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Simulation of *o*-Xylene Oxidation into Phthalic Anhydride: Rigorous Multitubular Catalytic Reactor Modelling and Exportation into the Process Flowsheet

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Abstract

The aim of this case study is to develop a process model including both heat integration and separation processes by means of ASPEN PLUS simulation software.

Previous studies have attempted to develop kinetic models or to retrieve optimal policies for operating the process multitubular catalytic fixed-bed reactor. This time a rigorous model is developed in ASPEN CUSTOM MODELER and exported into the process flowsheet. Then, the different postulated models are compared and evaluated.

The equation-oriented option in ASPEN PLUS enables rapid convergence and suggests encouraging future prospects in optimization.

Keywords: Aspen Plus, Aspen Custom Modeler, Exportation, Phthalic Anhydride

1. Introduction

The production of phthtalic anhydride is of practical relevance in large-scale organic synthesis, with a wide application in the Chemical Industry. Partial oxidation of *o*-xylene with air excess leads to the production of phthalic anhydride and releases noticeable quantities of heat. The reaction product is recovered by cooling the reaction gases in a two-stage process where liquid (condensation) and solid (desublimation) product streams are separated. The raw phthalic anhydride is then purified by stripping and distillation.

Previous works have focused on the study of the reaction network (Anastasov, 2003; Ross and Calderbank, 1971) and the achievement of the optimal operation policies of the reactor, including its optimization (Anastasov and Nikolov, 1998; Papageorgiou and Froment, 1996; Calderbank et al., 1977).

However, due to the complexity of the process, including a multitubular catalytic fixed-bed reactor, batch units (such as switch condensers and an intermediate storage vessel) and recycle loops, the simulation of the overall process has not been performed yet.

The most recent versions of ASPEN PLUS (permitting not only the sequential-modular simulation but also the equation-oriented one) avoid convergence troubleshooting when working with complex process diagrams containing nested recycle loops.

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Operation unit models which are not included in the ASPEN PLUS model library can be user-programmed and imported from ASPEN CUSTOM MODELER. Thus, a rigorous steady-state two phase model for describing the multitubular catalytic fixed-bed reactor is developed in this study. Additional models for the switch condensers and the intermediate storage vessel are also used.

The results obtained from the model are then checked with the data taken from literature (Ray and Sneesby, 1998).

2. Study of the Process

The production process of phthalic anhydride is quite a complex process, involving several side reactions and by-products. For this reason, the nature and quantity of catalyst used and temperature control in the reactor arise as relevant factors to consider in order to reach the required selectivity towards the final product: phthalic anhydride.

A rigorous description of the above-mentioned chemical reactions implies the knowledge of its mechanism and kinetic equations alike.

Some by-products have been identified owing to side reactions in competition with the desired one. Besides, three pre-products formed in previous series reactions lead to the synthesis of the product (PA, C_8H_{10}). These products (see Figure 1) are identified as benzoic acid (BAC, $C_7H_6O_2$), methyl-maleic anhydride (MMA, $C_5H_4O_3$), maleic anhydride (MA, $C_4H_2O_3$), *o*-tolualdehyde (*o*-TAL, C_8H_8O), *o*-toluic acid (*o*-TAC, $C_8H_8O_2$) and phthalide (PH, $C_8H_6O_2$). If oxidation conditions become more aggressive, partial or total combustion of the reactants takes place, so that the reaction products are carbon monoxide (when operating with low oxygen to reactant ratio), carbon dioxide (stoichiometric oxygen surplus in the feed stream) and water.

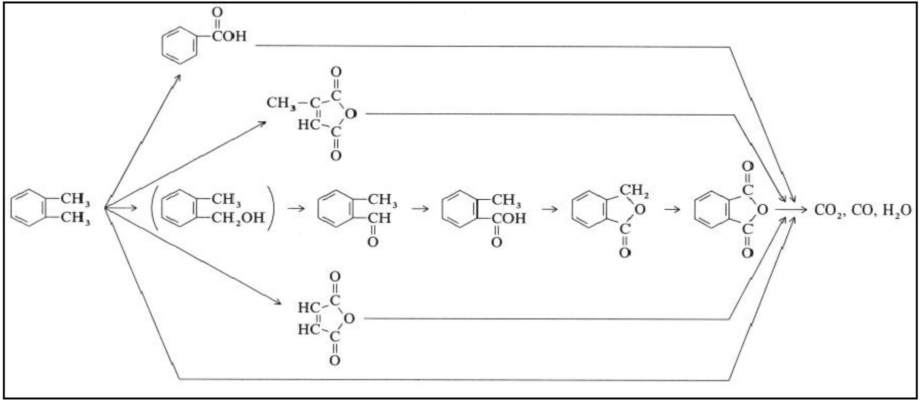

Figure 1. Oxidation of o-xylene reaction mechanism

The general layout of a phthalic anhydride production plant allows us to distinguish three different sections, which are set out below.

2.1 Reaction Section

The initial part of the phthalic anhydride production process flow diagram is the reaction section, where the reactants are initially dosed and led to the inlet pressure and temperature conditions of the catalytic reactor, which holds the reactions on the inside of thin tubes filled with catalytic vanadia-titania pellets or rings. Inside the shell of the reactor, a continuous flow of molten salt allows temperature control.

2.2 Condensation Section

After the reaction section, the cooling and condensation of the reaction gases is necessary in order to recover the product. Heat exchange operations (including both latent and sensitive heat) are involved, playing a major role in the heat integration of the final process. Partial liquefaction of the gas outlet stream of the reactor is carried out in a heat exchanger called after-cooler, obtaining a liquid stream rich in phthalic anhydride. Afterwards, the gas stream still containing an important amount of product is alternatively desublimed in a couple of switch condensers. A heated stirred buffer tank allows us to obtain a continuous flow of the product.

2.3 Purification Section

Finally, the required purity of the product is achieved by means of a purifying train consisting of a stripping column, focused on the removal of the compounds that are more volatile than phthalic anhydride. Depending on its purity, they might be likely to revalue. After that, a rectification column leads to the desired phthalic anhydride recovery from the top of the column while the heavy waste is recovered from the bottom.

3. Process Flowsheet and Modelling

Most of the units involved in the process are successfully described by the available mathematical models in the ASPEN PLUS model library. The implemented user-defined models are discussed next.

3.1 Multitubular Catalytic Fixed-Bed Reactor

The selected model for describing reactor behavior is a steady-state length distributed model. It involves two phases (both the reaction gases and the catalytic solid) for transformation inside the tubes and a single phase (the molten salt) for the liquid in the shell.

The following assumptions were initially considered for modelling:

- Mass and heat axial dispersion in the gas phase. No radial dispersion is considered due to the small diameter of the tubes.
- Heat conduction in the solid phase.
- Constant overall coefficient of heat exchange between the shell and the tubes.
- Both constant and variable effectiveness factor throughout the reactor, due to the possibility of graduating catalyst activity.

Under these assumptions, mass balance for the *i* component involved in the *j* reaction is:

$$\left.\begin{array}{l} D\cdot\dfrac{d^2C_i^G}{dz^2}=\dfrac{d}{dz}\left(u\cdot C_i^G\right)-\left(1-\varepsilon\right)\cdot\eta\cdot\rho_P\cdot\left(-r_j\right) \\ \left(1-\varepsilon\right)\cdot\eta\cdot\rho_P\cdot\left(-r_j\right)=a\cdot k_G\cdot\left(C_i^S-C_i^G\right) \\ \qquad C_i^G\Big|_{z=0}=C_{i0} \qquad \left.\dfrac{dC_i^G}{dz}\right|_{z=L}=0 \end{array}\right\} \tag{1}$$

Heat balance for the gas phase:

$$\left.\begin{array}{l} E^{G}\cdot\dfrac{d^{2}T^{G}}{dz^{2}}=\dfrac{d}{dz}\left(u\cdot\rho_{G}\cdot c_{PG}\cdot T^{G}\right)-\left(1-\varepsilon\right)\cdot\eta\cdot\rho_{P}\cdot\sum\left(-r_{j}\right)\cdot\left(-\Delta H_{r\,j}\right)+U\cdot\dfrac{2}{R}\cdot\left(T^{G}-T^{F}\right)\\ \left(1-\varepsilon\right)\cdot\eta\cdot\rho_{P}\cdot\sum\left(-r_{j}\right)\cdot\left(-\Delta H_{r\,j}\right)=a\cdot h_{G}\cdot\left(T^{S}-T^{G}\right)\\ \qquad T^{G}\Big|_{z=0}=T_{0}^{G}\qquad\dfrac{dT^{G}}{dz}\bigg|_{z=L}=0 \end{array}\right\}\tag{2}$$

Heat balance for the solid phase (catalyst and support):

$$\left.\begin{array}{l} k_{S}\cdot\dfrac{d^{2}T^{S}}{dz^{2}}=a\cdot h_{G}\cdot\left(T^{S}-T^{G}\right)\\ \qquad\dfrac{dT^{S}}{dz}\bigg|_{z=0}=0\qquad\dfrac{dT^{S}}{dz}\bigg|_{z=L}=0 \end{array}\right\}\tag{3}$$

Heat balance for the heat-exchange fluid (molten salt)

$$\left.\begin{array}{l} E^{F}\cdot\dfrac{d^{2}T^{F}}{dz^{2}}=\dfrac{d}{dz}\left(u\cdot\rho_{F}\cdot c_{PF}\cdot T^{F}\right)+U\cdot\dfrac{2}{R}\cdot\left(T^{F}-T^{G}\right)\\ \qquad\dfrac{dT^{F}}{dz}\bigg|_{z=0}=0\qquad\dfrac{dT^{S}}{dz}\bigg|_{z=L}=T_{0}^{F} \end{array}\right\}\tag{4}$$

Different operation conditions, kinetic models for the reactions and reactor parameters were considered from literature (Anastasov et al., 1998; Anastasov, 2003) to verify the model.

Mass and heat transfer coefficients were estimated with ASPEN CUSTOM MODELER. The model consistent in ASPEN CUSTOM MODELER needs the definition of two auxiliary sub-models for importing-exporting the input and output data in order to be concordant with the port definition of the material streams in ASPEN PLUS.

3.2 Switch Condensers and Buffer Vessel

The initially-developed model for the switch condensers and the buffer vessel is a batch model, built in ASPEN CUSTOM MODELER language, that involves different phases: the lean reaction gases, the cooling diathermic oil, the solid product that accumulates from the gas desublimation (which is periodically unloaded into the buffer vessel, where it melts within the liquid phthalic anhydride obtained from the liquefaction stage) and the liquid that is recovered in the stirred tank.

Batch models cannot be imported into ASPEN PLUS. The presence of two switch condensers working alternatively and a buffer vessel allows us to obtain a continuous product flow with a homogeneous concentration of phthalic anhydride, so that we have used the steady-state ASPEN PLUS model comprising a *phase separator* and a *heat exchanger* to describe these equipments (see Figure 2).

3.3 Process Flowsheet

The simulates process flowsheet studied, shown in Figure 3, includes the ASPEN CUSTOM MODELER exported reactor model and the model used for the condensation section. Recycle loops are considered, due to the heat integration of the process.

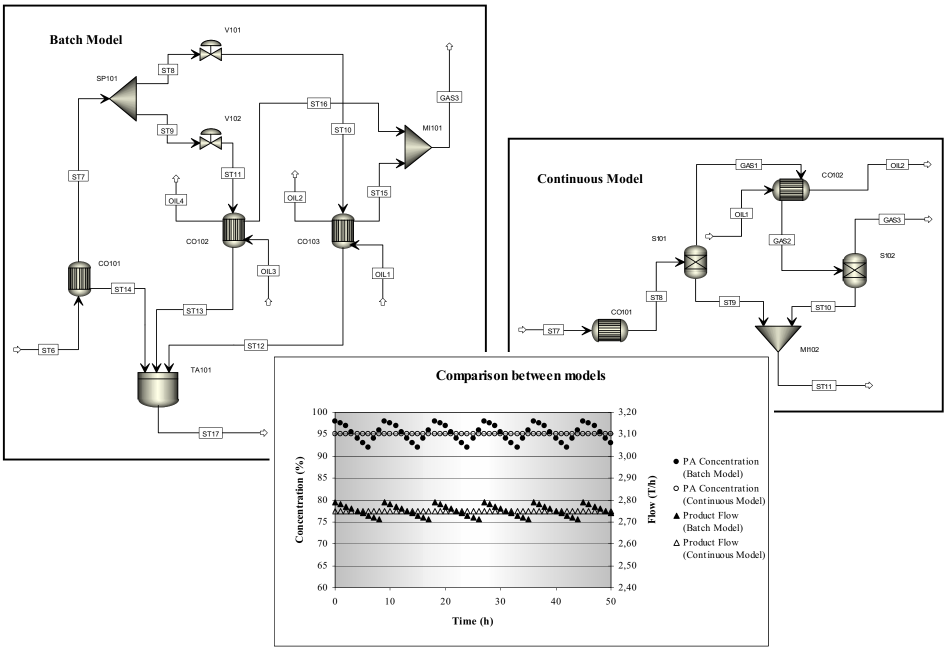

Figure 2. Comparison between the rigorous batch model and the continuous model used

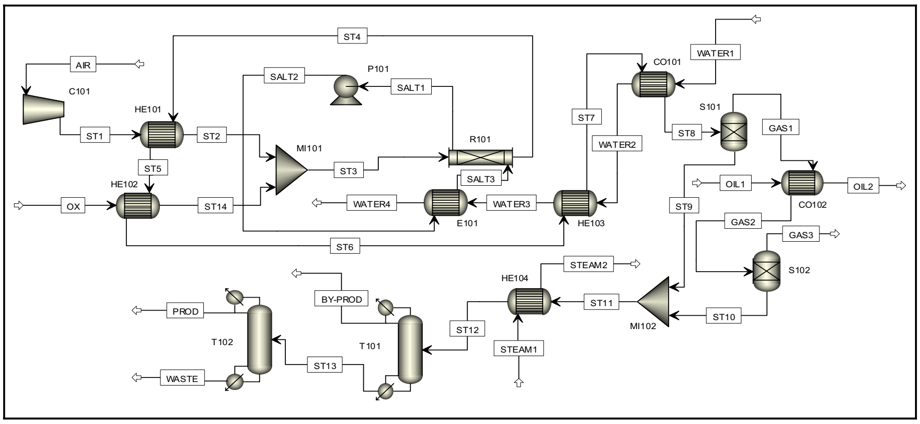

Figure 3. Phthalic anhydride production process. Simulation flowsheet.

4. Results Discussion

The kinetic models proposed by Anastasov (2003), Papageorgiou and Froment, (1996); Calderbank et al., (1977) and Ross and Calderbank, (1971) predict the total conversion of the *o*-xylene when operating with inlet temperature over 200ºC, but postulate the formation of different by-products. Assuming pure *o*-xylene as raw material, the mechanisms that do not consider the formation of the BAC by-product (the only one less volatile than the PA product) do not allow us to justify the existence of the rectification column, ouing to the fact that no heavy wastes to be removed are synthesized.

Using graduated catalyst (20% of catalytic particles in the first 0.5 m of the reactor, 40% in the following 0.5 m and 100% in the rest) enables easier temperature control and provides higher yields in the PA product (1.10 kg PA/kg *o*-xylene).

Increasing the flow of reactants facilitates mass and temperature transport in the catalyst. If residence time is reduced from 1.3 s (4950 kg/h production in a reactor of 13500 tubes 3.5 m x 0.0025 m) to 1.0, the rigorous model can be approached by the *plug flow reactor* (PFR) model, included in the ASPEN PLUS model library (see Figure 4), which is accurate enough.

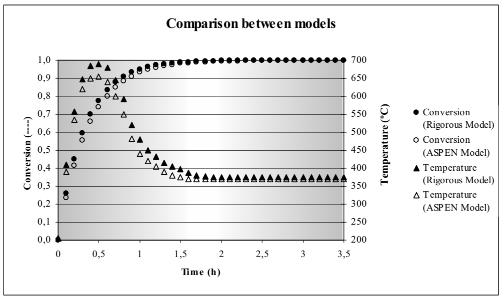

Figure 4. Comparison between the rigorous catalytic model and the PFR model

5. Conclusions and Future Perspectives

The developed model is flexible, permitting both short-cut (if desired) and rigorous analysis of the process. Different operation conditions and raw materials (such as naphthalene and n-pentane) can be considered.

The equation-oriented technique facilitates convergence and allows deeper analysis of the process, such as design specifications, parameter estimation, data reconciliation and, mainly, optimization. In this direction, cost analysis and heat integration could be attempted.

References

Anastasov, A.I., 2003, Chem. Eng. Sci., 58, 89.

Anastasov, A.I., and V.A. Nikolov, 1998, Ind. Eng. Chem. Res., 37, 3424.

Calderbank, P. H., K. Chandrasekharan and C. Fumagalli, 1977, Chem. Eng. Sci., 32, 1435.

Papageorgiou, J. N. and G. F. Froment, 1996, Chem. Eng. Sci., 51, 2091.

Ray, Martyn S. and Martin S. Sneesby, 1998, Chemical engineering design project: A case study approach. Gordon and Breach Science Publishers, Second Edition.

Ross, G. L. and P. H. Calderbank, 1971, , Chem. Eng. Sci., 26, 2003.