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02835



Distribution:
LIMITED

ID/WG.99/7
6 August 1971

United Nations Industrial Development Organization

Original: ENGLISH

Second Interregional Fertilizer Symposium

Kiev, USSR, 21 September - 1 October 1971
New Delhi, India, 2 - 13 October 1971

Agenda item III/1a

RECENT ADVANCES IN AMMONIA PRODUCTION TECHNOLOGY^{1/}

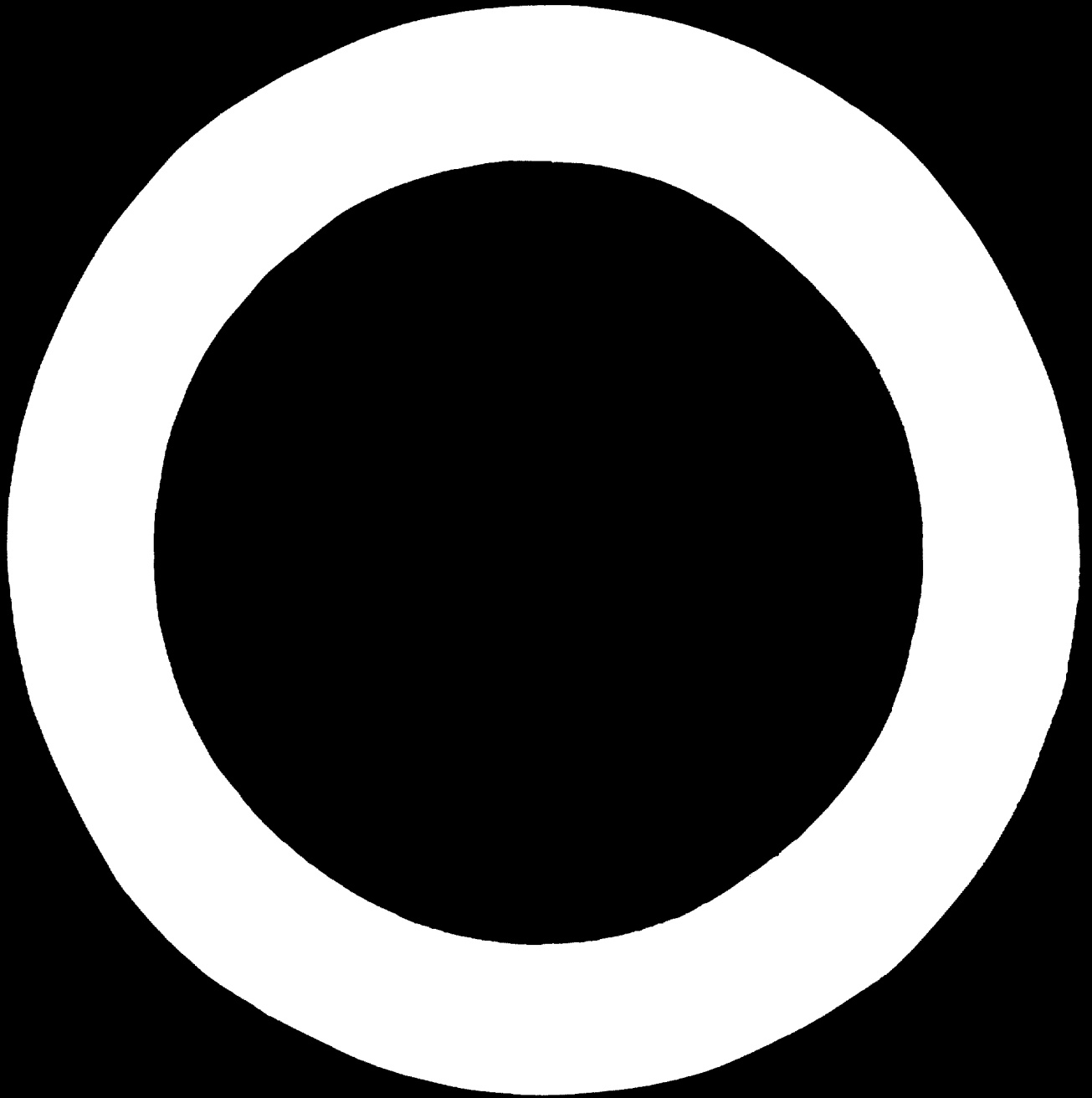
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1. It is the purpose of this paper to summarize the major advances that have been made in ammonia plant design in recent years. The advances cited are of importance in that they have contributed significantly toward smoother, quicker initial commissioning operations, and toward improved on-stream availability of these ammonia plants. The presentation is directed primarily toward advances which apply to large-scale ammonia plants, that is, plants of capacity of 600 tons per day or over, and to advances which have in fact been demonstrated in such plants. It is beyond the scope of this presentation to discuss advances still in the development or demonstration stage. Included are discussions of recent advances in feedstock desulfurization, steam-hydrocarbon reforming, carbon dioxide removal, and ammonia synthesis.

2. Desulfurization of natural gas feedstocks has become more sophisticated in recent years. In most natural gas based ammonia plants designed several years ago activated carbon, fortified with metallic additives, was utilized for feedstock desulfurization. This material was adequate for processing of pipeline gas, usually containing relatively low sulfur concentrations. At that time, pipeline gas was usually purified by the natural gas supplier to a level of 10 ppm or less of sulfur. This small residual sulfur was invariably hydrogen sulfide or mercaptan, both of which could be adequately removed by the promoted carbon. In addition, the gas supplied by pipeline was free of heavy hydrocarbons, compressor oils, and the like. This consideration is extremely important because such heavy hydrocarbons are selectively adsorbed by activated carbon, thereby blocking the adsorption centers on the carbon and rendering it ineffective for adsorption of hydrogen sulfide or mercaptans. For a number of years the industry operated perfectly satisfactorily with such carbon desulfurization systems.

3. In recent years, however, experience has tended to indicate that the simple carbon desulfurization was not completely satisfactory. As the natural gas pipeline approached, and sometimes possibly exceeded rated capacity, increasing evidence of heavy hydrocarbons in pipeline gas became apparent. When heavy hydrocarbons such as butane or any higher molecular weight material, enters a carbon drum even for a short period of time the effectiveness of the carbon drum may be completely nullified. This can occur under conditions such that operators are completely unaware of the change, principally because the change of gas composition in terms of composition, heating value or molecular weight is extremely small. There have even been reported instances of carbonyl sulfide in natural gas, probably as a consequence of still undetermined phenomena in gas processing plants. Carbonyl sulfide is not removed by activated carbon.

4. For plants equipped with carbon desulfurizers, a reasonable expedient has been the installation of continuous titrometers for sulfur monitoring. The commercially available instruments for this service, while probably not of sufficient precision for accurate measurements on an absolute basis, are adequate for plant control purposes. Many operators have adopted these instruments and have found that, if calibrated periodically against more refined laboratory methods, they are useful operating guides and are satisfactory indicators of significant or rapid change in sulfur content of the purified gas. Most operators use such instruments as a guide to carbon regeneration frequency. The general practice is to regenerate on a regular frequency basis, and more often if the titrometer so indicates. A sulfur reading of 0.2 ppm is the generally accepted criterion for regeneration.

5. On new ammonia plants, those designed within the last two years, there has been a strong tendency to include desulfurization equipment capable of removing sulfur even in the presence of heavy hydrocarbons, and of removing the more re-

fractory sulfur compounds such as carbonyl sulfide. There are several means for accomplishing this objective, two examples are given.

- a) Natural gas is first desulfurized with activated carbon, which is still the most economic means for maximum sulfur removal most of the time. However, as a backup, a hot zinc oxide desulfurizer is provided. The gas exit the carbon desulfurizer is preheated to a temperature of approximately 400°C and passed into a vessel containing a fixed bed of zinc oxide. At this temperature zinc oxide is highly effective for chemical reaction with hydrogen sulfide and mercaptans even in the presence of heavy hydrocarbons. The zinc oxide is of course converted to zinc sulfide by chemical reaction. In addition, at this temperature zinc oxide is effective in removing carbonyl sulfide, provided that the initial concentration of carbonyl sulfide is reasonably low, as is usually the case. This system is relatively inexpensive in terms of both capital charges and operating cost. Since the zinc oxide merely serves as a back-up, or guard, its consumption is relatively low. After the zinc oxide has been converted it is usually discarded, as recovery or regeneration of the small quantity involved is not economic. Preheating the natural gas to 400°C is not a penalty, inasmuch as it is required that the gas be preheated prior to reforming anyway.
- b) A more sophisticated desulfurization system comprises mixing the natural gas with hydrogen, in the form of recycled synthesis gas, preheating the mixture to 400°C, and passing the mixture over a bed of cobalt molybdate catalyst and then over a bed of zinc oxide. The cobalt molybdate serves to catalyze the hydrodesulfurization reaction whereby organic sulfur of almost any type likely to occur in natural gas is converted to hydrogen sulfide. The resultant hydrogen sulfide is then removed from the gas by the zinc oxide, which converts to zinc sulfide. This method of desulfurization is somewhat more

costly in respect to both capital costs and operating costs, principally because of the necessity to recycle a portion of the ammonia synthesis gas back to the desulfurizer. This recycle is still relatively small, representing only a fraction of one percent of the total synthesis gas. However, this desulfurization technique represents the most advanced and sophisticated desulfurization system employed for natural gas desulfurization, and is deemed adequate for almost any natural gas likely to be encountered.

6. Engineering of steam-hydrocarbon reformers has advanced in recent years, these advances being perhaps more accurately classified as refinements. Nevertheless, they have improved reformer on-stream availability considerably.
7. Ammonia plant primary reformers contain hundreds of catalyst tubes. The tubes are about 8 to 12 cm in inside diameter, and about 10 meters in length, and are filled internally with catalyst particles, generally about 1.5 cm to 2.0 cm in size. The tubes are fabricated of 25 percent chrome, 20 percent nickel alloy, and operate at a temperature of approximately 300-930°C. The tubes are arranged for parallel gas flow, -that is the gas is distributed in a uniform manner to each of the hundreds of tubes at the inlet or top end, and gas is collected at the outlet or bottom end. The tubes are arranged in groups of 40 or 50 tubes, in an assembly sometimes called a "harp".
8. As the reformer furnace is heated, the harp expands of course, and if any uneven expansion occurs severe thermal stresses will be developed. Techniques have been refined for assembly and erection of the harps to minimize the axial and bending stress experienced during and after heating of the reformer. An example is in the assembly sequence, which requires that the field welds be made in such sequence that axial stress is essentially zero. Another example is in the procedure for field recalibration of springs used to support the tubes; each spring is adjusted within narrow tolerances to assure uniform support for the

harp, and to assure that no single tube or group of tubes is subjected to an undue axial load. Numerous similar engineering and fabrication modifications have been made, including improvement in the all-important matter of quality control as applied to both shop and field work.

9. In addition to the care exercised by the engineering and construction organization concerned with design and erection of the plant, maintenance procedures have also been refined and expanded. Periodic recalibration of support springs, careful inspection of welds, monitoring of operating temperature and similar procedures have increased reformer availability significantly. Detailed maintenance procedures and manuals are prepared and should be carefully followed.

10. The catalyst used in primary reformers has experienced considerable improvement in recent years. Improvements include use of support material with improved long term strength characteristic, formulation of catalyst with improved long term activity and even improvements in the heat transfer characteristics of reformer catalyst.

11. Support materials used on earlier catalyst, subject to the severe conditions of temperature and pressure experienced in modern large scale ammonia plants, frequently suffered severe loss of crush strength after periods in service as short as several months. Crush strength, measured by simple laboratory techniques, lost as much as three quarters of the initial value. While this degradation did not invariably cause difficulty, there have been instances in which catalyst crumbling has occurred as a consequence of the loss of crush strength. Since this crumbling meant increased resistance to flow, plant throughput could be affected. Furthermore, if crumbling occurred in some of the tubes, rather than all of the tubes (and this is in most instances what tends to happen) then flow through tubes containing crushed catalyst would tend to be lower. Again the overall effect is one of reduction of plant throughput.

12. Therefore improvement in formulation of reformer catalyst support materials is a significant improvement which has occurred in recent years. While the presentation of the technical details of the support composition is beyond the scope of this presentation, the effect of the change is noteworthy.

13. Catalytic activity and catalyst physical strength are interrelated. Useful catalyst life can be terminated by either loss of activity or loss of strength; conversely, good long term activity with poor long term strength, or vice versa, is of no particular value.

14. Overall catalyst activity has not been a critical factor in recent years, but a phenomenon termed "hot bands" has caused occasional loss of production. The "hot band" phenomenon is characterized by loss of activity at one particular zone in the reformer, a critical point at which methane content is still relatively high, and temperature is also relatively high, and at which consequently the rate of reaction expressed as quantity of carbon reacted per volume of catalyst is maximum. At the point at which this absolute reaction rate is maximum, many catalyst exhibited premature aging and subsequent loss of activity. Because the chemical driving force is high at this particular location, high catalytic activity is not required and a moderate catalytic activity is adequate. New catalyst formulations have been developed which, while of somewhat lower initial activity, have far superior ability to maintain activity than the more active catalysts used earlier. This is an interesting example of an instance in which catalyst activity indicates a superior life, and is, in the overall, a better catalyst.

15. Another recent development in primary reformer catalyst technology has been a relatively simple idea to improve heat characteristics. The designer of a reformer tube is required to strike a classical engineering balance between heat transfer characteristics and pressure drop. The factors which tend to increase

heat transfer are the very factors which, unfortunately, tend to increase pressure drop; the engineer strives to find the optimum balance.

16. In a reformer tube the requirements for heat transfer are greatest near the inlet end, where the bulk of the chemical reaction heat as well as sensible heat is required. The pressure drop consideration is greater at the outlet end, where gas volume is greatest. Therefore dual catalyst systems have been introduced to take advantage of this consideration. In one system, for example, small size catalyst particles are used at the inlet and large size particles at the outlet. This combination serves to increase the heat transfer characteristics at the inlet end and to decrease the pressure drop at the outlet end. This has been adopted in several plants as a means for increasing throughput or conversely permitting more efficient reformer operation.

17. Carbon dioxide removal systems design is another area in which considerable development has been achieved in recent years. Several years ago, amine systems such as monoethanolamine were used in almost every instance in which energy costs were relatively low, and activated hot potassium carbonate processes such as Gasmarco-Vetrocoke, Benfield, Carsol or Catacarb, were used in instances in which energy costs were relatively high. The hot potassium carbonate processes require considerably less energy than amine systems, and for this reason were favored where energy costs were high. On the other hand, initial capital charges for carbonate systems were higher, and therefore a "payout" consideration entered into the economic basis for selection.

18. Over the past few years the hot carbonate processes have benefited from significant developments. New and improved corrosion inhibitors have proven adequate to permit use of less high cost alloy steel for equipment design. Experience has been gained to demonstrate the effectiveness of new and improved packing materials in carbonate service, causes of earlier problems with sludge formation have been identified and eliminated, concern with foaming tendency has

been reduced by better operating techniques and, perhaps most important, experience gained on large scale plants has permitted designers to offer "tighter" designs, using plant data as a basis for such designs.

19. The overall effect of improvements in the various hot carbonate processes has successfully reduced the initial capital cost of the hot carbonate processes to the point at which the difference in capital cost between hot carbonate process and an amine process is indistinguishable. This has been accomplished while still maintaining a significant advantage in energy requirements for operation in favor of the hot carbonate process. Thus the economic incentive is today clearly in favor of the hot carbonate processes, and in fact in most large ammonia plants currently in design or recently started the hot carbonate process, in one of its proprietary forms, is used for carbon dioxide removal.

20. The ammonia synthesis loop represents another area in which engineering developments have been made in the past few years. The principle adopted several years ago, -use of two cases of centrifugal compressors using proven compressor technology, -resulted in a synthesis pressure of approximately 150 atmospheres for the 600 and 1000 ton per day plants then under design. As plant size increased, and as compressor technology increased, synthesis pressures have risen to levels of 200 to 240 atmospheres. This pressure of course is not notably high, as synthesis pressures of 300 to 330 atmospheres were very common a decade ago. Of course, plants were of much smaller capacity then. Plants today which utilize pressures of 200-240 atmospheres are in the over-1000 ton range, say 1300 tons per day.

21. In some instances the choice has been made to adopt three cases of centrifugal compression, and then the optimum synthesis pressure is even higher, up to about 300 or 320 atmospheres.

22. Several proprietary ammonia converter designs have made an appearance in

commercial operation in recent years. Among these are designs by Topsøe, ICI and Kellogg. In each case a quench-type catalyst system is used in an effort to improve the initial vessel cost and/or vessel pressure drop.

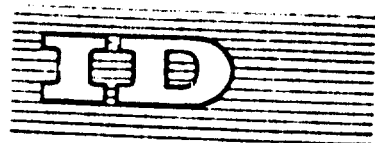
23. Topsøe's radial flow converter contains two sections of catalyst chambers, one above the other, in a vertical cylindrical pressure vessel that is of small enough diameter to permit full-diameter closure, even for capacity in excess of 1600 tons/day. The synthesis gas flows radially, outward in one section and inward in the other, the relatively short distance of travel permitting use of small catalyst particles. Temperature control is facilitated by feed the inlet gas in three portions, one of which is introduced at the periphery of the pressure vessel to keep the walls cool, and another is fed through a heat exchanger through which the converted gas is exhausted.

24. ICI's converter contains a single annular bed of catalyst surrounding a central heat exchanger. Quench gas is introduced at several intermediate points down the catalyst bed by means of specially designed gas distributors. The gas distributor, or lozenge, distributes quench gas with good efficiency of mixing while at the same time reducing the volume occupied by quench zones. No interbed support grids are required, and catalyst loading and discharging procedures are simplified.

25. The synthesis catalyst used today is virtually the same as that used several years ago; therefore the new converters do not offer a new catalyst but rather a more economical vessel for catalyst containment. The Topsøe and Kellogg converters, by using a small particle size, also offer a reduction in catalyst volume coupled with a characteristically lower pressure drop for a given synthesis circuit flowrate. All three converters have been proven in commercial service.

26. Kellogg's design features a series of horizontal "slabs" of catalyst con-

tained in a horizontal pressure shell, with quench introduced between slabs. The synthesis gas flows down and through the first slab of catalyst, crossflow to the axis of the converter. The gas is quenched and made to flow, by means of a system of baffles, to the upper surface of the second adjacent slab of catalyst, and so on through the converter. The horizontal arrangement offers a large cross-sectional area of flow through the catalyst beds yet permits using a shell diameter that is within the fabrication limits of full closure.



Distribution:
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ID/OC/99/7 SUMMARY
6 July 1971

United Nations Industrial Development Organization

Original: ENGLISH

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Agenda item III/1a

SUMMARY

RECENT ADVANCES IN AMMONIA PRODUCTION TECHNOLOGY^{1/}

by

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This paper summarizes recent advances in ammonia production technology. The presentation is directed primarily toward those advances of the last 5 - 6 years which have been demonstrated in large scale commercial plants. Included are discussions of advances in feedstock desulfurization, steam-hydrocarbon reforming, carbon dioxide removal, and ammonia synthesis.

Feedstock desulfurization systems have become more sophisticated in response to increasing instances in which natural gases containing particularly refractory sulfur compounds have been adopted for industrial use, and these systems are described.

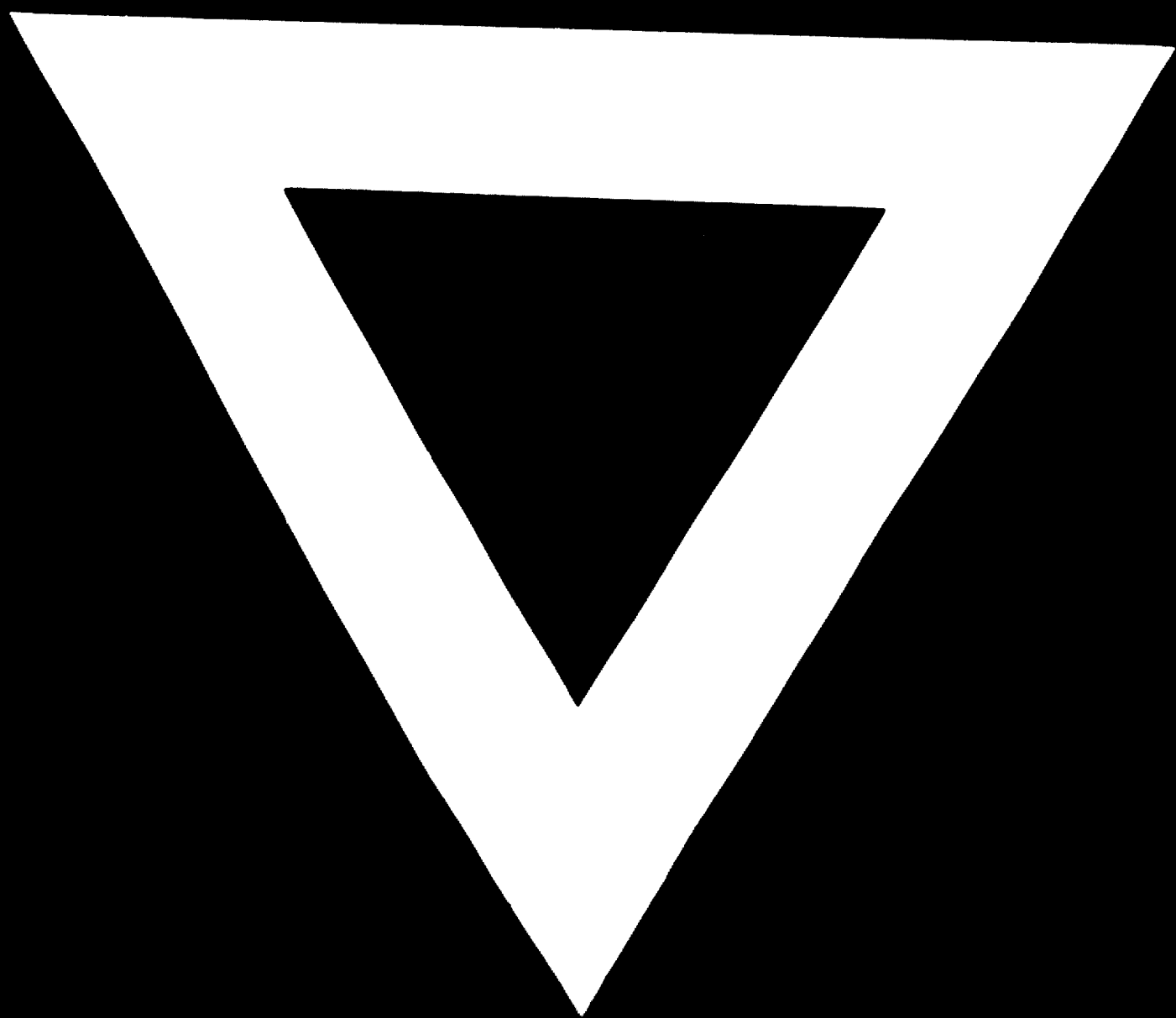
Steam-hydrocarbon reforming advances have been primarily in the area of improved metallurgical and engineering quality control, and in the area of improvements in catalyst formulation. Both of these advances have improved the performance of steam reformers.

Carbon dioxide removal systems design has advanced by the development and improvement of the various activated hot potassium carbonate processes. The successful operation of these systems has improved the cost-efficiency performance of the newer ammonia plants.

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Ammonia synthesis design has advanced by the further development of centrifugal compressors, by the development of improved ammonia converters, and by a trend toward higher synthesis pressures than were used in plants designed a few years ago.





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