm we developed was run on these values of 'Ea' and 'ka' on this way values of unknown parameters was retrieved in this way.

Approach to design the continuous plant

Connecting batch reactors in series to make a system of CSTR (continuous stirred tank reactors) is the best way one can transform the batch system into a continuous system. In order to make best utilisation of available resources and introducing minimal modification into the plant, a design connecting the six reactors in series with one reactor working as mixer tank and the remaining five as CSTR was proposed. Such arrangement would give higher conversion compared to a single reactor having same capacity of the six reactors combined. The proposed design of reactor is depicted below:
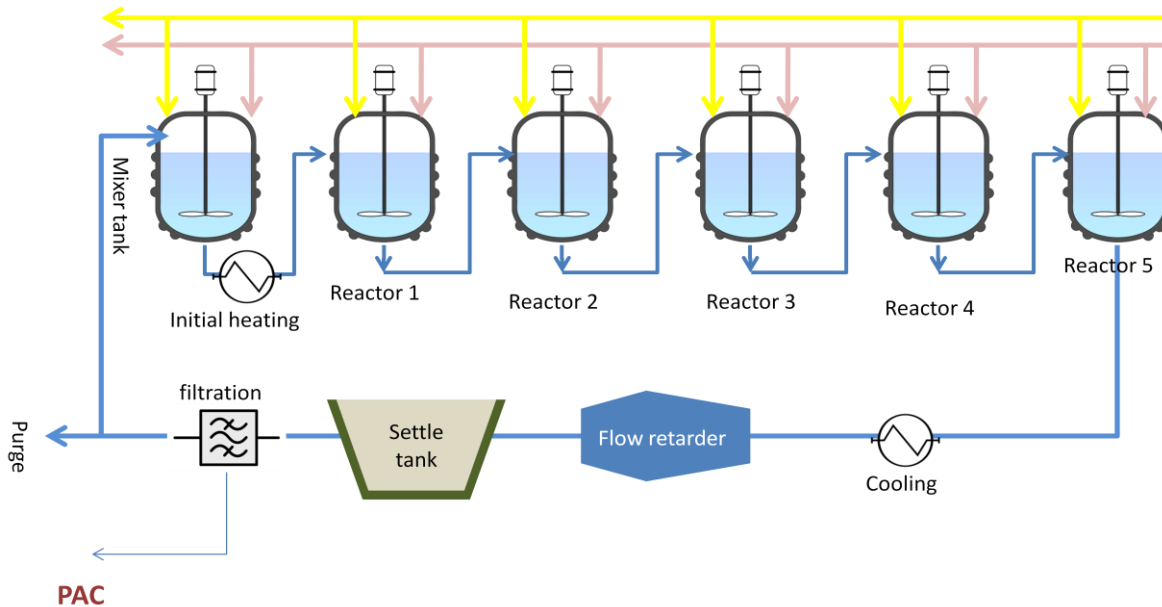
Since we desire higher conversion of alumina, an obvious choice would be taking excess HCl in the feed (taking any reactant in excess increases the rate of reaction as well the conversion of the other reactants, provided no side reactions occurs). The only issue was to separate out PAC from the unreacted HCl, since PAC is highly soluble in HCl. An experiment was carried out in RnD lab to separate HCL from the solution via distillation. Concentrated HCl, which in its pure aqueous form fumes at room temperature and pressure, could not be separated from its PAC solution even at 100 degC. The conclusion was: 'it is unfeasible to use excess HCl due to its high solubility with our final product PAC, which would make its separation difficult'. Therefore the alternate choice was opted, i.e using excess ATH. We had to study solubility of ATH in PAC as well as HCl. It was observed through experiments that ATH is sparingly soluble in water, HCl and PAC as well. Hence it was decided to use excess PAC in reactants' feed.

Simulation of continuous plant

Based on the optimised value of heat of reaction, heat transfer coefficient, activation energy and Arrhenius factor retrieved from the MATLAB programme, another programme was written to simulate the proposed continuous plant in steady state operation. Following equation was written and solved in the simulation for each reactor-

$$x = \left(\frac{V_0 \; k \; c_a^{\frac{2}{3}} c_h}{c_{aprev} \cdot F}\right)$$

V_0 = volume of the reactor
c_a = concentration of ATH in present reactor
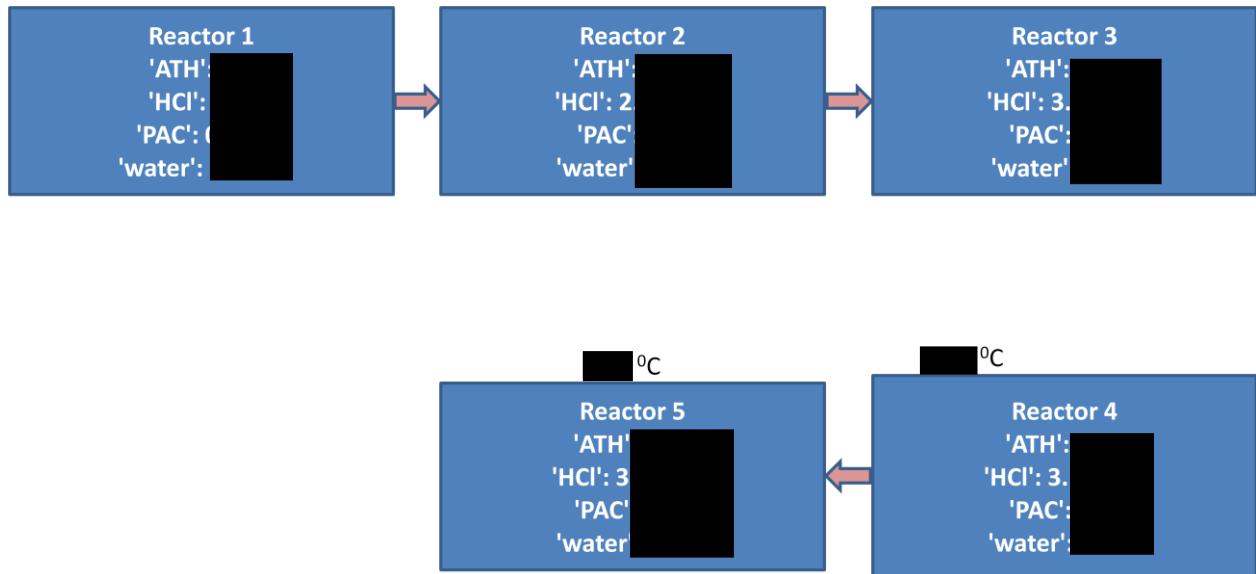x = conversion of the ATH in present reactor
F = flow rate (in and out) of the reaction mixture
c_{aprev} = concentration of ATH in preceding reactor
k = rate constant

Bisection method was used to solve above equation and for each of the five reactors, following results were obtained:

Parameter	Value
PAC to HCl molar ratio	██
net_conv w.r.t HCl	██
PAC_production	████ ns/day
PAC mass fraction	██

Variable	Range	Units
Reactor1 – temp	██	^0C
Reactor2 – temp	██	^0C
Reactor3 – temp	██	^0C
Reactor4 – temp	██	^0C
Reactor5 – temp	██	^0C
Feed flow rate	██	lit/hr
ATH feed conc	██	mol/lit

Additional equipments

The proposed continuous plant requires additional equipments, mainly to fullfill three purposes i)a continuous plant requires automation and rigorously designed control system in order to keep track on product quality as well as to ensure if the plant is operating under safety limits, ii)operations in continuous process need to be fast and more adjustable, iii)The unreacted feed needs to be separated from the final product and recycled

Controllers, sensors, and automated valves/switches would be required to fullfill the first purpose. For the second purpose, the external heat exchangers are needed for preheating of the reaction mixture, inlet feed of the reactants have to be present in each reactor to compensate any disturbances may arisen from previous reactor(s) and obviously additional piping system to implement these. To serve the third purpose, since we have used ATH in excess, we cannot pass the product outlet directly to the filtration unit as an excess amount of ATH can cause significant damage to the filters. A flow retarder and a separation tank have been proposed to ease the work of filtration units. A flow retarder will essentially slow down the velocity of flow (and not the flow rate) of the final feed, which will ultimately reduce the turbulence and would make easier to separate unreacted ATH. The retarded flow will be passed through a settle tank, where around 70% if the sludge will be settled down. Remaining sludge will be removed from filtration unit(s).

Dynamic equations to design a control system

Our previous analysis of the continuous plant assumed steady state operation. The analysis would be incomplete if we do not consider the setup time of the plant, stability and safety.

Following set of equations are proposed for the dynamic operation of the plant:

$$T_r = a_r T_{rin} + b_r T_{rout}$$

$$T_w = a_w T_{win} + b_w T_{wout}$$

$$Q_r = T_{rd} T_r V_r \ (Cp_a c_a + Cp_h c_h + Cp_p c_p + Cp_w c_w)$$

$$\frac{dV_r}{dt} = V_{in}^* + V_a^* - V_{out}^* - V_s^*$$

$$V_r \cdot \frac{dc_a}{dt} = c_{hin} V_{in}^* + c_{av} V_a^* - c_{aout} V_{out}^* - k.c_a \ c_h \ V_r^*$$

$$V_r \cdot \frac{dc_h}{dt} = c_{hin} V_{in}^* + c_{hv} V_a^* - c_{hout} V_{out}^* - 3.k.c_a \ c_h \ V_r^*$$

$$V_r \cdot \frac{dc_p}{dt} = c_{pin} V_{in}^* + c_{pv} V_a^* - c_{pout} V_{out}^* + k.c_a \ c_h \ V_r^*$$

$$V_r \cdot \frac{dc_w}{dt} = c_{win} V_{in}^* + c_{wv} V_a^* - c_{wout} V_{out}^* + 3.k.c_a \ c_h \ V_r^*$$

$$sumin = T_r V_{in}^* (Cp_a c_{ain} + Cp_h c_{hin} + Cp_p c_{pin} + Cp_w c_{win})$$

$$sumout = T_r V_{in}^* (Cp_a c_{aout} + Cp_h c_{hout} + Cp_p c_{pout} + Cp_w c_{wout})$$

$$V_r \cdot \frac{dQ_r}{dt} = h.A.(T_w - T_r) - \Delta H.\frac{dc_a}{dt} + sumin - sumout$$

$$Cp_w.m.\frac{dT_w}{dt} = F_{in} T_{win} - F_{out} T_{wout} - h.A.(T_w - T_r)$$

T_r = mean temrature of the reactor in Kelvins
T_{rin} = temperature of reactor inlet
T_{rout} = temperature of reactor outlet
Q_r = total amount of heat inside the reactor given by
V_r = volume of the reactor
c_a = mean concentration of ATH in the reactor
c_{ain} = conc. of ATH in reactor inlet
c_{aout} = conc. of ATH in reactor outlet

h = heat transfer coefficient between reactor and the jacket
A = area of heat transfer
T_w = mean temperature in jacket
T_{win} = temperature of jacket inlet
T_{wout} = temperature of jacket outlet

F_{in} = inlet flow rate of water or steam into jacket
F_{out} = outlet flow rate of water or steam from jacket
V_{in}^* = inlet flow rate of reaction mixture into reactor
V_{out}^* = outlet flow rate of reaction mixture from reactor
V_a^* = flow rate of feed stream into the reactor
V_s^* = flow rate of HCl fumes from reactor to scrubber
m = mass capacity of the jacket
Cp_w = Heat capacity of water

Pressure inside the reactor can be give by VLE relation of reaction mixture, which can be determined if the quantities listed above are known.

Above system of equations can be analysed using process control theory to determine setup time of the plant and the required controller system(s) ensuring the stability and safety of the plant. At a reactors scale, a proposed control system would be a combination of cascading and split control, based on the controlled parameters and manipulated parameters we have for a given reactor as given below
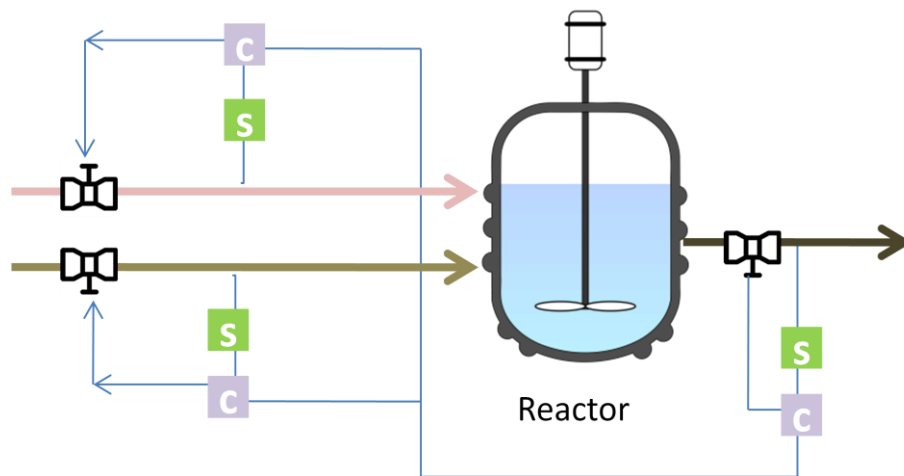
Constant parameters
heat transfer coefficient between jacket and reactor
area of the heat transfer in a reactor
inlet concentration of entity 'a' } x4
inlet temperature
volume of the reactor
mass of water contained in jacket
mass of steam contained in jacket
molar heat capacity of entity 'a' } x4

Manipulated variables
inlet flow rate of reaction mixt.
outlet flow rate of reaction mixt.
intlet flow rate of AH stream
intlet flow rate of HCl stream
outlet flow rate of HCl from sparger
inlet flow rate of water/steam in jacket
outlet flow rate of water/steam in jacket

Controlled variables
outlet concentration of entity 'a' } x4
mean temperature of the reactor
outlet temperature reactor
reactor pressure

Conclusion:

- The model utilized numerous assumptions and therefore the plant is being described in a fuzzy logic. For example, we do not know precisely what the rate law of the reaction is. We however obtained an range under within the rate law expression should lie.
- The final result was produced based on the suggestion that the daily production of the continuous PAC plant must surpass production of the existing batch plant
- There were many aspects of the reaction system that cannot be described without performing specific experiments, like the VLE of the reaction mixture.
- In order to carry out a more complete analysis of the plant, one needs to do rigorous analysis on the dynamics of the plant and process control theory.

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