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PLANT DESIGN AND ENGINEERING

SPECIAL REPORT

Improve engineering via whole-plant design optimization

New simulation methods identify cost-effective advantages early

H. MARTÍN RODRÍGUEZ, Repsol (Technology Unit), Madrid, Spain;
A. CANO, Process Systems Enterprise, Inc., Cedar Knolls, New Jersey; and
M. MATZOPOULOS, Process Systems Enterprise Ltd, London, UK

Process design requires consideration of many trade-offs. Some equipment decisions may improve the economics of the units under design but negatively impact the project's total economics, as well as the operability of the plant as a whole.

By considering the entire plant simultaneously during design, it is possible to balance decisions that result in the *overall* best economics. This article describes the design of a propylene oxide (PO) process for Repsol. This facility design included a complex multi-tubular reactor (MTR) and a separation section with many distillation columns (two involving reaction and one using azeotropic distillation), plus large recycle flows. Through model-based engineering (MBE) and optimization techniques, substantial economic advantages to the process development were discovered by the design engineering team.

Background. Many companies, including Repsol, Lyondell, Shell and others, use styrene monomer (SM)/PO technologies to co-produce SM and PO. As shown in Fig. 1a, ethylbenzene (EB) is treated with oxygen to form ethylbenzene hydroperoxide, which is then used to oxidize propylene to PO. The resulting 1-phenylethanol is dehydrated to produce styrene.

This is a mature technology, involving a complex process and large capital investment. A major disadvantage for PO producers is the strong dependence of its economics on the variable SM market.

Repsol's policy of diversification led the company to initiate a research project to explore new technologies for PO production via the epoxidation of propylene using hydrogen peroxide (H₂O₂), as shown in Fig. 1b. Success of this research project led to the development of a commercial-scale process for the production of several hundred thousands tpy of PO.

The hydrogen peroxide to PO (HPPO) process has a number of advantages. In particular, it is simpler, requires a lower capital investment and yields less byproducts.

Approach to process development. Repsol began the process development project and decided to take a MBE approach to improve process understanding, develop insights, accelerate development and ensure discovering the best possible design with optimal process economics. Development involved a significant experimental phase, including the construction and operation of dedicated pilot plants. Experimental data was then used in conjunction with design and optimization models, combined with the best engineering practices and commercially available modeling platforms.

Model-based engineering. The MBE approach combines first-principles engineering mathematical models of process physics and chemistry with experimental data to produce high-fidelity

Fig 1(a)

SM/PO: Ethylbenzene to SM and PO

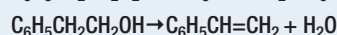
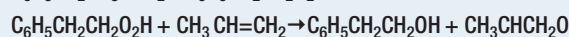
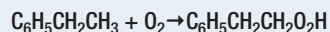


Fig 1(b)

Hydrogen peroxide route to PO

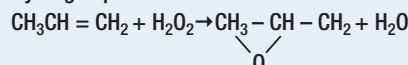


FIG. 1 Process reaction for producing PO.

predictive models of the key process operations. Once a model of sufficient accuracy is established, the model—rather than the experimental data—is used to optimize process design and operation.

This approach allows a much more comprehensive, effective and faster exploration of the process design space than can be achieved by experimentation alone. Also, it allows technology risks to be quantified and addressed systematically.

Key to MBE is *model-targeted model-based experimentation*, where experimentation is focused on maximizing the predictive accuracy of the model rather than addressing individual aspects of process design. The models are used to design further experiments aimed at yielding the maximum amount of information, thereby reducing time and cost involved by the experimental program. Fig. 2 illustrates a typical approach.

Applying MBE to new process development has many benefits. The key advantage is the ability to determine the optimal equipment design, operating conditions, overall process design and even optimal operating procedures. Alternatives can be rapidly screened and poor designs eliminated, with only the most promising alternatives going to pilot or demonstration plant testing for verification. The existence of a predictive model makes it easy to accommodate changing requirements and specifications during process design and to re-optimize for new conditions.

Another major advantage is that the combination of models and experimental data can be used to improve the effectiveness of the whole experimentation process. Model-based data analysis provides accurate parameter values as well as estimates of parameter reliability—information that can be used in formal risk assessment and to provide a quantitative assessment of where further experimental R&D effort should be focused.

The models capture corporate knowledge in such a way that it can easily be transferred between different groups within the organization, facilitating an integrated design approach.

The process. The process is shown schematically in Fig. 3. The reacting mixture enters an MTR where an exothermic catalytic reaction yields PO and several byproducts. The reaction products

are fed to a separation section, where the product (PO) is purified to the required quality. Solvent and unused reactants are recycled to the reactor.

Multi-tubular reactors. MTRs are widely used throughout the petrochemical/chemical and refining industries for exothermic catalytic reactions. However, their behavior is highly complex, with good design and consistent operation difficult to achieve. An MTR contains a large number—sometimes 20,000 or more—catalyst-filled tubes within a shell through which cooling fluid passes. Often, each tube is divided into several sections, each packed with a different catalyst and/or inert material, and designed to promote different reactions.

Heat generated by the reactions in the tube catalyst beds is typically removed by cooling liquid—often molten salt, but, in this case, cooling water—flowing through the shell side. There is strong interaction between shell and tubes: the temperature of the cooling fluid outside a tube influences the rate of reaction inside it, which, in turn, affects the amount of heat produced and transferred to the cooling medium at that point; and different tubes indirectly affect each other via their interactions with the cooling medium.

A good design is achieved by adjusting key aspects of the shell and tube bundle geometry to minimize variations in temperature profile from one tube to another. Uniformity of temperature profiles across tubes facilitates optimization of operating conditions to achieve better conversion and fewer side reactions, thus increasing plant throughput and reducing separation costs. It also enhances catalyst life by reducing the likelihood of hotspot formation and the consequent progressive catalyst burnout that results in poor conversion and controllability with early catalyst replacement.

Separation section. The separation section is an equally complex part of the HPPO process. The original design included many distillation columns (one involving azeotropic distillation and two involving chemical reactions). The model of the separation section involved 25 components, including reactants, solvent, product, byproducts and impurities. Beyond the intrinsic complexities of the MTR and separation section, a further layer of complication was introduced at a flowsheet level by the existence

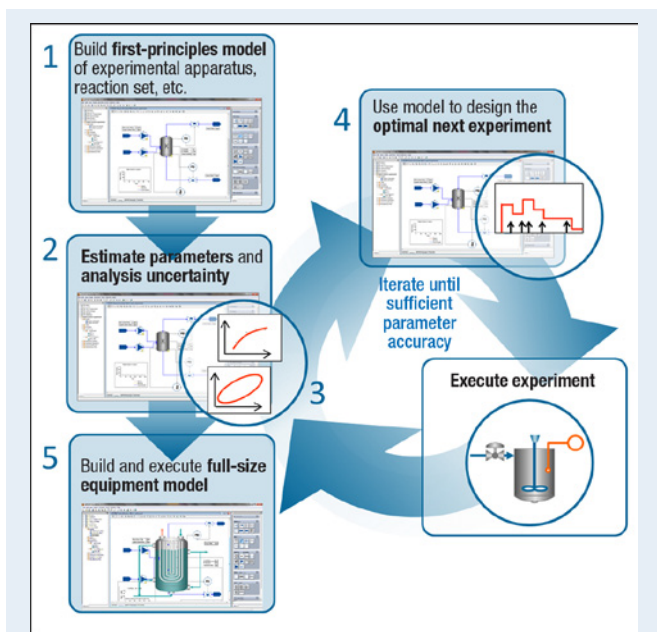


FIG. 2 Model-based experimentation processes.

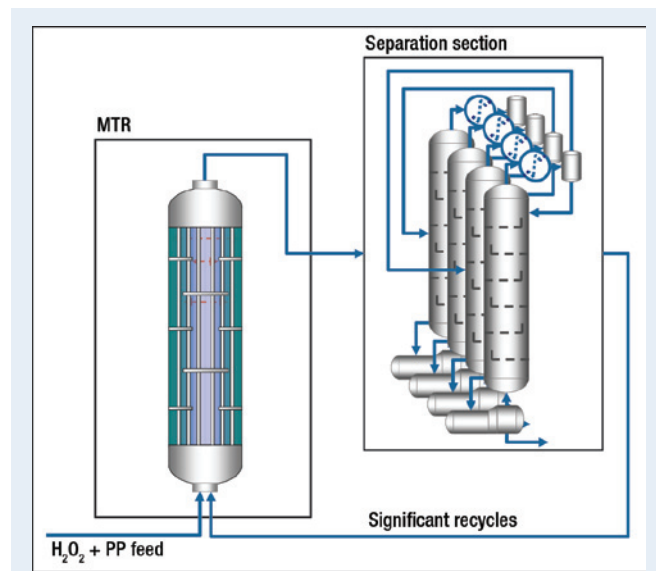


FIG. 3 The new PO process schematic.

of a number of significant recycles, as well as possibilities for heat integration that needed to be considered.

Process development: project phases. The process development was done in three major phases:

Phase 1: Experimentation. Extensive pilot-plant experimentation was undertaken to identify chemical kinetics and determine heat transfer characteristics. It was guided and supported by models of the experimental equipment.

Phase 2: Process design and optimization. Detailed equipment and process models incorporating the physical and chemical phenomena identified during Phase 1 were used to construct the whole-plant flowsheet model. This model was then used for the evolutionary design of the commercial-scale process.

Phase 3: Heat integration. The Phase 2 design was further improved by considering heat integration options in the optimization.

The initial plan for the development of the new process envisaged the reactor and separation section being designed and optimized sequentially. However, it was quickly realized that, because of the close coupling of reaction and separation stages, it was essential to optimize the design of both sections simultaneously. This is a general characteristic of processes involving reaction and separation.¹ Optimizing the reactor separately from the separation section can result in large recycle flows, which will increase the capital and operating costs of the separation section. Conversely, maximizing conversion in the reactor in an attempt to reduce separation costs will typically result in a reactor that is too large. The optimal level of conversion (and, therefore, the optimal reactor size) can be found only by considering reaction and separation costs simultaneously.

Phase 1—Pilot-plant experiments. This phase was to accurately identify chemical kinetics and determine heat transfer characteristics. Experimentation was done on a single-tube pilot plant. Over 60 pilot-plant experiments were conducted with various catalysts. The experimentation phase followed the classic step-by-step model-targeted experimentation approach shown in Fig. 2:

Step 1—Build first-principles model of experimental apparatus. A detailed model of the tubular reactor experimental rig was developed using off-the-shelf models that took account of all relevant heat and mass transfer phenomena, as shown in Fig. 4. This included limitations in the mass-transfer rates to the pellets and, more importantly, for liquid-phase systems—where the diffusion coefficients are very low and the intra-particle transport limitations are severe—in the catalyst pores *within* the pellets.

The catalytic reaction was thus modeled using a detailed catalyst pellet model with radially distributed intra-pellet variations. The catalyst-filled tube was represented by an axially and radially distributed model. A rigorous approach was used for the modeling of the thermodynamic and transport properties of the reaction mixture.

Step 2—Estimate parameters using model of experimental apparatus from Step 1. The model from Step 1 was used to

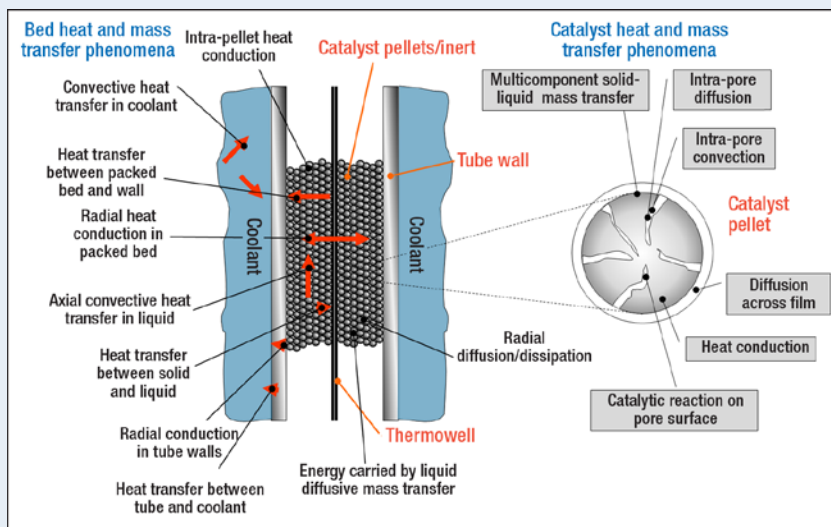


FIG. 4 Phenomena considered in the catalyst pellet and fixed-bed model.

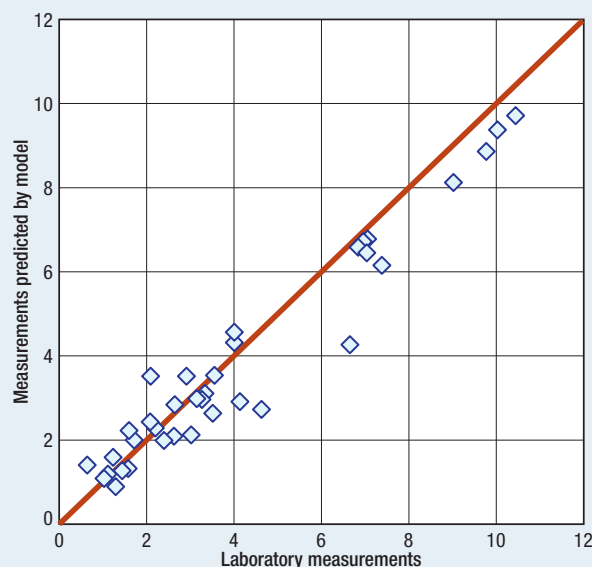


FIG. 5 Predicted component lab values (y-axis) against the actual measurements (x-axis) for 38 experiments.

estimate reaction kinetic and heat transfer parameters from experimental data. Rigorous mathematical techniques for simultaneous estimation of multiple parameters in nonlinear models using multiple experimental data sets were used for this purpose.

Step 3—Perform model-based data analysis. The confidence (uncertainty) information generated for each parameter by the Step 2 parameter estimation was used to determine where the most significant areas of risk inherent in the data were, and thus where subsequent experiments should be focused.

Step 4—Design additional experiments if necessary. Using the model constructed in Step 1, it was possible to propose several new experiments that would maximize information content in critical areas—for example, by replacing propylene by PO in the reactor feed, and co-feeding PO and propylene.

Steps 2 to 4 were repeated until the estimated values of key parameters (primarily the main reaction kinetic parameters) were

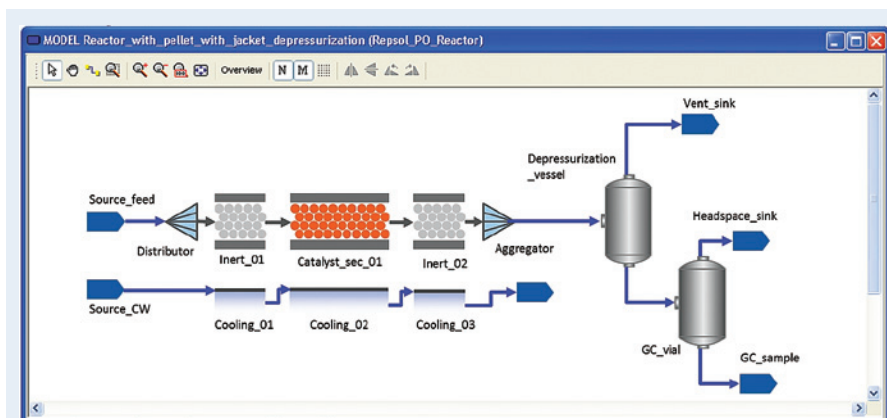


FIG. 6 Pilot-plant model showing inert sections, catalyst bed and cooling jacket.

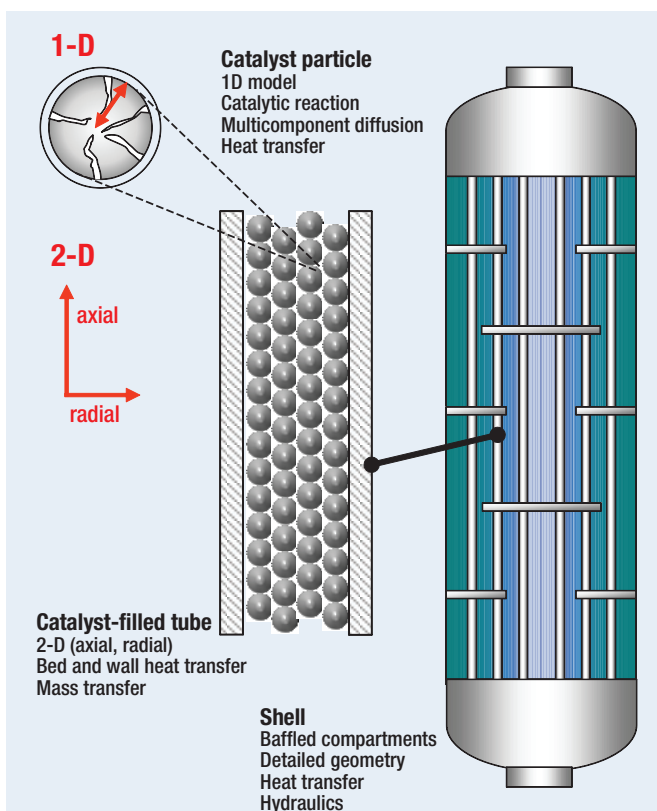


FIG. 7 Reactor sub-models: Key phenomena and relationships shown.

considered sufficiently accurate. Fig. 5 shows the accuracy of fit for concentration of one of the reaction products.

Pilot-plant model. Fig. 6 shows the flowsheet constructed in Step 1 to represent the pilot-plant reactor. The reactor tube comprised a central section (about a meter long) filled with catalyst pellets, with inert bed sections placed at the beginning and end of the tube.

The two flash units simulate the sampling procedure. The first vessel simulates depressurization from high pressure to atmospheric conditions, and the second the increase in temperature to ambient during gas chromatograph injection. Modeling the sensors is an important requirement for correct mass balance reconciliation and interpretation of lab data. The model used for data

analysis should reflect the physical reality of the experimental setup as closely as possible.

Feedback to experimentation. Following initial use of the model to analyze data gathered earlier, the project team was able to make numerous recommendations with regard to the experimental setup. These included replacing cooling coils with a cooling jacket operated in the turbulent regime, improving control, adding thermocouples for temperature measurements at locations determined by the analysis, and modifying sampling approaches. It was also possible to make recommendations on the catalyst pellet design to minimize side reactions.

Interestingly, the initial results also identified and quantified biases in thermocouple readings, effectively using the predictive model as a calibration instrument to correct pilot-plant measurements. This allowed more precise estimation of heat transfer and kinetic parameters to be obtained in subsequent experiments. The ability to use information from the model-based data analysis to identify improvements to experimental setups helps to maximize the quality of information collected. This is one key advantage of the MBE approach.

Phase 2—Process design and optimization. Once acceptable parameter accuracy was attained through experimentation, the validated model of the key phenomena could be used as the core of the commercial reactor model for process design. As mentioned earlier, it was important to consider the trade-off between the reaction and separation economics. As a consequence:

- All work during the design phase considered the reaction and separation sections (including recycles) simultaneously.
- Due to the large number of decision variables involved, the design was posed formally as an optimization problem and solved using rigorous mathematical techniques, in preference to attempting a trial-and-error analysis based on repeated simulations involving the variation of a few variables at a time.

Modeling the reactor. The optimal design of the MTR, involving complex phenomena occurring within a large number of tubes as well as complex cooling fluid behavior on the shell side, presents a significant challenge in itself—even before integration with the separation section is considered. Model-based techniques can help to ensure an axial tube-side temperature profile that favors the desired reactions. To achieve this, it is necessary to accurately quantify heat transfer at all points throughout the reactor, taking into account the fluid dynamics on the shell side and reactions occurring in the tubes simultaneously.

The model of the complex liquid-phase MTR to be used in the full-scale new PO process was constructed using commercially available catalyst and fixed-bed reactor component models (Fig. 7). As the shell side comprised a number of compartments separated by baffles, lumped cooling models were used, with each compartment being assumed to be perfectly mixed.

Modeling of separation section. The base case separation section design was taken from a steady-state design obtained using

TABLE 1. Optimization decisions regarding reactor design

1. Tube pitch (relative to tube outside diameter)
2. Minimum average coolant velocity within tube bank
3. Mass fraction of H ₂ O ₂ in the feed stream (a measure of the amount of solvent used)
4. Molar ratio of PP to H ₂ O ₂ in the feed
5. Concentration of H ₂ O ₂ in the H ₂ O ₂ raw material stream
6. Number of active reactors
7. Number of baffles in the reactor shell
8. Tube length
9. Cooling water inlet temperature
10. Space time (reciprocal of kmol H ₂ O ₂ /hr per kg catalyst)
11. Reactor process stream inlet temperature.

standard flowsheeting tools. This flowsheeting model was implemented within the design modeling environment using similar steady-state equilibrium distillation column models.

On initial analysis, it quickly became apparent that the calculated performance and economic of the process were heavily dependent on the accuracy of the thermodynamic model. To improve its accuracy, binary interaction parameters in the activity coefficient model were fitted for 21 binary pairs using data from commercial databanks, as well as from targeted vapor-liquid equilibrium (VLE) experiments carried out in-house or commissioned to external laboratories. The result was a set of highly accurate parameters for the composition ranges of interest.

Model implementation—overall. The models described above were implemented in commercially available process design software capable of handling the physical and chemical complexity of the MTR, the convergence challenges of the recycles, and numerical complexities of the optimization. The flowsheet was constructed from standard model libraries. A custom-cost module was added for the optimization calculation.

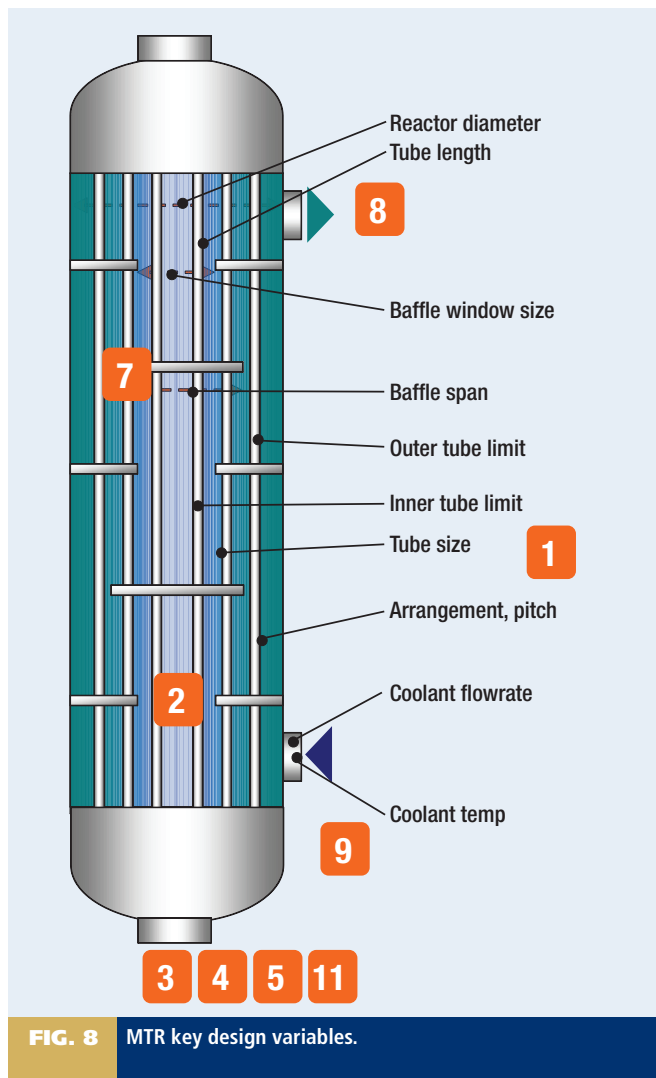
Reactor model and separation models were constructed and initially solved separately. The models were then integrated and recycle loops closed. Once an initial solution was reached, the team had a model that was capable of being used for optimization for the whole plant design.

Optimization. The optimal design of the new PO process was determined via an economic-based optimization calculation that maximized the annual profit,¹ i.e., the difference between the value of the products created and the total annualized cost (TAC).

Any such design must satisfy a number of key constraints and this is obtained by resolving a large number of design and operational decisions that are available to the designer. These are discussed later.

Design objective function. TAC brings together recurring operating costs (€/yr) with capital costs (€/yr), by applying an annualization factor (AF), which has units of year⁻¹ and represents the trade-off between capital investment costs and operating costs. High values of the AF bias designs in favor of smaller equipment and larger consumption of raw materials and utilities.

In its simplest form, the AF is equal to the interest rate used to evaluate capital investments. This would assume infinite equipment life without the need to replace it. It has been shown that

**FIG. 8** MTR key design variables.

net present value (NPV) formulae can be translated into the TAC framework by a suitable definition of the annualization factor.² AFs used can be as high as 1/yr. For the current project, a value of AF = 0.4/yr was selected.

Total annualized profit (TAP) maximization was chosen as the objective function for the design optimization. As the production rate was fixed as a design criterion, maximizing TAP gives the same results as minimizing TAC. The objective function was formulated as:

$$TAP = \text{Annual operating margin} - \text{Total equipment cost} \times AF$$

where:

$$\text{Annual operating margin} = \text{Annual revenue} - \text{Annual cost of raw materials} - \text{Annual cost of utilities} - \text{Annual cost of catalyst}$$

Constraints. Any valid design and operating conditions must satisfy a number of key constraints, including:

- Quality constraints on product, for example, maximum ppm levels of several impurities

¹ The term "process optimization" is often used loosely to mean any form of process improvement. The optimization referred to here is a true mathematical optimization, i.e., determining the mathematically-best solution given the data provided. The validity of the optimal solution of course depends highly on the predictive accuracy of the underlying model.

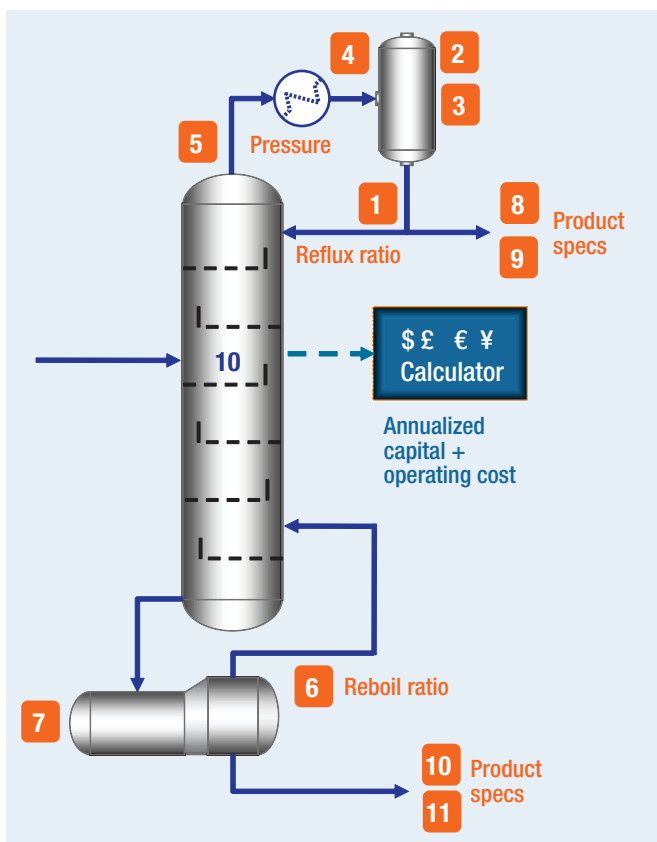


FIG. 9 Typical distillation column key design variables—operating conditions and specifications.

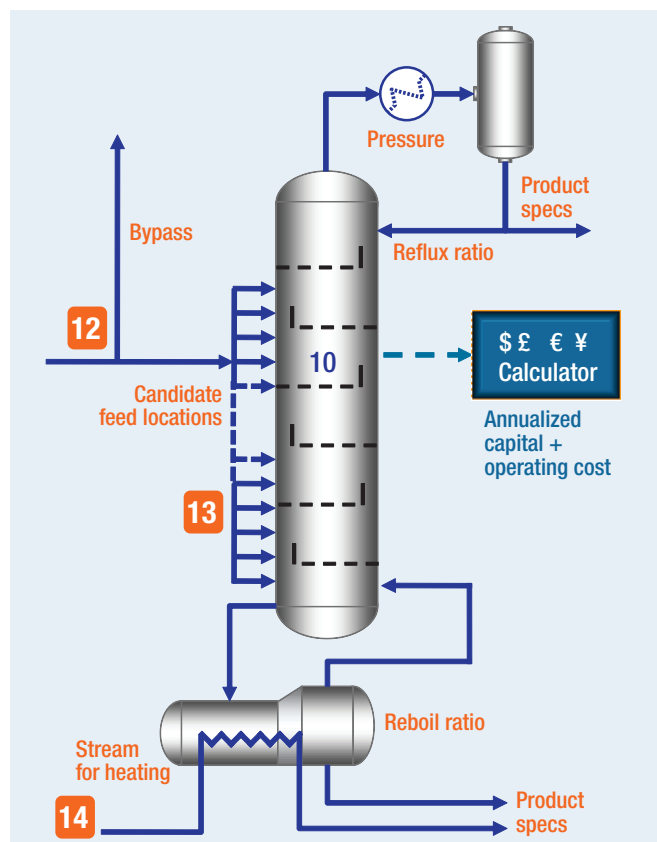


FIG. 10 Typical distillation column key design variables—product goals and configuration.

TABLE 2. Optimization variables for separation section of new PO design

Category 1—Operating conditions

1. Condenser reflux ratio
2. Condenser temperature
3. Condenser pressure
4. Condenser temperature approach
5. Column top pressure
6. Reboiler boil ratio
7. Reboiler temperature

Category 2—Product specifications*

8. Concentration of component *x* in the overhead distillate stream
9. Fraction of component *x* entering the column that is recovered in the vapor distillate stream
10. Mass fraction of component *x* in the bottoms stream
11. Mole fraction of component *x* in the bottoms stream

Category 3—Column or flowsheet configuration (Fig. 10)

12. Fraction of feed stream not bypassing the column. This was used to allow the optimizer to make structural decisions on flowsheet alternatives (for example, to allow for potential removal of some columns in the original flowsheet).
13. Feed tray location. The optimizer was allowed to consider a number of alternatives, selecting the one that gave the economic maximum.
14. Heat integration options (see Phase 3).

*These were applied to the intermediate streams between columns (the final product stream qualities are *constraints* rather than optimization variables).

- Safety constraints, for example, maximum oxygen concentrations—arising from decomposition of unreacted H_2O_2 —in potentially explosive streams
- Coolant supply and return temperature constraints
- Effluent concentration constraints determined by environmental considerations
- Reactor shell-side minimum and maximum velocity constraints required to prevent tube fouling and tube erosion, respectively
- Constraints on reactor and column dimensions, due to road transport considerations for equipment manufactured offsite.

Optimization decision variables. These are the design parameters—equipment dimensions, operating conditions and so on—that are varied during the optimization to maximize the value of the objective function. In the final design stages, there were 49 decision variables in total. Most of these were continuous variables—for example, reflux ratios that could be varied between a minimum and maximum value during optimization. However, the optimization included some discrete (or integer) decisions, for example, feed tray location or “on/off” variables representing stream routing decisions. The optimization decisions relating to the reactor design included, as shown in Fig. 8 and Table 1.

The optimization variables relating to the separation section design were divided into three categories, as summarized in Table 2. Different optimization variables were used for each column, as shown in Figs. 9 and 10, depending on the key design criteria for the column; between two and four variables were used per column.

Optimization methodology. The optimization phase helped develop a deep understanding of the process. More than 10 optimization runs were done, each providing new insights into the process and its design, and leading to the consideration of more design alternatives via introducing new decision variables. Thus, each successive optimization resulted in improved process economics.

Verifying design via hybrid process/CFD modeling.

The MTR model applied for the optimization-based design made use of velocity and pressure-drop correlations for modeling the shell side. Based on empirical data, such correlations allow a reasonable account of reactor behavior to be incorporated within a whole-plant optimization framework.

However, once the final design is obtained, it is highly desirable to perform a full hydrodynamic calculation to provide an extra check on whether all relevant constraints are met. In the case of the new PO process, one important consideration related to the minimum velocities of the coolant throughout the shell. Because changing conditions within the shell also affect the tube-side behavior, the entire reactor design needed to be validated.

Accordingly, detailed computational fluid dynamics (CFD) models of the shell side were implemented and then combined with the tube-reaction models, using a proprietary hybrid modeling interface (Fig. 11) to produce a fully coupled hybrid model of the MTR.³

The hybrid model was also used to decide between configuration alternatives for baffle type (disc-and-doughnut vs. single-segmental configurations) and distributor design (homogeneously distributed inlets vs. distributors comprising a discrete number of slits) and showed that the chosen options were indeed viable in terms of the detailed fluid flow characteristics. Fig. 12 lists selected results.

Phase 3—Heat integration. In the final stage of the design, pinch analysis was carried out. Heat integration routes were introduced where there was any potential benefit, with the optimizer allowed to select process streams instead of utilities in certain reboilers to reduce the total steam cost.

Optimal new PO process design. The optimal design represented large savings in operating and capital cost with respect to the initial base case. Two columns were eliminated entirely from the separation section. One was found to have negligible separation effect; the other, used for treating a waste stream, was found to have a steam cost that exceeded the cost of sending the stream directly to wastewater treatment.

The final design for the MTR ensured that tube behavior and performance were practically uniform across the entire tube bundle. The heat integration yielded significant operating cost savings with attractive return on investment; payback was less than four months.

Conclusion. During the course of the design optimization described in this article, the value of the TAP increased by several tens of millions of €/yr, with approximately €5 million/yr saved by eliminating just one distillation column. The optimization resulted in an economically viable and robust process.

At the outset of the project, the practicality of applying this level of design optimization to an MTR or separation section

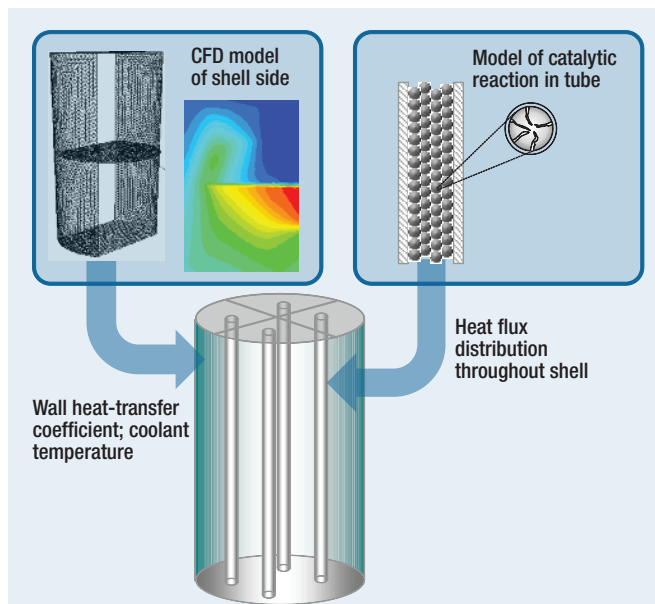


FIG. 11 Combining shell-side CFD and tube catalytic reaction models for hybrid simulation via proprietary software interface.

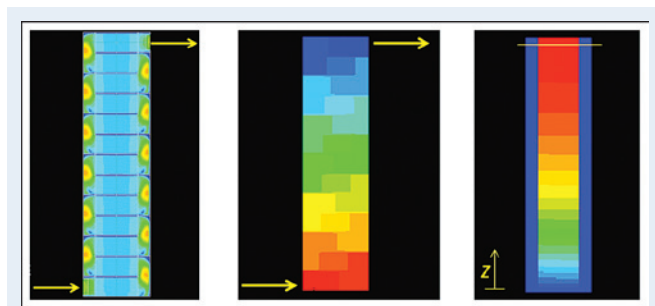


FIG. 12 Selected results from the CFD verification step for the MTR coolant side: from left to right, profiles for coolant velocity, coolant pressure drop and PO conversion.

separately using detailed first-principles models was virtually unknown. Even less clear was the feasibility of optimizing the combined process. In addition to delivering an economically-optimal design, the project proved that:

- Whole plant optimal design is now a viable technology and capable of significant savings—both in terms of capital expenditure (CAPEX) and operating expenditure (OPEX).
- Models are sufficiently accurate to be able to reflect the effects of small changes in physical configuration, for example, tube pitch or tube diameter in the MTR.
- Complex configuration decisions, such as the location of distillation feed trays, can be taken into account.
- Optimization technology is suitably powerful and robust, and capable of large optimizations that include combinations of many continuous and discrete decisions.
- Model-based data analysis helps to make the experimentation phase shorter and more effective.
- MBE can be applied from the experimental stage onwards. Indeed, the earlier model-based techniques are brought to bear during process development and design, the better.

The methods used in this design are suitably general and can be applied to any process plant and they are available via commercially-available simulation and modeling tools. Although the case presented here involved process design, the methodology applies to both design and operations. In fact, the rigorous models used for conceptual design are also suitable for detailed engineering and operation stages of the project. **HP**

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Hilario Martín Rodríguez is a senior technologist at Repsol, Madrid, Spain. He has 13 years of experience in process design, modeling, optimization and applied mathematics in the oil & gas, refining and chemical industries. He is also Associate Lecturer at the Chemical Engineering Department at Valladolid University, Spain. He has a M.Sc. degree in mining engineering from the Madrid Polytechnic University, Spain.

Alejandro Cano is a principal consultant at Process Systems Enterprise Inc., Cedar Knolls, New Jersey. He has 10 years of experience in the application of high-fidelity modeling to complex processes involving chemical reactions and separations across many different industries. He has a Ph.D. in chemical engineering from the Massachusetts Institute of Technology.

Mark Matzopoulos is chief operating officer at Process Systems Enterprise Ltd, London, UK. He has 30 years of experience in the development and application of process simulation and modeling tools in steady-state and dynamic simulation and plant optimization in the oil & gas, refining and chemical industries. He has a chemical engineering degree from the University of Cape Town, South Africa.

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