

# Dinamikus szimulátor fejlesztése: Fenol előállítása kumolból

*Development of dynamic process simulator: Phenol production from cumene*

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## **Összefoglaló**

Megbízható és biztonságos technológiák tervezése az egyik legfontosabb feladatuk a mérnököknek. Dinamikus folyamat szimulátorok fejlesztése segítheti a mérnököket, hogy a veszélyes állapotokat felmérjék, valamint ezek tapasztalatot nyújthatnak az üzemeltető operátoroknak is. Ilyen célból készítettük el egy fenol előállító rendszer dinamikus szimulátorát. Fenol előállítása kumolból egy intermedieren keresztül történik, ami a kumol-hidroperoxid (CHP). A CHP jelentős hőfejlődés közben bomlik, ami a reaktor elfutásához vezethet. Az elkészített dinamikus szimulátort a jövőben biztonsági elemek, megoldások tesztelésére, összehasonlítására és azok fejlesztésére tervezzük felhasználni.

## **Summary**

Engineers' one of the most important task to design reliable and safe technologies. Development of dynamic process simulators can help engineers to identify hazard conditions, which can also give experience for operators. For this purpose a dynamic simulator of phenol production system has been developed. Phenol production from cumene happens through a formation of intermediate, called cumene-hydroperoxide (CHP). CHP can decompose easily in exothermic reactions resulting reactor runaway. In the future, the developed dynamic simulator will be used to test, compare and improve safety elements.

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## **Introduction**

Chemical engineers' most crucial task is to design reliable and safe process systems to produce valuable chemical products. Usually, the biggest challenge in such a task is the optimal design of the conversion system, which starts with the characterization of the safety operating conditions to ensure the prevention of any undesirable situation.

Engineers have applied steady-state process simulators for years now to explore the operating regimes of optimal and hazard conditions. Nowadays process dynamic simulators (DPS) become more and more important, and it already has a widespread use. The major application of DPS is in the development of operator training simulators with the aim of training operational staff of chemical technologies. Process operators can learn:

- chemical plant start-up and shutdown situations;
- handling process interlocks and trips;
- steady-state operations at different operating points etc.

Dynamic simulators help to understand the chemical technology, plant control theory and operation. It provides confidence in normal and abnormal operations. Moreover, in dynamic simulations engineers are able to check and develop control systems before the actual start-up. Another possibility in dynamic simulator is designing, developing and testing safety systems to avoid any possible unsafe situations. Modified operating parameters can lead to malfunctions, and these can be prevented if the operators know well the behavior of the technology.

This work is about to develop a dynamic simulator of a hazard reactor system, on which we will be able to test the behavior of the system due to some possible malfunctions, and to design safety elements to decrease the risk of these malfunctions. As a case study, production of phenol was chosen based on cumene oxidation with air.

CHP is an intermediate in this technology containing weak oxygen bonds, which can decompose upon exposure to acids, bases, contaminants, heat etc. This highly exothermic decomposition can lead to development of reactor runaway, which can cause the exposition of reactor.

### Case study

Almost all used phenol is from synthetic processes. Hercules and BP Chemicals started to develop the cumene-hydroperoxide (CHP) route to phenol. Nowadays worldwide phenol production is based on this technology [1].

Phenol producing from cumene takes two reaction steps. The first reaction is the oxidation of cumene (1), where air bubbles through liquid cumene. The second reaction is cleaving CHP under acidic conditions to produce phenol as product and acetone as a co-product (2). Both reactions are highly exothermic.



Oxidation of cumene is auto-catalyzed by CHP, and proceeds via a free-radical mechanism. This mechanism causes many side-reactions which take place simultaneously. Quantity of by-products can be reduced by optimizing the process conditions. The main oxidation byproducts are dimethyl-benzil-alcohol (DMBA) and acetophenone (AP). Main byproducts are formed in the next reactions (3-4):



CHP concentration and temperature have positive effect on the quantity of byproducts. Therefore, the CHP concentration should be kept 25-30%, and the temperature is decreased as the CHP concentration increases [2]. The second main reaction is the acid-catalyzed cleavage of CHP to produce phenol and acetone. Many reactions occur as a result of free-radical mechanism. Primary side reactions here are forming DMBA from cumene and CHP, and forming acetophenone plus methanol from CHP [3].

For the purpose of developing dynamic simulator, a simplified reaction kinetic has to be identified. J.P. Fortuin carried out the oxidation reaction of cumene at 110 °C and 120 °C, and measured the concentration of CHP in function of time [4]. Hattori carried out the oxidation reaction at 120 °C temperature too, but with different initial CHP concentration [5]. Weber measured at 100 °C the concentration of main byproducts in function of time [6].

Reaction kinetics has been identified based on the above mentioned measurements and (1, 3-4) reaction steps considered as a part of the reaction mechanism. The fit of the model is shown in Figure 1. The following reaction rate equations characterize the kinetics. The identified kinetic parameters for oxidation reaction are shown in Table 1.

$$r_{ox} = k_{0,ox} \cdot \exp\left(-\frac{E_{A,ox}}{RT}\right) \cdot c_{cumene} \cdot c_{CHP}^{0.5} \quad (5)$$

$$r_{s1} = k_{0,s1} \cdot \exp\left(-\frac{E_{A,s1}}{RT}\right) \cdot c_{CHP} \quad (6)$$

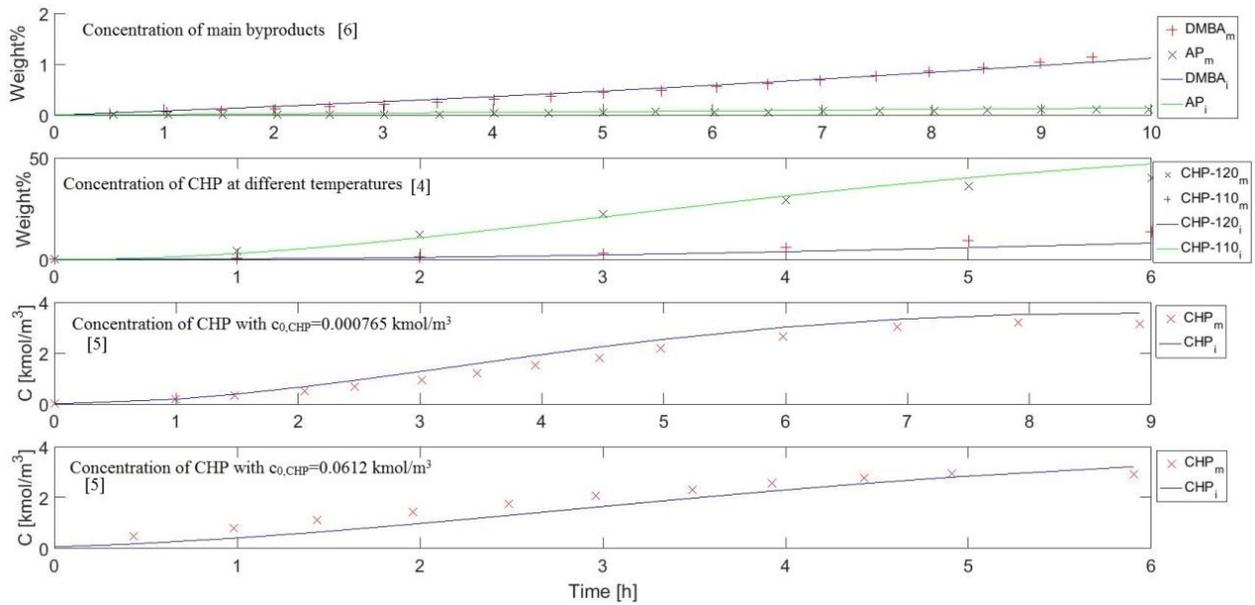
$$r_{s2} = k_{0,s2} \cdot \exp\left(-\frac{E_{A,s2}}{RT}\right) \cdot c_{CHP}^{0.5} \quad (7)$$

Cleavage of CHP occurs under acidic conditions. Beside the production of phenol, two side reactions take place, which are the same as in oxidation reaction. Levin measured that acidic conditions influence the reaction rates, therefore the by-side reactions have different reaction kinetic parameters and equations in oxidation and cleavage section. The following reaction rate equations characterize the kinetics, where  $m=126.7 \text{ m}^3/\text{kmol}$ . Levin identified the reaction kinetic parameters for the acid-catalyzed cleavage, which are shown in Table 1 [3].

$$r_p = k_{0,p} \cdot \exp\left(-\frac{E_{A,p}}{RT}\right) \cdot \exp(m \cdot c_{acid}) \cdot c_{acid} \cdot c_{CHP}^2 \quad (8)$$

$$r_{s3} = k_{0,s3} \cdot \exp\left(-\frac{E_{A,s3}}{RT}\right) \cdot c_{cumene} \cdot c_{CHP} \quad (9)$$

$$r_{s4} = k_{0,s4} \cdot \exp\left(-\frac{E_{A,s4}}{RT}\right) \cdot c_{CHP} \quad (10)$$



**Figure 1.** Fit of the kinetic model (continuous lines) to the measured data (markers)

**1. Table.** Reaction kinetic parameters for oxidation and cleavage

Reaction step		Pre-exponential factor ( $k_0$ )	Unit	Activation energy [kJ/kmol]
Oxidation section (identified)	(1) reaction	$7.4214 \cdot 10^{19}$	$[\text{m}^{4.5}/(\text{kmol}^{1.5} \text{ h})]$	$1.5650 \cdot 10^5$
	(3) reaction	$1.6119 \cdot 10^{18}$	[1/h]	$1.4607 \cdot 10^5$
	(4) reaction	$2.2752 \cdot 10^{18}$	$[\text{m}^{1.5}/(\text{kmol}^{0.5} \text{ h})]$	$1.5169 \cdot 10^5$
Cleavage section	(2) reaction	$2.8800 \cdot 10^{21}$	$[(\text{m}^3/\text{kmol})^2/\text{h}]$	$1.5100 \cdot 10^5$
	(3) reaction	$6.3000 \cdot 10^{15}$	$[\text{m}^3/(\text{kmol} \text{ h})]$	$1.1510 \cdot 10^5$
	(4) reaction	$5.2200 \cdot 10^{14}$	[1/h]	$1.2550 \cdot 10^5$

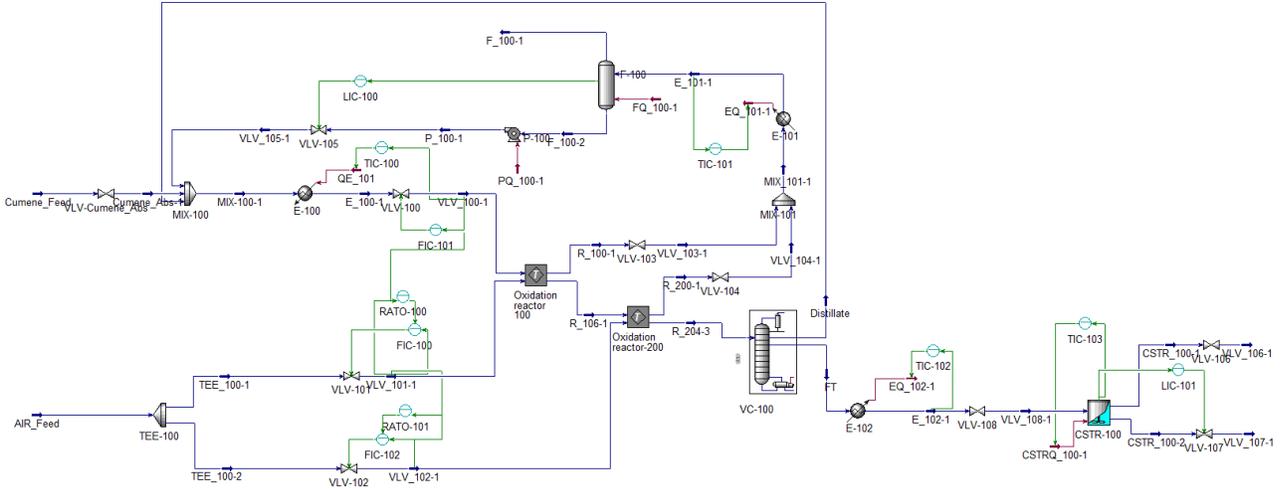
### Dynamic simulator of reactor system

Dynamic simulator of above mentioned reactor system has been developed in Aspen HYSYS. The major processing steps are the following:

- liquid-phase oxidation of cumene to CHP in series-flow bubble columns;

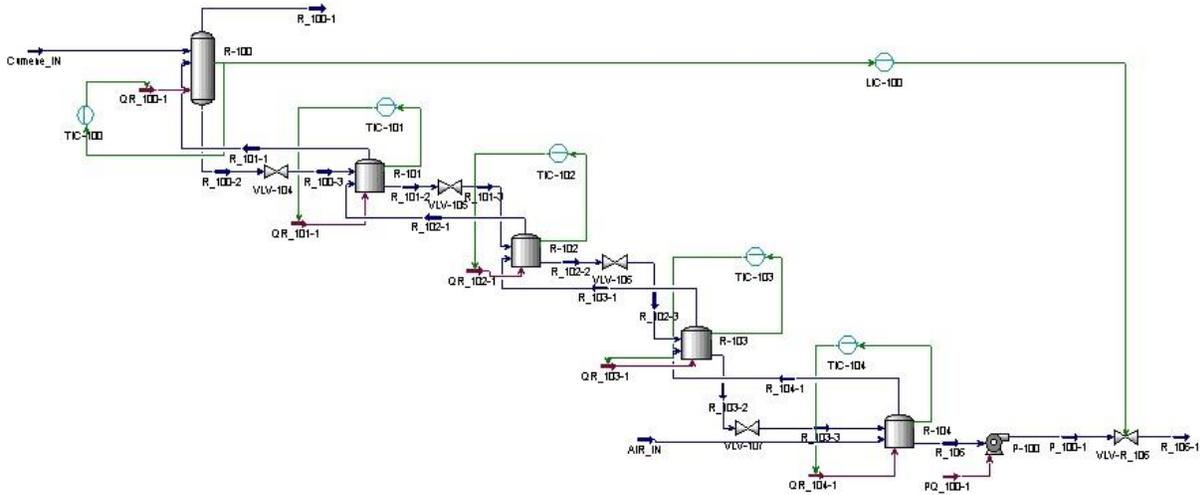
- concentration of CHP under vacuum;
- acid-catalyzed cleavage of concentrated CHP to produce phenol and acetone.

The dynamic simulator of investigated system is shown in Figure 2. The bubble columns have five sections, with inner cooler. The simulator of oxidation column was developed by four tank and a flash. All section is temperature controlled, and also the level of column is controlled. Air from oxidation columns contains cumene and CHP too, therefore this air stream is cooled down via E-101, and the liquid organic phase is separated from air in F-100 flash. Liquid phase is recycled to oxidation section.



**Figure 2.** Simulator of reactor system

In the oxidation section the fresh cumene with recycled cumene streams are pumped to bubble columns. Two oxidizers are in series with respect to cumene, but in parallel with respect to air. Cleaned atmospheric air is used for reaction. The residence time is between 5-6 hours overall. The dynamic simulator of the oxidation section is shown in Figure 3.



**Figure 3.** Simulator of oxidation sections

Concentration of CHP occurs under vacuum. Packed column is used to separate the cumene from CHP. Cumene comes as a distillate, and recycled to oxidation columns. Concentrated CHP (~60 w%) comes as bottom product, and flows to the cleavage section. Dynamic simulator of vacuum column is shown in Figure 4.

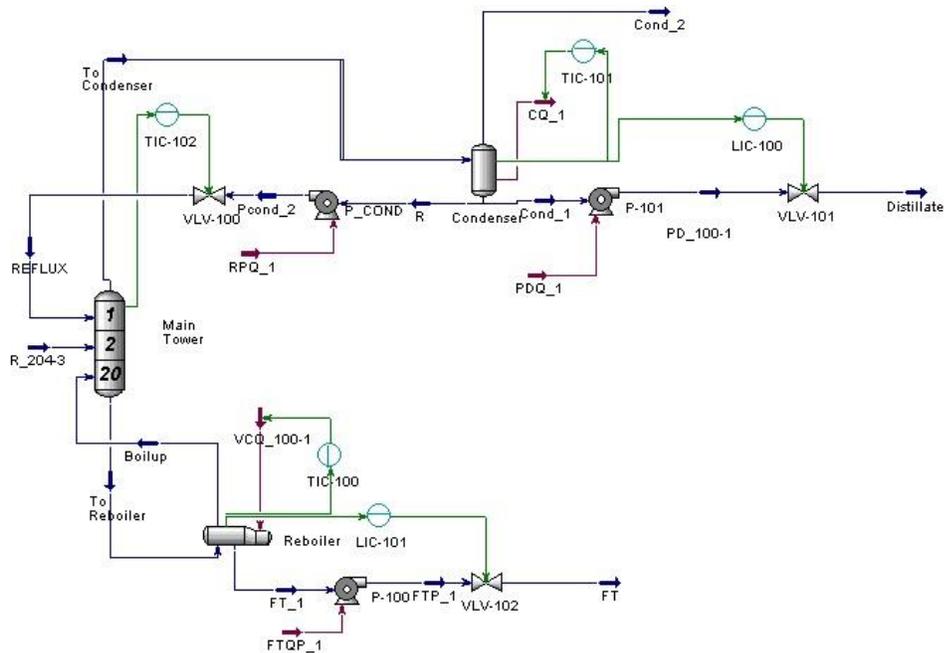


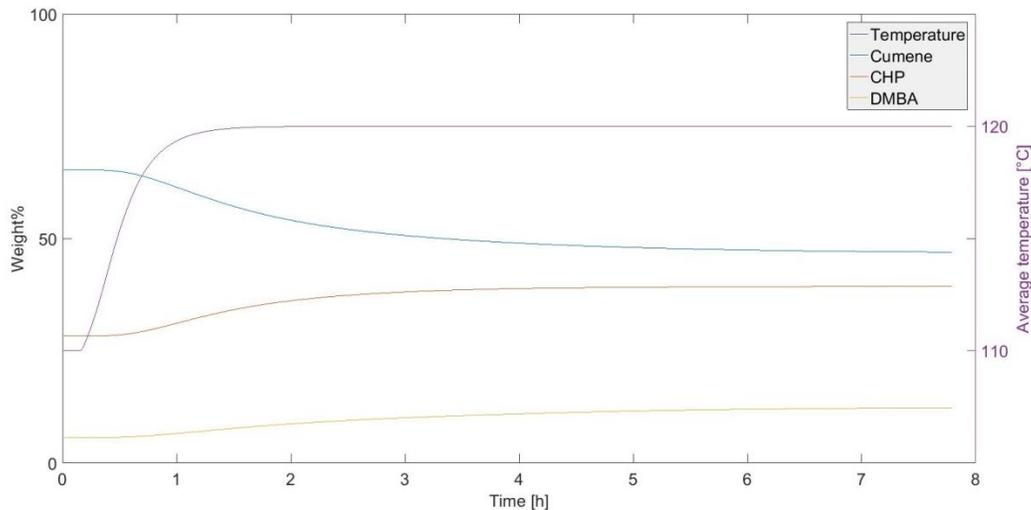
Figure 4. Simulator of vacuum column

Cleavage of CHP occurs in a continuous stirred tank reactor (CSTR). Beside the level controlling, temperature is need to be controlled due to highly exothermic reactions. Conversion and selectivity of oxidation sections, and also of the cleavage section is shown in Table 2.

2. Table. The calculated conversion and selectivity in the system

	Oxidation section 1.	Oxidation section 2.	Cleavage reactor
Conversion [%]	18.28	9.93	95.01
Selectivity of main product [%]	78.69	72.98	96.32

Effect of temperature increase in second oxidation section has been analyzed, where the setpoint of temperature controllers increased from 110 °C to 120 °C. As a result of temperature increase the concentration of cumene decreased, but the concentration of CHP and DMBA increased due to higher reaction rate, which is shown in Figure 4. Five temperature controllers operate here for the five column sections, but only one temperature is indicated in Figure 5., which is the average of present values with respect to time.



**Figure 5.** Cumene, CHP and DMBA concentration trajectories in the second oxidation section due to temperature increase

## Conclusion

In this paper simplified oxidation reaction kinetics has been identified based on measurements found in literature, and also the dynamic simulator of reactor system of phenol production technology has been developed in Aspen HYSYS. The simulator gives reliable results based on the identified reaction kinetics. Therefore, it is applicable to model operation malfunctions, hazard situations and safety elements. In the future, the gained experience during this work can be applied in the development of dynamic simulators including hetero-catalytic reactors, like the production of high hydrogen content (in molecular structure) fuels from vegetable oils by hydrocracking.

## Acknowledgement

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