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# NEW TECHNIQUES FOR SOLVENT RECOVERY AND ELIMINATION OF WASTEWATER EMISSIONS DURING VACUUM PROCESS OPERATIONS

By

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## Methylene Chloride Recovery Clean Air Act

The pharmaceutical and chemical process industries are concerned with controlling volatile organic compound (VOC) emissions for several reasons: to meet environmental regulations, for increased worker safety, and to minimize product losses. Various methods can be used including flaring and carbon adsorption. These techniques are end-of-the-pipe solutions and are not integral with the process operation itself.

An improved technique for the recovery of solvents during reaction, distillation, evaporation, drying, filtration, mixing, and other vacuum operations is the APOVAC vacuum system. The skid-mounted, engineered package is based upon a single stage liquid ring vacuum pump. The system allows for the recovery and reuse of clean solvent with minimum air emissions and zero liquid emissions. VOC and biological oxygen demand (BOD) regulations are met by this technology.

The paper reviews the technical details of the system and presents test results and on-site operational data. Specific case histories involving methylene chloride recovery and acid/toxic gas neutralizations are also included.

## ABSTRACT

The APOVAC® Solvent Recovery System provides for recovery and reuse of clean solvent, compliance with VOC rules and elimination of wastewater emissions. Test results and on-site operational data are provided. Case histories illustrate methylene chloride recovery and acid gas neutralization.

## Keywords:

Liquid Ring Vacuum Pump  
Solvent Recovery  
Engineered System  
Wastewater Emissions  
VOC Emissions

## 1. The Industrial Environment

In the chemical processing industry (CPI) the generation of vacuum is a necessity. Many chemical processes take place more easily, more quickly and more efficiently under vacuum than under atmospheric pressure, thus allowing better product quality at lower production cost. Some processes require, at different stages, vacuum and pressure, such as in vacuum or warm gas convection drying in Nutsche filter-dryers. If it is a "wet" process involving the use of solvents then solvent recovery becomes an important consideration because of cost savings associated with its recovery as well as environmental benefits.

These objectives have stimulated the development of the APOVAC system concept which is based on the principle of closed loops or circuits. Since its development, the APOVAC system has enhanced today's chemical process technology through solvent recovery and recycling, elimination of wastewater effluent, and reduction of gas emissions thus contributing to a technically efficient and environmentally acceptable operation.

## 2. APOVAC System Concept

The underlying design of the APOVAC system is the combination of vacuum generation and solvent recovery through condensation in a closed circuit system composed of a liquid ring vacuum pump (LRVP) plus a subsequent cooler as shown in Figure 1. The incoming gas stream is cooled in the LRVP and loses its solvent load during the passage through the pump and the subsequent ring-liquid cooler. Condensation occurs in the system due to

compression and cooling in the pump. The ring liquid and condensate (solvent) are collected in a central collection tank which is combined with the system ring liquid cooler where the temperature rise due to the pumping and condensation process is eliminated. An optional exhaust gas cooler further reduces the exhaust gas temperature and provides additional condensation. For the liquid components, the ring liquid is the same as the process solvent such that the latter can then be recycled directly into the production process since it is free from any contamination.

In this basic APOVAC system, three closed circuits exist as shown in Figure 1.

- an internal ring liquid circuit between the pump and the cooler
- an external process liquid (solvent) circuit between the APOVAC system and the chemical processing unit
- an external cooling medium circuit between the APOVAC cooler and the coolant supply

The APOVAC system is self-contained, free from internal contamination, and requires, for its proper functioning, only energy for pumping and cooling. As an addition to a wet process chemical production unit, it allows the efficient recovery and recycling of solvents thus helping to reduce production cost, consumption of energy and solvent, and environmental pollution.

## 3. APOVAC System Design

### 3.1. Liquid Ring Vacuum Pump Features

The central part of any APOVAC

system is the liquid ring vacuum pump (LRVP). A vaned impeller rotates eccentrically in a cylindrical housing with cyclically increasing and decreasing gas chambers to generate a suction and a compression area in the pump. A rotating liquid ring acts as a sealant between the impeller and the housing. Figure 2 shows this design. In this context, the LRVP is the component of choice because of its vacuum generation capability and its various other functions as outlined below:

- heat exchanger function due to the thorough mixing effect between ring liquid and conveyed gas resulting in a strong cooling effect and a nearly isothermal gas compression
- condenser function due to compression and cooling of the gas stream
- reactor function between ring liquid and conveyed gas for neutralization
- tolerance to liquids and solids which may enter the pump
- capability to work as a vacuum pump or as a compressor

### 3.2. Functional System Concept

These useful features of liquid ring vacuum pumps allow APOVAC systems to be designed to a small number of simple but very efficient principles:

- Combination of functions:
  - Pump: condenser; cooler; reactor; gas conveying unit for pressure and vacuum service
  - Ring liquid: solvent; condensate
  - Cooler/Tank: cooling unit for ring liquid; condenser for solvent; collector for ring liquid and solvent condensate
- Separation of functional elements:
  - Separate circuits for cooling media avoid

contamination of process liquids and allow different temperature levels in different system stages.

- Integration in closed circuits: Several closed circuits maximize reusability of process liquids and minimize internal contamination and losses.
- Flexibility and adaptability: The APOVAC system and its components can easily be adapted or modified relative to size, ring liquid requirements, materials choice, control devices, accessories, etc. according to user requirements.

### 3.3. Gas Temperature Profile and Energy Balance

Since condensation is generally the critical process step of any APOVAC system, its temperature profile at a given operating pressure level is of vital interest. In each APOVAC system, three different temperature levels prevail. An optional exhaust gas condenser would increase this number to four. The incoming gas stream of a temperature  $T_1$  is cooled in the pump through its contact with the ring liquid and leaves the pump discharge together with part of the ring liquid at the temperature  $T_2$ . In the subsequent countercurrent ring liquid cooler, the gas temperature drops down to  $T_3$ . If an exhaust gas condenser exists, another cooling step down to  $T_5$  takes place. The liquid ring temperature in the system oscillates between  $T_2$  and  $T_4$  as a consequence of the energy-dissipating pumping process on the one side, balanced by the cooling performance of the liquid ring cooler on the other side. This is graphically shown in Figure 3.

The energy balance of a typical APOVAC system handling inert gases saturated with solvents must consider several elements, as shown in Table 1. The relative size of each element for air at 10°C saturated with water is also given. It is important to note that the solvent recovery rate of the APOVAC system at a given pressure level depends primarily on the temperature of the exhaust gas. The APOVAC design ensures the discharge of the gas stream at the lowest possible system temperature (i.e. after the ring liquid cooler).

#### 4. Environmental Control: Air & Wastewater

A plant site is required to meet many environmental rules for air emissions and wastewater emissions. The new Clean Air Act (CAA) of 1990, for example, will be tougher than ever and will require a 90% reduction in emissions by the year 2000 for 189 major chemicals. Table 2 lists the 1990 CAA "Most Wanted" list, many of which are used by the CPI. Of these compounds, over 50 percent are solvents that are typically used as ring liquids in the APOVAC system. In terms of wastewater emissions, the Clean Water Act allows a plant to discharge only the pollutants that are contained in its permit.

There are many ways to address VOCs and other forms of air pollution. Solutions include carbon adsorption systems, scrubbers, catalytic oxidation, and thermal incineration with regenerative heat recovery. For wastewater control, filtration, distillation, settling tanks, and chemical treatment are common techniques.

The above discussion focuses on pollution control as an end-of-the-pipe solution and looks at each waste stream as an individual problem. The most effective approach for environmental control is a "total-system" view point. The APOVAC system solves both the air and wastewater problem as part of the process solution. Wastewater emissions are eliminated as the ring liquid is the same solvent as the process fluid.

VOC rules are met by the uniquely designed ring liquid cooler operating on the high pressure side of the LRVP. Table 3 illustrates the dramatic effect of this cooler on exhaust gas solvent load for different solvents. Finally, for difficult or high-load solvent recovery, a precondenser or exhaust gas condenser can be added. Sections 5 and 7 illustrate examples of a total process approach to solving a pollution problem, rather than a quick (and expensive) fix to a specific exhaust stream emission problem.

#### 5. Areas of Application

APOVAC systems with the previously described features find a wide field of applications as described below:

##### - Drying

The APOVAC system operates as a vacuum pump with solvent recovery for conventional vacuum drying. In addition, it can be used as a compressor for filter-cake "blowing" and/or convection drying. In these applications, emissions can be virtually eliminated by circulating an inert gas, usually  $N_2$ , with intermediate condensation at elevated pressure and low temperature. In convection

drying, the gas is reheated before recycling to the dryer or filter-dryer. Figure 4 shows a typical vacuum/ convection drying installation.

#### - Distillation

Running these processes under vacuum lowers the distillation temperature and helps save costs. APOVAC units generate the required vacuum and recover evaporated condensibles carried away with the air leakage.

#### - Crystallization

Crystallization in wet processes requires the removal of solvents. The crystallization process is often accelerated or better controlled under vacuum. The APOVAC units ensure the necessary vacuum plus the recovery of the process liquids.

#### - Stripping of Solvents (Recovery of Solvents from Waste Air Streams)

In the case of adsorption, solvents are attached to a suitable medium, e.g. activated carbon. When the adsorptive capacity is reached, the solvent must be removed and ideally recovered. This is often achieved by applying heat and vacuum or pressure. APOVAC units generate vacuum and/or pressure and recover the solvents released. APOVAC compressor systems in addition allow a smaller sized system, and more efficient solvent recovery than non-pressurized systems. Finally, as pretreatment for waste air streams prior to the end-of-pipe installation, they recover between 60 to 90 percent of the solvent load, thus reducing the burden on final gas treatment unit.

#### - Degassing of Extruder, Kneader, and Compounding Units

Many chemical compounds contain a certain amount of volatile compounds from their manufacturing

process. During thermal and mechanical processing like extrusion, kneading, and compounding these volatiles are released, especially at elevated temperatures, and must be removed. The removal process is helped significantly by the application of vacuum. APOVAC systems generate the vacuum and recover the condensible part of the volatiles. The tolerance of a liquid ring pump to small particles which are frequently released is an additional benefit.

#### - Waste Air & Water Scrubbing for

#### Neutralization and Purification

The close contact of the conveyed medium with the ring liquid allows specific reactions to take place in the pump such as neutralization of acids or deodorization of odorous gas streams. In the former, the ring liquid is a caustic solution which, in contact with the acid gas stream, results in the removal of the acid and the formation of salts in the ring liquid. The ring liquid has to be treated regularly to remove the salt generated. A similar purification effect can be achieved with odorous gas streams through a selection of suitable ring liquids. A static-mixer, shown in Figure 5, with a side stream of the ring liquid to scrub the process gas upstream of the pump significantly helps to increase the neutralization efficiency.

#### - Chemical Vapor Deposition

In this metal coating process, compounds of metals like aluminum, titanium and others, are deposited on the desired materials. The resulting process acid gases can be neutralized in APOVAC systems using an alkaline ring liquid.

#### - High Vacuum Applications

For applications that demand increased vacuum, a fully

integrated gas ejector can be incorporated. This ejector design, as shown in Figure 6, uses the vapor in the gas/vapor space of the collector tank as the motive gas force. The result is increased vacuum without the use of fresh air or nitrogen. Organic emissions and gas consumption are reduced as compared to conventional air or steam jet ejector systems.

#### - Replacement of Existing Vacuum Systems

The APOVAC unit can replace existing steam jets where there is high water usage, environmental problems, or inefficiencies. For conventional oil vacuum pumps, replacement with an APOVAC unit can eliminate oil contamination problems as well as the high maintenance costs associated with these systems.

The most useful way of applying the APOVAC unit is to attach one system to each wet process unit, such as a dryer or crystallizer. Thus, a series of APOVAC systems are installed in a chemical production plant with each system being part of a specific production unit. The exhaust gas of each unit is collected and conveyed to a central system which meets all of the specific rules for exhaust gas quality.

#### 6. Return on Investment

The incentive for an investment into an APOVAC system is in most cases the need for vacuum generation combined with exhaust gas emission control and recovery of solvents. Experience has proven that the investment for an APOVAC system can often be paid back in a short time, generally less than one year, if the total costs associated with solvent utilization in the plant are considered. Table 4 illustrates a typical

return on investment (ROI) calculation that has been taken from a fine chemical production plant.

#### 7. Case History Installations

One of the major VOCs that must be controlled is methylene chloride ( $\text{MeCl}_2$ ). The following two case histories detail successful APOVAC installations. One is low temperature  $\text{MeCl}_2$  recovery while the other involves steam jet replacement and  $\text{MeCl}_2$  recovery/neutralization.

In this batch - granulation process, 200 Kg of  $\text{MeCl}_2$  is emitted. Solvent recovery is required due to environmental rules as well as for process economics. The user installed an APOVAC 2510 system with a precondenser, demister, exhaust condenser, and back pressure control. The ring liquid is  $\text{MeCl}_2$  with a chilled brine at  $-40^\circ\text{C}$  as the coolant. The result is pure  $\text{MeCl}_2$  recovery of greater than 96 percent, which is reused in the process.

A second installation of interest is a methylene chloride recovery/neutralization application. In this case, the application is a monomer batch reaction where 196 Kg of  $\text{MeCl}_2$  is steam-stripped at a final vacuum of 5 mm Hg. The issue facing the plant was that approximately 70 percent of the  $\text{MeCl}_2$  was lost to the atmosphere and the wastewater disposal system through the steam jets. A further complication was the presence of 5 percent water in the solvent, thus eliminating low temperature condensing as an option.

After conducting on-site test work, the user installed an APOVAC 2510 with an exhaust condenser and gas ejector. The

ring liquid is a 40 percent solution of potassium carbonate ( $K_2CO_3$ ), and the coolant is at  $0^\circ C$ . The  $K_2CO_3$  ring liquid provides for a phase separation as  $MeCl_2$  is not soluble in  $K_2CO_3$ . The  $MeCl_2$  is decanted from above the  $K_2CO_3$  in the receiver tank. Finally the  $K_2CO_3$  neutralizes the trace hydrochloric acid that is formed by the aqueous  $MeCl_2$ . The user recovered greater than 90 percent of the  $MeCl_2$  and eliminated wastewater emissions of an  $MeCl_2/H_2O$  mixture by replacing the steam jets.

## 8. Summary

This paper examined an approach to solving an emission problem that goes beyond a single-stream response. The 1990 CAA allows for site-specific issues to impact the selection of a control device. These include utility requirements, space, work force skill, disposal options, and secondary environmental impacts, such as wastewater and solids generation by the proposed equipment. The APOVAC unit addresses these issues and allows the user to solve an air and wastewater emission problem simultaneously with a single control device. This overall emission minimization approach provides benefits to several different groups associated with the plant and allows for a proactive response to pollution control.

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Table 1: Energy Balance

INCOMING	% OF TOTAL	OUTGOING	% OF TOTAL
Gas Heat	1%	Gas Compression Energy	17%
Solvent Cond. Heat	24%	Ring Liquid Cooling Energy	81%
Pumping Energy	75%	Exhaust Gas Cooling	2%

Table 2

## 1990 CAA Title III's "Most Wanted" List

Acetaldehyde	Dimethyl phthalate	Phthalic anhydride
Acrylic acid	Epichlorohydrin*	Propylene oxide
Acrylonitrile*	Ethyl benzene*	Styrene*
Allyl chloride	Ethyl chloride*	Styrene oxide*
Aniline*	Ethylene dichloride*	Perchloroethylene*
Benzene*	Ethylene glycol*	Titanium trichloride
Benzyl chloride	Ethylene oxide	Toluene*
1,3-Butadiene	Formaldehyde	Trichloroethylene*
Caprolactam	Glycol ethers*	Vinyl acetate
Carbon tetrachloride*	Hydrochloric acid	Vinyl bromide
Chlorine	Maleic anhydride	Vinyl chloride*
Chlorobenzene*	Methanol*	Xylenes*
Chloroform*	Methyl methacrylate	Hydrofluoric acid
Cresols/cresylic acid	Methylene chloride*	
Cumene	Phenol*	
Diethanolamine*	Phosphorus	

\*Solvents typically used as ring liquids in the APOVAC unit.

Table 3: Exhaust Gas Load as Percentage of 1 Kg Air

Ring liquid	(°C)	Circulation without gas cooling	APOVAC Unit
Acetone	-15	19.8	6.3
Methyl alcohol	- 5	8.6	2.5
Toluene	+10	12.2	3.3
Butyl alcohol	+20	8.5	2.7



Table 4: Economic Justification

APOVAC

- a. Investment Cost
- b. Installation Cost
- c. Total System Cost (\$)

SOLVENT Handled

- a. Quantity Recovered
- b. Recovered Value
- c. Raw Material Price
- d. Purchasing Value
- e. Additional cost for handling and stocking under safety conditions including loss of interest.
- f. Savings for increased life of flare (no HCl generation)
- g. Savings for reduced flare gas washing, neutralization, disposal or other treatment
- h. Miscellaneous
- i. Total Solvent Savings Per Year (\$/year)

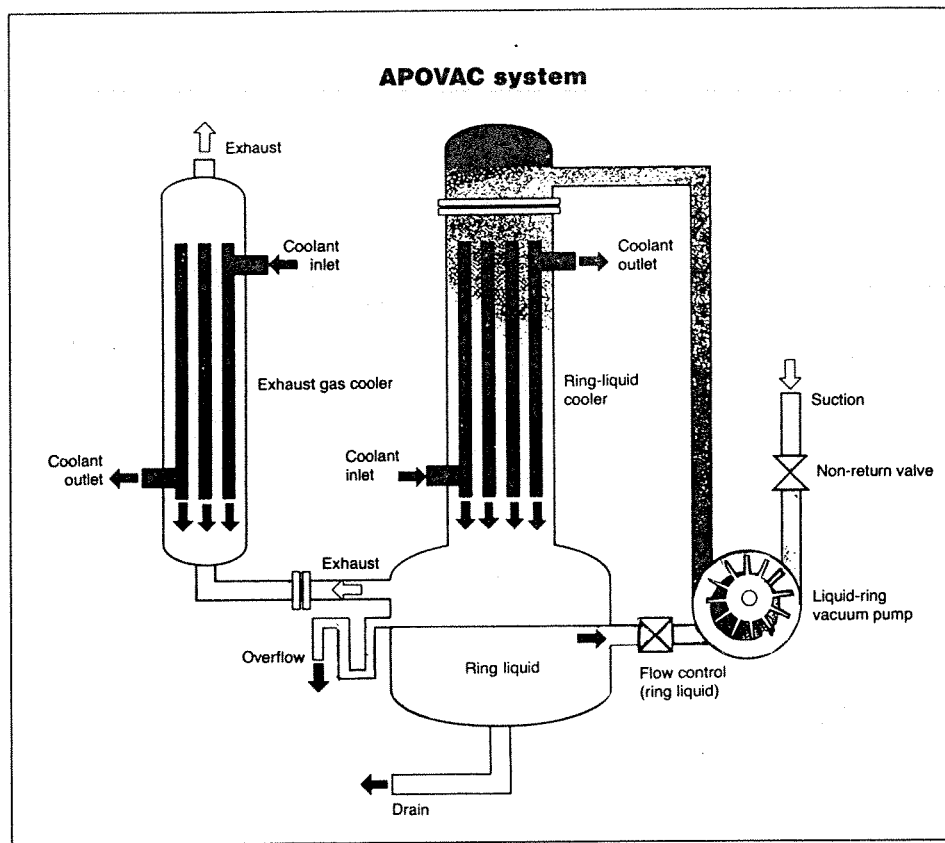
APOVAC System Annual Cost

- a. Depreciation
- b. Capital Cost
- c. Energy Cost
- d. Cooling Energy Cost
- e. Total APOVAC System Annual Cost (\$/year)

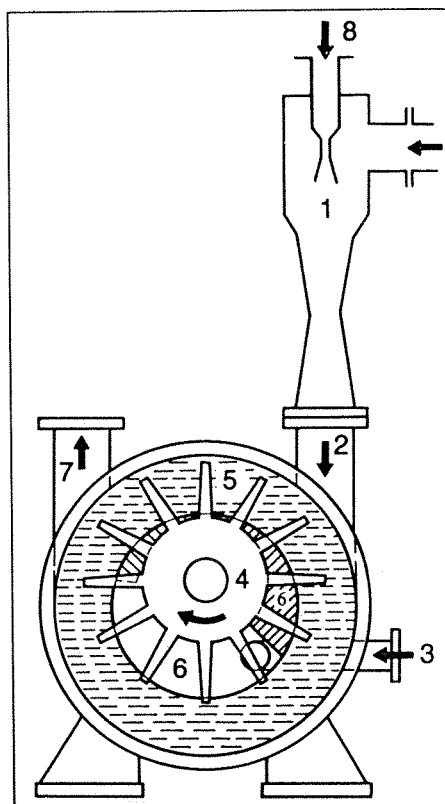
SAVINGS PER YEAR (\$): 2.i. - 3.e.

PAY BACK TIME (YEAR):  $1.c. \div (2.i - 3.e.)$

**Figure 1:** Schematic Representation of the APOVAC System



**Figure 2:** Operating Principle of Liquid Ring Vacuum Pump with Upstream Gas Ejector



1. Gas ejector
2. Gas intake
3. Ring liquid inlet
4. Vaned rotor
5. Ring liquid
6. Crescent-shaped cavity
7. Gas and ring liquid outlet
8. Motive gas

**Figure 3: Gas Temperature Profile and Energy Balance for APOVAC System**

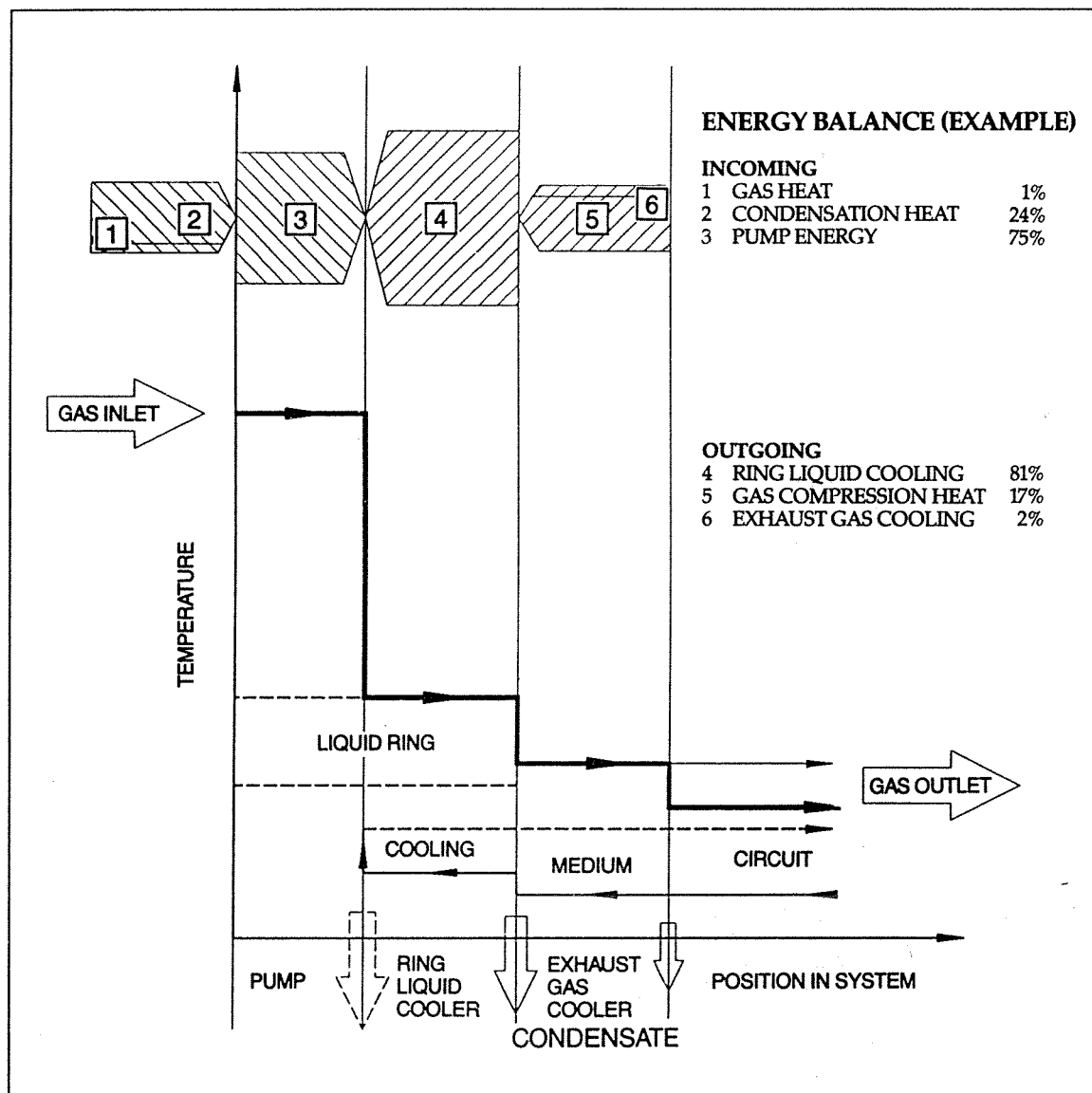
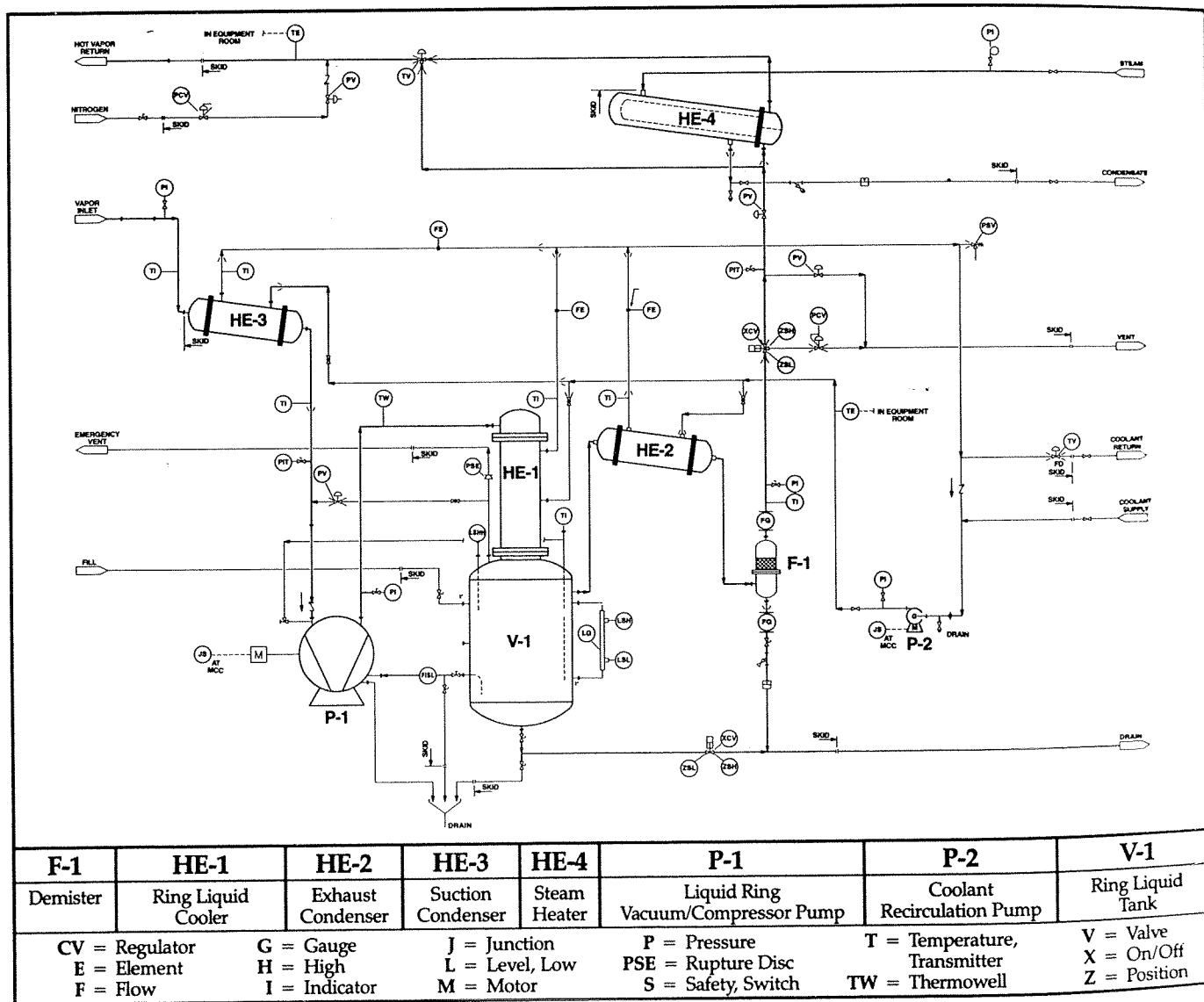
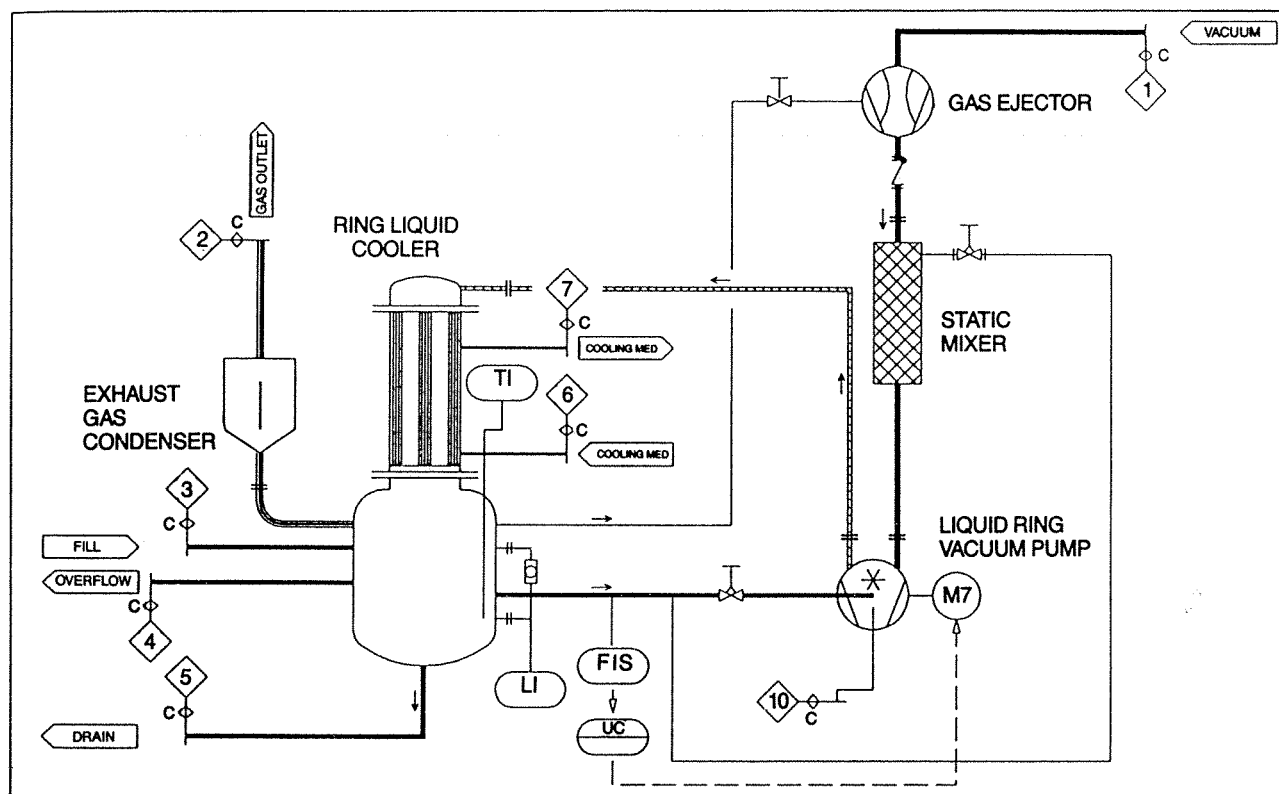


Figure 4: APOVAC Solvent Recovery Skid for Vacuum and Convection (Pressure) Drying



**Figure 5:** APOVAC Scrubbing Skid for Acid Gas Neutralization



**Figure 6:** Gas Ejector Using System Gas-Vapor as the Motive (Propulsion) Force

