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LOW-WASTE TECHNOLOGY IN SELECTED CHEMICAL PROCESSES

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CZECHOSLOVAKIA

Terminal report*

Prepared for the Government of Czechoslovakia
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of Dr. Peter Grau of The Prague Institute of Chemical Tecnnology

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I INTRODUCTION AND BACKGROUND

A. SCOPE OF THE PROJECT

The project opts to maximize the rational use and complete processing of natural resources thus leading to the conservation of raw materials and energy and improvement of environmental conditions in the country by reducing and/or eliminating wastes generated by the chemical industry.

Specifically the project focused on four widely used chemical technologies:

- oil refining with special attention to removal of sulfur compounds from petrochemical raw materials and products
- production of sulfuric acid with special attention to minimize SO_2 emissions and to use waste heat
- production of nitric acid with special attention to minimize NO_x emissions
- organic synthesis with special attention to replacement of traditional chemical reduction by non-waste catalytical hydrogenation.

The project staff was represented by specialists from the Prague Institute of Chemical Technology (University grade), who cooperated closely with appropriate industrial specialists in Czechoslovakia. Leading staff specialists visited during study-tours principle industries dealing with the above mentioned technologies in Austria, FRG and United Kingdom and discussed the problems also with counterparts at some universities and research institutes in visited countries. Their travel-reports are available at UNIDO.

It is also aknowledged valuable contribution to the project by Project-expert Prof. L.S.Gordeyev and Project-consultants Mr.J.Eimers and Prof.Dr.H.Schulz.

The output of the project was discussed internationally at the Workshop on Low-waste Technology in Selected Chemical Processes, which was held 23-24 October 1986 in Prague. About 25 specialists from developed and developing countries and from Czechoslovakia attended.

Also the representants of Czechoslovak chemical industries expressed their eminent concern to utilize the project outputs in the planning and management activities.

Principal project staff:

Prof. Dr. Petr Grau - Project Manager
Dr. Peter Lischke - Assistant Project Manager
Prof. Dr. Otto Weiser - Oil refining and Petrochemistry specialist
Prof. Dr. Jaroslav Poživil - Sulfuric acid specialist
Dr. Jiří Michálek - Sulfuric acid specialist
Prof. Dr. Jan Vosolsobě - Nitric acid specialist
Prof. Dr. Josef Pašek - Organic synthesis specialist
Dr. Jiří Červený - Organic synthesis specialist

B. PRINCIPLES OF LOW-WASTE TECHNOLOGY IN CHEMICAL PROCESSES

1. Introduction

The steady growth of the world's population has been accompanied by increasing industrialization in most countries and, inevitably, by a sharp increase in the consumption of the world's natural resources. At the present time, over 100 billion tons of various materials are extracted each year from the earth, and practically all the elements listed in Mendeleev's periodic table are used in industry.

The activities of man are linked with the accumulation of waste materials, the non-use of which is causing the consumption of natural resources to soar and the environment to deteriorate.

The wastes can be broken down into three groups:

- production wastes - leftovers of raw materials and intermediate products which have lost some or all of their quality and usability
- consumption wastes - products and substances already used earlier, of which the regeneration or further use is inexpedient economically
- side products - generated together with the primary product, not representing the desirable final objective of the production process in question.

Developments in the area of low-waste technologies are contingent on an interdisciplinary cooperation of a number of branches where the situation prevailing in both the sphere of production and that of consumption must be analyzed together with the pertinent effects on all components of the living environment, in order to arrive at a proposal for modifying and altering the production process so as to achieve in particular a perfect utilization of the raw materials being processed /from which the desired species is extracted as fully as possible/ and, on the other hand, also to enhance the value of the ballast matter or, should this prove to be impossible, to convert it to a form which will make it possible to return it to the natural environment with a minimum of environmental damage. Another important prerequisite is an economical use of all forms of energy, owing to the limited reserves of fossil fuels which today account for most of the negative effects arising from combustion and affecting the environment /health of the population, acid rainfall, damage to forests and agriculture, contamination by heavy metals/.

Other requirements imposed on the low-waste technology systems include limitations on the generation of all kinds of wastes /solid, liquid, and gaseous/ by the manufacturing processes and, in the consumer sphere, a high usability and dependability of the products themselves which otherwise would rapidly be converted to wastes of which the disposal again burdens the environment. The last stage which completes the whole production and consumption loop is a comprehensive utilization of the wastes from production as well as of the used products as raw materials recycled to the repetitive production process.

Introduction of low-waste technology represents an issue not just purely technical or economic but, as a matter of fact, one which also involves the implementation of a new philosophical approach displayed by man, a new attitude toward life. Of necessity, the ideals acknowledged as meeting man's requirements and desires will need some reassessment which might perhaps entail a trend toward more modesty on the one hand but, on the other hand, would provide an opportunity for securing a better future for the generations to come. Examples will be mentioned relating to the chemical and petrochemical productions, including the basic products, the kinds of wastes involved, and the ways of handling the problem. These data are listed in Table 1.

The recommendations which can be found in Table 1 do not represent a full-fledged solution to the problems faced. These problems can only be resolved by creating a low-waste production process. Non-waste production amounts to such an organization of production where the production wastes que cut down to a minimum or are entirely reprocessed to secondary material resources. Creation of non-waste technology relies on an implementation of the optimum process flow diagrams involving closed streams of materials and energy. A comprehensive utilization of raw materials is the fundamental principle.

Table I

Item No.	Production	Component directly endangered: w-water, s-solid, a-air	Present tonnage and waste classification HT, LT-high, low tonna of production; HW, LW-high, low waste coefficient	Problem description	Solution
1	2	3	4	5	6
1.	Sulphuric acid	A	HT, LW	SO_2 in end exhaust gases	Pressure absorption, scrubbing
2.	Nitric acid	A	HT, LW	NO_x exhalation	Reduction of NO_x, scrubbing, presure absorption
3.	Soda	W, S	HT, HW	Waste calcium chloride	Saturation of sodium hydrooxide by combustion CO_2
4.	Phosphoric acid and phosphorous fertilizers	W, A	HT, HW	Waste gypsum sludge SiF_4 exhalation	Use of gypsum for sulphuric acid, cement plaster. Absorption of SiF_4
5.	Chlorine, alkaline hydroxides	W, A, S	HT, LW	Mercury in waste water and ventilation air, chlorine exhalation	Diaphragma electrolyzers, Hg recovery from the waste. Not generally applicable

1	2	3	4	5	6
6.	Oil refining, benzen refining, acidic refining	W, S	HT, HW	Semiliquid refining waste containing sulphuric acid	Replacement by hydrogenation refining
7.	Oxidation processes (e.g. antrachinon)	W	LT, LW	Waste water containing manganeous or chromic salts	Catalytic oxidation by air or oxygen
8.	Reduction processes (e.g. anilin, aromatic amins)	W	HT, HW	Waste iron hydroxides, high salinity waste water	Catalytic hydrogenation of nitro-group
9.	Sulfonation processes (e.g. intermediates for tensides)	W	HT, HW	Sulfonation by a mixture of sulphuric and hydrochloric acid - high salinity wastes	Continuous sulfonation by gaseous SO_3+H_2
10.	Phtalic anhydride	W, A	HT, HW	Phthalic anhydride and side products wastes (maleinic anhydride, naphtoquinones)	Combustion of waste gases. Production of secondary chemicals
11.	Butadien	W, A	HT, HW	Ammonia and copper salts in waste water	Absorption in special organic solvents
12.	Acetylen	W, S	MT, HW	Diluted suspension of $Ca(OH)_2$	Pyrolysis of hydrocarbons
13.	Ethylenoxide Prophylenoxide	W	HT, HW	High salinity ($NaCl$, $CaCl_2$) from chlorhydrine production	Oxidation of olefines

1	2	3	4	5	6
14.	Phenol	W	HT, HW	High salinity wastes from sulfonation technology	Use cumen and its derivatives as raw material

2. The objectives of non-waste technology and related problems

2.1. The objectives of non-waste technology

These objectives can be defined as follows:

- to minimize production wastes and to make the wastes less detrimental to the environment
- to use raw materials and energy more economically
- to seek ways and means of further use of the waste products
- to produce environmentally acceptable products
- to extend the service life of products and to make them easier to repair.

2.2. The problems involved in the creation of non-waste technologies in the chemical industry

The chemical industry is a branch involving a broad spectrum of compounds being processed and produced, as well as a variety of techniques and processes. This is why a great number of specific problems which are difficult to generalize is typical of the industry. This is also demonstrated in Table 1 which includes data on just several kinds of production. The key to low-waste technology may rest with feedstock selection but also with the selection of process, apparatus, and design. Clearly, quite specific studies must be worked out to handle specific production projects and to develop the process variants. It is also evident that the methods of tackling the problem are different, as a rule, for mass production chemistry and for speciality chemicals.

The general principle applies that, as the production units grow larger, the technical standard of the process, its control, and its operation are also enhanced and frequently approach the non-waste technology level. At the same time, a combination of more kinds of mass production processes operated concurrently at one plant may bring about an improved interlinking in the use of feedstocks, wastes, water, and energy. However, attention must simultaneously be paid to hazards facing plants which are too large, where even a relatively minor operational defect may manifest itself by greatly damaging the environment.

It can be stated that in most countries, the chemical industry has to bear up with the authorities of the State enforcing limitations on the environmental effects of production. However, the existing chemical plants mostly repressent enclosed and rather inflexible technological entities where additions of new processes or new apparatus that would fundamentally cut the quantity and type of wastes produced are faced with difficulties. In such a case, an improved protection of the environment tends to be attainable preferably by installing pollution control facilities such as waste water treatment stations, off-gas cleaning apparatus and the like.

The most effective implementation of technology can be achieved when new facilities are being built. On the world-wide scale it is felt that literature sources which would deal with critical assessments of production processes from the angle of low-waste technology are rather scarce.

An attempt at establishing a draft system of criteria for the evaluation of technologies from the standpoint of wastes abatement can be found in the Appendix.

II SPECIFIC PART

A. REMOVAL OF SULFUR COMPOUNDS FROM PETROCHEMICAL RAW MATERIALS AND PRODUCTS BY HYDROGENATION AND EXPLOITATION OF HYDROGEN SULFIDE GAINED AS RECOVERED MATERIAL FOR FURTHER CHEMICAL SYNTHESES

1 REMOVAL OF SULFUR AND OTHER HETEROATOMS FROM HEAVY OILS AS OBTAINED FROM PETROLEUM, COAL AND FURTHER RAW MATERIALS

The fossil fuels as crude oil, oil sand shale, coal and natural gas consist not only of hydrocarbons but also of compounds which incorporate heteroatoms i. e., sulfur, nitrogen, oxygen and even metals. In their majority, these non-hydrocarbon components are detrimental to the quality of final products, and if disposed e. g. by combustion their impact on the living environment is very negative. Many refinery and petrochemical processes are therefore devoted to the removal of the heteroatoms. This is as well afforded for most of the catalytic hydrocarbon conversion processes.

The higher the boiling point of the hydrocarbon feedstock, the higher is its content of heteroatoms and the more difficult will be their removal. Hence, the refining of the high-boiling and residual feedstocks represents, both technically and economically, one of the greatest challenges faced in industrial processing of fossil fuels, and also concerns a fundamental ecological problem which has to be solved. Due to this situation both fundamental and applied research are focused on this problem worldwide, and the practical implementation of the results from research is increasingly important.

High-boiling and residual hydrocarbon fractions can be refined by means of physical methods, as extraction, adsorption, deasphalting, special distillation, thermal diffusion etc. These processes have two basic disadvantages: they are not universally applicable and they produce substantial quantities of wastes, which are frequently converted further only with great difficulties.

A universally advantgeous method for refining high-boiling and residual fractions is the hydroprocessing route. Many hydroprocesses have been developed in which at different severity of reaction conditions the undesirable components are removed and refined products with desirable properties are obtained. Most important hydroprocesses are the following:

- hydrofinishing
- hydrovisbreaking
- hydrodemetalization
- hydrotreating
- hydropyrolysis
- hydrocracking

In addition the hydroprocesses are very effective from the ecological point of view: the are of low- or even non-waste technology nature. Undesirable components are transformed to valuable hydrocarbons and heteroatoms are removed as their hydrogen compounds (H_2S, H_2O, NH_3) respectively metals. They are relatively easily separated from the hydrocarbon reaction products and are used for other chemical purposes.

From the economical point of view maaximum intensity and productivity of the hydrogenation processes must be achieved. Therefore generally (if it is technically and economically possible) catalytic processes are used. However for high-contamined feeds the application of catalysts is not feasible and other methods for ensuring a sufficient reaction rate of hydroprocessing must be sought.

Because of these interreactions some of the above mentioned problems, mainly those of ecological importance, will be treated in more detail in the chapters below.

1.1 Contents of heteroatoms and properties of heterocompounds in heavy oils of various origin and environmental impact of their uses

Heavy oils, that is oils of relatively high specific gravity, are rich in carbon and poor in hydrogen. Correspondingly their hydrocarbon composition is preferentially of aromatic and less of aliphatic and naphthenic nature. Heavy oils commonly are characterized by relatively high values of

- C/H atomic ratio
- multiring compounds
- average molecular weight
- asphaltenic compounds
- fraction of non distillable matter
- and compounds others than hydrocarbons which specifically contain such elements as Sulfur, Nitrogen, Oxygen, and the metals Nickel and Vanadium

Heavy oils are less attractive than light ones because of several reasons.

- Their simple use as a fuel is allmost not acceptable due to poor fuel properties and particularly due to the atmospheric pollution being encountered.

- Their use as a source for high quality motor fuels and burning fuels is generally possible with modern technology however relatively high investment and production costs are afforded.

- Heavy oils can be used as feedstocks for the production of chemicals as Hydrogen, Carbonmonoxide, Olefins and aromatics, however again the lighter oils or also the natural gas are the prefered raw materials as long as these are available due to much simpler conversion technologies being applicable.

However all the crude oils, even be light ones contain a certain fraction of residual oil, which has to be processed for final use specifications and as the resources of light oils become increasingly exhausted the heavy oils will be the main feedstock for high quality fuels and chemicals as well in the future. Therefore it is of greatest importance and must generally be recognized, that modern heavy oil processing and useage should approach the "non waste" principle as close as possible.

Contents of the heteroatoms Sulfur, Nitrogen and Oxygen in selected liquid fuels refering to petroleum oil from coal hydrogenation, tar from high temperature coal carbonization, shale oil and an oil from tar sand are given in Figure A-1 /1, 2/.

Petroleum can particularly be rich in Sulfur. Even the cited light Arabian atmospheric residue contains about 3.5 wt-% of Sulfur, a content, which is much too high for its direct use as a burner fuel because of nontolerable emissions of SO_2 and SO_3. The Sulfur content in the coal derived oils is relatively low, however the Athabasca bitumen, which has been extracted from a tar sand is particularly rich in Sulfur (~4.7 wt-%) again. Reactivity of sulfur compounds for hydrodesulfurization is relatively high however residual oil desulfurization is complicated by catalyst contamination from metals- and cokedeposition.

Sulfur in heavy fuels is prefereably bound in thiophenic rings which are constituents of multiring systems.

Nitrogen as a constituent of liquid fuels is primarily of less environmentals impact because of its lower concentrations and its main route of conversion during combustion to ammonia which is not so serious a contaminent of the atmopshere. However, when regarding the problems being encountered with Nitrogen in the fuel in more details it is seen that Nitrogen can be a more problematic contaminent than sulfur. Emissions of NO_x, which can be particularly harmful to needle trees in special situations, result from both, from the nitrogen in the fuel and from reaction with N_2 of the air during high temperature combustion of the fuel. In addition Nitrogen compounds are much more stable against hydrofining demanding for more severe reaction conditions, which result in higher costs for Hydrogen consumption, for higher reaction pressure and temperature reaction apparatures and for higher costs because of poorer selectivity towards the wanted products. Nitrogen occurs in fossil fuels mainly in derivatives of 5- and 6-membered rings (pyrrol and pyridine) as constituents of higher mulitring compounds. As outlined below in more detail the slow step of hydrodenitrogenation of a liquid fuel preveillingly concerns hydrogenation of an isolated carbocylic aromatic ring to which an amino group is being attached, which renders the C/N-bond reactive.

Oxygen is a main constituent of coal derived oils. (In petroleum it is only a minor constituent). In the original organic matter of coal the oxygen has been often observed as a bridging atom, connecting individual rings of the larger molecule. In the oils obtained from coal degradation Oxygen is mainly present in the form of phenolic OH-groups /3/.

Again the bond between oxygen and aromatic ring is rather stable and is only broken hydrogenolytically after weakening through satturation of the aromatic ring.

Metals (Ni, V) as constituents of heavy petroleum derived oils are largely associated to the complexing capability of nitrogen compounds such as porphyrins which prefereably takes up Nickel. These complexes are soluable in the crude oil and are rather stable. Demetallization mainly concerns hydrogenation of the conjugated system of double bonds of the ligand and its dinitrogenation. The metal is then deposited on the catalyst. Partiell demetallisation is obtained also through deasphalting of residual oils. Ni and V are typical constituents of petroleum residues however, not present in heavy liquids from coal as tars and pitches.

Regarding the environmentally most favorable uses of heavy oils second major route, which is not the subject of this study, should be kept in mind: gasification of the oil with oxygen and steam and purifying the synthesis gas from any contaminents before its further use for the production of Methanol, Ammonia, Gasoline and other products. In analogy, production of fuels and chemicals from coal via gasification is environmentally particularly beneficial. New coal gasification processes as HTW (Hochtemperatur Winkler)-Prozess, suited particularly for lignites, the Texaco-Ruhrkohle-Ruhrchemie entrained phase gasification process for any kind of coal and the Prenflow-process of Krupp-Koppers and Saarbergwerke which is under development as an extension to elevated pressure of the commercially successful Koppers-Totzek coal gasification.

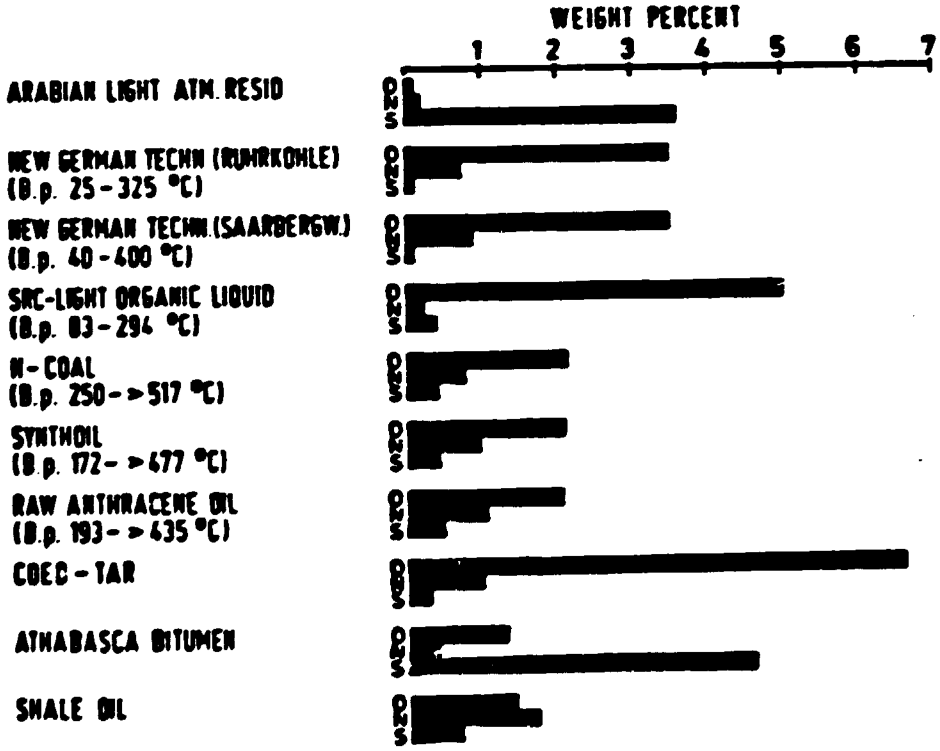

Fig. A-1: Content of oxygen, nitrogen and sulfur in selected liquid fuels

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1.2 Catalytic and non-catalytic processes for conversion of petroleum and coal derived oils to fuel oils and feedstocks for further deep conversion or refining

Recent trends in the petroleum industry exhibit substantial cutdowns in crude oil consumption and a reduction in production of petroleum residues to be used as fuel oils. The changes in structure of consumption of the petroleum products and especially of fuel oils can be derived from the data in Table A-1. It is clear from these data that in the countries regarded, the rate of consumption of petroleum products will drop in the 1980 - 1990 period and this trend should be strongest for fuel oils.

What attracts the eye in particular is the reduction of consumption of fuel oils envisaged for FRG and France (to about 50 %).

The task of effectively using petroleum residues has become prominent in research and development activities. Owing to the challenges faced and the demands with respect to experimental equipment and its operation, numerous agreements have been established for cooperation among, otherwise often competing, institutions. For instance, an association ASVAHL/Association for the upgrading of heavy oils/ has been etablished in France where, with participation of the French government, the petroleum groups ELF, IFP, and TOTAL have joined for cooperation in this areas.

At present nearly 50 processes are known which aime at the utilization of residual oils; out of these processes some 40 % are commercial. Their classification is shown in Fig. A-2. The individual processes attain different degrees of conversion, as is to be taken from Table A-2.

The following general conclusion can be drawn with regard to the individual processes and develompent trends:

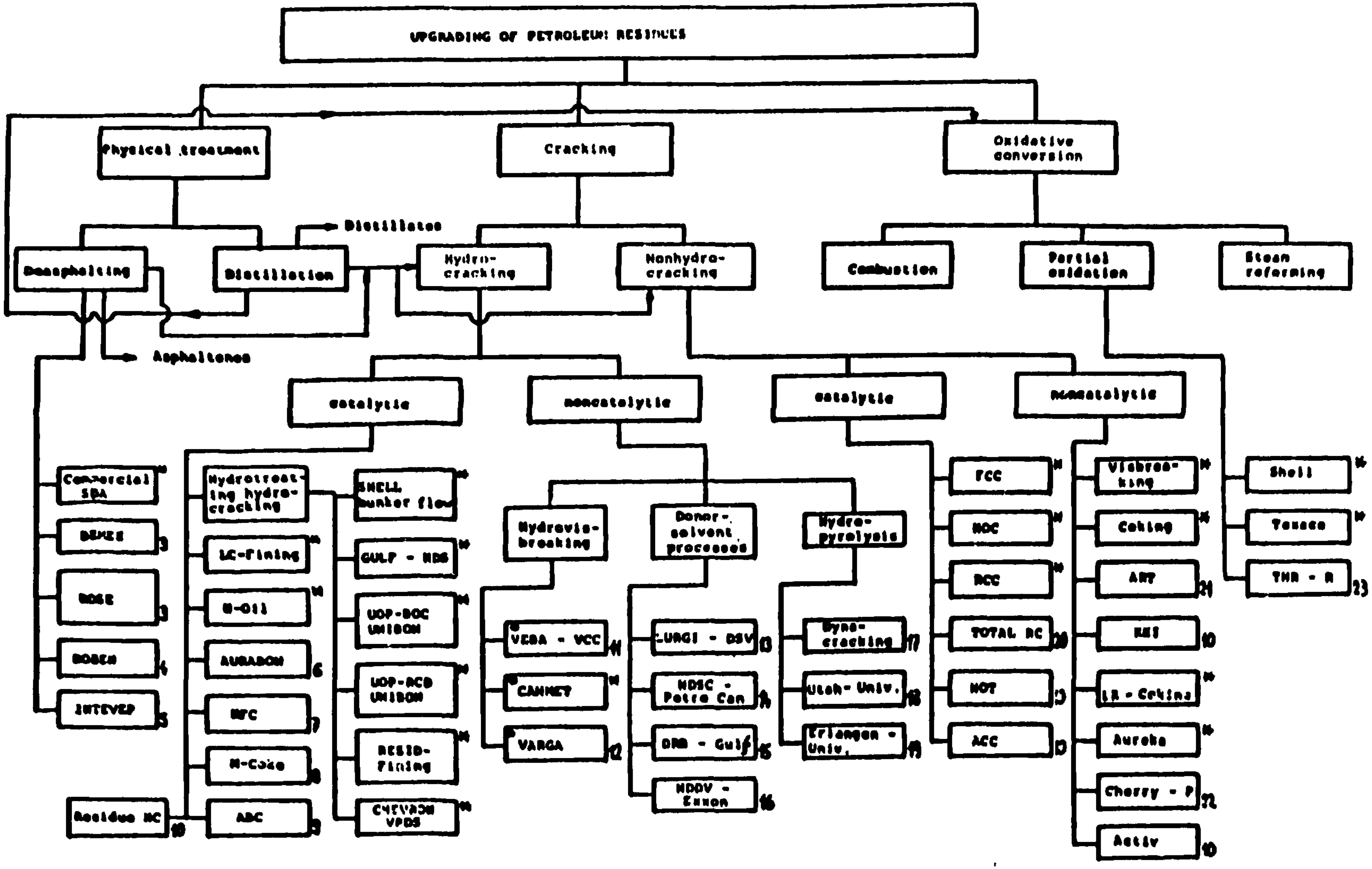

Fig. A-2: Upgrading of Petroleum Residues
x - Commercial scale processes; o - Application of once through-additives (catalysts) improving the conversion of thermal processes; number 2 - 23 = no. of reference

a) The fundamental difficulties faced in direct catalytic processing of residual oils which are due to the presence of asphaltenes and organometallic components in the case of hydrogenation processes can be overcome by means of the use of special catalysts which exhibit mainly the following properties:

- very high metals retention power
- very low coking tendency
- very large active areas
- appropriate porosity distribution
- moderate HDS and HDN activity

The catalytic reactor can profitably apply moving of the catalyst and its continuous regeneration.

The combination of HDM and HDS catalysts is advantageous in hydroprocessing of residual oils. A suitably selected ratio between HDM and HDS catalyst can regulate the degree of conversion and desulfurization.

Table A-3 presents an example of hydrotreating of an atmospheric residue for use as a feedstock for FCC or for the production of low-sulfur fuel oils (IFP results). Naturally, life time of the catalysts is limited in such a process. According to IFP data the catalyst operating costs are ca. 0.3 USD per bbl which amounts to 2 million USD per year as an indicative value /2/ for a facility of 1 million tons annual capacity.

Direct hydrodesulfurization of residual oils produces low-sulfur fuel oils in the simplest technological way, however due to an intensive deactiviation of the catalyst is very challenging both technically and economically. Therefore, such "indirect" processes of residual oil desulfurization come into use where the basic principle is, to limit the contact between the major contaminants present in the residual oil (i. e., organometallic components and asphaltenes) and the hydrodesulfurization catalyst, to which only the prerefined oils are fed. This is achieved as illustrated in Fig. A-3.

Table A-1: Development of consumption of petroleum products in the years 1980 - 1990 /1/

Country	Total of oil products 10^6 m^3/d				Residual of oil products wt.			
	1980	1985	2990	1980/90	1980	1985	1990	1980/90
France	0.293	0.247	0,201	- 31	27.7	22.1	14.1	- 49
FRG	0.347	0.319	0.307	- 12	18.6	9.5	9	- 52
Italy	0.264	0.287	0.262	- 1	47.7	47.6	41.3	- 13
Great Britain	0.212	0.208	0.197	- 7	28.8	23.5	22.5	- 22
Japan	0.327	0.322	0.316	- 4	38	33	28.4	- 25
USA	2.22	2.10	1.97	- 11	18.1	13.4	11.9	- 34
Czecho-slovakia				- 14				- 14

Table A-2: Residual oil conversion achieved in technical operation of different processes

Process	Conversion, range /%/ depending on severity of process conditions
Hydrorefining	0 - 33
Visbreaking	5 - 30
Hydropyrolysis	25 - 67
Coking	50 - 70
Hydrovisbreaking	55 - 70
Hydrocracking	60 - 95
FCC	70 - 88
Pyrolysis	75 - 85
DSV	82 - 92
Partial oxidation	97 - 100

Table A-3: Results obtained with a HDM-HDS catalyst arrangement applied for FCC feed preparation or fuel oils production /2/

Feed: atmospheric residue (Arabian Medium)

Feedstock - properties

Sp Gr	0.980
Visc., at 100 °C cts	70.5
Sulfur, wt-%	4.0
Conradson carbon, wt-%	12.2
C_5 insol., wt-%	9.9
C_7 insol., wt%	3.6
Ni. ppm	18
V, ppm	61

After 2000 hours of operation

Net conversion in 360 °C minus: 20.5 wt-%

Product properties residue 360 °C+

Sp Gr	0.927
Visc., at 100 °C cts	22.8
Sulfur, wt-%	0.24
Conradson, carsbon, wt-%	4.5
C_5 insol., wt-%	0.8
C_7 insol., wt-%	0.3
Ni. ppm	less than 1
V, ppm	less than 1

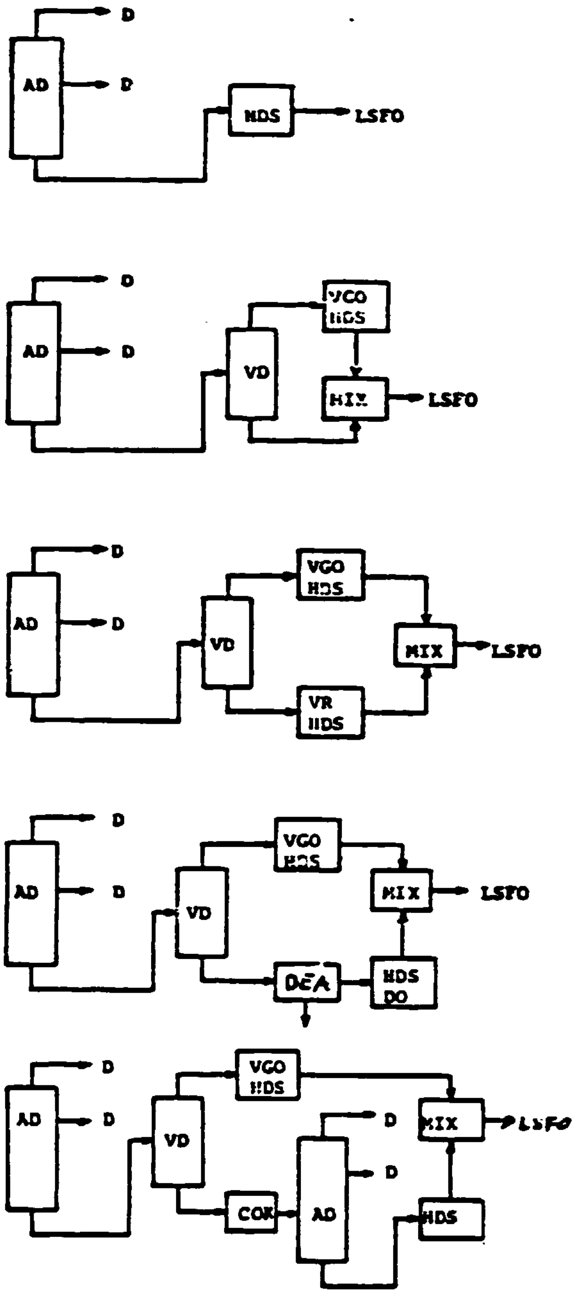

Fig. A-3: Examples of the most important schemes for production of low-sulfur fuel oils

AD - atmospheric distillation; VD - vacuum distillation; D - distillates; HDS - hydrodesulfurization; VGO - vacuum gas oil; SE - solvent extraction; COK - coking; MIX - mixing of fuel oils; LSFO - low-sulfur fuel oil; DEA - deasphalted oil;

b) Because the fundamental problems involved in direct catalytic residual oil conversion, the commercial tendencies appear to favour more widely the thermal route. The pure thermal variant is improved by the application of "additives" which exhibit only little catalytic effect and have their main importance in acting as "dischargers" for coking deposit. The coke precursors and other contaminants deposit preferentially on their surface, and not on the apparatus walls . Suitable additives are:

I. Amorphous and crystalline earths, Bayer`s mass (waste product from alumina production)

II. Low-temperature carbonization coke impregnated with iron compounds; here the adsorptive effect of the addition is combined with a moderate hydrorefining catalytic activity of iron (disposable catalyst).

c) The hydrogenation processes proceed more easily, when applying solvents with hydrogen donor properties, which produce hydrogen radicals required for the chain reaction of thermal cracking respectively satturation of unstable intermediates (e. g. the processes DSV, HDSC; HDDV - see Fig. A-2).

d) In catalytic hydrocracking processes a number of reactor-engineering means are applied to slow down catalyst deactivation:

I. "Protective" catalyst layers (guard reactors) are used for hydrodemetallizing the feedstock (this is done in a separate reactor or in the first layer of the hydrocracking reactor)

II. Catalyst "tailoring", i. e., optimization of chemical composition and texture, such as wide pores for the top layer and narrow pores for the bottom layer of the catalyst in the react

III. Use of moved catalyst particles (bunker flow, ebullating bed, slurry process); the catalyst can be continuously regenerated or replaced.

IV. Catalysts highly resistant to deactivating metals and cokeforming components are applied; special supports are used (such as Mg-Si for the ABC process /9/) or special zeolithes highly resistant to deactivication by metals (RCC process /24/) etc.

V. Special reactors are used: trickle phase with perfect distribution of the liquid phase and with wall effect elimination; reactors with ebullating or pseudofluid beds; slurry reactors etc.

e) As for the non-hydrogenative processes, the following trends can be noted as to be typical:

I. With respect to a wider chemical use of heavy oils (serve cracking and hydrocracking of VGO) the classical visbreaking has been modified to hydrovisbreaking

II. The coking processes are being optimized. The Flexicoking process with outstanding thermal efficiency can be taken as an example. The high efficiency is due to gasification of a part of the coke being produced so as to produce synthesis or fuel gas. A modification of fluid coking is the ART process with an inert carrier on which metals and coke deposit. A modification of delayed coking is the Japanese process EUREKA /25/ in which the formation of coke is inhibited by means of superheated steam and tars of high aromaticity are formed. These can be used as additives to raw materials in the production of metallurgical coke.

III. Efforts to extend FCC application as to cover residual oil processing have led to catalysts which are passivated against the deactivating effect of metals (Sb additives). Further progress obtained concerns the regeneration of catalysts which have been deactivated by metals (e. g., the DEMET III process). In a subsequent development, efforts have been undertaken to replace the FCC catalysts based on aluminosilicates by more resistant catalysts. For instance, the Japanese process HOT /10/ which is under develcmpent makes use of iron as a catalyst on which the following reactions proceed:

Cracking: $Fe_3O_4 + \text{feedstock} \rightarrow Fe_3O_4 \cdot \text{coke} + \text{oils} + \text{gases}$

Regeneration: $Fe_3O_4 \cdot \text{coke} + \frac{1}{2} O_2 \rightarrow Fe_3O_4 + CO$

$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$

$FeO + SO_2 + 3CO \rightarrow FeS + 3CO_2$

$3FeS + 5O_2 \rightarrow Fe_3O_4 + 3SO_2$

Reaction on incompletely oxidized iron: $3FeO + H_2O \rightarrow Fe_3O_4 + H_2$

Thus hydrogen is formed during cracking, and less coke is being produced.

IV. Processes are also under develompent whereby residual oils are used as feed for pyrolysis to produce basic olefinic, chemicals.

An important raw material of industrial chemistry which enjoys great perspectives is coal (not speaking of other carbonaceous materials such as tar sands and oil shales). Transformation of bitumen to high quality fuels or chemicals ranks among the most challenging developing processes both as a technical and economical goal. Such processes are highly important. They have a bright perspective particularly as the reserves of oil and natural gas will be nearer to exhaustion within medium terms of industrial planning.

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1.2.1 Fundamentals of hydrotreating of high boiling and residual heavy oils. Thermodynamics, kinetics and reaction networks of removal of individual heteroatoms.

Hydrogenative removal of Sulfur, Nitrogen and Oxygen from organic heterocompounds under formation of H_2S, NH_3, H_2O and the saturated hydrocarbons is generally feasable from the thermodynamic point of view at hydrorefining conditions as being 300 - 450 °C, and 30 - 300 bar.

The enthalpy of reaction for splitting of the bonds between heteroatom and carbonatom and saturation of the fragments with hydrogen is generally only weakly negative. However, the overall conversion includes commonly strongly exothermic reactions like the hydrogenation of aromatic rings, so that the process in generall is of exothermic nature.

Free reaction enthalpies of removal of S-, O-, and N-atoms through hydrogenolysis from the organic compounds are generally negative in the range of normal process conditions, however the overall conversion proceeds through a complex network of individual reactions and reaction steps and thermodynamic limitations may specifically interfere. Thus among all of the hydrocarbons methane is the thermodynamically most favoured compound and formation of methane has to be inhibited kinetically in the system. Similarly decomposition of most of the hydrocarbons to the elements carbon and hydrogen is thermodynamically possible. Coke formation which deactivates the catalyst is most probable from relatively high molecular weight asphaltenic compounds and is particularly retarded through increasing partial pressure of hydrogen.

The overall reaction rate generally increases with increase of partial pressure of hydrogen up to at least 150 bar. High partial pressures of hydrogen thus are generally favourable with respect to reaction rate and selectivity as well. Investment costs increase, however with the height of process pressure and therefore the minimum respective by economically optimum partial pressure and total pressure, respectively will be chosen for a process.

HDS, HDO and HDN conversions imply a mulitplicity of individual reactions and reaction steps. Regarding the composition of the heterocompound fractions each of the fractions (S, O, and N-compounds) consists of numerous substances, which are even difficult to determin qualifically. However the most abundant classes of heterocompounds in the different types of fuels have been identified and on the other hand, the most decisive slow steps in the reaction networks of HDS, HDO, HDN have been discriminated for several typical examples of model compound conversion. Severity of reaction conditions for removal of S-, O- and N-atoms increases in the order

HDS < HDO < HDN

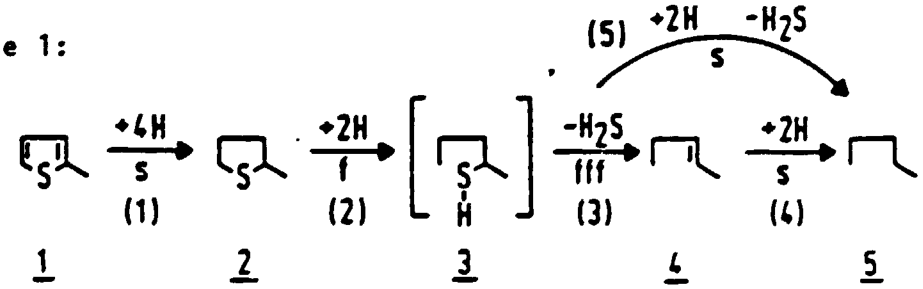
Hydrodesulfurization

The ease of removing sulfur hydrogenatively as H_2S from organic sulfur compounds depends strongly from the structure of substance. Aliphatic sulfur compounds as mercaptans and alkylsulfides which are the main sulfur compounds in natural gases and light petroleum fractions are very reactive.

Sulfur as a constituent of heavy oils predominantly is of thiophenic structure.

HDS-conversion of thiophene has been shown to follow the reaction path /26/:

Scheme 1:

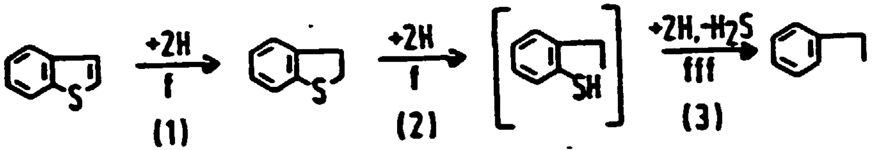


s = SLOW REACTION , f = FAST REACTION

Reactions (1) and (2) are similarly fast. The catalyst therefore has to be active as well for hydrogenation of rings with aromatic character (reaction (1)) and olefins (reaction (4)) as for splitting of C/S-bonds.

A model compound being more related to heavier oil hydrodesulfurization is benzothiophene /26/. Its hydrodesulfurization proceeds according to Scheme 2:

Scheme 2:



1 2 3 4

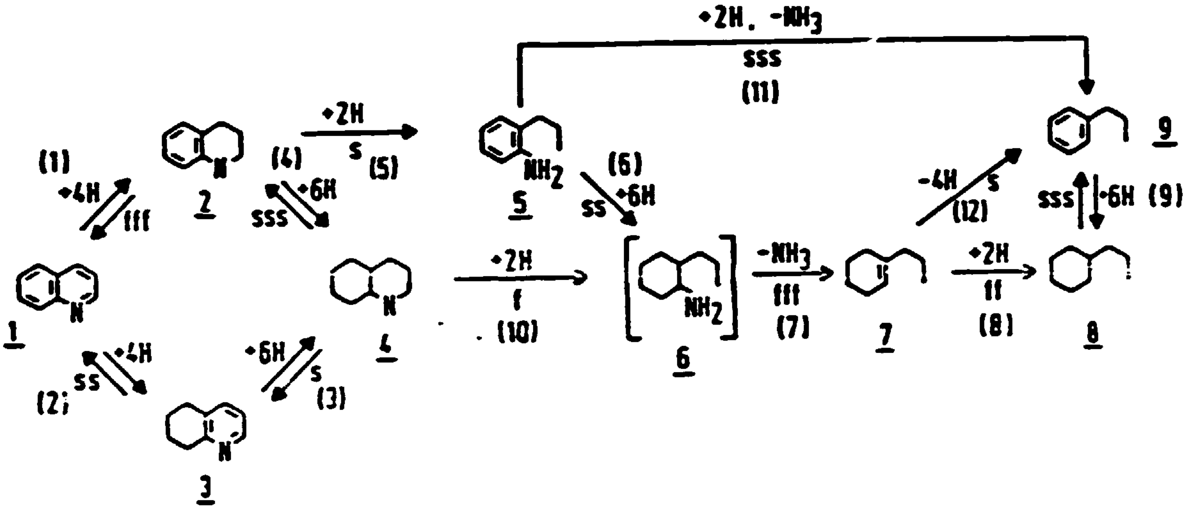
It is the most important feature of this scheme, that reaction (3) - the hydrogenolytic splitting of the bond between the sulfur atom and the aromatic ring - is feaseable without prior hydrogenation of the aromatic ring. This statement is very important, because it allows for complete hydrodesulfurization of an oil without hydrogenation of isolated carbocyclic rings, which is a particularly slow reaction; and this behaviour of sulfur compounds is different to that of corresponding oxygen and nitrogen compounds , where the bonds of the heteroatoms to the ring are much more stable.

With respect to sulfur in much higher molecular weight compounds the reactivity of the C/S-bonds will not be less, than in the model compound benzothiophene. However, for large molecules, as those of asphalthenes, it can be doubted that the necessary intimate contact of the bond which shall react with the active catalyst site is sterically possible. Hydrogen donorsolvents like tetralin can provide the hydrogen for saturation of radical fragments produced through breaking of C-S-bonds in such cases where catalytically activated hydrogen is not accessible. Naphtheno-aromatic compounds with hydrogen donor solvent properties are therefore very valuable constituents of reaction mixtures during hydrodesulfurization of heavy oils which suppress the tendency of coke formation.

Hydrodenitrogenation

Nitrogen compounds as constituents of fuel oils mainly are derivatives of pyridine, pyrrol and aniline. A typical model compound for hydrodenitrogenation is chinoline. Its denitrogenation reaction network is pictured in Scheme 3 /27/.

Scheme 3: Chinoline hydrodenitrogenation



The principles with significance of fuel oil denitrogenation are as follows:

- Hydrogenation of a heterocyclic ring (reaction (1)) in a dicyclic ring system like chinolin is much faster than that of a carbocyclic ring (reaction (2))

- Hydrogenation of one of the aromatic rings of a conjugated two ring system is much faster than hydrogenation of an isolated ring.

- A important intermediate is o-propyl aniline. It has been shown /28, 29, 30/ that the C/N-bond in anilines is very stable. Thus the isolated aromatic ring has to be hydrogenated in a slow reaction to make the C/N-bond reactive. It is due to this interrelation, that anilines accumulate in oils from coal hydrogenation, and it is a conclusion hereof that the slow steps of hydrodenitrogenation reaction networks is particularly that of hydrogenation of isolated aromatic rings of anilines.

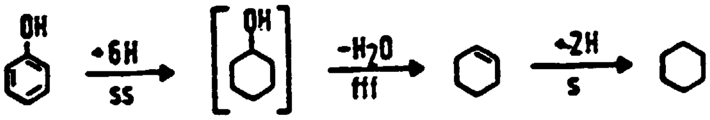
This again implies as a demand for hydrodenitrogenation systems to have high hydrogenation activity - and as a result for commercial hydrodenitrogenation - that necessarily high hydrogen consumption is associated as compared with hydrodesulfurization.

Hydrodeoxygenation

Organic oxygen compounds are major constituents of oils derived from coal through hydrogenation or pyrolysis. Irrespectively of the orginal structure the organic oxygen compounds in the oils are preferentially of phenolic nature, which reflects the high stability of the C/O-bond of the phenolic structure.

As the slow step of hydrodeoxygenation reaction networks the removal of oxygen from phenol therefore has to be regarded.

Scheme 4: Hydrodeoxygenation of phenol /27/



Similarly as outlined for aniline the aromatic ring of the phenol is hydrogenated in a slow reaction step the further reactions of oxygen elimination and saturation of the hydrocarbon fragment are comparatively fast.

With respect to hydrodeoxygenation of fuel oils it is concluded, that high hydrogenation activity of the system is desired, whereas hydrogenolysis activity can be kept low.

1.2.2 Catalysts for the hydrotreatment of heavy oils and their possible uses and restrictions

The hydrotreating catalysts, Co/Mo, Ni/Mo and Ni/W on supports as Al_2O_3 or Al_2O_3/SiO_2 have been introduced to heavy oil upgrading by Matthias Pier during his pioneering work on process development for coal liquifaction, in the 1930ies years. Since then only gradual improvements of the catalytic system have been achieved.

For removal of sulfur the $CoMoS/Al_2O_3$-System is best suited because it shows the highest activity at relatively low temperature /26/. Additionally the unwanted hydrogenolysis activity is low. During reduced crude hydrodesulfurization catalyst activity declines because of deposition of metals (Ni, V) on the surface and pore blocking due to coking of asphalthenes. Wide pore type catalysts have been developed for this application.

Removal of nitrogen needs higher reaction temperature and higher pressure than hydrodesulfurization, because the hydrogenation of isolated carbocyclic aromatic rings is involved. At higher reaction temperature NiMoS-catalysts are more active than CoMoS-catalysts /26/. Particularly for refining of coal derived oils which have elevated nitrogen contents as compared with petroleum fractions NiMoS-catalysts are best suited. /31, 32/.

Removal of oxygen is also performed adventagously with NiMoS-catalysts because again hydrogenation of isolated aromactic rings of the phenols has to be achieved /33/.

When mild hydrocracking is being desired to accompany hydrofining in order to produce lower molecular weight products than a catalyst support of adequate acidity, as Al_2O_3/SiO_2, is applied.

Such catalytic systems do yield additionally the reactions of bifunctional hydrocracking and hydroisomerization with olefinic hydrocarbons and carboniumions as reaction intermediates /34, 35/. Hydrogenation- and cracking-activity of the system have to be adjusted very properly for the actual purpose of application.

1.2.3 Comparision of hydrogenative and thermal routes of heavy oil processing

When comparing hydrogenative with thermal routes of heavy oil processing several aspects have to be taken into account:

- product distributions
- product qualities
- availability of appropriate processes
- feedstock properties
- investment costs
- production costs
- environmental impact

This complexity of the matter suggests no simple general solution but only best individual approaches.

Product distributions of the hydrogenative route can principally be regarded as favourable because of high selectivity and flexibility of the processes, high purity of products because of hydrofining properties of the catalytic conversion and high hydrogen to carbon ratio of the products. Thermal conversion generally produces a solid product (coke) in addition to liquids and gases and the yields of liquids are lower.

Product quality for the hydrogenative routes is generally superior to that of thermal routes. Products from thermal conversion are of unstable and unsaturated nature and need further upgrading. The yield of low value fuel gas is normally higher and particularly the coke being obtained is often only of low value because it contains much of the sulfur and the metals which were present in the heavy oil feedstock.

Thus the approach of fludized bed coking (Flexi coking) combined with burning and gasification of the coke and offgas and fuel gas purification or the Lurgi process which uses an inert circulating heat carier are favourable because no coke is being produced and no pollution of the environment encounterred.

The resently commercially most successful process of thermal residual oil conversion to coke and liquid plus gaseous fuels is that of delayed coking, because of its comparatively low investment and production costs. However, large scale application of this process could lead to a production of such amounts of coke, that these were not marketable. Proven processes of the hydrogenative type for heavy fuel oil conversion are available (see sections 1.3.1, 1.3.2, 1.3.3, 1.3.4) and the approach is particularly recommendable with respect to product quality, flexibility and nonwaste operation. However, relatively high costs are involved for hydrogen production and high pressure operation.

Feedstock properties are of minor technilogical impact for the coking processes and even the heaviest oils with high contents of asphaltenes, sulfur and metals can be processed. Feedstock properties must contrarily taken into account in detail for the hydrogenative route and catalyst and reaction condition adjusted properly.

Another environmentally particularly beneficial route of heavy fuel conversion, which is however not subject of the present expertise, is gasification with oxygen and steam at medium respectively high pressure. Commercial processes (Shell or Tecaco partial combustion processes) are available. All of the sulfur is being recovered as H_2S (and mainly converted to elemental sulfur) from the raw gas. Asphaltenes and metals in the feed don't affect the process. The clean synthesis gas can then be the feedstock for fertilizes and any high quality fuel (Otto motor and diesel motor fuel) or basic chemical (small olefins, aromatics, oxygenates etc.). This refers also to the modern area of fundamental research and process development of "C_1-Chemistry". Here not only heavy oils but also coal of any quality (high in ash and sulfur or lignites and hard coals which are not suited for hydrogenation) can be the ultimate organic matter which is being used. The actual option for one of the competing nonwaste technology routes is thus particularly governed by the availabilty of the different fossil fuels in a country

1.3 Examples of modern processes of heavy oil conversion and their major ecologic and economic relevance

As has been mentioned in chapter 1.2 the deep conversion of petroleum is based on its hydrogenative or nonhydrogenative cracking of the high-boiling and residual fractions for obtaining maximum yields of lower-molecular weight products which can be used as motor fuels, fuel oils, petrochemical feedstocks and other applications. The main reasons why numerous deep conversion processes are used in modern refineries are saving of crude oil to a maximum extend

- producing of high-quality products which can be used without pollution of the environment

- and, at the same time a sustantial increase in overall economy and flexibility.

For demonstration of these statements the following typical processing routes of high technical and ecological importance have been selected:

a) Mild hydrocracking of high-boiling petroleum fractions as an efficient and flexible process for producing low-sulfur fuel oils, components of lubricating oils, feedstocks for steam cracking and FCC and for producing of high-quality motor fuels;

b) Hydrovisbreaking of residual petroleum fractions for obtaining higher conversion rates and better product qualities than via visbreaking;

c) Desulfurization of residual oils, especially the combined process of solvent deasphalting and hydrorefining of deasphalted oil;

d) Direct coal liquefaction as a most important case of production of fuels and carbochemicals from substitute petroleum resources.

1.3.1 Mild hydrocracking as to be obtained in existing HDS-plants

Modern hydrocracking offers several possibilities for producing refinery products of excelent quality and valuable petrochemical feedstocks. The most important hydrocracking conversion routes are illustsrated in Fig. A-4 /1/.

Naphtha	→ **LPG**
medium distillates	→ **Gasoline**
Vacuumgasoil	→ **Gasoline**
	→ **Medium distillates**
	→ **Lubricating oil**
	→ Steamcracker-feed
	→ Mild Hydrocracking
Heavy oils	→ Distillates
Residues	→ Distillates

Fig. A-4: Alternatives of hydrocracking applications

The main reactions of the complex hydrocracking process are as follows:

- Hydrogenation of
  - olefins
  - monoaromatics
  - polyaromatics
- Hydrogenolysis of
  - organometalic compounds
  - sulfur compounds
  - nitrogen compounds
  - oxygen compounds

Hydrocracking and Hydroisomerisation of
- aromatics, hydroaromatics, (hydrodealkylation)
- naphtenes (hydrodecyclisation)
- paraffins (hydrocracking)
- paraffins (hydroisomerization)

The course of these reactions depends on the severity of the process i. e. it can be influenced by reaction conditions (temperature, pressure, space velocity, H_2/HC-ratio) and also by the type of the catalyst.

The main difference between conventional hydrocracking (HC) and mild hydrocracking (MHC) of vacuum gas oils is the control of catalyst and reaction conditions in such a way that hydrodealkylation, hydrodecyclisation and hydrosplitting of different hydrocarbon groups proceeds with most selectively and high flexibility.

The operating conditions may vary within a wide range /2/:

LHSV	0.5 - 1.5 h^{-1}
temperature	350 - 450 °C
hydrogen partial pressure	4 - 6 MPa
hydrogen recycle	250 - 500 m^3/m^3

The influence of reaction conditions on conversion rates is evident from Fig. A-5. Owing to cracking reactions and aromatic ring saturation, the consumption of hydrogen is higher than in the case of pure VGO - HDS, nevertheless it is lower in comparison with other types of hydrocracking (cf. Fig. A-6).

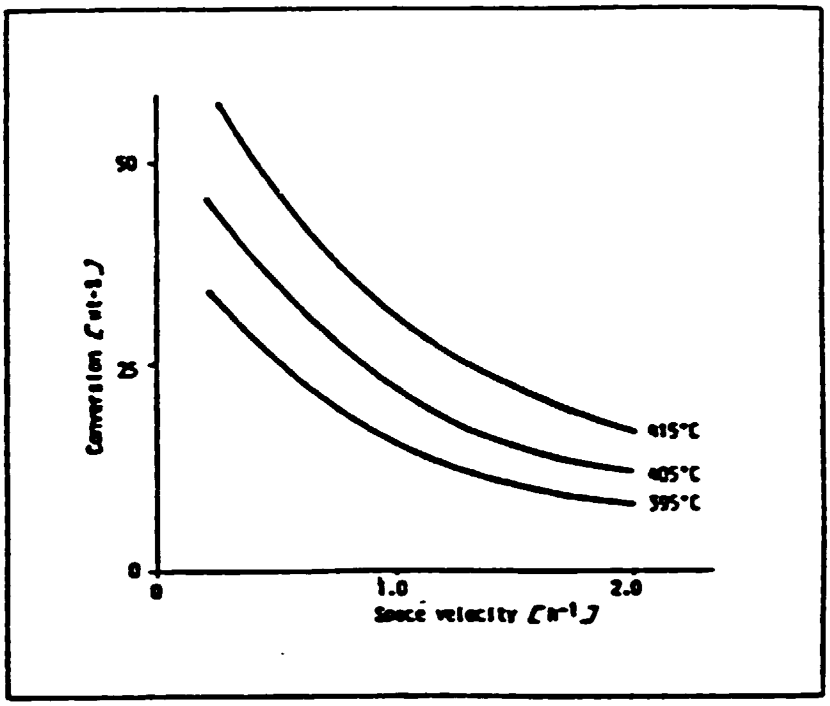


Fig. A-5: Effect of reaction conditions on VGO conversion

The field of application of MHC is relatively extensive:

- production of low-sulfur components of fuel oils;
- production of high-quality components of lubricating oils;
- production of diesel fuel and jet fuels of exellent quality;
- production Of FCC feeds;
- production of steam-cracker feeds.

It is particularly attractive, that MHC allows the use of existing HDS-units, i. e. there is a possibility of improving substantially the economy of a refinery when VGO - HDS overcapacity exists. The use of an existing HDS plant for MHC affords only low capital expenditure and slight engineering modifications.

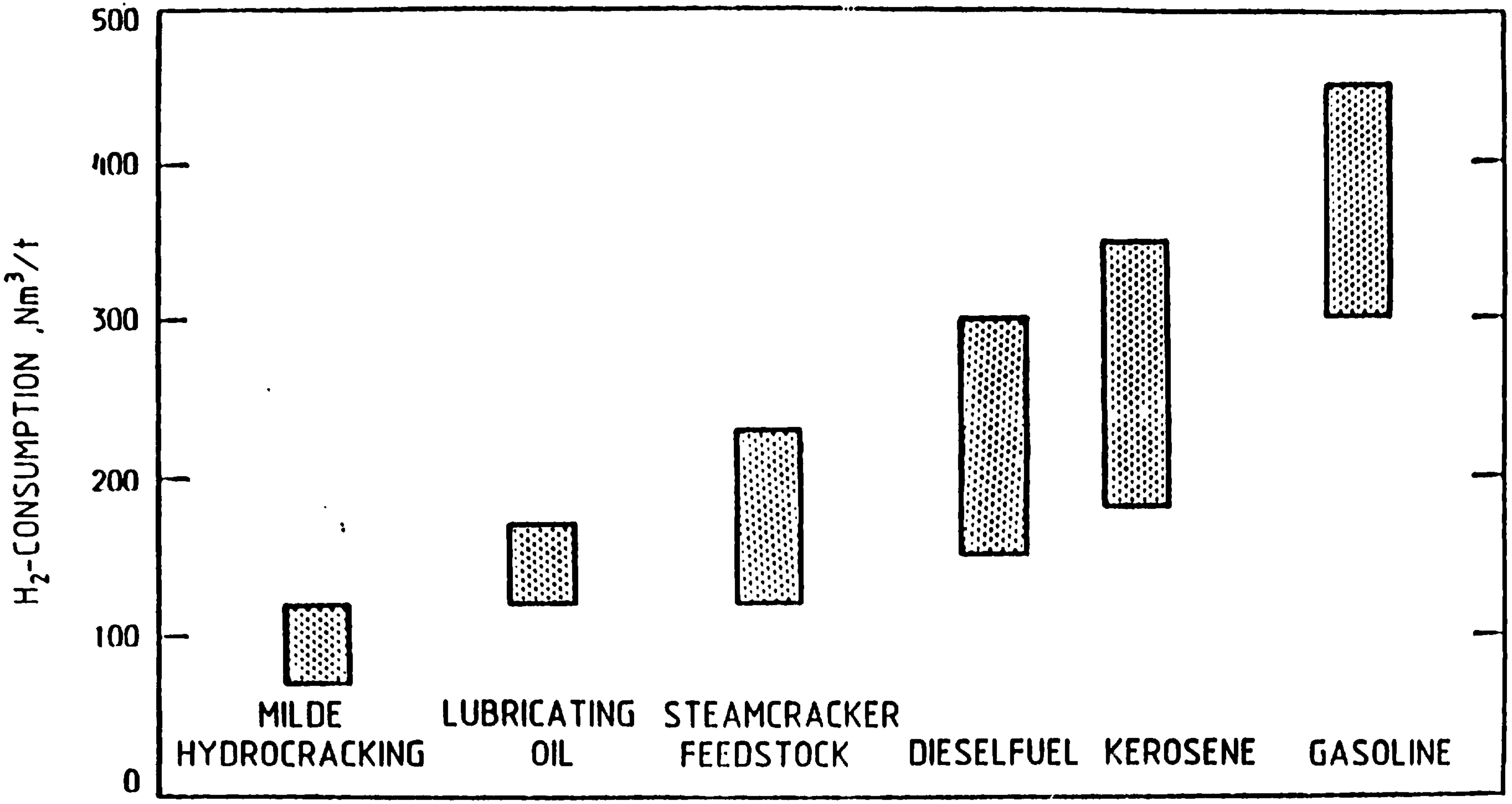


Fig. A-6: H_2-consumption in hydrocracking

The most important parameter influencing the performance of the MHC process is the choice of high efficient the catalytic system, which has to ensure simultaneously high hydrodesulfurization and hydrocracking rates.

E. g. BASF /2/ developed two hydrocracking catalysts of outstanding performance: M8-81 and M8-80S. Both catalysts contain Ni and Mo as active components supported on amorphons alumo-silicate with a moderate acidity. M8-81 is generally used in combination with a HDS catalyst of CoMo or NiMo type, the Catalyst M8-80S is characterized by both, hydrodesulfurzation and hydrocracking activity and it can be used without pretreatment catalyst.

Similarly, in the IFP-process the combination of the HDS catalyst HR 306 and the MHC catalyst HTH 544 /3/ is used.

Halder Topsøe A/S has developed special catalysts for MHC which, if the critical reaction temperature is not exceeded, exhibit high activity and stability /4/.

As an example of typical application of MHC in modern petroleum refining, the hydroprocessing of FCC feeds is discussed in more detail in the next chapter.

1.3.2 Hydroprocessing of catalytic cracker feeds

Commercial fluid catalytic cracking (FCC) today is of a high standards of technology particularly due to the major innovations outlined below:

I. Zeolite-type catalysts of high efficiency allow for a substantial increase in reaction rate and octane number of the gasoline;

II. The reaction now proceeds already in the riser allowing for shorter residence times with a narrower distribution;

III. Catalysts with special additives are made more resistant to the deactivating effects of metals present in the feedstock. The SO_2 and CO concentrations of the offgases from catalysts regeneration are also reduced.

Hydropretreating of a vacuum distillate as a catcracker feedstock increases the total conversion as well as yield and quality of gasolines obtained. Hydrotreating is particularly beneficial when residual fuel oils are used as part of the feedstock.

In this chapter, attention is being paid to hydroprocessing of catalytic cracker feeds. The following reasons create improved properties of the feedstock due to hydrogenation:

I. The content of aromatic compounds is reduced substantially and the content of paraffinic and naphthanic components increased correspondingly, thus cracking is facilitated and higher yields of gasoline are obtained.

II. Especially the polycyclic aromatic compounds are hydrogenated, making the mixture more resistant to coking; the aromatic compounds remaining after this hydrogenative treatment are mainly naphtheno aromatics which on hydrocracking, yield monocyclic aromatic hydrocarbons. Coking deposits are reduced and formation of aromatic gasoline is favored.

III. Hydrorefining reduces substantially the content of resins in the raw material, particularly in mixed feeds these most significant coke-precursors are being converted.

In principle, there are two modes of hydrotreating of vacuum gas oil (VGO, b. p. 623 - 823 K):

1. High-pressure hydrodearomatizing /7, 8/, which is associated with hydrorefining (desulfurization). The overall content of aromatics is reduced dramatically and the composition of the oil according to instance classes is fundamentally changed (Fig. A-7).

2. Mild hydrocracking /6, 7, 8/ where the reactions are similar, however, additionally there is a more pronounced reduction of the mean molecular weight (Fig. A-8).

Effective desulfurization is a positive feature of both these processes. As the degree of desulfurization is improved the cracking performance of the VGO is improved (see Table A-4). The yield of gasoline is increased and the deposition of coke on the cracking catalyst is minimized. The petrochemical useability of the by-products from cracking is improved: The amount of alkylate obtainable from the C_4 fraction is raised and the fraction of i-butylene is significantly increased.

Hydrotreating of VGO as a feed for catalytic cracking is a highly efficient process. This is illustrated by the operating data e. g. from the ÖMV refinery in Schwechat/Austria /5/: Hydrotreating proceeds on the hydrodesulfurization catalyst (HR 306) and a mild hydrocracking is obtained on the catalyst (HTH 544). The unit is operated under conditions as shown in Fig. A-9. The process is very flexible as depending on variation of the reaction conditions (cf. Fig. A-10).

Table A-5 lists the properties of the VGO feedstock and its product after mild hydrocracking. Table A-6 given a comparison of the cracking yields for the two feedstocks (reactor temperature 518 °C, pressure 0.16 - 0.18 MPa, regenerator temperature 740 °C, catalyst/oil ratio 5.6 - 5.9). The gasoline from the hydrogenated feed has a slightly lower RON because of a lower content of aromatics. The recycle oil has a substantially lower sulfur content due to hydrogenation of the feed, the anilin point is higher (lower content of aromatics) the Diesel index is also increased making it suitable for blending as a Diesel fuel component and a fuel oil of lwo-sulfur content.

Profitability of catalytic cracking is comparatively high with the hydrotreated feedstocks. For instance, under the conditions prevailing at the ÖMV petrochemical works in Schwechat the increase of total daily profit due to using hydrogenated FCC feedstocks is 28.5 % /9/.

Hydropretreating of FCC feedstocks also turns out to be of ecological importance: sulfur emissions are reduced in the use of these products as motor fuels or of the cycle oils as a fuel. The same applies to the catalyst regenerator of a cracking plant where a substantial reduction of SO_2 emission is achieved.

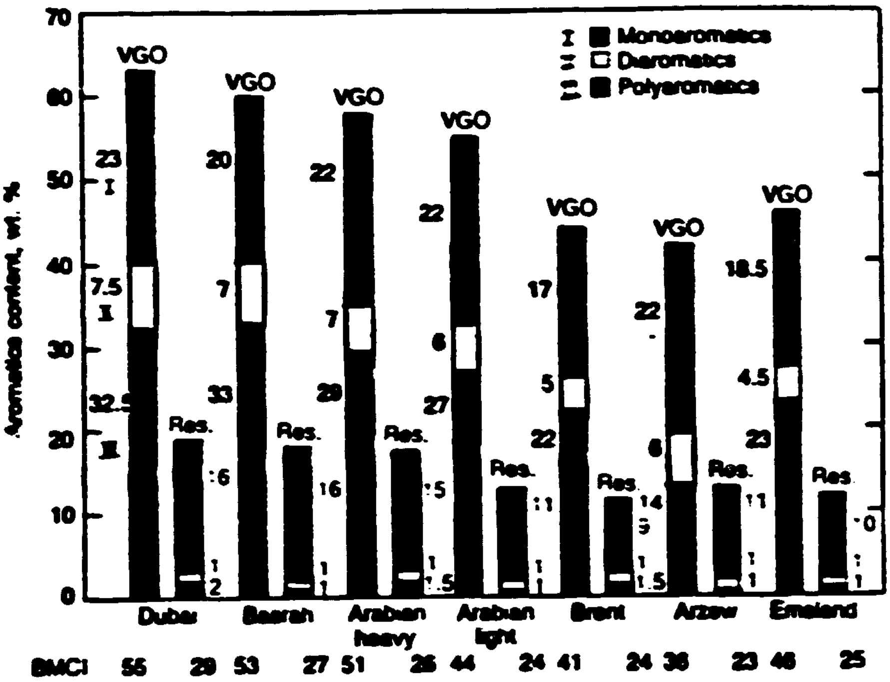


Fig. A-7: Yields of products, aromatics reduction in residue (>623 K) and group composition changes for hydrodearomatizing of different feedstocks (Results by BASF /7/).

Reaction conditions:

catalyst	$Ni-Mo/Al_2O_3$
pressure of H_2	15 - 20 MPa
temperature	613 - 653 K
WHSV	0,2 - 0,5 kg/liter/hour
gas/oil	0,3 - 2,0 cu.m/kg

Typical yields (wt-%):

C_1 - C_4	0.5
C_5 - 353 K (light gasoline)	0.5
353 - 458 K (heavy gasoline)	2.0
458 - 553 K (kerosine)	4.5
458 - 623 K (Diesel oil)	11.0
residue > 623 K	86.0

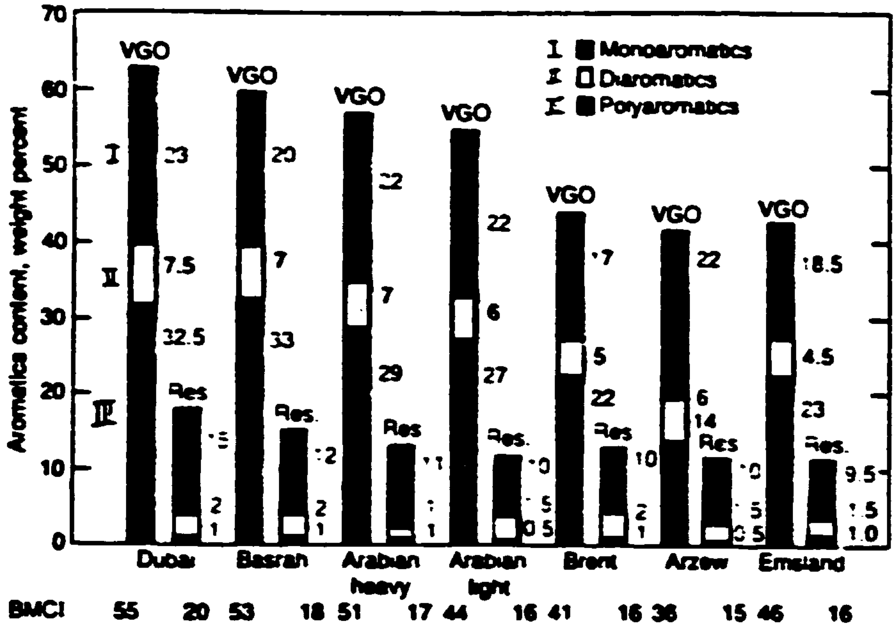


Fig. A-8: Yields of products, aromatics reduction and group composition changes obtained from MHC processing of different VGO feedstocks. (Results by BASF /7/):

MHC conditions:

catalyst	Ni-Mo/aluminosilicate
pressure of H_2	8 - 13 MPa
temperature	643 - 693 K
WHSV	0.6 - 1 kg/liter/hour
gas/oil	1 - 2 m^3/kg

Typical yields (wt-%):

C_1 - C_4	2.0 - 4.0
C_5 - 353 K (light gasoline)	2.0 - 3.0
353 - 458 K (heavy gasoline)	7.0 - 13.0
458 - 553 K (kerosine)	9.0 - 14.5
458 - 623 K (Diesel oil)	20.0 - 29.0
residue > 623 K	60.0

Table A-4: Effect of VGO hydrorefining on the results of catalytic cracking

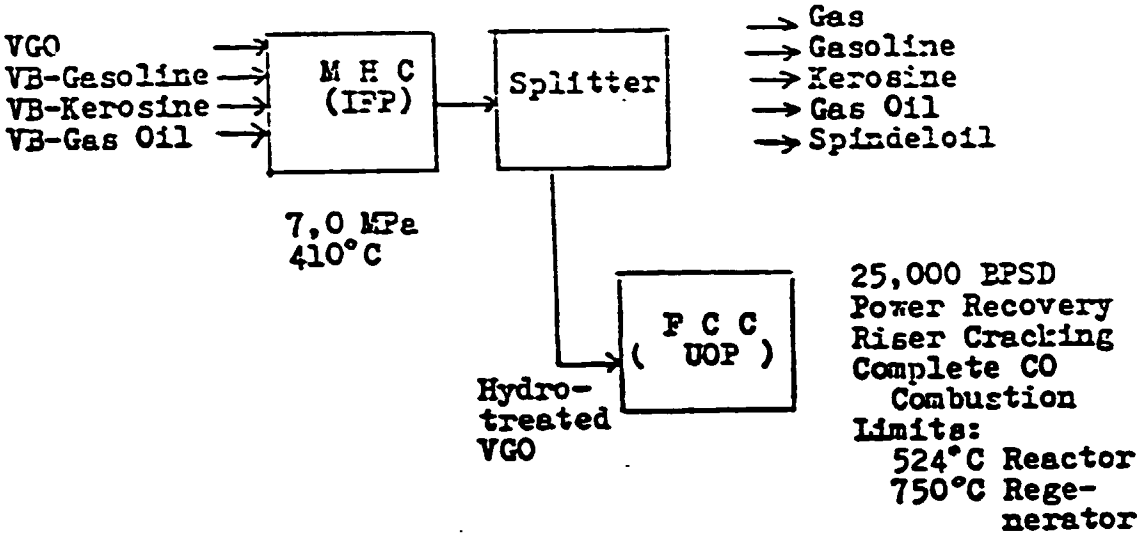
Feedstock	Untreated	Hydrorefined		
		A	B	C
S content. wt-%	2.68	0.53	0.28	0.01
Density	0.924	0.902	0.894	0.857
Total conversion, vol-%	78.1	80.7	81.7	92.0
Relative coke formation	1.0	0.78	0.76	0.43
Octane numer of gasoline (RON clear)	93.8	93.9	94.0	92.0
Potential quantity of alkylate, vol-%	33.6	37.2	37.1	41.8
Isobutene/butenes ratio in C_4 fraction, mol-%	0.68	0.72	0.79	0.81

Table A-5: Feedstock properties /5/

Type	Hydrotreated VGO	Unhydrotreated VGO
Denisty at 15 °C	0.905	0.934
Sulfur, pct wt	0.17	3.02
Basic Nitrogen, ppm	150	220
Conradson Corbon, pct wt	0.17	0.87
Aniline Point, °C	89.8	77.4
Bromine Number, g/100 g	2	4
Refractive Index 50 °C	1.4955	1.5087
Carbon/Hydrogen Ratio	6.67	7.02
Viscosity, cSt 50 °C	35.3	57.6
100 °C	-	10.2
Vanadium, ppm	0.17	1.2
Nickel, ppm	0.03	0.2
Iron, ppm	0.3	-
Copper, ppm	0.03	-
UOP-K	11.95	11.60
Distillation D1160 °C		
5	368	351
10	393	385
95	550	551
99	583	580
Elution-Chrom, pct wt.		
Anon Aromatics	55.9	44.2
Aromatics	43.6	52.8
Resins	0.5	2.8
Brandes, pct		
C_A	12.2	18.8
C_p	59.6	52.6
C_N	28.1	28.6

Table A-6: FCC yields (wt-%) /5/

Type	Hydrotreated VGO	Unhydrotreated VGO	Difference
Capacity, tons/day	3400	3200	
Gasoline EP 205 °C ASTM	57.3	49.0	+ 8.3
C_2 minus	3.9	5.2	- 1.3
Propane	1.4	1.4	0
Propylene	4.8	4.3	+ 0.5
i-Butane	1.9	2.2	- 0.3
n-Butane	0.4	0.6	- 0.2
Butenes	2.3	3.8	- 1.5
LCO, EP 390 °C ASTM	18.4	20.3	- 1.9
Clarified Oil	4.4	7.7	- 3.3
Coke	5.2	5.5	- 0.3
Conversion 250 °C			
Vol-%	78.7	74.4	+ 4.3
Wt-%	77.2	72.4	+ 4.8
Gasoline Selectivity			
Vol-%	88.4	81.2	+ 7.2
Wt-%	74.2	67.7	+ 6.5
CO Selectivity			
Vol-%	82.8	75.3	+ 7.5
Wt-%	80.9	73.6	+ 7.3
Gasoline + LCO			
Wt-%	75.7	69.3	+ 6.4



25,000 BPSD
Power Recovery
Riser Cracking
Complete CO
Combustion
Limits:
524°C Reactor
750°C Regenerator

Fig. A-9: MHC and FCC units /1/

MHC :

Catalyst: 50% HDS, 50% Mild Hydrocracking
Operating Pressure: 7,0 MPa
Operating Temperature: 410°C
Hydrogen Consumption: 7 kg / Ton FF

Feedstock:

Vacuum Gas Oil
Visbreaker Gasoline
Visbreaker Kerosine
Visbreaker Gas Oil

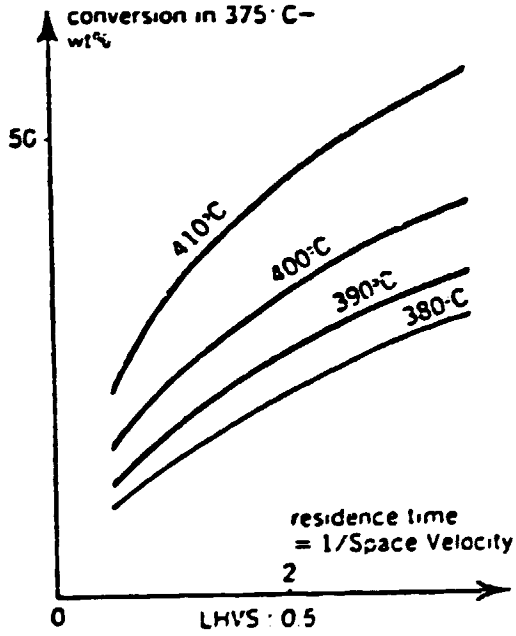


Fig. A-10: Low pressure VGO conversion with catalyst combination HR 306 + HTH 544 /1/
pH_2 = 3.5 to: 4.0 MPa

1.3.3 Hydrovisbreaking

When visbreaking of residual petroleum fractions is performed in the presence of hydrogen the main reactions are substantially influenced and their kinetics changed. In hydrovisbreaking the asphalthenes and resins are transformed to some extend into oils, which contain metals and nitrogen as porphyrins.

The following reaction scheme could be adopted for the hydrovisbreaking process /10/:

Reaktions of primary cracking:

I. Asphaltenes $\xrightarrow{H_2}$ distillates + condensed asphaltenes + gas + oils

II. Condensed asphaltenes $\xrightarrow{H_2}$ gas + coke

III. Resins $\xrightarrow{H_2}$ distillates + asphaltenes + gas + oils

IV. Oils $\xrightarrow{H_2}$ distillates + resins + gas

Reactions of secondary cracking:

V. Distillates $\xrightarrow{H_2}$ lighter distillates + gas

The concept of hydrovisbreaking is also based on the fact that the solubility of hydrogen in oil increases with pressure and temperature /11/. It operates at similar temperature and LHSV as hydrocracking and yields significantly higher conversion of the feed than visbreaking.

Hydrovisbreaking has a donor - solvent version, which is a modern development of the old Pott-Broche process. Donor-solvent-hydrovisbreaking uses a naphtenic fraction, which dehydrogenates at the reaction conditions used and produces hydrogen radicals available for the cracking reactions. The hydrogenated donor solvent fraction is then separated and recycled via a hydrogenation stage.

The application of donor-solvent principle is advantageous because it minimizes the make-up hydrogen requirement by retarding thermal cracking reactions which otherwise leads to the formation of undesired light fractions (C_4- and naphta).

For the reduction of coke formation, especially when the thermostability of the feed is low, some additives (which may exhibit a limited catalytic function at the same time) can be used in low concentration ($\leq$ 2 wt-%).

As once-trough-additives, e. g. "Bayer mass" (waste product of the alumina industry) or iron sulfide on lignite coke can be used /12/.

As an example, the Lurgi-Donor Solvent Hydrovisbreaking process is analyzed in more detail /13/:

The feedstock (vacuum residue, donor-solvent fraction and a part of the upgrading residue is heated in the presence of hydrogen (pressure 12 - 15 MPa) and enters the liquid phase reactor (soaker) upstream at a LHSV of about 0.5 - 1 h^{-1}, the reaction temperature (350 - 420 °C is adjusted according to the intended severity of the process. After leaving the reactor, the reaction mixture is cooled (to about 50 °C), the liquids are separated from the gas in a high pressure separator. Hydrocarbons in the gas phase are removed if required in a recycle gas scruber and a hydrogen-rich gas is obtained and used as the necessary make-up hydrogen and added to recycle system.

The product from the high pressure separator is split into distillates and residue (part of which could be used for H_2-production by gasification). The distillates are refined further in the hydrotreating section. Part of the 200 - 500 °C distillate is hydrogenated in a special donor-solvent generator where naphtenic type hydrogen-rich hydrocarbons are formed.

Typical results are shown in Table A-7 /13/. In this case, a low severity DSV operation for 90 % residue has been applied which avoids any coke formation or precipitation of metals.

Interesting conclusions can be drawn from the comparison of pure hydrovisbreaking and low severity donor-solvent hydrovisbreaking. In the conversion range 40 - 90 % the light hydrocarbon (C_4)-yield in donor-solvent hydrovisbreaking is only 50 % of that of pure hydrovisbreaking and similarly less hydrogen is consumend.

Intermediate distillate fractions from hydrovisbreaking can be hydrorefined in a conventional mode using e. g. 5 MPa hydrotreating for naphta upgrading and a 8 MPa process for the 200 °C + fraction.

Table A-7: Typical results of DSV of a Venezuelan heavy oil (90 % conversion of residue 500 °C + recycle ratios per 100 parts of heavy feed oil, containing 65 % of vacuum residue: 24 parts of residual recycle oil 500 °C + 14 parts of donor solvent /13/

	Heavy feed oil	DSV-product
Yields wt-% on feed:		
Inorganic gases	-	2.5
C_4-hydrocarbons	-	2.5
C_5 - 200 °C	-	20.1
200 - 500 °C	35	69.0
500 °C +	65	7.3
Chemical H_2 consumpt. (m^3/t feed)	-	152
Inspections:		
Sp. gravity (g/ma)	1.01	0.94
Av. mol. weight	470	252
H/C molar ratio	1.48	1.57*
Sulfur (wt-%)	3.9	2.66
V (ppm)	420	< 1 *
Ni (ppm)	100	< 1 *

*) in distillates 200 - 500 °C

It can be concluded that hydrovisbreaking is an efficient conversion process for upgrading of residual oils making their application much more acceptable from the ecological point of view.

1.3.4 Catalytic desulfurization of residual oils

As has been stressed before (cf. 1.2), the production of low-sulfur liquid fuels from residual oils ranks among the most important refinery processes for reducing SO_2 emissions which presently cause serious and increasingly more extensive environmental detoriation. In the introduction the principal possibilities of desulfurizing residual oils have been quoted. However, direct hydrodesulfurization on fixed bed catalysts is of limited applicability.

Among the highly efficient production routes for low-sulfur fuel oils the combination of deasphalting vacuum residues, hydrorefining of the deasphalted oil and blending of the refined deasphalted oil with other refinery streams is to be recommended.

A process to be presented below in more detail, has been developed at the Research Institute for Chemical Applications of Hydrocarbons (Czechoslovakia) in cooperation with the Bashkirian Science and Research Institute (USSR) where the deasphalting process DOBEN has been developed (14, 15). These studies performed in extended laboratory, pilot plant and industrial scale work, have been brought to the stage of actual project execution.

The process flowsheet showing also the balances for the production of fuel oils containing only 1 % S from a Romashkino crude is presented in Fig. A-11. Table A-8 lists the properties of the major fractions. Hydrodesulfurization of the vacuum distillate presents no difficulties and can be effected either by a classical route using more HDS or by application of mild hydrocracking, in order to obtain higher yields of motor fuels.

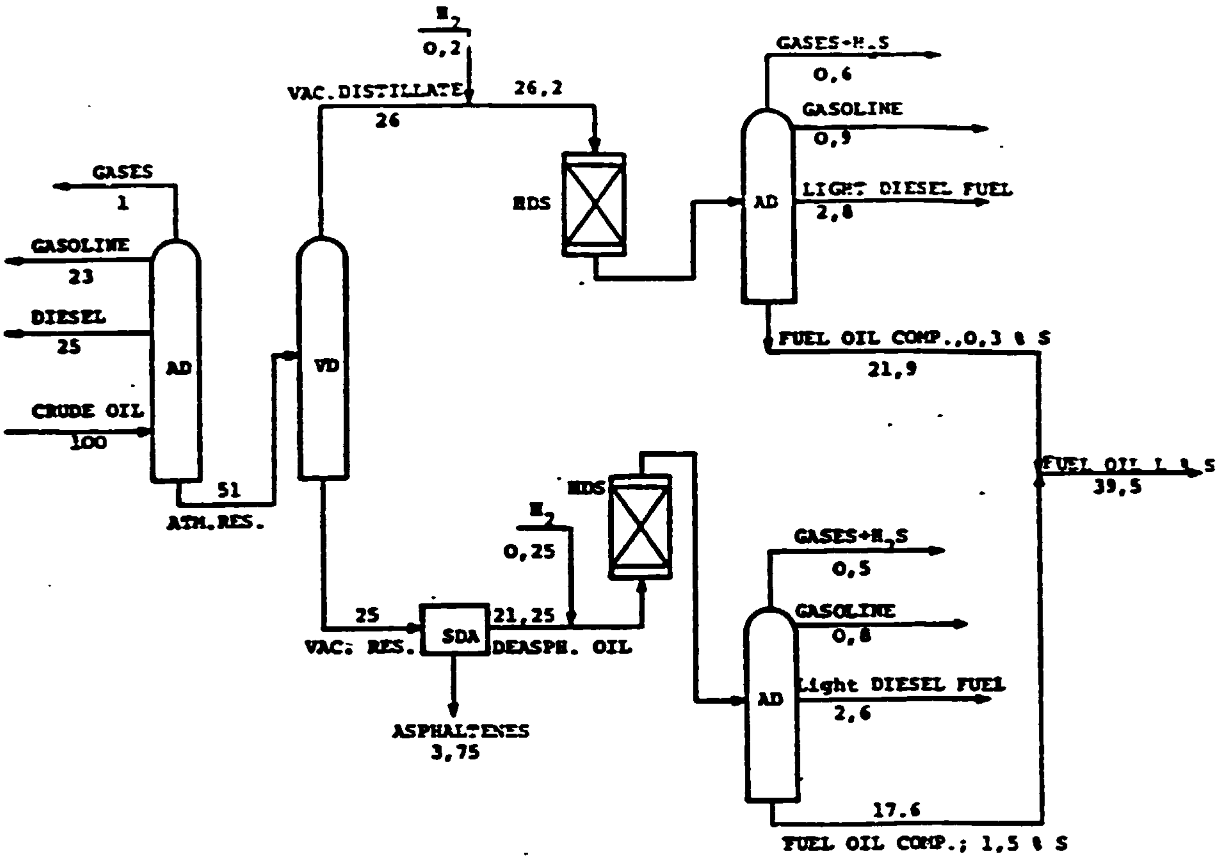


Fig. A-11: Production of fuel oils containing 1 % S by blending hydodesulfurized deasphalted oil with the vacuum distillate (balance data).

Table A-8: Characteristics of the atmospheric and vacuum residues and deasphalted oil as obtained from Romashkino crude oil

Distillation residue from Romashkino crude	Atm. resid 300 °C *	Vacuum resid 500 °C+ *	Deasphalted oil from vacuum resid
Yield, wt-%	49	25	21.5
Density at 20 °C, g/ml	0.960	1.010	0.986
Elemental compos. wt-%			
C	84.90	84.47	85.20
H	11.10	10.57	10.82
S	2.70	3.24	3.08
N	0.31	0.48	0.39
Molecular weight	510	820	740
Conradson carbon residue wt-%	10.5	18.4	12.5
Oils, wt-%	80.5	62.5	72.4
Resins, wt-%	14.6	27.0	26.8
Asphaltenes, wt-%	4.9	10.5	0.8
Ash, wt-%	0.054	0.076	0.032
Metals, ppm			
V	160	328	115
Ni	50	94	55
Fe	30	25	15
Viscosity, cSt/100 °C	52	860	220

*) Asphaltenes were determined using n-hexane, resins by adsorption on silica gel and desorption by a benzene-ethyl alcohol mixture 4 : 1. Other analyses as per CSSR standards.

A much more demanding operation is the hydrogenation of the deasphalted oil, a product which is similar to the atmospheric residue in some of its properties, however, containing a substantially lower amount of asphaltenes. Thus the hydrodesulfurization proceeds more easily and catalyst deactivation is slow. The conditions of pilot plant scale hydrodesulfurization of the deasphalted oil are outlined in Table A-9. The reaction proceeds on fixed bed catalyst (sulfides of group VI and VIII supported on a carrier having a specially modified texture); the feedstock is fed to the bottom of the reactor.

A fundamental prerequisite for successful commercial hydrodesulfurization of the deasphalted oil is the use of a highly active catalyst having a sufficient life time. Common hydrorefining catalysts for distillate feedstocks are rapidly deactivated by coking and by the metals introduced with the feed.

In Czechoslovakia, the carrier texture has been modified and other optimizing means have been taken in order to develop hydrorefining Ni-Mo and Co-Mo catalysts with substantially high resistance to deactivation. These catalysts permit desulfurization of deasphaltate (less than 1.5 wt-% S) and, simultaneously an effective metal removal (on a fresh catalyst, up to 2500 hours, the V and Ni removal is 80 - 90 %, whereas on a partly deactivated catalyst, up to 4500 operating hours, the average removal is 60 - 67 %).

The used desulfurization catalyst retains high quantities of nickel and, above all, vanadium. For example, a Co-Mo catalyst which had been used to desulfurize 2700 kg deasphalted oil per 1 liter catalyst, was found to contain 12.5 and 2.8 wt-% of V and Ni, respectively. Hence, the exhausted desulfurization catalyst represents a much more concentrated source of vanadium than the natural ores, and processes have been worked

Table A-9: Hydrodesulfurization of desasphalted oil. Reaction conditions and properties of products.

Data		Laboratory	Pilot
Temperature	°C	380 - 420	380 - 420
Pressure	MPa	10	10
LHSV	vol/vol.h	0.5	0.5
H/HC ratio	Nm^3 H_2/m^3	1000	1000
Duration of run	h	2500	2100
Hydrogen consumption	Nm^3/ton	103	85
Average product properties:			
Density at 20 °C	g/ml	0.930	0.950
Conradson carbon residue	wt-%	6.2	8.6
Pour Point	°C	- 12	+ 6
Kinematic viscosity	cSt/100 °C	13	45
Elemental analysis	wt-%		
C		86.57	85.96
H		11.52	11.45
S		1.20	1.30
N		0.34	0.39
Content of resins (silica gel)	wt-%	12.0	18.0
Content of n-C_6 asphaltenes	wt-%	2.2	1.3
Metals	ppm		
Vanadium		17	32
Nickel		13	20
Iron		15	11
Yields	w-%		
C_1 - C_4 (without H_2S)		1.6	1.4
C_5 - 200 °C		5.0	2.0
200 - 350 °C		18.0	12.0
350 - 525 °C		31.0	24.0
525 °C +		43.0	59.0

out (e. g. by Lurgi /16/) by which this vanadium can be recovered.

A special problem is the effective utilization of asphaltenes, the by-product obtained during feedstock deasphalting.

One of the possibilities, tested successfully in Czechoslovakia, is to add the asphaltenes to bitumen to be used in the construction of roads, in cases where the bitumen properties do not meet the standards asphaltene additions alter the original, unsuitable group composition of the bitumen and can improve some of its properties.

Another suitable technique of processing asphaltenes has been elaborated by Lurgi Co. in collaboration with the Venezuelan research institute INTEVEP S. A. (subsidiary of Petroleos de Venezuela S. A. /17, 18/). Deep deasphaltizing can be applied to prepare asphaltenes. The flow diagram of this process is reported in Fig. A-12. The feedstock is mixed with an aliphatic solvent (e. g., a mixture of C_5 - C_8 alkanes). Asphaltenes are precipitated in the form of fine particles and separated from the liquid. The underflow stream from the separator contains between 40 and 60 % by wt of asphaltenes and is dried to recover the solvent and to obtain the asphaltenes as a fine powder. Typical results from deasphalting a Venezuelan crude oil with hexane as solvent are given in Table A-10. High deasphalted oil yields were obtained (more than 87 % of the crude).

The asphaltenes obtained can be subjected to coking by the LR-Coking process (Lurgi-Ruhrgas /18, 19, 20/). The principle of this technology is shown in Fig. A-13. The feedstock is fed to the reactor in liquid or solid form. In the reactor the asphaltenes are mixed with particles of hot coke, which has been obtained in the process and is used as a heat corrier. The reactor is a special double screw mixer in which the feed and the heat carrier are blended.

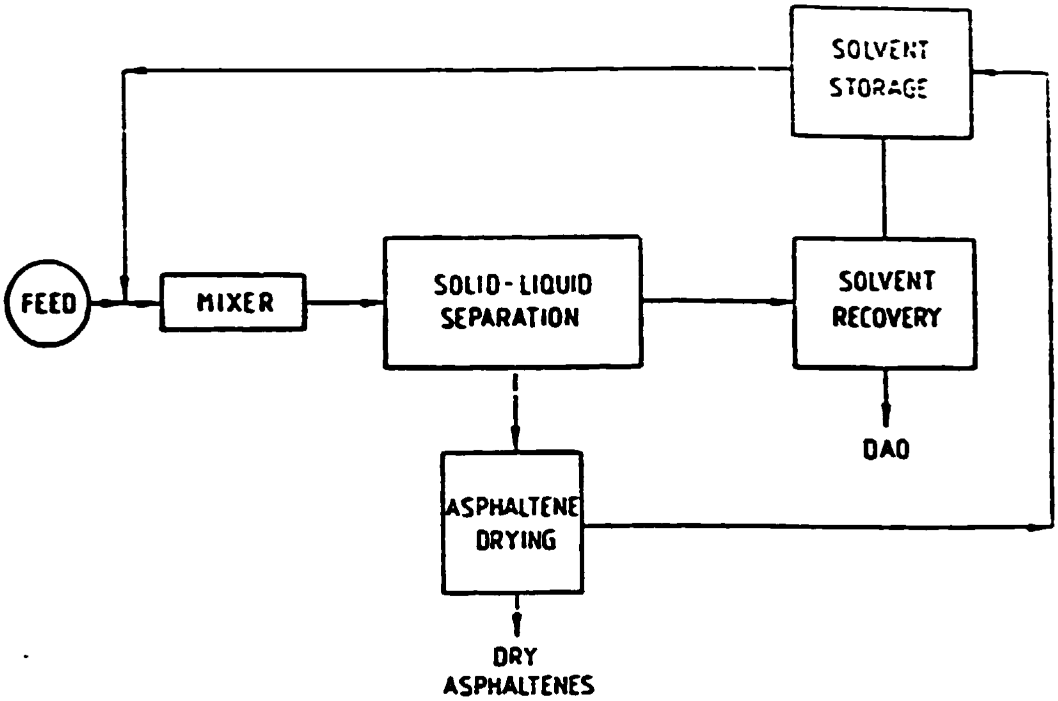


Fig. A-12: INTEVEP deep deasphalting process

Table A-10: Crude oil deasphalting

Solvent Properties	Feed	DAO	Hexane Asphaltenes
Yield % W	100.0	87.4	12.6
API Gravity	12.2	14.8	- 8.5
Specific Gravity 60/60	0.9847	0.6972	1.15
Sulphur % W	3.0	1.8	4.32
Nitrogen % W	0.54	0.40	1.58
Conradson Carbon % W	10.3	6.3	38.40
C_7 Asphaltenes % W	8.2	1.9	-
Vanadium ppm	330	165	1480
Nickel ppm	77	41	326
Viscosity			
CST + AT 140 °F	630	150	-
CST ü A 210 °F	72	31	-
Softening Point °C	-	-	220
Dropping Point °C	-	-	270

The volatile products are separated from the coke, cooled, and the vapors condensed. The fine coke particles are transferred to the liftpipe in which they are transported upwards pneumatically with an air stream and thereby partly burned, and heated up. In the collection bin the hot coke is separated from the flue gas and recycled to the reactor.

The main products of the LR-Coking process are

- coke
- coker liquids (free from heavy metals)
- high-calorific coker off-gas

Figure A-14 provides a summary of the main results of the LR-coking of asphaltenes. Clearly, the quality of the liquid products is improved as the coking temperature is lowered.

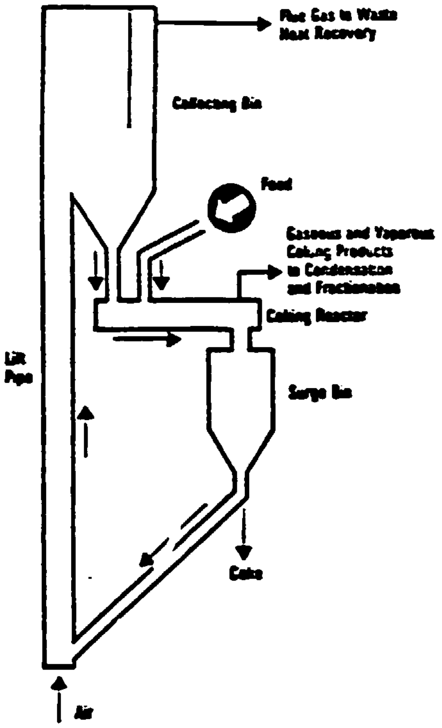
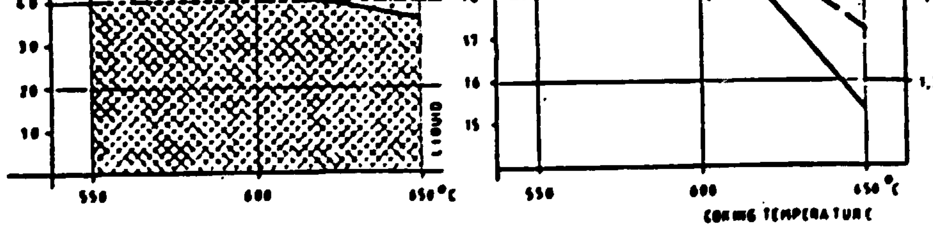


Fig. A-13: Principle of the LR-coker



COKING PRODUCT DISTRIBUTION

LIQUID PRODUCT PROPERTIES

Fig. A-14: Bench scale LR-coking of the hexane asphaltenes

However, there is a practical minimum temperature owing to the requirement of producing a coke with a low content of volatiles. This coke is a good fuel that can be burnt in power stations.

The coker liquids are stabilized by common hydrogenation processes if desirable.

Hydrotreating of the deasphalted oil can be performed as a single-stage operation but the recommended method is to apply a two-stage process; metals are removed 60 - 80 % in the first stage using special catalysts and this oil is subjected to finishing refining using common desulfurization catalysts (e. g., of the Co-Mo type).

An example of the effectiveness of deasphaltized oil hydrorefining using the INTEVEP demetalizing catalyst in the first stage and a commercial Co-Mo catalyst in the second stage, at ca. 10 MPa pressure, 375 - 400 °C temperature, and LHSV 0.4 h^{-1} is furnished by Table A-11 /17, 18, 19, 20/.

Table A-11: Deasphalted oil hydrotreating

Product Yield	Feed	Hydrotreated Product
H_2S/NH_3		2.65
C_1 - C_4		1.70
C_5 - 375 °F		6.50
370 - 650 °F		30.50
650 - 950 °F		38.40
Hydrogen Consumption SCF/BBL		1000
Liquid Product properties		
API Gravity	14.8	23
Sulphur wt-%	2.8	0.55
Nitrogen wt-%	0.4	0.31
Asphaltene C_7 wt-%	1.9	0.6
Conradson Carbon wt-%	6.3	3.0
Viscosity cST at 140 °F	150	22
Vanadium ppm	165	12

Conclusion

The alternative route of desulfurization and chemical upgrading of residual oils through a combination of deasphalting and hydrorefining of the deasphalted oil has been shown as technically feasible and profitable. The hydrogenated deasphalted oil represents a low-sulfur fuel oil or a low-sulfur component suitable for blending so as to obtain fuel oils with reduced sulfur contents.

The asphaltenes produced can be used as a blending component in the production of asphalts destined for road making and for other proposes. Alternatively it can be submitted to coking so as to produce petroleum coke suitable for use as a fuel for power stations and, on the other hand, to obtain liquid coker products which, after hydrotreating, can be used as motor fuel.

1.3.5 Direct coal liquefaction and hydrogenative processing of the primary products

Heavy oil conversion and conversion of coal to motor and heating fuels and to organic chemicals proceeds in comparable processes and coprocessing of coal and heavy oil petroleum fractions can circumstantially be particularly beneficial.

It again depends basically on the type and properties of the fossil fuel which is available domestically or could be obtained from the world free market. However fluctuations in world market energy prices, especially for petroleum are very hectic, so that it is neither reasonable nor recommandable to found any medium or long term energy political decissions on the present weakness of the world oil market. Thus the development of processes for coal hydrogenation can be very actual even today in specific cases.

Basis for any decission, if and according to which process a coal hydrogenation plant will be built, is the kind of coal which shall be converted. The ash content should not exceed the value of e. g. 10 wt-%. Accordingly South Africa produces more than 4 million tons of liquid fuels from a coal with more than 25 % ash annually via the route of coal gasification and subsequent Fischer-Tropsch CO-hydrogeantion /21/. A high sulfur content of the coal is adventageous for liquifaction. Bituminous coals of high reactivity are best suited. Lignites can also be hydrogenated successfully. However, the range of different lignite properties is very broad and its suitability for hydrogenation varies correspondingly.

Basis for all modern coal hydrogenation processes is still the classical development of Bergins and Pier (IG-Process). A flow sheet is given in Fig. A-15 /22/.

Hydrogen was then produced by means of coke gasification. The highest possible yield of oil was then achieved at pressures up to 700 bars. The residue of hydrogenation (ash and unreactive asphalthenes) was separated from the product stream by means of centrifuging, a procedure, which works not very satisfactorily. This residue was pyrolized to yield additional liquids and a remaining coke of very poor quality, containing the ash and the iron catalyst which was only deposited then.

A modern development based on the former German technology is that of Ruhrkohle and Veba, who have build a 200 t/d pilot in Bottrop and operated it successfully for several years /23/.The designed feed and product composition and the process conditions are shown in Table A-12.

Another process, related closely to the former IG-technolgoy, is that of Saarbergwerke (GfK, Gesellschaft für Kohleverflüssigung), which has been demonstrated in a 6 t/d pilot plant /24/. The process flow sheet is shown in Fig. A-16.

As compared with the classical IG scheme the following changes have been made.

- The feed slurry of coal, recycle oil and catalyst is heated partially through direct internal mixing with hot condensed reaction products.
- Separation of volatile products and residue of hydrogenation is obtained via a vacuum flash evaporization.
- The residue remains a still pumpable mass and shall be used for hydrogen production via partial oxidation. The feasebility of this process has been demonstrated successfully by Ruhrkohle/Ruhrchemie in their high pressure partial oxidation pilot plant which has been designed for coal gasification /25/.

The adventages of this use of the hydrogenation residue are that of an perfectly nonwaste technology approach. The reaction pressure can be taken as only about 300 bar, because

Table A-12: Feed and products (design) and process conditions of the coal oil pilot plant Bottrop /23/

		t/d
Feed:	Coal (m. a. f.)	200
	Ash	10
	Catalyst	8
	Hydrogen	12
		230
		t/d
Products:	Gases (C_1- C_4)	40
	Light Distillate	26
	Middle Distillate	66
	Residue	80
	H_2O, CO, CO_2, H_2S, NH_3	18
		230
Process Conditions:	Pressure	300 bar
	Temperature	485 °C
	Spec. Throughput	0.5 $t/m^3 \cdot h$
	Solids Concentration in Slurry	42 %

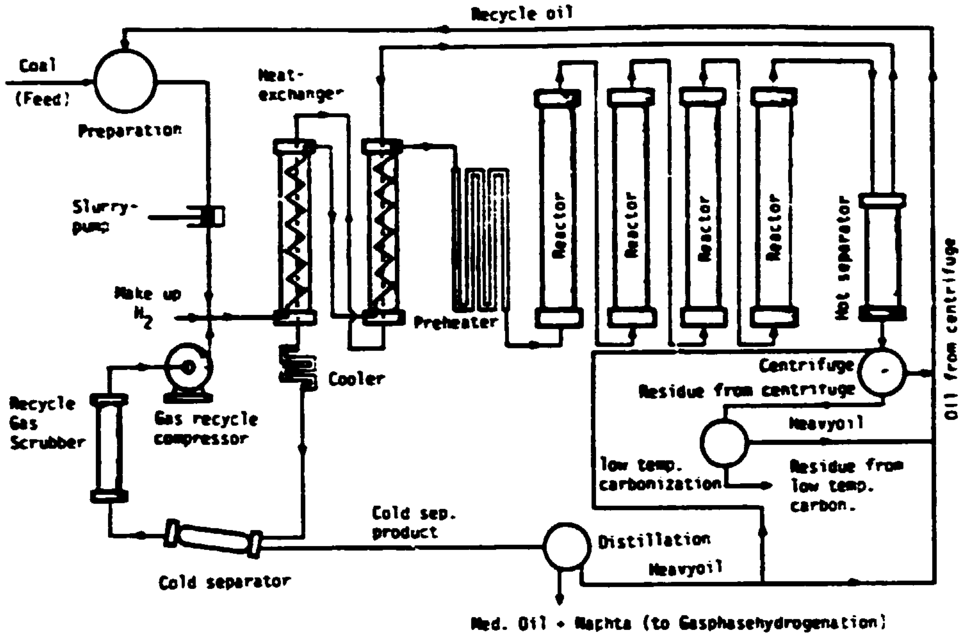


Fig. A-15: Flow sheet of the IG process

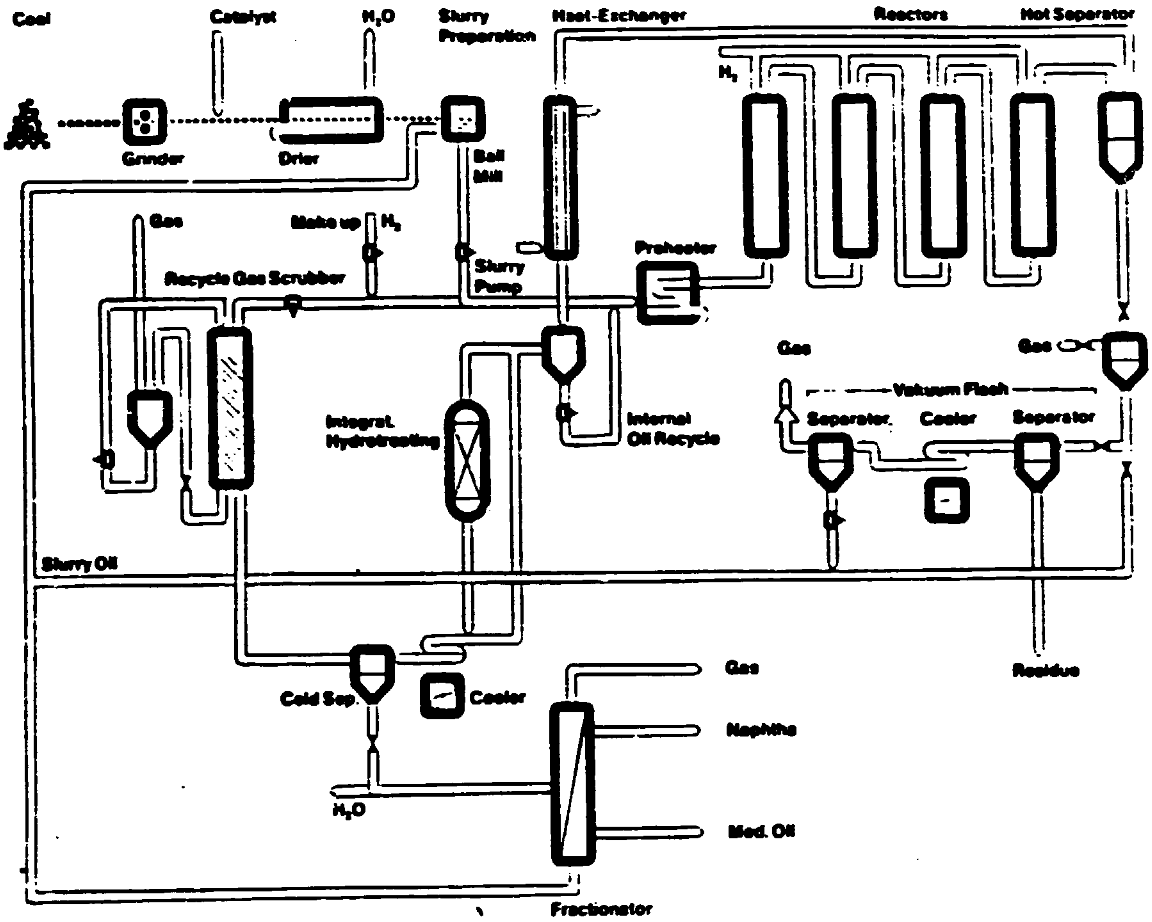


Fig. A-16: Pilot plant for coal liquefaction simplified flow diagramm (Saarbergwerke /24/)

nonreactive asphalthenes are no longer recycled to the reactor.

Following results have been published.

Table A-13: Composition of the bituminous coal (w-% on a dry basis)

ash	6.2
volatiles	37.2
Carbon	77.8
Hydrogen	5.2
Nitrogen	1.6
Sulfur	1.0
Chlorine	0.5

Table A-14: Product composition (in wt-% of the dry an ash free feed coal

C_1 - C_4		17.9
Oil		51.7
C_5 -200 °C	= 14.2	
200 - 325 °C	= 34.9	
> 325 °C	= 2.6	
Bitumen		21.0

The same pilot plant has been used for coprocessing of coal together with a residual mineral oil. As shown in Table A-15 the yield of distillable oil is substantially increased and consumption of hydrogen lowered. If one assumes the yield of oil from coal to be the same as when processing the coal individually then the degree of conversion of the residual oil to distillable oils amounts to 80 %.

Table A-15: Product yields from coprocessing of bituminous coal (83.7 wt-% maf) coke oven tar (7.8 wt-%) and residual oil from heavy oil hydrogenation (6.5 wt-%). (Values given in wt-% of the feed)

C_1 - C_4		15.9
Oil yield		57.0
C_5 -200 °C	12.8	
200 - 325 °C	27.7	
> 325 °C	16.5	
Bitumen		19.1

Typical data characterizing the product oils as according to the coal described in Table A-13 are given in Table A-16.

Table A-16: Characterization of the oils obstained by coal hydrogenation

	C_5 - 200 °C	200 - 325 °C	> 325 °C
sp. Gr. kg/m^3	855	977	1010
Mol. weight kg/kmol	109	166	235
Elemental compos. wt-%			
C	83.4	86.6	89.3
H	11.3	9.4	7.7
N	0.6	1.0	1.5
O	4.7	3	1.4
S	0.036	0.04	0.06

Reaction conditions for running the pilot plant were given as:

Feed coal	3.1 - 6 t/d
Temperature	460 - 483 °C

It has also been tested to conduct the refining of the hot volatile products from coal slurry phase hydrogenation directly. After condensing some of the higher molecular weight compounds in a hot trap, the product stream is being fed to a refining reactor. The flow sheet of this process mode is shown in Fig. A-17. Results as compared with conventional refining of the products are given in Table A-17.

Table A-17: Characterization of oil from coal hydrogenation as obtained and after refining (A in situ refining, B refining results by BASF, /26/

	A: In situ refining		B: Convention, refing	
	feed oil	product	feed oil	product
sp gravity, kg/m^3	960	870	950	860
mass per mol, kg/mol	157	150	140	130
Analysis (wt-%)				
C	86.7	87.7	85.9	87.3
H	9.8	12.2	9.7	12.7
N	0.7	0.1	0.8	0.0003
O	2.7	0	3.5	0
S	0.06	0.004	0.05	< 0.0001

Pyrosolprocess

Saarbergwerke have also anounced a new process of coal liquefaction in which the bituminous coal is hydrogenated only midly to an uptake of hydrogen of about 2 wt-% and the heavy oil together with the suspended solids is fed to a hydrocoker. Fig. A-18 shows the product composition as a function of severity of reaction conditions respectively the consumption of hydrogen.

Additionally the maximum content of ash of the feed coal is given as a function of severity of conversion.

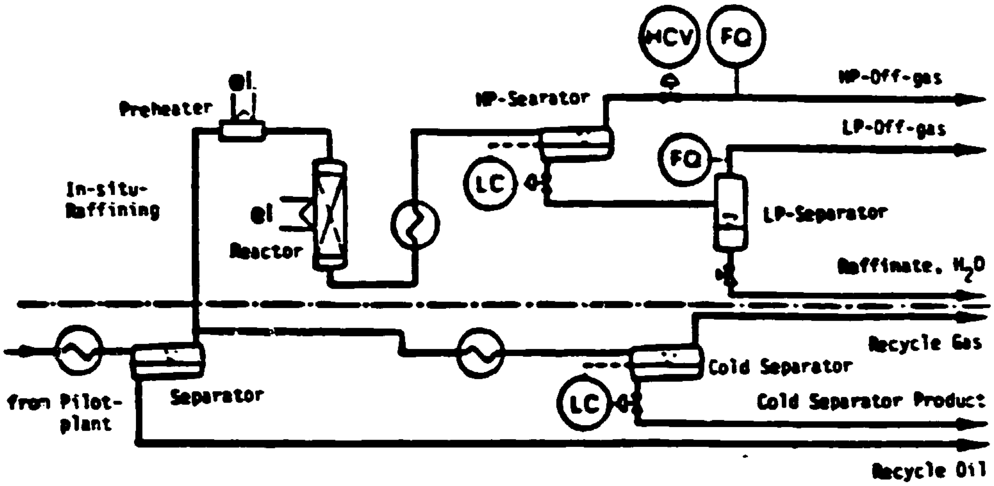


Fig. A-17: Flowsheet of the In-situ-raffination /24/

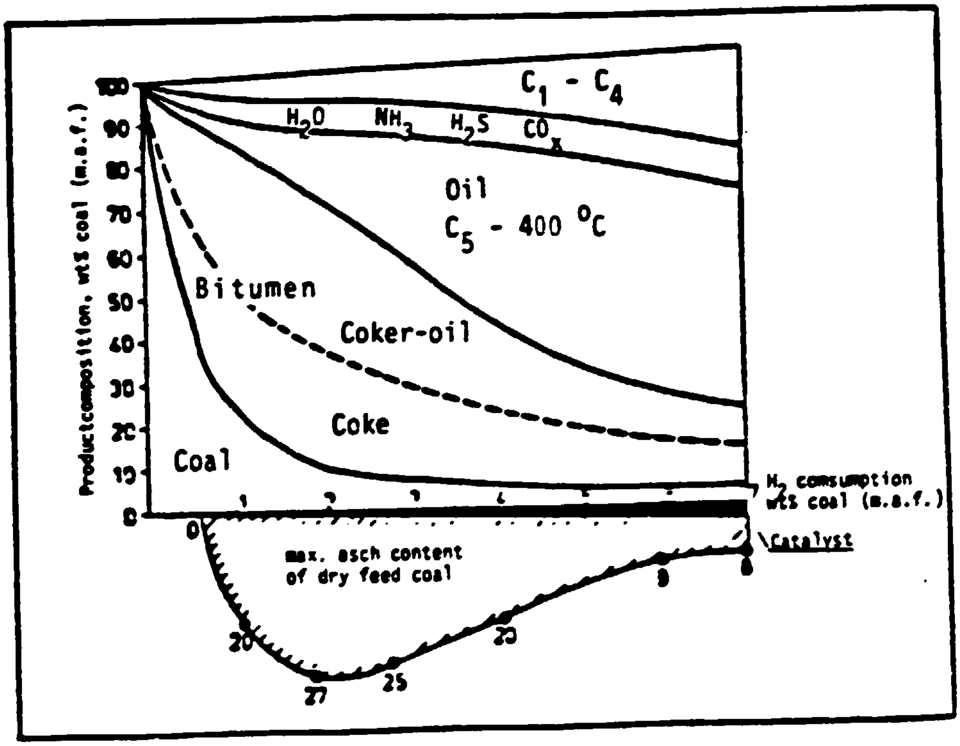


Fig. A-18: Product composition of the coal hydrogenation as a function of the degree of hydrogenation (H_2-consumption)

The adventages of this process are

- less hydrogen consumption
- higher yield of oils
- and the possibility of converting cheaper coals with higher ash content

Fig. A-19 shows the flow sheet of this process.

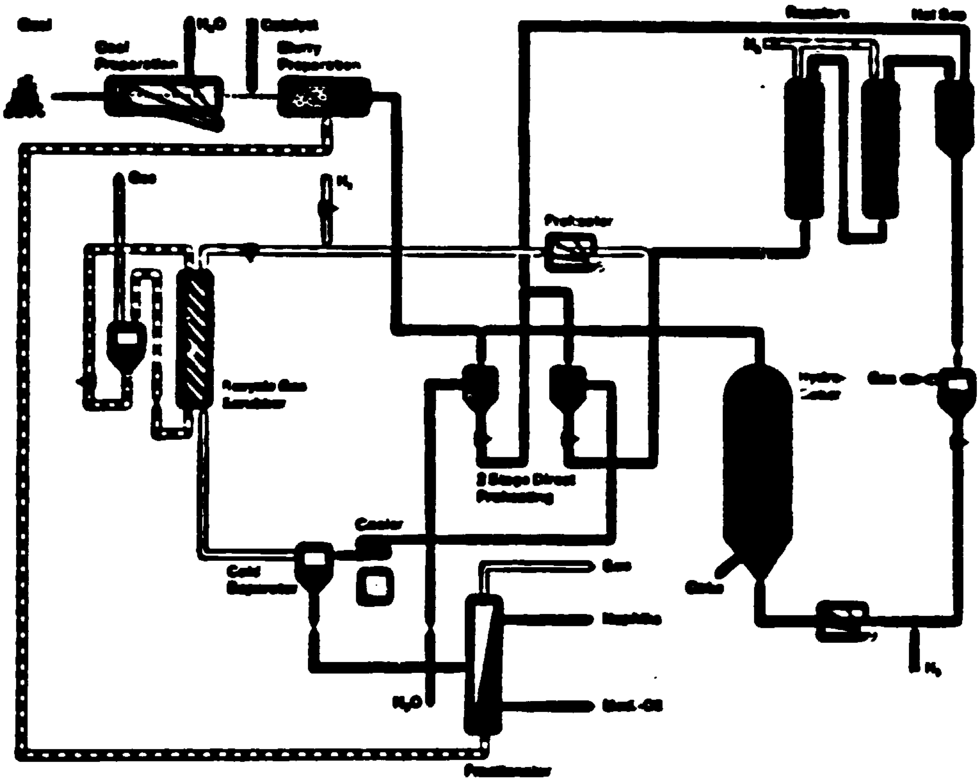


Fig. A-19: Pyrosol process for coal liquefaction. Simplified flow diagramm /24/

Salzgitter/Imhausen high pressure process

In this processes the reactor consists of a long high pressure tube (256 m) the ratio of length to diameter is ca. 10,000. The pressure range is indicated as 700 - 1500 bar. A pilot plant with a capacity of 75 to 220 kg/h feed coal has taken into operation in 1984 in Lahr (FRG).

The expected advantages of this process have been described as follows:

1. High specific through put due to relatively high reaction temperature and pressure. The high reaction temperature at shorter space time is possible without coking due to the high partial pressure of hydrogen.

2. Reduced formation of hydrocarbon gases and asphaltenes because of high reaction pressure and short space time.

3. Increased selectivity of oil formation due to the uniform residence time distribution as pertinent for the tube reactor.

4. Increased reaction rates because of high concentration of dissolved hydrogen.

5. Reduced tendencies of coking and formation of diposites in the reactor because of the high hydrogen partial pressure and the relatively high linear velocity of the reaction mixture and the simple geometry of reactor.

BCL-Process (Brown Coal Liquefaction Process)

A 50-ton-per-day pilot plant has been built and is being put into operation at Morwell (Victoria, Australia). This process has been developed by Nippon Brown Coal Liquefaction Co., Ltd.

The specific features of this process which spezifically take into account the properties of brown coal feed material are the following:

1. Deweeting of the coal is obtained via evaporation at 140 - 200 °C after preparing a slurry with the organic solvent.

2. Hydrogenation is performed in a conventional reactor (disposable catalyst added to the slurry, 430 - 460 °C, 150 bar). However the recycle solvent being used is partly the

hydrogenated middle distillate and hydrogenated deashed oil with favorable hydrogen donor properties.

3. Deashing of the liquid product is obtained with the help of a diluting solvent. In a settler the ash and the catalyst form a sludge together with the preasphaltenes. The sludge from the settler bottom is fed to a gasifier.

In all of the modern coal liquefaction processes the present requirements of a nonwaste technology are taken into account.

Locations for hydrogenation plants will be particularly dictated by the availability of cheep coal as in Australia, Canada, USSR, China, USA or Columbia.

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2. CHEMICAL USES OF SUFLUR AND HYDROGEN SUFLIDE AS OBTAINED FROM THE HYDROTREATING PROCESSES

2.1 Introduction

The traditional use of sulfur is for the production of sulfuric acid. About 90 % are consumed for this purpose. The remaining 10 % are used in paper industry, agriculture, for production of some important thio-organic chemicals, and elsewhere.

The main sources of elemental sulfur are as follows:

- (Frasch) mined sulfur
- hydrogen sulfide from natural gas
- hydrogen sulfide or sulfur obtained by removing sulfur from petroleum products and other perspective substitutes of petroleum as tar sand and oil shale
- sulfur from coal gasification
- sulfur from the flue gases of power plants

The dominance of Frasch mined sulfur was passed in the 1970s by sulfur recovered from fossil fuels and these sources are likely to satisfy all demands of the various industries. For instance, in the early 1980s coal combustion was the largest individual source of sulfurdioxide emissions to the atmosphere with about 100 million tons/year, equivalent to 50 million tons/year of sulfur.

Because of increasing amounts of recovered sulfur, its new applications are very specific and attractive. The most important fields where substantial quantities of sulfur can be consumed are the following /1 - 6/

- sulfur asphalt
- sulfur concrete
- sulfur coatings
- sulfur foams
- sulfur based composites and
- special thio-organic chemicals.

Sulfur asphalt /5/ is a mixture of asphalt, mineral aggregate and sulfur. Sulfur reduces the viscosity of the asphalt and improves the workability of the paving mixture. Sulfur asphalt can be laid without rolling compaction. The increased structural strength of sulfur asphalt in comparison to conventional asphalt allows its use for reducing winter cracking and deformation of road surfaces in summer. Sulfur also improves the resistance to water stripping. Paving products of high sulfur content are very stiff so that a reduction in paving thickness may be possible. The content of sulfur in the sulfur asphalt usually varies from 25 to 35 wt-% depending on the type of mineral aggregate and its intendend use. There exist several sulfur asphalt technologies for mixing and handling (Shell, SNEA, Gulf, Bureau of Mines, Pronk, ÖMV, etc.). In principle, all these technologies include mixing of solid or liquid sulfur, hot asphalt, and hot mineral aggregate. The mixing temperature is very important because above 160 °C, sulfur starts to show dehydrogenation properties acompanied by H_2S formation which results in making the asphalt more viscous. The lowest possible temperature and contact time while preparing the final mixture are desirable from the ecological point of view, because emission of H_2S and sulfur dust, which acts irritatingly to the eyes is minimized.

Experiences hitherto acquired with the use of sulfur asphalt are very satisfactory. For example, six demonstration roads have been constructed in Austria, with best results.

Sulfur concrete /1, 2, 3/

When sulfur is mixed with the hot mineral aggregate at temperatures above 120 °C (120 - 150 °C) a concrete-like material is obtained after cooling. To decrease sulfur fragility and improve the durability of the sulfur concrete under changing weather conditions several additives have been used which modify the plasticity of sulfur and the shape of its crystals.

Several processes for the production of sulfur concrete are available (the most important ones are those of Sulfur Innovations Ltd., ÖMV and SUDIC). These technologies differ mainly in particle size distribution, type of the sulfur plastifiers being used, and in process control equipment. Important advantages of the use of sulfur concrete are as follows:

- It can be applied at temperatures below 0 °C
- It obtains its final strength very quickliy in about several hours
- It has a superior performance in corrosive environments.

Some disadvantages make the application of sulfur concrete impossible for certain kinds of constructions:

- Is looses its structural strength at temperatures above 100 °C
- Sulfur dioxide is formed on burning.

An unconventional use of sulfur is the improvement of the strength and durability of the concrete by impregnating its pores and surface with liquid sulfur. By this means the compressive strength and the resistance to the attack by salt solutions and acids is improved. Additionally water adsorption is weakened and the frost resistance being increases.

Sulfur coatings /1, 2, 3/

The high resistance of sulfur to chemical attack led to its use as a coating. Nevertheless, additives must be applied for producing coatings with excellent properties:

- Addition of unsaturated hydrocarbons or other monomers prevents the formation of the crystalline state and stabilizes the long-chain polymer modification of sulfur

- Compounds for terminating chaine propagation reactions are added to restore a low viscosity

- Fibres and other filler materials are added to increase the mechanical strength.

The main applications are as follows:

- Protection of concrete structures in corrosive environments
- Stabilization of earthworks and mineral tailings piles or dumps
- Repair material for cracks
- Coatings for irrigation ditches, retention ponds, etc.
- Coating urea with sulfur as slow release fertilizer

There are several companies and institutions which developed protective sulfur coatings: South West Research Institute, Chevron Chem. Co., ÖMV, and others.

Sulfur foams /1, 2, 3/

The main constituent of sulfur foams are:

- Chemically modified sulfur
- Foaming agent
- Special additives

The most important propertiy of sulfur foam is its high resistance to compression as compared with foams based on polystyrene and polyurethane.

The main advantage of sulfur foam is the possibility of its production on site, even under conditions of adverse weather. The foams show exellent thermal insulation properties and are particularly suited for preventing frost damages to roads.

Sulfur-based composites /1, 2, 3/

Sulfur is a suitable component of some composites, mainly used in civil engineering. For example, light and easily built structures can be erected by means of surface bonding of block-like materials. The blocks are normally stacked, and a mixture consisting of plasticized sulfur and other additives is applied to the outside surface of the wall. Such walls show higher resistance to tension than conventional walls made of mortar joining material.

Production of special thio-chemicals

Conversion of sulfur or hydrogen sulfide to special chemicals can be very advantageous and especially in integrated petrochemical plants can substantially contribute to overall economy with the possibility of making use of what originally were wastes or by-products as H_2S and sulfur. The corresponding important and challenging problems are discussed in the next chapters.

2.2 Syntheses and applications of technically important thio-chemicals

2.2.1 Survey and application of the major technically important thio-chemicals based on petrochemistry

The range of applications of the main primary thio-chemicals produced on a petrochemical basis is rather broad. A survey of applications is listed in Table A-18. The following comments apply to the table:

a) In addition to the metallurgical applications, the use of thio-chemicals for the odorification of fuel gases is a traditional area. As related to the growing natural gas distribution pipe-line networks, production of odorification agents (to be added to the natural gas) has substantially increased. This application is of world-wide interest.

b) In petrochemistry, selected thio-compounds such as dimethyl sulfide, dimethyl disulfide - find use as modifiers for some metal catalysts, as supported platinum used in reforming. The addition of thio-compounds (dimethyl sulfide and dimethyl disulfide) to the feedstocks for thermal conversion (particularly to medium oil fractions) has a strong effect on reduction of coke formation and improves the economy of the process. In petrochemistry, dimethyl sulfoxide is an important solvent which is used to a growing extend for extraction of aromatics.

c) In the production of rubbers and other polymers a few thio-chemicals are important. Aliphatic mercaptans are used as chain transfering agents and molecular weight controlling agents in polymerizations; Without their addition the produced rubber would have a too high molecular weight. Among the mercaptans used for this purpose, the tertiary dodecyl mercaptan and the n-dodecyl mercaptan yield the

Table A-18: Application of petroleum-based thio-chemicals

Area	Application	Thio-chemical
Metallurgy Rare metal extraction	Sulfiding agents for metallic surfaces, extration of metals	liquid H_2S, dimethyl sulfide
Odorization of gases	Providing odor for natural and other gases	ethyl mercaptan n-propyl mercaptan isopropyl mercaptan tertiary butyl mercaptan dimethyl sulfide diethyl sulfide tetra hydrothiophene
Petrochemistry	Modifying agents for catalysts anti-coking agents to be added to feeds for pyrolysis, extraction of aromatics	dimethyl disuflide dimethyl polysulfide dimethyl sulfoxide
Production of rubbers and other polymers	Chain propagators in radical polymerization reactions	n-octyl mercaptan n-dodecyl mercaptan tertiary octyl mercaptan tertiary nonyl mercaptan
	Additive to polymer Prevulcanization inhibitor Synthesis of additives for PVC Solvents for polyurethane foams and acrylics	tertiary dodecyl mercaptan esters of thioglycolic acid cyclohexyl mercaptan thioglycolic acid
	Special polysulfidic sealants	dimethyl sulfoxide high molecular weight polysulfides
Tribology	High-pressure additives for oils used in cutting and grinding	tertiary dodecyl polysulfide
Building of roads	Thio-elastomer additives for asphalts	special polysulfides
Phytotherapy - plant treatment	Synthesis of herbicides and insecticides; solvents for these syntheses	methyl mercaptan ethyl mercaptan dimethyl disulfide dimethyl sulfoxide thiophenol
Pharmaceuticals	Intermediates of synthesis, and solvents	thiobutyramide thioacetic acid ethane dithiol dimethyl sulfoxide
Cosmetics	Intermediates in the synthesis of cosmetic products	thioglycolic acid
Fodder production	Synthesis of methionine	methyl mercaptan
Glassmaking and pottery	Color glazes (gold) for glass and China	pinene mercaptan

highest efficiency, but further thiols are also suited such as the tertiary nonyl mercaptan, tertiary octyl mercaptan, etc. The use of esters of the thioglycolic acid as a PCV stabilizer is also noticeable.

Cyclohexyl mercaptan ranks among the basic raw materials for synthesizing the prevulcanization inhibitor N-cyclohexyl thio-phtalimide, a thio-chemical of growing significance for the production of the lates generations of tyres. Another prospective trend in macromolecular technology is syntheses and application of sulfur-containing polymers which exhibit particular properties.

Also worth mentioning are the appliction of dimethyl sulfoxide as a solvent for polyurethane foams and acrylates and the application of special higher-molecular weight polysulfides (e. g. the French product named Sulkot) in the production of sealants.

d) In tribology, it were mainly the polysulfides like tertiary dodecyl polysulfide which found application as high-pressure additives for cutting, grinding and special transmission oils. These non-corrosive additives which exhibit great thermal stability and oxidation resistance have high sulfur content, and mix easily with the basic oils. They have recently found considerable expansion. Several well proven products are commercially available, e. g., Elf-Aquitgaine operates a facility in their Lacq works where sulfidic bottoms from the production of mercaptans are processed to type TPS 20 and TPS 32 additives with outstanding properties.

e) Modern roadbuilding faces the task of constructing high duty roadway capable for withstanding today's frequently quite enormous traffic under any weather and climate conditions. Modern bitumen mixtures are improved by polysulfide additives or the convantional roadway surfaces are coated with protection layers that contain thioelastomer additives (e. g. the French product Thiostone). Polysulfides of higher molecular weights, obstained as by-products during producing of mercaptans and sulfides, are the raw material of these special products.

f) In modern agriculture highly effective insecticides and herbicides manufactured by processes involving certain thio-chemicals are of importance.

Among the synthetic insecticides the product Systox from BAYER, which contains 0,0-diethyl-0-/2-ethylmercaptoethyl/thiophosphate (XIV) and 0,0-diethyl-S-/2-ethylmercaptoethyl/tiophosphate as the active species has to be mentioned. The substance from which the production of Systox is started is 2-ethylmercaptoethanol, prepared directly from ethyl-mercaptan and ethylene oxide. The same starting material is used in synthesizing Metasystox and Ekatin.

In the production of herbicides methyl mercaptan and ethyl mercaptan find application in the syntheses of symeric traizines of the Simetryn type.

Beyond Simetryn, a number of products has been marketed by Geigy These include Demetryn, Ametryn, Terbutryn, Prometryn, Dipropetryn.

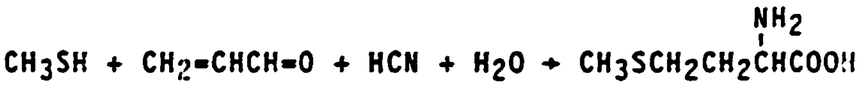
Modern agrochemistry can not operate without pesticides, made from basic thiochemicals. The major thiols used in the production of agrochemicals include CH_3SH, C_2H_5SH, n-C_3H_7SH, n-C_4H_9SH, n-$C_8H_{17}SH$, thiphenol and 2-mercaptoethanol. Further processes of herbicide and insecticide synthesis also make use of dimethyl disulfide as a thiomethylating agent, and dimethyl sulfoxide as a suited solvent.

g) In the production of pharmaceuticals the main intermediates and raw materials which are used for syntheses include thiochemicals such as ethane dithiol, thioglycolic and thioacetic acids, and also dimethyl sulfoxide which, in many cases, provides a suitable reaction medium.

h) In the cosmetic industry the major sulfur containing substance is thioglycolic acid; Elf-Aquitaine is the leading European producer hereof.

i) Modern fodder production is within those areas where sulfur-containing compounds are most prominent, particularly, because of synthetic-methionine of which the production grows steadily worldwide. The world production of this compound amounted to ca. 30,000 tons in 1970 and has grown to 100,000 tons in 1978. According to estimates by Monsanto, the annual increase of production rate in the 1980s should be 5 - 10 %.

The over-all reaction for synthesizing methionine commercially is



$$CH_3SH + CH_2{=}CHCH{=}O + HCN + H_2O \rightarrow CH_3SCH_2CH_2\overset{\overset{NH_2}{|}}{C}HCOOH$$

This means that methyl mercaptan is becoming an important industrial thiochemical.

In Europe, Rhone-Poulenc is the greatest producer of methionine. Other important methionine producers in the world are Elf-Aquitaine (France), Degussa (Germany), Sumitomo, Nippon Soda and Nippon Kayaku (Japan), Ugilor (France) and Monsanto, Dow Chemical, and Dupont (USA). A remarkable capacity for methionine production is also available in the USSR. Construction of a joint methionine production facility was also considered by Poland and Czechoslovakia.

Methionine, in terms of its annual production ranks second after L-glutaminic acid among the amino acids. Nutritionally the two optical isomers are equivalent allowing for a direct chemical synthesis of D,L-methionine.

j) The glass making and pottery industry makes use of special mercaptans, of the terpenic series. These substances find application in the production of decorative color coatings for glass and chinaware.

2.2.2 Survey of production trends of thio-organic chemicals and the theoretical principles of the thiolating reactions

Modern production of thio-organic chemicals on the basis of petrochemicals represents a rational and economically established system of predominantly catalytic reactions with hydrogen sulfide, yielding the desired products in a very straight forward manner with a minimum of intermediates. A simplified diagram of these production-routes is shown in Fig. A-19.

Commercially the basic thio-organic chemicals are formed by catalytic thiolation of suitable oxygen-containing substances or by catalytic addition of H_2S to olefins /7/. The simplest mode of producing thiols and sulfides is the addition of H_2S to the double bond. These addition reaction may, in technical practice, proceed in accordance with or against Markownikoff`s rule:

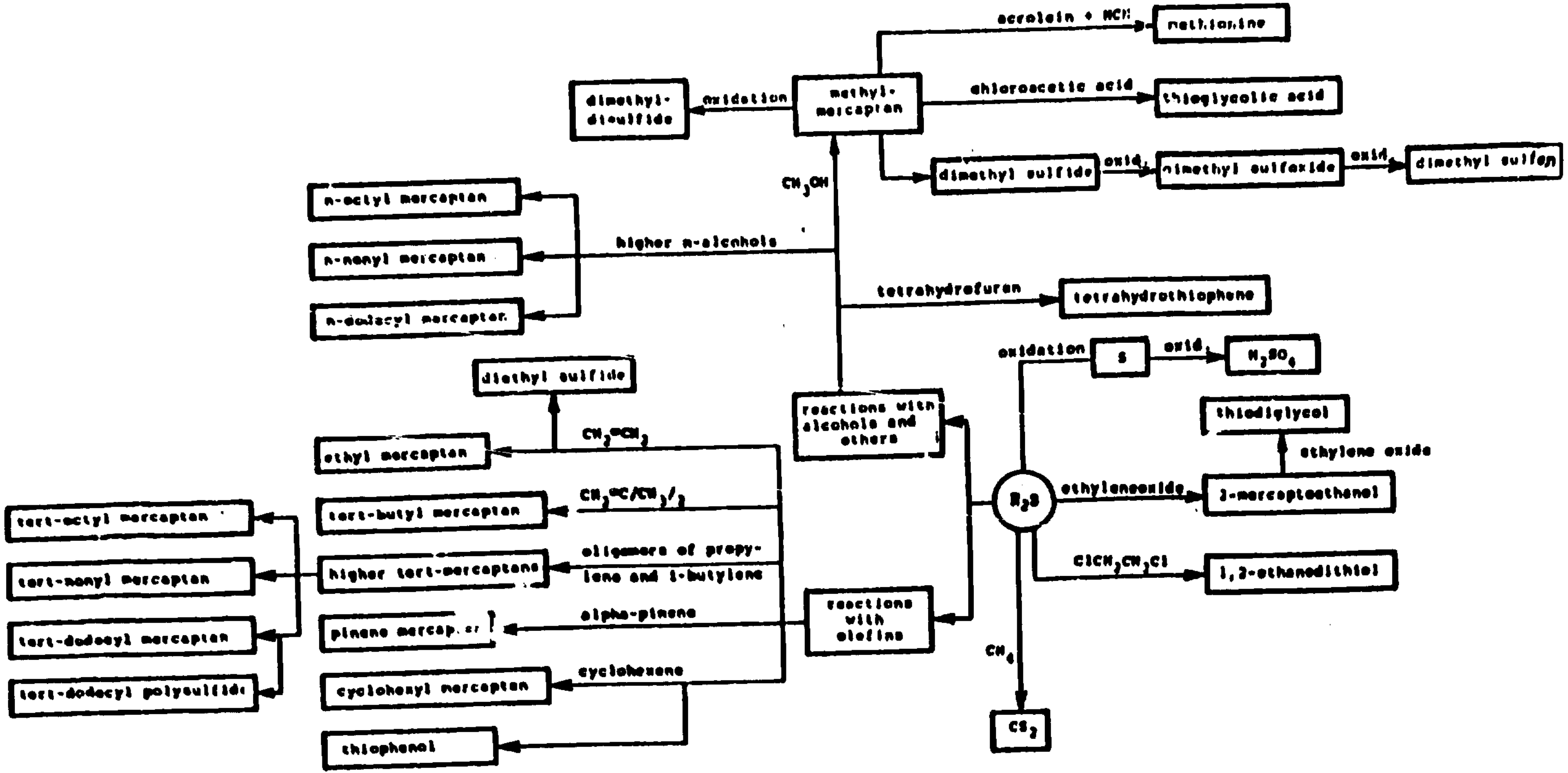
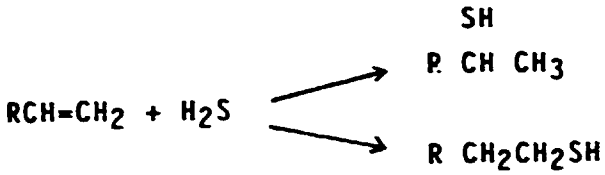


Fig. A-20: Survey of the technically most important thio-organic chemicals



$$RCH{=}CH_2 + H_2S \begin{cases} \longrightarrow R\,\overset{SH}{CH}\,CH_3 & (1) \\ \longrightarrow R\;CH_2CH_2SH & (2) \end{cases}$$

Secondary reactions in the system involve direct synthesis of sulfide, addition of mercaptans to alkenes, or dehydrosulfuration of thiols:

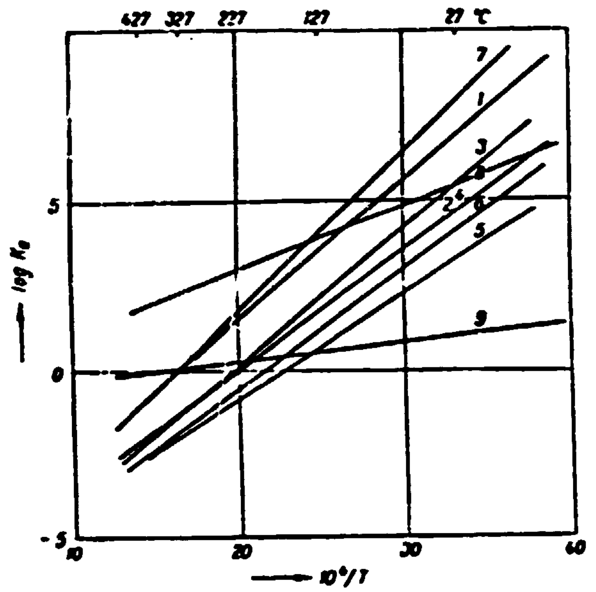
$$2\ RCH_2{=}CH_2 + H_2S \rightarrow RCH_2CH_2SCH_2CHR \qquad (3)$$

$$RCH_2CH_2SH + RCH{=}CH_2 \rightarrow RCH_2CH_2SCH_2CHR \qquad (4)$$

$$2\ RCH_2CH_2SH \rightarrow RCH_2CH_2SCH_2CH_2 + H_2S \qquad (5)$$

Figure A-21 lists the equilibrium constants for the reactions (1) - (5) as a function of temperature for small olefins. Clearly, most of these addition reactions are thermodynamically limited above 300 - 320 °C, so that, considering the requirement of high conversion, the temperature range actually available is up to about 250 °C.

When the production of thio-organic compounds by H_2S addition to olefins operates near the chemical equilibrium, the composition of the product mixture can be influenced significantly by varying the reaction conditions. This is seen in Fig. A-22 which gives an example of the equilibrium concentrations of ethyl mercaptan and diethyl sulfide for the reaction of H_2S addition to ethylene. It is obvious that the selectivity of the process is affected by all the major reaction parameters, i. e., the molar ratio C_2H_4/H_2S, temperature, and pressure.



1 - $C_2H_4 + H_2S \rightleftharpoons C_2H_5SH$

2 - $CH_3CH = CH_2 + H_2S \rightleftharpoons CH_3CH_2CH_2SH$

3 - $CH_3CH = CH_2 + H_2S \rightleftharpoons CH_3CH(SH)CH_3$

4 - $CH_3CH_2CH + H_2S \rightleftharpoons CH_3CH_2CH_2CH_2SH$

5 - $CH_3C(CH_3) = CH_2 + H_2S \rightleftharpoons CH_3CH(CH_3)CH_2SH$

6 - $CH_3C(CH_3) = CH_2 + H_2S \rightleftharpoons CH_3C(CH_3)(SH)CH_3$

7 - $C_2H_4 + CH_3CH_2SH \rightleftharpoons (C_2H_5)_2S + H_2S$

8 - $2\ CH_3SH \rightleftharpoons (CH_3)_2S + H_2S$

9 - $2\ CH_3CH_2SH \rightleftharpoons (CH_3CH_2)_2S + H_2S$

Fig. A-21: Equilibrium constants as function of temperature for selected addition and dehydrosulfuration reactions

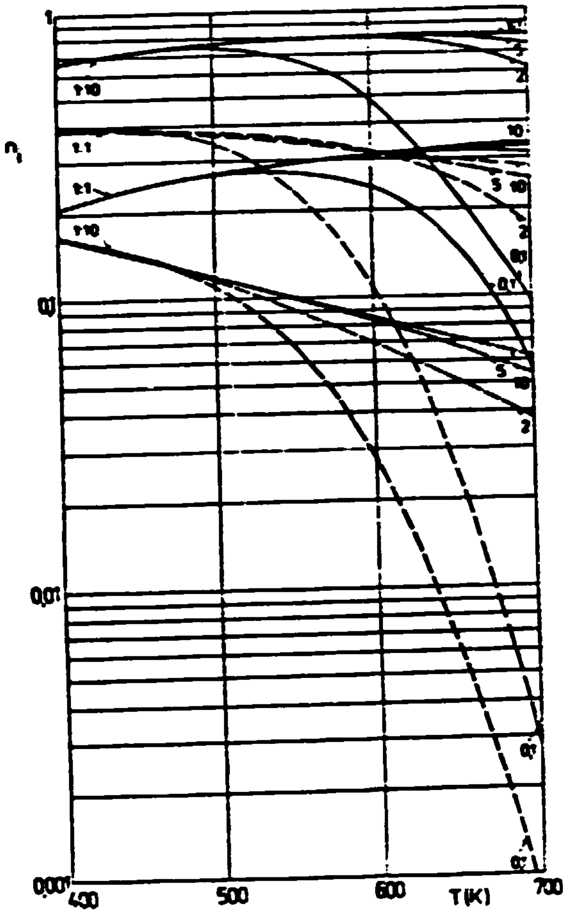


Fig. A-22: Equilibrium yields of products obtained by H_2S addition to ethylene

_______ ethyl mercaptan

_ _ _ _ diethyl sulfide

n_i number of moles of product per 1 mol C_2H_4

0.1, 2, 5, 10 total pressure in MPa

1 : 1, 1 : 10 ratio C_2H_4 : H_2S

The second basic reaction for commercially producing thio-organic chemicals is thiolation (or reductive thiolation) of suitable oxygen or nitrogen-containing substances:

$$RCH_2CH_2OH + H_2S \rightarrow RCH_2CH_2SH + H_2O \qquad (6)$$

$$RCH_2CH_2OCH_2CH_2R' + H_2S \rightarrow RCH_2CH_2SCH_2CH_2R' + H_2O \qquad (7)$$

$$RCH_2CH_2OCH_2CH_2R + 2\ H_2S \rightarrow 2\ RCH_2CH_2SH + H_2O \qquad (8)$$

$$RCH_2CH{=}O + H_2S + H_2 \rightarrow RCH_2CH_2SH + H_2O \qquad (9)$$

$$RCH_2COCH_2R + H_2S + H_2 \rightarrow RCH_2CH(SH)CH_2R + H_2O \qquad (10)$$

$$RCH_2COOH + H_2S + 2\ H_2 \rightarrow RCH_2CH_2SH + 2\ H_2O \qquad (11)$$

$$RCH_2COOR' + H_2S + 2\ H_2 \rightarrow RCH_2CH_2SH + H_2O + ROH \qquad (12)$$

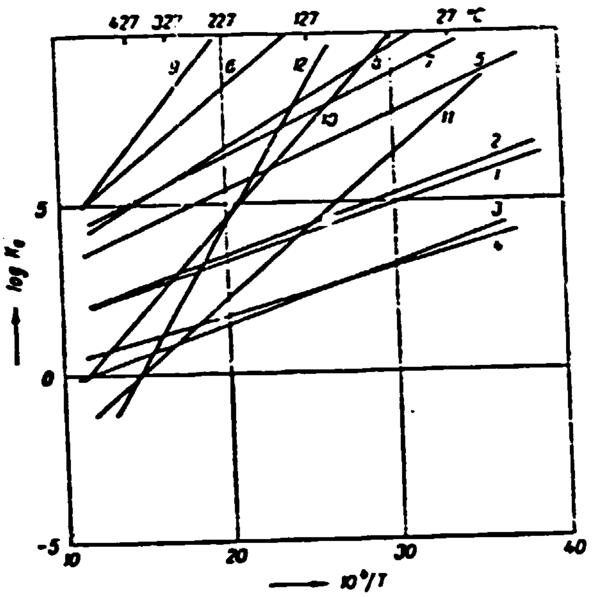
$$RCH_2COOR' + 2\ H_2S + 2\ H_2 \rightarrow RCH_2CH_2SH + R'SH + 2\ H_2O \qquad (13)$$

$$RCH_2C{=}N + 2\ H_2S + 2\ H_2 \rightarrow RCH_2CH_2SH + NH_4HS \qquad (14)$$

The equilibirum constants for some of the thiolation reactions are shown in Fig. A-23. As compared with the addition reactions, these equilibrium constants are substantially higher (= yielding water as a reaction product) and the reactions can be run at substantially higher temperatures and consequently proceed at higher rates.

Both kinds of thiolation are exothermic and, hence, an intensive removal of reaction heat from the reactor is of engineering significance.

In practice, all thiolation reactions require catalysis to proceed smoothly. Most of the catalysts used belong to eigher of the two types:



1 - $CH_3OH + H_2S \rightleftarrows CH_3SH + H_2O$

2 - $C_2H_5OH + H_2S \rightleftarrows C_2H_5SH + H_2O$

3 - $n\text{-}C_3H_7OH + H_2S \rightleftarrows n\text{-}C_3H_7SH + H_2O$

4 - $n\text{-}C_4H_9OH + H_2S \rightleftarrows n\text{-}C_4H_9SH + H_2O$

5 - $(CH_3)_2O + 2\ H_2S \rightleftarrows 2\ CH_3SH + H_2O$

6 - $(CH_3)_2O + H_2S \rightleftarrows (CH_3)_2S + H_2O$

7 - $(C_2H_5)_2O + 2\ H_2S \rightleftarrows 2\ C_2H_5\ SH + H_2O$

8 - $(C_2H_5)_2O + H_2S \rightleftarrows (C_2H_5)_2S + H_2O$

9 - $C_2H_5OH + 1/2\ S_2(g) + H_2 \rightleftarrows C_2H_5SH + H_2O$

10 - $CH_3CH = O + H_2 + H_2S \rightleftarrows C_2H_5SH + H_2O$

11 - $CH_3COCH_3 + H_2 + H_2S \rightleftarrows CH_3CH(SH)CH_3 + H_2O$

12 - $CH_3C \equiv N + 2\ H_2 + H_2S \rightleftarrows C_2H_5SH + NH_3$

Fig. A-23: Equilibrium constants for the thiolation of alcohols and for reductive thiolation of carbonyl compounds and nitriles.

I. Lewis'type acids ($AlCl_3.BF_3$) used at low-temperature (-30 to 100 °C) and low-pressure. They are applied either as such or in the form of suitable complexes (e. g. with CH_3OH, ethyl ether, olefins, etc.). Other acid catalysts include phosphoric acid supported on an inert carrier, and certain alumosilicates.

II. Heterogeneous sulfidic catalysts on supports used either as such or obtained by conversion of starter catalyst systems involving metals, oxides, or salts. They are used both for H_2S addition to unsaturated bonds and for thiolation of oxygen as well as other suitable starting compounds.

2.2.3 Selected examples of the synthesis of major technically important thio-organic chemicals

2.2.3.1 Low-temperature synthesis of tertiary dodecyl mercaptan /8/

A typical example is the synthesis of dodecyl mercaptan, important in the production of macromolecular susbstances. The Elf-Aquitaine process flowsheet is shown in Fig. A-24. A tetramer of prophylene (b. p. 180 - 215 °C) is led from the tank 1 to the upper part of the reactor 2 packed with Rasching rings where a contercurrent saturation with H_2S takes place. A catalyst complex ($AlCl_3$ bonded to olefin or to finished mercaptan) is added from the tank 3 and the reaction proceeds in the bottom part of the reactor 4 maintained at a low temperature (ranging from -30 to +10 °C. A mixture of H_2S and CO_2 used as the thiolating agent 16 is fed to the reactor bottom and flows upwards as bubbles through the liquid reaction mixture. The product of reaction is purified in the separation vessels 5 and 7, and is led to the continuous densitemeter 9, the washing section (washers 10 and 11 with acidified and untreated water, respectively) and then to the distillation column.

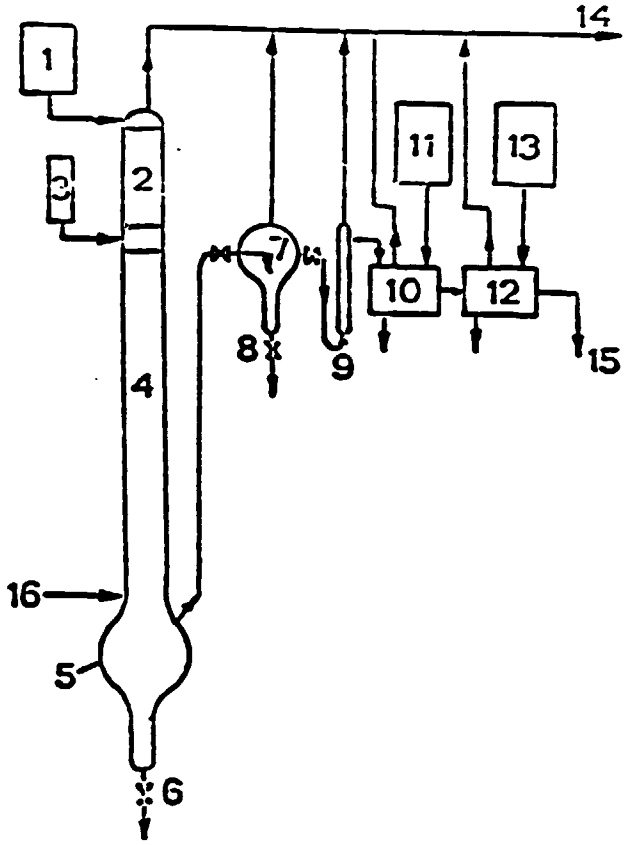


Fig. A-24: Process flowsheet of tert. dodecyl mercaptan production in Lacq

2.2.3.2 Production of pinene mercaptan /9/

This is an example of high-temperature H_2S addition using heterogeneous catalysts. The product is pinene-mercaptan, the basic component of golding overcoats for glass and china such as are made in Czechoslovakia.

Turpentine (high grade alpha-pinene), together with elemental sulfur and hydrogen (at a ratio such that H_2S is produced at an optimum stoichiometric excess related to the olefin and in the presence of a sulfide catalyst (molybdenum tungsten, and nickel sulfides individually or mixed, as such or supported on Al_2O_3) is heated to 200 - 250 °C in an autoclave. During the reaction the addition product is controlled with respect to the content of mercaptanic sulfur and the conversion is terminated as soon as the optimum mercaptanic sulfur content is obstained. In case of this synthesis being performed in a flow reactor, H_2S which had been prepared in an independent process is introduced, and an optimum volumetric flow rate is chosen. Unreacted (and, in part, isomerized) hydrocarbons are separated from the product of reaction by distillation and the finished product obtained from the distillation operation is a pure pinene mercaptan fraction which is a mixture of positional and stereo isomers.

2.2.3.3 Production of methyl mercaptan /10/

The production of this important thiol is an example of the thiolation of alcohols using heterogeneous catalysts. A typical flowsheet can be found in Fig. A-25. Methanol (containing 0.5 - 1.0 wt-% water) and H_2S are preheated to the temperature of 400 °C and, at a pressure of 0.7 - 1 MPa, the mixture is fed into the reactor packed with a catalyst which contains K- or Na-thiotungstate on Al_2O_3. The LHSV of methanol is approximately 0.4 - 0.5 h^{-1}. The reaction product is cooled and led to a stabilizing column where the unreacted H_2S is separated (in order to be recycled) with a small fraction of

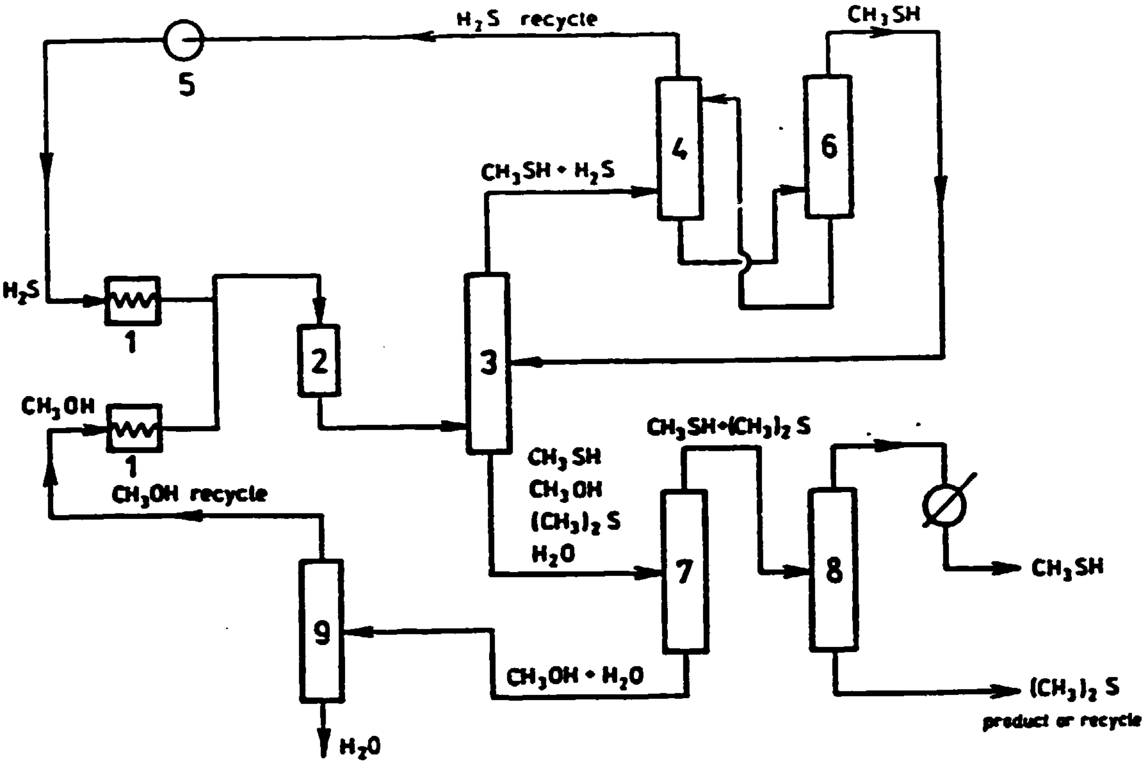


Fig. A-25: Process flowsheet of the thiolation of CH_3OH

1 - preheater
2 - reactor
3 - stabilizer
4 - absorber
5 - compressor
6 - stripper
7, 8, 9 - distillation columns

CH_3SH which is retained in the adsorber. The stabilized product consisting of CH_3 [illegible] $(CH_3)_2S$, CH_3OH, and water is fractionated in a series of distillation columns, yielding pure CH_3SH and $(CH_3)_2S$. The unreacted methanol is dried and recycled.

The higher tiols can be produced similarly.

2.2.3.4 Production of sulfur-containing odorants /11/

The production of efficient odorification agents expands together with the consumption of natural gas for heating purposes. An important requirement imposed on the odorants is a high sensoric effectiveness and, simultaneously, a high stability of odor during the distribution of the gas. The lower mercaptans and sulfides, individually or mixed, provide the most effective odorification agents. These substances account for the greatest fraction of all odorants produced by specialized companies (e. g. Elf-Aquitaine, Phillips Petrol., Pennwalt, etc.).

The C_4-fraction from the steam cracking process, after its dienes and acetylenes have been removed, is allowed to react with H_2S on a sulfide catalyst at 250 °C and 5 - 10 MPa pressure to a mixture of C_4-mercaptans and sulfides. The product is separated by means of distillation and the mixture of C_4-mercaptans is ready for application as a strong odorifiction agent.

2.3 Conclusion

a) As the resources of petroleum become more exhausted, the fraction of crude oils with higher sulfur content which is supplied for processing increases. The expected increase in coal consumption to replace oil in conventional power stations is necessarsily expected also to produce larger amounts of sulfur oxides.

The sulfur to be avialable from these two potential sources should be sufficient to cover the demand of the chemical industry.

b) There will be a gradual implementation of high-efficiency processes for desulfurization of combustion gases. No pollution arising from sulfur emission in offgases from power stations and heating plants can be tolerated after the year 2000; this is imperative if serious ecological catastrophes are to be avoided.

c) In spite of the upward trend of sulfuric acid production, which is due mainly to the increasing production of fertilizers required to boost agricltural yields in the developing countries, substantially larger quantities of sulfur will become available for use in further branches of the chemical and consumer industries.

d) A number of applications of sulfur may in the future increase the demand for sulfur substantially; this concerns primarily the sulfur asphalts and concretes but also various sulfur containing composites, special sulfur-containing polymeric substances, and thio-chemicals.

e) Certain thio-organic chemicals are of great importance for nutrition of the Earth's growing population, particularly in the developing countries. This concerns above all d,l-methionine which, through fodder fortification, is a prerequisite for a substantial boost in meat production. Expanded production of sulfur-based insecticides and herbicides will be caused by an intensification of plant production.

f) Hence, the new trends in the use of sulfur tackle two fundamental problems of develompent of the modern society - the yield novel, progressive products having outstanding applicability and, simultaneously, they provide for an effective protection of the living environment because the noxious sulfur compounds are prevented from burdening the environment.

g) Last but not least, the untraditional applications of sulfur are rather profitable, thanks to the fact that waste and by-products, often harmful ecologically, are converted at relatively low capital costs to products of considerable value having superior applicability.

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SOME ADDITIONAL OBSERVATIONS

The present expertise comprises a general part dealing with the principles of low-waste technology and a specific part devoted to four selected areas of chemical industry to which the following conclusions are related.

The contents of sulfur in the crude oils being recovered and used as well as in the coal which are mined is generally growing and simultaneously, there is an intensification of the necessity of removing it either from the offgases and exhausts after combustion or alternatively, prior to combustion from the fuels being used for power generation transportation, and as chemical feedstocks.

Important developments are recently underway in deep conversion of crude oil where high-boiling distillates and substantially the residual oils are used as a source of high-grade fuels and petrochemical feedstocks. Substantial progress has been achieved in the production of low-sulfur fuel oils, in the innovation of coal liquifaction, and chemical processing of carbochemical products.

Conversion of the high-boiling and residual petroleum feedstocks is obtained via highly effective catalytic and thermo-catalytic hydrogenation processes in which the undesirable elements (sulfur, nitrogen, oxygen, metals) are eliminated and upgraded fuel oils are produced, which can also more easily be processed in catalytic or thermal conversions, such as pyrolysis, fluid catalytic cracking, production of lubrication oils, etc.

Most important among the new processes are: catalytic desulfurization and hydrocracking of residual oils, mild hydrocracking and hydrovisbreaking. These processes are highly effective technologically they are more economic because of reduced energy consumption, and they meet the ecological requirements of low-waste technology.

An important complement to modern hydrorefining and hydrocracking processes is the non-traditional use of hydrogen sulfide and elemental sulfur. The production of sulfur asphalts and concretes, of special sulfur-containing composites, and of organic thiochemicals presents a substantial economic and ecological contribution to the traditional oil refining and petrochemical chemical industry.

Sulfuric acid is one of the most widely used chemicals. Its world production, ranks first among all individually produced chemicals. Thanks to this it contributes substantially to the individual national economies. Because the greatest part of the sulfuric acid being produced is used in the production of fertilizers, it is obvious that the development of sulfuric acid production is related to the solution of problems of food supply in the developing countries.

5. PRODUCTION OF SULFURIC ACID

1. Background

Sulfuric acid ranks among the principal products of the chemical industry. The extent of sulfuric acid production and consumption in individual industrially advanced countries may be regarded as one for the criteria by which the standard of the entire chemical industry can be judged. Most of today's chemical plants had their beginnings in the past century linked exactly with the production of sulfuric acid. As the other chemical technologies developed the consumption of H_2SO_4 kept increasing and its importance to the present-day chemical industry certainly has not dropped a single point. According to incomplete data, estimates of present sulfuric acid production figures worldwide run as high as 120-130 million tons in terms of 100% H_2SO_4.

The high production of sulfuric acid and the relatively low costs of raw materials were conducive to making the present sulfuric acid production plants to be of high standard both technologically and technically, so that even the production proper is rather inexpensive. This is due primarily to the high degree of utilization of the feedstock which is 98-99.5%, unparalleled elsewhere within the industry, and also to high utilization of the reaction heat for rising steam and producing hot water, and to high reliability and dependability of the process equipment. Inasmuch as the operating modes of the individual apparatuses of the production line are relatively stable, the application of simple regulatory loops or even of control computers to control the process presents no difficulties and, with a minimum of servicing, the operation can proceed in modes near the economic optimum.

All these factors reflect favorably on the profitability of production, chiefly in the case of the most advanced high-capacity plants where the cost of turning out 1 ton of product are substantially lower than in the case of various other starting materials and intermediates used by the chemical industry.

Another advantage of using sulfuric acid is that not only can any arbitrary concentration of aqueous H_2SO_4 solutions be used but also the H_2SO_4 solutions containing dissolved SO_3 - the fuming sulfuric acid - at any content of free sulfur trioxide, up to pure 100% SO_3. In this way can be created various environments exhibiting various activities of individual ions, of free SO_3 etc., to suit e.g. the organic syntheses.

At the early stages of development of the chemical industry the greatest amounts of sulfuric acid had been used to produce superphosphate, to pickle steel sheets and plates, to process ores, produce sulfates, to provide electrolyte for lead storage batteries, etc. While these areas of consumption gave no indication of falling consumption, other outlets have been added more recently to include the production of man-made fibres, caprolactam, nitro compounds /as part of nitration mixtures/, the requirements of sulfonation reactions, etc., which all represent a large consumption of sulfuric acid.

Even though the storage of sulfuric acid nor its transportation at shorter distances presents no difficulties, it is more advantageous, with a view to the great extent of consumption, to have the sulfuric acid produced on site or at least near the site where it is consumed.

Therefore, from the aspect of constructing and developing the chemical industries of the developing countries, it is of advantage to take off, just as it had been the case dozens of years ago in what today are the advanced countries, with the production of the primary intermediates which are less challenging technologically and which include sulfuric acid, fertilizers, NH_3, HNO_3 and the like. The developing countries no longer have to go all the way unaided committing the same errors but rather, may put to use the experience of the advanced countries, thus avoiding some of the problems which had to be overcome in the process of years.

Not speaking of the fact that a certain number of variants is available from which to choose technically and technologically, including opportunities for processing various raw materials, the greatest importance is attached to utilizing the experience acquired in handling the problems of environment protection. In the case of H_2SO_4 this problem can be broken down into two parts. The first one relates to the protection of the environment right during production, i.e., mainly the pollution by unreacted SO_2 exhalates and by H_2SO_4 mist. The other one is linked with the ways the H_2SO_4 produced is consumed and, possibly, with subsequent utilization of its waste solutions. Taking the liberty of some simplification, we can state that the dominant part of sulfuric acid produced will eventually be absorbed by the soil, the water streams, and the seas, with accompanying environmental damage.

If we may assert the claim that the first group of problems has been successfully mastered by now and that it is merely an issue of economics to find out how far we need to go with abatement and control of pollution, we cannot say the same of the second group of problems. At the present time, the processing of waste sulfuric acid solutions presents one of the most challenging problems which will have to be dealt with in the nearest future. For this reason, the present report will also go into the question of waste H_2SO_4 regeneration and reprocessing, inasmuch as by closing the loop of H_2SO_4 production - consumption - and regeneration we would cope not only with an issue of environment protection but also with one of the base of raw materials and of the H_2SO_4 production methods.

2. Outline of H_2SO_4 production

2.1. The products

When describing the process, some of the methods adopted for solution may be interlinked with the properties of the substances being processed and of the products. For this reason, monographs dealing with sulfuric acid production frequently pay attention to the properties of all the substances met with in route of the production process. In our case, only the products obtained will be described. More detailed information on the substances and products can be found in literature /1-5/.

The product encountered most widely at the sulfuric acid production plants is the so-called concentrated H_2SO_4 which contains 94-98% H_2SO_4. It is of advantage from the aspect of the technological use that sulfuric acid solutions of over 90% concentration can, at ambient temperature, be stored in tanks made from plain-carbon steel. Diluted sulfuric acid solutions having less than 85% H_2SO_4 corrode the steel, for the protective film of $FeSO_4$ is dissolved in such solutions. This is why lead or selected plastics are used.

Dissolution of sulfur trioxide in concentrated sulfuric acid yields the fuming sulfuric acid which contains various concentrations of free SO_3. Compounds of the type $H_2SO_4.nSO_3$ - polysulfuric acids - can be identified in a crystalline form at lower temperatures; they are also known in the form of salts.

In addition to concentrated and fuming acid, the sulfuric acid plants also turn out 100% SO_3.

2.2. Raw materials for sulfuric acid production

If we regard the historical development of H_2SO_4 preparation and production, we may state that any sulfur-bearing substance can be used as raw material as long as it can be transformed to SO_2 or SO_3 by some process. However, today's production of sulfuric acid which is of so great an extent must also meet other conditions, such as an abundant supply of given raw material having a determined standard quality /reserves for several decades/, acceptable price, low contamination, etc.

The material which at the present time, can be said to best satisfy these requirements, is elemental sulfur. The other sulfur compounds formerly used have gradually lost their importance as far as production proper is concerned. If they still are used, it is mostly for the reason that some outlet is sought for waste SO_2. This is why we usually classify such sulfuric acid production methods as desulfurization methods. In the combustion of sulfur-containing fuels, the amounts of sulfur dioxide which enter the atmosphere in the European countries as pollutants would suffice for the production of all sulfuric acid in those countries. In reality, however, owing to reasons both technical and economic, the sulfur dioxide from offgases is not yet retained industrially to a greater extent, so that most of the sulfur dioxide enters the atmosphere where it oxidizes to sulfur trioxide and, in the form of sulfuric acid /as acid rainfall/ is return to the surface of Earth.

When using sufficiently pure elemental sulfur /which is the most expensive of all the sulfur raw materials/, the entire processing line of the sulfuric acid production plant can be much simplified. In technical practice this amounts to low capital outlays, high operating reliability, and easy process control. In contrast to that, when other raw materials are used the entire process flowsheet becomes more complicated, the production is more prone to defects and requires more demanding inspection and control. For this reason, even if very inexpensive sulfur raw materials are used, such methods of production are no longer more adventageous economically than is the production of H_2SO_4 from elementar sulfur.

The situation is quite different under such conditions where waste sulfur dioxide has to be processed which may have been produced e.g. in roasting of polymetallic sulfidic ores or in desulfurization of combustion gases, etc. Since recently, another case can be added to the above examples, namely that of waste sulfuric acid and sulfates processing where no suitable use can be found for them, nor any other method of disposal.

On the whole, it can be stated in relation to the raw materials issue that, in cases where it is our intention to produce H_2SO_4 solely as an intermediate product in either an industrially advanced country or a developing country, the method which presently is most advantageous economically is to produce the sulfuric acid from elemental sulfur. Only in such cases where, within the framework of e.g. a specific chemical, metallurgical, or power generating plant, the question must be faced of the exhalation of SO_2, SO_3, H_2SO_4 wastes, and waste sulfates, the solution to this problem may be combined with sulfuric acid production. At the general level it is rather difficult to enter considerations of profitability, because that is determined entirely by the prevailing local conditions.

Such solutions were relatively successful where several wastes or low-value substances containing sulfur could be disposed of simultaneously. For example, the thermic decomposition of waste H_2SO_4 or waste sulfates at temperatures of 600-900 C provides an outlet for fuels /heating oil, coke, coal/ of high sulfur contents which could not be burnt in ordinary combustion processes. In this case it is also the sulfur contained in the fuel used for H_2SO_4 production which is utilized.

Fundamental differences among the H_2SO_4 production processes arise from whether or not a SO_2 gas free from any impurities is produced by the combustion which can be used without further cooling and cleaning for catalytic oxidation to SO_3, or whether the SO_2 carries mechanical and other impurities that would have to be removed prior to oxidation. In the case of sulfuric acid being produced from pure sulfur, the SO_2 can be oxidized directly. In all other cases it is a roaster gas containing mechanical impurities, ashes, dust, water vapor, catalytic poisons /chiefly As_2O_3 from ores/ etc., which must be removed prior to the catalytic oxidation, as a rule using some combination of dry and wet processes /dust settling, dry electrofilters - washing towers, wet electrofilters, roaster gas drying/. Owing to the fact that, at the present time, it is more advantageous economically for the industrially advanced countries to produce sulfuric acid from sulfur, we will limit ourselves to this method in the treatment presented below. Should a sufficient source of waste SO_2 become available in some developing country as the result e.g. of sulfite ores processing, this would warrant an independent study.

2.3. Sulfuric acid production from sulfur

Adhering to the same production principle we may meet facilities in the industrially advanced countries which produce sulfuric acid to capacities ranging from 50 to 2,500 tpd.

The raw material - sulfur of min. 99.9% purity - is brought to the production plant either in solid or in molten condition. All subsequent handling at the production plant usually involves molten sulfur /m.p. 119 C/, even the supply of sulfur in stock for several weeks of production is maintained in molten condition in heat insulated storage tanks. The sulfur is metered out into the combustion furnaces following only filtering on plug filters; several per cent kieselguhr is added to the sulfur as filtration material.

2.3.1. Sulfur dioxide production

Sulfur combustion by dry air proceeds in furnaces rather similar in design to steam boiler fireboxes where heavy oil or other liquid fuels are burnt. The only difference is that sulfur is burnt in dry air, of max. 0.1 g water per 1 Nm^3. The sulfur is sprayed into the combustion area by special burners. It is the design and proper operation of these burners which largly decide the rate of combustion which is described by the equation

$$S + O_2 \longrightarrow SO_2 \qquad \Delta H = -295 \text{ kJ}$$

The combustion temperature may reach 1200 C. The sulfur/air combustion ratio is maintained at a value such that the sulfur dioxide gas produced contains 9-12% SO_2 and 9-11% O_2. Only in those cases where some of the roaster gas is used for the production of 100% SO_2, the gas produced here is allowed to contain up to 18% SO_2 (3% O_2).

The combustion air is taken in from the atmosphere by a rotary blower, across a dedusting filter. The overpressure at the blower is so selected as to exactly cover the pressure loss of the entire production line which is 20-50 kPa. Subsequently, the air is dried by concentrated sulfuric acid /98% H_2SO_4/ in packed absorbers. The humidity retained by the drying sulfuric acid depends on climate and season and covers 20-60% of all water necessary for sulfuric acid production.

The sulfurous gas formed by sulfur combustion is cooled at the preheater and at the water banks of the steam boiler to the working temperature of the vadadium catalyst which is 400-420 C. Some 0.9 - 1.2 tons of steam at 4 MPa can be produced per 1 ton of H_2SO_4 output.

2.3.2. Sulfur dioxide oxidation to sulfur trioxide

This reaction, $SO_2 + 1/2\ O_2 \rightleftarrows SO_3$ at $\Delta H = -95$ kJ, proceeds very slowly if unaided, so a vanadium catalyst is used to speed up the reaction. The converter group, constituted by the catalyst beds and auxiliary equipment required to maintained the desired temperature conditions, is the most essential part of all the production equipment as far as the process control is concerned, inasmuch as it is its proper operation which alone can make it possible to obtain the necessary conversion of SO_2 to SO_3. With the so-called single-stage conversion the yield of SO_3 from SO_2 can in practice reach 98%. Even though a number of ingenious designs of the contact unit had been proposed, the one used worldwide today is a very simple and reliable design where the structure is composed of four to six adiabatic beds, with inter-tray cooling by integral heat exchangers. The flowsheet showing the connections within the contact unit can be seen in Fig. B-1.

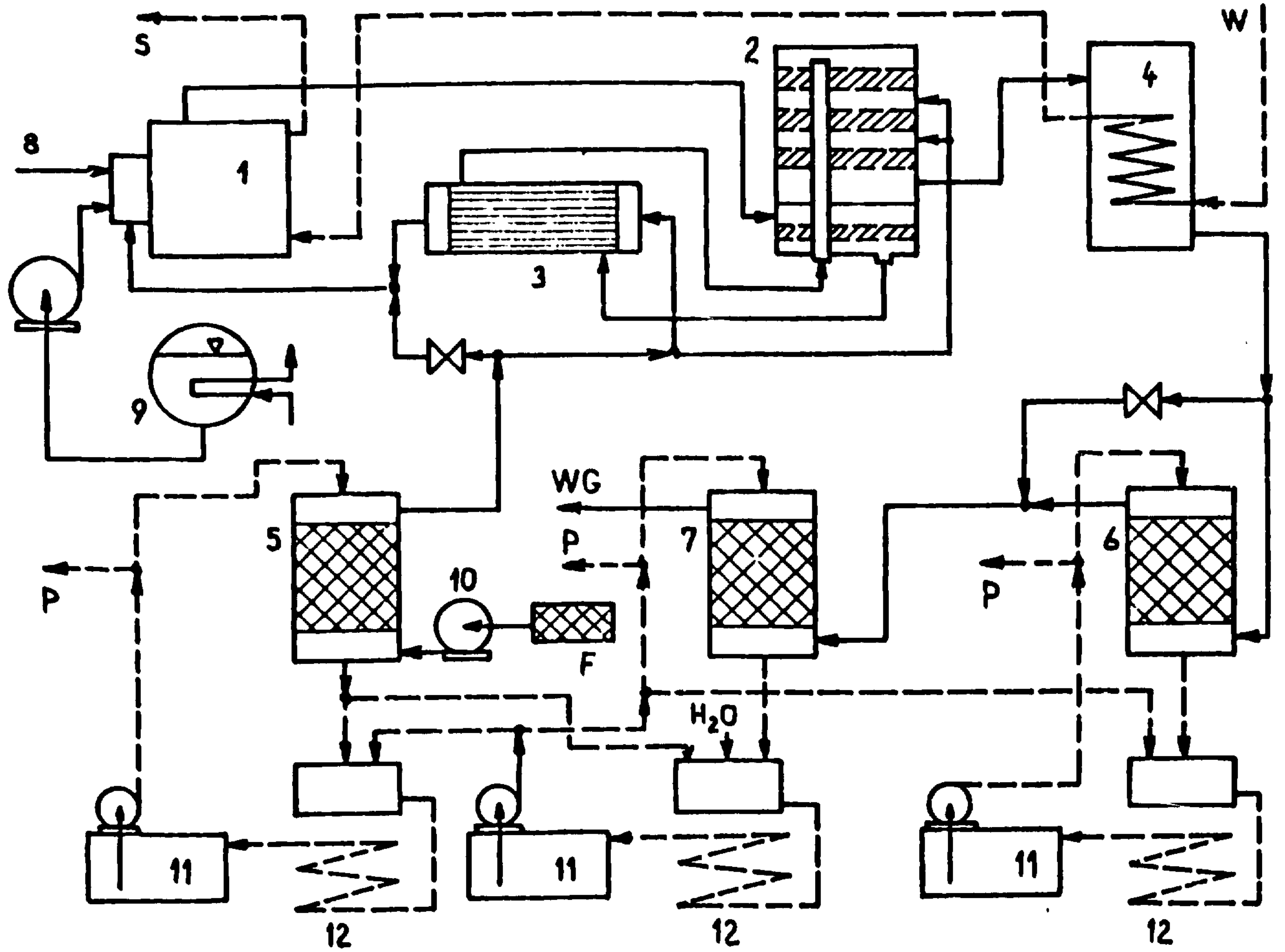

Fig. B-1 Sulfuric acid normal catalysis process. S - Steam, W - Water, WG- Waste gas, 1- Waste heat boiler, 2- Converter, 3- Heat exchanger, 4- Economizer, 5- Air dryer, 6- Oleum absorber, 7- Final absorber, 8- Sulphur, 9- Tank for heating oil, 10- Main blower, 11- Intermediate acid tank, 12- Acid Cooler, P- Product H_2SO_4, F - Air filter.

We cannot go into detail when considering the problems relating to reactor design. The problem reduces to proposing the most advantageous catalyst distribution to the individual trays and, at the same time, proposing such temperature conditions for the individual trays as to maximize the conversion at the reactor outlet, obtainable with given production and with given type and quantity of catalyst. As has already been mentioned, the maximum conversion is 98% in an optimized situation, but in cases where unsuitable conditions, fluctuations, or defects intervene it may be substantially less /e.g., merely 95%/.

The gas leaving the reactor is aftercooled either at the water banks of the steam boiler or by an economizer, and is led to the last process stage.

2.3.3. Sulfur trioxide absorption

The reaction taking place is

$$SO_3 + H_2O \longrightarrow H_2SO_4 \qquad \Delta H = -50\ kJ$$

Sulfur trioxide reacting with water or with aqueous sulfuric acid solutions - having a certain water vapor tension - would only yield H_2SO_4 in the form of hard-to-retain mist, so this is why the absorption of SO_3 is done in concentrated H_2SO_4 /97%/. It can be seen in Fig. B - 1 that the absorption and drying towers constitute one unit where the acid is processed under common control. The heats of reaction and dissolution which are generated in these two processes must be removed from the acid loops by cooling water. The temperature and concentration conditions in air drying as well as in absorption can be taken from Fig. B-1.

When fuming sulfuric acid is the desired product there are two absorption towers - the first one is the oleum tower where oleum having up to 30% free SO_3 can be produced, the second one is the so-called monohydrate tower where the remaining gaseous SO_3 is turned into 98% H_2SO_4. Only the second tower is used unless oleum is to be made.

The offgases from the absorption tower pass over filters /demisters/ where entrained H_2SO_4 droplets are retained, and thence to the stack and to atmosphere. The offgases contain approximately 0.2% SO_2. In smaller production plants, this is not a concentration which would threaten the neighborhood of the plant. Difficulties may arise however in the case of the larger production units.

As has already been mentioned, the over-all conversion of sulfur dioxide to sulfur trioxide is 98% at the most, which means that 2% of the sulfur dioxide processed is an effluent which goes to the atmosphere, there to be gradually oxidized to sulfuric acid and, eventually, to return to Earth in the form of acid rain. For example, thus, a sulfuric acid plant of 1000 tpd capacity emits sulfur dioxide in quantities yielding 20 tpd H_2SO_4 in the atmosphere. Such amounts of sulfuric acid can be disregarded neither ecologically, nor economically. For this reason, considerable attention is paid to trapping the unreacted sulfur dioxide emitted by sulfuric acid production plants.

3. Control of sulfur dioxide emissions from sulfuric acid plants and possible processing of sulfur dioxide from other sources

Atmospheric pollution by sulfur dioxide ranks among the prominent ecological problems of this time. This is why a considerable attention is devoted to issues of retaining and further use of the sulfur dioxide. In spite of substantial costs already incurred in efforts to find a solution, the problem has not yet been successfully resolved. The challenge becomes greater as the total quantity of exhalates to be processed grows higher but also as the SO_2 dilution (as a rule, 0.05-0.2%) and the contents of mechanical contaminants (dust and ashes) are increased. For instance, in the case of a 800 MW power station fired by lignite, the offgases leave the stack which has a cross section of 80 m^2 at a linear velocity of 15-20 $m\ s^{-1}$. Under such conditions it is a formidable problem to retain even just some of the sulfur dioxide, and the problem is technically unsolvable at present.

A certain degree of success at SO_2 retention has only been attained in the case of smaller pollution sources which however are without significance for the over-all balance of sulfur dioxide pollutant. This only solves the local problems of cities and certain outdoor localities. The sulfuric acid production plants can also be counted among the successful cases of SO_2 pollution control.

It has already been said that a conventional sulfuric acid production facility makes use of no more than 98% of the sulfur raw material, whereas the remaining 2% is turned to the SO_2 pollutant. A number of methods are theoretically available but only some of them have been applied in practice.

3.1. Alkaline washing

This is a rather simple unit technologically. A packed absorber is used to absorb the SO_2 residues in $NaOH$, Na_2CO_3, or NH_4OH solutions. When properly designed the absorber process will reduce the SO_2 content down to 0.0001 % SO_2 in the exit gas. The sulfite solutions produced are then processed to crystalline salts. A wider acceptance of the method is hindered by the limited outlets for these salts, where e.g. in photochemicals production, the requirements regarding purity are rather stringent, too.

3.2. The double conversion method

This method has become generally widespread in recent years, even though its implementation cannot be said to have avoided all problems. The principle of the method is very simple and consists in that the catalytic oxidation is discontinued on reaching 90-94% SO_2 conversion, whereupon the gas is cooled and the SO_3 produced is removed in the so-called intermediate absorber. The sulfurous gas containing up to 1% SO_2 is then heated to the catalyst working temperature and the reaction is allowed to continue. The theoretical attainable conversion is 99.99% and, in practice, 99.5% is actually attained. The sulfur trioxide produced is absorbed again in the final absorber. The gas leaving the final absorber contains no more then 0.05% SO_2 - and this means that a mere 0.5% SO_2 produced is not used by the H_2SO_4 production process and becomes an effluent. In contrast to sulfuric acid plants operated without the intermediate absorption, the exhalations are cut down to about 1/4 of their original value. This method also has the advantage of producing only the desired product which is sulfuric acid.

A drawback can be seen in that the contact unit connections are somewhat complicated, that one or even two large gas-gas type heat exchangers are needed, and that the amount of generated steam is slightly less - thus reducing the degree of heat utilization.

A further reduction of exhalations from the sulfuric acid production plants would indeed be theoretically feasible by "adding-on" yet another absorption unit but, owing to the necessity of working with highly diluted gases /99.95% of inert components/ the process would no longer be of any economic benefit. The alkaline washing can be used again but, of course, the absorption of sulfur dioxide from this highly diluted gas proceeds very slowly.

3.3. Sulfur dioxide oxidation in the liquid phase

These methods are based on trapping the residual sulfur dioxide in water and then oxidizing it. The forst of these methods which has found a practical application is known under the name "Sulfacid". SO_2 and O_2 from the diluted gas are trapped in a diluted aqueous solution of sulfuric acid where the reaction takes place. This is accelerated by the presence of certain metal ions /Fe^{3+}, Cu^{2+}, Co^{3+} etc./ which can be either dissolved or bonded to active charcoal. The method suffers from the disadvantage that the maximum obtainable sulfuric acid concentration is 25% /and may actually run as low as 10-20%/ and the product can be contaminated with the metal ions used.

This is a way to treat gases having 0.1-2%SO_2 and min. 5% O_2, whereas at higher sulfur dioxide contents the requirement for O_2 is that its concentration in per cent be five times as high as the SO_2 concentration. Sulfur dioxide conversion to sulfuric acid is about 90%. The diluted sulfuric acid obtained can be used in some other production or, in the case of sulfuric acid production plants, as a replacement for the process water supplied to the absorption loops.

Another such process of treating the waste gases by SO_2 absorption is the so-called PERACIDOX process whereby SO_2 is oxidized by H_2O_2 additions to the circulating solution. At variance with the foregoing method, no catalyst is required to oxidize the SO_2. One of the variants of this method is a process where a part of the circulating sulfuric acid is oxidized in an electrolyzer to a mixture of H_2O_2 and $H_2S_2O_8$ or to Caro's acid.

The drawback of the PERACIDOX method is the rather high consumption of H_2O_2 or of electric power for the oxidation. For this reason the method cannot be used e.g. as a substitute for the intermediate absorption but can only find application in the treatment of offgases which leave the plant downstream of the intermediate absorption.
Except for the concentration of the acid /max. 30% H_2SO_4/ the process parameters can be adjusted with a rather wide latitude so that the degree of SO_2 retention as well as the H_2O_2 or power consumption can be varied to suit the local conditions. Just as with the SULFACID process, the sulfuric acid produced can be used as a replacement of the process water.

A number of other methods for SO_2 retention were proposed but have not so far found application to any appreciable extent.

4. Sulfur dioxide oxidation catalysts

From the aspect of raw sulfur utilization and the quantity of sulfur dioxide pollutant produced, it is the contact unit which is of key importance in any sulfuric acid production plant. This is where the catalytic oxidation of sulfur dioxide to sulfur trioxide takes place according to the equation: $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3 \quad \Delta H = -95\ kJ$

This equilibrium reaction would not proceed spontaneously, so a suitable type of catalyst must be used. Even though, theoretically, a whole range of catalysts are applicable, only the vanadium catalysts are used in practice. This type of catalyst can be obtained from several important producers. Hence, a certain latitude is possible when designing the contact unit, concerning the catalyst selection, its loading, and the operating conditions. It is true that every supplier of the vanadium catalysts does specify in the form of documentation the properties of the individual types or offers the so-called engineering service - i.e., pertinent reactor design calculations including the process conditions, but it is believed that the designing be better done independently of the suppliers.

4.1. Vanadium catalyst quality assessment

High-quality vanadium catalyst must exhibit a high catalytic activity throughout the range of operating temepratures, an adequate mechanical strength, normal life extending over 5-10 years, and must be reasonably priced. Only some of these properties are accessible to laboratory measurements.

The mechanical strength can be ascertained rather easily. The particles are tested for compression strength and wear resistance. Both these methods are applied and the sample groups are ranked by decreasing strength, which may be either the compressive strength of the tablets, or the wear resistance. As for the wear test, the procedure usually adopted involves wear by the same particles in an empty drum of the laboratory ball mill or some similar device. The values found must only be regarded as relative values, inasmuch as these measurements are taken at ambient temperature while in the reactor, the catalyst operates at temperatures ranging from 400 to 600 C, i.e., under conditions where its mechanical properties are quite different. As indicated by practical experience, those catalysts which are stronger mechanically are less prone to particle deformation and to wear during operation; also, they do not become damaged by handling, thus attaining a longer life.

Another important property is the catalytic activity. Even though it is the main mission of the catalyst to speed up the reaction, the catalytic activity as a factor should not be overestimated in practical evaluations - for instance, even a highly active catalyst is of no use in the process unless it possesses a sufficient mechanical strength - which means that one should look for a catalyst which would be mechanically strong and, as the same time, highly active. In reality, these two properties tend to be somewhat mutually exclusive, because to attain a higher activity one needs to increase the porosity and the mean radius of the pores, which in turn detracts from mechanical strength.

4.2. Ensuring reliable operation at the contact unit

These are reasons which make it advantageous in designing and constructing the sulfuric acid production plants to use only such types of catalysts which have proven well in long-term operation in commercial facilities and which exhibit properties that can be checked in so-called reference units. Unless this is true one cannot guarantee a sufficient operations reliability and a long catalyst life in the contact unit.

At the present time, some 10 companies deal in the production and distribution of the vanadium catalysts. Inasmuch as the supplier of the catalyst assumes liability for dependable operation of the reactor as a whole, it is common these days that the supplier's company personnel takes care of packing the reactor with the contact mass, on the basis of design and optimization calculations. Simultaneously, checks are made of the technical condition of the reactor, its insulations, measuring devices, etc.

Years of experience with operating sulfuric acid production plants suggest that technologically, it is of advantage to adhere to certain conditions which are stipulated by the reactor and catalyst manufacturers to ensure reliable, extended operation:

1. When handling the catalyst and also when operating the reactor, the vanadium catalyst must never be contacted with water, because once it becomes humid a part of its catalytic activity is lost for good. For this reason, not even the water vapor from the startup furnace offgases must enter the reactor. Prior to shutdown of the sulfuric acid plant, the sulfur trioxide bonded onto the active component of the catalyst must be allowed to desorb for a sufficient period of time. In case that any free sulfur trioxide remains in the catalyst, the latter is turned strongly hygroscopic and picks up water even from atmospheric humidity.
2. Owing to the fact the active component of the vanadium catalysts is melted during the reaction (at 400-600 C), the sulfurous gas must be practically free from any microscopic dust particles. Unless this is so the porous

structure of the catalyst becomes clogged with dust. At higher dust contents in the gas or in the case of insufficiently strong catalyst particles /fragmentation/, even the area in-between the catalyst grains of the bed becomes clogged.

3. Catalyst life is adversely affected by every more significant alteration of the process operating mode. This concerns mainly an extended overheating of the catalyst beyond the maximum admissible temperature /620-640 C/ but also fluctuations of the temperature conditions as a conseoquence of changes in sulfurous gas concentration, gas feed interruptions, short shutdowns without undue temperature drop, as well as long shutdowns connected with reactor cooling. If properly run the production plant should not have more then two extended shutdowns in a year.

4. From the point of view of maximum utilization of the contact unit, it is imperative that modeling and optimizing techniques be used to ascertain what are the economically most advantageous operating conditions /relation between process line load and output, sulfurous gas concentration, catalyst activity, and the temperature conditions/. For the purpose of these calculations, regular measurements /during shutdowns/ must be made of the true catalytic activity of catalysts from individual trays, and corrections of the process must be made on the basis of the results. Over the service life period of the vanadium contact mas /up to 15 years/, one has to reckon of course with a gradual fading of catalytic activity.

It is the reliable operation of the contact unit which determines not only the degree of utilization of raw sulfur but also the opportunities for using the reaction heat for rising steam. The next Chapter is devoted to these problems.

5. Waste heat utilization in sulfuric acid production

5.1. Background

When assessing the suitability of this or that sulfuric acid production plant, and important part is played by the utilization of the waste heat generated in the process. Its rational use is generally advantageous for the developing countries of which many are poor in the power resources, and is of advantage from the environmentalist's point of view as well, because of the partial replacement of the combustion of solid or liquid fuels, representing the essential source of pollution.

The most important sources of heat in the production of sulfuric acid are the chemical reactions - combustion of the sulfur-bearing raw material which mostly is elemental sulfur, and oxidation of the sulfur dioxide to the sulfur trioxide. Heat is also liberated in various physico-chemical processes - air drying by sulfuric acid, sulfur trioxide absorption in sulfuric acid, and in diluting the sulfuric acid. Finally, heat is also produced by certain physical operations, e.g., a turbine blower heats up the air while compressing it for sulfur combustion. This list makes it evident that heat is liberated at different temperature levels and at various conditions relating to output, the state of the heat-carrying medium, and the corrosion of equipment. Hence, the degree of utilization of heat at various sulfuric acid production plants is different and as a rule, amounts to 55-60% of all the heat generated. The individual methods of utilizing this heat and the possibilities of enhancing the energy consciousness of the sulfuric acid making process will be treated below.

5.2. Utilization of high-potential heat

The reaction heats of sulfur combustion and sulfur dioxide oxidation are usually used for rising high-pressure steam. A steam boiler is installed immediately downstream of the sulfur combustion furnace, most frequently as a unit designed integrally with the furnace. The furnace gas is heated by the reaction heat of sulfur combustion to 900-1200 C depending on SO_2 concentration in the gas. In the steam boiler it is cooled down to 400-460 C depending on the desired gas input temperature at the contact reactor inlet. The reaction heat of SO_2 oxidation is withdrawn from the gas after each individual reactor tray. Other steam boiler sections, steam superheaters, or economizers are used for cooling the reaction gas from the temperatures of 440-620 C and for preheating the feedwater for the steam boiler or for preheating air needed for sulfur combustion in heat exchangers. Hence, the liberated heat again is used for rising steam. As an example may serve a production plant of 1000 tpd H_2SO_4 capacity which produces 60 tons of overheated steam per hour at 2.1 MPa pressure.

5.3. Opportunities for raising the steam production

At a given production rate of sulfuric acid, i.e., at a given amount of sulfur for combustion and SO_2 for oxidation, the amount of the generated steam will depend on the balance of the sulfur combustion unit and the contact unit. At the same time, the amount of heat carried away from the system considered by the exit gas will significantly depend on the sulfur dioxide concentration in the gas. The more diluted the gas is, the more nitrogen and oxygen must be heated and the higher are the losses of heat due to gas leaving for the absorption loops. From this angle, it is disadvantageous to cool the reaction mixture in-between the trays by admitting cold air, a method which is rather frequently used still.

In principle, what is required is the highest possible gas concentration, which not only improves heat utilization but also pushes down the consumption of power for driving the blower, thanks to lower pressure loss. In older plants, because of fear from too low conversion, the operating concentration of SO_2 was 9% at the point of zero conversion; a value of 10% is regarded as standard, but the authors had an opportunity to witness a concentration of 11.5% in a successfully operating plant /BASF Ludwigshafen/.

Another important opportunity for raising the generation of steam is to reduce the gas temperature at the inlet of the absorption loops, and to use its heat e.g. for preheating the feed water for the boiler or of air for the furnace. As a rule the temperature of the conversion gas is maintained at 180-200 C, for fears of corrosion by the liquid phase condensing from the reaction gas. With a suitable design of the heat exchanging apparatus /without "cold spots"/ and with their advantageous interconnection, the gas temperature can be lowered to 150°C without giving rise to oleum condensation, as the authors had an opportunity to see for themselves e.g. at the sulfuric acid production plant of Hoechst in Frankfurt/Main.

The production of steam can also be raised by increasing the temperature of the inlet streams, and here the possibilities are relatively limited - the temperature of air at the outlet of the dryer can be boosted from 40-50 C to 60-70 C by changing the temperature of the circulating acid, without incurring a rise in the water content in the air beyond the value of 0.1 g/Nm^3 which is required in order to minimize corrosion by the condensing oleum. Also the gas temperature at the exit of the intermediate absorption can be raised by shifting the operating mode of the absorber toward the higher temperatures, i.e. to 75 C and even higher from the usual 65 C. It means that pumps and coolers provided with an improved corrosion protection must be available. As we were able to see at Donauchemie Co., one of the intermediate absorbers had operated at acid temperature of 130 C downstreams of the mixer, and the corrosion problems were overcome by using properly selected materials.

As for the consumption of energy, the question of installing a blower in the process line is of importance. In the blower the air is heated by the compression heat and when located ahead of the dryer, this heat must be removed in the acid cooling loop because the air temperature on leaving the dryer is constant and given by the feed temperature of the dryer acid. When the blower is located downstreams of the drying tower the heat of compression is taken to the furnace and, in the adjoining steam boiler, is utilized for rising steam.

At the present the blower is mostly situated at a location ahead of the dryer absorber, for fear from corrosion by sulfuric acid mist. However, the problems arising from entrained liquid have been eliminated by introducing the demisters. As we were able to witness e.g. at Donauchemie and Hoechst in Frankfurt, where the blowers are situated downstream of the dryer, corrosion presents no problem in spite of the fact that the blower is made of plain-carbon steel.

5.4. Utilization of low-potential heat

A principal turning point in the efforts for increasing the utilization of energy at the sulfuric acid production plants is represented by utilizing the waste heat from the absorption loops. This allows to raise the degree of heat utilization from the usual 55-60% to 80-90% of total heat liberated. Most heat is liberated in the intermediate absorber, less in the final absorber; relatively little heat is liberated in the dryer or the oleum absorber. On the whole, a total heat output of 27 MW has to be withdrawn from the acids in the absorption loops, e.g. in a production plant of 1000 tpd H_2SO_4 capacity.

Utilization of the waste heate from the absorption loops is contingent on resolving a whole number of problems - installation of suitable compact exchangers, connecting them in a way such as to minimize the heat exchanging surface, and availability of a suitable consumer of the heated water. The compact coolers are understood to be enclose exchangers of the type liquid-liquid, or sulfuric acid - water. The hitherto most widely used cast iron spray coolers or air coolers are poorly suited for the job. At present the compact coolers have already become less capital-intensive, even in cases where the heat is not utilized and they take up less space. Out of the compact coolers available, those which are commonly used in the world include plate coolers, tube coolers with anodic protection, and tube bundle coolers made of PTFE. The modular plate coolers are manufactured from high alloy materials /Hastelloy C/ and exhibit a heat transfer coefficient of 2000-4000 W $m^{-2}K^{-1}$. As a rule, for reasons of material and sealing, they are approved by the manufacturers only for use at acid temperatures max. 100 C, but otherwise they are highly advantageous and impose little demand on floor area. The teflon tube bundle coolers by DuPont impose practically no limitations as concerns the acid temperature, and are free from corrosion. Owing to the low velocity of flow of the acid in the tubes and to the low conductivity of PTFE they have relatively low heat transfer coefficents /ca 250 W $m^{-2}K^{-1}$/ and, therefore require more space. They are more expensive, too. The compact tube bundle coolers with anodic protection are made of alloy steels having heat transfer coefficients of 400-600 W $m^{-2}K^{-1}$. Various companies would approve their use for various maximum admissible temperatures of the acid - 100-130 C. The operation of anodically protected coolers requires automatic control and great care, and may therefore be less suited for the developing countries. As an example, let us outline the cooler operation at Donauchemie Co. (Tab. B-1):

Table B-1

	acid temps.		water temps.		flow rate
	inlet °C	outlet °C	inlet °C	outlet °C	water m^3/h
cooler with anodic protection	100	83	63	83	175
plate cooler made from Hastelloy C	90	75	55	75	150
teflon tubelet cooler DuPont	130	110	100	110	320

What may be decisive for the economic effectivity of warm water utilization is the outlet opportunities - i.e., the consumers. It is best if there is a need right at the chemical plant - e.g., for phosphoric acid solution thickening, in rayon staple production, etc. Relatively extensive is also the utilization of warm water for heating, either within the plant or of whole towns /e.g., Helsingborg, Sweden/. Heating of hothouses is also common.

An interesting possibility for using waste heat from the absorption loops is to convert it to electric power using the fluorocarbon Rankin cycle where the waste heat of the acid is used to evaporate a low-boiling liquid. The vapor drives a turbine and is then condensed and recycled to transmit more heat. The system is similar to the steam turbine principle for the case of the turbine operating in a closed cycle, the only difference being the use of a liquid having a boiling point lower than that of water, so that the system can be operated with lower-potential heat source.

6. Sulfuric acid production plants - project and process optimization

6.1. Background

Sulfuric acid production plants have attained to a considerable degree of perfection during their many years of development in competition of the world's forefront companies. In spite of this, the individual projects and operating conditions differ from each other rather profoundly. This is due to the local conditions - raw materials selection, product quality, product destination, waste heat utilization possibilities, standard of the inspection, control, and maintenance personnel, etc. A plant which is best under given conditions need not be satisfactory at some other location or in another country. This is why it is important to comprehensively assess both the production plant proper and its links to its environment, in order to select the best - optimal - variant from those available. Evaluation of a whole number of variants without expensive experimenting can be done by the use of computers - with methods of mathematical modeling and optimization of the chemical processes. It ought to be realized that, with a view to the large production volumes involved in the case of sulfuric acid, relative savings of no more than just fractions of a per cent amount to millions in terms of annual profits, so that the payoff of the optimization operations undertaken is high.

6.2. Mathematical modeling of sulfuric acid plants and their parts

Mathematical modeling ranks among the basic rationalization techniques available to the design of the sulfuric acid production plants. Modern computers make it possible to scan a whole number of variants to the behaviour of the equipment, including emergency situations which cannot be modeled on the actual unit. Hence, the simulation calculations render it possible to work out specific technical solutions more rapidly, less expensively, and without any hazards which might be involved in actual operating experiments, for e.g. the modifications to the process conditions in the case of changes in the amounts of quality of raw materials, in the case where the material or engineering requirements are to be cut down, or when eliminating production line bottlenecks, etc. They also take into account the possible interactions of units, tune in their interlinking relationships, i.e., the systems approach is implemented. It is an advantage of the processes involved in the production of sulfuric acid that they have been studied rather thoroughly and are understood well enough to allow for modeling and/or optimization using reliable thermodynamic, kinetic, and chemical-engineering data available. The mathematical models are most often used in conjunction with optimization techniques.

6.3. Optimizing sulfuric acid production plants

A design of a sulfuric acid production plant including its process conditions usually involves a great number of variants of various kinds, of which all meet the basic requirements which is the production of a product of given quality, and also satisfy other limitations such as those arising from environmental standards and the like. The designs differ from each other in their individual parameters such as e.g. the temperature profile of the reactor, the quantity and quality of catalyst for individual treys of the reactor, the type of certain pieces of equipment, etc. What is understood under the term optimization is the identification of the best solution, best design, or best operating conditions in terms of a chosen criterion, with respect to the existence of various limiting conditions concerning mainly the values which the individual variates may assume. The criterion of success in optimization, which is called the object function, usually represents some economic parameter of the process, e.g., the cost incurred per 1 ton of sulfuric acid produced.

The objective proper of the optimizing calculations is to scertain the values of the variable parameters, so as to make the object function attain its extremum -

maximum or minimum. At the present time, abundant suitable optimization techniques are available for solving the individual types of optimization problems, which need not be described here.

The conterpoint of an expert´s job in assessing the sulfuric acid plants is on the one hand to formulate the optimization problem, i.e., to set the object function, to select the intervening variables, and to specify the limitations - and on the other hand, to evaluate the results and to draw conclusions relevent to practice. In the text below, therefore, we shall list examples of several optimization problems already solved in the area of sulfuric acid production.

6.3.1. Optimizing the inlet temperature for the vanadium catalyst bed

The essential element of the sulfuric acid production plant is the contact reactor where sulfur dioxide is oxidized. It plays a decisive part as far as the burdening of environment by sulfur dioxide pollution is concerned. The better the contact reactor is operated, the lower is SO_2 pollution. At the same time, merely by properly controlling the temperature profile of the reactor we may contribute to pollution abatement without incurring any capital outlays.

The exothermic reversible reaction taking place at the individual adiabatic beds of the multi-tray reactor at given flow rate and composition of the reacting gas is controlled solely by changes of the inlet temperatures. Temperature has a twofold effect on the yield of the SO_2 oxidation. On the one hand, a rise in temperature brings about a higher reaction rate and, on the other hand, causes a reduction to the value of equilibrium conversion at which the reaction rate is zero. Hence, the task of optimization is to find such temperatures at the inlets of the individual reactor trays at which the degree of SO_2 conversion at the reactor outlet will be maximum. One of the available search methods involving nonlinear one-dimensional optimization is applied - e.g., the golden section method. The result then is the optimum inlet temperatures for the individual catalyst layers, for different reactor outputs and reacting gas concentrations at which the SO_2 conversion at the reactor outlet is maximum. The study of the effect of small changes of the system parameters allows then to find the ranges within which these parameters should be held. Thus we arrive at a complete documentation as may be required for an optimized control of the reactor and for minimum SO_2 pollution.

6.3.2. Optimizing the catalyst distribution to beds of adiabatic reactor

In the case of adiabatic multi-tray reactors for SO_2 oxidation, the variables which significantly influence the degree of conversion include the total quantity of catalyst used, its distribution to individual trays, and its quality /kinetic parameters, pressure loss, and life time/. The effect of temperature has already been treated in Paragraph 6.3.1.

An important problem is the determination of the total quantity of catalyst to be used, and especially its distribution to the individual trays of the reactor, so as to maximize SO_2 conversion at reactor outlet. By a suitable redistribution of a given quantity of catalyst among the individual trays and by simultaneous determination of the optimum temperature conditions we may contribute to SO_2 pollution abatement even in the case of the standing sulfuric acid production plants, without any capital outlays. However, no single, general recipe for catalyst apportioning to the trays can be defined. It always depends on its kinetic properties which differ in the low-temperature and the high-temperature range and differ for gases of different concentrations. A combination of several types of catalyst can sometimes be used to an advantage. Therefore, it is necessary when determining the distribution of catalyst to the reactor trays to always apply the optimization of the degree of conversion, i.e., for every production output and SO_2 concentration in the reacting gas, and for every catalyst used. The object function is the SO_2 degree of conversion at reactor outlet. The intervening variables considered are the gas temperatures at tray inlets and the catalyst weights at the trays. Thus the problem may involve 8-10 intervening variables, depending on the number of trays. Methods of multidimensional nonlinear optimization must be employed here. The results obtained from the calculations showed that the SO_2 conversion can be increased and the SO_2 pollution can be reduced by redistributing the catalyst.

6.4. Importance of the computer methods

The aforementioned examples were intended as demonstrations of the potential of computer technology in contributing toward the control of pollution and, in general, toward rationalization of the sulfuric acid production plants, be it at the design stage or at the level of operating the existing plants. A great number of other problems were also solved - determination of the optimum concentration of SO_2 in the reacting gas, the synthesis of an optimum network of heat exchanging apparatus for the purpose of utilizing the waste heat, or a comprehensive simulation of the entire sulfuric acid production facility.

In all cases was the application of the mathematical modeling and optimization techniques highly profitable and it can only be recommended that it become an inseparable part and parcel of design and project assessments, including proposals for the construction of new sulfuric acid production plants in the developing countries.

7. Conclusions

Part B dealt with the production of sulfuric acid and also with its environmental effects and with opportunities for cutting down the wastes, particularly for SO_2 pollution abatement.

The sulfuric acid process has been chosen on account of reasoning that this is the truly mass-produced chemical where the production standard and the level of consumption have a direct bearing on the industrial maturity rating of the country, and also because ranking among the biggest consumers of sulfuric acid is the fertilizer industry, of paramount importance to the solution of the food problem of the developing countries.

The selection of specific technology for the sulfuric acid process as well as the design and interlinking of apparatus and the raw materials to be used make a rather comprehensive issue where a great number of local factors, availability of inputs, manpower skills, waste heat utilization, etc. all ought to be considered, with different solutions representing the optimum under different conditions. Nevertheless, a number of specific solutions based on the analysis performed can be defined:

1. The pollution problem of the H_2SO_4 plant working from elemental sulfur has been overcome with success by the double catalysis technology which warrants a total SO_2 conversion higher than 99.5%. Emissions of SO_2 can be pushed down even further, to amounts of no concern to the environment, by the Peracidox process if the facility is to be located in a densely populated area.

Proper operation of the contact reactor - which, for the purpose of attaining a sufficiently high SO_2 conversion, is the key apparatus - also is contingent on a proper catalyst selection; this matter was dealt with in Chapter B-4.

2. The pollution problem relates to the utilization in production of waste heat which can substitute in part the combustion e.g. of solid fuels, thus alleviating pollution. While the use of high-potential heat for rising steam is common, the use of lower-potential heat sources by adequate consumers has been recommended here and the related engineering requirements have been outlined.

3. Considerable ecological problems are provokes by sulfuric acid wastes. Description was given of how this problem appears to be coped with successfully using thermic decomposition - recycling and fresh acid production.

4. Of importance to the developing countries is also a high production reliability coupled with nonexacting requirements for maintenance and service. It is also for this reason that facilities where sulfur is worked to sulfuric acid can be recommended for the developing countries. In contrast to plant where other sulfur-bearing raw materials are processed, the facility which starts from elemental sulfur is very simple and reliable, its operation is stable and is not maintenance-intensive. As for process control, this can be mastered without difficulty using either manual

controls or simple computerized control systems.

It can be stated in conclusion that, as long as the recommendations made in Part B are adhered to, a sulfuric acid production facility can successfully be operated without unduly burdening the atmosphere by SO_2 emissions and other pollutants.

At the same time, such production represents an important source of steam for the associated productions at the chemical combine where the new facility is built, totalling some 1.2 tons steam per 1 ton H_2SO_4 produced.

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C. PRODUCTION OF NITRIC ACID

1. Introduction

1.1. General

The production of nitric acid bases totally on the raw material ammonia.

This ammonia is burnt and the resulting NO - NO_2 gases are absorbed in water giving nitric acid and waste NO_x gases.

In past times when only pressure-less installations were Known the waste gases contained about 3000 ppm NO_x. The development of acid resistant turbocompressors brought the use of nitric acid plants operating at pressures of 0,3 - 0,4 MPa and reduced the NO_x content in the gases to about 1200 - 1500 ppm.

A further improvement was the development of sieve - trays which enabled operation at pressures 0,7-0,8 MPa.

Computer designed absorption towers, together with constructional improvements allow now optimal yields and industrial plants designed on this base reach, when using cold cooling water, emission values of less than 200 ppm NO_x.

This development allowed to design and install plants with increasing capacities. The following Table I shows the increase of average capacity during the period 1950 - 1985.

Table C-1

Period	Average capacity of nitric acid plants expressed as tpd HNO_3
1950 - 1955	160
1956 - 1960	200
1960 - 1965	270
1966 - 1970	280
1970 - 1975	515
1976 - 1980	950
1981 - 1985	1200
from 1985 onward	up to 1500

The first dual pressure plants with capacities up to 1500 mtpd are now under construction as by Grande Paroisse for Rostock/DDR and by Uhde for Norsk Hydro Fisons Ltd GB and for Chemie Linz/Austria

1.2. Development of nitric acid production in C.S.S.R.

Production of nitric acid started in 1954 in the C.S.S.R. at present there are 18 plants in operation, divided over 5 locations :

Lovosice
Duslo Sala
Semtin
Ostrava and
Strazske

The total production amounts to ca $1x10^6$ tons HNO_3 100 % per annum.

The nitric acid produced is a base for the manufacture of fertilizers. The quantity of N in fertilizers is ca 600.000 tons/year. Together with another 100.000 tons imported nitrogen, the total quantity of N in fertilizers is about 700.000 tons. On an agricultural area of 6.800 ha this means a consumption of 105 kg/ha.

The ammonia necessary for this fertilizer production is partly produced in C.S.S.R. plants, partly imported from U.S.S.R.

From the 18 nitric acid plants mentioned, two plants are foreign deliveries : one in Duslo Sala and one in Ostrava.
The other 16 plants are designed and constructed by C.S.S.R. groups.

In 1985 the nitric acid production was as follows

Lovosice	350.768	tons HNO_3	100 %
Duslo Sala	369.020	"	
Semtin	106.459	"	
Chemko Strazske	76.185	"	
Ostrava	68.100	"	

making a total of 970.532 tons HNO_3 100 %

This production was achieved in 7196 hours of operation, making an average production of 134,87 tons per hour.

The main problems which encountered the C.S.S.R. producers are :

- environmental pollution
- saving of energies
- saving of raw materials
- effectiveness
  - a) from agricultural point of view
  - b) from economical side.

In environmental pollution the czechs made good progress in the reduction of NO_x in waste gases.

In 1978, with a total production of 1.017.600 tons there was an average NO_x emission of 12,6 kg NO_2/t HNO_3 equivalent to 1723 kg NO_2 per hour.

In 1985 these figures reached following values :

production	970 532	tons
emission	2,84	kg NO_2/t HNO_3
	383	kg NO_2/hour

This means only 21,5 % of the values reached in 1978.

The C.S.S.R. authorities prescribe for old plants a maximum allowable emission of 10 kg NO_2/t HNO_3 and for new plants a maximum allowable emission of 2 kg NO_2/ /t HNO_3 in the following a review is given with regards to the emission values of the plants (figures for 1985).

Plant	kg NO_2/t HNO_3
SCHZ Lovosice	
I - IV	1,89
V	0,89
Duslo Sala I - IV	1,45
Krebs - plant	2,0
VCHZ Semtin ZL	18,85
Ry	0,85
Chemko Strazske I	7,35
II	0,35
MCHZ Ostrava	5,50
Average	2,84

It can be seen from these figures that only the plants

VCHZ Semtin ZL
CHEMKO Strazske and
MCHZ Ostrawa give results

far over the value of 2,0 kg NO_2/t HNO_3 where as the Krebs plant Duslo Sala is just on the border.

The plants SCHZ V,VCHZ Ry and Chemko II apply the total catalytic reduction; the plants SCHZ I-IV and Duslo I - IV apply selective NO_x reduction.

Alkaline absorption is applied in the plants MCHZ, Chemko I and VCHZ ZL.

The Krebs plant Duslo has pressure absorption.

It may thas be stated that the plants, working with alkaline absorption give unsatisfactory results in the reduction of NO_x values.

Savings in raw materials and energies.

From data, received from Chemopetrol Lovosice, the cost per ton of HNO_3 can be analyzed as follows.

Raw materials + energies (incl. credit for energy)	Kčs	770,45
Catalyst	"	29,56
Personnel	"	8,73
Repair, maintenance	"	41,52
Amortisation	"	30,79
Fixed costs, overheads	"	141,17
Total	"	1022,22

The official sales price in C.S.S.R. is Kcs 1100/t.

This analyses shows that 75 % of the total cost amount to raw materials and energies.

This means that if a reduction of the total costs could be reached this could only be obtained by reduction of the costs for raw materials and energies.

An assumed reduction of the costs for raw materials and energies of 10 % will bring down the total costs to about 945 Kcs.

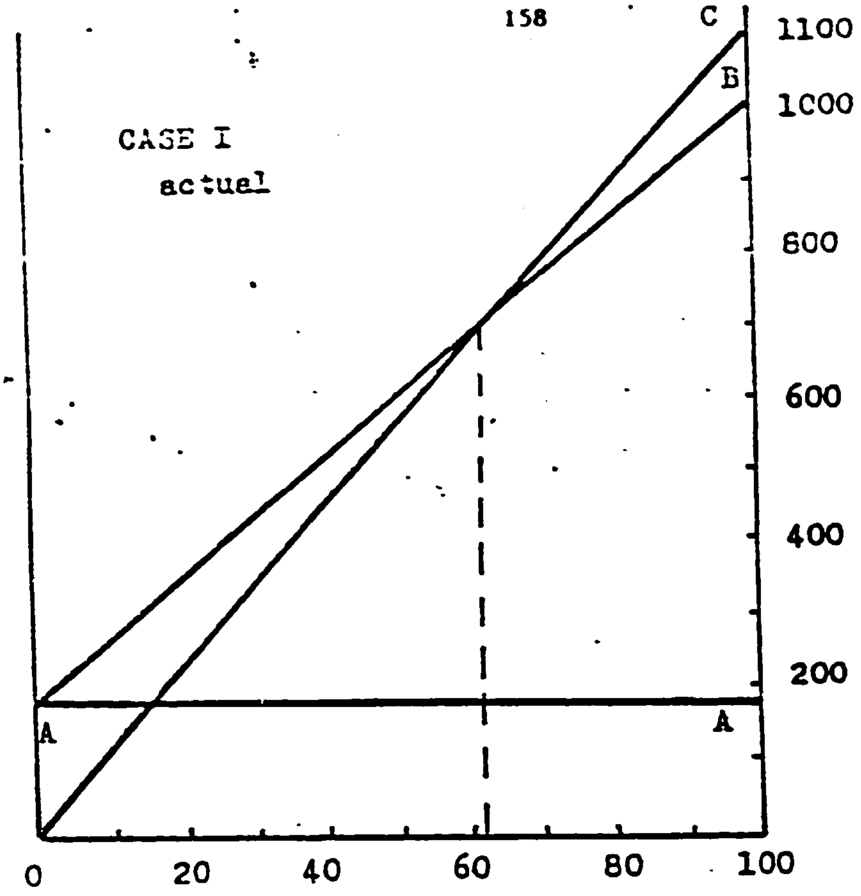
For these two cases the break-even-point has been constructed.

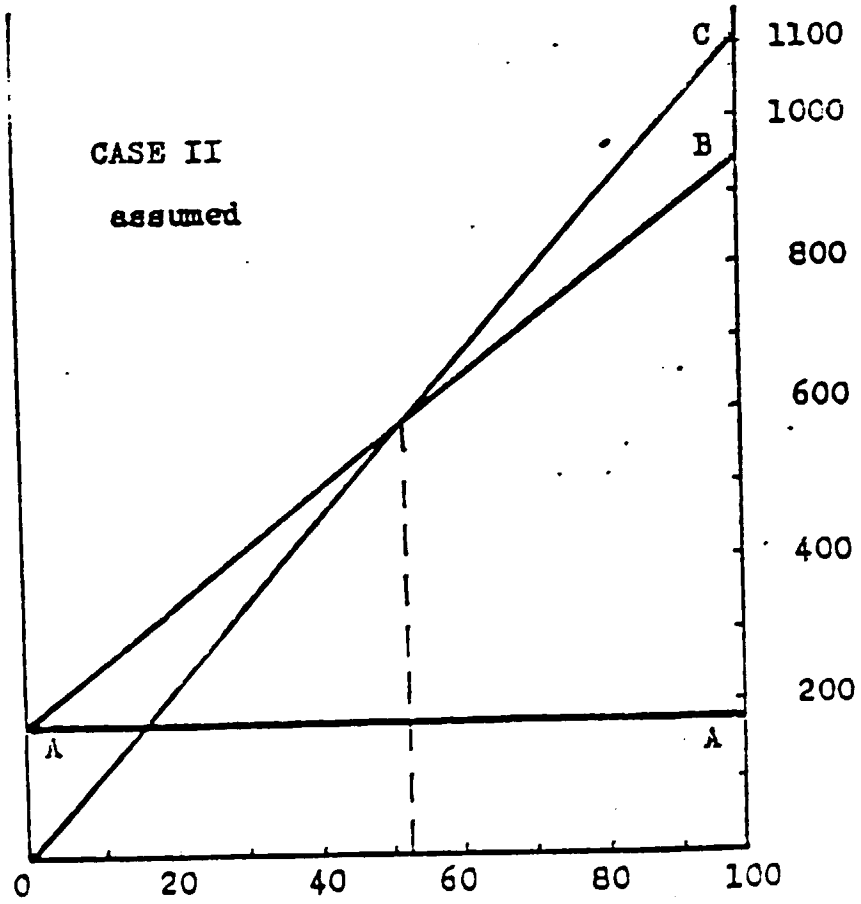
In the graphs the line

A.A denotes the fixed costs
A.B the variable costs
O.C the sales price

From the graph it can be seen the the break-even-points shifts from 61 % in the actual case to 52 % in the assumed case.

Means how to arrive at lower costs will be discussed in Chapter "Conclusions".


CASE I
actual
C
B
A
A
1100
1000
800
600
400
200
0
20
40
60
80
100


CASE II
assumed
C
B
A
A
1100
1000
800
600
400
200
0
20
40
60
80
100

1.3. Agricultural economics

The scope of this report doesnot deal with this point.

It may be stated that improvements could be reached by training the farmers to apply the right amount of fertilizer on the right time for the right cultures.

This should be cleared with governmental agricultural institutes and laboratories.

1.4. Foreign activities

The C.S.S.R. not only designed and constructed nitric acid plants in C.S.S.R but also intends to participate in the world market.

For this purpose a combination of following groups has been formed :

- Chemoprojekt Prague / projects
- UACH Prague, Academy / calculations process
- Chemopetrol Lovosice / supply of know-how
- VUCHZ Brno - Prague (Chepos) /design of equipment
- ZVU Hradec Kralove (Chepos)/Supply of equipment

In negotiations with potential customers this group acts as a unity.

This group deals not only with nitric acid plants but also with the RENOX - process for selective reduction, developed in CSSR.

2 . Nitric acid processes

The production of nitric acid from ammonia bases on following reaction equations :

1) $4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$

2) $2\ NO + O_2 \rightarrow 2\ NO_2$

3) $3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$

Reaction 1) is favoured by low pressure, reactions 2) and 3) are favourably influenced by high pressures.

These facts enable the selection of different combinations in combustion and in absorption.

In practice following combinations have been developped :

- Combustion and absorption at medium pressure	0,4 - 0,6 MPa
- Combustion at medium pressure	0,4-0,6 MPa
absorption at high pressure	0,5-1,4 MPa
- Combustion and absorption of high pressure	0,7-1,0 MPa

Combustion and absorption at lower pressures are obsolete, because at pressures $< 0,3$ MPa the waste gases contain more than 2000 ppm NO_x which causes heavy environmental problems.

The medium, dual and high pressure plants all have the following features :

Ammoniagas is mixed with air and burnt on a platinum-rhodium catalyst. The heat of reaction is utilized to generate superheated steam and to heat the tail gas from the absorption.

The generated steam and heated tail gas can be used in a turbine and expander to drive the compressor.

The nitrous gases are absorbed to form nitric acid in a sieve-tray column with internal cooling coils.

The three processes differ in the following :

a) medium pressure process

The tail gas is heated and forced to a catalytic NO_x reduction. From there the tail gas is expanded to regain part of the energy.

b) dual pressure process

The NO_x - gas from the combustion must be increased in pressure by an NO_x- compressor to meet the higher absorption pressure.

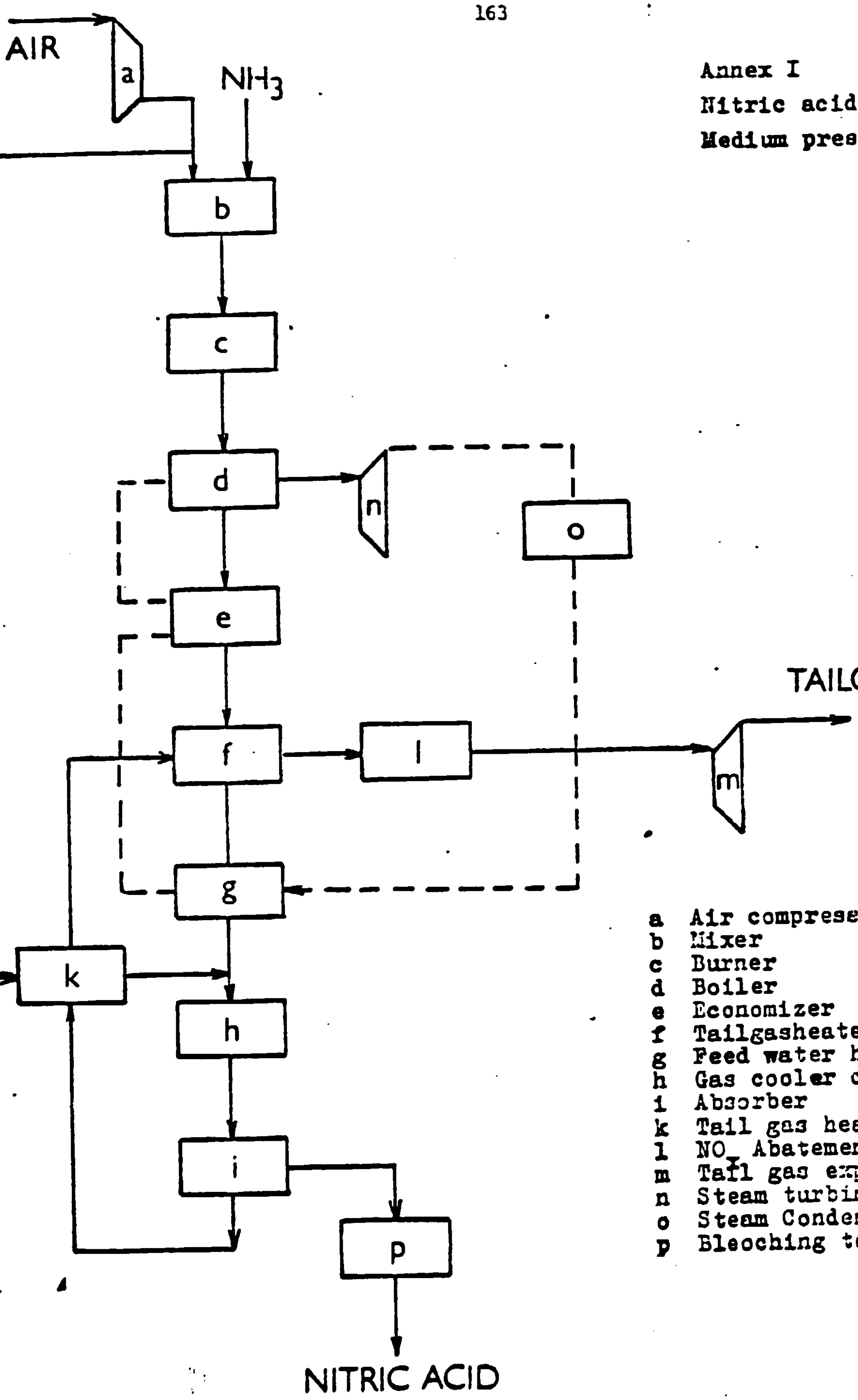
c) high pressure process

The air compressor has intercoolers, the tail gas after the expander is subjected to further heat exchange.

In each case the NO_x content in the tail gas will be below 200 ppm.

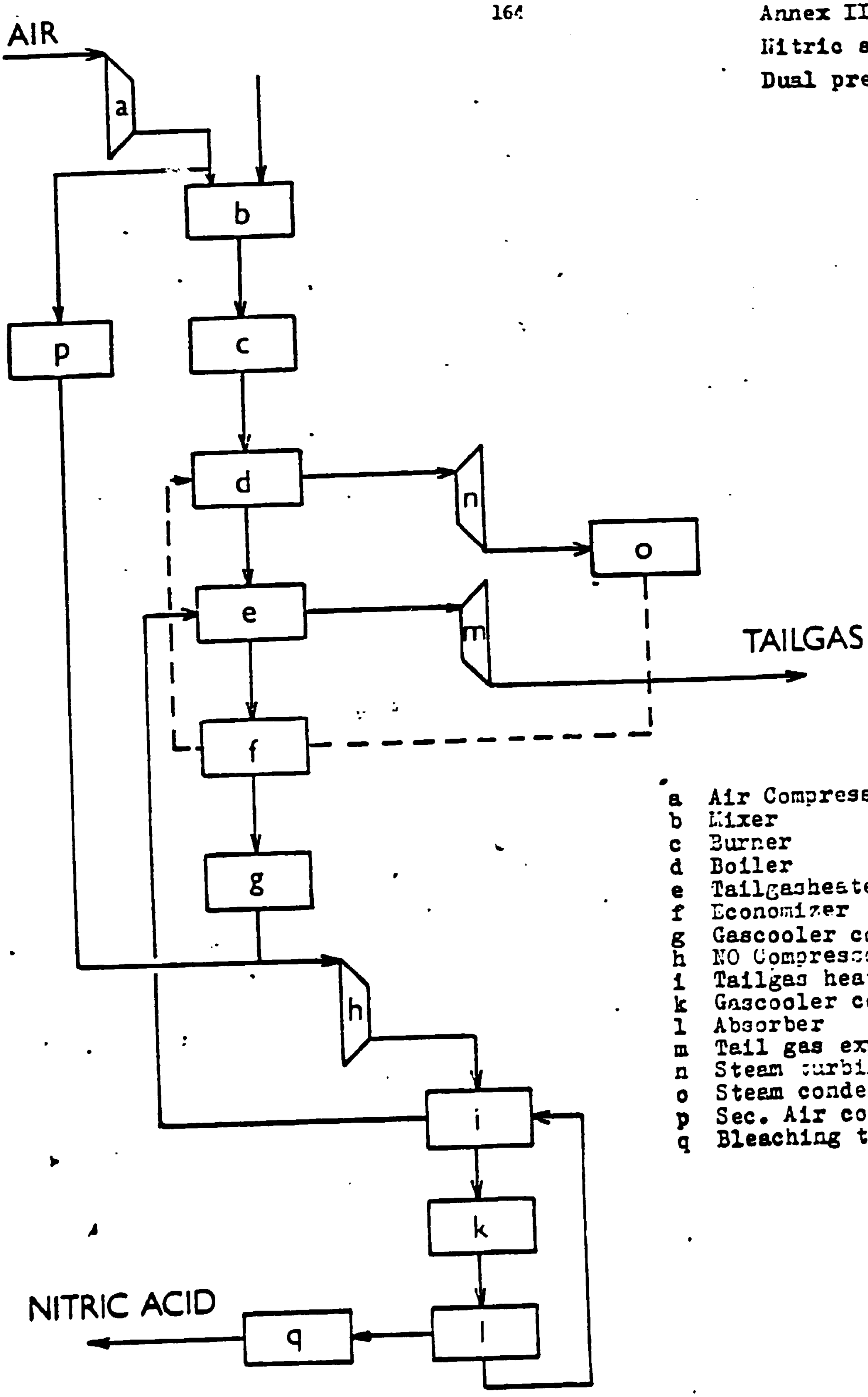
For Medium pressure process see	Annex I
for Dual pressure process see	Annex II
for High pressure process see	Annex III

Annex I
Nitric acid plant
Medium pressure



a	Air compressor
b	Mixer
c	Burner
d	Boiler
e	Economizer
f	Tailgasheater
g	Feed water heater
h	Gas cooler condenser
i	Absorber
k	Tail gas heater I
l	NO_x Abatement
m	Tail gas expander
n	Steam turbine
o	Steam Condenser
p	Bleoching tower

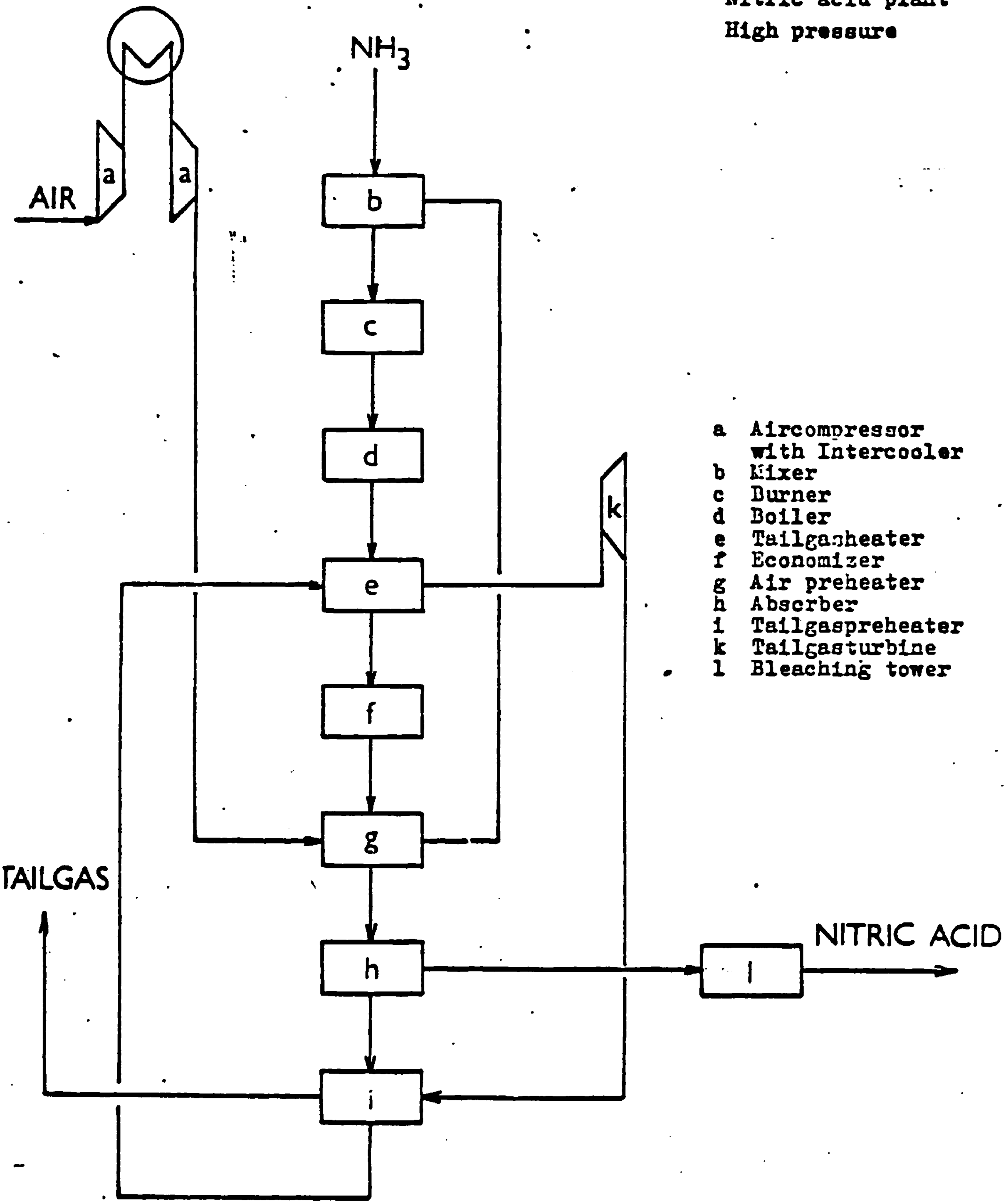
Annex II
Nitric acid plant
Dual pressure



a	Air Compressor
b	Mixer
c	Burner
d	Boiler
e	Tailgasheater II
f	Economizer
g	Gascooler condenser
h	NO Compressor
i	Tailgas heater
k	Gascooler condenser
l	Absorber
m	Tail gas expander
n	Steam turbine
o	Steam condenser
p	Sec. Air cooler
q	Bleaching tower

Annex III

Nitric acid plant
High pressure



a	Aircompressor with Intercooler
b	Mixer
c	Burner
d	Boiler
e	Tailgasheater
f	Economizer
g	Air preheater
h	Absorber
i	Tailgaspreheater
k	Tailgasturbine
l	Bleaching tower

The medium pressure process is economical for capacities up to 500 mtpd HNO_3 100 %. The NO_x content in the tail gases is high - about 600 ppm, sothat a selective reduction mast be included.

The dual pressure process is the most economical for capacities over 500 mtpd. Plants can now be constructed in one line up to capacities of 1500 mtpd. The NO_x content in the waste gases is lower than 200 ppm, normally 125 - - 150 ppm.

The high pressure process needs smaller equipment due to the higher operations pressures and is hence from economical point of view attractive.

A disadvantage is that the live time of the catalyst is short sothat more plant shut downs are required for changing catalyst. Also the yield of combustion is lower as in the other processes.

Honti (1) gives following parameters.

Operating Parameters for Ammonia Oxidation

Operating pressure	0,1 MPa	0,35 MPa	0,8 MPa	1,05 MPa
NH_3 concentration (vol %)	11,5-12,5	10,5-12,0	10,3-10,5	9,5-10,3
Gauze temperature (^oC)	790-850	870	920	940
Conversion efficiency (%)	97-98	96-97	95-96	94-95
Pt.loss (g/t HNO_3)	0,05-0,07	0,14-0,18	0,28-0,30	0,30-0,35
useful life of gauze pad (months)	6-12	3-6	2-3	1,5-2,0

3. Emissions in nitric acid plants and methods to fight these emissions

Emissions in nitric acid plants are visible as brown tail gases, this brown color being due to the NO_2 content. NO gases are not visible, other nitrous oxides are negligible.

When constructing new plants today there are a number of techniques that can be adapted to keep the waste gas concentration low and to adhere to the values required by the legislator. It can be said that the availability of highly efective sieve trays allows to design the process with flue gas concentrations of 400 - 700 ppm NO_x on an economical base.
If these values are still too high further possibilities must be investigated as there are
- extended acidic absorption, physical absorption
- alkaline absorption
- molecular sieves
- catalytic processes.

The advantages and disadvantages will be discussed now :

3.1. Extended acidic absorption

Due to improved energy recovery it has been possible to increase the pressure in the absorption and to apply highly effective sieve trays. At pressures over 0,8 mPa and by increasing the number of absorption trays an NO_x content of less than 200 ppm can be achieved.

An existing plant can be equipped with a newly-built high pressure absorption, an existing high pressure plant can be extended by one additional absorption tower.

Extended absorption can be applied but at some expense as the volume of absorber increases roughly proportional to (C_{NO_x})$^{-0,5}$ (2). In order to reduce absorber sizes, the use of a higher absorption pressure may be desirable.

An extended absorption process is economic up to 130 - 150 ppm.

If lower figures are required, either the absorption pressure must be increased and/ or the absorption column extended in height.
It must be mentionned that this will reduce the economic situation of the plant.

3.2. Alkaline absorption

This process gives better absorption by using alkaline liquids in the last part of the absorption column instead of water. In the case plant pressures above 0,5 MPa colorless waste gases and concentrations below 200 ppm

NO_x can be reached.

Well known as scrubbing liquid is Sodium hydroxyde solution, which forms sodium nitrite and sodium nitrate.

The process can be attractive ,if a market is available for the nitrites or nitrates.

Another possibility is to chemically wash with an urea solution. This process is not so attractive as at first a weak ammonium nitrate solution is obtained and at second expansive urea must be used to destroy the nitrous oxides.

3.3.Molecular sieves

The principle of the molecular sieves is the absorption of NO_2 at low temperatures and desorption at higher temperatures. They consist of minerals and mixtures of silicates, alumina or potassium, calcium and or sodium. With this process very low values of less than 50 ppm can be reached.

The equipment needed for this process is expensive and desorption at higher temperatures necessitates an expenditure of energy.

To allow continuous operation it is advisable to have 3 systems :

the first system absorbs NO_x
the second system is desorbed
the third system is cooled down

3.4.Catalytic processes

There are two different types of processes, the one using hydrogen or hydrocarbons, the other using selective catalytical combustion.

The main distinction between the two processes is that hydrogen or hydrocarbons react primarily with oxygen. When the oxygen in the tail gas is burn the excess of fuel reacts with NO_x and forms N_2.

The selective catalytic combustion uses ammonia and forms N_2 and H_2O after intermediate reaction.

The process using hydrocarbons as fuel has been applied mainly in the U.S.A. Aplication in other countries is very restricted, mainly due to following reasons

- high fuel costs
- problems due to presence of sulphur
- limited lifetime of catalysts
- nitrous oxide emissions are decreased but additional hydrocarbon emissions are released into the atmosphere. Question : are reasonable NO_x emissions more acceptable then colorless but larger hydrocarbon emissions.

The legislation of the Federal Republic of Germany has set the emission limit of hydrocarbons to 200 mg C/m^3 tail gas corresponding to ca 375 ppm CH_4.

In the U.S.A. emission values up to 5000 ppm CH_4 are measured.

The process of selective reduction with ammonia has been known for several years and depends on the fact that nitrogen oxides in nitric acid tailgas can be converted on a V_2C_5 catalyst with ammonia in accordance with following reaction equations.

$$3\ NO_2 + 4\ NH_3 \longrightarrow 3{,}5\ N_2 + 6\ H_2O$$

$$3\ NO + 2\ NH_3 \longrightarrow 2{,}5\ N_2 + 3\ H_2O$$

In the process the waste gases of the absorption are heated up to the catalysts operating temperature which lies between 250 and 350 °C and are then forced through a reactor, where the a.m. reactions take place. The treated gases are then blown to atmosphere.

The installation of selective catalytic purification in old plants as well as the operation of this purification presents no problems.because it has the least influence on other process parameters.

4. Materials of construction and corrosion in nitric acid plants

The nitric acid industry has to use for the prevailing corrosive conditions special stainless steels. Stainless steels are defined as iron based alloys with at least 12 % chromium.

They are classified as

- martensitic steels with 11,5 - 18 % Cr
- feoritic steels with 14 - 30 % Cr
- austenitic steels with 16 - 26 % Cr

The austenitic steels are the most widely used in the fertilizer industry due to their good corrosion resistance and good welding properties.

In nitric acid plants the material mostly used is a low carbon version of the standard Cr-Ni steel, the AISI 304 L or its equivalent, the german 1,4306. This material in general provides good resistance to intergranular corrosion. If the material is used for service at higher concentration and elevated temperatures it is found that sometimes intergranular corrosion will appear.

The reason is the presence of C, Si, P and S in higher amounts but still within the specification. To avoid this phenomenon it is advised to use materials with amounts of the mentioned elements far below those specified.

Investigations of the influence of the elements C, Si, P and S led to the development of a new special stainless steel. This steel, classified as AISI 310 L or 1,4335 shows folowing analyis.

C max 0,020 %

Si	max	0,030	%
P	max	0,020	%
S	max	0,015	%
Cr		24,5	%
Ni		20,5	%
Mn		1,8	%

In this steel the high amount of Cr as well as the low impurity levels contributes to better corrosion resistance.

Among the different manufactures the SANDVIK 2 RE 10 (4) and the UDDEHOLM UHB 25 L may be mentioned.

This material shows in HUEY test (with boiling 65 % nitric acid) extremely low corrosion rates.

The grade has been succesfully used in tailgas heaters and cooler condensers in nitric acid plants, where formation and reboiling of nitric acid droplets may occur.

In one plant 304 L tubes failed after 18 months in service in a cooler condenser. After retubing with 2 RE 10 the tubes have now been in service for over 5 years without any sign of attack (3).

In many plants cooling water is of bed quality and may contain high amounts of chlorides. In such plant a special stainless steel with composition.

C	max	0,020	
Si	max	0,4	
P	max	0,020	
S	max	0,015	
Cr		25	%
Ni		22	%

Mo 2,1 %

gives the best results for a cooler condenser since it has excellent resistance to nitric acid solutions. Owing to the high chromium and molybdenum content it has good pitting corrosion resistance.

Due to the Ni content it has good resistance to stress corrosion cracking. Both types of corrosion may occur on the cooling water side. A typical trade classification is SANDVIK 2 RE 69.

The main points in nitric acid plants where corrosion may occur are :

- the wet parts of waste heat users
- the inlet of tail gas heaters
- the hot parts of cooler condensers, especially uncooled walls.

and it must strongly be recommended to consider the application of these types of stainless steels in order to prolonge life of equipment.

5. Safety considerations in operation of nitric acid plants

Although modern nitric acid plants are designed with utmost consideration for safety aspects, certain hazards may not be overlooked because they can lead to damaging effect to human life, industrial property and to environment.

In nitric acid production ammonia is oxidised with air. The liquid ammonia is vaporized by means of warmed cooling water before entering the ammonia air mixer. The air and ammonia flow rates are monitored, the proper mixture is obtained by ratio control. The ammonia concentration remains below the explosion level, which lies between 15,5 and 23 vol % NH_3 at 0,1 MPa and 100 °C. If liquid ammonia in the form of small droplets is entrained with the ammonia gas the flow-ratio-controller cannot act on this increased amount of ammonia.
This means, that the lower explosion limit will be exceeded and the consequence is that an explosive mixture enters the combustion section causing an explosion in this part of the plant.

Unreacted ammonia forms ammonium salts when in contact with nitric acid. The salts formed are ammonium nitrite and ammonium nitrate.

Generally the formation of ammonium nitrate takes place in the cooler condensor or boiler feed water preheater when the first nitric acid is formed.

Very small droplets of ammonium nitrate solution are formed and transported to the NO gas compressor where they are deposed, mainly in the first stages of the compressor. In the compressor the nitrate deposits may cause heavy vibrations due to imbalance and in greater quantities they may load to explosions.

It is therefore necessary to clean the compressor by injection of water or steam.

This cleaning must be excuted continuously during the start up phase of the ammonia burner until complete activity of the catalyst gauzes. During normal operation this cleaning must be done once per shift.

Passing of unreacted ammonia through the burner can be monitored by the ammonium nitrate content of the nitric acid formed in the cooler condenser. When the ammonium nitrate content exceeds continuously 100 mg/ltr. after start up the combustion is incomplete and the burner should be inspected.

Explosive mercury compounds (azides) may form if compressed ammonia containing gases come in contact with metallic mercury. Thermometers, pressure gauges and the like installed on ammonia bearing equipment or piping should therefore not be of the mercury type.

In the scope of the safety considerations it must be clear that accidents can be avoided if the production plant is always kept clean and in technically proper condition. Also following rules must be followed :

- Escape ways and fire escapes must be kept free
- Absorption towers must only be mounted if a serviceable gas mask is carried along
- Protective covers on mobile parts of the equipment must be orderly fixed
- Cleaning work on running engines should not be made
- In case of open erection holes handrails must be provided

For a good training of all operating people the method od HAZOP (hazard and operation) should be followed.

With this simulator type training method all possible deviations, irregularities or operating faults can be given in and the appropriate means to resolve these can be studied.

6. Economy of operation

The economy of operation for the three processes described depends on a number of local conditions as :

- installation costs
- prices of raw materials
- plant size
- cooling water temperature
- costs of energy
- labour costs
- local NO_x-emission requirements
- capital costs

and final decision can be taken only after calculation for each individual case.

For a comparison of the three processes, MP, DP and HP, the main consumption figures are given in attached Table I.

From this table it can be seen that for the MP- and DP-processes the consumptions of NH_3 and Pt are acceptable, for the HP process, these figures are high. A factor which especially plays a role in the calculations at high costs for ammonia and platinum.

In order to compare the production costs for 1 t HNO_3 100 % in the MP and DP process a calculation was made for MP and DP processes each with capacities of 360, 600 and 1100 mtpd HNO_3 100 %.

The calculations include

- raw material costs
- amortisation, taken as 10 % of installed costs
- labour, overheads and maintenance, taken as 25 % of installed costs.

Table II gives the costs of raw materials and energies for 1 t HNO_3 100% for both processes.

The prices taken were supplied by the staff of SCHZ-Lovosice. The installed costs used base on W-European conditions.

a) MP	360 mtpd	$\$\ 12,5 \times 10^{6}$
	600 "	$\$\ 17,8 \times 10^{6}$
	1100 "	$\$\ 28,5 \times 10^{6}$
b) DP	360 mtpd	$\$\ 14,0 \times 10^{6}$
	600 "	$\$\ 17,1 \times 10^{6}$
	1100 "	$\$\ 25,4 \times 10^{6}$

Table III gives the total costs for 1 t HNO_3 in both processes.

The influence of varying raw material costs on the price of 1 t HNO_3 has already been discussed in Chapter II. 2.

The tables show that, starting from 600 mtpd, the Dual Pressure-Process is most economic.

TABLE C-2

Comparison of consumption figures
expressed per 1 t HNO_3 100 %

Process type		MP	DP	HP
Operating pressure	MPa	0,6	0,5/1,2	1,0
Ammonia	kg	283 +	280	287
Yield on ammonia	%	95,5	96,8	94
Platinum	gr	0,15	0,15	0,30
Boiler feed water	t	0,3	0,3	0,3
HP excess steam 2,5 MPa 400°C	t	0,75	0,95	0,5
Cooling water at 10°	m^3	130	140	140
Electric energy	kWh	9	8	8
Process water	t	0,5	0,5	0,5
Catalyst change after months		5-6	5-6	1,5-2

All processes with NO_x
emission < 200 ppm

+ NH_3 consumption for
selective reduction included

Table C-3

	Unit	Unit price kcs	Medium pressure		Dual pressure	
				kcs/t HNO_3		kcs/t HNO_3
Ammonia	t	2600	0,283	735,80	0,280	728,00
Catalyst	gr	402,9	0,15	60,44	0,15	60,44
Boiler feed water	t	1,98	0,3	0,59	0,3	0,59
Cooling water	m^3	0,65	130	84,50	140	91,00
Process water	t	1,32	0,5	0,66	0,5	0,66
El. Energy	kwh	0,40	9	3,60	8	3,20
Steam credit	t	125	0,75	-93,75	0,95	- 118,75
costs/t HNO_3	kcs			791,84		765,14

Table C-4

Production costs per t HNO_3 100 %

A Medium Pressure

mtpd		360	600	1100
Raw materials, energies.		791,84	791,84	791,84
Amortisation.		66,80	57,09	49,85
Overheads, Labour, Maintenance		167,00	142,72	124,62
Cost /t HNO_3	kcs	1025,64	991,65	966,31

B Dual Pressure

mtpd		360	600	1100
Raw materials, energies.		765,14	765,14	765,14
Amortisation		74,80	54,86	44,45
Overheads, Labour, Maintenance.		187,01	137,16	111,25
Cost/t HNO_3	kcs	1026,95	957,16	920,84

7. Developments in catalyst-manufacture

Catalysts are defined as materials which influence the velocity of chemical reactions without participating. Although catalytic action is already known for centuries, industrial application started from about 1800. Known is the example of burning hydrogen over platinum as discovered by Dobereiner in 1823.

Catalysts play an important role in todays human life.
It may be remembered that, without the catalytic synthesis of ammonia, feeding the worlds population would be impossible.

The firstnitric acid plants operated with a platinum-catalyst in the form of coils made from Pt-sheets.

Lateron these coils were replaced by gauzes made from Pt-wires 0,06 - 0,07 mm filament and 1024 mesh/cm^2.
It was found that addition of rhodium to the platinum increased the yield of combustion.
At present practically all nitric acid plants operate with catalysts consisting of 90 °/. Pt and 10 °/. Rh.

The Prague High School of Chemical Engineering developped a catalyst, the active element being cobalt. Good results were obtained with this patented type, named AMCX.
In Chemko-Strazske the number of gauzes could be reduced from 24 to 8+AMCX.
In preparation is a trial in Duslo.Sala where a combination of Degussa-Pt-recovery and Amox is expected to bring reduction of number of gauzes as well as savings in Pt-losses.

This is at present the aim of scientifists, savings in expensive Pt-consumtion.

The trend is to replace part of the Pt gauze by a non-noble metal. Investigated is the behaviour of catalysts made on Fe_2O_3 and Al_2O_3 base (USSR-catalyst KH-2T). This catalyst was used as 2nd stage and decreased the Pt-losses to 0,09-0,10 gr/t HNO_3 at operation 0,710 MPa and 860 - 920 °C.

Good results were also obtained in using Cr_2O_3 as catalyst.

Tests were carried out in a two-stage process with a Cr_2O_3 - catalyst being substituted for the Pt-catalyst. The total oxidation degree was 0,95 at 570 - 900 °C. It has also been found that the service life of a Cr_2O_3-catalyst and its selectivity with respect to the oxidation of NH_3 were significantly higher than those of a catalyst composed of Fe_2O_3 and Cr_2O_3 (95/7).

In the recovery of platinum a new system developed by Engelhard - Degussa, palladium is the main component. This system recovers up till 80 %.

8. Conclusion

1. In C.S.S.R nitric acid is produced in 18 plants. Operational records show that most of these plants function well. The plants which were visited made a good impression and the personnel showed good knowledge.

In a few plants these are problems with NO_x emissions. As has been shown in Chapter 1.2. these problems are met in the plants operating with alkaline absorption.

Probable reasons may either be found in

- unsatisfying operation of the absorption section of the nitric acid plant
- problems with saturation of the scrubbing liquid
- design of the scrubbing section

As a first step for the improvement of these plants it has been agreed, in a discussion with Prof. Dr. Skrivanek, Head of the Chemical Engineering Dept of the Prague High School, that this institute will investigate the reasons for this unsatisfactory operation. The institute will then make proposals for modification and improvement.

As a further step it has been agreed that two of the three plants will be equipped with an additional selective reduction.

For the design of new plants the required capacity determines the process type.

2. As has been shown for capacities up to 500 mtpd HNO_3 the medium pressure process is the most economical. In order to obey legislative regulations with respect to NO_x emissions a treatment of the tailgases must be provided.

From the four possibilities described in Ch. 3 it is recommended that the selective reduction method should be preferred. This method gives low emission values, about 100 - 150 ppm.

For plants with capacities over 500 mtpd the dual pressure process should be selected.

This process is in this range (500 - 1500 mtpd and over) the most economical. Plant costs are less than with the medium pressure process and with absorption pressures of 0,8 - 1,1 MPa and using cold cooling water NO_x emissions of 50 - 100 ppm can be reached.

3. High pressure plants can only be recommended when capital savings due to reduction of investment cost and elimination of nitrons gas compressor at least compensate for lower yield, higher catalyst losses and more frequent shut-downs. Low ammonia prices and increasing interest rates favour also the mono-high. pressure type plants.

For more economical operations new plants should be equipped with improved plant instrumentation and also the possibility of computer control should be considered.

An evalution of HP and DP processes is given by Voelker (5).

4. For the improvement of existing plants the methods of selective reduction as well as an extended absorption may be proposed.

As has been stated in Ch. 3 the method of extended absorption causes extra expenses as the absorber volumen increases proportionally to

$$\left[C_{NO_x}\right]_0^{-1,5}$$

where C_{NO_x} denotes the local mole fraction of nitrons gas at exit of absorber.
A higher absorption pressure, if possible to be applied, may reduce the absorber size.

5. Important for the acceleration of the oxydation reaction is a certain excess of oxygen.
This oxygen must be supplied somewhere after the combustion selection in order not to dilute the ammonia-concentration in the mixed gas.
Adding secondary air minimizes the quantity of effluent nitrons

As too less O_2 slows the oxydation and too much O_2 dilutes the C_{NO_x} the secondary air supply must be so regulated that the O_2 concentration lies between 0,04 and 0,05 mole fraction at the exit of the absorber.
Finally a reduction in temperature may increase the HNO_3-output.
By this reduction the gas-phase equilibrium moves towards the formation of more nitric acid A decrease in temperature of 5°C improves the absorption rate and increases the acid strength by about 2 %.

6. In a nitric acid plant energy is brought in with the combustion of ammonia.
The outgoing energy is in the form of steam, for electric energy generation or for export.

Energy consumers in the plant are the air compressor and the NO compressor.
Energy suppliers are steam turbine and tail gas turbine.

Essential improvement of plants consist of optimal utilization of process heat for energy recovery.

Dual pressure plants operate with tailgas temperatures of 350 - 400 °C. It is possible to have a higher tailgas preheating which may improve the waste heat utilization.
The tailgases may be preheated up to ca 600 °C the remaining heat content in the tail gas after the turbine can be used to produce an extra quantity of steam.

It can be calculated that in such a case for a plant with capacity 1000 mtpd HNO_3 the energy profit will be about 550 KW.

This proceder needs however a more expansive tailgas turbine and a second boiler.

It must be studied from case to case if the profit of the gain in energy allows the installation of this supplementary equipment.

7. With regards to materials of construction following recommendations can be made:

It is of utmost importance to use in the critical parts of a nitric acid plant, as these are:

wet parts of waste heat users
inlet of tail gas heaters
hot parts of cooler condensors

only these materials with very low amounts of impurities as C, Si, P and S.
Examples are SANDVIK 2 RE 10 and UDDEHOLM 25 L or the modified AISI - 304 L.

It is of importance to investigate the behaviour of the materials to be used as construction materials for those parts with the aid of the HUEY test. However the use of those materials should be restrieted to areas of very severe corrosion, due to the higher cost.

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D. REPLACEMENT OF CHEMICAL REDUCTION BY CATALYTIC HYDROGENATION IN PRODUCTION OF ORGANIC SUBSTANCES

1. Replacement of chemical reduction by catalytic hydrogenation-a survey

Table D-1 gives a listing of the most common cases where chemical reduction can be replaced by catalytic hydrogenation, including those cases where catalytic hydrogenation is irreplaceable.

Table D-1 Survey of the reduction reactions

Starting substance or type	Product or type	Chemical technique replaced
double bond	saturated bond	-
conjugated double bonds	partially or completely satd.	Na, Zn
acetylenic bond	part. saturated	Na, Zn, electrochem.
aromatic ring	cycloparaffinic ring	Na, HI
aromatic heterocycles	saturated heterocycles	Na, Zn, electrochem., formic acid
aldehydes, ketones	alcohols, hydrocarbons	Na, $LiAlH_4$, Meerwein-Ponndorf, Clemensen, Wolf-Kižner, electrochem.
imines, oximes	amines	Na, Zn
acids	alcohols, hydrocarbons	$NaAlH_4$, electrochem., HI
esters of acids	alcohols	Na, $LiAlH_4$
chlorides of acids	aldehydes alcohols	$LiAlH_4$ LiH

Table D-1 continued

amides of acids	amines	electrochem., Na, $LiAlH_4$
nitriles of acids	amines	Na, $LiAlH_4$
halogenides	hydrocarbons	Na, HI
nitro-substances	lower reduction stages nitro-group reduction	Fe, Zn, sulfides, electrochem., $SnCl_2$, etc.

The breakdown of processes in this study has been approached from the aspect of the reduced bonds as follows:

A. reduction of multiple bonds between two carbons
B. reduction of aromatic rings
C. reduction of carbonyl compounds
D. reduction of nitro-substances
E. reduction of other nitrogen-bearing compounds
F. hydrogenolytic cracking.

2. Reduction of multiple bonds between two carbons

2.1. Double bond hydrogenation

On an industrial scale the reduction of bonds between two carbons is done nearly always by catalytic hydrogenation. This is a process that became mass-implemented to the greatest extent, mainly in various refining technologies and in hydrogenation of fats. Recently there has been a considerable expansion of either a partial or a total hydrogenation of cyclo-oligomers /mainly of ethylene and butadiene/ in conjunction with the production of new types of special-purpose monomers and macrocyclic compounds. Also of importance is the partial hydrogenation of cyclopentadiene to cyclopentene, the monomer for specialty rubbers.

Catalytic hydrogenations of double bonds do not constitute a classical example of replacements of the earlier known chemical reductions by more advanced catalytic processes and, hence, are only mentioned for the sake of completeness, to round off the picture of the reducible functional groups.

2.2. Triple bond hydrogenation

In analogy to the case of the double bond reduction, the triple bonds are reduced much more often by catalytic hydrogenation than by chemical reduction processes. In organic synthesis as such, it is the partial hydrogenation of triple to double bond which is much preferred to the rather unfrequent total hydrogenation which proceeds up to the paraffinic C-C bond.

Palladium-based catalysts which, moreover, very often receive special pretreatment, are used most widely in the selective catalytic hydrogenation of triple bonds. Certain other catalysts such as skeletal iron and copper are also believed to possess a high selectivity for triple-to-double bond hydrogenation /1,2/.

Ranking among the most important commercial processes in the past was the hydrogenation of acetylene to ethylene as it was run e.g. in Germany. The same principle is used considerable expansion of either a partial or a total hydrogenation of cyclo-oligomers /mainly of ethylene and butadiene/ in conjunction with the production of new types of special-purpose monomers and macrocyclic compounds. Also of importance is the partial hydrogenation of cyclopentadiene to cyclopentene, the monomer for specialty rubbers.

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Ranking among the most important commercial processes in the past was the hydrogenation of acetylene to ethylene as it was run e.g. in Germany. The same principle is used presently in the purification of ethylene to remove admixtures of acetylene, formed during the pyrolytic processing of hydrocarbon fractions. Acetylenes are similarly removed in the processing of the pyrolytic C_4 hydrocarbon fraction if this is to be used for the production of 1,3-butadiene by what is called the CAA process /isolation using ammonia solutions of copper salts/ through partial hydrogenation on palladium catalysts under mild reaction conditions /so-called kalthydrierung/. Another example is furnished by the commercial application of Favorski's synthesis in the production of isoprene from acetone and acetylene by the SNAM process, where 2-methyl-3-butyne-2-ol is subjected to mild hydrogenation /at 30-80°C, 0.5-1 MPa/ on a palladium catalyst to yield the appropriate olefinic alcohol.

The high selectivity of palladium catalysts during triple bond hydrogenation can be tracked down to the high difference between the adsorptivities of the triple and the double bonds, so that the substance with olefinic bonding which is formed is displaced from the catalyst surface by the alkyne-type feedstock and is only capable of hydrogenation at a very low concentration of the alkyne substrate. The difference in adsorptivity is made even more pronounced in a number of cases due to catalyst modification by metals, alkalies, pyridine and quinoline, carbon monoxide, etc. Inasmuch as the selectivity of triple bond hydrogenation falls off with rising temperature, the reaction conditions preferred are rather mild.

The case of triple bond hydrogenation also is not to be regarded as a typical replacement of established chemical reduction reactions by hydrogenation.

catalysts and hydrogenated in the second stage on platinum group metals and, more recently, also on highly active nickel catalysts.

It is the nickel catalysts which, on the whole, have found their widest application exactly in the hydrogenation of aromatics. They are at a disadvantage at higher temperatures, owing to the hydrogenolytic effect. For this reason the process must often be conducted under somewhat more moderate conditions while resorting to higher-activity catalysts. Cases exist where not even this is of help - the arylhalogenides cannot be hydrogenated sofar to reasonable yields of cyclohexyl halogenides, inasmuch as the hydrogenolysis of the halogenide which is aromatically bonded proceeds much more easily than the catalytic hydrogenation of the aromatic ring.

The fact that the aromatic ring, in contrast to other functional groups, is relatively difficult to reduce renders it impossible, or rather difficult at the least, to prepare certain other substances featuring the cyclohexanic skeleton.

For instance, nitrobenzene cannot be hydrogenated to nitrocyclohexane, nor arylolefins to cyclohexyl olefins; hydrogenation of acetophenone to cyclohexyl methyl keton or to alcohol meets with difficulties. In the last-mentioned case, Ru or Rh catalysts are necessary which are capable of hydrogenating the aromatic ring under relatively mild reaction conditions such that the hydrogenation of the keto-group or the hydrogenolysis of the hydroxy-group need not occur yet.

A special case of aromatic ring hydrogenation is represented by the hydrogenation of aromatic hydroxy-compounds to cycloparaffinic ketones, which in fact is a partial hydrogenation. The greatest importance must be accorded to the hydrogenation of phenol proper to cyclohexanone required for caprolactam production, of resorcin to 1,3-cyclohexanedione, and of beta-naphthol to beta-tetralone. The palladium catalyst, because of its considerable selectivity, has proved useful for these reactions, but once again the reaction conditions ought to be mild /temperature of max. 100°C/. In some cases the catalyst is subjected to partial deactivation /by N-ethyl morpholine etc./. Procedures have also been worked out which make use of nickel catalysts; alkaline media are used /Ra-Ni, 50°C, 7-10 MPa, addition of H_2O + NaOH/. Yields of about 90% are obtained and most of the residue is the products of total hydrogenation.

It is clear from what has been said above that not even the hydrogenation of aromatic rings belongs to the classical examples of chemical reductions being replaced by catalytic hydrogenations.

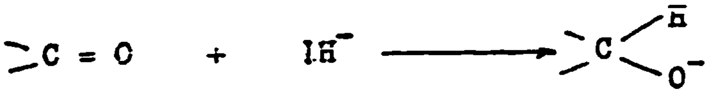
4. Reduction of carbonyl compounds

The reducibility of the carbonyl function depends on what groups are bonded to the carbonyl carbon. The reduction of aldehydes is the easiest, the reduction of ketones is more difficult. The carbonyl group in acids and their derivatives resists reduction to a considerable extent. A great number of chemicals can be used as reduction agents /and, in some of the cases, interesting side reactions occur which can be put to practical use/, or, alternatively, the reduction can be effected through catalytic hydrogenation.

4.1. Chemical reduction of carbonyl compounds

Carbonyl in aldehydes and ketones can be reduced to a pertinent alcohol or even a methyl group or methylene. The reduction to alcohol can be effected chemically using a variety of methods: by metals, hydrides, electrolysis, by hydrogen iodide, and by the Meerwein-Ponndorf method /3/ /i.e., by isopropyl alcohol in the presence of aluminum isopropyl alcoholate/.

When metals and hydrides are used as reduction agents, it is assumed /4/ that the reduction proper is effected by the hydride ion



$$>C=O \quad + \quad 1H^- \longrightarrow >C\begin{smallmatrix}\diagup \bar{H}\\ \diagdown O^-\end{smallmatrix} \qquad (1)$$

$$>C\begin{smallmatrix}\diagup H\\ \diagdown O^-\end{smallmatrix} \quad + \quad H_2O \longrightarrow >C\begin{smallmatrix}\diagup H\\ \diagdown OH\end{smallmatrix} \quad + HO^- \qquad (2)$$

Reduction by metals can proceed in either an acidic environment /e.g., Zn + mineral acid/ or an alkaline environment /sodium in wet ether, sodium amalgam, etc./.

The carbon atom of the carbonyl group is presumably attacked by electrons from the metallic surface on which the carbonyl groups is attached by chemisorption at the time when the reaction is taking place. It is necessary however that a donor of protons /water, acid, alcohol/ be present in the system, in order to bring to completion the transformation of the carbonyl group into an alcoholic group:

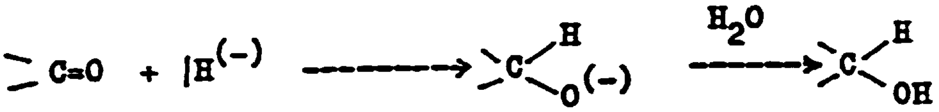
$$\underset{\uparrow 2e}{>C=O} \quad + \quad /Zn/_x \longrightarrow >\bar{C}-O^- \quad + \quad Zn^{(2+)} \quad + /Zn/_{x-1} \qquad (3)$$

$$>\bar{C}-O^- \quad + \quad 2\,H_2O \longrightarrow >CHOH \quad + \quad 2OH^{(-)} \qquad (4)$$

Another reaction which appears feasible is the direction reaction of protons with the electrons of the metal:

$$Zn \longrightarrow Zn^{(2+)} + 2\,e \qquad (5)$$

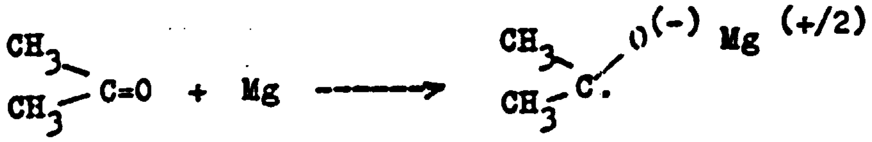
$$H^{+} + 2e \longrightarrow |H^{(-)} \qquad (6)$$



(7)

The same mechanism can also be proposed for the electroreduction of ketones on a metal cathode. The reaction diagrams indicate that the reaction is to be conducted in a polar medium.

When ketones such as acetone are reduced in a less polar environment /in benzene/ using suitable metals /magnesium/, the reaction proceeds differently: the carbonyl group reacts with the metal electrons yielding a radical-ion which is doubled due to the absence of protons in the reaction medium. The reaction products are pinacols



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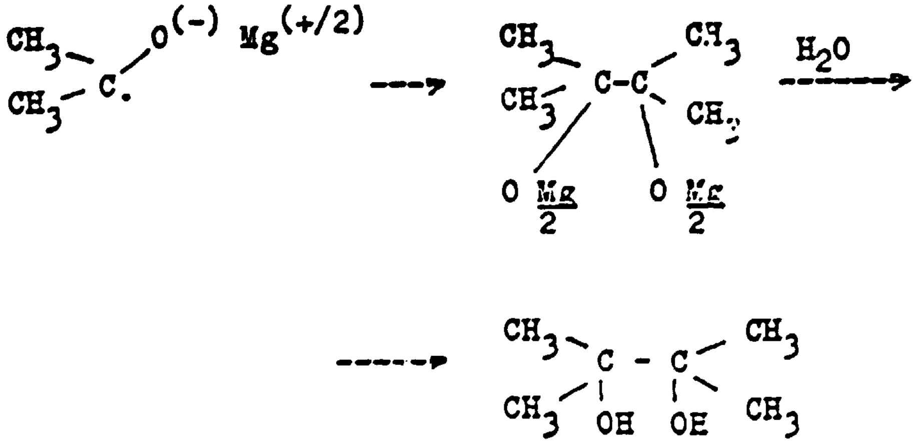


(9)

At suitable reaction conditions the pinacols may become the chief reaction products /reduction by sodium, amalgamated magnesium and aluminum, electrolysis//3/.

Reduction of carbonyl to methyl or methylene can be effected by ordinary techniques only with such compounds that have their carbonyl group adjacent to the aromatic ring. Frequently encountered reactions include the transformation of aromatic aldehydes and ketones to hydrocarbons as the result of reduction by sodium, lithium-aluminum hydride, zinc, hydrogen iodide, or electrolysis. By the last two methods the aldehydes and ketones can be turned to hydrocarbons quite universally, in spite of the absence of an activated carbonyl. The same products are obtained by reduction using the Clemmensen technique /ketone or aldehyde reduction by amalgamated zinc in hydrochloric acid medium/ or by two-stage reduction using the Kižner-Wolff technique. The latter reaction consists in the preparation of a hydrazone of the aldehyde or ketone by letting it react with hydrazine which, on heating with strong alkalies, splits off its nitrogen and yields a hydrocarbon /thus the initial carbonyl is converted to a methyl or methylene group/.

A survey of these reactions can be found in literature /5,6/.

The aforementioned reductions can obviously be also accomplished by catalytic techniques /cf. Chapter 5.3./. However, cases also exist where catalytic hydrogenation would accomplish nothing. For example, catalytic hydrogenation cannot be used to turn nitro-benzaldehydes to nitrated benzyl alcohols, owing to an unfailing formation of pertinent amino-derivatives on all known catalysts /whereas e.g. the aldehydic group can be reduced by $NaBH_4$ while retaining almost quantitatively the nitro-group/. Reactions of this type find application in the production of specialty pharmaceuticals.

4.2. Catalytic hydrogenation of carbonyl compounds

Most of the chemical reductions of carbonyl compounds, alluded to in the foregoing Section, can be effected by catalytic hydrogenation.

Catalytic hydrogenation of aldehydes is easier to perform than that of ketones but, at the same time, substantially more difficult than the hydrogenation of other easy-to-reduce groups /e.g., nitro-groups, double bonds, etc./. When using high-activity catalysts based on noble metals, it can proceed even at moderate temperatures /up to 100°C/ but if less active catalysts are used /Ni, Co, Fe, Cu/ it may become necessary, particularly if ketones are to be hydrogenated, to operate at higher temperatures and, owing to reasons of equilibrium, also at higher pressures, as a consequence. The reaction may proceed in either the gas phase or the liquid phase, depending on the nature of the reactants. Of greatest technical importance is the hydrogenation of higher aldehydes from oxosynthesis. Frequently used are copper-based catalysts, capable of catalyzing a selective hydrogenation of the carbonyl groups while keeping intact some other reducible functions in the molecule, such as the double bonds, the benzene ring, or the furane ring.

Reduction of carbonyls in aldehydes and ketones down to the methyl or the methylene group can also be done by catalytic hydrogenation at elevated temperatures. Palladium-based catalysts are used most frequently here.

5. Reductions of nitro-compounds

The reduction of nitro-compounds is governed by a rather complicated mechanism and proceeds via a number of intermediates which sometimes can also be the final products depending on conditions.

Schematically the individual intermediate stages can be represented as follows:

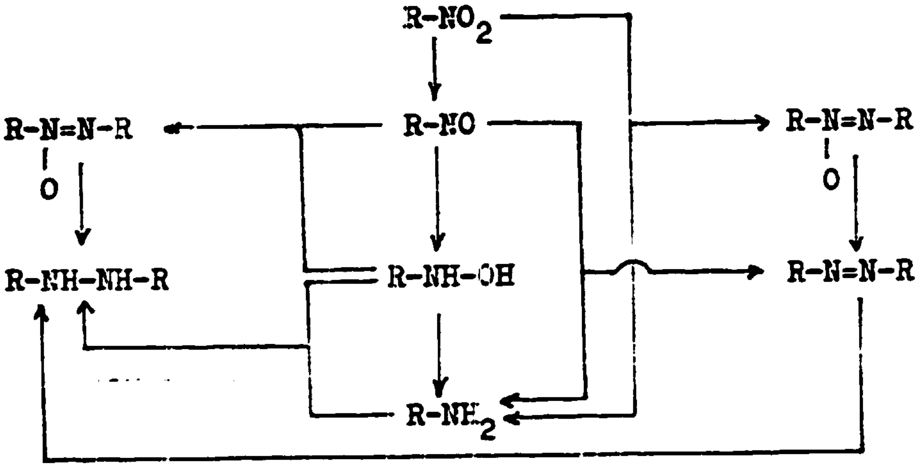


Fig. D-1 Reduction of aromatic nitro-compounds

In the first stage the aliphatic or cycloaliphatic nitro-compounds also yield a nitroso-compound which, inasmuch as it contains the nitroso-group on either the primary or the secondary carbon, can also exist in a tautomeric form /isonitroso form/ as an aldoxim /R-CH=N-OH/ or a ketoxim /$R_2C=N-OH$/. As a consequence to the existence of such forms we also meet compounds among the products of reduction of the aliphatic nitro-substances that cannot occur in the aromatic series. The reduction can be represented by the following diagram:

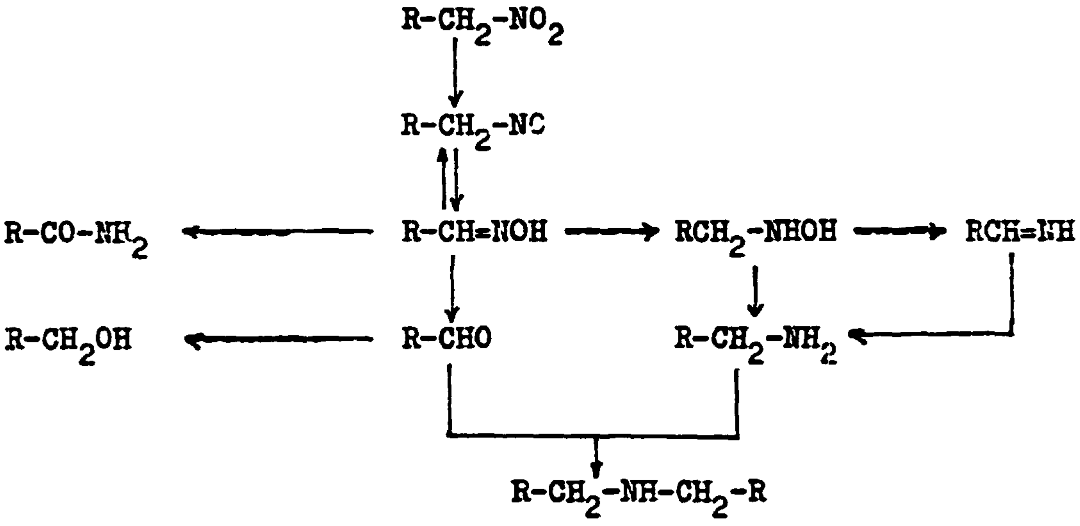


Fig. D-2 Reduction of aliphatic nitro-compounds

The nitro-group can be reduced by nearly all reducing agents. Those used most frequently include iron, zinc, tin, stannous chloride, and sulfides, with amines as the major product.

Should the hydroxylamine stage be retained, the reduction is conducted by amalgamated aluminum or zinc in a moderately alkaline environment of a salmiac or calcium chloride solution. Under certain conditions, electrolysis can yield hydroxylamines, too. The stage of the nitroso-compounds can be obtained e.g. by electrolysis, in the case of the aromatic nitro-compounds as starting material. Nitrobenzene can be reduced catalytically to nitroso-benzene using carbon monoxide.

The reaction proper which yields nitroso compounds is an electrophilic substitution, but one which involves a low-reactivity nitrosyl cation, N=O. It is used for the preparation of nitroso-compounds /or, of amino-compounds, after reduction/ from those derivatives of the aromatic hydrocarbons which posses strong class I. substituents. Nitrosation proceeds selectively to the p-position and is used e.g. in the production of p-nitroso dimethyl aniline, p-nitroso phenol, alpha-nitroso-beta-naphthalene, etc.

Aliphatic nitro compounds can be converted to oximes by catalytic hydrogenation or by reduction by zinc in acetic acid.

Reduction by zinc of the nitro compounds in strongly alkaline environments yields hydrazo compounds. The reduction of aromatic nitro compounds, nitroso compounds, and azoxy compounds by lithium-aluminum hydride is brought to a halt at the stage of the azo compounds.

The azo compounds are reduced to hydrazo compounds by milder agents like sodium amalgam, amalgamated aluminum, zinc in alcohol, or stannous chloride. Splitting to amines occurs in the case of a more energetic action of zinc, iron, or tin and in the case of reductions by titanium /III/ chloride, hydrosulfide, and hydroiodic acid.

The nitro groups of aromatics cannot be reduced by sodium borohydride, however energetic reduction agent this may be. Sodium borohydride may however accomplish the regeneration of certain metals and ions which are capable of reducing the nitro group and, thus, act in fact as indirect reduction agents in the presence of catalytic amounts of these metals and ions /7/.

Partial reductions of aromatic polynitro compounds are mostly accomplished using stannous chloride and sodium or ammonium sulfide. Stannous chloride and titanium /III/

chloride are used to selectively reduce the nitro group in the ortho position, as sulfides are used to reduce it in the para position, in the case of homolytic 2.4-dinitro derivatives of benzene.

The reduction products of the nitro substances find application in a number of branches of the chemical industry, chiefly in the production of dyestuffs, and also in the construction trade, in the pharmaceutical industry, in agriculture, etc.

5.1. Chemical reduction of nitro compounds

5.1.1. Reduction of nitro compounds by metals

5.1.1.1. Reduction of nitro compounds in acid media

Béchamp is credited with the discovery in 1854 of the reduction of nitro compounds by metals in an acid medium; he worked with the iron - acetic acid system. Today, the reduction by iron in the hydrochloric acid medium is the most frequent. Other metals such as Zn, Cu, or Al are rarely used, inasmuch as the reductions are then too costly, the products can only be separated with difficulty, and economic considerations make it imperative to recover the metals used. Zinc is used for the reduction of some insoluble and hard-to-reduce nitro compounds, and tin in hydrochloric acid is sometimes replaced by a solution of stannous chloride in the same acid. Stannous chloride acts somewhat more moderately and is well suited e.g. for the reduction of just one nitro group in dinitro compounds; this reaction proceeds smoothly in alcoholic solutions.

Out of the other acids /hydrochloric acid may sometimes form small amounts of chlorinated amines, under stimulation by high acid concentration, high temperature, and slow admission of the reduction agent/, worth mentioning as the one most frequently used is sulfuric acid which is particularly suitable in cases where arylhydroxyl amine rearrangement to hydroxyaryl amine is the desired reaction, and also acetic and possibly also formic acid in cases where undesirable hydrolysis might intervene. Protons can also be supplied by methanolic hydrogen chloride, water, or aqueous solutions of salts /sodium, ammonium, calcium, baryum chloride; ferrous and ferric chlorides/. To improve the solubility of the nitro sobustance, organic solvents are sometimes added /methanol, ethanol, pyridine, etc./.

Considerably less acid is used than would correspond to the full dissolution of the iron used, e.g. by the equation

$$Fe + 2HCl \longrightarrow FeCl_2 + 2H \qquad (10)$$

This is made possible by the fact that, in principle, it is not the nascent hydrogen /8/ produced by dissolving iron in hydrochloric acid but, rather, the iron converted into the oxide Fe_3O_4 or into a mixture of FeO and Fe_2O_3 /with the latter oxide dominating/ which is the agent responsible for the reduction proper.

Even though the reduction mechanism remains somewhat unclear, it is known that the electrons are supplied by iron; hence, the reaction is best described by the formal equation

$$4RNO_2 + 9Fe + 4H_2O \longrightarrow 4RNH_2 + 3Fe_3O_4 \qquad (11)$$

Gray iron is the form of iron which is most suitable. Thanks to their chemical heterogeneity, cast irons are rather reactive in the case of wet oxidation /wet corrosion/, owing to the possibility of galvanic microelements being set up where oxygen which stimulates iron oxidation is liberated at the anode. In commercial reductions, slightly over 2 mols of iron is used for the reduction of 1 mol of the nitro compound. A quantity of 0.06 to 0.1 mol acid per 1 mol nitro compound is sufficient. The effect can be regarded as catalytic, consisting probably in the activation of iron. Once the reaction is underway the substance being reduced picks up protons from water, the iron is oxidized to ferrous and ferric ions, and their dehydration yields Fe_3O_4. Thus the water is recycled so that 3.5 mols water per 1 mol nitro compound is sufficient.

Depending on the amount of iron and the reaction conditions, it is sometimes possible to halt the reaction at one of its intermediate stages /azoxy, azo, and hydrazo compounds/ but most often the products desired are diamines. Low quantities of acid and water must be used for the partial reductions, in order to avoid nitro amine dissolution and thus to protect it from continued reduction.

As a rule the reductions are conducted in such a way that the nitro compound is added to a boiling mixture of iron, water, and acid or acidic catalyst. Heat is removed by cooling the water vapor or the vapors of the azeotropic mixtures of water with organic substances. Adequate agitation is important to provide for good heat and mass transport. In the case of the Béchamp reduction the environment is highly corrosive, and considerable erosion can also take place due to the presence of solid iron particles. As a rule the reaction installation is made of cast iron or is lined with cast iron plates and acid-resistant stoneware or tiles.

The requirements imposed on the purity of the reduced nitro substances are seldom stringent, and it is of particular advantage that residual acid from the previous operation - nitration is not much of a problem. The yields, as a rule, are nearly quantitative.

The arrangement used to conduct the operations is to be illustrated by the description of the reduction of m-nitrobenzene sulfonic acid which follows: A small amount of water of iron sludge filtrate from previous washing is introduced into the reaction, and finely ground cast iron dust is admitted to the stirred liquid. After heating by steam to about 70°C a small quantity of hydrochloric acid is slowly admitted and, having allowed the violent boiling to subside, the mixture is heated to moderate boiling which brings to completion the etching of the cast iron dust. It is the purpose of this operation on the one hand to prepare a ferrous chloride solution as an electrolyte and, on the other hand, to etch the iron particles and to strip oxides off their surface in order to activate it. During etching, hydrogen is liberated and, inasmuch as the raw materials used are of commercial grade, also hydrogen arsenide and hydrogen phosphide.

After etching, the m-nitrobenzene sulfonic acid is admitted in the form of a wet paste of its sodium salt. It is metered out so as to keep the reductor contents boiling.

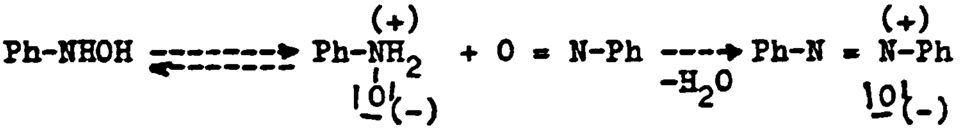
On completion of the reduction, the iron transferred to solution is precipitated by soda and the iron sludge is retained on pressure filters. The sludges obtained, containing iron oxides, are washed and eventually calcined, giving mineral paint pigments /9,10/ such as brown, red, or black. If ammonium chloride is added during the reduction together with ferrous chloride, even yellow-tinted pigments can be obtained. Attempts were also made to process the wast sludges to abrasives. Despite all these experiments the by-

-products from Béchamp's reductions are in fact unwanted wastes, with negative environmental impact.

Owing to progress in engineering over the past years, the extent of production of the aromatic nitro compounds by Béchamp-type reductions has shrunk, and a trend of replecement by catalytic hydrogenations has been evident. Nevertheless, the Béchamp process still survives in some cases such as in the production of toluidines, xylidines, metanilic acid, certain aromatic derivatives of naphthalene, and certain diamines. Conversion of the Béchamp process from batch to continuous operation has also been accomplished /11,12/. For instance, by continuous reduction the Bayer A.G. is producing diaminostilben disulfo acid, used for optical brighteners in detergents.

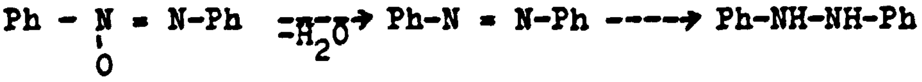
5.1.1.2. Reduction of nitro compounds in alkaline media

When nitro compounds such as nitrobenzene are to be reduced by metals in an alkaline medium /of which the system Zn + NaOH is the most frequent/, then the N-phenylhydroxyl amine produced via nitrosobenzene reacts with the unreacted nitrobenzene, yielding azoxybenzene by condensation of these two compounds:



$$\text{Ph-NHOH} \rightleftharpoons \text{Ph-}\underset{|\underline{O}|^{(-)}}{\overset{(+)}{\text{N}}}\text{H}_2 + \text{O = N-Ph} \xrightarrow[-H_2O]{} \text{Ph-N = }\underset{|\underline{O}|^{(-)}}{\overset{(+)}{\text{N}}}\text{-Ph} \qquad (12)$$

Azoxybenzene is then further reduced to azobenzene and hydrazobenzene as the final product:



$$\text{Ph - }\underset{O}{\text{N}}\text{ = N-Ph} \xrightarrow[-H_2O]{2H} \text{Ph-N = N-Ph} \xrightarrow{2H} \text{Ph-NH-NH-Ph} \qquad (13)$$

The hydrazo substances are isomerized with facility to diamines of the diphenyl series, important in the production of azo dyes.

The reduction process can be illustrated by the following stoichiometric equations:

$$2\ PhNO_2 + 5\ Zn + H_2O \xrightarrow{NaOH} Ph\text{-}NH\text{-}NH\text{-}Ph + 5\ ZnO \qquad (14)$$

Zinc oxide is hydrated

$$ZnO + H_2O \longrightarrow H_2ZnO_2 \qquad (15)$$

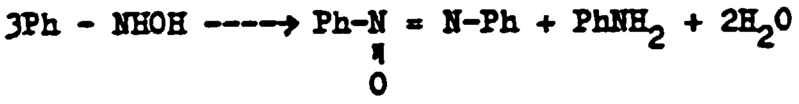
and reacts with sodium hydroxide giving zincate

$$H_2ZnO_2 \quad + \quad 2NaCH \rightleftharpoons Na_2ZnO_2 + 2H_2O \qquad (16)$$

The over-all reaction is described by the equation

$$2RNO_2 + 5Zn + 10NaOH \longrightarrow R\text{-}NH\text{-}NH\text{-}R + 5Na_2ZnO_2 + 4H_2O \qquad (17)$$

As a by-product the reaction may yield aniline, formed by successive reduction of phenylhydroxyl amine or by its disproportionation:



$$3Ph - NHOH \longrightarrow Ph\text{-}\underset{\underset{O}{\downarrow}}{N} = N\text{-}Ph + PhNH_2 + 2H_2O$$

(18)

It is advisable therefore that the phenylhydroxyl amine should not accumulate in the reaction mixture but rather should be allowed to react with nitroso benzene. This is aided by rising temperature and the sodium hydroxide concentration. Aniline can also be formed by reduction of azoxy benzene or even by decomposition of hydrazo benzene at an elevated temperature:

$$2Ph - NH - NH - Ph \longrightarrow 2Ph - NH_2 + Ph - N = N - Ph \qquad (19)$$

These reactions also are supported by higher alkali concentration and higher temperature. In practice, therefore, the first reduction stage is conducted at temperatures not higher than 95°C and at the highest possible concentration of the hydroxide, of which the whole amount required for the reaction /0.1 to 0.2 mol per mol nitro benzene/ is added at this stage. The second reduction stage is then carried out after the reaction mixture has been diluted with water, at a temperature of about 80°C. In technical practice, an excess 15-30% zinc is used beyond the amount determined from Eq. 17 , but no more than 5-10% of the theoretical amount of sodium hydroxide. In this case, just as in the case of reductions conducted in acidic media, the transitory soluble catalyst obtained is subject to hydrolysis which is promoted, moreover, by the presence of metals. Sodium zincate is hydrolyzed while sodium hydroxide is reclaimed and the insoluble hydrated zinc oxide is precipitated:

$$Na_2ZnO_2 + (x+1)H_2O \rightleftharpoons ZnO\ (H_2O)_x + 2NaOH \qquad (20)$$

Hence, the foregoing reactions proceed thanks to the effect of sodium hydroxide which keeps regenerating in the presence of zinc.

The waste product obtained is hydrated zinc oxide, used in the production of lipotom, salt of vitriol, or zinc metal /by electrochemical reduction/. However, the presence of organic species tends to considerably interfere with further processing. A strongly alkaline environment is produced in practice solely by sodium hydroxide; as for the applicable metals, it is mainly zinc but, to a limited extent, also iron, lead, amalgamated sodium, or amalgamated aluminum. The reduction is performed in reactors made of carbon steel and provided with vigorous stirring.

As benzidine is formed by rearrangement of hydrazo benzene, o-toluidine is obtained from o-nitro toluene, o-dianizidine from o-nitro anisole, benzidine-2,2′-disulfonic acid from m-nitrobenzene sulfonic acid, and other intermediates of dyestuffs production are obtained similarly /13, 14/.

5.1.1.3. Reduction of nitro compounds in neutral and slightly alkaline media

The reduction of nitro compounds by iron in neutral salt solutions at elevated temperature yields amines. Neutral reduction in cold solutions, using metals other than iron, especially zinc, allows to discontinue the process at the stage of beta-arylhydroxyl amine.

$$Ph\text{-}NO_2 + 2Zn + 3H_2O \longrightarrow Ph - NHOH + 2\ Zn\ (OH)_2 \qquad (21)$$

Ammonium chloride is the best electrolyte for this reaction.

The hydroxyl amine derivatives can also be obtained by reductions of the nitro compounds with Zn amalgam in the presence of alum, with Al amalgam in nonaqueous solvents containing calculated additions of water, with Al in ammonium chloride solutions, with Zn in the calcium chloride solution, with Zn and Pb in acetic acid electrolytes, etc.

5.1.2. Reduction of nitro compounds by sodium dithionate

Sodium dithionate is mainly used in the reduction of anthraquinone and of indigoid derivatives. It is rarely used in the reduction of nitro compounds because of its relatively high price, and that mostly in the production of vat dyes.

The dithionate either is available as such or is prepared only during the reaction concerned, by adding Zn dust to a sodium hydrogen-sulfite solution. The latter method is used for the reduction of indigo and also for the preparation of o-aminophenol from the pertinent nitro-derivative. The reduction is described by the equation

$$2NaHSO_3 + SO_2 + Zn \longrightarrow Na_2S_2O_4 + ZnSO_3 + H_2O \qquad (22)$$

Sulfur dioxide is required for this reaction, and is obtained by introducing a mineral acid into the reaction mixture during the reduction.

5.1.3. Reduction of nitro compounds by sodium sulfite and hydrogensulfite

The reductions by sodium sulfite and hydrogen sulfite can be expressed by the following equations:

$$PhNO_2 + 3\ Na_2SO_3 + H_2C \longrightarrow PhNH_2 + 3\ Na_2SO_4 \qquad (23)$$

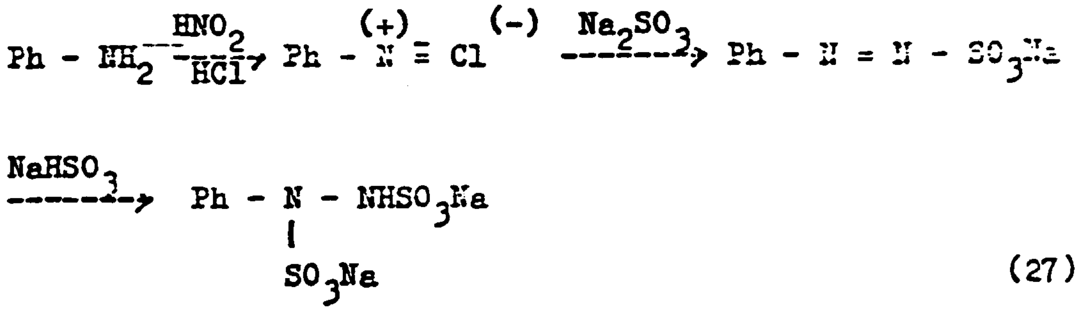
$$2\ PhNO_2 + 6\ NaHSO_3 + 2H_2O \longrightarrow 2\ PhNH_2 + 3\ Na_2SO_4 + + 3\ H_2SO_4 \qquad (24)$$

$$Ph/H/NO_2 + 2Na_2SO_3 + NaHSO_3 \longrightarrow Ph/SO_3Na/NH_2 + + 2Na_2SO_4 \qquad (25)$$

$$Ph/H/NO_2 + 6\ NaHSO_3 \longrightarrow 2\ Ph/SO_3H/NH_2 + + 3\ Na_2SO_4 + H_2SO_4 \qquad (26)$$

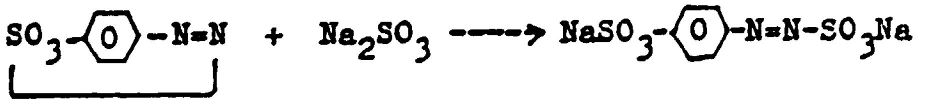
In a single reaction stage this process yields amines on the one hand, and ortho and para aminobenzene sulfonic acids on the other hand. As a rule the reaction is made to proceed by excess $NaHSO_3$ and abundant sodium hydroxide is added to produce the required amount of the neutral sulfite.

Reductions by the mixtures of $NaHSO_3$ and Na_2SO_3 and by a small amounts of Zn are used in the production of phenyl hydrazine from aniline. Aniline is first converted to an diazonium salt by nitrous acid, and then the salt is reduced further, as expressed by the equation



$$Ph - NH_2 \xrightarrow[HCl]{HNO_2} Ph - \overset{(+)}{N} \equiv \overset{(-)}{Cl} \xrightarrow{Na_2SO_3} Ph - N = N - SO_3Na \xrightarrow{NaHSO_3} Ph - \underset{\substack{| \\ SO_3Na}}{N} - NHSO_3Na \qquad (27)$$

A similar method is employed in the production of phenylhydrazine-4-sulfonic acid. Diazotation of sulfanilic acid is the first stage. Then the reaction mixture is admitted into a sulfide solution. The pertinent diazo sulfate is formed first, and by reaction with more sulfite it is turned to hydrazine sulfate and, eventually, to hydrazine disulfonate:



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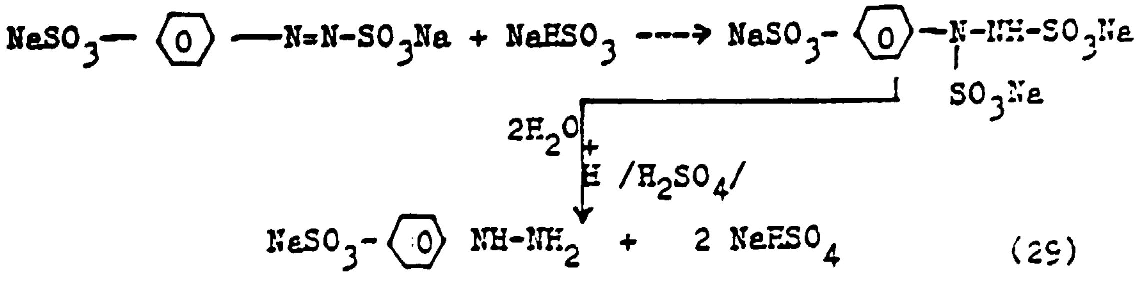

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In the naphthalenic series, a frequent reduction is that of 1-nitroso-2-naphthol to 1-amino-2-naphthol-4-sulfonic acid by hydrogen sulfite.

5.1.4. Reduction of nitro compounds by sulfides

The reduction proceeds in alkaline environments and the sulfides used most often are the sodium sulfide Na_2S, the sodium disulfide Na_2S_2, the sodium hydrogen sulfide NaHS, and the ammonium sulfide $(NH_4)_2S$.

The reaction with sodium sulfide yields sodium hydroxide, as evidenced from the equation

$$4RNO_2 + 6Na_2S + 7H_2O \longrightarrow 4RNH_2 + 3Na_2S_2O_3 + 6NaOH \qquad (30)$$

Reductions by hydrogen sulfide or by sodium disulfide yield only the sodium thiosulfate while the alkalinity of the medium remains largely unchanged:

$$4RNO_2 + 6NaSH + H_2O \longrightarrow 4RNH_2 + 3Na_2S_2O_3 \qquad (31)$$

$$RNO_2 + Na_2S_2 + H_2O \longrightarrow RNH_2 + Na_2S_2O_3 \qquad (32)$$

The chief problem connected with reductions by the sulfides consists in finding a way of disposing with the sodium thiosulfate wastes, a condition which must be met to offset the high price of the sulfides. Utilization of the waste is hindered by the presence of organic species and tends to be rather problematic. When other polysulfides are used, the one additional product is sulfur, a source of even more complication:

$$RNO_2 + Na_2S_3 + H_2O \longrightarrow RNH_2 + Na_2S_2O_3 + S \qquad (33)$$

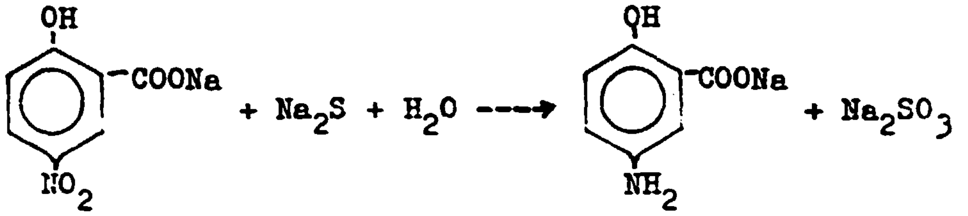
With sodium sulfide used for the reduction, the sodium hydroxide produced is often a nuisance. If of higher concentration it creates conditions in the reaction environment which favor the production of azoxy compounds; these cut down on the yield and impair the quality of the primary product. Owing to this circumstence the reaction must be conducted so as to obtain conditions such that the hydroxide does not accumulate in the reactor. This is why ammonium sulfate, sodium hydrogen carbonate, or mineral acid solutions are added to modify the alkalinity of the reaction medium:

$$2\ NaOH + (NH_4)_2\ SO_4 \longrightarrow Na_2SO_4 + 2\ NH_4OH \qquad (34)$$

$$NaOH + NaHCO_3 \longrightarrow Na_2CO_3 + H_2O \qquad (35)$$

$$NaOH + HCl \longrightarrow NaCl + H_2O \qquad (36)$$

Addition of magnesium salts is another possibility; pH is then regulated by removing the sodium hydroxide in the form of magnesium hydroxide precipitate, at the same rate at which the sodium hydroxide is formed. When using Na_2S the the formation of sodium hydroxide can sometimes be avoided by working with crystalline sodium sulfide $Na_2S.9H_2O$, rather than with its diluted aqueous solutions. In practice the nitro compound is melted with the sodium sulfide crystals, at temperatures up to 110°C. This is the way to produce e.g., the amino salicylic acid:



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The reductions by sulfides are mostly used to effect partial reductions of aromatic dinitro compounds /of m-dinitro benzene to m-nitro aniline, of 2,4-dinitro phenol to 2-amino-4-nitro phenol, of trinitro phenol to picraminic acid, of 2,4-dinitro anisole to 2-amino-4-nitro anisole, etc./, the reductions of aromatic nitro compounds which contain halogens, the preparation of amino-azo compounds, and reductions in the anthraquinonic series. Ammonium sulfide and hydrogen sulfide used in cold media can reduce nitro compounds to corresponding hydroxyl amines.

5.2. Catalytic hydrogenation of nitro compounds

5.2.1. Hydrogenation of nitro compounds to amino compounds

Inasmuch as the nitro group lends itself very easily to hydrogenation, the reaction can in principle be performed without affecting any other reducible groups of the molecule. Also aiding this purpose is a suitable selection of catalysts /copper catalysts for the hydrogenation of aromatic nitro compounds in the gas phase are inactive toward the aromatic ring/ as well as of the reaction conditions /mild reaction conditions such as, frequently, room temperature and normal pressure, are mostly sufficient for hydrogenating the nitro group/. The nitro compounds can be hydrogenated in either the gas or the liquid phase, and the choice must respect the properties of the reactants as well as of the products. In the case of liquid phase hydrogenation, a solvent is used as a rule which dissolves the reaction water thus homogenizing the liquid phase. This need not necessarily be homogenized but homogenization is advantageous, though, owing to a sufficiently rapid mass transport. It is often the case that water which is not dissolved in the organic layer will strongly impede the reaction by adsorbing onto the catalytic surface and causing the catalyst particles to cluster. Thanks to the fact that, as a rule, the aromatic amines are more soluble in the organic solvents than the nitro compounds, the batch process can also be led in the liquid phase in such a way that the solid reactant is partly dissolved in the system and partly suspended; as it reacts it keeps entering the solution so that eventually the amine is completely dissolved. Owing to the nitro group reductions being highly exothermic /-500 kJ/mol/, it is an important engineering problem to consider the removal and utilization of the reaction heat. The catalytic hydrogenation of aromatic nitro compounds to amines provides us with a classical example of cases where the chemical reduction by the Béchamp method is replaced by a modern catalytic process. Several specific examples of such replacements are outlined below.

Aminobenzene sulfonic acids

Reduction of the nitrobenzene sulfonic acids to corresponding amino acids proceeds most often in the form of water-soluble sodium salts. Out of the chemical methods available, the most frequent ones include the reductions by sulfides /15, 16/, by sodium borohydride in the presence of transition metal salts such as $CoCl_2$ /17/, or by hydrazine in the presence of ferric chloride /18/.

These processes can, at an advantage, be replaced by catalytic hydrogenation, mainly one where the catalysts used are on the basis of palladium /19-23/, platinum and rhodium /21/, nickel /22, 23/, or nickel promoted with palladium /24/.

Aminohalogen benzenes

Many chloranilines, chiefly 4-chloraniline and 3,4-dichloraniline, are important components in the synthesis of efficient herbicides. They can be prepared by catalytic hydrogenation of the corresponding chloro nitro benzenes, using various catalysts like Ni, Ru, Pd, Rh, etc. Hydrogenolysis of the C-Cl bond and the successive hydrogenation of the aromatic ring, most likely to occur in acidic media /25, 26/ at higher temperatures and pressures, makes the process somewhat complicated. The degree of hydrogenolysis can be substantially mitigated by proper selection of catalyst and the reaction conditions /27 - 37/. Similarly, the subsequent aromatic ring hydrogenation can also be suppressed. Buffer solutions are used to maintain a suitable pH /6 - 7.5/, and sometimes the reaction is allowed to proceed directly in an alkaline environment to dispose of thy hydrogen chloride formed, if any.

Methyl ester of 4-aminobenzoic acid

The methyl ester of 4-aminobenzoic acid is produced as an intermediate product by the process which eventually yields isocain, a local anesthetic. The methyl ester used to be prepared by reducing the corresponding nitro acid with iron in a hydrochloric acid medium according to Béchamp, followed by esterification. In commercial application this process suffers from a number of drawbacks. Considerable quantities of ferric sludge are produced, and the repetitive acido-basic transition not only leads to an increased consumption of inorganic chemicals but also, above all, contributes to waste water salinity.

For the esterification reaction of 4-aminobenzoic acid, the esterification catalyst used is sulfuric acid. A great excess of sulfuric acid must be used, owing to the presence of the amino group. On completion of the reaction the free sulfuric acid as well as that bonded to the amino group is to be neutralized with ammonia. Wastes amount to 1.7 tons of ammonium sulfate per 1 ton of methyl ester produced. When adopting a modified esterification technology where the process is run at higher temperatures and pressures, the quantity of ammonium sulfate produced is somewhat lower. Moreover, there is 2.9 tons of ferric sludge /in terms of Fe_2O_3/ and 1.7 tons of sodium chloride as wastes per 1 ton of methyl ester produced.

These shortcomings are eliminated by a process making use of catalytic hydrogenation. This consists in 4-nitrobenzoic acid being esterified by methanol in the presence of a small amount of mineral acid, followed by catalytic hydrogenation of the methyl ester of 4-nitrobenzoic acid to methyl ester of 4-aminobenzoic acid. Not only is it of advantage that the Béchamp reduction is substituted for by catalytic hydrogenation, but also the esterification of the nitro acid is substantially more advantageous than that of the amino acid. When the 4-aminobenzoic acid is esterified by methanol the basic amino group affects the acid-catalyzed reaction by bonding an equivalent amount of catalyst /sulfuric acid/ on the one hand, and by the ammonium cation thus formed being less likely to add another proton, as required by the esterification mechanism, on the other hand. If 4-nitrobenzoic acid rather than 4-aminobenzoic acid is subjected to esterification, the quantity of sulfuric acid required is less by at least one mol per 1 mol of the organic acid. Since the ester obtained would succumb to hydrolysis under the conditions of Béchamp´s reduction, some other method of reduction is necessary, and catalytic hydrogenation is the best.

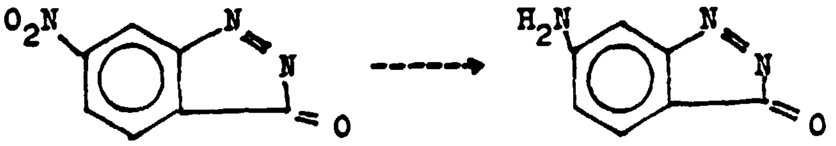
A suitable catalyst for this hydrogenation is e.g., palladium on active carbon; methanol is a suitable solvent precluding potential over-esterification which might be due to the acidic properties /38/ of the Pd-H system should other alcohols be used. As a consequence to the low solubility of the methyl ester of 4-nitrobenzoic acid, the operating temperature must be elevated /60 - 100°C/. Catalysts based on copper, free from the danger of aromatic ring hydrogenation, may also be considered but care must be taken to avoid hydrogenolysis of the ester group, inasmuch as the copper-based catalysts would generally require high-temperature operation.

3-Aminobenzene sulfofluoride

One of the intermediates required for the synthesis of color components for photographic materials is 3-aminobenzene sulfofluoride, produced by Béchamp-type reduction /39/ from the corresponding nitro compound. The reduction can be replaced by catalytic hydrogenation on Pd/C catalyst /40/ or possibly on Raney nickel /40, 41/.

6-Amino-3-indazolone

Another example is the replacement of the reduction of 6-nitro-3-indazolone by stannous chloride in a hydrochloric acid environment by catalytic hydrogenation using platinum or palladium catalysts:



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The nitro group alone is reduced while the other reducible groups are retained. The operating range is 20 - 100°C at 0.1 - 10 MPa pressure in the environment of monomethyl - or monoethyl-ether of ethylene glycol, or possibly of acetic acid. Isolation of 6-amino-3-indazolone occurs in the hydrochloride form /42/. The nitro groups in the positions 4, 5, or 7 can be reduced in a similar way.

3-Nitraniline

Even though the nitro group is very easy to hydrogenate, successful attempts were made to selective hydrogenate just one nitro group in dinitro benzenes using skeletal nickel or platinum and palladium black. The selectivity of the process is said to be controllable /43, 44/ by catalyst selection and by catalyst modification by species such as pyridine; the kind of solvent used may also be significant.

5.2.1.1. Application of the aromatic nitro compounds

Aniline is the one aromatic amine which enjoys the widest application. It is used in the production of polyurethanes, rubber chemicals, agrochemicals, dyes, photochemicals, pharmaceuticals, etc.

2,4-Toluene diamine is used in the production of toluene diisocyanate for polyurethane foams and elastomers, for paints, sealants, etc. The toluene diamines are produced by catalytic hydrogenation of dinitro toluenes which are formed by nitration at ratios of 80% of the 2,4-form to 20% of the 2,6-form, over a wide range of reaction conditions if different catalysts are used /Pd/C, Ra-Ni, Ni on various carriers/.

p-Phenylene diamine serves as anti-oxidant for polymers and oils, and also as anti-ozonant for rubbers and special polymers /polyamides/. The compounds used as anti-ozonants are various derivatives of p-phenylene diamine which however are not produced from the mother compound. Diisocyanate from the m-isomer is used in polyurethanes production. All these isomers are used in the photographic and dyestuffs industries.

Of great importance to the pharmaceutical industry, the photographic industry, and also as intermediates for the production of dyestuffs, are aminophenols and their sulfonated derivatives. Those finding the widest application are:

2-amino phenol; 2-amino-4-nitro phenol; 2-amino-4-chloro phenol; 2-amino-5-nitro phenol; 3-amino-4-hydroxybenzene sulfonamide; 2-amino-6-chloro-4-nitro phenol; 2-amino-4,6--dinitro phenol; 2-amino-4-chloro-6-nitro phenol; 2-amino-4,6-dichlorophenol; 2-amino-4-chloro-5-nitro phenol; 2-amino-3,4,6-trichloro phenol; 3-amino phenol; 4-amino phenol; 4-amino-2-nitro phenol; 2,4-diamino phenol; 5-amino-2-hydroxybenzoic acid; 4-acetamino phenol; 2-amino-1-phenol-4-sulfonic acid; 6-amino-4-nitro-1-phenol-2-sulfonic acid; 6-amino-4-chloro-1-phenol-2-sulfonic acid; 6-amino-1-phenol--2,4-disulfonic acid.

Reductions of corresponding nitro alcohols yield alkanol amines, emulsifying agents. The most important compounds of this group include:

2-amino-1-butanol; 2-amino-2-methyl-1-propanol; 2-amino-2--methyl-1,3-propandiol; 2-amino-2-ethyl-1,3-propandiol; 2-amino-2-/hydroxymethyl/-1,3-propandiol.
In these cases, too, the chemical reduction is replaced by catalytic hydrogenation.

Table D-6 Applications of selected aromatic amino compounds

Compound	Commercial derivatives and applications
o-toluidine	triphenyl methane dyes, safranin dyes
m-toluidine	dyes
p-toluidine	alkali red 9, acid green 25
2,3-xylidine	dyes
2,4-xylidine	soluble red 7, Violet 14
2,5-xylidine	p-xyloquinone, soluble red 26, Violet 7
2,6-xylidine	dyes
3,4-xylidine	synthetic riboflavin /vitamin B2/
3,5-xylidine	azo dyes
o-anisidine	synthesis of guaiacol, direct red 24
m-anisidine	soluble red 1
p-anisidine	dyes
o-phenetidine	dyes
p-phenetidine	phenacetine, anti-oxidant, dyes
p-cresidine	FD § C red 40
o-chloroaniline	dyes
m-chloroaniline	dyes
p-chloroaniline	azo-copulation components 10 and 15
2,5-dichloroaniline	dyes
3,4-dichloroaniline	herbicides, dyes
2-aminobenzene sulfonic acid	dyes, acid yellow
3-aminobenzene sulfonic acid	other dyes, acid orange 1, basic yellow 3,80
4-aminobenzene sulfonic acid	other dyes, intermediates for syntheses, analytic chemistry

Table D-6 continued

o-nitroaniline	orange 7, red 14, other dyes
m-nitroaniline	intermediate for organic synthesis and dyes, disperse yellow 5, yellow 1
p-nitroaniline	dyes, p-phenylene diamine, anti-oxidant
2,4-dinitroaniline	orange 5, other dyes
2,4,6-trinitroaniline	detonator

5.2.2. Hydrogenation of nitro compounds to lower stages of reduction

Hydrogenation can be so conducted as to produce, under suitable reaction conditions, not an amino compound but, rather, a lower reduction intermediate as the final product, or possibly the product of its subsequent conversion which no longer is due to hydrogenation. Thus, nitrobenzene can be hydrogenated to phenyl hydroxyl amine /obtained chemically by reducing nitrobenzene with zinc in a NH_4Cl solution/ which rearranges to 4-amino phenol in an acidic environment.

Hydrogenation of nitrobenzene to phenylhydroxyl amine has been described extensively in literature. Tsenyuga et al. /45/ have conducted this reaction in a heterogeneous solvent system benzene-water using various catalysts /skeletal Nb, promoted skeletal Ni, catalysts based on Nb, Pd, Cr, and other metals on supports/. Using a catalyst prepared from a Ni-Al alloy containing 0.3% Fe and max. 0.1% Cu, phenylhydroxyl amine was obtained under optimal conditions with a yield of 60%, at an aniline content of max. 15% in terms of nitrobenzene.

Another paper /46/ describes the use of Rh/C and Pd/C catalysts in the presence of $Co/EDTA/_3/NO_3/_2$ /EDTA = ethylene diamino tetraacetic acid/. Better results were obtained with the Pd/C catalyst - 80% yield at 50% conversion.

Heterogeneous catalysts based on Rh and Pd were used by yet another author /47/.

Yield was investigated as function of the character of carrier, the nature of solvent, the nature and concentration of the complex-forming ion /Co^{2+}, Ni^{2+}, Fe^{2+}/ and the ligand attached to it /ethylene diamine, oxicoumarin, triphenyl phosphine, nitroso naphthol, acetyl acetone/, the ratio of the components of the catalytic system used, and temperature. The yields obtained ranged from 44 to 80%.

A German patent /48/ has described the hydrogenation of nitrobenzene to phenylhydroxyl amine in 80% ethanol containing max. 2% dimethyl sulfoxide in the presence of a Pd/active carbon catalyst, under normal conditions.

Phenylhydroxyl amine rearranges to 4-amino phenol in an acidic environment. In practice, the two reaction stages are usually combined - the reduction is allowed to proceed directly in the acidic environment /49/, e.g. by the Al + + H_2SO_4 system. In order to obtain p-amino phenol by catalytic hydrogenation of nitrobenzene, this must be conducted in an acidic environment where the aforementioned Bamberger--type rearrangement from phenylhydroxyl amine to p-amino phenol is possible. According to a Japanese patent /50/ the hydrogenation can be performed in the presence of an aqueous sulfuric acid solution on Pt/C, Pd/C, or Rh/C catalysts with an organic solvent added /dibutyl ether, caproic acid, n-octanol, 2-ethyl-1-hexanol/, at 80°C and 0.2 MPa. Other patents are also known /51, 54/ which make use of the Pt catalyst. The reaction conditions are analogous to what has been described above, and the yields amount to some 80%. The reaction may also proceed at room temperature and the atmospheric pressure of hydrogen /55/. The use of other catalysts, viz., MoS_3/C, PtS/C, CoS, WS_3, PtS_2 in the presence of H_2SO_4, NH_4HSO_4, H_3PO_4 has also been patented /56, 57/, at temperatures of 120-155 °C and at about 3 MPa pressure. The yields of 4-amino phenol were up to 82%. Another example where the product of an incomplete reduction of the nitrogroup is desired is the preparation of hydrazo benzene. It is prepared chemically by reducing nitrobenzene with zinc in a strongly alkaline environment. According to a Soviet patent /58/ it can be prepared by catalytic hydrogenation of nitrobenzene on a nickel or platinum catalyst, in the presence of pyridine.

6. Reductions of other nitrogen-bearing compounds

6.1. Reduction of triple bond between carbon and nitrogen

Reduction of the triple bond of nitriles yields imines which can be transformed further in various ways. Addition of hydrogen yields primary amine; reaction with primary amine forms a Schiff base which is reduced to secondary amine. If the reduction of nitriles is carried out in an environment in which the transient imine is susceptible to hydrolysis, it is possible sometimes to retain the aldehyde or even the alcohol. The reduction of nitriles to amines is done catalytically using sodium in alcohol, lithium-aluminum hydroxide and zinc in hydrochloric acid. Reduction to aldehyde is successful if a limited amount of lithium-aluminum hydride is used /otherwise yielding amine/, or with stannous chloride /by Stephen's method/. The hydrogenation rate of the nitrile groups is lower than that of the C=C double bond. Thus, the unsaturated nitriles are usually hydrogenated to saturated amines. However, when using a selective catalyst, such as Raney cobalt for the hydrogenation of nitriles, the nitrile group can be hydrogenated preferentially. Chemical reduction methods are described in literature, e.g. /59 - 61/, whereas the catalytic methods are treated in other references /62 - 64/. Of greatest practical importance is the production of hexamethylene diamine, used to produce Nylons and intermediates for light-fast polyurethanes.

6.2. Reduction of double bond between carbon and nitrogen

The double bonds present in imines and oximes are easily reduced catalytically, by sodium in alcohol, sodium amalgam, amalgamated aluminum, lithium-aluminum hydride, zinc in acetic acid, and by electrolysis. Amines are the products if either of the two types of compound is the reactant. The imines need not be isolated to prepare the amines. It is sufficient if a mixture of aldehyde or ketone with ammonia or primary or secondary amines is treated with hydrogen in the presence of a catalyst /most frequently, based on cobalt or nickel/ or with formic acid /the Walach-Leuchart method/. Alcohol can also be used instead of the carbonyl compound, the alcohol being partially dehydrogenated under the prevailing reaction conditions.

6.3. Reduction of double bond between two nitrogen atoms

Hydrogenation of azobenzene on Pd/Al_2O_3 catalyst in ethanol can be used to prepare hydrazo benzene /65/.

A reaction of interest rather then of commercial potential is the reduction of the azo groups by hydrogen iodide which performs the reduction of this group without affecting any nitro groups that might be present in the molecule /unless they are in the ortho-position to the azo group/.

6.4. Reduction of nitrosamines, nitramines, and diazonium salts

Nitrosamines and nitramines reduce to hydrazines or a reduction-split to amines and ammonia. The former reaction type predominates in the case of reduction by zinc, sulfites, and by electrolysis, whereas the latter is encountered in the case of reductions by tin and iron.

The diazonium salts are reduced similarly. Addition of two hydrogen atoms splits them to nitrogen and a hydrocarbon residual, by four equivalents they are reduced to hydrazines. The replacement by hydrogen of the diazonium group is effected by stannate, the reduction to hydrazines is achieved by zinc, stannous chloride, sulfites, and hydrogen sulfites. The diazo compounds can also be reduced in a variety of ways. Either the product is hydrazines /by zinc in alkali/ or they are split to amine and ammonia /by zinc in acetic acid, by amalgemated aluminum/, or the N_2 group is replaced by two hydrogen atoms /by hydroiodic acid/

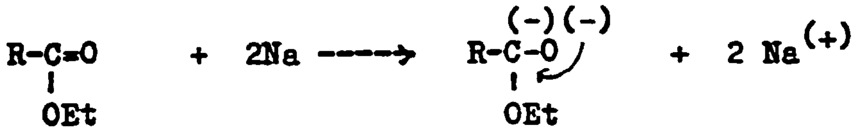
7. Reductive splitting

Reductive splitting of various chemical bonds may frequently be aimed at in the case of chemical transformations, but on the other hand it may constitute an undesirable side reaction which detracts from the yield of the primary product being prepared by reduction. Under the hydrogenation conditions the hydrogenolysis of the C-C bond is not very common. It does occur though, mainly during the hydrogenation of sterically stressed systems /cyclopropanic, cyclobutanic rings/ and compounds incorporating bonds which have become weakened chemically /splitting of beta-ketoacids, beta-dicarbonic acids/. Reductions of hydroxyl groups, mainly from carbons adjacent to aromatic rings, are rather common. The reduction of benzyl alcohol to toluene proceeds even under moderate conditions of catalytic hydrogenation and may be brought about even by sodium, sodium amalgam, lithium-aluminum hydride, zinc, and stannous chloride. Etherified and estherified hydroxyls also split off easily if activated by the neighborhood of aromatic rings, whereas the aromatically bonded hydroxyls would not split off unless drastic conditions are employed /high-temperature, high-pressure hydrogenolysis, distillation with zinc dust/. The vicinity of a double bond also facilitates the reduction of the hydroxyl group /by sodium in liquid ammonia, by hydroiodic acid/.

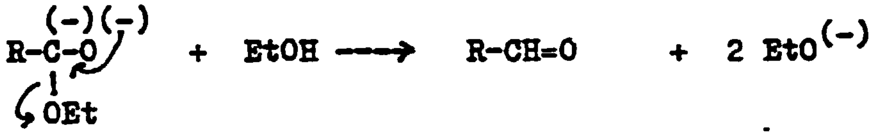
Carboxyl can be converted by reduction to the aldehydic group but also to alcoholic or even to methylene group. The conversion to alcohols is most common, brought about usually by lithium-aluminum hydride or by electrolysis.

In cases of aromatic acid reductions where the splitting of the hydroxyl yielding alcohol is facilitated by the vicinity of an aromatic ring, the reduction may proceed down to methyl. Non-activated carboxyl can be reduced to methyl by hydroiodic acid or by electrolysis.

Esters are easier to reduce than free acids, again mostly to alcohols. The reduction agents are lithium-aluminum hydride or sodium in alcohol /the Bouveault-Blanc method/. The reaction apparently proceeds via corresponding aldehyde:



$$\underset{\mathrm{OEt}}{\mathrm{R{-}\overset{|}{C}{=}O}} + 2\mathrm{Na} \longrightarrow \underset{\mathrm{OEt}}{\mathrm{R{-}\overset{|}{C}{-}\overset{(-)(-)}{O}}} + 2\,\mathrm{Na}^{(+)} \qquad (38)$$



$$\underset{\mathrm{OEt}}{\mathrm{R{-}\overset{|}{C}{-}\overset{(-)(-)}{O}}} + \mathrm{EtOH} \longrightarrow \mathrm{R{-}CH{=}O} + 2\,\mathrm{EtO}^{(-)} \qquad (39)$$

$$\mathrm{R{-}CH{=}O} + 2\mathrm{Na} + 2\,\mathrm{EtOH} \longrightarrow \mathrm{R{-}CH_2OH} + 2\,\mathrm{EtO}^{(-)} \qquad (40)$$

Dissociation of the O-Et bond at the first reduction stage is made easier by the negative charge of oxygen bonded to the same carbon atom.

The Bouveault-Blanc reduction, discovered in 1903, came to be used commercially in the year 1930. As it involves a high sodium consumption, of 4 mol per 1 mol alcohol, it has never become widespread and is only used in the production of some special alcohols. An analogical reaction is the reduction of amides by sodium in alcohol /the Landenburg-Vishnegradski reduction/.

Certain esters can be reduced to alcohols also by zinc, or electrolytically. In sugar chemistry an important reaction is the reduction of lactons /internal esters/ to aldehydes by sodium amalgam and sodium-boron hydride.

From chlorides of acids the alcohols are obtained by reduction using lithium-aluminum hydride. Of much greater practical importance however is the preparation of aldehydes by catalytic hydrogenation of acid chlorides known as the so-called Rosenmund reduction. From salts of acids the aldehydes are derived by reduction using sodium amalgam or electrolysis /mercury cathode/ where the reduction is performed in the presence of an aromatic amine /p-toluidine/ which reacts with the aldehyde to a benzylidenic compound which can be hydrolyzed to obtain the aldehyde.

The yields of alcohols obtained by reduction of acid anhydrides are usually low, except for the reduction of phthalic anhydride by zinc which leads to the formation of o-carboxy-benzyl alcohol or phthalide in more substantial quantities.

Amides of acids can be reduced to primary amines by lithium-aluminum hydride or electrolytically. With sodium in alcohol the products are amine but also an alcohol, formed by combination of reduction with hydrolysis and another reduction. Cyclic amides /lactams/ and imides can be reduced by lithium-aluminum hydride and by electrolysis to cyclic amines.

Amides and imines incorporating a group susceptible to enolysis

$$- NH - CO - \rightleftarrows - N = \underset{|}{C} - OH \qquad (41)$$

can be reduced by zinc or by phosphoric bromide to compounds containing the group $-N=CH-$.

Reduction of the carboxylic to the alcoholic group is more difficult than that of the carbonyl group. As a rule the catalytic hydrogenation of free acids is avoided /acids attack some of the catalysts chemically, problems may arise with the reaction water/. Much more frequent is the hydrogenation or hydrogenolysis of esters or amides of acids. It is here that the so-called Adkins catalysts are used /based on CuO - Cr_2O_3/ which are highly selective for this process. One has however to use higher temperatures and pressures (over 250 °C, over 10 MPa). Free acids which may sometimes be present in small quantities in the ester reactants can be bonded by adding alkalines (MgO). The use of ZnO - Cr_2O_3 based catalysts is less common (being less active they require even higher operating temperatures, about 300 °C), and the same applies to Re-based catalysts. The process has found widest application in the production of higher fatty alcohols from fats or synthetic fatty acids. The operating conditions are 20-30 MPa and about 300°C temperature, with 90-95% conversion. The starting material is triglyceride, processed by over-esterification by methanol to corresponding methyl esters

$$C_3H_5(OOCR)_3 + 3\ CH_3OH \xrightarrow{CH_3ONa} 3\ RCOOCH_3 + C_3H_5(OH)_3 \qquad (42)$$

which are then subjected to hydrogenolysis. Unsaturated fatty alcohols are produced in a similar way, too. A special case of the reduction of aldehydes and ketones is the so-called reductive catalytic amination, of which the so-called Wallach-Leuchart reduction is a chemical reduction analogy. It is only the catalytic process which is of commercial importace. It is based on two concurrent reactions - condensation of carbonyl compounds with ammonia or amines, and hydrogenation of the imines formed (cf. Chapter 6.2). Of industrial importance is the hydrogenolysis of oxirane compounds, e.g. of styrene oxide to 2-phenyl ethanol. This is done using nickel or palladium based catalysts /66 - 68/. Also the hydrogenolysis of substituted 1,3-dioxanes on CuO-Cr_2O_3 based catalysts, which replaced the formerly used reduction by sodium in alcohol, finds application in the perfumes industry /69/.

Replacements of the halogen by hydrogen take place most often by hydrogenolysis using palladium or platinum and nickel.

Iodine splits off most easily, bromine is less active, and chlorine is difficult to detach. The alkyl fluorides are highly resistant to hydrogenolysis. A reactive halogen can be reduced by sodium amalgam, zinc in a neutral medium, by iron, tin, stannous chloride, chromium (II) chloride, and sometimes by sulfite. An unactivated halogen requires the use of sodium, lithium-aluminum hydride, zinc, or hydroiodic acid.

Palladium catalyst is ordinarily more suitable for the hydrogenolysis of the C-halogen bond than is the platinum catalyst as it is not too much deactivated by the hydrogen halogenide formed. The reaction is rendered easier by the presence of bases and polar hydrocyclic solvents /70/. In contrast, it is retarded by the use of nonpolar solvents (ethyl acetate, benzene, cyclohexene) /71, 72/. Hydrogenolysis of aromatically bonded fluorine occurs only under conditions such that the ring is hydrogenated, too /73/.

The palladium catalyst is highly active for hydrogenolysis even under mild reaction conditions, and this is why it is used e.g. for removal by hydrogenolysis of the protective groups in the case of various syntheses, such as the groups -OCOR, -OR, $-NR_1R_2$, etc.

Certain other reduction reactions also represent a hydrogenolysis in the true sense of the term. These are e.g. the reductions of nitro compounds which are dealt with elsewhere, inasmuch as certain bonds are split in the process there. However, from the standpoint of what has become the accepted classification of the reduction reactions, they still do belong under the heading of hydrogenation, and this viewpoint is adhered to in the present study, too.

8. Hydrogenation catalysts

Metals and also metal oxides and metal sulfides are the most frequently encountered active components of the hydrogenation catalysts. Metals (as conductors) and oxides and sulfides (as semiconductors) are capable of catalyzing those reactions where electron transfers occur. As for metals, those most widely represented as hydrogenation catalysts are the group VIII. metals (Fe, Co, Ni, Pd, Pt, Rh, Ru, Re) and the group I. metals (Cu). Oxides, in contrast to metals, exhibit a substantially lower activity and find a major application in dehydrogenation reactions which, as a rule, are made to proceed at higher temperatures than the hydrogenation reactions. Some of them however are also used in hydrogenations (if conducted at high pressures and temperatures). These are mainly Cr_2O_3, Fe_2O_3, $CuO-Cr_2O_3$, $ZnO-Cr_2O_3$, WO_3, and MoO_3. The metal sulfides also are not highly active but are greatly advantageous in that they are insensitive to sulfur compounds which deactivate a great majority of the hydrogenation catalysts. Again, they are used in hydrogenations carried out at high temperatures and pressures; those most widely used are NiS, WS_3, CoS, MoS_3, and their combinations.

The catalyst proper may be constituted by a pure active component (Pt, Pd, Rh black, Raney type catalysts etc.) but, more frequently, this active component is applied onto a support (mostly active carbon, gamma-alumina, silica gel, diatomaceous earth, etc.) where an advantage is wrung from the high specific surface and where the particle shape can be influenced. This makes it also possible to control the mechanical strength of the catalyst, its thermal stability, service life-time, and the properties of the active component proper. Another component that may be contained in the catalysts is the promoters which enhance activity, or the modifiers which affect activity as well as selectivity. Most of the promoters are metals, most of the modifiers are also metals or metal salts or certain organic substances. The table below lists examples of frequent application of the individual types of hydrogenation catalysts, in keeping with their most specific properties.

Table D-7 Application of the hydrogenation catalysts

Catalyst	Specific properties	Application in hydrogenation
Pt	tendency to hydrogenolytic splitting	aromatic rings, aliphatic ketones, special pharmaceutical hydrogenations, benzene
Pd	to be avoided in the case of aromatic rings and aliphatic ketones	selective hydrogenation of acetylenes and dienes, Rosenmund reduction
Rh	less susceptible to hydrogenolysis then Pt, only limited splitting of O- and N- substituents	aromatic rings at normal pressure at T below 100 °C; pyridine, quinoline, and furane derivatives
Ru	low activity in double bond hydrogenations; well suited for aqueous media, inhibited in alkaline and non-aqueous media; resists sulfur, free from hydrogenolytic effects	aldehydes and ketones under mild conditions, aromatic amines and alcohols to cyclohexane derivatives, high-pressure hydrogenation of carbonic acids
Re		hydrogenation of unsaturated carbonic acids and amides
Fe	mainly for NH_3 synthesis	
Co	less active than Ni, low activity in double and triple bond hydrogenations	nitriles - selectively to primary amines

Table D-7 continued

Ni	requires higher T, p; Cannizzaro type disproportionation in the hydrogenation of aldehydes; hydrogenolytic effects	acetylenes, olefins, aromatics, nitro compounds, nitriles, oximes, carbonyl compounds, dehydrohalogenations
Cu	leaves aromatic rings unattacked	aromatic nitro compounds
CuO-Cr_2O_3	inactive in double and triple bond hydrogenations as well as in aromatic ring hydrogenations	aldehydes, amides, esters of carbonic acids
ZnO-Cr_2O_3		unsaturated acids to unsaturated alcohols
NiS, WS_3, CoS, MoS_3		double bonds and aromatics with S present; 200-300°C at high pressure

The costs of the catalyst often amount oto a significant share of the production costs. Despite their high price it is rather often that catalysts based on the platinum group metals are used in industry. Table D-8 gives a survey of the supply and demand of platinum in the Western world (derived from data by Johnson Mattey, (GB).

Table D-8 Platinum and palladium supply and demand: Western World

Supply	Platinum					Palladium				
	1980	1981	1982	1983	1984	1980	1981	1982	1983	1984
South Africa	2,320	1,800	1,960	2,070	2,310	870	910	820	790	950
Canada	130	130	120	80	150	170	160	160	110	190
Others	30	30	30	40	40	60	70	70	80	90
	2,480	1,960	2,110	2,190	2,500	1,100	1,140	1,050	980	1,230
USSR sales	340	370	380	290	250	1,240	1,430	1,550	1,560	1,690
Totals	2,820	2,330	2,490	2,480	2,750	2,340	2,570	2,600	2,540	2,920
Demand by region										
Western Europe	290	420	330	330	410	330	300	350	470	550
Japan	940	1,150	1,050	950	1,140	690	820	890	1,220	1,350
North America	980	700	710	720	870	840	820	830	830	1,000
Rest of Western World	120	160	230	180	170	170	150	180	180	200
	2,330	2,430	2,320	2,180	2,590	2,030	2,090	2,270	2,700	3,100
Western sales to Comecon/China	30	30	30	20	30					
Movements in stock	460	(130)	140	280	130	310	480	330	(160)	(180)
Totals	2,820	2,330	2,490	2,480	2,750	2,340	2,570	2,600	2,540	2,520

100 in the table = 100 000 ounces troy
The West and the western world = all territories except the USSR, other Comecon countries and the People's Republic of China

The subsequent table, Table D-9, gives an indication of the demand broken down to individual industries, for the same territory.

Table D - 9 Platinum and palladium demand by application in Western World (total)

	Platinum					Palladium				
	1980	1981	1982	1983	1984	1980	1981	1982	1983	1984
Auto	680	640	645	615	725	300	270	290	300	340
Chemical	260	250	260	245	290					
Dental						520	480	590	820	960
Elatrical	210	185	170	175	190	590	800	840	1,110	1,260
Glass	140	100	85	105	140					
Hoarding	-	-	45	90	170					
Jewellery	560	755	765	715	775	180	210	220	180	190
Petroleum	130	140	65	20	15					
Others	350	360	285	215	285	440	330	330	290	350
TOTALS	2,330	2,430	2,320	2,180	2,590	2,030	2,090	2,270	2,700	3,100

100 in the table = 100.000 ounces troy

Platinum is first and foremost a high-technology metal whose unique properties render it irreplaceable in many key industrial processes and make it strategically of great importance.

Platinum is still under the spell of the allmighty dollar, low inflation, and high real interest rates that have afflicted all precious metals for the past four or five years. Political events continue to exert no more than passing influence. On the open market, platinum picked up strongly early in 1983 from its mid-1982 lows, but began to slip gradually in the final quarter. There was a brief respite in February and March 1984 when the price neared $ 400 per oz (ounce Troy) as the doller weakened momentarily and, for once, markets reacted to the situation in the World. Through the rest of 1984, with nothing to check the slide, the price drifted steedily down to a two-and-a-half year in London of $ 289.50 on December. By the end of January, 1985 the spot quotation was around $ 275 and all eyes remained firmly fixed on the dollar.

Palladium has performed strongly over the past two years, during which demand has increased by 37 % to 3.1 million oz in 1984. Influenced by the new Soviet policy and firming demand, the open market price for palladium began climbing sharply late in 1982, and by mid-January 1983 had more than doubled in two months. The 1983 average was $ 134.50 against $ 66.35 in the previous year. In 1984, after moving up even further to a first quarter average of $ 158.35 (the highest since the end of 1980) and a 1984 high of $ 163 in April, the market weakened in the second half. Although historically less a prey to speculation, palladium caught some of platinum´s lethargy at the turn of the year, and was down to $ 113-114 at one point in mid-January 1985 from a second half peak of $ 150 on November. Soon after, there were growing signs that the market pessimism had been misjudged and that palladium had strong recovery potential in view of its underlying industrial strength. It was trading in the range of $ 126-131 at the end of January, 1985. The minor pgms (platinum group metals), i.e.: rhodium, ruthenium, iridium, and osmium) had an exciting year in 1984, after attracting little attention for some time. The rhodium price rose gently through 1983 to $ 345 in January 1984. By July 1984 it had reached $ 700, ended the year at around $ 900, and broke the psychological $ 1,000 barrier on January, 1985.

The ruthenium price increased fourfold to $ 165, having neared $ 200 at one stage. Although supplies of iridium appeared adequate, the price put on $ 130 during 1984 to $ 465. A renewed buying program added 1,800 oz to the U.S. stockpile in the last quarter of 1984, bringing the total holding of iridium to 29,590 oz. Following a long spell at $ 140, the osmium price took off strongly in March 1984. After flirting wirth $ 1,000 in September, osmium ended the year at around $ 900.

With a view to the soaring prices of the platinum metals, their application involves the use of special equipment and techniques and is governed by special regulations to minimize losses in production, handling, processing, reclaiming, etc.

The hydrogenation catalysts are produced by quite a number of companies. Tanking among the biggest producers are BASF, Shell, ICI, Girdler, Harshaw, Degussa, Ruhrchemie, Engelhard, Nikki, Procatalyse, Doduco, Johnson Matthey Chemicals, Leuna Werke and, in Czechoslovakia, the ČSSP Chemical Works in Záluží.

8.1. Regeneration of precious metals from used catalysts

The useful life of catalysts in a given process is influenced by a number of factors. As a consequence of their effects the catalysts are subject to gradual changes in properties which are outwardly manifested by loss of activity.

In the continuous processing units the catalysts must be regenerated from time to time so as to maximally restore their catalytic efficiency. Even then the catalyst, having passed a number of working and regeneration cycles, will reach the stage one day where it has to be replaced. These cycles, i.e., their duration, are very much process dependent and are influenced both by the properties of the catalyst proper and by the character of the process (temperature conditions, feedstock composition, side reactions, etc.). The service lifes of catalysts are of the order of months or years.

The price of the active metal proper constituting a substantial part of the catalyst production costs, it goes without saying that all the users of catalysts make efforts to reclaim the precious metal from the catalyst in a usable form and at maximum yield.

A number of catalyst manufacturers in the world obviously are also engaged in precious metal reclamation from used catalysts. Worth mentioning are e.g. Degussa, KCE, Doduco, Haereus, Engelhard, etc. Some catalyst producers even enter contract relations such that the catalyst is only rented out to the user and must be returned to the manufacturer when it is no longer active. Any disputes concerning the precious metal contents in either fresh or used catalysts can be settled by the "arbitration laboratory" (Griffith in London), the ruling of which is to be accepted by the two parties to the dispute.

The price of catalyst reprocessing may vary to some extent depending on the precious metal content, and the average losses of the precious metals due to reprocessing fluctuate from 0.8 to 3.0 wt.%, depending on metal type and content and on the type of carrier.

During a study tour undertaken within the framework of the UNIDO project, the authors of the present report paid a visit also to Johnson Matthey Chemicals Ltd. facility in Royston where the problems of precious metal based catalysts, their prices, and the prices of their regeneration were considered in discussions. This firm is the world's largest manufacturer of automobile catalytic converters. The largest part of these converters are manufactured in their branch office in USA, where exhaust converters are obligatory in cars. These converters radically reduce the pollution of cities by waste gases and are being gradually introduced also in other countries.

A certain problem still consists in the so far uneconomical way used for the regeneration of the active component of the catalyst (Pd, Pt, Rh); thus, the converters used also represent questionable wastes. Under the circumstances, an extension of the use of the converters to include all cars would contribute to a faster exhaustion of the limited stock of platinum metals.

The price of the palladium catalyst and the costs of regeneration of Pd from the catalyst based on active charcoal were also discussed. The price of the new catalyst containing 3% Pd consists of two components: 20 pounds sterling per one kg of dry catalyst, plus the price of palladium contained in it. The present-day price of palladium is something below 3 pounds starling per one gram. The costs of regeneration of Pd are: 1.45 pounds/kg of catalyst used, plus 140 pounds per one kg of regenerated palladium. The firm guarantees a 98% yield on Pd in the regeneration. If a 100% recovery of metal is required, the price of 2% Pd should be added to the regeneration costs given above, i.e., about 60 pounds per kg of regenerated Pd. Hence, production costs of a new catalyst are higher than those, e.g., of firm Haereus (37 DM/kg catalyst + the palladium price), and also the regeneration costs are somewhat higher.

The return of 100% of the metal, where the regeneration due loss is made up by the firm that performed the regeneration, is a way of by-passing, to an extent, the regulations governing the exports of precious metals.

The price of the Ru catalyst is 25 pounds sterling per kg, plus the price of the metal. The price of ruthenium is now approximately the same as that of palladium, i.e., something below 3 pounds per kg. The regeneration of Ru is said to be more difficult due to the volatility of its oxide, and is therefore more expensive than that of Pd.

The catalysts based on active charcoal are burnt in a multipurpose furnace after use. Since they obtain the used catalyst from many users, and the catalyst contains also mechanical impurities (e.g., filter cloths, bottles, and the like), the burning equipment should be simple. Probably it is a grid furnace with a stream of gas used for burning. The metal is received only in the ashes as this is the case with the Haereus company. The used catalysts as such are inhomogeneous to such a degree that no determination of a representative metal content is possible.

A number of processes were developed for isolation of the precious metals from used catalysts. It is very important that these processes be perfect, inasmuch as the catalyst costs represent a substantial portion of the over-all costs of the hydrogenation processes and, as such, are determining for the economy of production as a whole.

9. Apparatus for catalytic hydrogenations

The basic piece of equipment for a hydrogenation facility is the reactor. Inasmuch as the reaction system in question is a multiphase system, the number and condition of the phases constitutes a criterion of the classification of hydrogenation reactors:

Reactors for gas phase hydrogenation: the compounds to be hydrogenated and hydrogen form a gas mixture which passes through a reactor packed with catalyst particles - this is a two-phase system.

Reactors for liquid phase hydrogenation: a liquid compound to be hydrogenated, or its solution in a suitable solvent, and hydrogen gas are in contact with a solid catalyst - this is a three-phase system. This type of reactor can be further devided into three groups:

- batch autoclaves with suspended catalyst,
- continuous reactors with suspended catalyst,
- continuous reactors with fixed bed catalyst.

The substances which are hydrogenated in the gas phase are, as a rule, simpler compounds exhibiting lower boiling points and treated in great quantities. Hydrogenation of benzene to cyclohexane or catalytic reduction of nitrobenzene to aniline are typical examples. With these processes, ordinary apparatus is used and the behavior of the reactors has been analyzed in detail in availabel literature. Much more numerous are the liquid phase hydrogenations, and it is exactly on this type of hydrogenation reactions that the present report is focused. Liquid phase hydrogenation requires special equipment such as pumps for transporting the catalyst suspension, and filters which may be more costly than the reactor itself and whose reliability is essential for smooth operation of the entire production line.

In principle, any liquid phase hydrogenation can be performed using any of the aforementioned three types of reactors, but the proper selection of an economically optimal reactor does require a certain amount of experience. The discussion in this study relating to the problem of reactor type selection is based on the author's abundant experience with the development and operation of numerous industrial hydrogenation facilities.

9.1. Reactors for gas phase hydrogenation

Prodigious literature is devoted to analyzing the catalytic reactors for gas phase reactions, and this has more than once been treated synoptically in monographs and textbooks /74, 75, 76/. Hence, just a few selected technological problems will be discussed here.

9.1.1. Reactor with heat exchange and adiabatic reactor

In a tubular reactor with heat exchange, the reaction heat derived from the hydrogenation reaction is removed from the catalyst layer across the tube wall to a cooling medium which may be water, boiling water, or an organic heat transfer agent. In an adiabatic reactor which is of simpler design, the evolved reaction heat increases the temperature of the reaction mixture. No precisely defined criterion of selection between these two types of reactors is available. It is always possible in principle to meet the condition for the adiabatic reactor, viz., that the adiabatic rise in temperature must not exceed an admissible temperature range defined by various factors. The adiabatic heating can be modified nearly arbitrarily by excess hydrogen allowed to circulate in the reactor node. Even though the adiabatic reactor is very simple, it is not always that it offers the optimum solution:

/a/ as the excess of hydrogen (i.e., the molar ratio of hydrogen to hydrogenated compound) increases the costs incurred in recycling the hydrogen are rising. The importance of this factor diminishes with increasing pressure, owing to lowering the compression ratio at the recycling compressor;

/b/ as the excess of hydrogen increases, the hydrogenation rate mostly slows down and the reactor size increases;

/c/ recycling of large amounts of hydrogen requires large size heat exchangers, wide pipings, and bulky fittings;

/c/ the tubular reactor can better utilize the reaction heat of hydrogenation, mostly for steam production;

/e/ the volume of the catalyst in the tubular reactor is subject to design limitations. Reactors having over 10,000 tubes and over 20 m^3 catalyst volume are unique products of mechanical engineering. The limiting size of the reactor goes down as pressure goes up.

In the history of catalytic reactors, contradictory phenomena may be encountered. For instance, the very first system of catalytic reduction of nitrobenzene to aniline at BASF /Germany, F.R./ was adiabatic and used a hydrogen/ /nitrobenzene molar ratio of 200. The reactors built today all incorporate heat exchange and are operated at molar ratios of 10-20. An interesting development took place in the case of reactors for methanol synthesis by hydrogenation of carbon monoxide. The early reactors had $ZnO-Cr_2O_3$ catalysts and were adiabatic multilayer reactors operated at 30 MPa pressure. The application of the copper catalyst, of higher activity, has made it possible to reduce the reaction temperature and thus also pressure, down to 5 MPa, which in turn has allowed for the use of a tubular reactor offering an excelent utilization of the reaction heat (the Lurgi process). The tubular reactor however is limited as to its size and, apparently, the growth of the production capacities up to 2000 tons daily per reactor over the last years tends to prefer the adiabatic reactor which operates at about 10 MPa pressure (the ICI process).

Inasmuch as the growing pressure tends to suppress the disadvantages of the adiabatic type of reactor as listed under (a), (b), and (c), the adiabatic reactors are being given preference particularly for high pressure hydrogenations and in the case of large production capacities. In contrast, the tubular reactors are met more frequently in the case of hydrogenations conducted at pressures not exceeding 2 MPa.

3.1.2. Fixed bed or fluidized bed of catalyst

A fluidized bed of catalyst approaches an ideal mixer and, thus, is practically isothermic; the danger of overheating is at its minimum here. Also, the fine grains of the fluidized catalyst are more effective, with a view to internal diffusion, than are the grains having around 5 mm in size which are commonly used in the fixed bed arrangement; in the case of the latter grains the internal surface utilization is no higher than just 10-50%. In spite of the bright outlooks which had been predicted for the fluidized reactors just a few years ago, they have not become too widespread. Considering the requirement of high conversion of the reactant, the fluidized reactors are exposed to the danger of break-through of the unreacted feedstock, owing to so-called bubble fluidization.

Undisputably, the fluidized reactors are at an advantage in that the deactivated catalyst can be continuously regenerated, and this is why they have carried the day unambiguously in the area of catalytic cracking. As for catalytic hydrogenations, however, the deactivation of the catalyst proceeds rather slowly. Nevertheless, e.g. in nitrobenzene hydrogenation to aniline, the fluidized reactors (the American Cyanamide process) compete with tubular reactors (the NIOPIK process, USSR; Sumitomo, Japan; Moravien Chemical Works, Czechoslovakia).

9.1.3. Apparatus for gas phase hydrogenation

Figure D-3 depicts a typical structure of an installation incorporating a tubular reactor. Control circuits are denoted by internationally accepted symbols.

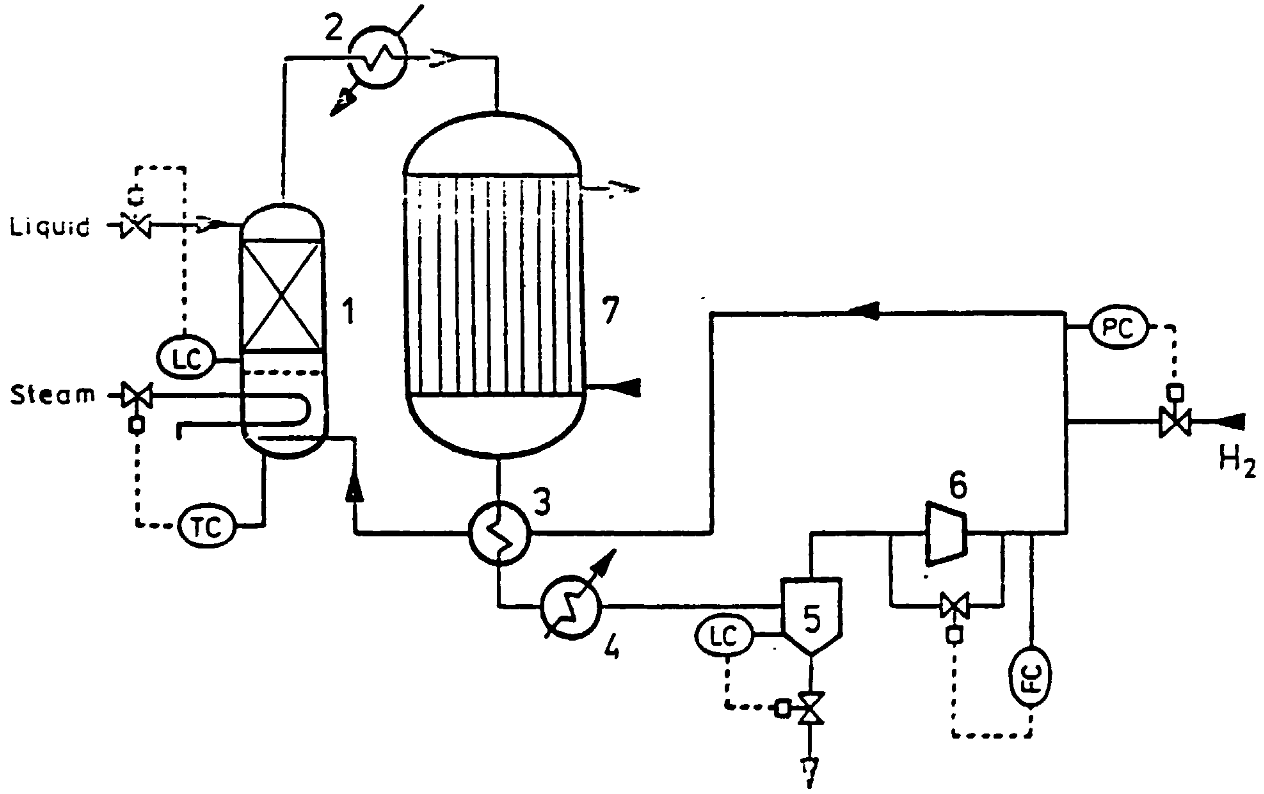


Fig. D-3 Schema of apparatus for gas phase hydrogenation:

1 - evaporation of compound to be hydrogenated into a stream of hydrogen; 2 - feed preheater; 3 - heat exchanger; 4 - cooler; 5 - hydrogen/liquid separator; 6 - recycling compressor; 7 - tubular reactor

Various compression engines are used for hydrogen recycling. The type of engine to be used depends primarily on the capacity desired:

- piston compressors - used rather seldomly, and only exceptionally at pressures up to 1 MPa. Their limiting output at 1-2 MPa pressure is approximately 20,000 Nm^3/h,
- screw compressors - are used for outputs of 1000-20,000 Nm^3/h and are very reliable,
- centrifugal compressors - for outputs over 20,000 Nm^3/h,
- blowers of various design - for compression ratios up to 1.7; being substantially cheaper than compressors they are expedient if the pressure loss of the apparatus is to be reduced below a level at which the use of blowers becomes feasible.

The hydrogenated compound is mostly allowed to evaporate in a stream of hydrogen; this is done by either bubbling the hydrogen through a layer of heated liquid or in tubular evaporators using the falling film principle. Inasmuch as the catalyst can become deactivated even by low quantities of the higher-b.p. substances, it is expedient to have a rectification element incorporated in the evaporator (Fig. D-3).

9.2. Liquid phase hydrogenation

Two monographs appeared recently, devoted to the kinetics and chemical engineering problems of the reaction system liquid - gas - solid phase /77, 78/. Therefore, we shall limit ourselves to pointing out certain important chemical engineering aspects of designing the hydrogenation apparatus, and to expanding these by our own experience. Adequate attention will also be paid to the auxiliary equipment which tends to be neglected when discussing reactor technology.

9.2.1. Hydrogen transport in the three-phase system

The compound being hydrogenated only reacts with hydrogen on the catalyst surface and, hence, must be transported toward a catalyst particle by diffusion through the liquid medium. Hydrogen is first dissolved in the liquid and then it diffuses through it toward the catalyst surface. Both the hydrogen molecules and the substrate molecules diffuse via the pores of the catalyst to its internal surface. Thus, there operate several transfer processes in the system, and the rate of each of them may in fact influence or even control the hydrogenation rate. As a rule it is only the transfer of hydrogen which becomes subject of studies; this can be accounted for by several circumstances:

(a) The concentration gradient is the driving force of mass transfer. As the hydrogen concentration in liquid ordinarily is much lower than the substrate concentration, the driving force of hydrogen transfer can only assume very low values, even in the case where there is a zero concentration of hydrogen in the layer which immediately adjoins the catalyst surface.

(b) The hydrogenation rate frequently is of the zeroeth order with respect to the substance being hydrogenated, and this is why a drop of its concentration near the catalyst surface against the bulk liquid concentration will not affect the reaction rate. The hydrogenation rate with respect to hydrogen is usually of the 1st order.

(c) Hydrogen must first dissolve in the liquid phase, and this as a rule is the slowest stage of transport which, accordingly, exerts the greatest influence.

At very low reactant concentrations, i.e., just prior to completion of a batch hydrogenation process or in a continuous stirred reactor, the arguments listed sub (a) and (b) lose their validity and the diffusion of substrate toward the catalyst surface may become the controlling process. For example, with certain proprietary processes of aniline production (ICI, Tolo-Chimie), nitrobenzene is hydrogenated in the liquid phase in a continuous reactor equipped with a stirrer, at a nitrobenzene concentration of 0.0001%, and in this case the hydrogenation rate is influenced by the diffusion of the nitrobenzene.

The path of hydrogen from the gas phase to the catalyst particle surface or the hydrogen concentration drop are illustrated in Fig. D-4 on the basis of the film theory. As a rule the resistance at the gas side can be disregarded, the mass transfer coefficients in the liquid at the g-l interface (k_L) and at the l-s interface (k_s) are approximately the same. This holds true for the agitated particles suspension where, moreover, the mass transfer coefficient is nearly independent of the agitation rate. Hence, by agitation the mass transfer is only influenced by the gas-liquid interfacial surface (a).

For the hydrogen dissolution rate in the liquid it holds that

$$r = k_L \, a \, (C^{+}_{Hl} - C_{Hl}) \qquad (43)$$

where a is the interfacial area g-l per 1 m^3 of mixture (m^{-1})

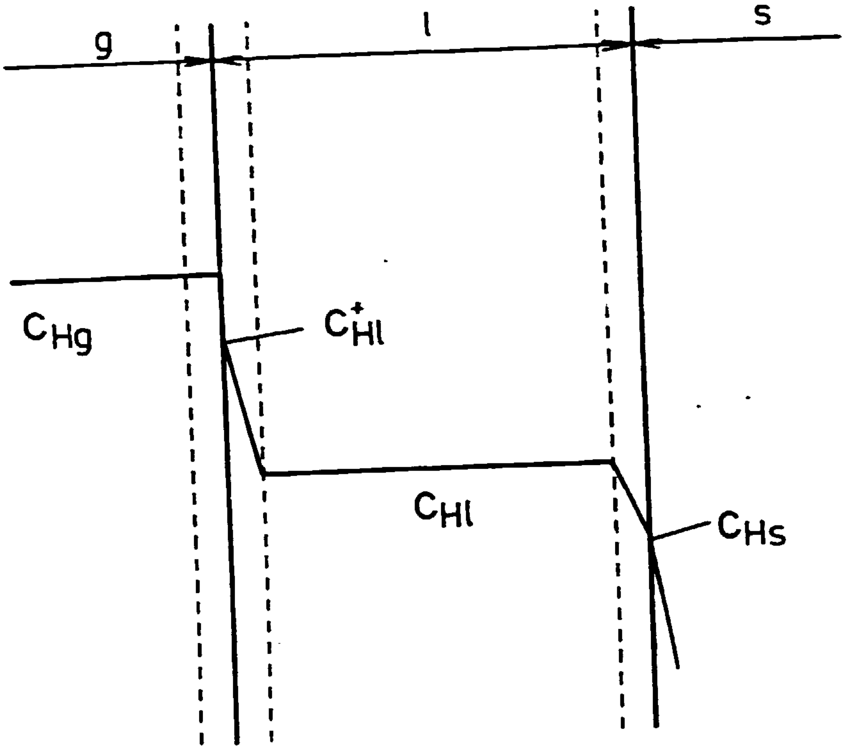


Fig. D-4 Scheme on hydrogen transport from gas phase into liquid and through liquid to catalyst surface

C^{+}_{Hl} is the hydrogen equilibrium concentration in the liquid corresponding to the hydrogen partial pressure in the gas phase

C_{Hl} is the hydrogen concentration in the liquid bulk (mol m^{-3})

The rate of hydrogen transfer to the surface of the catalyst particles is

$$r = k_s a_s m \; (C_{Hl} - C_{Hs}) \qquad (44)$$

on the condition that $k_s \approx k_L$

where a_s is the external surface of catalyst particles ($m^2 kg^{-1}$)

m is the weight of catalyst per 1 m^3 of mixture ($kg\ m^{-3}$)

C_{Hs} is the hydrogen concentration just above the catalyst surface.

The value of k_L can e.g. be calculated using the expression proposed by Calderbank /79/:

$$k_L = 0,42 \left(\frac{D_H}{\nu_L}\right)^{1/2} (\nu_L g)^{1/3} \qquad (45)$$

where D_H is the diffusion coefficient of hydrogen

ν_L is the kinematic viscosity of liquid ($m^2\ s^{-1}$)

g is the acceleration due to gravity ($m\ s^{-2}$).

The mass transfer coefficient depends above all on the viscosity of liquid,

$$k_L \approx \text{const.}\ \nu_L^{-2/3} \qquad (46)$$

and this is why with viscous liquid the kinetic mode of operation is more difficult to attain. Hence, stirring systems which guarantee a high level of gas dispergation in the liquid find application in hydrogenations involving fats and other similar substrates.

The external surface of suspended powder catalyst is of the order of 1,000-10,000 m^2/m^3 (the true value $a_g m$), the surface of bubbles in the same volume of mixture usually is lower by one order of magnitude. Therefore, it is rather the effect of the g-l interfacial surface on the hydrogenation rate than the effect of diffusion toward the catalyst surface which is encountered. The kinetic region is understood to be that mode of operation where the whole volume of the liquid is saturated with hydrogen to the maximum i.e. equilibrium, concentration. In well designed reactors with suspended catalysts /autoclaves with stirrer, bubble towers/ the kinetic mode of operation is commonly achieved (cf. Chapters 9.2.2 and 9.2.3).

In a trickle bed reactor where the liquid trickles through a fixed catalyst layer the g-l and l-s surfaces are roughly equal to each other. The rate of hydrogen diffusion across the flowing film of liquid depends above all on the film thickness and, thus, on the spraying density. In this case it is only with low activity catalyst that we may approach the kinetic mode of operation; the actual hydrogenation rate usually is 30-70% of the kinetic rate (Chapter 9.2.5.).

The diffusion of hydrogen in liquids is slower by three orders of magnitude than that in gases, and this keeps low the utilization of the internal surface of a porous grain of the catalyst. With the suspended powder catalyst having a grain size below 0.05 mm there is a nearly total utilization, whereas with the granules for the fixed bed having a mean size of 5 mm the utilization is no higher than just 1-5 %. The catalysts for the trickle bed reactors are therefore made is such a way as to have the active component only in the surface shell of the granule. This can well be done when the catalyst is prepared by impregnating the carrier with the active component; it finds application chiefly in the case of catalysts based on precious metals.

9.2.2. Batch autoclaves

Figure D-5 presents a simplified view of an autoclave with stirrer.

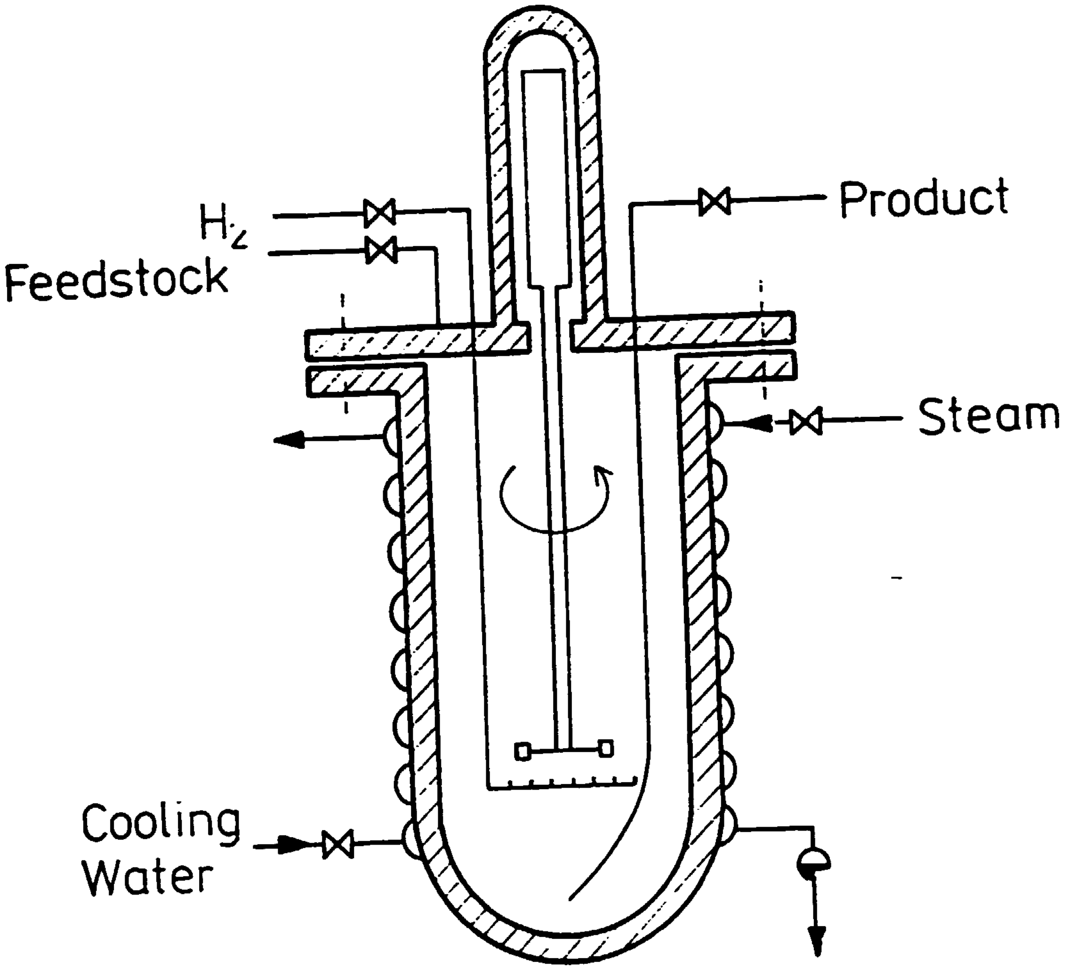


Fig. D-5 Autoclave with glandless stirrer

9.2.2.1 Agitation

Turbine stirrers are most widely used. The distance between the level of liquid and the stirrer must not exceed 1m in order to permit vortex generation required to drawn in hydrogen by suction from above the liquid level. Introducing hydrogen below the turbine of the stirrer would facilitate the high dispergation of gas but this measure is effective only when the hydrogen is being brought in continually. A suitable design is that of stirrers with two elements of which the top one provides for gas dispergation and the bottom one agitates the liquid bulk and prevents the catalyst from settling down. The net input on the stirrer ought to be at least 2 kW m^{-3}. Commercial autoclaves are usually operated at 5-20 rps and, in this region, the hydrogen absorption rate /$k_L a$/ increases rapidly, nearly as high as the square of the rps value /77/.

An important problem of design is the sealing of the stirring axle. Mechanical sealings are used for pressures up to 5 MPa, double sealings with oil counterpressure are used at higher pressures. However, preference is nowadays given to sealing less stirrers with magnetic couplings /Fig. D-5/.

The hollow shaft stirrer is frequently mentioned in literature but rarely used in practice; hydrogen suction from the area above the liquid is effected through this axle, and the stirrer arms dispergate it within the liquid. Laboratory autoclaves commonly use the pulsating stirrers which however have not found much application with the large size autoclaves. The firm Buss /of Switzerland/ offers hydrogenation autoclaves with ejector dispergation of hydrogen. An ejector, as is well known, generates a g-l interfacial surface higher one order of magnitude than that generated by a stirrer, and this is markedly manifested in reaction rate enhancement during the hydrogenation of viscous liquids. Problems relating to stirrer sealing are avoided but nonetheless, the pumping of the catalyst suspension through the ejector is also complicated, owing to abrasion.

An interfacial area of 200-300 m^2/m^3 can also be obtained by bubbling the hydrogen through the bulk of a liquid. - Here the energy required for dispergation is not supplied to the stirrer but to the hydrogen circulating compressor. However, the bubble column find more application for the continuous processes, even though the batch hydrogenation applications are possible, too.

9.2.2.2. Autoclave heating and cooling

A common design involves heating and cooling by a mantle or by tubes welded to the outside of the autoclave. Owing to reasons of corrosion, it is expedient to use water cooling and steam heating, with two separate tube systems. Cooling by internal helix is highly efficient but makes the construction of the autoclave interior more complicated.

9.2.2.3. Operating pressure and autoclave capacity

Owing to reasons of design the maximum volume of autoclaves decreases as the hydrogenation pressure increases.

Autoclaves of up to 30 m^3 capacity are made for pressures of about 2 MPa. Hydrogen at 2 MPa pressure is produced by steam reforming of hydrocarbons and is commonly available at large plants. In such a case, it is well advised to design the hydrogenation process to operate at this pressure because even the equipment then is relatively inexpensive; the reason is that it can be made by welding whereas the high-pressure autoclaves are forgings. Autoclaves equipped with stirrers and designed for pressures of 10-20 MPa are manufactured to capacities of max. 5 m^3.

At plants where work with pressure vessels is out of the ordinary, we may meet with opinions that, for safety reasons, it is better hydrogenations be conducted at only a moderate overpressure. This, in most cases, is an erroneous conclusion. Up to about 10 MPa pressure the hydrogenation rate usually is directly proportional to the hydrogen pressure, so if we reduce the pressure we must compensate for the decrease in reaction rate by increasing the catalyst concentration. At high catalyst concentration and low pressure it is only with difficulty that the kinetic mode of operation can be obtained in the hydrogenation process. Pressures below 1 MPa must be regarded as absolutely ineffective.

9.2.2.4. Batch autoclave operating mode

With a view to possible initiation of an explosion of the air-hydrogen mixture by the catalyst, it is recommended that the autoclave be thoroughly flushed with nitrogen prior to charging each batch. However, if the hydrogen is completely discharged at the end of a hydrogenation and if then the autoclave is flushed with nitrogen and the nitrogen again is replaced by hydrogen, this cuts down on the time utilization of the apparatus and induces great losses of hydrogen in the autoclave is operated in this manner. The following procedure is more economical: on completion of the hydrogenation the hydrogen pressure is reduced to 1-2 MPa and the liquid mixture is pushed out of the autoclave by the residual pressure of hydrogen while the eventual pressure of gases in the autoclave is 0.3-1 MPa. Then the new batch is pumped into the autoclave, i.e., the liquid substrate with suspended catalyst. With the autoclave operated in this way, no cooling is needed and the heat capacity of the autoclave is used for preheating the new batch. Often, in this way, the batch can be heated up to a temperature at which the hydrogenation already proceeds at a sufficient rate, so that the autoclave heating can be dispensed with entirely.

Two ways of admitting hydrogen are practiced with the batch autoclaves - continuous admittance, and periodic admittance. If the hydrogen is being admitted continuously under the stirrer turbine, the dispergation of gas is better and this method enables the kinetic mode of operation even with less effective stirrers. In the case of the hydrogen being admitted periodically, the pressure varies between a minimum and a maximum value. From the pressure drop one may judge on how the hydrogenation is proceeding, and a stop in the pressure drop is an indication of the end of hydrogenation. This is the chief advantage in contrast to the continuous admittance of hydrogen where the end of hydrogenation must be indicated in some other manner, e.g., by analyzing the liquid substrate. In the case of periodic admittance the hydrogen must be dispergated from the area above the liquid bath which imposes more stringent requirements on stirrer operation.

The combination of both these methods is of advantage; most of the substrate is hydrogenated at a constant pressure while the hydrogen is being admitted continuously, and only after the hydrogenation rate /indicated by hydrogen flow rate measurements/ will have dropped below a certain level the inflow of hydrogen is interrupted and the hydrogen pressure drop in the autoclave is monitored.

9.2.3. Continuous hydrogenation with suspended catalyst

For continuous hydrogenation with suspended catalyst, the options available are to use just one autoclave or more autoclaves in series, or frequently, column reactors with hydrogen circulation /Fig. D-6/.

9.2.3.1. Bubble columns

The basic characteristic of the bubble column is the rate of gas flow /u_g/ related to the entire cross section of the tower. On the value of u_g depend the gas holdup ε_g and the rate of hydrogen transport from gas to liquid as expressed by the simplex k_La /s^{-1}/. A certain minimum gas velocity must be maintained also with regard to keeping the catalyst in a homogeneous suspension. Published measurements /77/ suggest that the bubble columns attain k_La values lower by a factor of 3 to 5 than vessels equipped with stirrers.

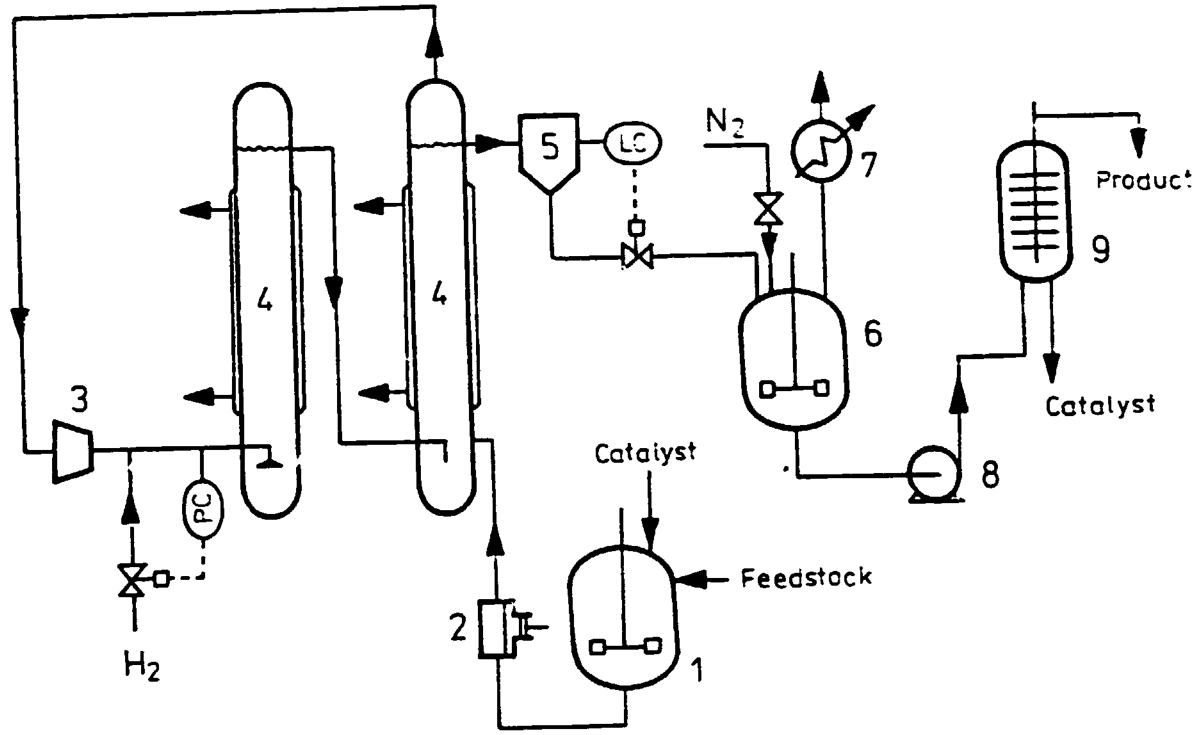


Fig. D-6 Schema of continuous slurry hydrogenation in bubble columns

1 - preparation of catalyst suspension in compound to be hydrogenated; 2 - diaphragm slurry pump; 3 - compressor; 4 - reactors; 5 - tank with level indicator; 6 - slurry receiver; 7 - reflux condenser; 8 - pump; 9 - pressure filter

To hold the catalyst in suspension, a hydrogen velocity $u_g = 0.02\text{-}0.03$ m s^{-1} is sufficient, and this velocity is also enough, in most cases, for reaching the kinetic mode of operation for the hydrogenation process. At velocities higher than 0.05 m s^{-1}, foaming of liquid and nonuniform bubbling are frequent; large bubbles occur side by side with the small bubbles. According to our industrial experience, the hydrogen velocities of 0.02-0.05 m s^{-1} can warrant the kinetic mode of operation at an absorption rate of about

5 kmol H_2 h^{-1} m^{-3} at 5 MPa pressure. As the catalyst concentration is increased, the hydrogenation rate grows higher and one has also to select a higher velocity, but such situations are encountered rather infrequently. At the streaming velocities of hydrogen of 0.02-0.05 m s^{-1} the gas holdup is $\varepsilon_g \approx 0.1$, which means that the bubbles take up some 10% of the total mixture volume.

The value of the gas-liquid interfacial area depends only slightly on the primary distribution of hydrogen. Small bubbles will gradually coalesce and the specific surface area is pushed down as the distance from the distributor is increased. Despite this it is expedient to distribute the hydrogen uniformly across the reactor cross section, e.g., by perforated tubes or at least by several nozzles. The hydrogen distribution also relates to the necessity of making the choice between passing the hydrogen from tower to tower in parallel or in series. As for the liquid, a series of towers represents sequential flow, and the hydrogen can be led in parallel or, together with the liquid, in series. Obviously, the amount of circulating hydrogen is greater in the case of the parallel arrangement, but the recycling compressor operates at a lower compression ratio. From the point of view of the investment costs, of power consumption for hydrogen recycling, and also of simplicity of control, it is better the use the series connection. In that case, what enters the second and subsequent reactors is a mixture of liquid and gas so that it is impossible to use a distributor with small perforations.

9.2.3.2. Axial mixing

Stirred autoclave can be regarded as an ideal mixer, whereas the bubble column is a system with limited axial mixing.

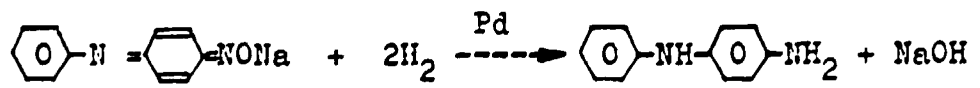
Numerous hydrogenations are controlled by zeroeth-order kinetics as far as the hydrogenated species is concerned, and this is why the mixed reactor /CSTR/ can be used even for a high reactant conversion. This is how nitrobenzene is hydrogenated to aniline in a stirred autoclave, to a conversion exceeding 99.999%. This however is an exception rather than a rule. The zeroeth order of the hydrogenation usually applies only at conversions of up to 90-95 %, and many hydrogenations, particularly the hydrogenation aminations, have an order considerably higher than zero. In such cases the CSTR would perform very poorly and the flow of the liquid must be made to approach the plug flow. In this connection, it is useful to know the intensity of axial mixing in the bubbled tower, and this can be measured by the axial mixing coefficient D_{Lax}. Deckwer /80/ correlated the experimental data obtained by several authors using the equation

$$D_{Lax} = 2,7\ d_T^{1,4}\ ug^{0,3} \qquad (47)$$

where d_T is the tower diameter.

Other authors as well have found the axial mixing of the liquid to be strongly influenced by the tower diameter /77/. According to our measurements conducted at a tower of 1 m diameter and 12 m liquid height at a hydrogen velocity of 0.03 m s^{-1}, this tower can be regarded as equivalent to two mixers connected in series. Axial mixing can be limited by baffles.

As an example of an expedient utilization of limited axial mixing can be presented the hydrogenation of a water-methanol solution of the 4-nitrosodiphenyl amine sodium salt /81/



(48)

This hydrogenation is controlled by zeroeth-order kinetics with respect to substrate up to 65% conversion, whereas further on the effective order is 0.65. A 100% conversion of the nitroso compound is required. With a view to the low stability of the reactant the hydrogenation is performed within the temperature range of 70-100 °C, at 5 MPa operating pressure. Adiabatic heating of the reaction mixture is 70 K. A palladium catalyst is used. The highest hydrogenation output was achieved in a plug flow reactor where however the liquid feed had to be preheated while the reactor itself had to be cooled. If a system providing adequate axial mixing is selected, the hydrogenation can be conducted adiabatically with cold feed, reaching a high specific output. In three towers of which each corresponds roughly to two mixers, the distributions of conversion and temperature are as follows:

	conversion %	temperature °C
No. 1 reactor	70	75
No. 2 reactor	98	95
No. 3 reactor	100	96

With most hydrogenations the final product is usually more stable than the unsaturated reactant, but cases exist where the selectivity of the hydrogenation is influenced by axial mixing. Such an undesirable consecutive reaction is hydrogenolysis, e.g., when esters of fatty acids are hydrogenated the desired alcohol is splitted to hydrocarbon:

$$\begin{aligned} RCH_2COOCH_3 \xrightarrow{H_2} \; & RCH_2CH_2OH + CH_3OH \\ & \hookrightarrow \xrightarrow{H_2} RCH_2CH_3 + H_2O \end{aligned} \qquad (49)$$

9.2.4. Handling catalyst suspensions

The powder catalyst must be metered out into the reactor, and must again be separated from the hydrogenation product. Especially in the case of continuous hydrogenations, these operations tend to involve serious difficulties.

9.2.4.1. Catalyst metering

For a continuous reactor the catalyst is always to be metered out in the form of a suspension; for a batch autoclave a dry catalyst can be used but this is not expedient, either. Pumping of catalyst suspensions always involves abrasion and clogging of pump valves. The catalyst is either mixed within the substance to be hydrogenated /or its solution/, or is pumped seperately in the form of a concentrated suspension in some pure solvent. Either method has certain advantages:

/a/ When metering out the catalyst together with the substance to be hydrogenated, the suspension contains a low percentage of solid particles and pump abrasion is relatively low. In cases where the suspensions involved are particularly thin, it is possible to apply ordinary centrifugal or plunger type pumps.

/b/ When metering out the catalyst in the form of a concentrated suspension, ordinary pumps can be used for the major part of the clean liquid feed and the special pump can be used only to handle the catalyst suspension. Separate metering of catalyst also allows for an operative control of the catalyst concentration in the reaction mixture.

Various types of pumps are used to pump suspensions into the reactors or onto the filters:

- centrifugal pumps up to 2 MPa pressure as long as the concentration of the solid phase is max. 1% and the abrasive wear is not too high,

- pumps with excentric worm up to 1 MPa, even at high catalyst concentrations,
- diaphragm pumps or, less frequently, flushed plunger pumps or twin cylinder pumps at higher pressures.

9.2.4.2. Catalyst filtering

For safety reasons the hydrogenation product is not filtered using the hydrogen pressure in the reactor. The product being discharged from the reactor is expanding, expulsing hydrogen by desorption, and only then it is filtered. The filters mostly used are sealed pressure filters of various design. For low outputs, these are bag filters or cartridge filters, while vertical or horizontal plate filters are used at higher outputs. The filtration cake is removed from the plates by vibration /filters made by BHS, FRG, the so-called Niagara filters, etc./, by centrifugation /the Funda filter by CHEMAP, Switzerland, the Hercules Filter by Seitz, FRG/, or by scraping. The pressure filters tend to be equipped with automatic filtration cycle control. The pressure filters can handle 0.3-2 m^3 of suspension per hour per 1 m^2 of the filtering partition. The size of the filter area must also be chosen with a view to the amount of solid particles, inasmuch the filtration must as a rule be discontinued as soon as the cake is 20-30 mm thick.

It is advisable that a small safety filter be included downstream of the main filter. This is usually an inexpensive bag or plug filter.

In hydrogenations involving higher catalyst concentrations, it would not be feasible to continuously meter out and filter the catalyst. In such cases the catalyst is separated by settling and is returned to the reactor. Only the fine particles of catalyst are filtered /Fig. D-7/. A special case of this design is represented by the fluid operating mode of the bubbled tower, whereas in catalytic hydrogenations this system has not found acceptance.

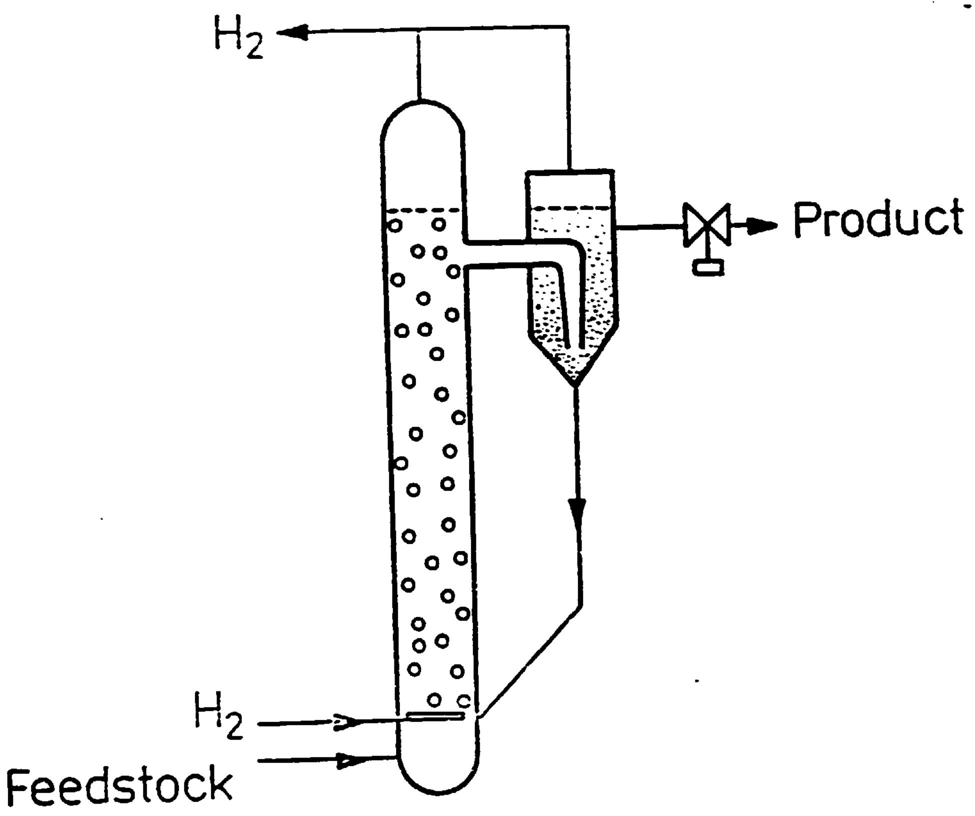


Fig. D-7 **Bubble reactor with internal recycling of catalyst**

9.2.5. Reactors with fixed bed of catalyst

These are applied as either the trickle-bed reactors or the fixed-bed reactors with cocurrent upflow with dispergated bubbles of hydrogen /Fig. D-8/. Under certain conditions of flow however, even in the case of cocurrent streams of liquid and of hydrogen flowing downwards the catalyst bed may become flooded with the liquid. The trickle bed is encountered more frequently in catalytic hydrogenations. The

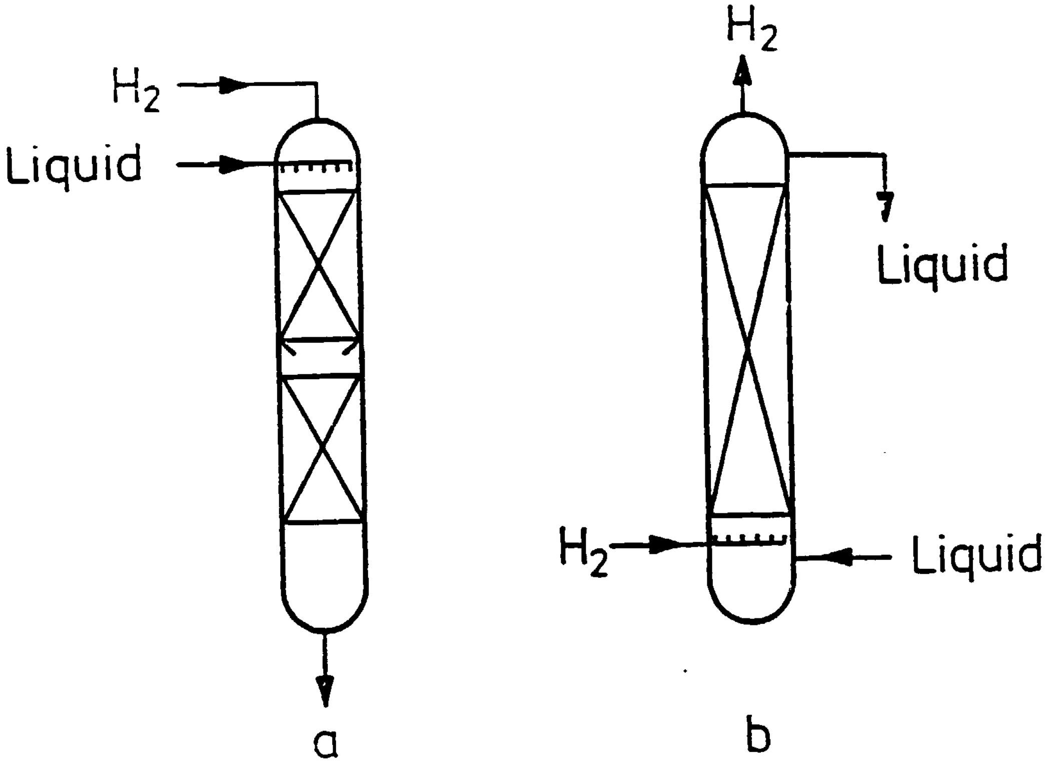


Fig. D-8 Reactors with fixed bed of catalyst

a - trickle-bed reactor

b - fixed-bed reactor with cocurrent upflow

reactor with cocurrent upflow has the advantage of perfect wetting of the granules and less danger of local overheating. However, the flooded bed imposes higher demands on the mechanical strength of the catalyst granules and usually requires hydrogen recycling, whereas the trickle bed can often be operated with only a stoichiometric amount of hydrogen.

9.2.5.1. Hydrogen transport in the trickle-bed

With both the liquid and the hydrogen being led cocurrently from top to bottom, the mode of operation of the trickle-bed depends on the gas and liquid flow rates. At a certain velocity of flow the trickle flow will convert to pulsed flow, or to foaming flow in the case of foamy liquids. The boundaries of the two modes were studied e.g. by Charpentier and Favier /82/ and by other authors /77/. In the region of pulsed flow there is an actual danger of the unreacted feed penetrating into the product. Even in the region of low velocities, i.e., under the trickle flow mode, the effective gas-liquid interfacial area is somewhat higher than the geometric surface area of the particles. In fact, some of the gas is dispergated as small bubbles within the trickling liquid film. As the velocities of flow of the two media grow higher, the interfacial area increases in proportion to the rising pressure loss of the bed which is a measure of the energy transmitted to the gas-liquid system and on which the friction force between the two phases is dependent. In the trickling film of liquid there always is a transverse hydrogen concentration gradient and, as a rule, the rate attained amounts to 20-70% of the kinetic hydrogenation rate /83/.

Utilization of the internal surface of the catalyst granule having 5 mm in diameter is no more than 1-5%. In spite of the fact that the trickle bed reactor contains 50-200 times more catalyst per unit volume then the reactor with suspended powder catalyst, the specific outputs of both types are roughly the same.

9.2.5.2. Adiabatic mode of trickle bed reactors

Most of the industrial hydrogenation reactors of trickle bed type are cylinders having 0.2-2 m in diameter and 5-20 m in height. The removal of reaction heat across the wall is ineffective and the reactors are operated adiabatically. As an exception, tubular trickle bed reactors can be encountered, which however require a complicated distribution of the liquid in the individual tubes.

A number of ways are used of how to adapt the adiabatic heating of the reaction mixture so as to conform to an admissible level:

/a/ In certain cases the reactant is so much diluted in the feedstock that the adiabetic temperature increment is very small. An example is the hydrorefining /desulfuration/ of oil fractions, removal of traces of nonsaturated compounds /acetylenes/ from hydrocarbons, etc.

/b/ The substance to be hydrogenated is intentionally diluted by some solvent or reaction product. In the hydrogenation of nitriles the nitrile is diluted by liquid ammonia which not only reduces the adiabatic heating but, at the same time, suppresses the formation of undesirable secondary amines.

/c/ The adiabatic heating is modified by excess hydrogen which is recycled. The hydrogen can be introduced at several points along the reactor height which allows for an operative control of the temperature profile of the reactor.

9.2.5.3. Catalyst bed arrangement

With increasing reactor height the density of spraying at given catalyst volume is increasing simultaneously favorably affecting the distribution of liquid within the bed. At low density of spraying the whole catalyst surface is not wetted and this may bring about local overheating and may extend the scope of the side reactions. With increasing density of spraying the liquid film thickness increases, causing an increase in the diffusional path for hydrogen, but it has been demonstrated experimentally that this does not detract from the rate of hydrogenation; this can be accounted for by an increase in interfacial area or even by better wetting of the catalyst granules.

Of negative impact on reactor performance is the so-called wall flow. It has been ascertained that the wall flow is less pronounced in a bed of porous catalyst particles than in a bed of non-porous particles. In spite of this, laths have to laid along the reactor walls to convey the liquid away from the wall, into the catalyst bed.

To obtain a uniform distribution of liquid across the reactor, one can use distributors developed for packed rectification columns. Uniform wetting of catalysts requires a minimum spraying density of about 3 m^3/h per 1 m^2 of reactor cross section. Some hydrogenations proceed so slowly that even this minimum spraying density is hard to attain. At selected elevations /spaced at 3-5 times the reactor diameter/ the distributions of the liquid are repeated, taking the liquid away from the reactor walls at the same time. When the catalyst is divided among several beds the mechanical loading of the granules due to the dead weight of the bed is also reduced. However, some operators use just one bed of catalyst even in reactors as high as 20 m. The partitioning of the catalyst packing into several levels is also done in the case where the reactor temperature is controlled by admitting cold hydrogen at several points.

9.3. Industrial reactor design - upscaling

9.3.1. Batch autoclaves

The batch autoclave usually have stirrer of an aeration efficiency high enough to always reach the kinetic mode of hydrogenation. This makes it easy to transfer laboratory data by upscaling, inasmuch as the specific output and selectivity are identical for both the laboratory and the full-scale reactor. Sometimes the big reactor attains somewhat higher outputs, owing to deactivation of a part of the catalyst in the laboratory installation. Hence, the upscaling operation reduces to just the problem of heat removal which however is easy to solve by calculation.

9.3.2. Continuous slurry reactor

Kinetic data from laboratory batch reactors is easily available. In cases where the continuous apparatus consists of a series of stirred autoclaves, it can be modeled as a cascade of ideal mixers.

More complex and risky is the transfer of the kinetic data from a batch reactor to a bubble tower, even supposing that the latter is operated in the kinetic mode. Several factors which cannot be forecast to any sufficient accuracy are involved here:

/a/ The degree of axial mixing can be expressed from published correlation equations but its effect on selectivity, within a system of several reactions, need not be sufficiently represented by measurements taken in a batch reactor.

/b/ If the catalyst is separated by settling and is returned to the reactor /Fig. D-7/, it is difficult to envisage how much of the catalyst is in the reactor and how much in the settling tank. Moreover, the recycling of the suspension adds to axial mixing in an undefined manner.

/c/ In our practice we have met with a case of partial settling of catalyst in the reactor; consequently, the cascade of hydrogenation towers exhibited a specific output higher than the laboratory autoclave. The difference between the catalyst concentration in the liquid feed and its true concentration in the reactor cannot be predicted but, within certain limits, can be regulated by changing the hydrogen flow velocity.

It is especially the factors sub /b/ and /c/ which require experiments to be run on a pilot installation. The pilot scale measurements are intended to widely scan the effects of hydrogen flow on the hydrogenation process. The approximate ratio of tower diameter and height expected for the full scale reactor should be adhered to at the pilot plant.

9.3.3. Trickle-bed reactors

The first information on the hydrogenation process on catalyst granules can be obtained from a modified laboratory autoclave: a bucket holding the granulated catalyst is placed in the axis of the autoclave, and a modified stirrer is used to pump the hydrogen saturated liquid across the catalyst layer.

Experiments are run very often using laboratory trickle bed reactors having 0.1-1 m bed height, i.e., at a very low spraying density. Such experiments may yield distorted results, also owing to the high share of wall flow. As a rule, the outputs reached in a bigger reactor are higher. Hence, even the small experimental unit should have the highest possible layer of catalyst as the density of spraying is the most essential criterion for reactors of such type. The hydrogen flow velocity affects performance only in the pulsed flow region, i.e., in the regime of high phase-interaction.

Great uncertainty is brought into the data transfer by the thermic effects of the side reactions for which the kinetics and reaction heat can only be ascertained to low precision. For this reason, some operators recommend that the upscaling be done gradually, always by just one order of magnitude. Measurements of the temperature and concentration fields in an experimental reactor and a kinetic analysis of the nonisothermic data thus obtained which is to be applied to the gas phase catalytic reactions /84/ can be recommended even for the trickle-bed catalysts. This procedure allows to make away with some of the intermediate stages involved in upscaling.

9.4. Reactor type selection

In principle, any of the three reactor types discussed above can be used for any given hydrogenation. It is true however that difficulties and useless costs are avoided if the proper selection is made.

9.4.1. Trickle-bed reactor or slurry reactor

The trickle bed reactor features a number of advantages over the slurry reactor hydrogenation:

- no pumping and filtering of the catalyst suspension is required, making the apparatus less expensive,
- the clear liquid does not cause any wear of pipings and fittings,
- catalyst handling is hazardous for in the powder form it is pyroforic,

- the three above advantages are reflected in a higher reliability and safety of the hydrogenation facility.

The advantages of the trickle-bed reactor are that significant as to make it advisable that the first question asked when developing a hydrogenation process should be: "can this hydrogenation be performed in a trickle-bed reactor?". There are several limitations however to the application of the trickle bed reactor:

/a/ the adiabatic mode of operation
Reaction heat is difficult to remove from the trickle bed. In most cases however this can be taken care of by modifying the adiabatic heating so as to conform to an admissible limit, so this limitation is not insurmountable.

/b/ the capacity of equipment
It is often claimed that the continuous trickle-bed reactor is poorly suited for small scale productions and for variable production programs, i.e., as a multipurpose facility. The batch autoclaves with stirrers tend to be recommended in such cases. In fact, however, the trickle bed reactors fit very well also the requirements of low production capacities and even those of a variable production program. Transition to hydrogenation of some other compound does not present problems any greater than in the case of the stirred autoclave.

/c/ catalyst life time
Rapid deactivation of the catalyst is the greatest obstacle to using a trickle bed reactor. Owing to the low utilization of the internal surface of the granules, rapid deactivation is conducive to a high consumption of catalyst, substantially higher than in the case of slurries. Frequent replacements of the catalysts are just as unsuitable.

Indeed the trickle bed reactor ought to be regarded as unsuitable in cases where the catalyst life time is less than 1 month.

/d/ process selectivity
In the region of internal diffusion, the side reactions and consecutive reactions can display greater impacts on the process. Limitation by selectivity occurs however only with more complicated reaction systems.

It is solely the short catalyst life time and the process selectivity which can be regarded as serious objections to using a trickle bed reactor.

9.4.2. Batch or continuous slurry hydrogenation

The production capacity is the major selection criterion. The continuous slurry hydrogenation is clearly destined for larger production units, of a lower feed rate boundary of about 1 m^3 of liquid per hour.

In some processes the batch autoclaves are even used in the case of higher capacities, with regard to selectivity. In the continuous arrangement the selectivity may grow worse as a consequence of axial mixing for a poorly adjustable end of hydrogenation. Even though, e.g., continuous processes of glucose hydrogenation to sorbitol have been developed involving both a suspended catalyst /slurry/ and a trickle bed reactor, it is the batch autoclaves which are chosen even for capacities exceeding 10 ktons annually, owing to product quality requirements.

9.5. Safety at work during hydrogenation

Hydrogen forms an incendiary mixture with air at 4-75% H_2 and the explosive range is 18-59% H_2. The hydrogen self-ignition temperature in air is 485 C. The explosivity of the hydrogen-air mixtures is underlined once again by the initiation effect of the hydrogenation catalysts. Explosion or fire due primarily to hydrogen may propagate by ignition of the hydrogenated substance. This is why the catalytic hydrogenation is more demanding as concerns apparatus design as well as the quality of operation and servicing than are the chemical reductions. This also is one of the reasons why the chemical reduction agents continue to be used.

With regard to safety of operation at the hydrogenation facilities, several principles can be forwarded which should be adhered to whenever installing and operating a hydrogenation process:

/a/ The design of apparatus incorporates a minimum of piping connections and a minimum number of fittings which potentially might turn leaky.

/b/ Hydrogen is a light gas and is dissipated rapidly in the atmosphere. Hence, the hydrogen concentration at apparatuses installed as open facilities cannot, in the case of minor leakage, reach the limit of explosivity. Instances are known where the explosive mixture was formed exactly under the roofing of the building where the facility was housed. Therefore, compressor rooms where roofing is required must be provided with wither natural or forced air draught systems.

/c/ In the case of slurry hydrogenation the dry catalyst must not come into contact with hydrogen and air. The apparatus must be kept clean and catalyst residues must be removed instantly. Hard-to-remove rests of the catalyst on the outer surface of apparatus can be deactivated by spraying with sulfide solutions or with organic sulfur-bearing compounds.

/d/ The hydrogenation apparatus is to contain only the indispensable volume of inflammable matter. Apparatuses containing more inflammables, such as storage tanks, must be situated at a sufficient distance from the pressure apparatus.

/e/ Defective seals of piping and apparatus joints and junctions represent the most frequent cause of explosions and fires. Hence, it is most important to properly choose the sealing materials.

<u>Metallic seals</u> are used in all instances to handle pressures over 10 MPa. For medium pressures, the national standards permit the use of asbestos seals of the tongue and groove system but even here the metal-reinforced or all-metal seals of mild steel, aluminum, copper, etc. are gaining ground.

The apparatus tends to spring leaks mainly during shutdown at which time the apparatus temperature is changing. After every shutdown it is necessary therefore to the check the apparatus for leakage, first using an inert gas.

/f/ It is recommended that the apparatus be checked once a day or even once every shift for leakage using a detector of inflammables. Early detection of small leakage forestalls serious emergencies. The detectors may also be permanently installed in particularly dangerous locations, with limit overstep signaling.

/g/ It is recommended that the high-pressure hydrogenation apparatus be equipped with so-called <u>emergency drainage</u>. In the case of danger, e.g., of a substantial leakage of the reactor, the valve for rapid de-pressurizing of the reactor can be activated by depressing a single pushbutton, and other valves such as those for cooling, inert gas, etc. will open simultaneously.

9.6. Sources of hydrogen

Hydrogen is usually available at large chemical plants since it is used in the synthesis of ammonia, methanol, in hydrorefining of oil fraction, etc. For these purposes the hydrogen is produced as a rule by the so-called steam reforming of hydrocarbons, mainly of natural gas. This method of production yields hydrogen at 2-3 MPa pressure, which is sufficient for many hydroganations.

As for the contents of catalytic poisons the petrochemical hydrogen is of sufficient purity, the hydrogen sulfide content usually is lower than 0.1 ppm. Inert gases may however be present, mainly methane and nitrogen, to concentrations of 1-30 vol.%. Such diluted hydrogen is poorly suited for hydrogenations. In the batch autoclave the inert gas would accumulate above the level of liquid, which may even bring about a complete stop of the hydrogenation process. In continuous apparatus a certain quantity of gases must be discharged during the process to maintain an admissible level of the inerts but, in every case, the hydrogenation proceeds at a lower concentration of hydrogen then is that of the incoming hydrogen. With a view to the 1st order of hydrogenation to hydrogen, this cuts down on the reactor output and the gas being discharged represents hydrogen losses.

A recent technique used to remove the inerts from hydrogen is the molecular sieves /the so-called PSA process, delivered e.g. by Linde AG./, or the inerts are separated using polymere membranes /the PRISM process, Monsanto/.

In certain plants the hydrogen is produced as a side product from sodium chloride electrolysis. In the case of amalgam electrolysis the hydrogen is contaminated with mercury which is a catalytic poison. Apparatus for hydrogen cleaning by adsorption on treated active charcoal is usually supplied as part of the delivery of the electrolysis facility.

In some plants there is no hydrogen available and thus, the introduction of hydrogenation is contingent on the provision of hydrogen. Not counting the capital-intensive steam cracking of natural gas, moderate quantities of hydrogen can be secured in two ways:

/a/ By transporting hydrogen in pressure cylinders on truck trailers. One trailer can be loaded with about 1000 Nm^3 of hydrogen and in this way, daily consumption rates lower than 3000 Nm^3 can be saturated. It is obvious that effectivity will depend on how far the hydrogen would have to be hauled. Hydrogen thus provided is up to one order of magnitude more expensive than that available from the distribution networks of a petrochemical plant.

/b/ By water electrolysis which may cover hourly consumption rates of up to 500 Nm^3 hydrogen. Pressure electrolyzers can even be ordered which produce hydrogen at about 3 MPa pressure /the processes Lurgi, Lonza/. Electrolytic hydrogen is 3-4 times more expensive than petrochemical hydrogen, and 4 kWh/Nm^3 is the power input for the electrolysis.

10. Conclusions

Reduction agents such as iron, sodium, zinc, sulfides, etc., commonly used for the reduction of organic substances, are being replaced to a growing extent by catalytic hydrogenation. For instance, as far back as 30 to 40 years ago the use of sodium in the reduction of higher fatty acids to alcohols has been supplanted by catalytic hydrogenation, and iron came to be replaced by hydrogen during the last two decades in the production of aniline from nitrobenzene. The major reason of this trend is the oxidation products of the reduction agents, which as a rule are wastes difficult to handle and hardly of any use. To illustrate this on the production of aniline, some 4-5 tons of wet iron oxide sludges which, moreover, omitting aniline to the atmosphere by evaporation, are turned out per 1 ton of the product.

In the past, the substitutions of such reduction agents by hydrogen were regarded economical solely in the case of large production capacities but, as catalysis and the hydrogenation technology have become more advanced, they find application even in relatively low production volumes, such as in the preparation of dozens of dyestuff intermediates.

A survey has been given of the reduction reactions, indicating how the replacement by catalytic hydrogenation is done, i.e., specifying catalyst selection and the reaction conditions. Inasmuch as the precious metals palladium and platinum are used rather frequently as catalysts, the study has also addressed their recent pricing trends and the cost evaluation methods to be adopted when these catalysts are applied.

Production equipment descriptions as well as the discussions concerning hydrogenation type selection are largely based on the authors' practical experience with developing and commercializing numerous hydrogenations. It is not always at chemical plants that hydrogen is readily available, and this is why a chapter has also been devoted to the sources of hydrogen. Attention has also been paid to presenting the principles of safety at work which apply to the hydrogenation facilities where hydrogen is nearly always handled at elevated temperature and pressure.

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III. CONCLUSIONS

The present report comprises a General Part dealing with the principles of non-waste technologies and a Specific Part devoted to four selected technologies of the chemical industry to which are related the conclusions outlined below.

The contents of sulfur in the crude oils
as well as in the types of coal being used
are incessantly growing and, in parallel, there is an intensification of the necessity of removing it either from the offgases and exhausts after combustion or, alternatively, prior to combustion while using the raw materials for power engineering, transportation, and chemical purposes.

Intensive developments have been underway since recently in the deep processing of crude oil where mainly the high-boiling distillates and, above all, the residual oils are used to produce high-grade fuels and petrochemical feedstocks. Substantial progress has been achieved in the modern production of low-sulfur fuel oils, in the innovation of coal liquefaction, and chemical processing of carbochemical products.

Conversion of the high-boiling and residual hydrocarbon feedstocks is effected by modern, highly effective catalytic and thermo-catalytic hydrogenation processes whereby the undesirable components (sulfur, nitrogen, oxygen, metals) are eliminated from the feedstocks and quality fuel oils are produced, together with starting materials which lend themselves much more easily to further catalytic or thermic processing, such as the feedstocks for pyrolysis, fluid catalytic cracking, production of lubrication oils, etc.

Worth mentioning in the first place from among the new processes used for such purposes are: catalytic desulfurization and hydrocracking of oil residues and carbochemical raw materials, mild hydrocracking, and hydrovisbreaking. These processes are highly effective technically, are economical because of lower energy consumption, and meet the ecological requirements relating to the low-waste technologies.

An important complement to the modern hydrorefining and hydrocracking processes is the non-traditional use of the liberated hydrogen sulfide or of elemental sulfur produced from this hydrogen sulfide. The production of sulfur asphalts and concretes, of special sulfur-containing composites, and of organic thiochemicals represents a substantial economic and ecological contribution to traditional refinery and petrochemical production.

Sulfuric acid ranks among the most widely used products of the chemical industry. As to the extent of production, it ranks first in the world out of all individually produced chemical compounds. Thanks to this it is of paramount importance to the development of individual national economies and to the development of the chemical industry. Inasmuch as the greatest share of sulfuric acid produced is destined for consumption in the production of fertilizers, it is clear that the development of sulfuric acid production has an impact on the solution of the problem of food in the advancing countries.

The analysis made and the report present make it clear that the selection of specific production technology, the design and interconnection of apparatus, the selection of raw materials, and the links to subsequent chemical productions amount to a rather complicated question which must be solved with respect to the prevailing local conditions.

The fundamental question - i.e., the question of minimizing sulfur dioxide pollution - is solved at the present time by using a double conversion technology which can warrant a degree of SO_2 to SO_3 conversion higher than 99.5%. This very high efficiency, unparalleled in the case of other chemical productions, also relates to the selection of proper catalysts and to an optimization of its operating conditions in a commercial reactor.

From the ecological viewpoint, another problem being faced is that of disposing of and using the waste solutions of contaminated sulfuric acid. This problem is successfully solved in conjunction with the use of high-sulfur residual fuel oil. Contaminated H_2SO_4 solutions at concentrations higher than 50% and even sulfate solutions can be used for thermic decomposition in furnaces fired with this kind of fuel oil.

From the economic viewpoint, a question which is essential for the sulfuric acid production plant is the utilization of waste heat for rising steam.

On the basis of recommendations given in Part B, an effective production of sulfuric acid can be designed so as to suit the particular requirements of the country in question while guaranteeing living environment protection from damage.

Nitric acid ranks also among basic inorganic chemicals important for chemical industries, espesially for the production of fertilizers.

As has been shown the medium pressure process /0,4-0,6 MPa/ appears to be the most advantageous for capacities up to 500 mtpd HNO_3. The NO_x concentration in the tail gas is, however, high /about 600 ppm/ and selective reduction must be applied.

For capacities over 500 mtpd the dual process is the most economical and shows also low level of NO_x in tail gas. Combustion is at medium pressure, while absorption at high pressure /0,5-1,4 MPa/. The concentrations of NO_x in the tail gas are lower than 200 ppm, normally 125-150 ppm.

It has been documented by full-scale data on operation from 18 plants in Czechoslovakia that application of low-waste technology principles can guarantee emissions lower than 2 kgs NO_2/t HNO_3. Present average figure is 2,84 kg NO_2/t HNO_3 and the best plant produces as little as 0,35 kg NO_2/t HNO_3. Further improvement of the average figure is expected in near future. Appropriate ways and means are reccommended in the report.

Attention was paid also to operational and environmental safety of the process, especially to construction materials resistant to corrosion. Recent development in energy conservation and waste energy utilization was also assessed.

The chemical methods of reduction of organic compounds entail the necessity of disposing of the products of the reduction agents. As a rule their use is very problematic and, mostly, such products represent detrimental wastes exerting a negative effect on the environment. From this standpoint, then, the replacement of the reduction agents by hydrogen, which acts as a reducing species in the presence of hydrogenation catalysts, is very much welcome.

The present study surveys the chemical reductions of organic compounds, presenting a classification by type of group to be reduced and indicating the appropriate method to be used in the substitution by catalytic hydrogenation. The next part is devoted to catalysts - their specific properties, most frequent applications, and regeneration. The front-ranking producers are listed and the trends are shown which can be discerned in the development of prices of the precious and rare metals that have been considered in recent years for the preparation of catalysts. Attention is paid to equipment for catalytic hydrogenations - the reactor types for gas as well as liquid phase hydrogenation, the methods of heating and cooling, and the questions of catalyst metering and separation involving a number of practical aspects are analyzed.

The concluding part presents the guidelines for safety at work with hydrogenation and sources of hydrogen.

APPENDIX

1. Criteria for evaluation of low-waste and non-waste technologies

As already mentioned, assessment of the various effluents emitted is problematic. Solutions proposed for input/output analysis, however, are normally based on linear production relationships. Corresponding models permit not only economic but also ecological parameters such as pollution emission, as well as raw material and energy consumption to be taken into account.

Within the scope of such model calculation can be determined the share of pollution accounted for by final products and by intermediate products.

The most important steps of the method applied are the selection of criteria to be taken into account in the evaluation. It is possible to rank the criteria into four groups:

- the criteria of environment protection
- the economic characteristics
- the technological characteristics
- the social criteria.

1.1. The criteria of environment protection

The environmental criteria group selected for the evaluation of the various technologies contains three major sub-groups:

- Criteria based on material and energy balances
- Criteria relating to environmental standards
- Economic criteria.

The criteria belonging to this group indicate the qualitative relationships of air, water, thermal pollution, and waste production.

1.1.1. Criteria based on material and energy balances

Specific polluted end gas and waste water per unit production. This relative indicator allows for an analytical comparison of similar operations and technologies in the stage of both design and execution. All the criteria to be shown here are denoted by the letter C and a subscript.

C1 = end gases /final product
C2 = waste water/final product

Specific fresh air and clean water consumption relating to unit of final product

The lower the figures, the more favorable the technology.
C3 = air requirement / final product
C4 = water requirement / final product

Ratio of the amount of purified end gases and waste water to the total amount of end gases and waste water.

These criteria are of major environmental importance but they also characterize the technical level of the technology.

C5 = purified end gases /total end gases

C6 = purified waste water /total waste water

Production criteria

These indicators express the amount of final product that could be produced /theoretically/ from the material lost in waste water and end gases. The lower their value, the more favorable the technology. The equivalent amount of the final product can be calculated from the material balance.

C7 = equivalent final product / final product

Waste produced per unit of final product

This gives the absolute amount of waste relating to unit of final products. The lower its value, the more advantageous the technology. Its value can be determined by measurement or it can be calculated.

C8 = waste / final product

Waste produced per unit of raw meterial

The lower its value, the more favorable the technology. The value can be both measured and calculated.

C9 = waste / raw material

Ratio of utilized and total amount of waste

This figure indicates how much of the waste produced by a technology can be utilized either within or outside the production facility. Its value can be either measured or calculated. The closer its value to unity, the more favorable the technology.

C10 = utilized waste / total waste

Heat loss or heat pollution criteria

These indicators are of major importance when low-heat consumption technologies are evaluated. Their values can be measured or calculated.

C11 = actual heat consumption / final product

C12 = theoretical heat consumption / actual heat consumption

C13 = exergy of total products / exergy of feed materials

General environmental noise level

Criterion for environmentally harmfull components can be written as additivity by weight coefficients.

1.1.2. Criteria related to environmental standards

Ratio of discharged and permitted pollutent concentration in air and waste water

These indicators can be either determined by analytical methods or calculated from material balances. The permitted values change from one country to another.

C14 = discharge concn. in end gases / permitted concn.

C15 = discharge concn. in waste water / permitted concn.

The ratio of pollutent emission and permitted discharge levels

C16 = emitted pollutants in end gases / permitted emission

C17 = emitted pollutants in waste water / permitted emission

Toxicity indicator

C18 = toxic material / final product

Note: exergy = maximum possible use of work

Epidemiological indicators, environmental effects, corrosion/erosion indicators etc. should be evaluated by specialists.

1.1.3. Economic criteria

Capital investment criterion

This indicator shows the ratio of capital investment in environment protection to total capital investment.

C19 = capital investment in environment protection
/ total c.i.

Operation criterion

C20 = operating costs of environment protection
/ operating costs

Waste processing criterion

This is an indicator which is to take account of the costs of waste abatement and control, plus the costs of waste transportation and dumping, and also of the profits that can be derived from waste utilization.

1.2. The economic characteristics

Methods which use economic categories for the description of technological systems allow for more reliable characterization of technologies and selection between variants of given technology.

The economic criteria can be classified into three groups:

/a/ Investment characteristics of a technology
/b/ operational characteristics of a technology

/c/ economic consequences of the environmental effects caused by the implementation and operation of a technology.

For the purpose of evaluation of the essential quantitative characteristics of the technology, its production capacity is needed.

The criteria used for economic evaluation of various technologies may differ from country to country and most of them are commonly used in assessments of the feasibility of projects.

1.3. Other technological considerations

The aim of the technological evaluation is to examine the technological system and to evaluate the technical level of the system. It is worth considering the following aspects of the problem:

- which system elements, process parameters, and interface conditions are most conducive to producing wastes and energy losses;
- which of the waste streams can be re-used.

Evaluation of a system should incorporate the following information:

/a/ Sophistication of the technology /number of process stages; the yield of wastes at each stage and their toxicity; provision of waste processing within the enterprise; necessity of creating an individual enterprise for waste processing; necessity of waste transportation; necessity of using special materials, equipment, and instruments; employment of new methods for the analysis of raw materials, products, and wastes; complexity of starting and setting-up a non-wast process/.

/b/ Analysis of inputs /amount and purity of raw materials used, amount and purity of auxiliary materials used, energy required/.

/c/ Analysis of the operating characteristics /capacity of plant with respect to most advanced technologies, degrees of freedom under control, use of computers/.

/d/ Analysis of environmental outputs /air pollution; water pollution; thermal pollution/.

Process development may involve experimenting, theoretical analyses, mathematical modeling, and optimization from the point of view of environment protection.

1.4. Social considerations relating to non-waste technologies

The social criteria include:

- Effects of technology on man, the working conditions /climatic factors, noise, maximum physical labor, monotonousness of work, health hazards/.
- Effects of technology on the social climate /work force and its composition, educational and cultural changes/.
- Evaluation of technology from the aspects of public relations /public opinion about the desirability of the technology/.

2. Plan of action for minimizing waste of energy and raw materials for selected chemical processes

The initial step is the selection of a system for study. Then it is necessary to define the system boundaries.

The next step is to have a complete picture of material flows in the system, a material balance.

Third, the energy requirement of each process is assessed, as are the shares of output energy that can be utilized.

The fourth step includes calculation of the criteria. Mathematical modeling of the process may be employed.

The fifth step is to appropriately select the technology and apparatus.

The sixth step is to optimize new low-waste and non-waste process variants and to recalculate the criteria.