

ENERGY RECOVERY FROM SULPHURIC ACID PLANTS

BY

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Paper presented at AICHE Joint Florida Section Meeting
Clewwater Beach, Florida, May 19-20, 1978.

I INTRODUCTION

With the uncertainty of oil prices and the rapidly escalating cost of energy, it has become more and more important to search for ways to recover waste heat from chemical process plants, and to ensure that the recovered energy is put to optimal use.

The manufacture of sulphuric acid via the sulphur burning process is a highly exothermic process. Whereas it is standard practice to recover "high-grade" heat as steam from the combustion of sulphur and catalyst oxidation of SO_2 to SO_3 , a significant amount of "low-grade" heat in the acid circulating system is usually rejected to the cooling water.

With the advent of new technology and the rising price of energy it is now technically and economically feasible to recover this "low-grade" heat to provide hot process water or electrical energy using a fluoro-carbon power cycle.

This paper gives an account of how such energy recovery is being achieved in several operating plants and also describes other energy recovery projects under study.

II ENERGY DISTRIBUTION IN A SULPHURIC ACID PLANT

A typical sulphur burning double catalysis/double absorption sulphuric acid plant is illustrated in Figure 1. Ambient air is dried by countercurrent contact with sulphuric acid and compressed by a blower before being fed to the sulphur furnace, where it combines with molten sulphur yielding a gas containing 8 - 12% SO_2 at a temperature from 1500 - 2000 °F.

The gas is then cooled in a waste-heat boiler to the 750 - 850°F range and flows to a multi-bed converter where the catalytic conversion of SO_2 to SO_3 takes place. The reaction heat is recovered by raising steam and reheating the return gas to the converter after SO_3 absorption in the intermediate absorber tower. The absorption of the SO_3 is carried out in the intermediate and final absorber towers by countercurrent contact with 98% acid. Overall conversion of better than 99.7% is achieved. The residual SO_2 in the stack gases is below 350 ppm.

The heat of dilution in the dry acid system, the heat of absorption in the absorber acid system, and the sensible heat of gas transferred during its contact with the acid are rejected to the cooling water in the acid coolers. The acid strength in the drying and absorption system is maintained by the cross transfer of acid between these systems. Product of either 93% or 98% acid can be taken from the drying or absorption system, respectively.

The heat released during the different steps of manufacturing of sulphuric acid is listed in Table 1. For a 1000 STPD plant 204.4 MM BTU/HR. are released during the reactions leading to the formation of the acid product. Adding to this, the heat of compression of the combustion air and subtracting the heat losses (approximately 3% of the total heat released) leaves a net surplus of 204 MMBTU/HR. which must be removed from the process.

Table 2 shows how this energy leaves the plant. 55 to 60% of the total heat is recovered in the form of high pressure

steam and is available to perform useful work on the site. The "high-grade" heat used to raise steam comes from the sulphur combustion and SO_2 oxidation steps. The remaining 40 - 45% of the heat traditionally leaves the plant as waste heat. About 94% of this waste heat is removed in the acid cooling systems and the remaining small amount leaves via the stack gas and the product acid.

The actual distribution of the heat going to the steam production and that removed in the circulating acid coolers depends on several factors (1, 2) such as:

- (1) the humidity of air entering the drying tower
- (2) whether the blower is located before or after the drying tower
- (3) the temperature of the gas to dry and absorber towers,
- (4) the product acid strength
- (5) the type of acid system used, and
- (6) whether the plant uses a single or double catalysis/absorption process.

Table 3 shows typical heat loads for the different acid cooling duties on a 1000 STPD plant. The exact distribution may vary depending on the above factors as well as the acid cross flow arrangement.

III LOW-GRADE ENERGY RECOVERY

From the foregoing discussion it is clear that significant amount (about 40%) of the total surplus energy is generally rejected as waste heat in the acid cooling system. Up until

recently the heating value of this "low-grade" heat has been ignored, primarily because of relatively low value of energy and the lack of adequate acid cooling equipment made its recovery impractical and uneconomical.

Taking the current cost of fuel oil at \$0.37/USG, and the furnace efficiency at 80%, the cost of equivalent heat is \$3.25/MM BTU. Thus, if all the waste heat from the acid were recovered and put to use it would represent a saving of about \$2.24 million/year. However, in some cases the heat from the dry and product acid may not be as easily recoverable because of its lower temperature level. Even for this situation, with recovery from the absorber acid only, the saving is quite substantial (about \$1.90 million/yr.). Hence with current energy prices there is a very definite incentive to recover the circulating acid heat.

To recover this energy, the acid cooling equipment employed must be capable of complete containment of the cooling fluid, be able to operate at high temperatures, be able to operate at high pressure while at the same time, meeting the reliability standards required for continuous production. For these and other reasons we believe the CIL anodically protected shell and tube acid coolers (3) are best suited to this application.

At Chemetics we have pursued two basic approaches to "low-grade" energy recovery from the sulphuric acid plants. In the first approach water is heated to the 175-200°F range and is made available for various end uses. The second approach generates electrical power using a fluoro-carbon power cycle.

IV HOT WATER GENERATION

Figure 2 illustrates the first energy recovery system using Chemetics acid coolers which was commissioned in 1974 on National Lead Industries' 2 x 900 STPD acid plants at Sayreville, New Jersey. Here the acid heat from the product and the dry acid coolers is utilized to directly preheat boiler feed water from 60°F to 118°F, recovering 9.3 MM BTU/HR. This represents a saving of \$195,000/yr (at 1975 energy prices) with a payback period for the coolers of 9.0 months. This early installation demonstrated that the Chemetics coolers could reliably be used for direct heating of boiler feed water.

For boiler feed water applications the sensible heat required for preheating boiler feed water is not sufficient to remove all the heat from the acid cooling duties. Taking an average steam production of 1.1 ton/ton acid produced, the maximum heat that can be utilized for this purpose on a 1000 STPD is about 12.8 MM BTU/HR. heating boiler feed water from say 60 to 200°F. This would free up about 13,500 lb/hr of L.P. steam generally used in deaerator, for other use on the site.

Figure 3 shows another application of direct process water heating. Here about 49.7 MM BTU/HR from the absorber acid of a 600 MTPD sulphuric acid plant of Boliden at Skelleftehamn in Sweden, is recovered in a demineralized water loop which is heated up to 170°F. The hot water is subsequently flashed to generate 22 ton/hr of steam under vacuum. This steam is then used in a downstream SO₂ stripping process. A trim cooler operating on seawater is placed in the loop to remove the total

heat when the steam generation is not required. This installation has been in trouble-free operation since December 1976. At a current value for heat of \$3.25/MM BTU the energy savings represents \$1,361,000/YR with a payback period for the Chemetics coolers of 6.2 months.

Another energy recovery installation for Boliden at Helsingborg in Sweden is illustrated in Figure 4. In this installation about 37.2 MM BTU/HR of intermediate absorber heat from 750 MTPD acid plant is recovered in the demineralised water loop in which water is heated up to 197°F. The demineralised water in turn heats water which is circulated to heat the houses of the town of Helsingborg.

A seawater trim cooler is included in the demineralised water loop to handle the seasonal variation of the town heating demand. The project was successfully started up in April 1978. Provisions have also been made to recover a further 16.6 MM BTU/HR from the final absorber acid.

Chemetics has installed a number of such energy conservation systems, and is currently carrying out engineering studies on several other interesting applications. These include boiler feedwater preheating, domestic water heating, wash water heating for a Titanium Dioxide process, heating water to concentrate phosphoric acid, and preheating seawater for desalination process. In all cases the economics favour operating the acid plant at the highest acid temperature possible. Such installations offer an extremely attractive payback on investment and will no doubt become even more attractive in the future with escalating energy costs plus any added

incentive to be provided by the Government to conserve energy.

In the existing plants where older cooling equipment needs to be replaced, the payback period is even more attractive. In these cases the return on investment can be based upon the incremental cost of the extra cooling surface required to follow the energy recovery route as opposed to rejecting the heat into cooling water.

These energy recovery applications are typified by high tube wall temperatures and low water side velocities and special care has to be taken in the design and choice of material for these coolers. The tubing material is normally 316L stainless steel for most fresh water cooling applications. However, in cases of heat recovery applications the material is upgraded to provide necessary resistance to stress corrosion cracking at the elevated temperatures. It should be noted that the tube material used in the exchanger is dictated by water side considerations, and not by the acid side.

V ELECTRICAL POWER GENERATION

The second approach to recovering energy is to convert the low grade heat into electrical power, using a flurocarbon Rankine cycle.

This system is similar in concept to the sulfuric acid plant waste heat steam system, the difference being that the flurocarbon is contained in a closed loop, where it is repeatedly compressed, heated, vaporized, expanded, then condensed. Fig. 5

illustrates the concept on a temperature entropy diagram for the reversible expansion of R 114. Liquid is compressed from a to b via a circulating pump. From b to c heat is added to the compressed liquid to bring it to the saturation temperature by a preheater. From c to d heat is added to the saturated liquid in the evaporator to vaporize the fluoro-carbon. The vapor then passes through an expansion turbine where isentropic expansion (d to e) produces mechanical work which is transformed to electrical power via a generator. The remaining heat in the expanded vapor is rejected to the water cooling system in the condenser, represented by e to a.

The main advantage of this system is that the recompression of the fluoro-carbon is done in the liquid phase thus requiring little work input.

The equipment required for this system is schematically represented in Fig. 6.

The pump compresses the cold liquid fluoro-carbon to the required pressure, then delivers it to the preheater where it is heated to saturation temperature before passing into the vapor drum. The vapor drum is connected to a natural circulation evaporator, with the fluoro-carbon flowing through the tubes, and acid through the shell. The vaporized fluoro-carbon leaves the evaporator vapor drum and enters an expander, which drives an induction generator to produce electric power from the work done by the vapor, in expanding from high pressure to low pressure. The expanded vapor is then condensed in a water cooled shell and tube exchanger before returning to the hold tank.

The power generated from this type of system is dependent on two main factors:

- (1) The evaporation temperature of the fluoro-carbon, which is directly related to the temperature of the acid leaving the preheater (i.e. to the tower or to the pump tank) and to the heat load in the acid system.
- (2) The condensation temperature of the fluoro-carbon, which is a function of cooling water temperature and flow.

The optimum system maximizes the difference between these temperatures. Figure 7 shows the effect of cooling water temperature on power recovery. In this case the evaporation temperature is fixed at 205°F. The net power loss in the generated horsepower is 23% for a change in condensation temperature from 90°F to 120°F.

On retrofit systems it may not always be possible to optimise the recovery of this low grade heat with existing process layout or because of physical restrictions in terms of temperature and availability of the cooling water. Where process changes have to be made the heat loads should be redistributed in such a way that the energy is most easily recoverable, i.e. the absorber acid system.

On installations where the acid cooling system is being completely upgraded the acid coolers/fluoro-carbon heaters would be designed in such a way that a fluoro-carbon with a small volumetric flow would be used, this in turn would result in cost savings in the expander and associated piping. However, where a plant is already operating with Chemetics coolers it is possible to utilize some of these coolers, with modification, in the preheating duty, by selecting an appropriate fluoro-carbon that operates within the design

pressure rating of these units, however this would increase the physical size of the expander and associated piping because of increased gas volume. In all cases the boiler would require to be custom built due to the nature of its operation.

On a typical 1000 STPD sulfur burning sulfuric acid plant in the Florida area, with cooling water at an average temperature of 90°F it is possible to export 1000 kw/Hr. from the generator to the plant grid. At present electricity rates in Florida, the payback period for such an installation is approx. 3-5 years.

On new grass roots facilities there is greater scope to recover the low grade heat as electrical power. By careful distribution of acid heat loads, and by designing the acid circulation systems to make the higher level heat more readily available it is possible to recover an even higher proportion of this energy.

As in any new system, there is some degree of risk associated with realizing the claimed performance. However, we do feel that the equipment is well proven and of the highest integrity. It is only the interaction of the flurocarbon heat recovery system with sulfuric acid cooling which is untried.

In conclusion, with energy cost continuing to escalate, the low-grade waste heat from acid circulating that was traditionally rejected to cooling tower is rapidly becoming an affordable source of usable energy.

LITERATURE CITED

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TABLE 1

HEAT RELEASED DURING MANUFACTURE OF SULPHURIC ACID
(BASED ON 1000 STPD PRODUCTION RATE)

	MM BTU/HR.
(1) SULPHUR COMBUSTION: $S + O_2 \rightarrow SO_2$	108.9
(2) CATALYST CONVERSION TO SO_3 : $SO_2 + 1/2 O_2 \rightarrow SO_3 ::$	35.9
(3) ABSORPTION OF SO_3 : $SO_3 + H_2O \rightarrow H_2SO_4$	50.1
(4) DILUTION TO PRODUCT ACID $H_2SO_4 + nH_2O \rightarrow 93\% H_2SO_4$	4.8
(5) CONDENSATION OF WATER VAPOUR IN DRYING TOWER $H_2O (v) \rightarrow H_2O (l)$	4.7
TOTAL REACTION HEAT	204.4
+ HEAT OF COMPRESSION	5.6
- HEAT LOSSES	6.0
NET SURPLUS HEAT	204.0

TABLE 2

ENERGY LEAVING A SULPHURIC ACID PLANT

(BASED ON 1000 STPD PRODUCTION RATE)

	MM BTU/HR.	%
"HIGH-GRADE" HEAT FOR STEAM PRODUCTION	112.2 - 122.4	55 - 60
<u>"LOW-GRADE" HEAT</u>		
- DRY/ABSORBER SYSTEMS	76.5 - 86.7	37.5 - 42.5
- STACK GAS	4.1	2
- PRODUCT ACID	1.0	0.5

TABLE 3

DISTRIBUTION OF HEAT LOADS FOR ACID COOLERS

(BASED ON 1000 STPD PRODUCTION RATE)

DUTY		MM BTU/HR.
DRYING ACID	(93%)	10.2
INTER ABSORBER ACID	(98%)	49.0
FINAL ABSORBER ACID	(98%)	20.4
PRODUCT ACID	(93%)	2.0
TOTAL		81.6

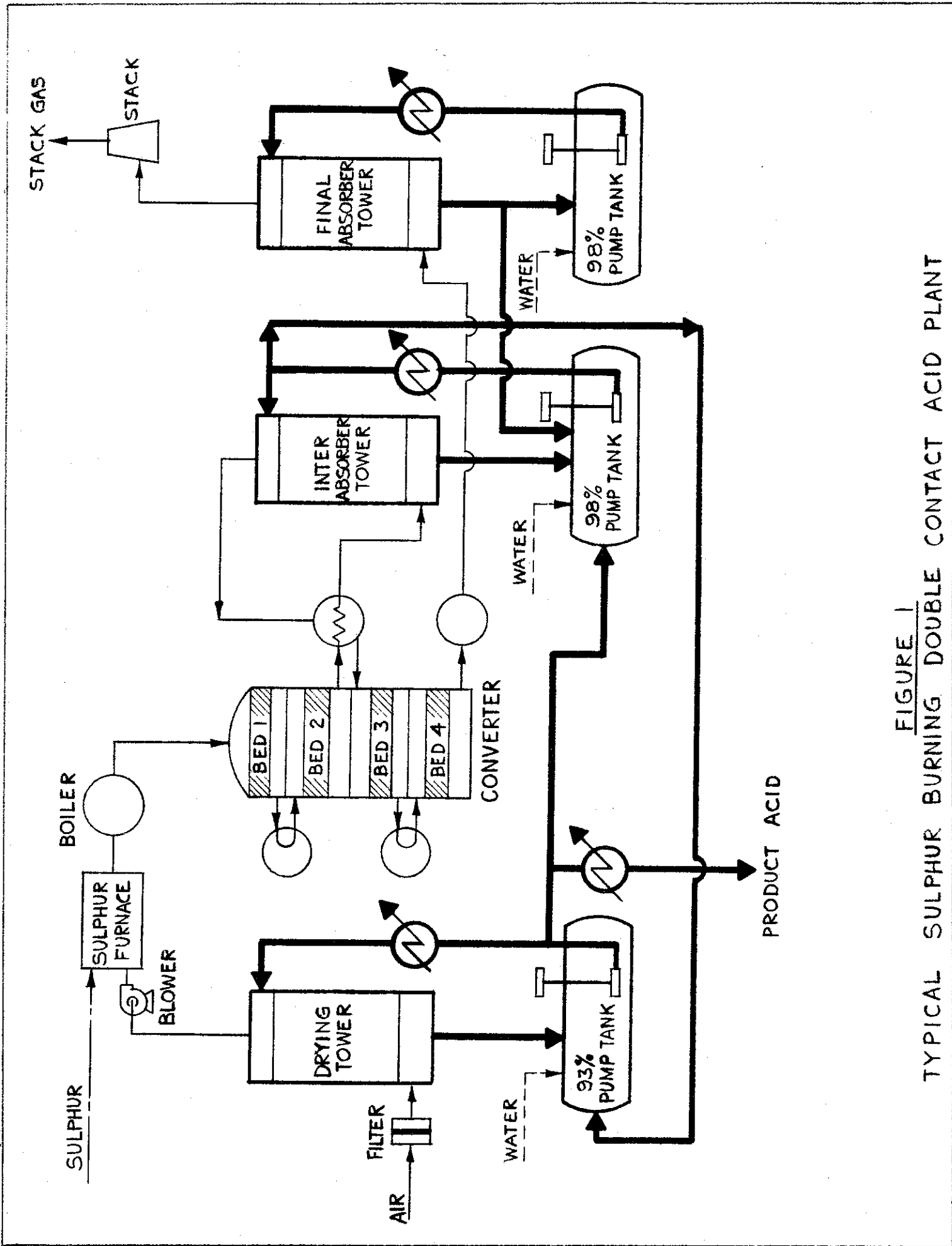


FIGURE 1
TYPICAL SULPHUR BURNING DOUBLE CONTACT ACID PLANT

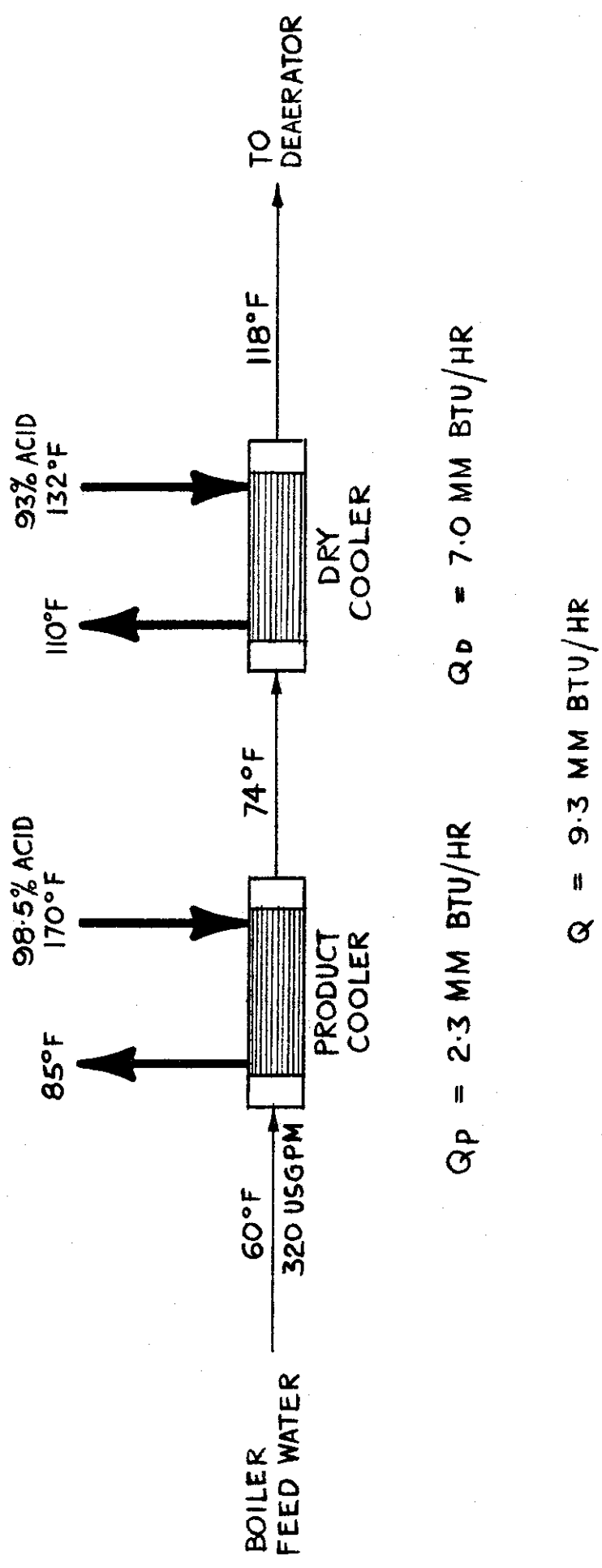
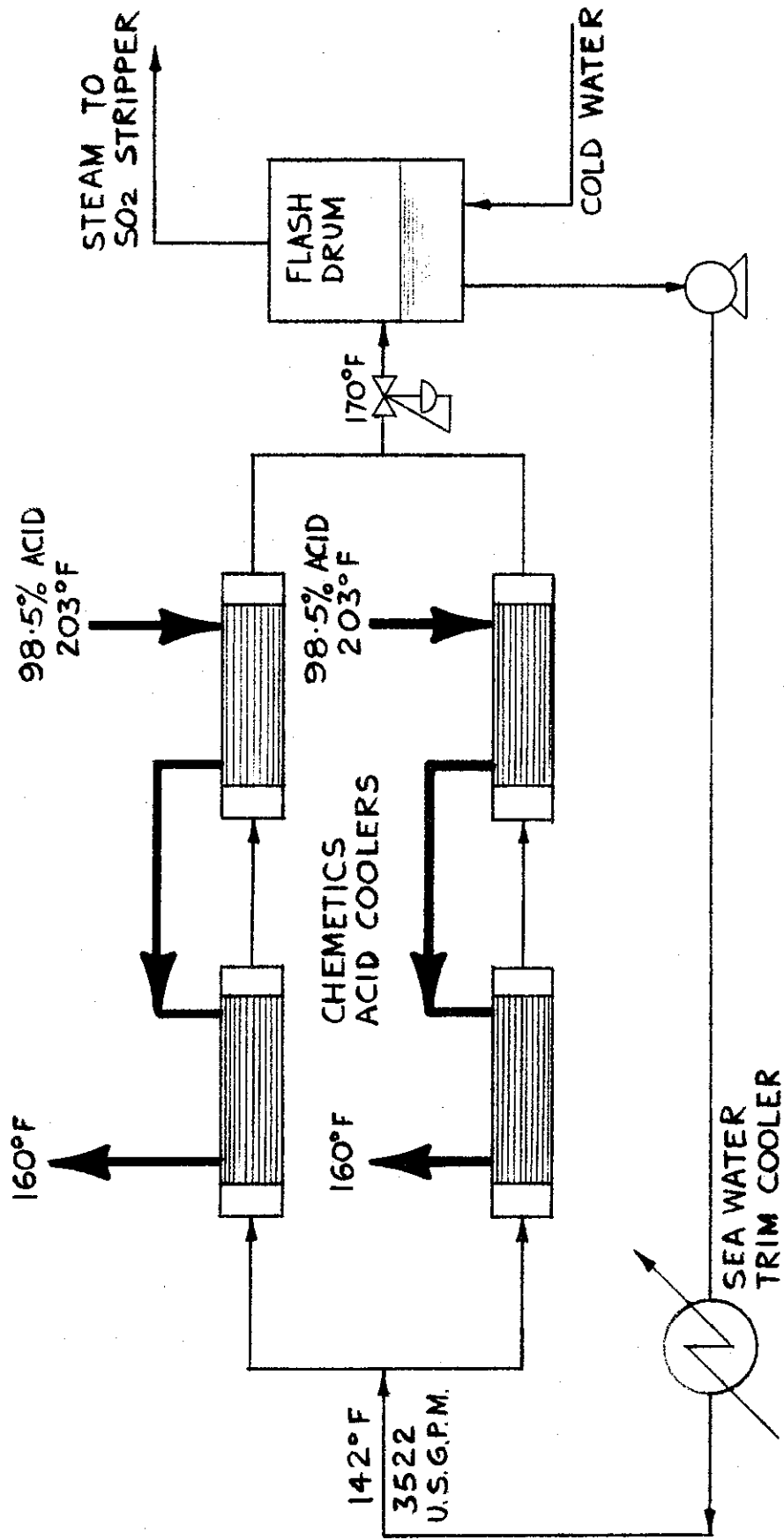


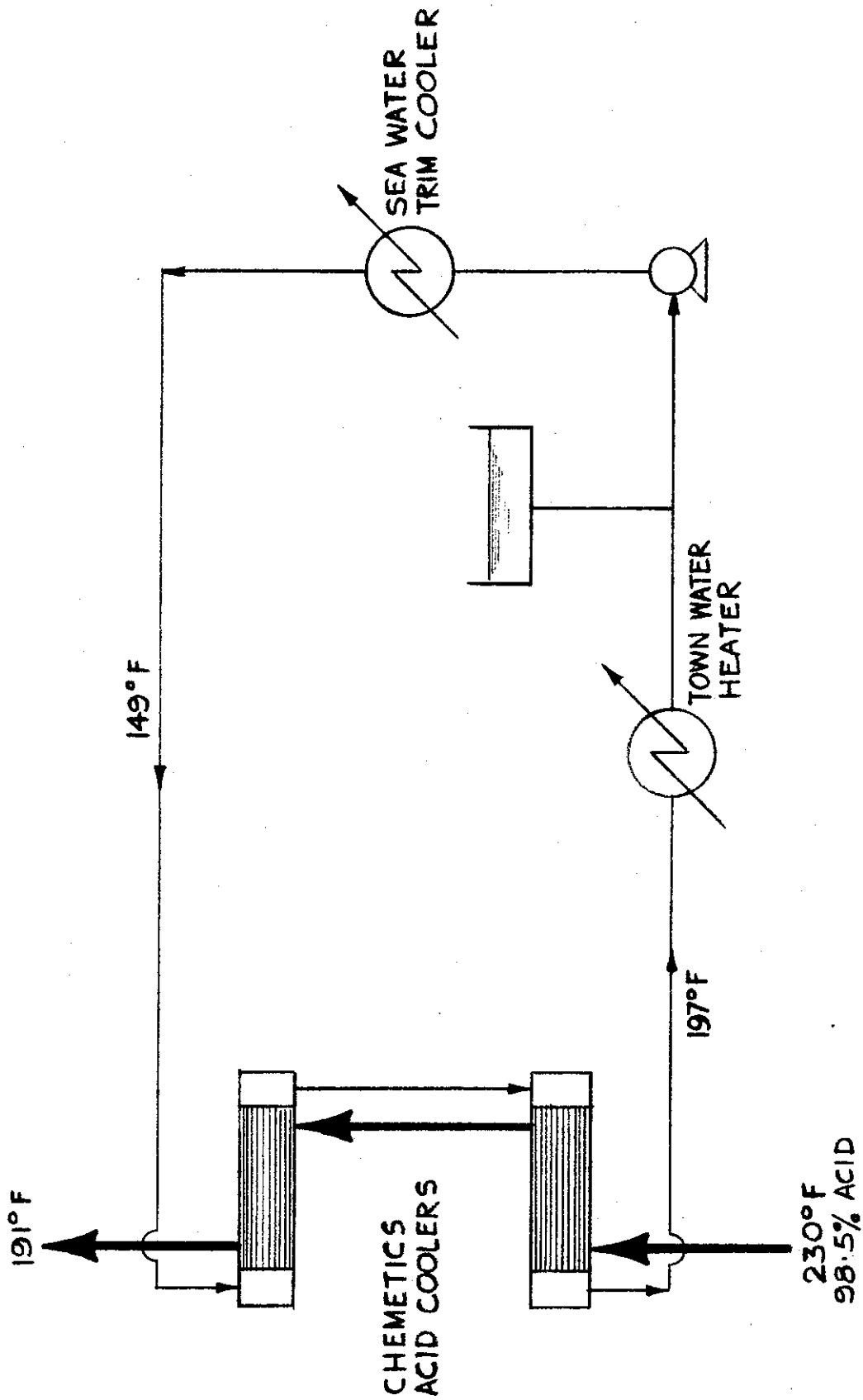
FIGURE 2
 BOILER FEED WATER PREHEATING SYSTEM FOR N. L. INDUSTRIES



$$Q = 49.7 \text{ MM BTU/HR}$$

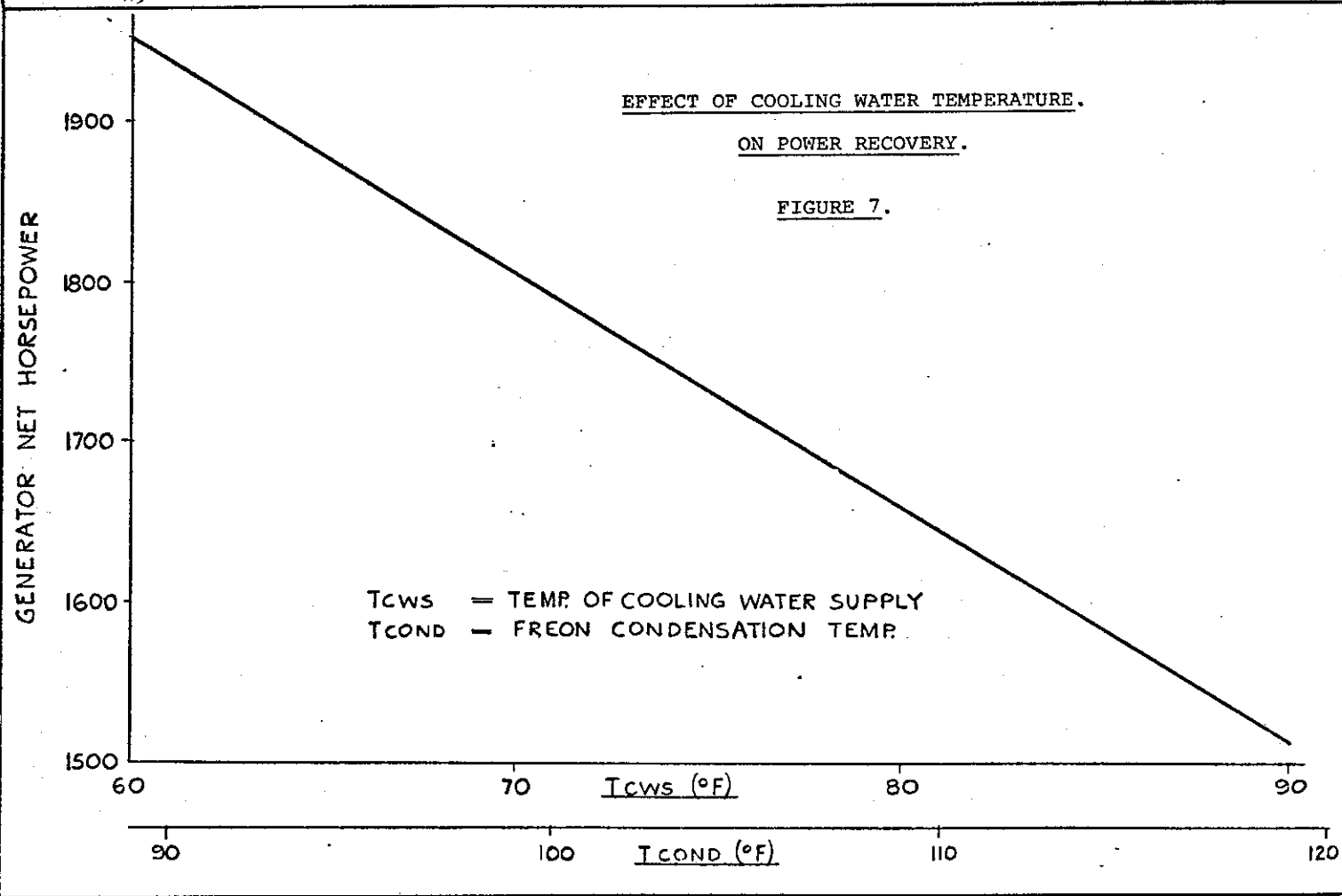
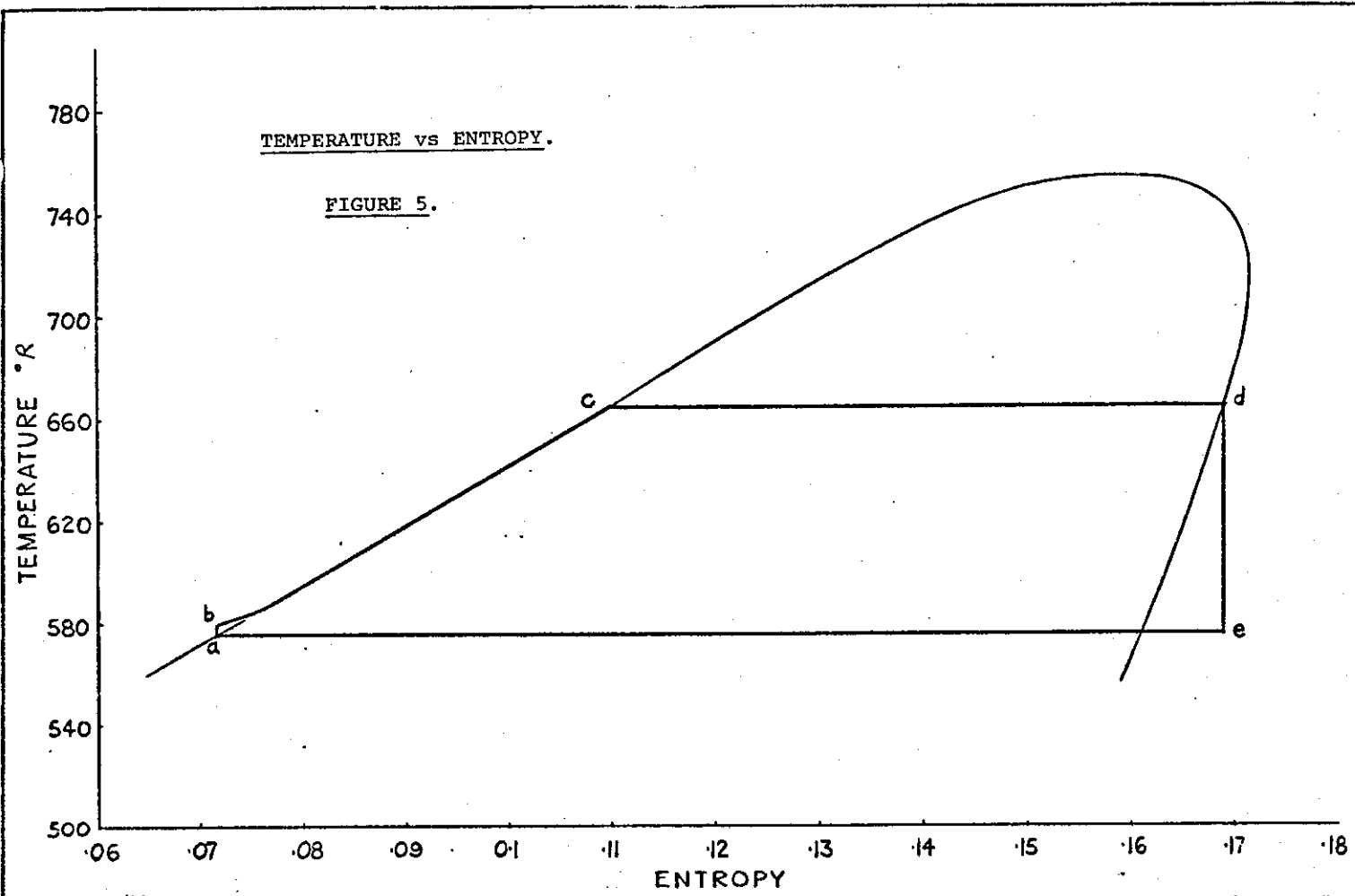
FIGURE 3

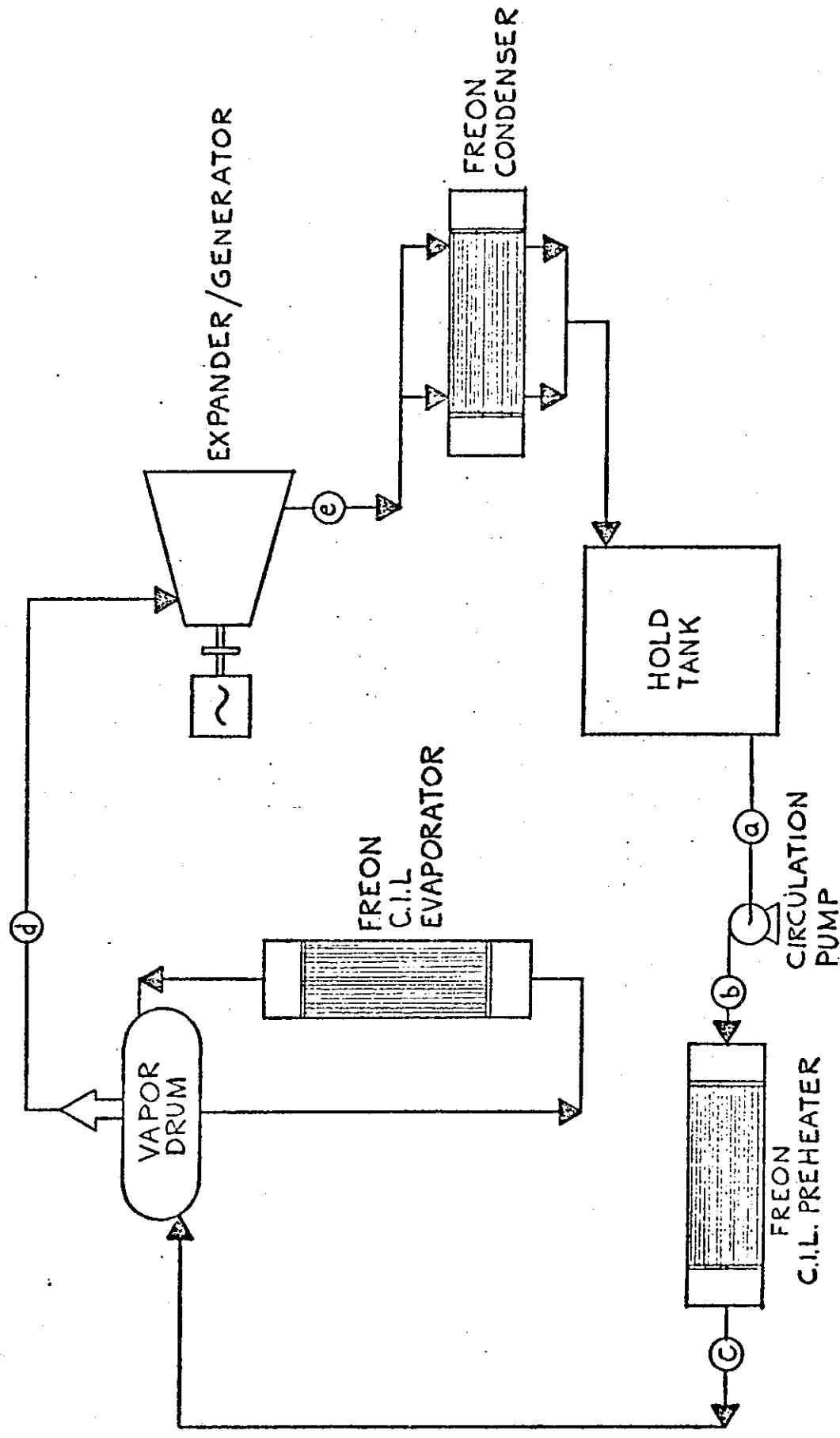
ACID HEAT RECOVERY SYSTEM FOR BOLIDEN, SKELLEFTEHAMN, SWEDEN.



Q = 37.2 MM BTU/HR

FIGURE 4
TOWN HEATING SYSTEM FOR BOLIDEN, HELSINGBORG, SWEDEN.





ENERGY RECOVERY SYSTEM.

FIGURE 6.