

**"SIMULATION AS A USEFUL TOOL  
IN EXAMINING WASTE PRODUCTION"**

by

**N. C. WOLFGANG\***  
and  
**L. W. AYRES\*\***

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# **SIMULATION AS A USEFUL TOOL IN EXAMINING WASTE PRODUCTION**

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## **Abstract**

Materials balance analysis provides a powerful tool for improving the accuracy of environmental-economic studies. It is possible to use current "off-the-shelf" computer models to create a database of standard industrial processes that are balanced in terms of individual chemical components. This paper outlines the procedures involved in the simulation of such industrial processes and presents a sample application.

a Ms Wolfgang, currently a student in the Chemical Engineering Department of Drexel University, Philadelphia, PA, USA, performed this work as an INSEAD summer intern in 1994.

## **Starting Points**

The economy can be visualized as a series of materials transformation processes. From an economist's perspective, the most important of these are production, consumption and exchange. It has become commonplace to regard each of these activities in economic terms; i.e., to consider each as a process by which value is added. However, several analysts have noted that this perspective essentially divorces the analysis of economic activities from the environment; i.e., it treats economic activity as if it were independent of the environment whereas, in practice, economic activities are embedded in the environment. The environment and economic activities are linked in two principal ways. The environment is a source of materials used in economic processes. The environment also acts as a sink for wastes arising from economic activities. Essentially, then, from an environmental perspective, economic activities are better visualized as ones of materials mobilization and transformation. What concerns the environmental analyst is how economic activities may disturb the environment. This perspective on the economy is at the heart of "industrial metabolism".

Against this backdrop, it is important to recognize that the economic perspective on economic activities is dominant. We have accurate and efficient methodologies already in place to account for economic operations in money terms. At the micro-level, each firm is required to keep books; i.e., a set of financial accounts. To ensure complete recording, elaborate systems of double-entry bookkeeping have been institutionalized. At the macro level, the sum of the value of either/both total production or total consumption provides a measure of national income, GNP. Economic accounting is facilitated by the use of a common unit of value, which allows all economic activities to be evaluated in monetary terms. By contrast, we have as yet only poorly elaborated systems to account for anthropogenic mobilization and transformation of materials. The lack of a system is, in part, attributable to the relatively recent recognition that such a system is needed. This recognition has arisen from increasing societal concern over the severity and incidence of environmental problems ranging from climatic change, through ozone depletion to regional acidification. The problem of developing a system to account for materials is compounded by the difficulties of specifying a single unit of account that has meaning; i.e., environmental relevance.

Nonetheless, even without an obvious solution to the "metric" problem, attempts are already well underway to provide inventories of the environmental impacts associated with economic activities. Depending on the interests of the analyst, inventorying may be undertaken for a range of units. These may be defined territorially, sectorially, functionally (e.g., in terms of plants or processes) and, most commonly, in terms of products or services delivered. The analysis of product and service life cycles is an approach to the inventorying of environmental implications of economic activity. The use of life cycle analysis (LCA) has been growing as the potential of the method to reveal information useful in corporate and public sector decision making has been recognized in an ever increasing set of applications. However, some analysts have noted that the method has several limitations arising, most particularly, from problems of data. There is a real danger that a potentially valuable tool in environmental-economic analysis could be discredited by inappropriate interpretation of results from doubtful LCAs [Ayres 1995].

The problem is essentially linked to the accuracy of basic data on unit processes, which are at the heart of any LCA. A major weakness is that published data on unit processes are often unbalanced. The mass and elemental composition of inputs to a process are not matched by a corresponding balance in the mass and elemental composition of process outputs. While a mass balance cannot ensure data validity, it is absolutely certain that data failing to satisfy a mass balance criterion must be invalid on either the input or the output side of the equation (possibly on both).

This problem is, in part, attributable to the long-standing dominance of the economic perspective in analyzing processes. Only inputs to and outputs from unit processes that are associated with economic costs have traditionally been considered "relevant" to the process description. As a result, it is common to see descriptions of processes that ignore inputs and outputs that are considered as "free" goods or "free" emissions, such as air, water, unreacted feedstocks, and many pollutants. Another cause of the problem is simply the lack of familiarity with materials accounting. Since data on materials flows are not routinely collected by any government agency, companies have no external reason to monitor materials use. Their only incentive arises from the general concern to track costs and eliminate inefficiencies in resource use. This does not amount to an imperative for full materials accounting but merely provides an incentive to minimize unnecessary losses of the most valuable materials. Materials that are not "valuable", but which may be emitted to the environment with serious environmental consequences, are unlikely to be recorded.

A secondary, but related concern, is that on an *ad hoc* basis the production of LCAs is expensive and seldom efficient. This is because there are high costs in data collection on upstream and downstream elements of lifecycle chains. Since the costs of collecting these data are high, and the data may not even be accessible (especially if an upstream or downstream process occurs within the jurisdiction of a third party) such data are also unlikely to have high levels of accuracy, and often do not satisfy mass-balance conditions.

## **Building a Database of Balanced Unit Processes**

These two aspects of the data problem - inaccuracy and inefficiency in data gathering - are best tackled by building a readily accessible database of balanced unit processes. However this is no trivial matter. It requires the following:

- An appropriate breakdown of production into sequences and chains of "unit processes".
- An accurate description of each unit process in terms of inputs, equipment used, pressure and temperature conditions, exposure times, etc.
- Process product yields.

To simplify the analysis of a production process, the process is conventionally divided into units (after the approach pioneered by Arthur D. Little). A unit process<sup>1</sup> is the smallest subdivision of an overall process that still constitutes a complete entity in the sense that it might theoretically be detached and moved (for instance) to another location. A unit processes can stand alone, with a definable set of inputs and at least one output that is a commodity with an economic value.

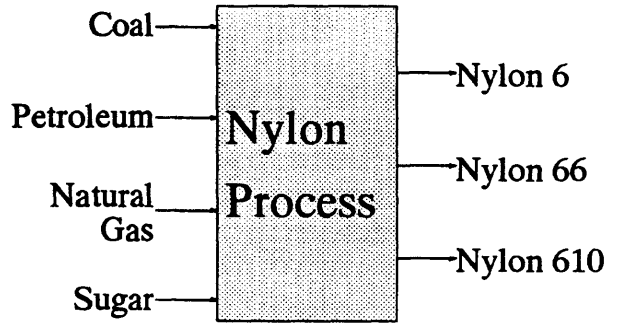


Figure 1. . "Black box" nylon production process

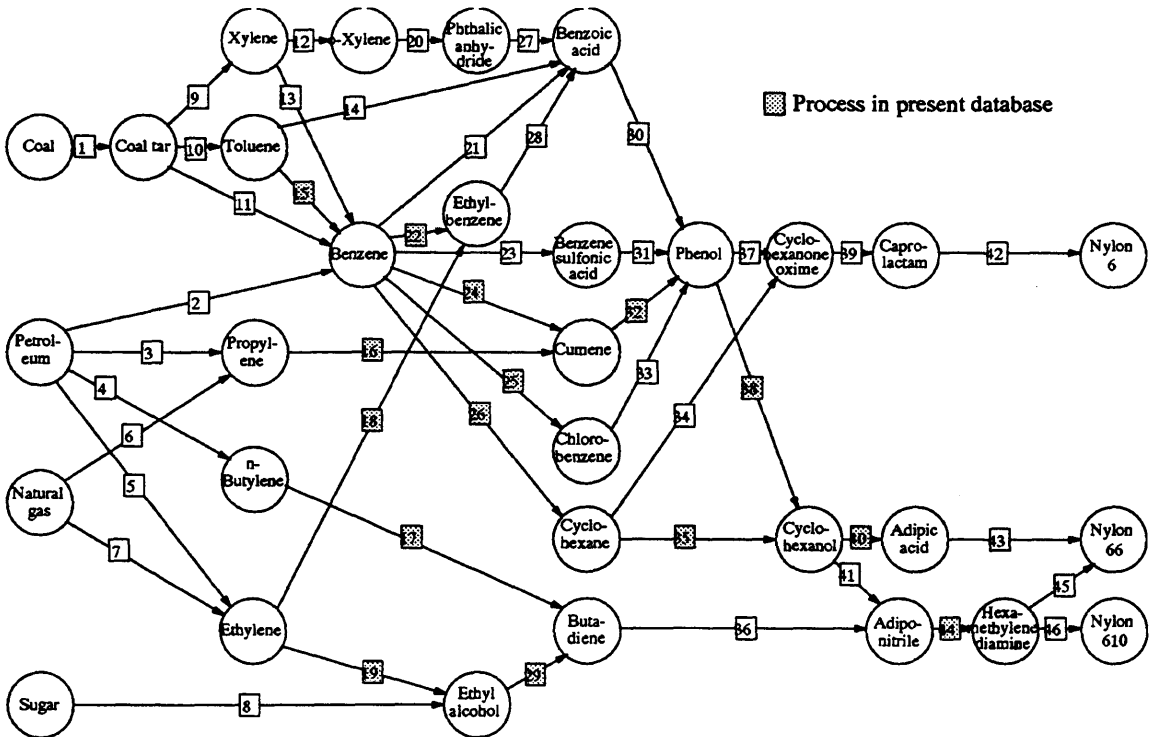


Figure 2. . Complete nylon production process

To illustrate this point, *Figure 1* represents the nylon production process. The nylon production process involves a number of upstream chemicals. The upstream processes can be outlined in greater detail by *Figure 2*, which shows a division into unit processes. The production of cyclohexane from benzene is one such unit process (labelled 26 in *Figure 2*). The advantage of this approach is that the same unit process often occurs in the production chain of many different major commodities. For example the production of chlorobenzene from benzene (labelled 25 in *Figure 2*) is used in the production of solvents as well as nylon. Unit processes can be linked together in many different ways to represent the production of different chemicals.

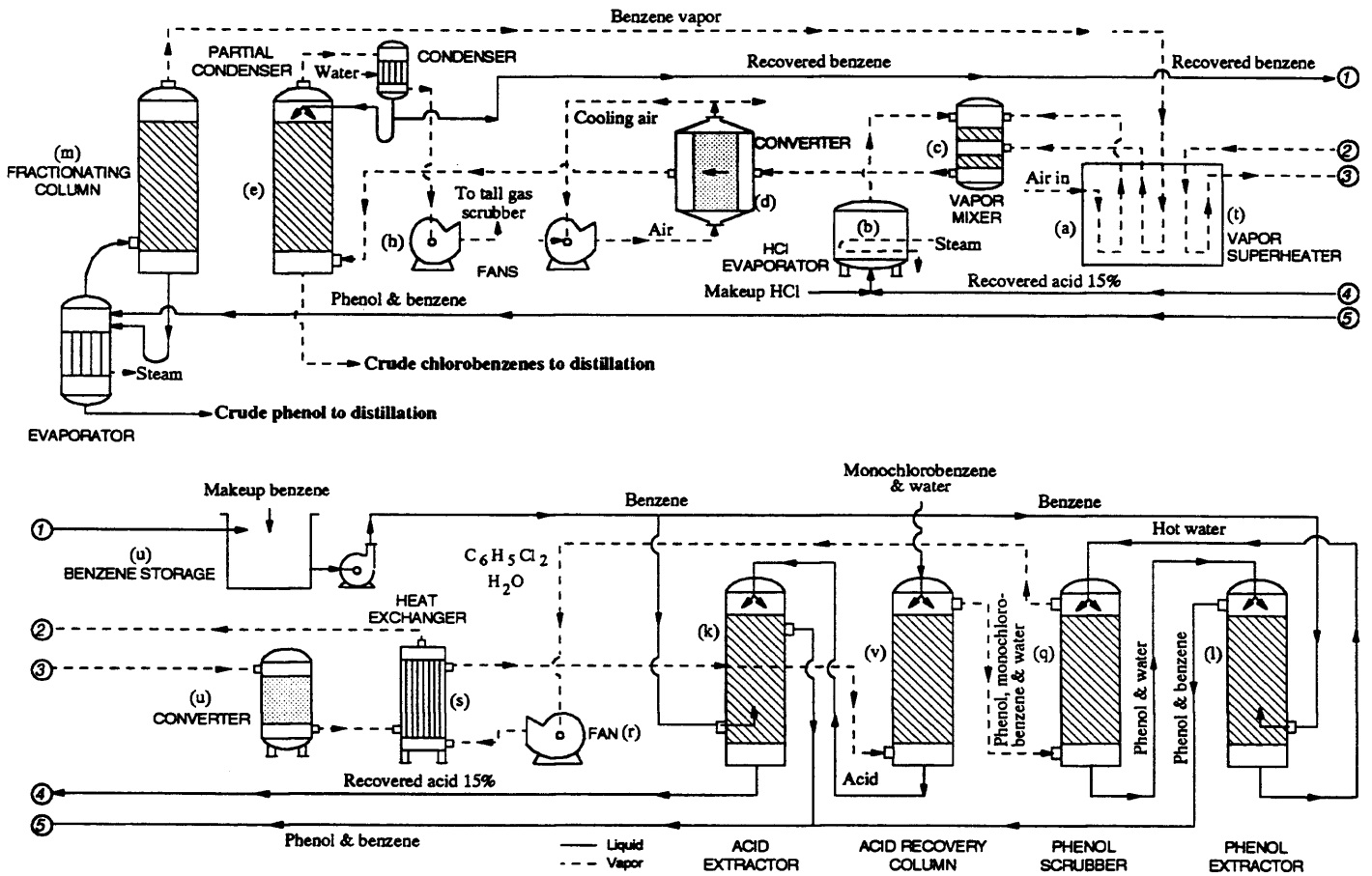


Figure 3. Complex Phenol Flowsheet

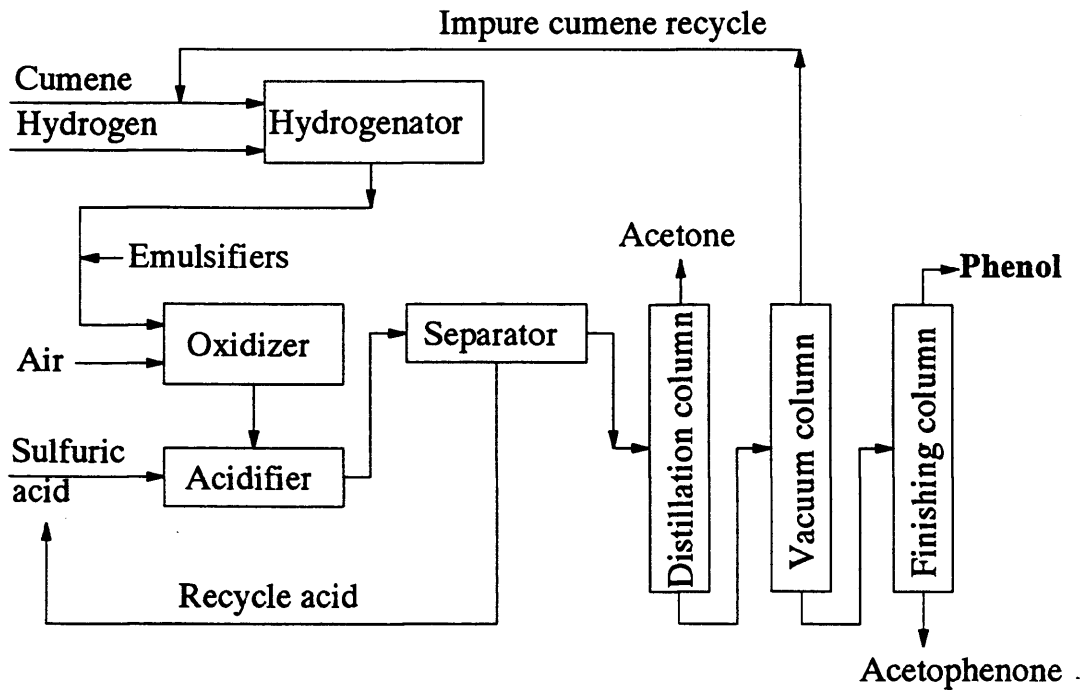
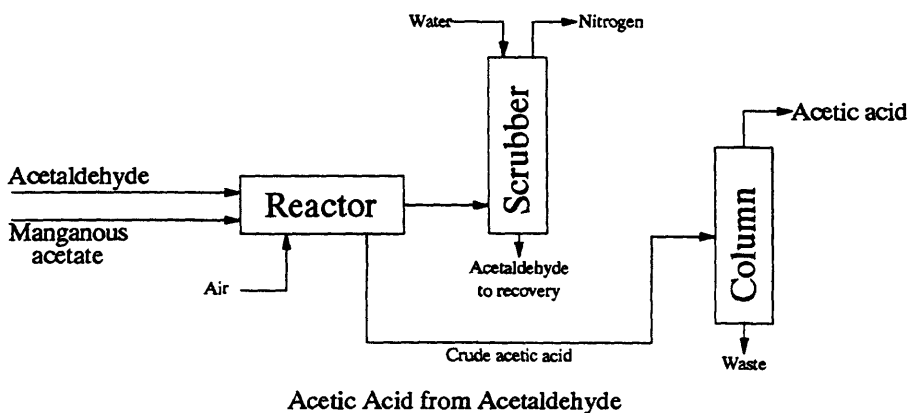


Figure 4. Simple phenol flowsheet. Source: [Lowenheim & Moran 1974]

Chemical process data at the unit process level can be found in a number of references [e.g. Lowenheim & Moran 1975; Kent 1983, Himmelblau 1989, Kirk & Othmer 1993, SRI 1989]. However, many unit process descriptions are oversimplifications of the actual process in that they provide only the amount of usable product as an output. They fail to include the waste products or sometimes even the usable side products. Quite often the process conditions (temperature, pressures, exposure times), flow rates, and yields are not available. Not only may there be missing data, but most references tend to have an economic slant concerning the relevant information, i.e. flow rates may be given in dollars/year instead of metric tons/year. Despite the incompleteness of such sources they can provide a starting point for a simulation. The next logical step is to create a flowsheet, a pictorial representation of the process. This includes arrows indicating inputs and outputs with as many reactors as necessary and lines indicating connecting streams. A flowsheet essentially consists of four basic stages, the feed streams, the process reaction stage, the waste definition stage, and the product streams. Flowsheets can be extremely complex or simple, as illustrated for phenol in *Figures 3 & 4.*

All chemicals necessary to carry out a process are represented by the feed streams. A stream can consist of one or more chemicals, with different flow rates. Flow rates are defined in either mass or molar units per unit time. The product stream(s) represent the total flow of material out of the process and usually consist of several chemicals. The sum of the feed stream flow rates are equal to the sum of the product stream flow rates, i.e. there is a mass balance.

The process reaction stage is the part of the flowsheet representing the chemical reactions necessary to produce the product. An example using acetic acid is shown in *Figure 5.* It includes all the reactors and operation blocks involved. This stage represents the actual process equipment.



*Figure 5. Process reaction stage: acetic acid*

During the process reaction stage, we model all the reactions involved in producing the final product, under ideal conditions. The only outputs for this stage are the product(s), by-product(s), and the unreacted reactant(s).

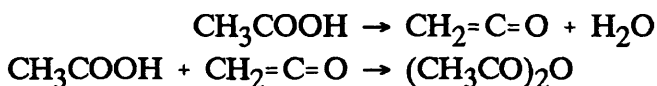
Owing to inevitable inefficiencies in the production process yields are always less than 100%. Yield can be defined as:

$$\text{Yield} = \frac{\text{Quantity of reactant converted to desired product}}{\text{Quantity of reactant converted}}$$

The yield is, however, more commonly specified as a conversion factor, which is defined by:

$$\text{Conversion} = \frac{\text{Quantity of reactant into process} - \text{Quantity of reactant out}}{\text{Quantity of reactant into process}}$$

These two ratios are not normally the same. The same value may result for a simple, one-reaction process where the reactant concerned is either converted to the product or comes out of the process unreacted. Differences occur when there is a side reaction involving the reactant. For example, consider the following two-stage reaction for producing acetic anhydride ( $(\text{CH}_3\text{CO})_2\text{O}$ ) from acetic acid ( $\text{CH}_3\text{COOH}$ ).



If the conversion of acetic acid to the intermediate ( $\text{CH}_2 = \text{C} = \text{O}$ ) in the first reaction were 100% then the overall yield of acetic anhydride from acetic acid would be zero. This is because if all of the acetic acid reacts in the first reaction then the second reaction could not occur at all. This sort of situation is not uncommon.

In the simulation, the waste definition stage occurs after the process reaction stage. This stage does not represent the actual process equipment but rather it represents all of the side reactions that could possibly occur to form unwanted products, i.e. wastes. Since the process stage is simulated under ideal conditions only the specified reactions occur. This is a simplification used for reasons of computational tractability and because we do not have all the information on the process. To simulate the generation of wastes the main product(s) is/are first separated from all other chemicals that are outputs of the process reaction stage to avoid the occurrence of a reverse reaction of the product(s). It may also be necessary to separate certain by-products for the same reason.

The stream containing the unreacted reactant(s) and other by-products is fed to a simulated "Gibbs reactor" which allows the chemicals to reach final chemical equilibrium. The final products of this last reaction stage constitute the simulated process wastes. The resulting stream is then recombined with the product stream to form an overall product stream. This overall product stream of the unit process is defined as a profile of chemical compounds, including both the product(s) and the wastes. The profile meets the materials balance criterion, element by element. The overall product stream can be divided into as many streams as necessary, by different methods, for ease of analysis. For example, in our unit process database the overall product stream is divided into a liquid stream and a vapor stream.



## **A Step-by-step Approach to Using Aspen Plus®**

There are many possible combinations of wastes in the output stream that would satisfy a mass balance. To calculate these by hand in an attempt to find the most plausible possibilities would take a Herculean effort and an enormous amount of time. It would be relatively impossible to develop a complete database of processes using manual methods. Fortunately, there are an increasing number of simulation programs available today for both networks and desk-top computers (e.g. *ASPEN PLUS*®, *PRO II*®) to aid in such a task. In creating our database *ASPEN PLUS*® and *MAX*® (a similar program to *ASPEN PLUS*®, also supplied by *AspenTech*, which is a more user friendly software package with limited capabilities) were used. *ASPEN PLUS*® and other such programs are intended to be used in designing and operating plants producing chemical products. These tools are designed to aid in process development, plant design, modification, and maintenance, and to help improve plant efficiency. *MAX*®, on the other hand, is normally used for teaching and is relatively inexpensive and easy to use.

In creating a balanced unit process one essentially simulates the relevant process conditions. A simulation can be as simple or as complex as is necessary. The actual simulation is data dependent. In specifying the process flowsheet, account must be given to whether or not the available data are sufficiently detailed to provide all required inputs. In cases where some input is lacking a more simplified flowsheet of the process must be used. For example a simple heat exchanger may require that heat transfer coefficients be specified; if these data are unavailable then a heater with a specific temperature output may be specified instead.

*ASPEN PLUS*® is more easily used with *ModelManager*®, a graphical user interface designed for *ASPEN PLUS*®. These programs allow the user to create a flowsheet using graphics, as well as aiding the user to the next logical step in the model design. *ASPEN PLUS*® is capable of simulating several different reactor types. These include a stoichiometric reactor, a Gibb's reactor, a yield reactor, an equilibrium reactor, a continuous stirred tank reactor, a plug flow reactor, and a batch reactor.

The reactor model that was most commonly used in constructing our data base is the stoichiometric reactor (RSTOIC). This is used to simulate a reaction in which both stoichiometry and reaction yield are known, but the reaction kinetics were unknown. This reactor can also simulate several reaction that occur in series under similar temperatures and pressures. A Gibb's reactor (RGIBBS) is used to simulate the waste emissions. It essentially calculates chemical and phase equilibrium by minimizing Gibb's free energy subject to atom balance<sup>2</sup> constraints. The equilibrium reactor (REQUIL), not offered in *MAX*®, also computes chemical and phase equilibrium but accomplishes this by solving stoichiometric chemical and phase equations. REQUIL is not used to calculate the waste outputs since it requires stoichiometric equations in which the wastes are already known. The yield reactor (RYIELD) is used to simulate a reaction where the specific reaction yields of each component is known. The continuous stirred tank reactor (RCSTR) is used when the reactor contents have the same properties as the outlet stream and reaction kinetics are known. The plug flow reactor (RPLUG) is used in the modelling of a reactor where there is no mixing in the axial direction, but there is perfect mixing in the radial direction. The reaction kinetic must be known for

**RPLUG.** The batch reactor (RBATCH) simulates batch or semi-batch reactors, and runs until a specific condition, specified by the user, is reached.

There are numerous ways to simulate the separation of chemicals. These fall into four different categories: splitters and separators, shortcut distillation columns, rigorous fractionations, and flashes. The splitter and separator models include a stream splitter, a component separator, and a two-outlet component separator. The stream splitter (FSPLIT) combines streams and then splits them into two or more outlet streams. All but one of these streams must have specified the fraction of the input flows in the stream. The component separator (SEP) can be used instead of distillation column when the details of the separation are not available. SEP separates streams according to splits specified on each component. The two-outlet component separator (SEP2) is similar to SEP but it allows for the specification of component purity. SEP and SEP2 are both simplifications of distillation or absorption and are used when there is limited information.

The shortcut distillation column models include a design model and a rating model of a single-feed, two-product distillation column with a partial or total condenser. Both models are of distillation columns; they only perform different calculations. The short cut distillation design model (DSTWU) estimates the minimum number of required stages and the minimum reflux ratio given specified recoveries for the light and heavy key components. The shortcut distillation rating model (DISTIL) calculates product compositions given the number of stages, reflux ratio, and the distillate to feed ratio, using the Edminster approach. *ASPEN PLUS*<sup>®</sup> offers an additional shortcut distillation model not available in *MAX*<sup>®</sup>, that is, a shortcut distillation model for complex columns (SCFRAC). SCFRAC is used to simulate columns such as vacuum towers and crude units and calculates, based on product specifications, product compositions and flows, number of stages per section, and heating or cooling duties.

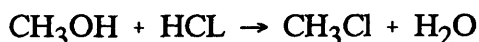
There are four separation models available. The most rigorous model (RADFRAC) is used to simulate all types of multistage vapor-liquid fractionations including stripping, absorption, and extractive and azeotropic distillation, as well as ordinary distillation. It is suitable for many operations but requires more specific information, such as pressure, circulation rate, temperature, temperature change, and vapor fraction. To simulate interlinked multistage fractionation units the MULTIFRAC model can be used. It can model more complex systems involving side stripper, external heat exchangers, bypasses, and others. An absorber model (ABSBR) is used to simulate simple absorbers and strippers without reboilers or condensers. Liquid-liquid extractors can be simulated using the EXTRACT model. Both ABSBR and EXTRACT are capable of handling multiple feeds, heaters/coolers, and liquid sidestreams. RADFRAC and EXTRACT are available in both the *ASPEN PLUS*<sup>®</sup> and *MAX*<sup>®</sup> packages, while MULTIFRAC and ABSBR are only in *ASPEN PLUS*<sup>®</sup>.

There are two flash models; a two-outlet flash model (FLASH2) and a three-outlet flash model (FLASH3). Both models simulate flashes, evaporators, knock-out drums, decanters and other single-stage separators. They separate streams into liquid and vapor streams. FLASH3, however, handles streams with two liquid phases and therefore has two liquid outlets, one for each phase, as well as the vapor outlet.

Other simulation blocks available include a heater/cooler model (HEATER), a two-stream heat exchange (HEATX), a multi-stream heat exchanger (MHEATX), and a stream mixer (MIXER).

The next essential step is to create a list of all the chemical species involved in the process. This includes the chemical inputs, the major outputs, by-products, and all possible wastes. A partial list of the critical organic pollutants occurring in simulations run to date is shown in *Table 1*.

To start the simulation, the chemical components involved in the main stoichiometric reactions are listed. Next, taking into consideration all of the elements contained in these components, a list of any possible chemical outputs (products, by-products, wastes) is created. For example, in the reaction of methanol and hydrogen chloride to produce methyl chloride:



the only elements present are hydrogen, oxygen, carbon, and chlorine. The only feasible wastes are those that include a combination these and no other elements. Chloroform ( $\text{CHCl}_3$ ) could be a possible waste. Hydrogen cyanide (HCN), by contrast, could not be a possible waste in this case, due to an absence of nitrogen among the chemical inputs.<sup>3</sup>

Table 1. . Large production &amp; priority organic pollutants

$\text{CCl}_4$	Carbon tetrachloride	$\text{C}_6\text{H}_4\text{ClNO}_2$	o-Chloronitrobenzene
$\text{CS}_2$	Carbon disulfide	$\text{C}_6\text{H}_4\text{ClNO}_2$	p-Chloronitrobenzene
$\text{CHCl}_3$	Chloroform	$\text{C}_6\text{H}_4\text{Cl}_2$	o-Dichlorobenzene
$\text{CH}_2\text{O}$	Formaldehyde	$\text{C}_6\text{H}_4\text{Cl}_2$	m-Dichlorobenzene
$\text{CH}_3\text{Br}$	Methyl bromide	$\text{C}_6\text{H}_4\text{Cl}_2$	p-Dichlorobenzene
$\text{CH}_3\text{Cl}$	Methyl chloride	$\text{C}_6\text{H}_5\text{Cl}$	Chlorobenzene
$\text{CH}_3\text{I}$	Methyl iodide	$\text{C}_6\text{H}_5\text{ClO}$	o-Chlorophenol
$\text{C}_2\text{Cl}_2$	Tetrachloroethylene	$\text{C}_6\text{H}_5\text{ClO}$	m-Chlorophenol
$\text{CH}_2\text{Cl}_6$	Hexachloroethane	$\text{C}_6\text{H}_5\text{ClO}$	p-Chlorophenol
$\text{C}_2\text{HCl}_3$	Trichloroethylene	$\text{C}_6\text{H}_5\text{NO}_2$	Nitrobenzene
$\text{C}_2\text{H}_2\text{Cl}_2$	1,1-Dichloroethylene	$\text{C}_6\text{H}_6$	Benzene
$\text{C}_2\text{H}_2\text{Cl}_4$	1,1,2,2-Tetrachloroethane	$\text{C}_6\text{H}_6\text{ClN}$	o-Chloroaniline
$\text{C}_2\text{H}_3\text{Cl}$	Vinyl chloride	$\text{C}_6\text{H}_6\text{ClN}$	p-Chloroaniline
$\text{C}_2\text{H}_3\text{ClO}$	Acetyl chloride	$\text{C}_6\text{H}_6\text{O}$	Phenol
$\text{C}_2\text{H}_3\text{Cl}_3$	1,1,1-Trichloroethane	$\text{C}_6\text{H}_7\text{N}$	Aniline
$\text{C}_2\text{H}_4\text{Br}_2$	1,2-Dibromoethane	$\text{C}_6\text{H}_{10}\text{O}_4$	Adipic acid
$\text{C}_2\text{H}_4\text{Cl}_2$	1,2-Dichloroethane	$\text{C}_6\text{H}_{11}\text{NO}$	Caprolactam
$\text{C}_2\text{H}_4\text{Cl}_2\text{O}$	Bis(chloromethyl) ether	$\text{C}_6\text{H}_{12}$	Cyclohexane
$\text{C}_2\text{H}_4\text{O}$	Acetaldehyde	$\text{C}_6\text{H}_{14}$	n-Hexane
$\text{C}_2\text{H}_4\text{O}$	Ethylene oxide	$\text{C}_7\text{H}_5\text{Cl}_3$	Trichloromethylbenzene
$\text{C}_3\text{H}_3\text{N}$	Acrylonitrile	$\text{C}_7\text{H}_6\text{O}_2$	Benzoic acid
$\text{C}_3\text{H}_4\text{O}$	Acrolein	$\text{C}_7\text{H}_7\text{Cl}$	Chloromethylbenzene
$\text{C}_3\text{H}_4\text{O}_2$	Acrylic acid	$\text{C}_7\text{H}_7\text{NO}_2$	o-Nitrotoluene
$\text{C}_3\text{H}_5\text{ClO}$	Epichlorohydrin	$\text{C}_7\text{H}_7\text{NO}_2$	p-Nitrotoluene
$\text{C}_3\text{H}_5\text{NO}$	Acrylamide	$\text{C}_7\text{H}_8$	Toluene
$\text{C}_3\text{H}_6\text{O}$	Allyl alcohol	$\text{C}_7\text{H}_8\text{O}$	o-Cresol
$\text{C}_3\text{H}_6\text{O}$	1,2-Propylene oxide	$\text{C}_7\text{H}_8\text{O}$	m-Cresol
$\text{C}_3\text{H}_7\text{NO}$	N,N-Dimethylformamide	$\text{C}_7\text{H}_8\text{O}$	p-Cresol
$\text{C}_3\text{H}_9\text{N}$	Trimethylamine	$\text{C}_7\text{H}_{10}\text{N}_2$	Toluene-2,4-diamine
$\text{C}_4\text{H}_2\text{O}_3$	Maleic anhydride	$\text{C}_7\text{H}_{16}$	n-Heptane
$\text{C}_4\text{H}_4\text{O}_4$	Maleic acid	$\text{C}_8\text{H}_4\text{O}_3$	Phthalic anhydride
$\text{C}_4\text{H}_6$	1,3-Butadiene	$\text{C}_8\text{H}_8$	Styrene
$\text{C}_4\text{H}_6\text{O}_2$	Vinyl acetate	$\text{C}_8\text{H}_{10}$	Ethylbenzene
$\text{C}_4\text{H}_8\text{Cl}_2\text{O}$	Bis(2-chloroethyl) ether	$\text{C}_8\text{H}_{10}$	o-Xylene
$\text{C}_4\text{H}_8\text{O}$	Tetrahydrofuran	$\text{C}_8\text{H}_{10}$	m-Xylene
$\text{C}_4\text{H}_8\text{O}_2$	1,4-Dioxane	$\text{C}_8\text{H}_{10}$	p-Xylene
$\text{C}_5\text{H}_8\text{O}_2$	Methyl methacrylate	$\text{C}_8\text{H}_{10}\text{O}$	2,4-Xylenol
$\text{C}_5\text{H}_{12}$	n-Pentane	$\text{C}_9\text{H}_6\text{N}_2\text{O}_2$	Toluenediisocyanate
$\text{C}_6\text{Cl}_6$	Hexachlorobenzene	$\text{C}_{10}\text{H}_8$	Naphthalene
$\text{C}_6\text{H}_3\text{Cl}_3$	1,2,4-Trichlorobenzene	$\text{C}_{10}\text{H}_{10}\text{O}_4$	Dimethyl phthalate
$\text{C}_6\text{H}_3\text{Cl}_3$	1,3,5-Trichlorobenzene	$\text{C}_{12}\text{H}_{14}\text{O}_4$	Diethyl phthalate
$\text{C}_6\text{H}_3\text{Cl}_3\text{O}$	2,4,6-Trichlorophenol	$\text{C}_{16}\text{H}_{22}\text{O}_4$	Dibutyl phthalate

### Example: Balancing a Unit Process Using Aspen Plus®

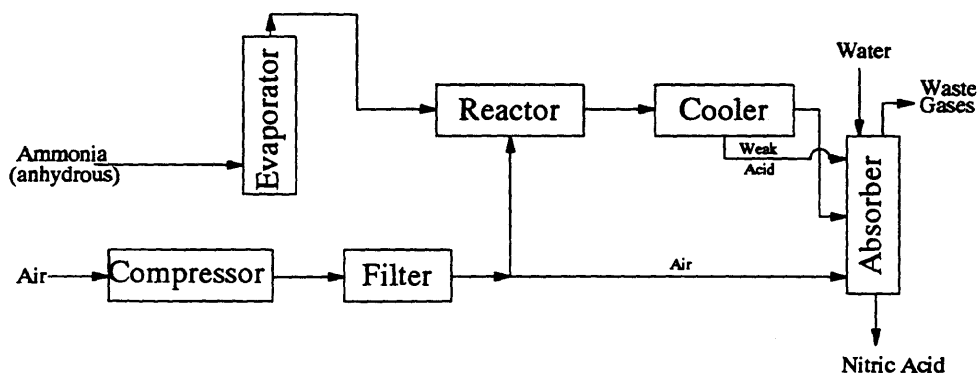
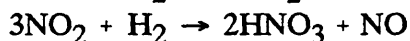
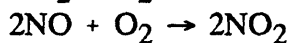
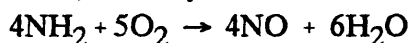


Figure 6. Flow diagram for nitric acid process. [Lowenheim & Moran 1975]

To demonstrate this method the production of nitric acid from ammonia has been chosen as an example. The process flow diagram is shown in *Figure 6*.

There are three reactions that occur, and they are as follows:



These reactions exhibit a 93 - 95% overall yield. A thorough description of this process can be found in [Lowenheim & Moran 1975] and [SRI 1989]. A brief description is as follows:

Air is compressed to approximately 100 psi and preheated to about 300 °C and then mixed with previously vaporized anhydrous ammonia. The 10% ammonia mixture is then passed through a reactor containing a platinum-rhodium wire-gauze catalyst at 750°C. Hot nitric oxides are formed and then cooled along with excess air. When compressed and absorbed in water, a concentration of about 60% is achieved.

This 60% concentrated nitric acid may be further reacted by different techniques to increase concentrations, but for the purpose of this example, the reaction ends here.

On the basis of 1 metric ton of nitric acid at 100% concentration, 290 kg of ammonia, 3600 m<sup>3</sup> of air, and 125 m<sup>3</sup> of water are required [Lowenheim & Moran 1975 p. 563 *et seq*]. Using the given information, a simulation flowsheet can be developed (*Figure 7*).

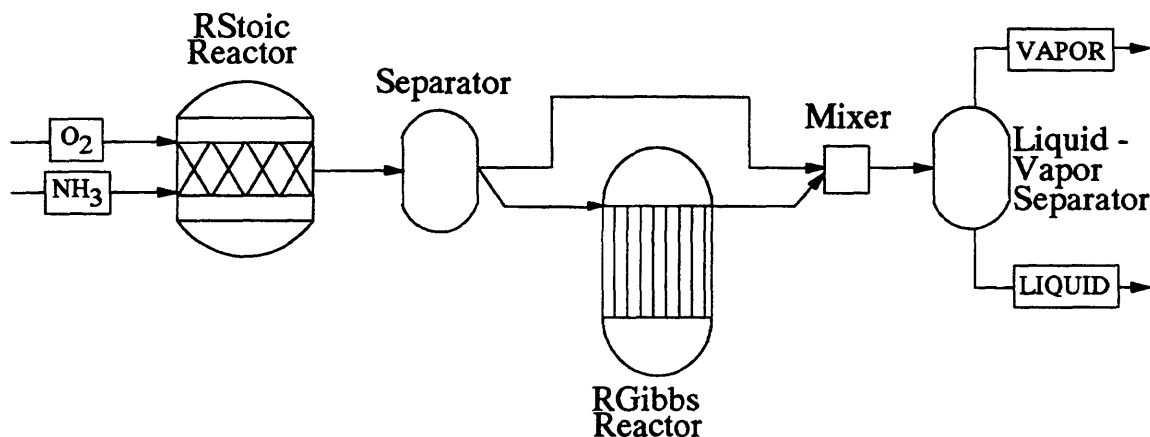


Figure 7. Simulation flowsheet for nitric acid process

The next step was to provide the program with a list of the chemicals involved. The major components in the production of nitric acid are listed: NH<sub>3</sub>, O<sub>2</sub>, NO, H<sub>2</sub>O, NO<sub>2</sub>, and HNO<sub>3</sub>. Taking into consideration that these components contain only nitrogen, hydrogen, and oxygen, a list of possible wastes must be developed. In this case the list of possible wastes is contained in the list of major components. The lack of carbon in the process severely limits the potential waste products. A process such as aniline from chlorobenzene by ammonolysis ( $C_6H_5Cl + 2NH_3 \rightarrow C_6H_5NH_2 + NH_4Cl$ ) would require nearly half of *Table 1* as a list of possible wastes since a larger number of elements is involved in the reaction. It is better to put more wastes than necessary in the list since any wastes that are not being produced can always be removed after the simulation has run.

Since only a volumetric value for air was given as an input, and not a value for the oxygen necessary for the reaction, the air must be divided into the individual chemical species present. It is necessary to add all chemicals present in air (*Table 2*) [Lide 1994] to the component list. (See *Endnote 3*.) The "Air-Sep" block of *Figure 7* is a yield reactor and is used to calculate the composition of the 3600 m<sup>3</sup> of air using the fractional volumes of the species present. The air then passes through a compressor where both the pressure and temperature are increased. From there it is fed into a stoichiometric reactor ("Process") along with ammonia. The three reactions are simulated in series, resulting in a yield of 95% nitric acid based on ammonia. The output of this stream contains only the products and unreacted by-products, which includes all of the components from the air.