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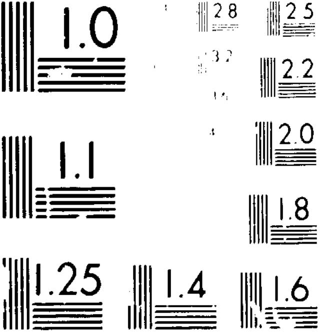

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REACTOR DESIGNS AND CATALYSTS FOR AMMONIA SYNTHESIS*

by

Umberto Zardi**

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CONTENTS

INTRODUCTION

In the chemical industry, and more particularly in the sector concerned with the production of basic products such as ammonia and methanol, plant capacity is constantly on the increase while at the same time the industry has been under great pressure to reduce energy consumption in view of the ever-increasing cost of raw materials and energy.

New technologies and new process schemes have been developed and high-capacity, low-energy plants are currently being built. Synthesis technology (reactors and catalysts) is also evolving fast to meet the new requirements for large plant capacity and low energy consumption which in some ways are conflicting.

The drastic reduction in synthesis pressure, made possible by the use of new types of catalyst, and large plant capacity have led to the development of reactors capable of accommodating large volumes of catalyst; ple equipment is thus being designed to minimize the loss of energy in synthesis gas (low pressure drop in the high recycle gas flow) and solve the problems intrinsic in the new large sizes,connected with the construction of large-size equipment, transport, maintenance and catalyst replacement. Table 1 shows the variations in characteristics of ammonia synthesis reactors from their origins to the present day.(1) As mentioned above, the development of new synthesis catalysts has been a determining factor in the designing of large, low-energy plants.

The developments in synthesis reactor design and in catalysts are reviewed in this article and the new Ammonia Casale synthesis reactor and catalyst are described in detail. Some of these developments have already provided a tangible answer to the different problems facing the industry and represent not only today's technology, but that of the near future as well, while others also mentioned in this article are no more than concepts to be assessed and proven in a more distant future.

STATE OF THE ART

Reactor designs

The axial flow design adopted for ammonia and methanol reactors in the past is still the most widely adopted solution today. The small size of the apparatus used in the past made it unattractive to adopt the radial flow designs proposed by various designers (2) to reduce gas pressure drop.

Most medium-to-large-capacity reactors (up to 2500 MTD in the case of methanol) even today are of the axial type, since it is not easy to change a well-established tradition, nor has it been easy to design problem-free cartridges with radial flow catalytic beds for large reactors. Catalyst shrinkage, in effect, has been a serious problem, affecting gas distribution in large-size radial beds.

The characteristic features of the various reactor designs lie in the way gas flows through the catalyst, the way temperature is controlled in the catalytic beds and in the reaction heat recovery system. The following is a brief review of the designs most frequently adopted:

First generation

- Ammonia Casale
  Single bed axial reactor with tube-cooled catalyst bed and calandria-type feed - product interchanger (Fig 1).
- Montecatini(3)
  Multibed axial reactor with interbed cooling by boiling water (steam generation) (Fig. 2).
- BASF(1)
  Multibed axial reactor with intercooling by gas injection (quench type) (Fig. 3).

- TVA(3)

  Single bed axial reactor with tube-cooled catalyst bed and calandria-type feed - product interchanger (Fig. 4).

- OSW(3)

  Multibed axial reactor with gas-gas cooling by heat exchangers between beds. Steam generation if desired (Fig. 5).

Last generation

- Kellogg(4)

  Multibed axial reactor with intercooling by gas injection (quench type (Fig. 6).

- Uhde(5)

  Multibed axial reactor with gas-gas cooling by heat exchangers between beds (Fig. 7).

- ICI(6)

  Single bed axial reactor with catalyst intercooling by gas injection through lozenge distributors (quench type) Fig. 8).

- Topsøe(7)

  Two-bed radial reactor with intercooling by gas injection (quench type) (Fig. 9).

- C F Braun(8)

  Two axial beds in separate vessels with an external heat exchanger between the two beds (Fig. 10).

- Ammonia Casale

  Multibed axial reactor with intercooling by gas injection (quench type), HP steam generation (Fig. 11).

- Montedison(9)

  Two-bed axial reactor with intercooling by steam generation (Fig. 12).

Synthesis catalysts

The catalysts commonly used for ammonia synthesis are based on promoted magnetite and are characterized by their chemical composition and particle shape. The most common ammonia synthesis catalysts are in the shape of irregular granules. The granulated product is obtained by crushing and screening a cooled melt.

The most widely used catalysts, available either in the oxidized state or prereduced, are: **Ammonia Casale SA, BASF AG, Imperial Chemical Industries (ICI), Haldor Topsøe and United Catalyst Inc.(UCI).**

NEW DEVELOPMENTS

Reactor designs: the new generation

- Kellogg(10)

Horizontal reactor designed by Kellogg for very large units where it is necessary to limit the pressure drop across the catalyst bed and to reduce reactor volume using small-size catalysts (Fig.13). The horizontal reactor operates in the same manner as the quench reactor, except that the gas flow is through shallow longitudinal catalyst beds called "slabs", contained in a removable carriage. Despite the use of a small particle size catalyst, pressure drop is low because of the large cross-sectional area. An efficient system is provided to mix converted gas from each slab with cold quench gas.

- Topsøe(11)

Series 200 reactor. According to the basic principle of the radial flow reactor the gas must pass only through a thin layer of catalyst, and consequently pressure drop through the catalyst beds is minimized. The Series 200 Topsøe reactor (Fig. 14) comprises a basket containing a catalyst section with two beds, one on top of the other, a gas-gas exchanger arranged centrally at the level of the higher catalyst bed and below this a heat exchanger. The main inlet gas stream, entering at the top of the reactor, flows downwards in the annular space between the shell and the basket, thus cooling the pressure shell, and enters the heat exchanger which is provided with a by-pass through which is admitted a cold gas flow.

- Ammonia Casale(12)

Axial-radial reactor with modular cartridge (Fig. 1.). The new Ammonia Casale design is a vertical reactor with stacked modular catalytic beds (modular cartridge). In each catalyst bed the gas flows through a first zone in a prevalently axial flow and in a second

zone in a radial flow (beds with split gas flow) (Fig. 16.)
Unlike conventional radial reactor designs, sealing at the top end of each layer is unnecessary, since the axial flow zone acts as sealing pad for the gas flow. An important simplification of the gas run is thus achieved with a minimum of pressure drop and a simple reactor cartridge which consists of catalyst baskets, each individual basket being individually detachable, and fitting one on top of the other with a simple sealed joint (Fig. 17).

The cylindrical bed walls are perforated along their whole length with the exception of the top portion, to ensure correct distribution of the gas flow. The height of the unperforated zone in the top portion is optimised according to the type of catalyst used and to the radial thickness of the bed in order to make the best possible use of the catalyst and of reactor volume.

Figure 18 is a general schematic view of a low-pressure ammonia reactor with two catalytic beds and internal exchanger after the first bed.

Figure 19 is a general schematic view of a low-pressure methanol reactor with three catalyst layers. In these reactors the cartridge has been designed according to the concepts described above.

This novel reactor design, mechanical details of which have already been tested in large-scale plants, is particularly suitable for low-pressure loops involving large volumes of catalyst and very high gas flow. With this new design column-like, high-yield and low pressure drop reactors can be built, minimizing transport, erection and maintenance problems.

Synthesis catalysts

The availability of new synthesis catalysts is fundamental to the success of new low-energy schemes for large-scale ammonia production. Such catalysts must satisfy the two basic requirements of high activity and low pressure drop, affected by catalyst volume and particle size and shape. The new catalysts recently developed to satisfy these basic requirements are described below:

- ICI(13)

  The new ICI ammonia synthesis catalyst contains, together with iron, cobalt from 1 to 20% w/w calculated as CO_3O_4. According to ICI the volume of the cobalt-containing catalyst required for a given ammonia output is under 75% of a corresponding cobalt-free catalyst and only 50% at the lower temperature at which the cobalt-containing catalyst is active (Table 4).

- The ACSA spherical catalyst(14 - 15)

  Numerous attempts have been made to produce ammonia synthesis catalysts in a regular shape (in the shape of small cylinders or spheres) by compaction or sintering of the powder.(16 - 17 - 18) In general the product so obtained had either inadequate mechanical characteristics or its activity was too low.

  Ammonia Casale has now developed a new process through which a spherical catalyst can be obtained having great mechanical strength and intrinsic activity at least equal to that of the best irregular-shape catalysts. According to the new process the basic product, conventionally obtained by melting, is finely pulverized and then pelletized and sintered. With this system it is particularly easy to introduce promoters to improve activity. With this new process, spherical catalysts have been produced starting from the conventional Ammonia Casale and other catalysts on the market. The spherical catalyst can be produced in the oxidized or prereduced state.

In Table 5 the chemical analysis and physical properties of the spherical catalyst are compared with some of the conventional irregularly shaped catalysts commercially available.

The diagram in Figure 20 shows the ratio of pressure drop of various sizes of catalyst in irregular granules and of a spherical catalyst to the pressure drop of a 7 mm spherical catalyst.

As the diagrams show, the pressure drop of the spherical catalyst is lower than that of the irregular granules catalyst of the same size. For example, a catalyst in irregular granules 12 - 21 mm in size (average size 14.6 mm) has a relative pressure drop of 0.85, while a spherical catalyst has a relative pressure drop of 0.52. It follows that by using a spherical catalyst:

at equal pressure drop a smaller size catalyst can be used, for example 5 mm diameter as against irregualr granules 8 - 10 mm in size, achieving an increase in activity of about 15%;

at equal activity and catalyst size the pressure drop will be lower. For example, by using a 9 mm spherical catalyst as against an 8 - 10 mm irregular granules catalyst, the pressure drop will decrease by about 50%.

POSSIBLE FUTURE DEVELOPMENTS

Reactor designs and synthesis catalysts

Many new ideas have been put forward during the last few years, by way of patents for new reactor designs and fabrication processes for new ammonia synthesis catalysts.

By reasons of space only bibliographic references are given below, which should enable those interested in this subject to carry out a more extensive study of the matter:

For reactor designs:

axial desings, see references 19, 20, 21 and 22

radial designs, see references 23, 24, 25 and 26

For new catalysts:

see references 27, 28 and 29.

CONCLUSIONS

The need to increase plant size and at the same time save energy is generating a new and improved technology for the synthesis of ammonia. New criteria have been adopted in the designing of high-pressure equipment, in sizes which even a few years ago were unthinkable, to facilitate its construction, handling, erection and maintenance.

The design of reactor cartridges has been greatly simplified to accommodate more easily large volumes of catalyst which must be quickly installed and replaced; new types of catalyst have been developed, with free-flowing characteristics and a low tendency to agglomeration and shrinkage.

Reactor volume can be conveniently reduced by using small-size catalysts and this is made possible by the low pressure drop baskets (transverse or radial flow) and by the regular shape of catalyst granules (pherical, for example).

The new cartridges with a stacked modular structure will greatly simplify the construction of large, single-train plants.

ACKNOWLEDGEMENT

The author would like to acknowledge his debt to those companies which have kindly contributed information and technical documentation.

Lugano, Switzerland, January 1982

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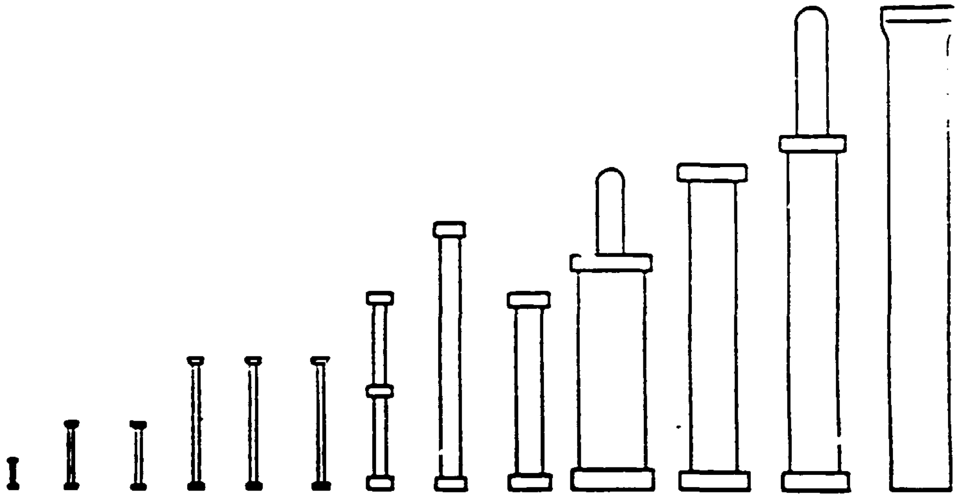
TABLE 1 - DEVELOPMENT OF THE AMMONIA REACTORS



Construction year	1910	1911	1912	1913	1913	1914	1915	1940	1956	1963	1969	1972	1980
Diametre in mm.	90	[illegible]	160	200	300	500	800	1000	1200	2900	2000	2400	2800
Length in m.	1.8	4	4	8	8	8	12	18	12	22	22	34	34
Weight in tons					3.5		65		105	270	386		
Catalyst volume in cu.m.					0.09		1.1		4.85	64	36	56	130
Operating pressure in bar					200		300		300	150	350	210	170
Production capacity tons/day					3.6-4.8		85		195	910	1200	1580	1500

TABLE 2 - CHARACTERISTICS OF DIFFERENT REACTORS

TYPE	GAS FLOW	TEMPERATURE CONTROL	CAPACITY RANGE	RELATIVE VOLUME OF CATALYST (1)	CATALYST BEDS: PRESSURE DROP (1) BAR	REACTOR VOLUME UTILIZATION %
LAST GENERATION						
Kellogg	axial	quench	up to 1300	1	5 to 6	-
Topsoe	radial	quench	up to 2500	1	2 to 3	-
ICI	axial	quench	up to 1300	1	5 to 6	-
Uhde	axial	gas/gas exchange	up to 1300	0.8	5 to 6	-
C F Braun	axial	external gas exchange	up to 1300	0.8	5 to 6	-
Ammonia Casale	axial	quench	up to 1300	1	5 to 6	-
Montedison	axial	heat recovery	up to 1300	0.8	5 to 6	-
NEW GENERATION						
Kellogg horizontal	transverse	quench	up to 2500	1	3 to 4	48
Topsoe Series 200	radial	gas/gas exchange	up to 2500	0.8	2 to 3	63
Ammonia Casale (modular cartridge)	axial-radial	gas/gas exchange	up to 2500	0.8	1 to 2	68

Notes:

1. Referred to the same operating conditions

TABLE 3 - INDUSTRIAL APPLICATIONS OF NEW REACTOR DESIGNS

(Reactors in operation)

TYPE	CAPACITY	LOCATION
Kellogg horizontal	1700 MTD	Japan
Topsøe Series 200	1350 MTD	Netherlands
	1000 MTD	France
Ammonia Casale (modular cartridge)	1000 MTD(1)	France
	1000 MTD(1)	France
	1000 MTD(1)	Rumania

Note: (1) Axial flow with modular cartridge

TABLE 4 - COMPOSITION AND ACTIVITY OF ICI'S COBALT CATALYST

Composition		Activity	
Fe_3O_4	balance		
CoO	5.2	450°C	134
CaO	1.9	400°C	144
K_2O	0.8	350°C	160
Al_2O_3	2.5		
MgO	0.2	100 = cobalt-free	
SiO_2	0.5	catalyst activity	

TABLE 5 - COMPARISON OF THE PROPERTIES OF SPHERICAL AND IRREGULAR-SHAPE CATALYSTS

CATALYST TYPE	ACSA SPHERICAL (Ce activated)	A & B(1) (Ce activated)	A(1)	B(1)
CATALYST SHAPE	spherical	spherical(2)	irregular shape	irregular shape
CATALYST SIZE mm	10	6 - 10	6 - 10	12 - 21
ANALYSIS FeO	29	31 - 32	32	31
Fe_2O_3	62.1	60.7 - 62.1	63.4	62
Al_2O_3, K_2O CaO, SiO_2, MgO	7.6	7 - 4.6	4.6	7
Ce	1.3	1.3		
PHYSICAL PROPERTIES				
- Bulk density Kg/cm^3	2.5	2.5	2.7	2.7
- Crush strength Kg	250	250	-	-
ACTIVITY(3)	100%	100%	100%	100%

Notes:

(1) Catalyst by other manufacturer

(2) Irregular-shape catalyst transformed into spheres with the ACSA process

(3) Reference activity of crushed catalyst

TABLE 6 - ENERGY REQUIRED FOR GAS CIRCULATION IN DIFFERENT TYPES OF REACTOR

	AMMONIA REACTOR (KWh/MT NH_3)	METHANOL REACTOR (KWh/MT CH_3OH)
AXIAL FLOW	44	48
RADIAL FLOW	37	—
AXIAL-RADIAL FLOW	32	35

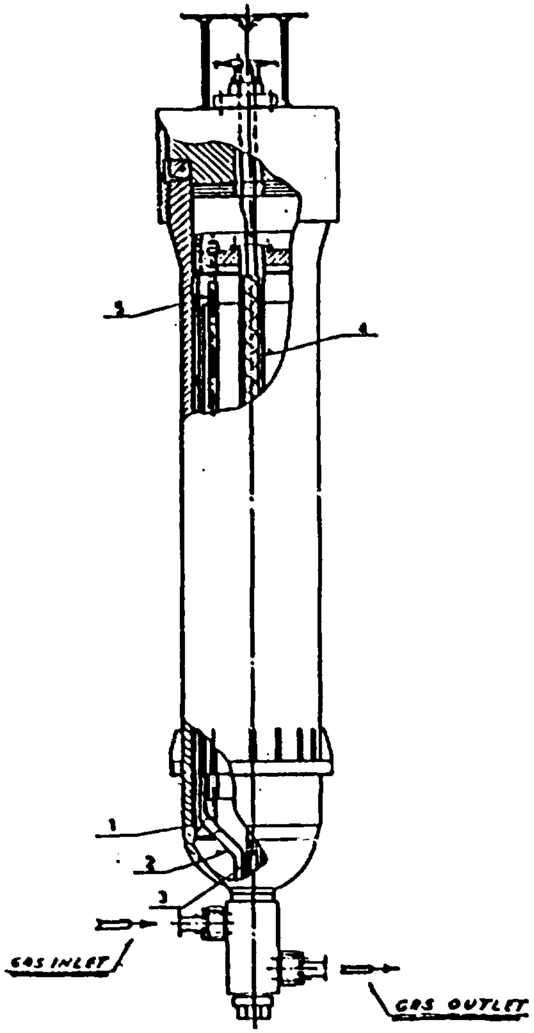


FIG. 1 SINGLE BED AMMONIA CASALE AXIAL REACTOR

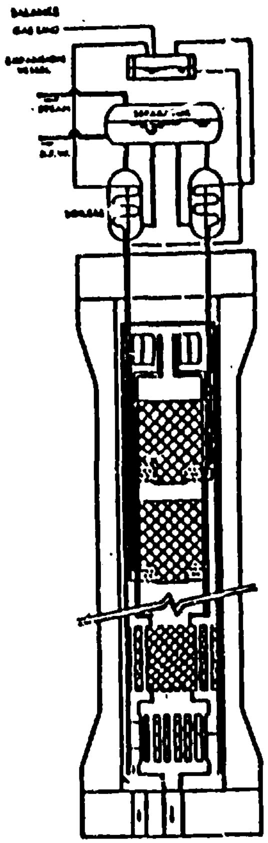


FIG. 2 MULTIBED MONTECATINI AXIAL REACTOR

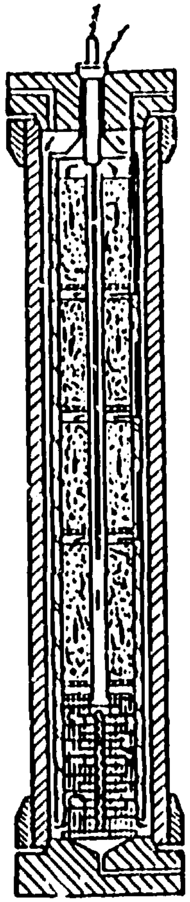


FIG. 3 MULTIBED BASF AXIAL REACTOR

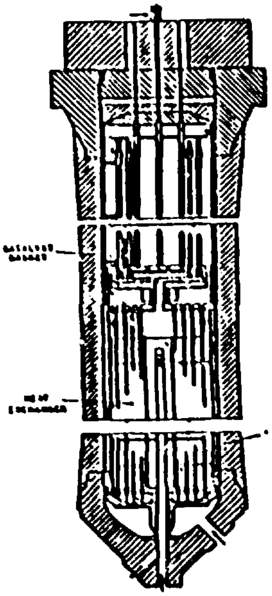


FIG.4 SINGLE BED TVA AXIAL REACTOR

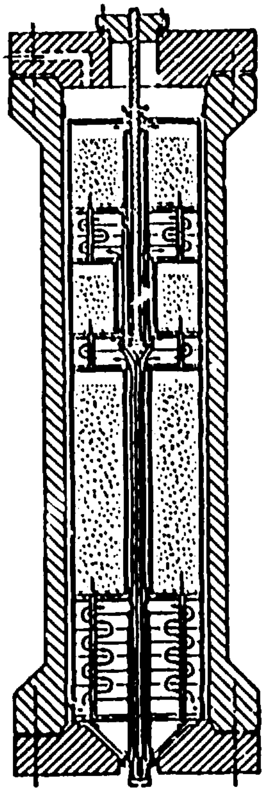


FIG. 5 MULTIBED O.S.W. AXIAL REACTOR

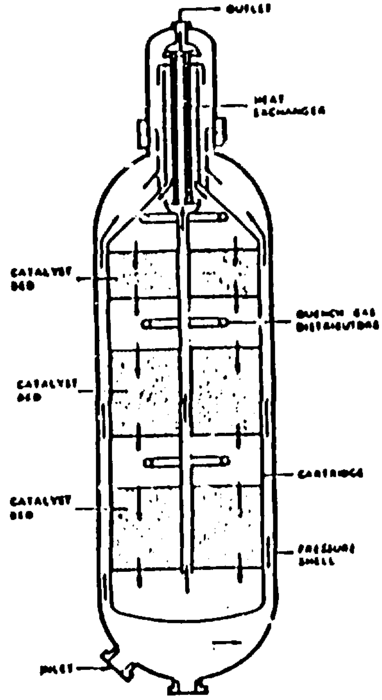


FIG. 6 MULTIBED KELLOGG AXIAL REACTOR

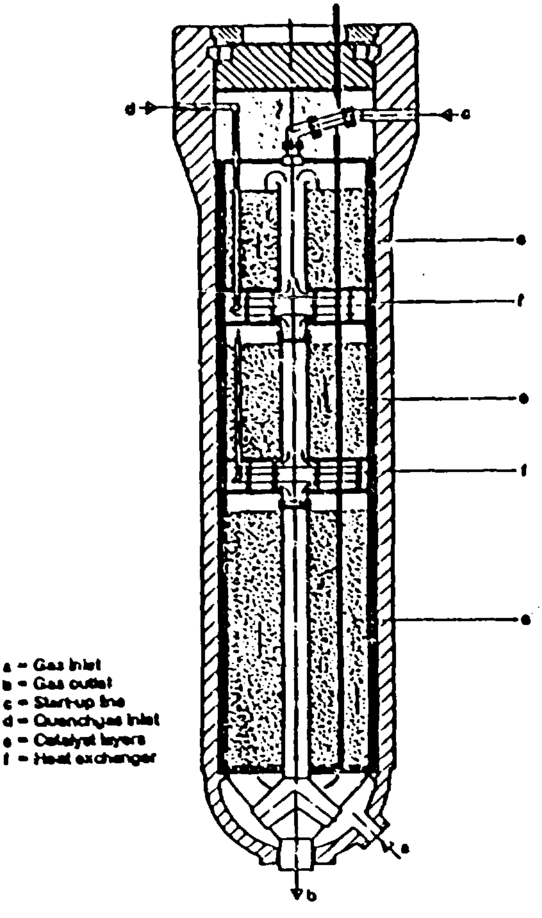


FIG. 7 MULTIBED UHDE AXIAL REACTOR

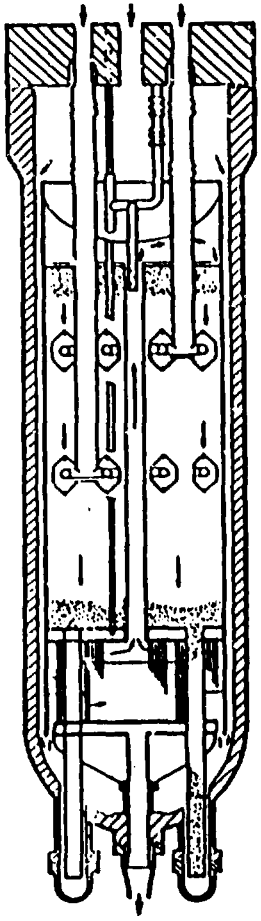


FIG.8 SINGLE BED ICI AXIAL REACTOR

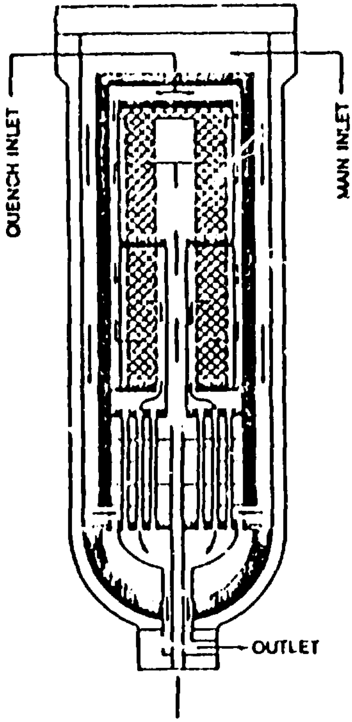


FIG. 9 TWO-BED TOPSOE
RADIAL REACTOR

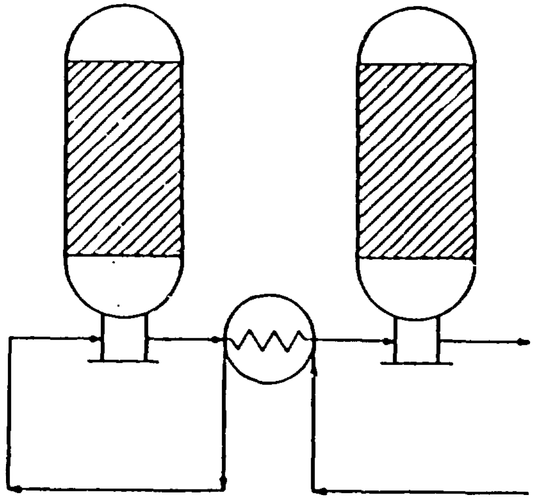


FIG. 10 TWO-BED C.F. BRAUN AXIAL REACTOR

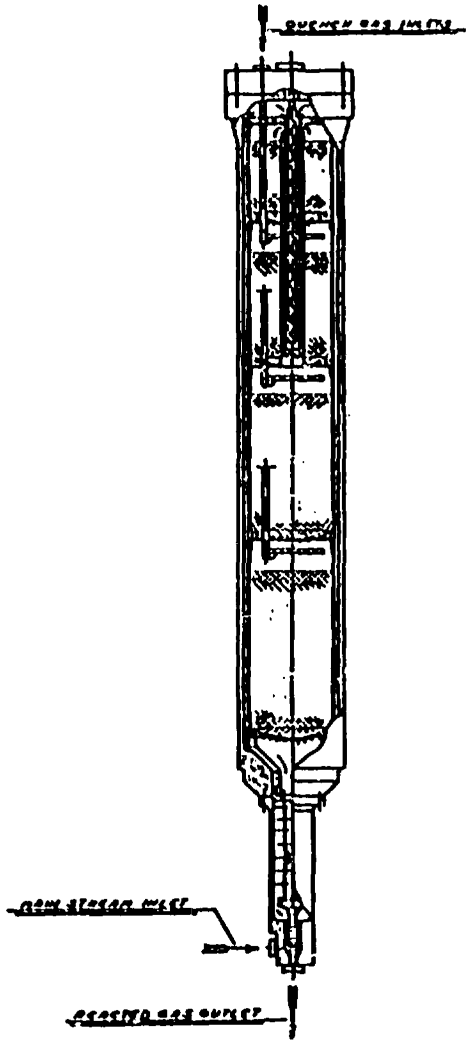


FIG. 11 MULTIBED AMMONIA CASALE AXIAL REACTOR

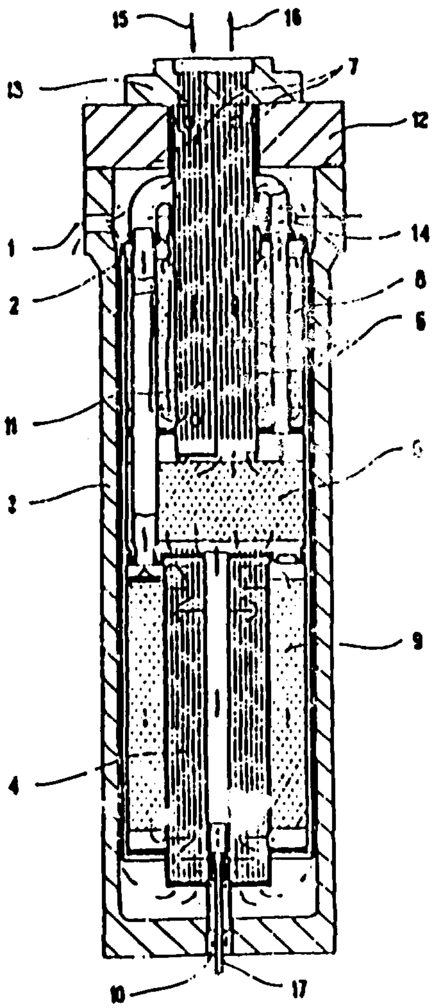


FIG. 12 TWO-BED MONTEDISON AXIAL REACTOR

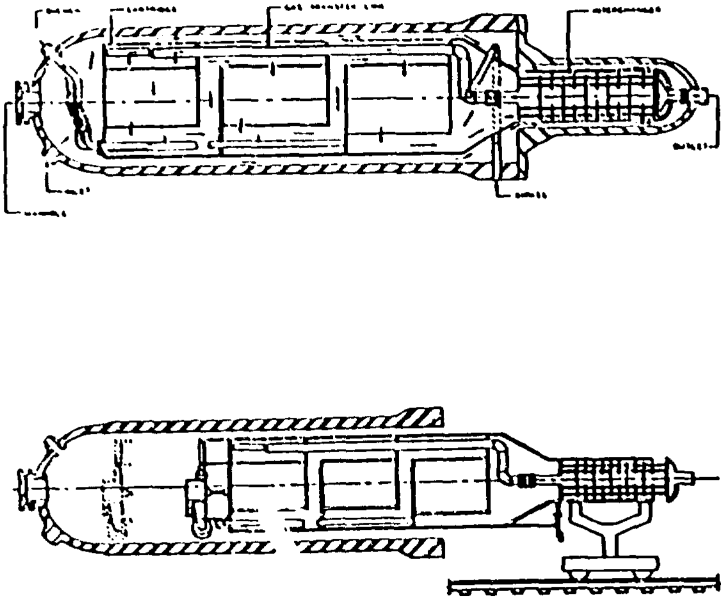


FIG. 13 KELLOGG HORIZONTAL REACTOR

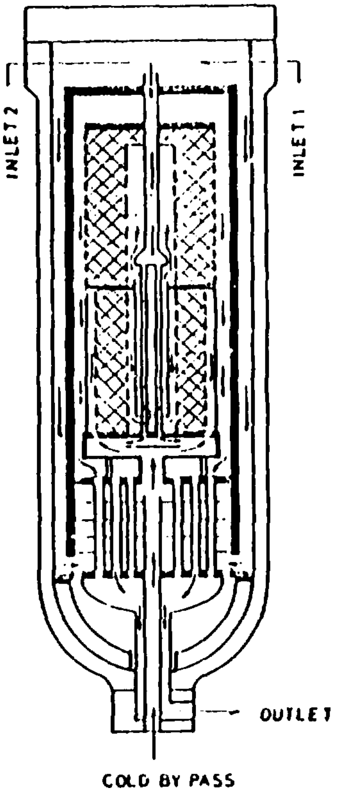


FIG. 14 TOPSOE SERIES 200
RADIAL REACTOR

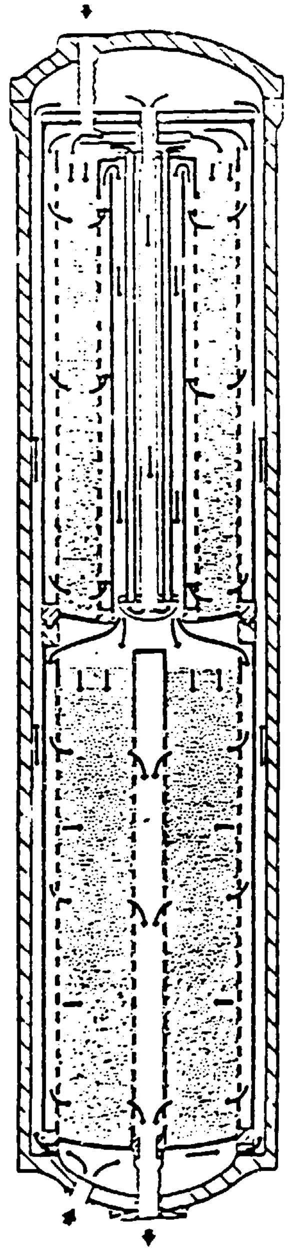


FIG. 15 AMMONIA CASALE
AXIAL-RADIAL REACTOR

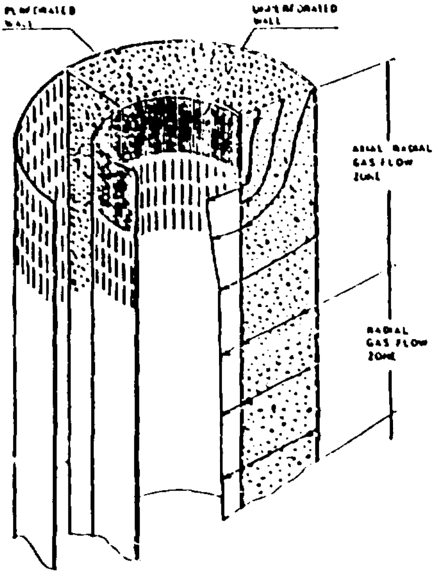


FIG.16 PERSPECTIVE VIEW OF TOP END OF BASKET WALLS IN THE A.C. AXIAL-RADIAL REACTOR

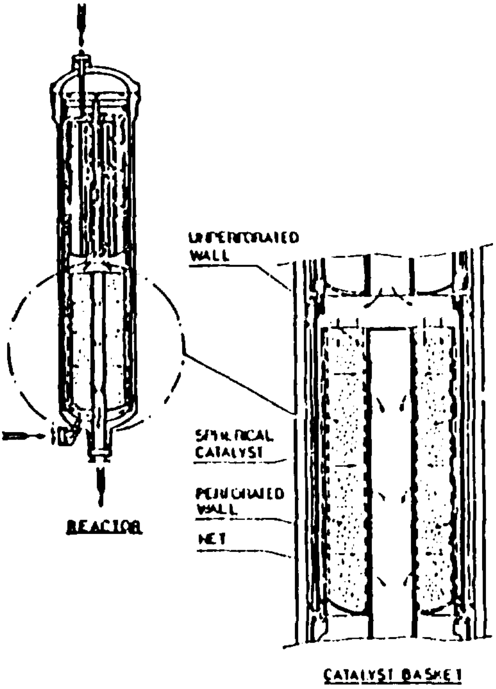


FIG. 17 GENERAL VIEW OF A CATALYST BASKET

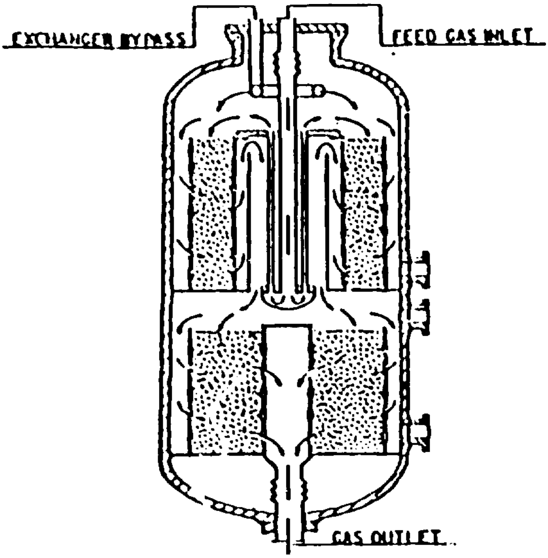


FIG. 18 GENERAL VIEW OF A.C. AXIAL-RADIAL LOW PRESSURE AMMONIA REACTOR

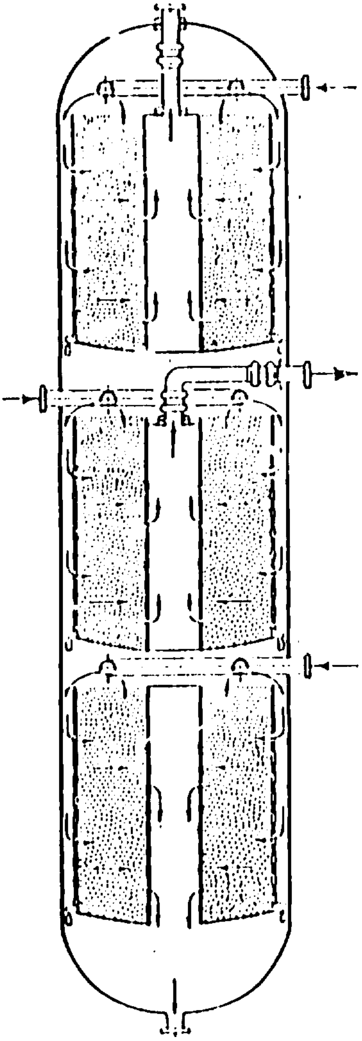


FIG.19 GENERAL VIEW OF THE AMMONIA CASALE AXIAL-RADIAL LOW PRESSURE METHANOL REACTOR

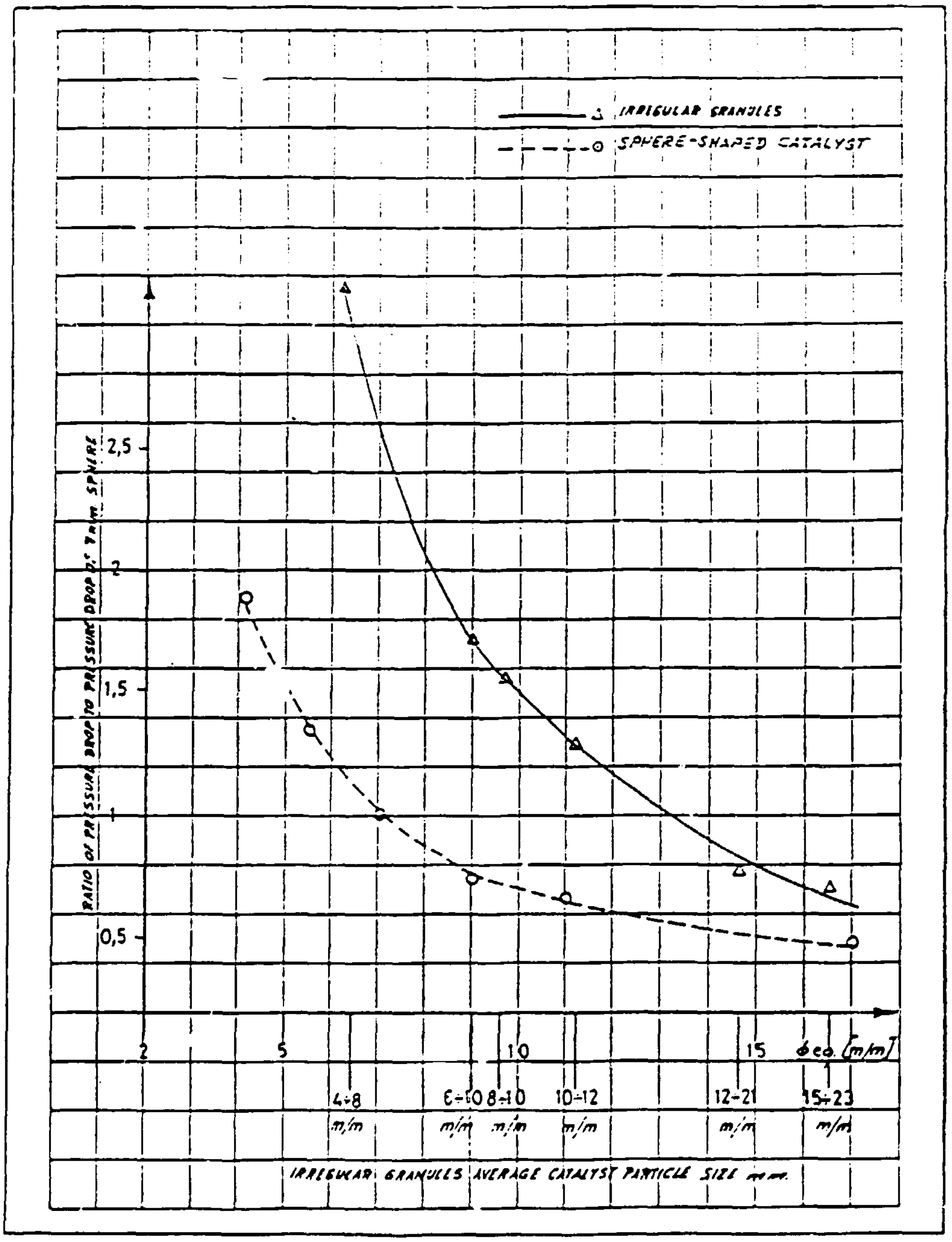


FIG 20 PRESSURE DROP DIAGRAM FOR SPHERICAL AND IRREGULAR-SHAPE CATALYSTS

The Company

Ammonia Casale SA is a Swiss company established in 1921. Its first activity was the industrial exploitation of Professor Casale's new processes for the synthesis of ammonia.

Ammonia Casale has played a leading role in the development of the ammonia and methanol industry in major world countries, including the People's Republic of China.

To date over two hundred plants have adopted the Casale technology.

The company continues to be actively involved in research and development work and consulting services and has recently achieved some very important results in the development of advanced technology in the field of ammonia and methanol synthesis and methyl fuels.

The Author

Umberto Zardi is the Managing Director of Ammonia Casale SA.
In the course of his twenty-five years' career he has also worked for Montecatini and Snamprogetti and has been involved in the development of ammonia, methanol and urea technology.