Sulphuric acid plant modelling

Technology is fundamental to the profitable design and operation of environmentally friendly phosphate and sulphuric acid plants and processes. In this study, **Chai Bhat** and **Ven Pinjala**, AspenTech examine how modeling technology can help in debottlenecking existing plants, achieving high product purity, increasing energy recovery, and automate process analysis to optimise plant operations.

aspenONE Engineering for Chemicals

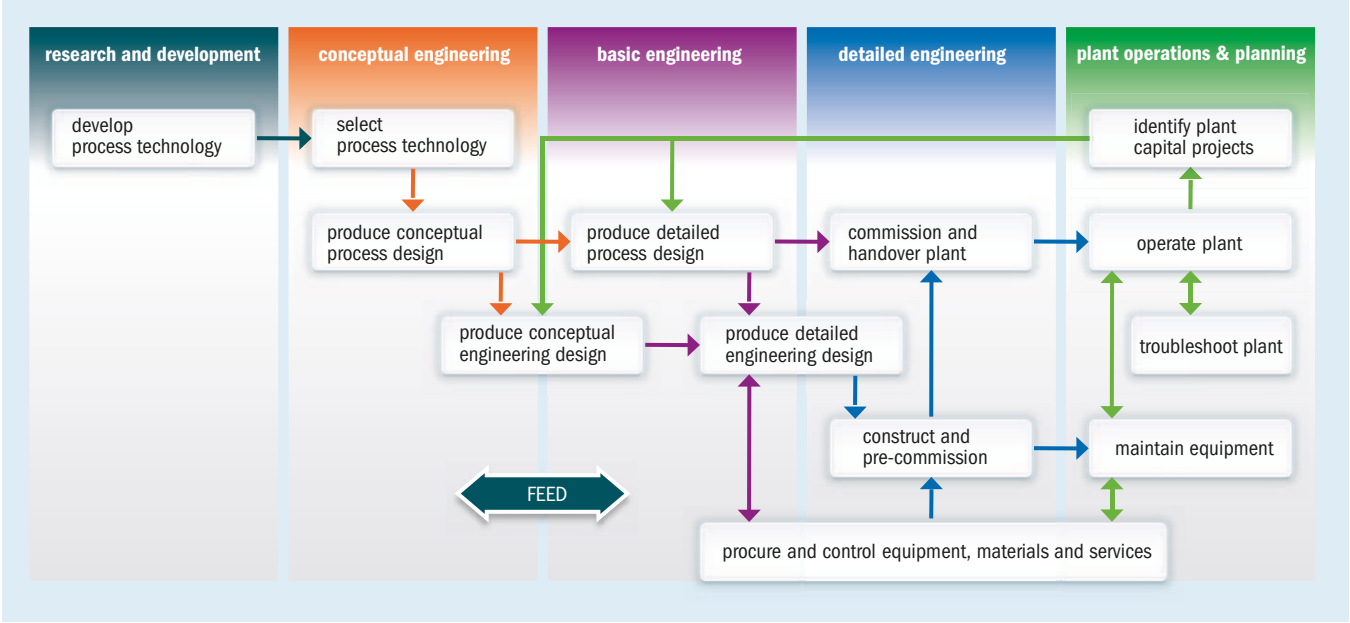
aspenONE Engineering enables engineers to model the sulphuric acid and phosphoric acid processes in one integrated environment. It has been successfully utilised by plant owners/operators, engineering and construction companies, and technology providers to improve yields, increase plant efficiency and quality, and reduce capital and operating costs.

Operation of a sulphuric acid facility can be challenging because of the high cost of maintenance of sulphuric acid plants, stringent requirements on SO_2 emissions, importance of energy efficiency, and accurate equipment sizing and rating. aspenONE Engineering has been successfully used by many companies to design every sub-process of the sulphuric and phosphoric acid plant in one integrated environment.

Aspen Plus is an integral part of aspenONE Engineering and contains the world's largest database of pure components and phase equilibrium data for conventional chemicals, electrolytes, solids, and polymers. The physical property database is regularly updated with data from the U.S. National Institute of Standards and Technology (NIST). Having accurate physical properties data is critical to the precision of the simulation results and directly affects the cost of process equipment. The electrolytes feature in Aspen Plus improves the accuracy of the vapour-liquid equilibrium calculations in the adsorption units of sulphuric and phosphoric acid processes.

Figure 1 illustrates the overall engineering workflow and life cycle process of designing a sulphuric acid plant. Based on the process concept and business objective, one can establish the performance of the concept and then improve the concept using conceptual design methodologies in Aspen Plus. The base case and the improved case economic feasibility can be compared using standard cost analysis environment such as Aspen Process Economics Analyzer. It

Fig 1: **Asset engineering lifecycle and workflow**



is also important to establish a detailed performance model for critical equipment. This helps identify a practical design option during the conceptual phase. The basis for these detailed equipment models needs to be consistent between the base case and the improved case.

After developing an improved process concept, Aspen Plus Dynamics can then test the process for safety, operability, and controllability issues; this defines the key control loops and the instrumentation for the process. Once the process control strategy and key instrumentation is defined, the definition of the process intent for the design is complete.

Aspen Basic Engineering can then be used to develop the FEED package, incorporating the PFD or process P&ID for the improved concept, equipment designs, data sheets, summary sheets and basic control loops and instrumentation. The process design information can then be further transferred into detailed P&ID and instrumentation environments.

The performance models developed for the process can be re-used for operational monitoring and improvement of the plant using Aspen Simulation Workbook. The performance model can also be deployed to non-expert users who may not have background in simulation to perform "what if analysis" studies over the web using Aspen Online Deployment[1].

Importance of physical properties

Sulphuric acid has consistently ranked no. 1 in world chemical production. Considerable work has been done in the steady state simulation area of sulphuric acid processes. Sulphuric acid models have been used to design, de-bottleneck, and troubleshoot plants, converter profile optimisation (with the Equation Oriented (EO) capability), evaluate catalyst purchases and rate present catalyst condition, energy recovery analysis, and to emulate gas-to-gas hex leaks. Some of the key variables in sulphuric acid production are: gas strength, production rate, stack SO_2, converter catalyst loading and temperature profile, acid strength, steam production, gas pressure drop, and gas dew-point.

Physical properties are the most important part of any simulation, it is critical to have accurate and updated physical properties to perform engineering calculations which eventually dictate the sizing and rating of plant equipment which affects the capital costs, operating costs, and safety of the plant.

Aspen Properties is part of aspenONE Engineering and provides state-of-the-art physical property methods, models, algorithms, and data that enables chemists and engineers to easily perform engineering calculations based on rigorous and proven thermophysical property models and data. It enables users to capture and deploy consistent physical property data and knowledge across the enterprise. Aspen Properties contains the world's largest database of pure components and binary parameter databanks.

For simulation of aqueous acids such as sulphuric acid and phosphoric acid processes it is recommended to turn the electrolytes feature on in Aspen Plus. In Aspen Plus, an electrolyte system is defined as one in which some of the molecular species dissociates partially or completely into ions in a liquid solvent, and/or some of the molecular species precipitate as salts. These dissociation and precipitation reactions occur fast enough that the reactions can be considered to be at chemical equilibrium. The liquid phase equilibrium reactions that describe this behaviour are referred to as the solution chemistry. In Aspen Plus, solution chemistry is often referred to simply as chemistry[2].

Solution chemistry has a major impact on the simulation of electrolyte systems. For non-electrolyte systems, chemical reactions generally occur only in reactors. In Aspen Plus, all unit operation models can handle electrolyte reactions[2].

Solution chemistry also impacts physical property calculations and phase equilibrium calculations. The presence of ions in the liquid phase causes highly non-ideal thermodynamic behavior. Aspen Plus provides specialised thermodynamic models and built-in data to represent the non-ideal behaviour of liquid phase components in order to get accurate results[2].

Equation oriented modeling

Sequential modeling (SM) is the traditional approach of modeling in Aspen Plus; SM solves each block in the flow sheet in sequence. SM is a viable option generally for flow sheets without too many recycle loops. However for larger flow sheets with multiple recycle loops SM can be very time consuming.

Unlike SM, equation oriented (EO) modeling does not solve each block in sequence. EO gathers all the model equations together and solves them together. EO is typically ideal for highly heat-integrated processes, process with multiple recycle loops, processes with numerous design specifications, process optimisation, and for process model tuning through data reconciliation and parameter estimation. EO solves much larger problems than SM and uses the same computational effort[3].

Rate based distillation

Aspen Rate-Based Distillation (formerly Aspen RateSep) is part of the aspenONE Engineering solution, and extends the functionality of Aspen Plus RadFrac distillation model with second-generation rate-based technology which accurately predicts simulation over a wide range of operating conditions. Aspen Rate Based Distillation uses sate-of-the-art mass- and heat transfer correlations to predict column performance, without the need of efficiency factors. This added degree of rigour is especially critical for modeling gas scrubbers, sour water strippers, azeotropic systems, reactive distillations, nitric acid absorption columns, narrow-boiling separations, and other highly non-ideal separation processes.

The rate-based modeling approach is superior to the traditional equilibrium-stage modeling approach that has been employed extensively in the process industries. The rate-based models assume that separation is caused by mass transfer between the contacting phases, and use the Maxwell-Stefan theory to calculate mass transfer rates. Conversely, the equilibrium-stage models assume that the contacting phases are in equilibrium with each other, which is an inherent approximation because the contacting phases are never in equilibrium in a real column.

The rate-based modeling approach has many advantages over the equilibrium-stage modeling approach. The rate-based models represent a higher fidelity, more realistic modeling approach and the simulation results are more accurate than those attainable from the equilibrium-stage models. The rate-based modeling approach can reduce the risk of inadequate designs or off-spec operation because the rate-based models explicitly account for the actual column configuration which affects column performance.

Designed to model reactive multistage separation problems rigorously and accurately, Aspen Rate-Based Distillation bal-

ances gas and liquid phase separately and considers mass and heat transfer resistances according to the film theory by explicit calculation of interfacial fluxes and film discretisation. The film model equations are combined with relevant diffusion and reaction kinetics and include the specific features of electrolyte solution chemistry, electrolyte thermodynamics, and electroneutrality where appropriate. The hydrodynamics of the column is accounted for via correlations for interfacial area, hold-up, pressure drop, and mass transfer coefficients. SO_2 stripping is a rate-limited process, and can be accurately modeled using Aspen Rate-Based Distillation[1,4].

Steady-state sulphuric acid model

This model simulates the production process of sulphuric acid from sulphur in a typical double absorption plant. The model includes the following features:

- A set of electrolyte components for this process
- Typical process areas including: sulphur burning, sulphur dioxide conversion, absorption of sulphur trioxide and the main streams connecting these units.

Table 1: **Components modeled in simulation**

Components	Component ID type
H_2O	CONV
H_2SO_4	CONV
SO_2	CONV
SO_3	CONV
S	CONV
N_2	CONV
O_2	CONV
$C_{10}H_{22}$	CONV
$H3O^+$	CONV
HSO_4^-	CONV
SO_4^{2-}	CONV
CO_2	CONV

- Definition of methods for calculating and reporting electrolyte systems
- Supports rigorous design, rating, or simulation by interfacing with the A program.

Table 1 lists the components modeled in the simulation.

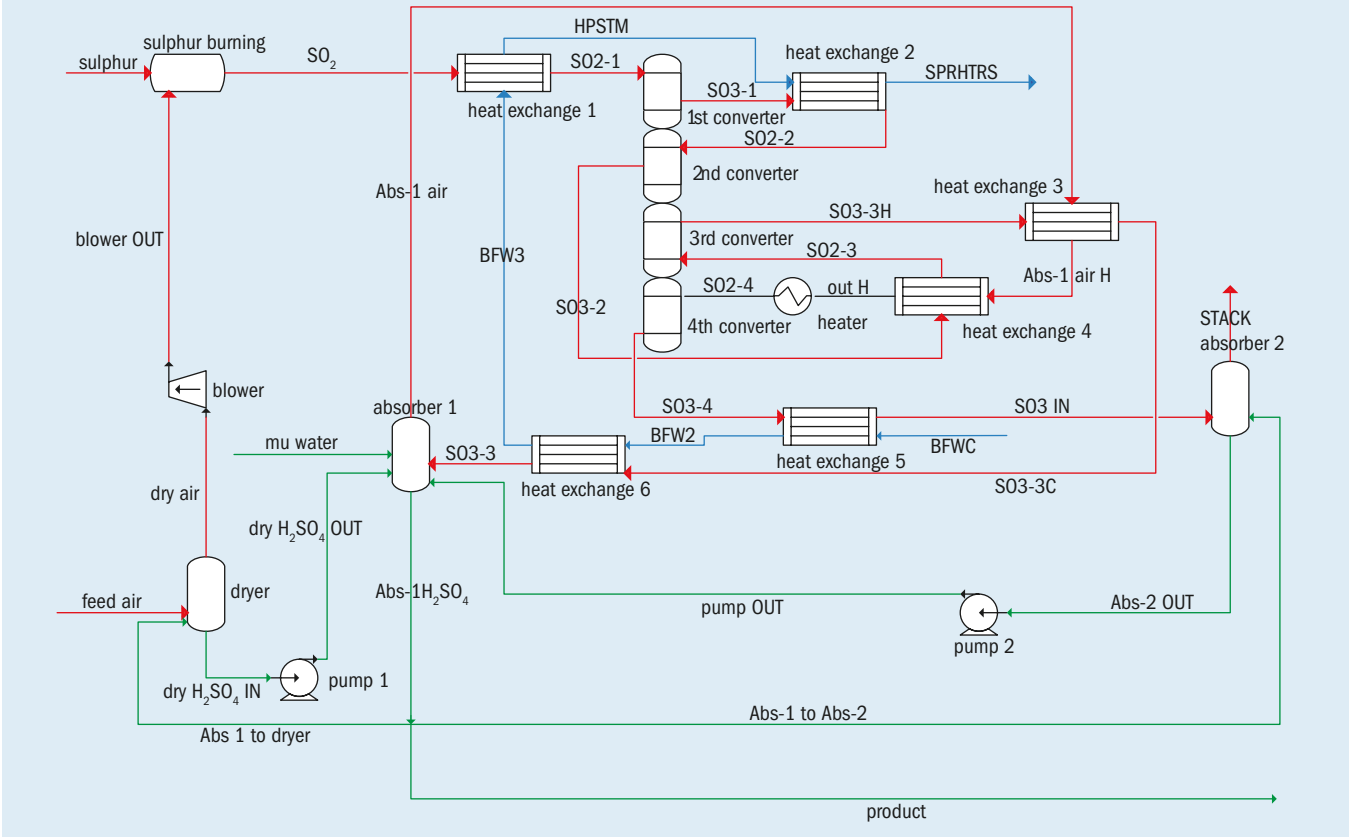
SO_2, O_2, N_2 and CO_2 are selected Henry's components. The Electrolytes Expert System can be used to generate electrolyte species and reactions. In this model, acidic species are treated as hydronium ion H_3O^+ and choose components H_2O and H_2SO_4 for the electrolytes system. In addition, the apparent component approach is used.

Figure 2 shows the process flow sheet which includes: air drying, sulphur burning, sulphur dioxide conversion, double absorption of sulphur trioxide, gas-to-gas heat exchangers, strong acid system and energy recovery system (steam system).

Sulphur is mixed with the dry air after the removal of water from the feed air in the drying column. An oxidation reaction takes place in the sulphur burner. Then the sulphur dioxide gas and the unreacted air are cooled from 2010°F to 750°F (1100°C to 400°C) prior to entering the first pass of the converter where sulphur dioxide is converted to sulphur trioxide.

Sulphur dioxide and air undergo the catalytic oxidation reaction in the converter. Since the heat released from the sulphur dioxide oxidation will increase the temperature of the catalysts, the equilibrium conversion rate will decrease. Therefore, the sulphur dioxide conversion process is divided into four stages and the temperature of the catalysts in each stage can be kept suitable by stepwise cooling among

Fig 2: **Asset engineering lifecycle and workflow**



the stages. Thus the reaction can get higher conversion and reaction rate.

In the double absorption process, the gas (SO_2, air and SO_3) from the third converter pass enters the inter-pass tower. After the generated sulphur trioxide is absorbed, the residual gas (SO_2, air) is heated again and enters into the fourth pass of the converter. The inter-pass absorber removes the SO_3 so the conversion in the fourth pass of the converter is increased. The gas out from the fourth pass of the converter enters the final absorption column. Stack SO_2 concentration is lowered below 500 ppm so the exhaust gas can be discharged to atmosphere.

The sulphuric acid (98.5%) from the inter-pass absorption column splits into three streams including the product stream, stream Abs-1ToDryer and stream Abs-1ToAbs-2. Stream Abs-1ToDryer will go to the dry column as de-hydrant. Stream Abs-1ToAbs-2 will go to the final absorption column as the absorbent. The sulphuric acid solution (98.9%) from the final absorption column and the sulphuric acid solution (97.7%) from the dry column will both enter the inter-pass absorption column as absorbent.

Table 2 provides a process summary.

The global property option used in this model is ELECNRTL. This option set is used for the simulations with non-ideal electrolyte solutions. ELECNRTL calculates liquid phase properties from the Electrolyte-NRTL activity coefficient model. Also, Henry's Law is used to calculate gas (SO_2, O_2, N_2 and CO_2) solubility in sulphuric acid. The Ideal property option is used for vapour phase at high temperature in the converter and heater unit operation. The STEAMNBS property option is used for the steam system (economisers, boiler, and superheater) unit operations.

The chemical reactions in this process include gas reactions, absorption reactions and acid chemistry. The reactors are modeled with the built-in models RGibbs for the sulphur burner, and RCSTR for the converter passes. And the sulphur trioxide absorption reaction takes place in RadFrac column. Table 3 lists the reaction units and corresponding Aspen Plus models

Reactions in each reactor and their specifications in Aspen Plus model are listed below and shown in Tables 4 and 5.

Converters – kinetic reaction

$$SO_2 + {}^1/_2 \rightarrow O_2\ SO_3$$

Absorption reaction

$$SO_3 + H_2O \rightleftharpoons H_2SO_4$$

Table 2: Process summary

Area	Purpose
Dryer	dry feed air
Sulphur burning	preparation of sulphur dioxide
Sulphur dioxide conversion	preparation of sulphur trioxide
Absorption of sulphur trioxide	preparation of sulphuric acid
Steam system	heat removal and steam generation

Table 3: Reaction units and corresponding Aspen Plus models

Reaction unit	Reaction type	Aspen Plus model
Sulphur burn	equilibrium	Rgibbs
Converters	kinetic	RCSTR
Absorption reaction	equilibrium	RadFrac

Table 4: Sulphur burn

Component	Valid Phases
N_2	Vap
O_2	Vap
SO_2	Vap
CO_2	Mixed
H_2O	Mixed

Acid chemistry

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

Sulphur burn is modeled using the Gibbs free energy minimum method in the RGibbs model. This determines the equilibrium composition of the products resulting from the many reactions that can occur.

The four converter passes in this process are modeled using four RCSTR reactors with user reaction kinetics. FORTRAN subroutine USRKIN represents the kinetics in all converter passes. USRKIN is included compiled and linked in file Rate1.dll. File sulphuric.opt holds the pointer to the .dll file. It is recommended you place all three files (.bkp, .dll, and .opt) in the same directory.

The first Real parameter of USRKIN is the volume of catalyst in litres. The second Real parameter is the activity of the catalyst. You may adjust these parameters to calibrate the model to reflect the performance of your plant.

Ionic equilibrium reactions in the liquid phase are modeled using Chemistry and the apparent components approach.

Absorption reaction is modeled using Radfrac. The major unit operations are represented by Aspen Plus models as shown in Table 6 (excludes reactor units).

HeatX block supports rigorous design rating or simulation by interfacing with the Aspen Shell & Tube Exchanger program.

Streams represent the material. The simulation is augmented with a combination of flowsheeting capabilities such as Convergence, Design Specs and Calculator Blocks.

Tables 7 and 8 tables outline the key

Table 5: Modelling of converter passes

Converter	Reaction ID	Subroutine Name	Values for parameters	
1st	Rate1	USRKIN	Integer	Real
			1	27000
			2	1.8
2nd	Rate2	USRKIN	Integer	Real
			1	31000
			2	1.8
3rd	Rate3	USRKIN	Integer	Real
			1	30000
			2	1.8
4th	Rate4	USRKIN	Integer	Real
			1	42000
			2	1.8

Table 6: Aspen Plus unit operation models used in the model

Unit operation	Aspen Plus model	Comments / specifications
Drying and absorbing towers	RadFrac	Rigorous absorption including absorption reaction and acid chemistry. Use a "pump around" to model acid-cooling and recirculation
Blower	Compr	Typical pressure rise ~142 in H_2O. Comp Block may also be used to model the steam turbine driver if you choose to add one.
Boiler, superheater, economisers, Gas-to-gas heat exchangers	MHeatX / HeatX	Using MHeatX block to model heat exchanger usually leads to faster and easier flowsheet convergence.

Table 7: Design specs used in the sulphuric acid model

Spec name	Spec (target)	Manipulated Variables
BURN-SO2	Set the SO_2 mole fraction out of SBURN to 0.11	Sulphur (feed of SBURN) mole flow
DS-1	Set the H_2SO_4 mass fraction of product acid IPAT to 0.985	MUWATER (pure feed water to IPAT) mass flow
STEAM	Set the temperature of steam from BLER to 750°F	BFWC (pure feed water of EC4A) mass flow

flowsheeting capabilities used in this model.

Note: In the simulation flowsheet, DUPL blocks are used to duplicate streams entered into the heat exchanger. All the duplicated streams are connected to a hierarchy model in which HeatX blocks are used to simulate heat exchangers. In this way, the flowsheet is not only faster and easier to converge, but supporting rigorous design, rating, or simulation by interfacing with the Aspen Shell & Tube Exchanger program.

This simulation will complete with run status "Results Available". Key stream simulation and process simulation results are shown in tables 9 and 10.

Table 8: Calculators used in the sulphuric acid model

Name	Purpose
C-1	Transfers the mass flow unit of stream IP-PRD from lb/hr to tons/day. Shows the temperature profiles of the burner and converters, UA of heat transfer equipment and flow and concentration of production. Uses Excel to perform this calculation. The Excel file is embedded in the file with extension .apmbd.

Conclusion

The sulphuric acid model provides a useful description of the process. The simulation takes advantage of Aspen Plus's capabilities of modeling electrolyte components. This includes automatic chemistry generation and the capacity of handling electrolyte reactions for all unit models. Aspen Plus provides specialised thermodynamics models and built-in data to represent the non-ideal behaviour of liquid phase components in order to get accurate results.

The model may be used as a guide for understanding the process and the economics, and also as a starting point for more sophisticated models for plant designing and process equipment specifying.

References

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Table 9: Key stream simulation results

Flowsheet variable		
Feed	air feed, lb/hr	224,000
	sulphur feed, lb/hr	26,906
	air/sulphur, mole ratio	9.36
	water for absorption column, lb/hr	2,236
	water steam for heat exchange, lb/hr	109,164
Product	sulphuric acid, lb/hr	83,317
	steam production, lb/hr	109,164
	psi	650
Waste	exhaust gas	179,826

Table 10: Process simulation results

Process variable			
Sulphur burner temperature, °F			1099
Water content of feed air, mole frac			0.029
Water content of dry air, ppm			5.53
Converter temperature, °F	In	Out	ΔT
PASS1	750	1114	364°F
PASS2	824	954	130°F
PASS3	810	858	48°F
PASS4	759	802	43°F
SO_2 in stack, ppm	283		
Sulphuric acid concentration, wt-%	98.5		
Sulphuric acid production, STPD	1000		