Modeling of a gas-liquid phase cumene oxidation process for efficient synthesis of cumene hydroperoxide (HPOC)

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Abstract. Cumene hydroperoxide (HPOC) have been extensively used as an important intermediate for developing and synthesizing cross-linking agents of large-scale production of plastics and rubbers. In the chemical industry, HPOC is widely produced by the cumene oxidation process, which is energy-intensive and highly exposed to safety hazards including severe fire and explosion incidents. In this contribution, the cumene oxidation takes place in the mixture of a gas-liquid binary system. The whole set-up of cumene oxidation process including synthesis, separation and purification was established and optimized by using Aspen HYSYS. In the modelling, cumene and O₂ were carried by the air flow into a liquid phase of aqueous base solution. The conversion of HPOC was high as 31% at optimum base concentration. We further modelled the distillation separation process considering a multi-stage distillation process. By reducing the pressure of distillation from 200 to 20 kpa, the HPOC separation was more efficient with significant composition differences between gas and liquid phase. Under the pressure of 20 kpa, the purity of HPOC reached high as 80% with minimum energy consumption in the liquid phase after two-stage distillation, and further purified by post-treatment to yield high-purity product.

1. Introduction
The process industries spend an estimated $500 billion annually worldwide in conceptual design, process engineering, detailed engineering, construction, startup and maintenance for chemical, refining, polymer and power plants. In order for chemical engineers to successfully execute these process and product studies, process modeling plays a key role in enabling technologies for process development and design, equipment sizing and rating, and process debottlenecking and optimization. In recent years, process modeling benefits the energy-efficient chemical processes for reducing petrochemical energy consumption, minimizing emission of toxic residues/ greenhouse gases for resolving environmental hazards within the chemical industry. Models allow the anticipation and control of an industrial process. Such modeling is made possible by using the Aspen HYSYS software.

Organic peroxides have been extensively used as intermediates in the development of large-scale production of plastics and rubbers as polymerization initiators and cross-linking agents for rubbers. Chemical engineering plants involving peroxide production are majorly based on cumene hydroperoxide (HPOC) as the raw material. From the upper stream, HPOC is a product of the conversion process of cumene, benzene or propylene. However, the HPOC conversion process is energy intensive and conversion is normally low due to the low-efficient gas reaction at high temperature. In contrast, the cumene oxidation in gas-liquid mixture has been proven to be an energy-
efficient process with its highly efficient mixing of the reagents, binary phase reaction system along with high conversion.

Our goal is to model a process of synthesis of cumene hydroperoxide by oxidation. To this end, the choices to carry out the modeling of this process will be presented. We tailored the catalytic base compounds in the liquid phase, the pressure-temperature in the separation process, and the system diagram involving multi-stage distillation to maximize the HPOC conversion as well as minimize the energy consumption of the system. In particular, this paper will justify the choice of the thermodynamic model, reactors, flow rates and separation operations.

2. Modelling and simulations

2.1. Reaction mechanism of the oxidation process

Cumene hydroperoxide (HPOC) is a liquid organic compound at ambient temperature and pressure. It is an important intermediate compound in the chemical industry. Indeed, it is found as a product in the conversion processes of cumene but also benzene and propylene. HPOC will then be used as raw material in the process of synthesis of phenol and acetone. The process for synthesizing HPOC from cumene is an oxidation reaction.

![Figure 1. Reaction formula of Cumene oxidation in the mixture of gas (80% of nitrogen and 20% of hydrogen) and liquid (85% water, 15% NaOH). The cumene in the carrier air phase reacted with O₂ to form cumene hydroperoxide (HPOC) in the organic liquid. C₉H₁₂ (PH) + O₂ → C₉H₁₂O₂ (HPOC).](image)

For our study we will rely on a process of oxidation of cumene from the literature (Figure 2).

![Figure 2. Block diagram of the cumene oxidation process. The distillation column for preconcentration (D₁). The distillation column for vapor concentration (D₂). The economizer preconcentrator (E). The reactors for cumene oxidation (R₁ to R₃). The washing column (L) and the effluent collection for post-treatment (Y).](image)
2.2. Selection of the thermodynamic model

The selection of a suitable thermodynamic model for the prediction of enthalpy ($H$) and phase equilibrium ($K$) is very important to process modeling. Selection of an inappropriate model will result in convergence problems and erroneous result. The thermodynamic model was chosen from a selection flow chart provided for this purpose.

We used the Peng–Robinson–Stryjek–Vera equation of state (PRSV) model for the whole process. During the reaction, the fluid is composed of cumene, air (80 % of nitrogen and 20 % of hydrogen), water and sodium hydroxide (85 % of the water, 15% NaOH). Therefore, the reaction takes place in a binary phase system with a mixture of gas and liquids.

Ideally, we should have selected the Kabani-Danner model, but the software indicated a lack of coefficient, especially for the HPOC. Same for SRKSV. As a hydrocarbon system, we finally defined our thermodynamic model as PRSV.

To improve the process, it would have been wise to make changes to thermodynamic models:
- for air alone: Ideal gas state equation
- for the organic phase (cumene + HPOC): PR or SRK (flowchart)
- for the aqueous phase (Water + NaOH): NRTL, UNIQUAC, Margules, Van Laar, Wilson.
Nevertheless, HYSYS displayed a lack of coefficients for these models. So, we used PRSV for the whole process.

![Figure 3. Flowchart for selecting the thermodynamic model.](image)

2.3. Selection of reactors and flows

According to Figure 2, the reaction of the oxidation of cumene is carried out in a cascade of three reactors in series. It remains to determine the type of reactor: Gibbs, equilibrium, conversion, CSTR, PFR. We chose a conversion reactor. Indeed:
- CSTR / PFR reactor: we found in the literature a value of the activation energy of the reaction. But we lacked a value for the kinetic constant.
- Gibbs Reactor: the model we chose did not include the free energies of all compounds.
- Reactor to conversion: according to several sources in the scientific literature, it is indicated that the conversion rate, relative to cumene, is between 20 and 50%. We therefore made the choice to adjust the parameters of the reactors and the reaction, in order to obtain a conversion rate of the order of 30% at the outlet of the third reactor. Indeed, by trial and error, we set a reaction rate equal to 10% to meet this condition. (After adding the recycling unit, the conversion rate then goes from 30 to 99%).

We work at 5 bars and at a temperature of about 100 ° C for each reactor (conditions recommended by the literature). We do not work with an adiabatic reactor to be able to evacuate the heat produced by the exothermic reaction. Output temperatures of 105 ° C are then imposed. This temperature ensures a good conversion of HPOC and avoids the appearance of parasitic reactions. Indeed, HPOC decomposes at high temperature and other reactions become dominant at the expense of converting cumene to HPOC.

To manage the temperature of the reactor, one can choose wisely the flow of air at the entrance. The literature recommends a molar fraction of oxygen in the vapor phase of our reactors of 6%. There is then room for maneuver on the kinetics and consequently on the temperature of the reactor. To regulate the air flow, we added 3 "adjust". One for each reactor. The value to be adjusted is the input airflow and the target value is the fraction of oxygen in the reactor outlet vapors. It is worth 0.06.

To prevent spurious reactions, it is necessary to add soda. However, according to the literature, it is indicated that, for a 100% sodium hydroxide concentration, the ratio between the flow rates of cumene and sodium hydroxide is:

\[
m_{\text{cumene}} / m_{\text{NaOH}} = 0.1 \times 10^3 / 5 \times 10^{-7} = 2 \times 10^8
\]

It is thus possible to determine the soda inlet flow rate by knowing the input rate of cumene.

3. Results and discussion

3.1. Effects of NaOH concentration on HPOC concentration

| Time interval (h) | Cumene (Kg/h) | Soda (mg/h) | T (°C) | HPOC (%) | pH | Phenol (ppm) | Acidity (ppm) | O2 (%) |
|-----------------|--------------|------------|--------|----------|----|--------------|--------------|--------|
| 0-62            | 0.1          | 5\times10^{-4} | 78.2   | 30.1     | 3.6 | 4            | 30           | 6.2    |
| 62-124          | 0.1          | 0          | 80     | 29.5     | -   | 4            | 30           | 6.2    |
| 124-186         | 0.1          | 0          | 80.6   | 27.3     | 3.3 | 28           | 55           | 6.5    |
| 186-248         | 0.1          | 5\times10^{-4} | 78.3   | 27.9     | 3.9 | 8            | 30           | 6.0    |
| 248-310         | 0.1          | 5\times10^{-4} | 78     | 29.0     | 3.8 | 4            | 25           | 5.8    |

From the table, we know that sodium hydroxide flow rates are obtained at different time intervals for a given cumene flow rate. And the fastest to reach the specified rate is during the first time-interval, when the flow rate of sodium hydroxide is 5\times10^{-4} mg/h.

3.2. Effects of temperature and pressure on cumene concentration

After reacting, cumene, HPOC and other components (water, NaOH) should be separated. Oxygen and nitrogen will be in the vapor phase of our reactor where they will be separated from cumene and water through flash distillation.

The liquid phase at the outlet of the reactor 3 is, for its part, washed and then distilled twice to obtain a stream composed of cumene and which will serve as a recycle and an HPOC stream. To
achieve this, the literature proposes to successively make two distillations. We will work at low pressure because it is easier to separate the two components.

Figure 4. Temperature of bubble (red solid diamond and red line) and dew (blue open square and blue line) points versus mass fraction of cumene ($x_{\text{Cumene}}$) in the mixture of gas (80% of nitrogen and 20% of hydrogen) and liquid (85% water, 15% NaOH) under 200 kpa. The bubble curve showed slightly higher temperatures (196-184 °C) than the dew curve (195-183 °C) in the $x_{\text{Cumene}}$ range of 0.10-0.90. The maximum temperature gap between the bubble and dew curve was 1.5 °C at $x_{\text{Cumene}}$ of 0.50.

Figure 5. Temperature of bubble (red solid diamond and red line) and dew (blue open square and blue line) points versus mass fraction of cumene ($x_{\text{Cumene}}$) in the mixture of gas (80% of nitrogen and 20% of hydrogen) and liquid (85% water, 15% NaOH) under 20 kpa. The bubble curve showed significantly higher temperatures (140-110 °C) than the dew curve (133-103 °C) in the $x_{\text{Cumene}}$ range of 0.10-0.90. The maximum temperature gap between the bubble and dew curve was 17 °C at $x_{\text{Cumene}}$ of 0.50.

These two graphs show the curve of temperatures of bubble and dew point of cumene with mass fraction, under two pressure conditions (200kpa and 20kpa). Figure 4 showed the simulated phase diagram of the gas-liquid mixture under 200 kPa. The temperature of bubble (red solid diamond and red line) and dew (blue open square and blue line) points versus mass fraction of cumene ($x_{\text{Cumene}}$) in
the mixture of gas (80 % of nitrogen and 20 % of hydrogen) and liquid (85 % of the water, 15% NaOH). The bubble curve showed slightly higher temperatures (196-184 °C) than the dew curve (195-183 °C) in the $x_{\text{Cumene}}$ range of 0.10-0.90. The maximum temperature gap between the bubble and dew curve was 1.5 °C at $x_{\text{Cumene}}$ of 0.50.

In contrast, the simulated phase diagram of the gas-liquid mixture under 20 kPa was significantly different. Figure 5 showed the temperature of bubble (red solid diamond and red line) and dew (blue open square and blue line) points versus mass fraction of cumene ($x_{\text{Cumene}}$) in the mixture of gas (80 % of nitrogen and 20 % of hydrogen) and liquid (85 % of the water, 15% NaOH) under 20kpa. The bubble curve showed significantly higher temperatures (140-110 °C) than the dew curve (133-103 °C) in the $x_{\text{Cumene}}$ range of 0.10-0.90. The maximum temperature gap between the bubble and dew curve was 17 °C at $x_{\text{Cumene}}$ of 0.50.

Comparing the above two figures (Figures 4 and 5), we conclude that as the pressure decreases, the difference between the two points is much more obvious. Thus, the composition difference between two phases becomes larger and beneficial to increase the efficiency for the separation at certain temperature. Thus, we chose 20 kpa for the pressure of the first distillation.

3.3. The outputs of distillation system

The first distillation allows, according to the literature to remove about 70% of cumene (molar). Cumene being more volatile, it will be found primarily in the distillate.

We can increase the distillation number to increase the purity of our final product. In our case, we will use two low pressure distillation columns in series. The advantage of a low pressure is initially to lower the boiling points. In addition, a low pressure facilitates the separation of the components because the dew and boiling curves are further away (Figures 3 and 4). The number of theoretical stages of the distillation column is then reduced. Thus, we will perform a first distillation at 20 kPa and then a second at 13 kPa.

In order to get an integrated system on the purity of distillate, we also need to define the operating conditions of our columns and their characteristics. We first positioned a "Shortcut column". We defined:

- The pressure of the condenser and the boiler
- The fraction of HPOC in the distillate
- The cumene fraction in the rack

After a first calculation, we obtain the minimum reflux rate $\tau_{\text{min}}$. We then define the reflux ratio of our column $\tau$ as being equal to $\tau = 1.5 \times \tau_{\text{min}}$. We then went from a shortcut column to a distillation column. We have integrated the data collected through the "Shortcut column": the number of optimal stages, the position of the inlet, the condenser and boiler pressure, the reflux rate. Then we imposed a specification on the purity of the distillate.

The withdrawn from the second distillation column, composed mainly of HPOC, is then brought to ambient temperature and pressure and mixed with water to obtain a final product with an HPOC molar composition of at least 80%. The distillates obtained during the two distillations are put under pressure and ambient temperature before being recycled.

3.4. Discussion: potential improvements

The first criticism we can make about our Aspen simulation is the simplification of the reaction mechanism. Indeed, there is a multitude of side reactions with a direct link to the cumene conversion rate. In addition, we make the assumption that our diet (excluding recycling) is composed of cumene only. A real installation should surely implement a first cumene purification. Indeed, the presence of phenol, acetone or acid is a poison for the conversion of cumene to HPOC.

The lack of data with respect to thermodynamic models and kinetics did not allow us to study all the reactors available to us. For the Gibbs reactor, we lacked free enthalpies. For the PFR and CSTR reactors, we had little kinetic data for a reaction mixture using sodium hydroxide.
In addition, we could have made heat exchangers at the entrance of our process which must be heated to 100 °C using the withdrawal of our second distillation and the distillate of the first column. However, it is not advisable to heat process start elements with end-of-process elements because the distance between them is accompanied by heat losses.

In conclusion, we benefit from the software Aspen HYSYS and models that capture the dominant physical and chemical behavior of chemical systems to simulate the production of HPOC and gradually separate the products to efficiently achieve the purified HPOC.

We may use these correlative models within a thermodynamic modeling framework to describe and validate available data and to extrapolate with reasonable confidence outside the range of available data. Databanks and correlations of known accuracy play key roles in engineering calculations and I believe, will have much more industrial applications.

4. Conclusions
In this contribution, a highly efficient cumene oxidation process was modelled by using a gas-liquid binary system. The whole set-up of cumene oxidation process including synthesis, separation and purification was established and optimized by using Aspen HYSYS. In the modelling, cumene and O2 were carried by the air flow into a liquid phase of aqueous base solution. The conversion of HPOC was high as 31% at optimum base concentration. We further modelled the distillation separation process considering a multi-stage distillation process. By reducing the pressure of distillation from 200 to 20 kpa, the HPOC separation was more efficient with significant composition differences between gas and liquid phase. Under the pressure of 20 kpa, the purity of HPOC reached high as 80% with minimum energy consumption in the liquid phase after two-stage distillation, and further purified by post-treatment to yield high-purity product. The current system provides an energy-efficient and safe alternative to the existing large-scale cumene hydroperoxide (HPOC) processes for developing and synthesizing polymerization initiators and cross-linking agents.

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