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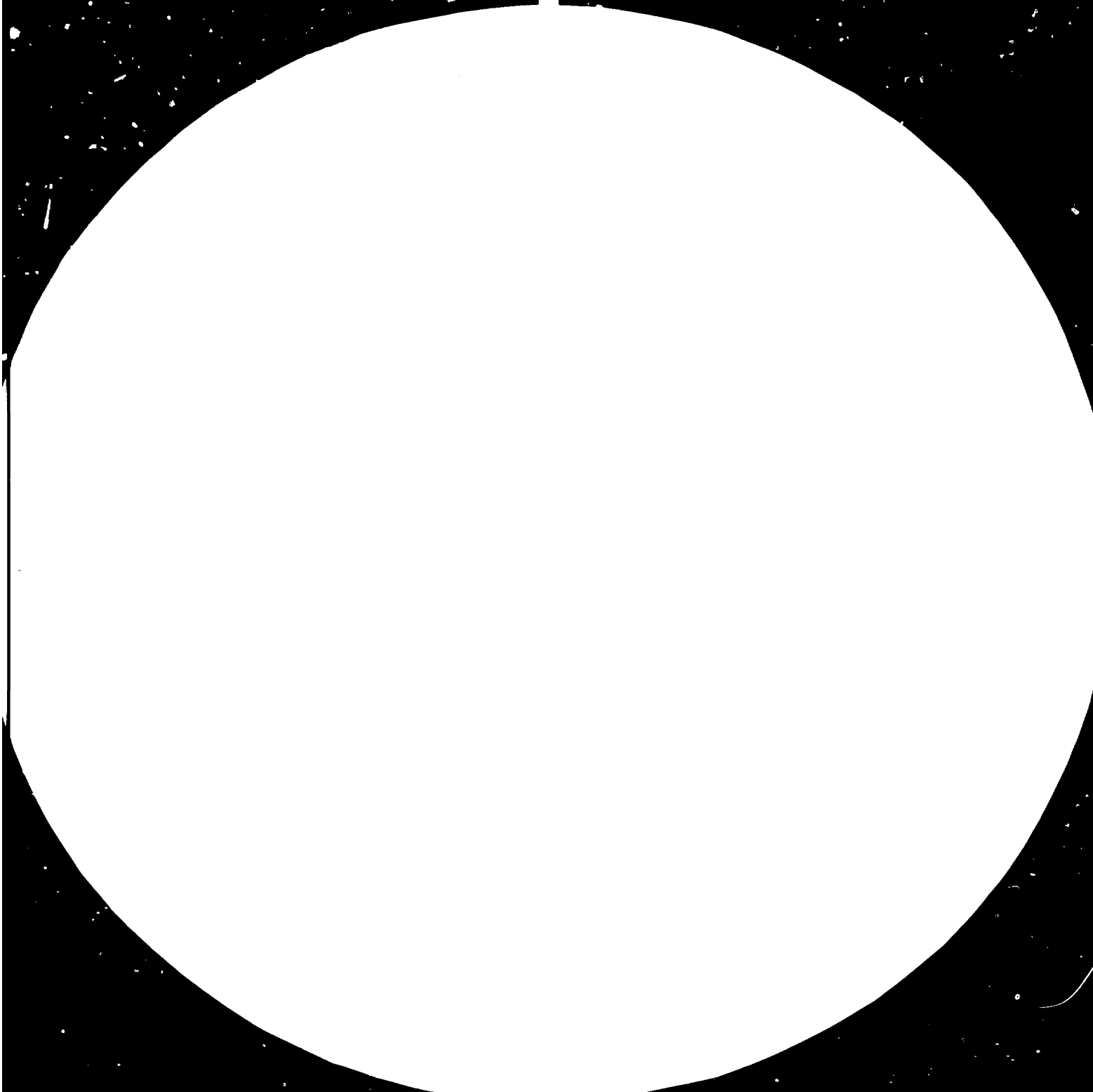
MICROCOPY RESOLUTION TEST CHART

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CRITERIA FOR SELECTING CO_2 REMOVAL PROCESSES*

by

Frank C. Brown**

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**   Process Group Head, Ammonia/Gas Processes, Humphreys and Glasgow Limited,
        22 Carlisle Place, London SW1P 1JA, United Kingdom

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SUMMARY

This paper examines the major processes available for the removal of carbon dioxide from synthesis gas streams produced by the catalytic steam reforming of natural gas. The development of these processes is followed and the up to date designs are described. It is shown that the improved versions of the established processes have similar overall performance to the newer physical solvent processes especially where 100% CO_2 recovery is required. However the simpler and in most cases cheaper physical solvent plants are likely to increase their number especially in circumstances where 100% CO_2 recovery is not required.

INTRODUCTION

This paper describes the development of the major processes available for the removal of CO_2 from gas streams produced by the catalytic steam reforming of natural gas. Starting with ethanolamines it also examines the hot carbonate processes before moving on to physical solvents. It finishes with a description of the latest variants of all these processes and following a statement on performance offers suggestions as to how designers should select the most appropriate for their specific applications.

HISTORICAL

Early ammonia units were based on coal derived hydrogen. The large quantity of carbon dioxide needing removal was washed out with water. In the USA operators saw the possibility of using the large quantity of cheap natural gas as an ammonia feedstock. Following work done by BASF and Standard Oil the tubular steam reformer was introduced in the mid thirties working at atmospheric pressure. Ethanolamines were found to be particularly suitable for CO_2 removal from the low pressure gas streams and before long the MEA process was completely dominant in the USA.

By the end of the fifties reforming plants were working at higher pressures and various inventors were working on processes requiring lower energy. In the USA Benson & Field at the U.S Bureau of Mines and in Europe Giammarco of Vetrocoke were developing the hot potassium carbonate process. Before long both were using activators to improve the dissolving rate of CO_2. Benfield used the higher boiling point diethanolamine while Vetrocoke used arsenic oxide.

In the sixties these two hot carbonate processes came to be completely dominant. In the USA MEA was still widely applied but Benfield and several imitators began to take orders.

In the mid seventies the process licensors began to respond to the need for better performance and most produced improved versions of their existing processes. By the end of the decade plants were operating using half the energy of those in operation at the beginning. At the same time several physical solvent processes were developed and began to take orders. Development continues and all the major processes have versions suitable for todays high energy costs and need for simple, reliable plant. We shall now examine these processes in more detail.

ETHANOLAMINES

Monoethanolamine in a weak aequeous solution was the first of this group of compounds to be used. The absorbtion, desorbtion and vapour pressure data is such that the absorbtion has to be carried out at about 40°C while the regeneration must be carried out at the boil which is over 100°C. These solutions are extremely corrosive if operated above 20% without inhibitors. Because of the low solution strength and the wide temperature difference between absorbtion and regeneration these plants have a very large reboil requirement of over 150 MJ/KG mol of CO_2, even when designed according to the arrangement show by fig. 1. Because of the high corrosion rates all exchangers operating over 70°C have to be made of stainless steel. The columns themselves are relatively short, about 20 trays, but the large expensive heat exchangers make the whole unit relatively costly.

In the early sixties a few designers produced units using two ethanolamines TEA and MEA. TEA behaves almost like a physical solvent having a relatively straight absorbtion isotherm. By just using flash and a slight degree of stripping, these early designs used TEA to remove about 60% of the CO_2 while the remaining 40% was removed by a MEA system. The effect was to reduce the overall energy requirements by about half compared with straight MEA.

However due to the lack of suitable corrosion inhibitors, the weak
solutions were still used and a great deal of stainless steel led
to a very expensive and complicated plant. Very few were built.
The big advance was the development by Union Carbide of a
synergistic corrosion inhibitor known as UCAR Amine Guard which
enabled much stronger solutions to be used. Many earlier plants
were revamped with considerable energy savings.

The next developments are covered in later sections.

HOT CARBONATE PROCESSES

In this section we shall describe the hot potassium carbonate
processes of Benfield and Vetrocoke which completely supplanted
the earlier cold processes. By operating hot with activator there
was a very small temperature difference between the absorber and
the regenerator. Combined with the high solution strength and
high carrying capacity the reboil requirements of these hot
processes were much lower than the competing MEA process. In
Europe natural gas was scarce and many plants used much more
expensive energy sources like naphtha and LPG. Although early
schemes were often single stage almost all later schemes used
split absorbers and many used split regenerators. Such a scheme
using lean and semi lean flows is shown in figure 2. Similar
arrangements were used by Benfield and Vetrocoke and the later
Catacarb and Carsol processes.

The lean solution from the base of the regenerator is pumped
to the top of the absorber through a cooler. This flow is about
twenty five percent of the total solution flow. The lean liquor
decends through the top part of the absorber where it removes the
CO_2 from the syngas down to about 1000 ppm. Half way down the
absorber the semi lean stream enters and flows to the base of the
absorber. The rich solution flows through an expansion turbine to
the top of the regenerator. At about two thirds of the way down
the partly regenerated semi lean stream is extracted and pumped to
the middle of the absorber, the remainder is more fully
regenerated as it drops to the base of the regenerator where the
make gas and steam reboilers are located.

By careful operation and attention to detail in the design, like the use of crevice free reboilers, these plants have become extremely successful following earlier teething troubles. The arsenic activated Vetrocoke was extremely good at resisting corrosion but suffered from the toxity of the solvent and from complex compounds whch tended to form and either block the plant or cause severe foaming. These latter prcblems were overcome, but the toxity problem was only solved by moving to glycine as the activator.

Benfield was the most successful of these processes with over 230 applications. At the end of this stage of developments the energy consumption had been reduced to about 100MJ/KG. MOL. of CO_2. In a later section we shall see how these processes were improved to almost half this figure.

PHYSICAL SOLVENTS

The other class of solvents are physical where the solubility of CO_2 closely obeys Henry's Law. The earliest used phy-ical solvent is water. However, apart from the very large Norsk Hydrc application there are no other modern examples. Since no heat is necessary to break a chemical bond these solvents can be used in almost isothermal operation. However, carrying capacity is very temperature dependent so refrigerated operation is necessary. Generally to be economic a solvent needs to have about four times the carrying capacity of water at about 10°C. There are now several solvents with this sort of performance among them are Selexol, Sepasolv MBE, Fluor Solvent and Purisol.

The Rectisol process which uses methanol as a solvent is rather different to these. Because of the high vapour pressure of methanol it has to be operated at the very low temperature of - 50°C. This gives the solvent a very high carrying capacity, about 20 times better than water, but produces a high refrigeration load and a very expensive plant due to the need to use low temperature alloys, however, cold methanol is such a good selective solvent that the Rectisol process was used for virtually all heavy oil partial oxidation plants built in the sixties and seventies.

In the last few years physical solvent technology has been very greatly developed so that now several processes provide the most serious challenge to improved versions of the established processes.

In fig. 3 is shown the normal configuration of the Selexol process as used by Humphreys & Glasgow. Since no sulphurous gases are present air can be used for the final stripping. Note the position of the refrigeration in the circuit. By locating the chiller on the rich stream before expansion it will in most cases result in the regenerated stream reaching the absorber a few degrees cooler. This is because the expansion and desorbtion steps remove more heat from the solution than the sum of the sensible heat of the stripping air and the pumping power. A problem with physical solvents is that, even using a vacuum flash, it is difficult to remove more than 85% of the CO_2 by pressure reduction alone. The remaining 15% leaves mixed with the stripping air. H&G have applied for a patent for the technique of using the process air for this stripping and so returning the CO_2 to the secondary reformer.

The figure immediately shows the other disadvantage of a physical solvent. It dissolves some of all the gases. These have to be flashed off with a little CO_2 and returned to the absorber by compression, this adds to the cost of the plant and to the power consumption. If very pure CO_2 is required then the recycle flow can be very large.

IMPROVED PROCESSES

From the mid seventies the designers of the chemical absorbent processes have been working hard to dramatically improve the performance of these processes. Almost all successful developments exploit the fact that the regenerated solvent contains a very large amount of heat. If this solvent is reduced in pressure a considerable quantity of steam can be flashed off. Since the pressure is reduced this steam requires some form of compression.

The earlier versions used steam ejectors to recompress this steam. These are relatively inefficient as compressors and only produced about a 20% reduction in reboil. By using mechanical recompression of this steam exterior reboil requirements have been reduced to 50%. Vetrocoke have chosen to use a different approach by having a second regeneration capacity at very low pressure which is thus able to use directly the flashed steam from the main regenerator.

The other developments concern TEA/MEA and BASF's MDEA. TEA behaves rather like a physical solvent while MEA is a most efficient chemical solvent. By using their corrosion inhibitors Union Carbide have developed this process into a two column system with a single flash tank. As both solutions are used much stronger than before the reboil levels are extremely low. BASF with MDEA (fig. 4) have operated this single solvent in a similar way on their Ludwigshafen plant for over ten years. MDEA has a very straight absorption isotherm so it performs very closely to a physical solvent. Unfortunately it is not particularly good at dissolving CO_2 so even with an activator the final absorber has to be extremely tall. However only one liquid is required and the reboil is very simlar to that of the TEA/MEA process

PERFORMANCE DATA

This performance data was supplied to H&G against a gas specification corresponding to an associated gas. Since the comparison cannot be exactly precise performance bands are used. Electrical power is converted at 12 MJ equivalent to 1 KW and then added to the reboil to give total energy.

BAND 1 Over 150 MJ/KG.MOL. (63,000 BTU/LB MOL)

    (A) MEA with under 20% solution strength

BAND 2 120 -150 MJ/KG MOL. of CO_2.

    (B) Union Carbide Amine Guard II.

BAND 3 100 - 120 MJ/KG.MOL. of CO_2.

    (C) Benfield single and double stage - non flash

    (D) Vetrocoke - arsenic and glycine activated

    (E) Catacarb

    (F) Carsol

    (G) Sulfinol*

    (H) Union Carbide Amine Guard IV.

BAND 4 80 - 100 MJ/KJ MOL CO_2

    (I) Benfield with steam ejector flash

    (J) Vetrocoke with two regenerator pressure levels

    50 - 65 MJ/KG MOL of CO_2

BAND 5 (K) Benfield, mechanical compression

    (L) BASF, MDEA.

    (M) Union Carbide Amine Guard VI

    (N) Catacarb, mechanical compression

    (O) Vetrocoke with inert gas assistance

BAND 6 30 - 50 MJ/KG.MOL of CO_2

    (P) Selexol with 100% CO_2 recovery

BAND 7 20 - 30 MJ/KG.MOL of CO_2

    (Q) Selexol

    (R) Sepasolv MBE

    *Sulfinol is a Shell process using a mixture of physical and chemical solvents.

NOTE: The position in the list has no significance within a band. Within performance bands it is generally true to say that erected costs are close. There are many factors governing precise erected costs which it is impossible to cover in this paper.

WHICH ONE TO CHOOSE?

Many factors will come into play here. With the more established processes there is a lot of plant data to enable a confident choice to be made. The more modern variants generally use well established VLE and kga data so the concern is more to do with the reliability of steam compressors and increased flash stages.

The physical solvents are generally very non corrosive and require large but cheap plant much helped by an almost total lack of heat exchangers of any significant size. Unfortunately they have little, if growing, operational experience and also use very expensive solvents which need good housekeeping to avoid high replacement costs.
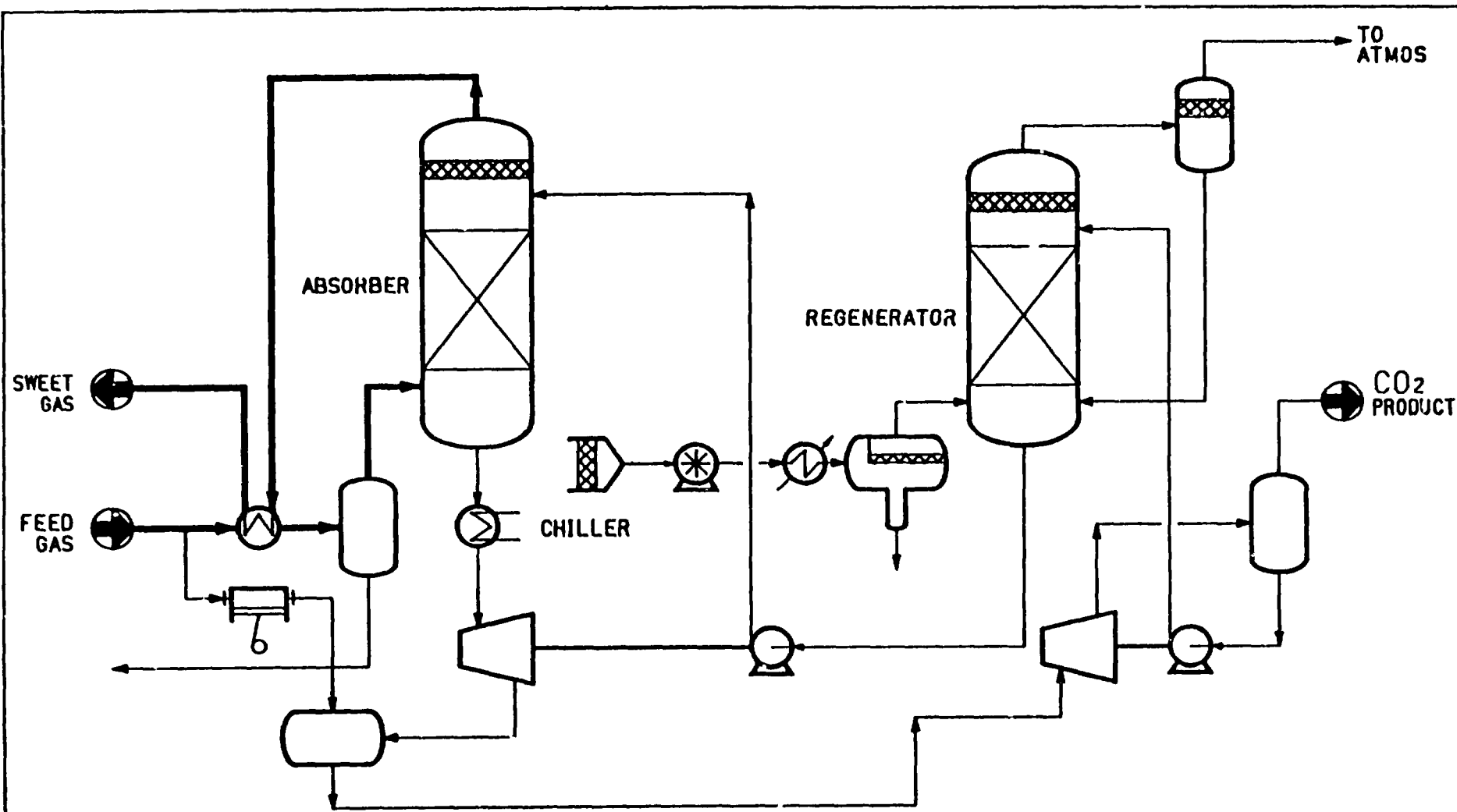
My feeling is that when 100% CO_2 recovery is required the improved processes are likely to take the business particularly in developing countries while in other circumstances the physical processes will gain ground rapidly.

ACKNOWLEDGEMENTS

FIG.1. MEA WASH.
THIS DRAWING ALSO COVERS UCAR AMINE GUARD II

FIG.2. BENFIELD SYSTEM.
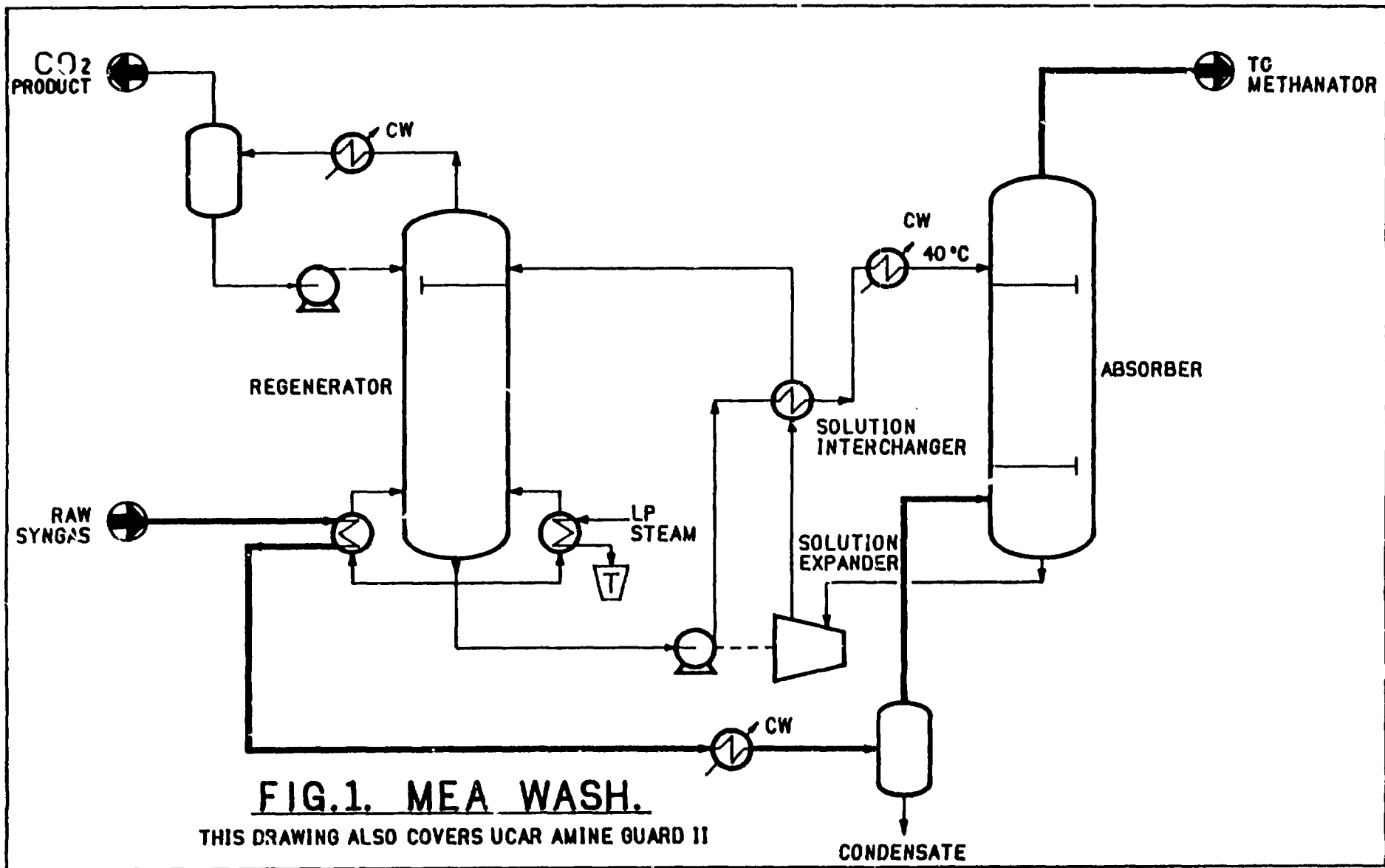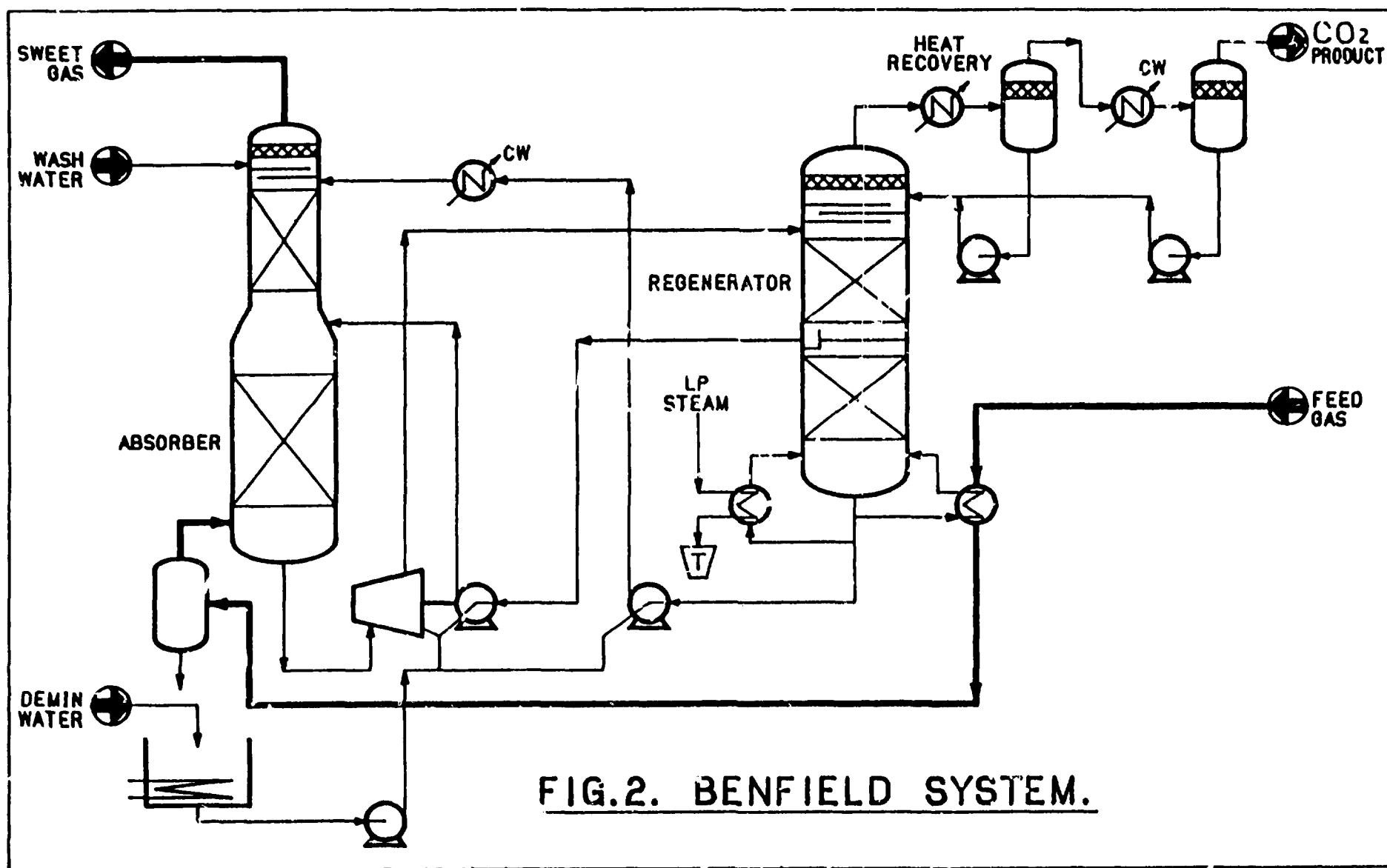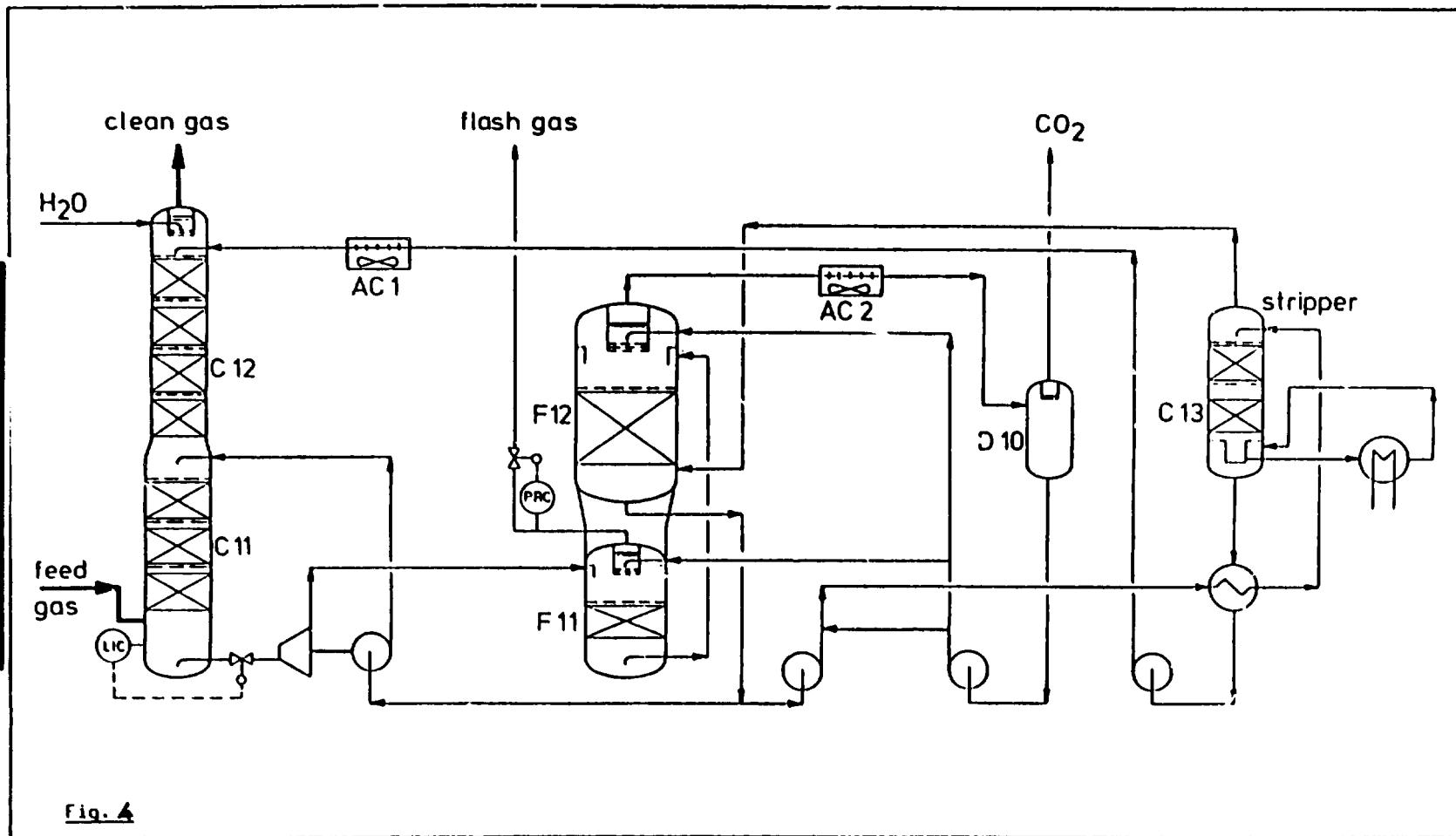
FIG.3. SELEXOL SYSTEM.

Fig. 4

Process diagram of a two-stage MDEA wash for the removal of CO_2 from synthesis gas

Volkamer