Monarch™ HRS Retrofit
A Technology Update

by
David L. Randolph III
Jeffrey P. Walser
John R. Horne
Walter M. Weiss

Presented at the
Regional Central Florida AIChE Meeting
May 1997

ENVIRO-CHEM SYSTEMS
Monsanto

14522 South Outer Forty Road
St. Louis, Missouri, USA 63017
314-275-5700
email: enviro-chem@ccmail.monsanto.com
Internet: http://www.enviro-chem.com

Monarch™ HRS Retrofit - A Technology Update

David L. Randolph III / Jeffrey P. Walser / John R. Horne / Walter M. Weiss
Monsanto Enviro-Chem Systems, Inc
St. Louis, Missouri 63178

ABSTRACT

The Monarch™, process increases the amount of recoverable energy from a sulfuric acid plant as high pressure steam. Monarch, a wet gas process, combines Heat Recovery System (HRS), steam injection, and condensing economizer. HRS has been well demonstrated over the last ten years recovering energy as medium pressure steam. Steam injection has been proven technically. The condensing economizer has been successfully demonstrated with over eight months of operation at Sud Chemie located in Germany. Condensing economizers recover energy as high pressure steam from the gas phase reaction of SO_3 and water vapor, and condensation of sulfuric acid. Operating data indicates corrosion rates and acid concentration are equal or better than predicated. Existing HRS's can be retrofitted with condensing economizers to increase overall energy recovery and plant capacity.

WHAT IS MONARCH

When Monsanto's patented Heat Recovery System (HRS) was introduced, opportunities for optimization and improvements quickly followed. An active research and development program, combined with experience gained from designing and operating full-scale systems, led to another major advance in energy recovery. This process, called Monarch, is based on the highly synergistic combination of two well proven technologies: HRS and the wet catalytic process.

There are two major features of this technology: First, essentially all the process heat is recovered as steam, which eliminates the need for cooling water in the acid plant. Second, heat is shifted from the production of medium pressure steam to the production of high pressure steam.

The manufacture of sulfuric acid by processing gas containing water, sulfur dioxide, and sulfur trioxide is a well established and proven technology. It is sometimes referred to as the wet catalytic or wet gas process. Such plants typically operate on feedstocks like hydrogen sulfide, which produce water when burned. The wet catalytic process can be characterized as an acid plant without a drying tower. Cooled combustion gases are taken directly to the converter, thus eliminating the capital cost associated with drying. Conventional vanadium catalysts have worked very successfully under these conditions. Enviro-Chem built such a plant for Climax Chemical in 1962. It operated for 25 years before the entire complex was shut down. Maintenance was equivalent to a dry gas plant.

The dew point of the gas stream after pass 3 of the converter ranges from about 410°F (210°C) to about 520°F (270°C). The lower end of this range is typical for a plant where ambient air is the main source of moisture. The upper end of the range is typical for a plant where steam injection is used to produce a nearly equimolar mixture of sulfur trioxide and water.

Wet sulfur trioxide-containing gas can be handled in carbon steel equipment provided the gas temperature is kept above the dew point. Carbon steel construction was used for the Climax Chemical plant. The relatively high dew point generally limits cooling equipment to boilers and superheaters. Equipment operated below the dew point must be constructed of alloys or other corrosion resistant material.

A flow diagram for the Monarch process is shown in Figures 1 and 2. Moist ambient air is drawn through a filter by the main blower. The compressed air is preheated prior to entering the sulfur burner. The air heater uses 150 psig (10 barg) steam from the HRS to heat combustion air, which shifts additional heat to high pressure steam production. The gas exiting the sulfur burner is cooled by a waste heat boiler and superheater before entering the first converter pass. A superheater after the first pass and a hot heat exchanger after the second pass are standard gas cooling equipment for these locations.

Dilution water, in the form of 5 psig (0.3 barg) saturated steam, is added to the gas leaving the third pass. As the gas is cooled in waste heat boiler #2 and condensing economizer 3B, some of the sulfur trioxide reacts with the water vapor to form sulfuric acid vapor. About one-fourth of this reaction heat is recovered in waste heat boiler #2 and three-fourths is recovered in economizer 3B. Some acid is condensed in the economizer which is designed using materials proven in HRS service to have very low corrosion rates for similar conditions. This heat of reaction and condensation is recovered as high pressure steam.

The gas leaving the economizer goes to a conventional HRS. From the HRS, the gas is heated in the cold and hot interpass heat exchangers before entering the fourth converter pass. The cold interpass heat exchanger is located after the fourth pass, so it is only exposed to dry gases with a low dew point. The cold gas leaving the cold interpass exchanger enters the hot interpass exchanger at a temperature above the dew point of the hot gas entering the hot interpass exchanger. The gas leaving the fourth pass is cooled in the cold interpass exchanger and economizer 4A before entering the final absorbing tower (FAT). From there, it exhausts to the atmosphere through the plant stack.

The acid from the FAT is pumped through the FAT acid cooler, which uses demineralized water to cool the acid. The cooled acid is then distributed to the FAT and the upper stage of the HRT. The water leaving the FAT cooler is further heated in the HRS preheater before going to the deaerator. The deaerator is operated at a pressure high enough to allow all the acid heat to be recovered.

The product acid cooler and the compressor lube oil cooler are the only cooling water requirements in the acid plant area. The only need for a cooling tower is for the steam condenser in the turbine generator area.

As the quantity or quality of recovered energy increases, the cost usually increases also. Different types of heat transfer equipment are utilized for cooling, with the selection depending on the type of plant and site specific requirements. Design heat transfer coefficients for different types of equipment are reasonably constant, hence, the cost of utilizing that equipment at a specific location in the process depends on the cost per unit area and the available temperature driving force. The most cost effective steam generating equipment tends to be economizers, superheaters, and boilers, in that order. Ultimately, the type of equipment and extent of heat recovery from a wet gas stream is an economic decision based on balancing the incremental cost of heat transfer area against the value of the additional power generated. In references (1) and (2), a condensing economizer was selected as the most cost effective means for increasing the production of high pressure steam. In 1990, the total plant investment equivalent for a 2750 STPD Monarch plant was 1380 $/kW.

Subsequent optimization in 1995 of the Monarch process has led to increased power generation. Table 1 shows a comparison of Monarch with a conventional design based on a 3750 STPD sulphur burning plant with 11.5% SO_2 (dry basis).

Table 1- Sulfur Burning Monarch

	CONVENTIONAL	MONARCH
High pressure Steam		
Pressure (psig)	900	900
Temperature, F	900	925
Production, klbs/hr	375	461
Production, lb/lb	1.20	1.48
Medium pressure steam		
Production, klbs/hr	0	46.4
Production, lb/lb	0	0.33
Electric Power		
Gross MW	45	69.5
Internal use MW	9	9
Net Export MW.	36	60.5
Capital Cost		
Acid plant M$ (a)	36	49
TG area M$ (b)	17	21
Total cost M$	53	70
Investment equivalent.		
Total Plant $/kW	1470	1160
Incremental $/kW		690

(a) - Includes acid production facility from sulphur pit through stack. Excluded are the utilities for water treatment, instrument/plant air, unloading, filtering and storage of sulphur, and storage and loading of product acid.

(b) - Includes power facility beginning at high voltage substation and also includes cooling tower for steam condenser and acid area requirements.

The results in Table 2 are based on generating maximum power. No low pressure steam export has been considered and internal power usage includes a motor driven compressor. In both the conventional and the Monarch cases, the net power will be reduced in a fertilizer plant by the amount of steam used for phosphoric acid evaporation and ejectors. If 163,000 lb/hr of 40 psig (3 barg) steam is extracted for the evaporators and 17,700 lb/hr of 150 psig (10 barg) steam is used for ejectors, sulfur melting, etc., the net power shown in Table 2 would be reduced by about 10 MW.

Compared to 1990, the estimated incremental cost of the Monarch plant over the conventional plant has increased due to the higher costs of stainless steel. However, a series of incremental changes in the Monarch flow sheet, as shown in figures 1 and 2, have increased the gross power production by more than 12%. As a result, the total plant investment equivalent ($/kW) has actually been reduced. The major changes can be summarized as follows:

- A 900 psig (62 barg) boiler has been added after pass 3.
- The 900 psig (62 barg) trim superheater has been moved to the exit of the main WHB.
- 150 psig (10 barg) steam from the HRS is superheated to 750°F (400°C).
- 900 psig (62 barg) boiler feedwater is preheated with 150 psig (10 barg) steam before going to the condensing economizer.
- All boiler feedwater is preheated in the economizer by gas from the fourth pass and in the HRS system by hot 440°F (227°C) acid.

HEAT RECOVERY SYSTEM

The HRS, a key element of the Monarch process, has flourished in the past ten years. The number of HRS units installed now totals 19 as shown in Table 2. Individual plant capacities range from 260 STPD to over 4850 STPD, and the total installed capacity is over 39,500 STPD. With the exception of a few excursions, these plants have experienced very low corrosion rates, less than 2 mpy (0.05 mm/yr), handling concentrated acid at temperatures well over 400°F (200°C). The latest HRS installation is for Anaconda Nickel. This is the largest single train sulfur burning acid plant in the world at 4850 STPD. Kennecott at 3850 STPD is the largest single train metallurgical acid plant in the world.

The most significant acknowledgment to our breakthrough in energy recovery was the patent issued to Enviro-Chem for the Heat Recovery System. The HRS has been the subject of numerous technical papers. From the initial conception until now, the basic process has not changed. The Heat Recovery System is basically an absorber that operates at about 400°F and uses a boiler to remove the absorption heat as steam (at up to 150 psig), instead of acid coolers (where heat is wasted by rejecting it to the cooling tower). The discovery that made this development possible is this: By increasing acid concentration in the absorber by less than 1%, rather common stainless steel alloys become virtually corrosion resistant at 400°F and higher.

The gas from the economizer enters the first of two stages in the Heat Recovery Tower (HRT). High temperature absorption and condensation occur in the lower stage. The upper stage is a cooler-condenser, where the gas is contacted with cool sulfuric acid to reduce sulfur trioxide and sulfuric acid vapor to normal levels. The gas is slowly cooled in the upper stage to minimize mist formation. Gas conditions leaving the tower are essentially the same as gas leaving a conventional interpass tower. Acid circulation through the tower absorbs heat from acid condensation and sensible gas cooling. The circulating acid is cooled in the HRS boiler. The cooled acid stream flows to the dilutor where it is mixed with boiler feedwater for trim concentration control, before returning to the first HRT stage.

The overflow from the HRT flows to the HRS heater where it is cooled by feedwater to the HRS boiler and high pressure (HP) boiler. This acid stream is further cooled in the HRS preheater before flowing to the final tower pump tank.

Like Monarch, HRS has been optimized to increase power production as can be seen in Figure 2. A similar system is employed where both HRS and HP boiler feed water is heated in the HRS heater by hot acid and in economizer 4A by hot gas. Then HRS steam is used to preheat just HP boiler feed water in a carbon steel vessel. Effectively, the HRS continues to act as a heat pump by transferring energy from the medium pressure system to the HP system where more power is produced. For HRS in a standard dry gas plant, there are numerous options with decreasing energy recovery such as increasing water circulation through the HRS heater and flashing it back in the deaerator. The added heat recovery depends on the power cost versus the cost of added surface and additional equipment.

STEAM INJECTION

This concept involves injecting steam into the process gas upstream of the HRS tower. The advantage is to react the SO_3 with the water vapor prior to entering the tower, thus reducing the acid concentration rise across the lower stage. A lower concentration rise allows for a higher inlet concentration at the same circulation rate. One of the benefits of this scheme is that it can be used to upgrade low pressure steam to 150 psig steam (provided the steam pressure is higher than the process gas pressure), by means of chemical reaction! Simply stated, dilution water in the liquid state is replaced with dilution water in the gaseous state - steam. All the heat of condensation (1000 btu/lb) is recovered thermally in the acid as sensible heat.

This concept was first modeled on Monsanto's flow sheet simulator to determine dewpoints, water to SO_3 ratios, and flow scheme. For the initial trial, approximately 30% of the dilution water was injected as steam. This would raise the gas temperature exiting the economizer from 370°F. to about 500°F. This significant temperature rise elevates the bulk gas temperature to well above the dewpoint. The significantly higher SO_3 to water vapor ratio insures that in the event of condensation, the liquid would form oleum.

A full scale field test was conducted on a nominal 2500 STPD acid plant. Of critical importance was where and how to inject the steam, especially considering that this was to be done in an existing carbon steel duct. Extensive measures were taken to be sure that the steam was dry at the injection point, to avoid damage to the injector and duct. Material selection for the injector was also important because in localized areas, the injector could see anything from steam to possibly hot, weak acid.

Early in 1993, full scale operation began. System performance was almost identical to the predictions. Steam production was up and corrosion rates in the HRS system were unchanged or down. Because less water was injected into the diluter, energy release and vibration were reduced. As an added benefit, there was an improvement in the stick test appearance and a reduction in the mist generation, measured by mist eliminator drainage. 304 ss corrosion coupons in the gas stream averaged a corrosion rate of only 0.4 mpy (0.01 mm/yr). Unfortunately, the existing carbon steel ductwork contained several cold spots. This dropped the localized gas temperature below its dewpoint which caused gas duct leaks.

In the future, as shown in Figure 3, a 304 SS mixing chamber with 310 SS mixing tabs will be used with a shock resistant ceramic steam injection nozzle. Steam is injected cocurrent to the gas flow. A sufficient duct length is provided with an elbow to obtain complete mixing. Computer simulations using computational fluid dynamics were used to confirm that gentle mixing will take place thus allowing the majority of the steam to mix in the center of the duct. This steam injection design will be installed in Namhae's new 1320 STPD standard HRS plant. Startup is scheduled for September of this year.

A secondary benefit of the demonstration in 1993 is verification of one concept of the Monarch process. Steam injection along with a condensing economizer, are the staple ingredients of Monarch. For this reason, plans were put in place to demonstrate the next unit operation, the condensing economizer. The long term test will confirm vapor -liquid-equilibrium, reaction, thermodynamic, heat transfer, and corrosion data on this key piece of equipment.

CONDENSING ECONOMIZER

The function of the condensing economizer is to shift hydration heat (SO_3 (g) + H_2O (g) $\rightarrow$ H_2SO_4 (g/l)) from the medium pressure HRS system to the high pressure steam system. The gas phase reaction is approximately 60%

complete at the economizer exit. Since the tube wall temperatures are below the dewpoint, some condensation heat is also recovered. The economizer is constructed of the same corrosion resistant alloy materials that have been proven in HRS Service.

The mole ratio of water to sulfur trioxide is kept below 1.05, which corresponds approximately to the concentration of the sulfuric acid azeotrope. This insures that the condensation product will have a concentration greater than the sulfuric acid azeotrope which is approximately 99%. The condensate concentration is not very sensitive to water vapor content. If there are excursions in the steam addition rate, the condensate film is maintained at a relatively high acid strength, where the corrosion rate is low. In fact, 140% of the stoichiometric water can be added without decreasing the condensate concentration below 98%. The excess water vapor passes to the HRT, where the large holdup of acid prevents the concentration from dropping rapidly. As the decreasing concentration is detected, the steam valve is throttled.

In cooperation with Sud Chemie in Germany, a full-scale demonstration economizer was put into service in their wet gas plant in August 1996. This plant is 130 STPD sulfur burning plant which burns a saturated waste air stream and H_2S gas, and has a high temperature interpass absorber downstream of the condensing economizer.

The economizer itself as seen in Figures 4 and 5 is a test unit incorporating special design features to enable analysis of thermal performance and corrosion. Special fin-to-tube welding procedures were developed to minimize crevices between the fin and tube. All applicable European codes were met. There are over 40 thermocouples located inside the unit to measure the temperature of the water and the gas at various passes. Individual water temperatures are measured for each tube row. The tubewall temperatures are measured throughout the unit. Over 40 corrosion coupons are installed in the gas and acid condensate below the tube bundle and within it at 3 locations. The flow of acid condensate and its conductivity are measured on-line. All of this data except for corrosion rates are sent to a nearby computer system and recorded.

The most important element of the operation of the condensing economizer was confirmation of the corrosion rates of the alloy materials. This would determine the lifetime expectancy and the final cost of the unit. Considerable data has been collected in the past on HRS corrosion coupon rates but in the 400 - 440 F temperature range. The condensing economizer operates in the 400 - 600 F range. As shown in Table 3 below, the corrosion rates of the coupons taken from the condensing economizer are extremely low ranging from no corrosion to a maximum of 1 mpy (0.025 mm/y). These very low corrosion rates insure the continued operating longevity of the condensing economizer.

Table 3- Corrosion Rates

LOCATION	RATE	# OF COUPONS
Bundle	Not Detectable	24
Bundle	0.14 - 0.35 mpy 0.0004 - 0.009 mm/y	8
Bottom	0.65 - 1.0 mpy 0.017 - 0.025 mm/y	12

The second important element of the condensing economizer was the verification of the heat transfer coefficient as it directly impacts the final cost of the unit. Measuring thermal performance is more difficult because it depends on consistent data at various operating points. Operating conditions must be compared to original design conditions. The data collected to date indicates that the overall heat transfer is within 10% of predicted which is typical for an economizer.

OTHER APPLICATIONS

The application of the condensing economizer was developed for the new Monarch process, but there are applications for existing plants already retrofitted with HRS. Steam injection in conjunction with the condensing economizer can be installed to shift the production of medium pressure steam to high pressure. Even though existing plants are the typical dry gas process, many of the benefits of Monarch can be attained by creating the wet gas directly before the HRS tower by using the steam injection vessel. The amount of steam injected is increased to make up for the water removed in the existing dry tower. Shown in Table 4 is a comparison for a 2600 STPD plant with the base case as HRS. Steam injection alone increases in medium pressure steam production by 12% which results in a 375 kW increase in power. With steam injection followed by the condensing economizer there is a 5% reduction in medium pressure steam but an increase of 13% of high pressure steam. The net result is an increase in power production of 1645 kW. Additional benefits include maximizing the acid concentration to stage 1 of the HRT and lowering the acid temperature to the HRS boiler.

TABLE 4- HRS Retrofit

	HRS	STEAM INJECTION	CONDENSING ECONOMIZER
STPD	2600	2600	2600
HP Steam, klbs/hr	244	244	277
HRS Steam, klbs/hr	108	121	103
30# Steam, klbs/hr	0	12	26
STG 1 Flow, gpm	5100	5200	5200
STG 1 Conc, %	98.64	99.0	99.0-99.3
Acid Temp, Deg F	433	440	429
Power Increase, kW	BASE	375	1645

This application is particularly advantageous in existing HRS plants where the turbine generator is at its maximum admission of medium pressure steam, but has additional high pressure steam capacity. Because the addition of steam injection with a condensing economizer reduces the heat load on the HRS, the plant capacity may be increased. On retrofit plants where HRS is being added, steam injection and condensing economizer reduces the cost of the HRS.

Each sulfuric acid plant must be evaluated based on its existing equipment and value of power to determine the best selection of energy recovery options. With the successful demonstration at Sud Chemie, the condensing economizer becomes a key piece of equipment for the designer. A new era will begin in which the value of the power produced from a sulfuric acid plant becomes as important as the sulfuric acid produced.

References

1) McAlister, D. R., Grendel, R. W. , Schneider, D. R., Shafer, J. R., and Tucker, J. S., "A Sulfuric Acid Plant for the 1990's", Preprints of Sulphur 1990 International Conference, Cancun Mexico, April 1-4, 1990, pg 267.

2) McAlister, D.R., and Schneider, D.R. (Monsanto Company) (1992): "Method for Recovering High Grade Process Energy from a Contact Sulfuric Acid Plant". US Patent No. 5,130,112.

Table 2

HEAT RECOVERY SYSTEM INSTALLATIONS

	CUSTOMER NAME	STPD CAPACITY	YEAR
19	Anaconda Nickel	4850	1998 Start-up
18	O.C.P./Morocco	2500	1998 Start-up
17	Namhae/Korea	1320	Sept. 1997 Start-up
16	Kennecott Copper/Utah	2000	April, 1995
15	Kennecott Copper/Utah	2000	April, 1995
14	Cargill (Seminole)/Florida	2200	Oct. 1992
13	Cargill (Seminole)/Florida	2200	Sept. 1992
12	Cargill (Seminole)/Florida	2200	Aug. 1992
11	PCS (Texasgulf)/North Carolina	3250	Oct. 1992
10	PCS (Texasgulf)/North Carolina	3600	Oct. 1992
9	IMC-Agrico (Agrico)/Florida	2500	Sept. 1992
8	IMC-Agrico (Agrico)/Florida	2500	July 1992
7	IMC-Agrico (IMC)/Florida	2700	Aug. 1991
6	Tessenderlo/Belgium	1100	Dec. 1989
5	Yong Nam/Korea	660	June 1990
4	Yong Nam/Korea	660	May 1990
3	Namhae/Korea	1500	Dec. 1987
2	Namhae/Korea	1500	Nov. 1987
1	Falconbridge/Norway	260	Aug. 1987

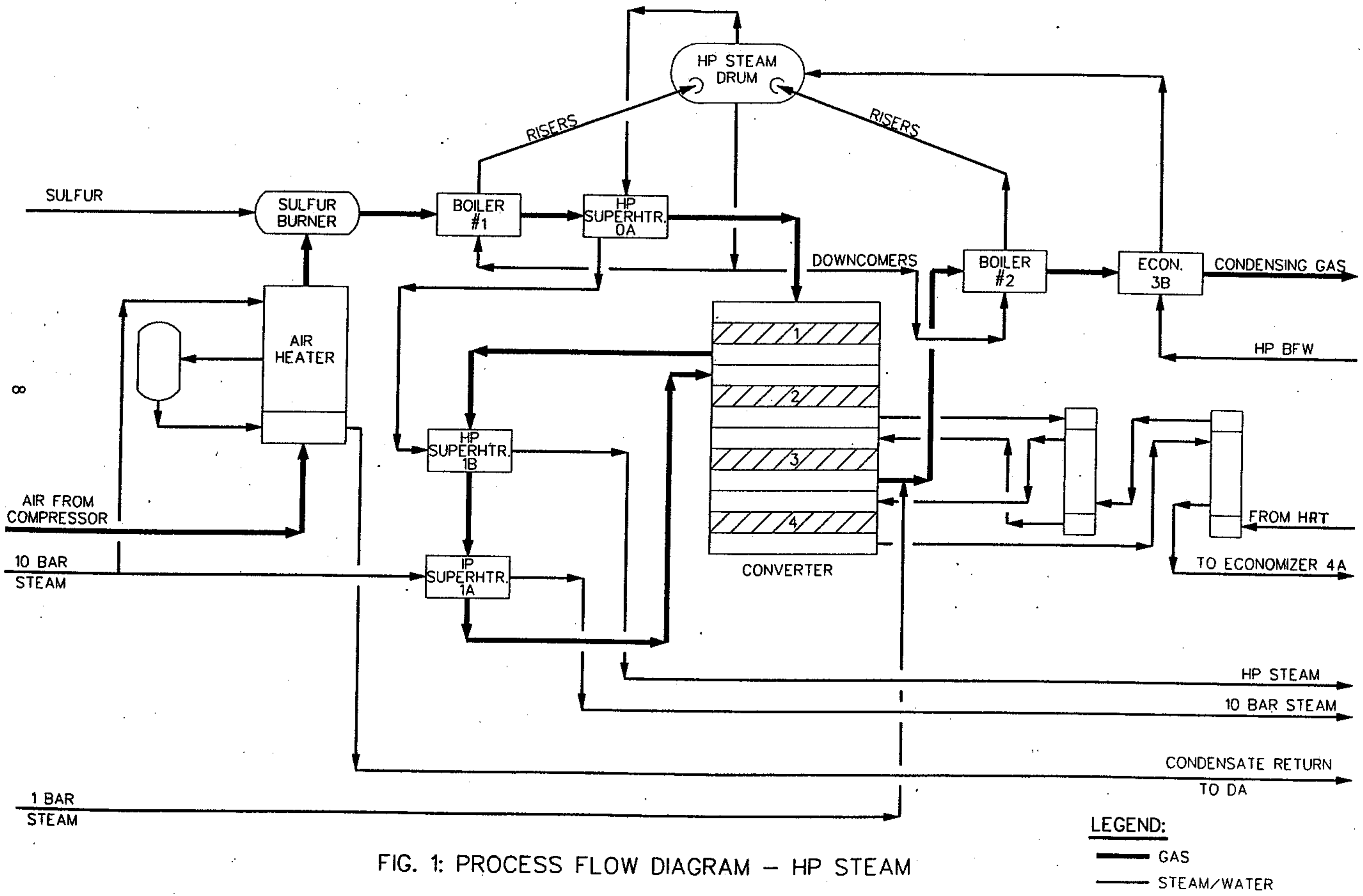

FIG. 1: PROCESS FLOW DIAGRAM – HP STEAM

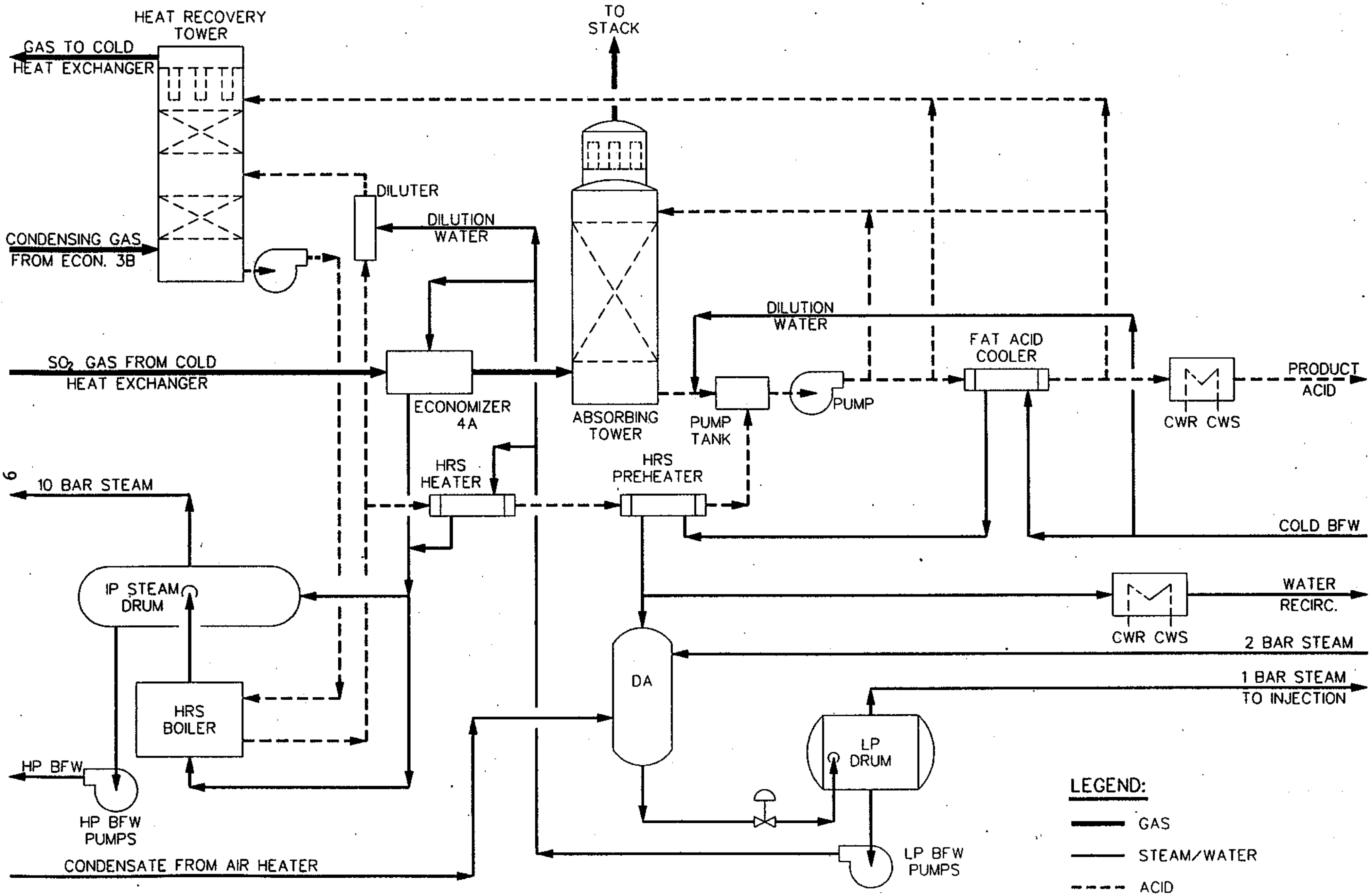

FIG. 2: PROCESS FLOW DIAGRAM – LP AND IP STEAM

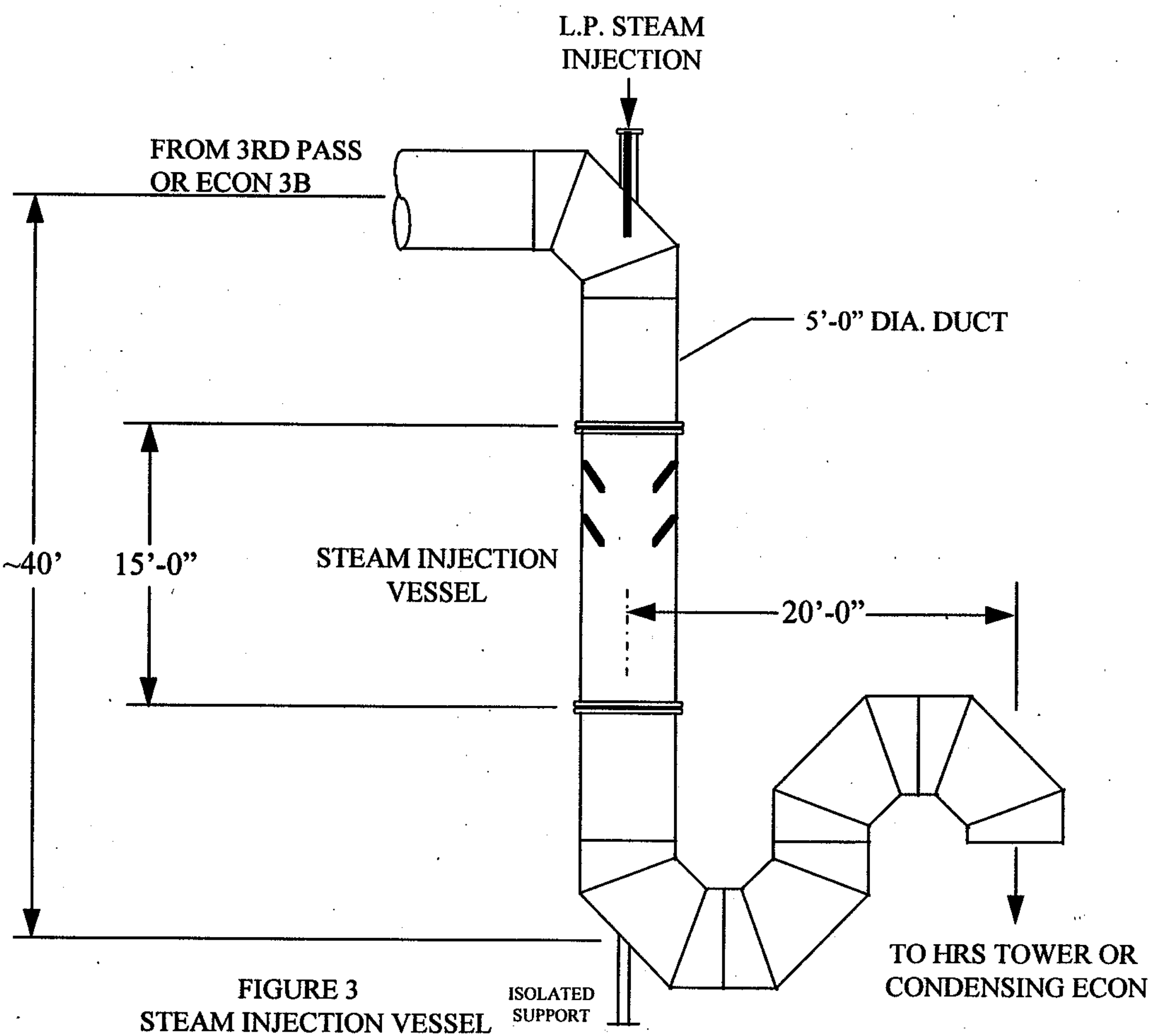

FIGURE 3
STEAM INJECTION VESSEL

Figure 4

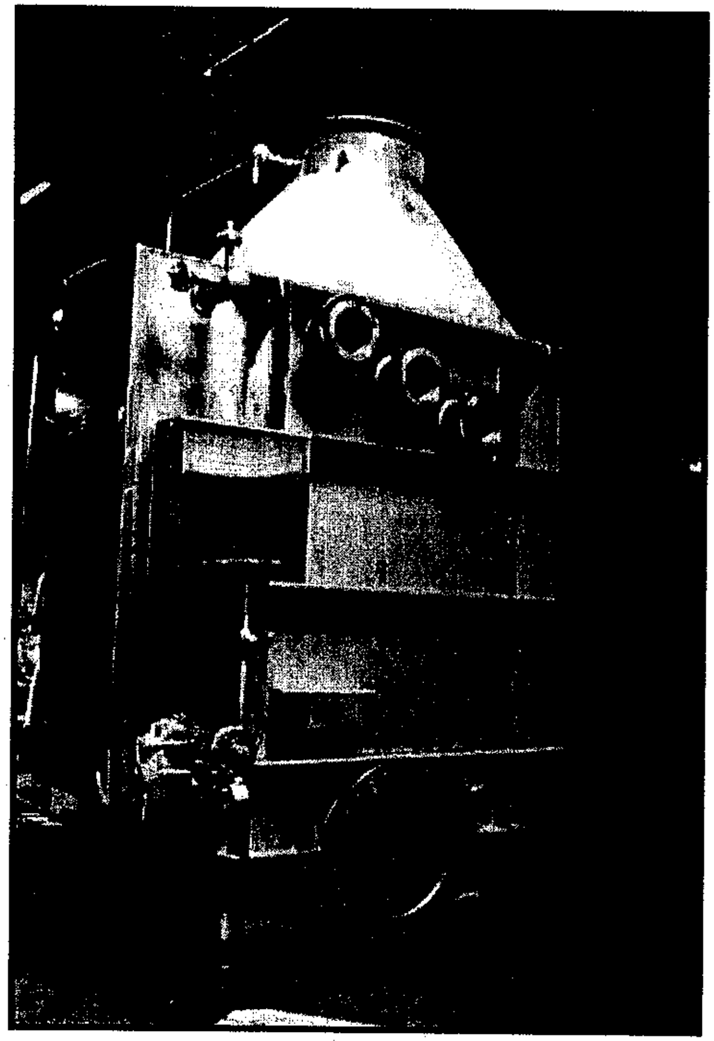

Figure 5