DYNAMIC SIMULATION OF THE CLEAVAGE SECTION IN A PHENOL PLANT FOR SAFETY ANALYSIS

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Abstract

The dynamic model of the cumene hydroperoxide (CHP) cleavage reactor in a phenol-from-cumene plant is developed in order to simulate its transient behavior. According to literature on safety many thermal runaways or explosion incidents are caused by the decomposition of organic peroxides because of the relatively weak oxygen-oxygen bond that is the basis for their reactivity and tendency for spontaneous and violent decompositions. This is what may happen in the cleavage section, where an accidental catalyst inhibition can cause CHP hold-up and possible thermal decomposition that depends on its concentration. Aim of the dynamic simulation is to prefigure and analyze all those scenarios relevant to non normal operating conditions that can flow to dangerous situations due to presence of a base coming from preceding sections that inhibits the cleavage reaction. Operation could become critical when the disturbance due to NaOH feed stops and catalyst action is restored in the reactor.

Keywords

Dynamic modeling, Disturbances, Safety, Tubular reactor, Cumene hydroperoxide cleavage.

Introduction

Process simulation models are essential components of the basic toolkit of process design teams. Traditionally, these simulations are static models and, sometimes, substantial engineering design margins are required for compensate to their limited abilities. When specialized dynamic modeling can be developed to investigate specific non steady-state scenarios, design uncertainties can be reduced.

Today increasing computing speed and software that is more advanced constantly extend the application of dynamic simulations to project elements that were out of practical reach until recently. Dynamic simulation allows the design engineer to investigate the time dependent behavior of a process, which leads to significant cost savings (optimized design margins, lower energy demands, enhanced plant operability, smoother commissioning) and to improved process safety.

It is on this latter aspect that we focus the dynamic simulation of the cumene hydroperoxide (CHP) cleavage reactor in a phenol production plant.

Hazard Analysis of the Phenol-from-Cumene Process

As it is well known, the production of phenol and acetone from cumene (Hercules-BP process) develops through five process operations:

1) Oxidation of cumene to CHP.
2) Oxidate settling and wash.
3) CHP concentration.
4) Cleavage of CHP to phenol and acetone.
5) Fractionation and purification of cleavage mixture into acetone and phenol.

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Each of the above steps involves many safety aspects mainly related to temperature (both the reactions are exothermic), explosive mixture cumene-air and CHP concentration.

An analysis of hazard associated to the first part of phenol-acetone plant, a series of cumene oxidation reactors, points out how the main risk in the oxidation section is the explosive mixture cumene-air (Pellegrini at al., 2001) although the most dangerous component seems to be cumene hydroperoxide. In fact, many thermal runaway incidents in chemical industries, during exothermic operations, are due to reactivity and instability of organic peroxides (Luo at al., 2001). In any case, to obtain high selectivity, cumene conversion is usually less than 40% so CHP concentration in oxidation reactors is rather low. Moreover the acidic by-products of the oxidation reaction that could catalyze the decomposition of CHP are neutralized by addition NaOH or sodium carbonate while temperature is controlled by cooling water (Fleming at al., 1976; Arendt at al., 1986).

In the following stripping section, operating at low temperatures, CHP is concentrated to approximately 80 wt. % and fed to the first of the two cleavage reactors.

Focus of our study is to analyze those scenarios that can be dangerous for the cleavage unit taking into account that failures occurring in preceding sections of the plant can affect normal operation of the cleavage reactors and lead to risk situations. The risk situation due to the presence of NaOH coming from the oxidation zone has been considered as example case.

The Cleavage Reactor and its Modeling

The cleavage reaction takes places in a tubular loop reactor with two sections where heat exchange to remove the heat of reaction is provided. There are two inlet flowrates: one, in the upper part of the reactor, is constituted by cumene hydroperoxide, acetone and some by-products; in the other, fed at the bottom, also a small percentage of sulphuric acid, which acts as catalyst, is present. The pump at the reactor bottom allows to re-circulate up to one hundred times the total feed: the high acetone content dilutes the heat released by the exothermic reaction.

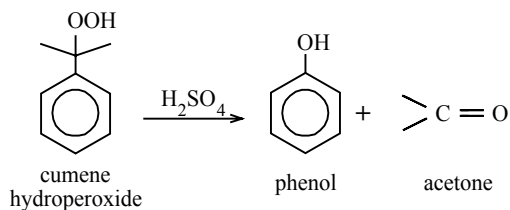The main reaction of cumene hydroperoxide acid cleavage to phenol and acetone:

Figure 1. Main CHP cleavage reaction.

is very exothermic ($\Delta \hat{H}_R = -1540$ kJ/kg CHP).

To keep loop temperature sufficiently low (70÷77°C) cleavage is conducted in a boiling mixture of acetone and phenol in order to operate with CHP dilute solutions and to remove heat reaction by evaporation of acetone (Caldi, 1999).
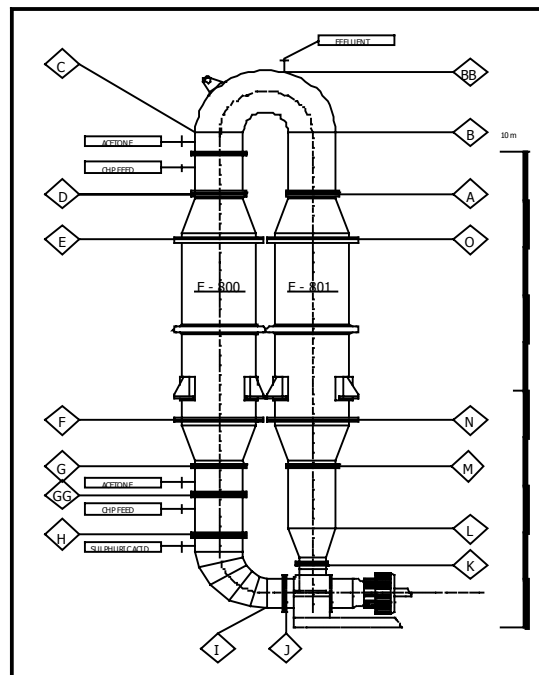

Figure 2. Cleavage reactor.

Since the acid catalyzed reaction of CHP is highly selective to phenol and acetone we consider the only kinetics of the main reaction, neglecting secondary reactions from CHP. It is a simple first order kinetics with respect to CHP and to catalyst:

$$r = kC_{CHP}C_{H_2SO_4} = k_0 e^{(E_0/RT_0 - E/RT)}C_{CHP}C_{H_2SO_4} \quad (1)$$

The kinetic constant k depends on both temperature and concentrations of water and phenol; for more details please refer to Cavalieri d'Oro et al. (1986), Cavalieri d'Oro (1990), Chen and Sjoberg (1980) and Caldi (1999).

The transient model of the reactor is given by a system of Partial Differential Equations (PDE) that represent the material and energy balances for each of the zones that constitute the equipment.

Axial development of the loop reactor is in agreement with a plug flow schematization, i.e. the variables of interest are intended to change only along the axial coordinate. So the mass and energy balances for the adiabatic regions and the water-cooled exchangers present, besides the derivative with time due to the transient condition, a derivative with the axial coordinate or, equivalently, with the contact time τ.

$$\begin{cases} \dfrac{\partial C_i}{\partial t} + \dfrac{\partial C_i}{\partial \tau_R} = \pm r \\[2mm] \dfrac{\partial T}{\partial t} + \dfrac{\partial T}{\partial \tau_R} = \dfrac{\left(-\Delta \bar{H}_R\right)\cdot r}{\bar{c}_{P_{m_\lambda}}^{L}\, C_{tot}} \end{cases} \quad (2)$$

$$\begin{cases} \dfrac{\partial C_i}{\partial t} + \dfrac{\partial C_i}{\partial \tau_R} = \pm r \\[2mm] \dfrac{\partial T}{\partial t} + \dfrac{\partial T}{\partial \tau_R} = \dfrac{\left(-\Delta \bar{H}_R\right)\cdot r}{\bar{c}_{P_{m_\lambda}}^{L}\, C_{tot}} - \dfrac{4U\left(T-T_e\right)}{D_T\,\bar{c}_{P_{m_\lambda}}^{L}\, C_{tot}} \\[2mm] \dfrac{\partial T_e}{\partial t} + \dfrac{\partial T}{\partial \tau_W} = \dfrac{4U\left(T-T_e\right)}{D_{eq}\,\hat{c}_{P_W}\,\rho_W} \end{cases} \quad (3)$$

Let's consider, as the first step, the solution of the above system under steady state condition, i.e. null derivative with time. We have experienced that a simple numerical approach is to solve the equations related to the adiabatic zones with a fourth-order Runge Kutta method while the two heat exchangers have been treated as a series of CSTRs (Continuous Stirred Tank Reactors) which corresponds to a forward Euler method. This latter choice, which leads to a system of nonlinear algebraic equations, allows to take better into account the presence of the countercurrent cooling water.

It is well known that a tubular reactor may be modelled as a continuous system as well as an infinite sequence of stirred tank reactors. Of course, beyond a given discretization number, the simulation results do not change significantly, i.e. asymptotic conditions are reached (Pellegrini et al., 1988).

A discretization corresponding to three cells for each exchanger is sufficient to give reliable values for CHP concentration and temperature along the cleavage reactor (as shown in Fig. 3 and 4 respectively), though asymptotic conditions are not perfectly reached.
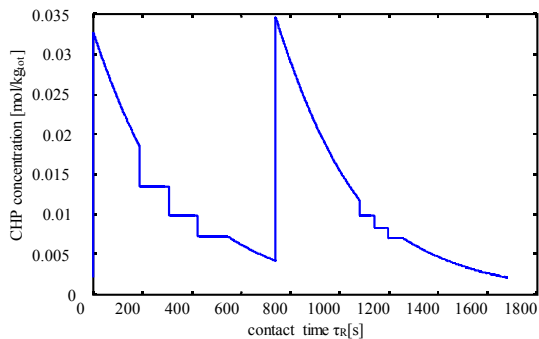

Figure 3. CHP profile with 3 cells for the heat exchangers.

Increasing the number of cells, NR, variables into the exchangers are depicted with more accuracy, but critical
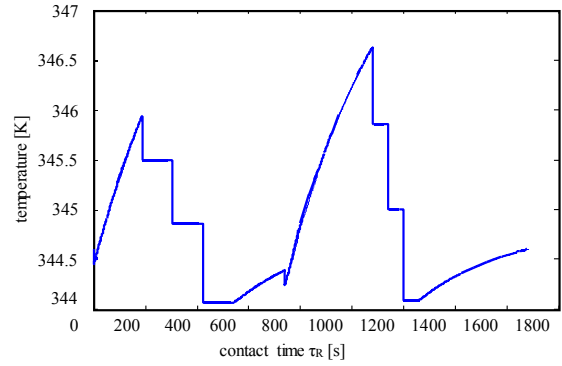

Figure 4. Temperature profile with 3 cells for the heat exchangers.

points (maximum temperature and CHP concentration) do not change considerably as shown in the following figure, where NR=10:
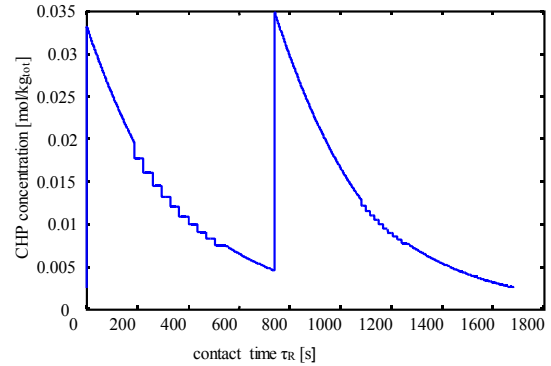

Figure 5. CHP concentration profile with NR=10.

A preliminary investigation of potential hazards due to the exothermic nature of the cleavage reaction has been performed by means of steady state simulations for increased values of catalyst concentration. Although reaction rate increases, the maximum values of temperature are almost the same of those obtained for the normal catalyst concentration, showing that there is no risk in this case.

Dynamic simulation

As a first step we approached the dynamic simulation by solving Eqs. (2) and (3) in complete form, i.e. by subdividing the axial coordinate and applying a finite difference method. So the PDE system is reduced to an Ordinary Differential Equation (ODE) one which can be easily solved (no stiffness problems arise). In the mean time we realized that since the reaction rate is very high, quasi steady-state conditions can be assumed for the process with remarkable savings from the computational point of view.

Before simulating the dynamic behavior an accurate analysis of the causes that can give rise to hazard situations in the cleavage reactor has been made.

The presence in the reactor of a base (NaOH) coming from the preceding section of cumene oxidation can involve high probability of risk. In fact the base neutralizes the sulphuric acid that acts as catalyst inhibiting the cleavage reaction and allowing the reactant hold-up.
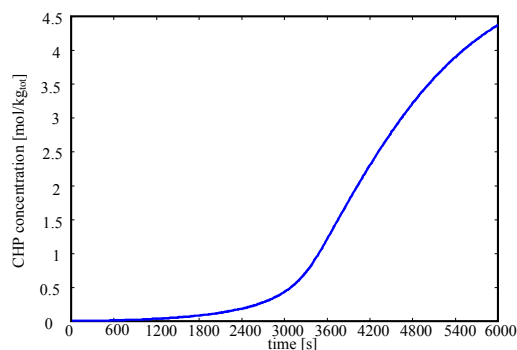

Figure 6. Profile of CHP concentration with feed polluted by NaOH

The course of the situation (i.e. to runaway conditions or not when reaction is no more inhibited) depends mainly on the elapsed time between the base injection and the recovery of the normal operation, as illustrated in the following figure, where explosion is avoided (duration of the disturbance equal to 30').
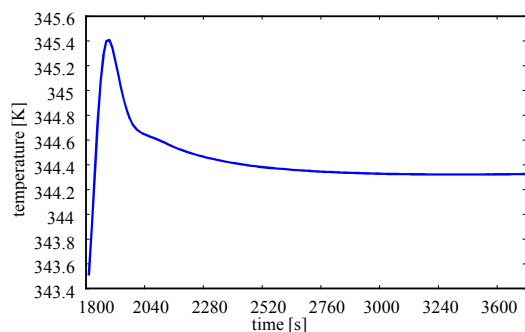

Figure 7 .Temperature profile with restoration of sulphuric acid concentration after 30'

Operation becomes critical if catalyst restoration occurs after 50': temperature can reach the mixture bubble point with consequent sudden evaporation of the liquid mass.

Conclusions

Dynamic simulation of a CHP cleavage reactor for safety purpose has been developed. A feed poisoned with a base which inhibits the reaction is considered. Time elapsed before recovering normal operating conditions is

an important variable to monitor in order to prevent runaway conditions due to CHP hold-up. Other scenarios relevant to cooling water failure have been analyzed in Pellegrini et al. (2003).

Nomenclature

C = concentration, mol/m^3

$\tilde{c}_P$, $\hat{c}_P$ = molar and mass specific heat, J/(mol·K), J/(kg·K)

D_T, D_{eq} = tube and equivalent diameter for exchangers, m

E = activation energy, J/mol

k = rate constant, m^3/(mol·s)

R = gas constant, J/(mol·K)

r = rate of reaction, mol/(m^3 s)

T, T_e = process side and water side temperature, K

t = time, s

τ_R, τ_W = process side and water side residence time, s

U = overall heat transfer coefficient, J/(m^2·K·s)

$\Delta\tilde{H}_R$ = heat of reaction, J/mol

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