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MINOX

A CATALYTIC DEOXYGENATION PROCESS FOR
IRRADIATED ORGANIC REACTOR COOLANTS

by

R. LOPES CARDOZO, H. NORDMEYER,
H. LANGENKAMP and C. CERUTTI

1971



Joint Nuclear Research Centre
Ispra Establishment — Italy

Chemistry Department
Organic Chemistry Service

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ABSTRACT

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OXYGEN
QUANTITY RATIO
REDUCTION
CATALYSIS
FOULING
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RADIATION CHEMISTRY

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for the ESSOR reactor at the J.N.R.C.,
Ispra

MINOX, a Catalytic Deoxygenation Process

for Irradiated Organic Reactor Coolants *)

1. Introduction

The realization of the organic cooled reactor concept is, besides other factors, especially depending on a successful handling of the fouling phenomenon. Investigations of the origin of this phenomenon come to the conclusion that among those fouling constituents and promoters which are present as dissolved molecules in the coolant, the oxygen-containing organic compounds seem to contribute preferably to the fouling capacity (1-5).

Oxygen-containing compounds are already present in the virgin coolant. Geiss, Klose et al. (6) separated such compounds as benzantrone and fluorenone from virgin OM-2 coolant in amounts of 10-20 ppm per compound. In general, the virgin coolant contains 200-300 ppm of organically bound oxygen, so that many other compounds are present.

The concentration of oxygen-containing compounds increases remarkably upon irradiation and pyrolysis when the coolant comes into contact with air or water. During OMRE - CORE II operation values of up to several thousand ppm of organically bound oxygen in the form of phenylic, carbonylic and carboxylic compounds have been detected. The highest values were found after opening of the reactor core, due to oxidation of the free radicals present (7). At the same time, fouling tests showed an increase of the fouling rate. On the other hand, fouling was reduced in the presence of hydrogen used as cover gas (8,9).

*) Manuscript received on 16 December 1971

It is not possible to exclude all oxygen contacts of the circulating coolant in practice (e.g. in-leakage of water from the secondary circuit) and, therefore, it should be tried to remove continuously all the oxygen-containing compounds which promote fouling.

A certain amount of oxygen, which is bound to highly polymerised or condensed organic molecules will be removed together with the heavy high boiling fractions of the coolant during distillation or extraction processes. But this is by far not enough and does not prevent fouling inside of the coolant circuit. Attapulugus clay adsorbent treatment - as proved in our laboratories (10,11) - is not specific and accompanied by isomerization and cracking reactions which cause undesirable changes in the coolant composition.

In oil industry, hydrosulphuration is a standard operation. For such processes, e.g. the Shell "Trickle" process (12), CoO.MoO_3 -catalysts at 300-400°C and hydrogen pressures up to 100 atm. are used, whereby 90% or more desulphuration is obtained. Also nitrogen- and oxygen-containing compounds are removed to an appreciable extent (13). It seemed thus promising to investigate the merits of a comparable process for the deoxygenation of organic reactor coolants. Besides, also dechlorination and desulphuration effects could be expected. The aim of the present study was to find suitable catalysts and conditions for such a hydrotreatment process - called "MINOX" - resulting in a maximum, selective deoxygenation without changing the coolant composition.

2. EXPERIMENTAL

2.1. Oxygen model compounds

The investigations commenced with the study of the diphenylmethane formation from pure benzophenone in function of temperature, contact time, hydrogen pressure and catalyst employed. The reaction



has been selected as model reaction, because it is easy to control by gaschromatographic analyses, even in coolant mixtures.

In order to obtain a clear picture of the feasibility of the MINOX process for the deoxygenation of the many classes of oxygen-containing organic compounds that may be encountered in practice, not only benzophenone but various other model substances were selected for study. Especially the following compounds have been used in pure state or in mixtures with OM-2 coolant:

- o- and p-hydroxydiphenyl,
- 2,5 - diphenyl - 1,4 - benzoquinone,
- anthraquinone,
- 9 - anthracenecarboxaldehyde,
- benzanthrone (1,9 - benzanthr - 10 - one),
- diphenylene oxide.

2.2. Coolants applied

In the organic cooled O.M.R.E. - and ORGEL - type reactors polyphenylic mixtures are used as coolants. The actual reference coolant for the elaboration of the MINOX process was the OM-2/PROGIL mixture, consisting of o-, m- and p-terphenyl. The process has then been proved with two other types of coolants: the OM-D/PROGIL, which is an eutectic mixture of o- and m-terphenyl and diphenyl, and with HB - 40 / MONSANTO, which is identical with SANTOWAX-R hydrogenated to 40%. Composition and analyses of the virgin coolants and some of their physical properties are enlisted in table 1.

The experiments with spent coolant mixtures have been executed with OM-2/PROGIL irradiated at 320, 380 and 420°C during the BLO - 3 operations in the MELUSINE reactor at the C.E.N. Grenoble.

2.3. Catalyst screening

For the hydrodeoxygenation of the coolant a long-life catalyst combining a highly specific efficiency for oxygen removal with a low cracking activity is desirable. The coke production rate on the catalyst surface must be kept at a minimum. For this purpose, acid-free supports should be chosen. The catalyst should possess a good mechanical, chemical and thermal stability in order to allow column operation and repeated activation and re-generation procedures!

The catalysts which have been successfully used in the screening program are enlisted in table 2. Co, Ni, Mo, Pt and Pd are the active elements on γ - Al_2O_3 - supports, used as pellets, spheres and in extruded form of different size. The chemical composition of some of the catalysts is given in table 3. The effects of a H_2S - pretreatment for CoMo - and NiMo - catalysts have been investigated in several runs.

2.4. Equipment

Preliminary catalyst screening tests have been executed at 1 atm. hydrogen pressure in a glass equipment with 5 or 50 g samples of pure oxygen-containing organic compounds with up to 20%w catalyst. The main parameters studied were reaction time and temperature.

At higher hydrogen pressures, a one liter autoclave equipped with an electromagnetic agitator was used for heating batches of 0,5 l each. Comparable standard conditions have been: 40 atm. H₂-pressure, 300°C reaction temperature and 4 hours contact time.

Column experiments were at first carried out in a lab - scale pressurized loop (loop "Gastone", see figure 1) of stainless steel (V₄A) at temperatures of up to 350°C and H₂-pressures up to 15 atm. Column dimensions: d=40 mm, l=530 mm. The column has been operated in downflow. Charge rates up to 5 l/hr have been processed.

The final installation of an ameliorated semi-technical pressurized loop (loop "63", see figure 2) with better heating rate controls and thermoisolations and easily exchangeable columns allowed the extension of the hydrotreatment experiments at higher gas flows to a H₂-pressure of 30 atm. and 400°C temperature, reaching finally hydrocracking conditions. The column (d = 40 mm, l = 1000 mm) has been operated in downflow direction, introducing the hydrogen directly at the upper column entrance.

All samples destined for oxygen, chlorine and sulphur analyses have been degasified by passing through of nitrogen gas for at least 1 hour at 120°C. The nitrogen was previously purified from traces of oxygen with a hydrogen activated copper catalyst and dried with molecular sieve material.

2.5. Analytical methods

Qualitative and quantitative gaschromatographic analyses^{x)} have been used as analytical tool for the detection of changes in the coolant composition and in the composition of the organic model compounds. The oxygen and chlorine contents could be analyzed by neutron activation analyses^{y)}, the sulphur contents by X-ray fluorescence spectrography^{z)}. The high polymere contents in the coolants and the coke production rates on the catalyst surface have been estimated by special fractional thermogravimetric analyses (14). Thermogravimetric analyses served also for estimations of the water contents and determination of the optimum activation temperatures for the catalysts. Specific surface, pore volume, average pore size and pore size distribution measurements of the catalysts before and after treatment have been executed by the B.E.T. gasadsorption method (SORPTOMATIC instrument/C.ERBA).

x) executed by Mr.F.Geiss, y) Mr.F.Girardi and z) Mr.G.Vos
and co-workers

3. RESULTS

3.1. Deoxygenation

The results of the preliminary batch and autoclave experiments concerning the formation of diphenylmethane from pure benzophenone are expressed in figures 3,4 and 5.

At 1 atm. hydrogen pressure (fig.3) conversion is very low. Even after contact times of up to 24 hours, only the sulphur activated CoMo-catalyst reaches more than 15%, while the same not activated catalyst shows no reaction. Augmentation of the hydrogen pressure soon leads to higher conversion rates, as can be seen in figure 4. At 30 atm. pressure the diphenylmethane formation is about 30% and it follows from extrapolation that the desired high conversions can be expected at 40-50 atm.. This has been proved by later autoclave experiments with coolant mixtures, where 40 atm. have then been chosen as standard pressure.

The temperature dependency of the benzophenone - diphenylmethane reaction is given in figure 5 for two catalysts. The reaction temperature for most of the autoclave experiments has been fixed on 300°C in order to avoid pyrolysis effects at 4 hours standtime. For the column operations where contact times are several minutes only, temperatures up to 400°C could be employed without causing pyrolysis effects.

After having reached optimum conditions for the benzophenone - diphenylmethane conversion, the deoxygenation of other oxygen-containing organic compounds has been tried under the same conditions. Table 4 gives the results of some of the autoclave experiments where pure oxygen model compounds have been added to virgin OM-2 coolant. All added compounds of the phenylic, carbonylic and carboxylic types have been successfully deoxygenated with the exception of benzanthrone. Deoxygenation of this highly condensed compound was incomplete, whereas diphenylene oxide, a member of the heterocyclic group of compounds in which oxygen is bound to a more stable ring position, has been found quite refractory to the hydrotreatment. Column runs showed the same results (e.g. experiments G-25 and G-26 in table 5). The deoxygenation of the oxygen model compounds has been controlled by gaschromatographic analyses. The gaschromatograms of figures 6 and 7 show the complete disappearance or conversion of the added compounds.

The efficiency of the deoxygenation experiments has been calculated as the quantity of oxygen converted (to H₂O) during the run, expressed in percent of the initial oxygen content of the sample.

$$E = \frac{(a - b) \cdot 100}{a} , \quad \text{where } E = \text{efficiency (in\%)} ,$$

a = initial	}	oxygen content (in ppm)
b = final		

This is valid for the batch and autoclave experiments. For the column treatments the deoxygenation efficiency has been calculated as an overall efficiency, where the final oxygen content (b) is representing an average value of all half-hour samples (c) taken during the (eight hours) run. In this case

$$b_{\text{ool}} = \frac{\sum c}{n}, \quad \text{where } n = \text{number of samples taken during the run}$$

The conditions and results of the deoxygenation experiments executed in the lab-scale loop "Gastone" and in the semi-technical loop "63" are summarized in tables 5 and 6. Maximum deoxygenation has been obtained in the loop "63" with up to 98% efficiency for OM-2 coolant with 10,000 ppm initial oxygen content, benzophenone as model compound and CoMo-catalyst. Under comparable conditions there is no significant difference between OM-2, OM-D, HB-40 and even OM-2 spent coolant mixtures containing up to 8% high polymers, efficiencies being in the range of 95-98%.

The residual oxygen content, which was about 200 ppm in the most successful experiments, is due to a not removable part of oxygen-containing compounds originally present in the virgin coolant. OM-2 coolant as furnished contains up to 300 ppm organically bound oxygen, about 200 ppm of which could not be removed by the mild hydrotreatment conditions applied (see experiment G-9 in table 5 and table 7). This residual oxygen seems bound not to radicals but to stable ring positions or to sites within condensed high polymers not accessible to the treatment. Its removal should be possible under more severe hydrocracking conditions. Hydrocracking, however, - besides raising the price of the process owing to its higher temperatures, hydrogen pressures and hydrogen consumption - causes undesired changes in the coolant composition and augments the coke formation rates to an extent which shortens the catalyst lifetime. Oxygen bound to condensed high polymers could be removed continuously together with these compounds by extraction or distillation processes which are proposed to keep the high polymer content in the coolant on the desired low level.

3.2. Dechlorination

Chlorine is contained only in small amounts of 1-5 ppm in terphenyl coolants (see table 1). It nevertheless contributes to the fouling formation (15,16) and is a very strong corrosion promoter for all metals forming reactor tube walls and claddings, especially for zirconium alloys (17). If zirconium alloys are used, a chlorine content of $< 0,2$ ppm in the coolant is recommended (18). Therefore, only highly dechlorinated terphenyl should be introduced in the reactor circuits. Besides, the installation of a continuously working dechlorination method, to be used for make-up coolant pretreatment as well as for in-loop clean-up seems to be indispensable. It has been tried to make the MINOX process available for this task, in order to combine deoxygenation and dechlorination in one operation.

The possibilities of dechlorination have been investigated during the deoxygenation column experiments with loop "Gastone" and loop "63". In most cases 10-20 ppm of organically bound chlorine have been added to the initial coolant sample, using 1 - Cl - anthraquinone as model compound. The results are enlisted in tables 5 and 6. The dechlorination efficiency has been calculated in the same way as described for deoxygenation in chapter 3.1.. The MINOX process has been found very effective for dechlorination. Optimum results have been obtained with loop "63", with efficiencies at about 99% for all coolants and spent coolant mixtures, residual chlorine contents ranging from 0,07-0,2 ppm.

3.3. Desulphuration

The sulphur content of virgin terphenyl coolants - undesired because of its contribution to corrosion and fouling (19) - has been detected in varying amounts from < 2-160 ppm. The effects of desulphuration obtained simultaneously with the oxygen removal in the MINOX process have been investigated in some autoclave and loop "Gastone" operations using OM-2/PROGIL coolant with initial sulphur contents of 50-200 ppm, in the presence of oxygen model compounds. The results are given in table 8 for the autoclave and in table 5 for the loop experiments.

In general, desulphuration combined with the MINOX conditions has been found incomplete, although in several cases desulphuration efficiencies have been obtained (calculated as described in chapter 3.1.) of up to 75% in the column operations and 85% in the autoclave. A residual sulphur content of > 20 ppm has been detected in the coolant even after the most efficient treatments. A large part of the sulphur compounds present are refractory to the hydrotreatment (probably compounds of the thiophene type ...). The maximum sulphur concentration accepted in Orgel type circuits is about 10 ppm (19). It is, therefore, recommended to provide only terphenyls with extremely low sulphur contents in order to avoid the installation of specific desulphuration devices.

4. PROCESS CONDITIONS

The MINOX process is envisaged as a continuously operated liquid-phase catalytic column hydrotreatment in a reactor coolant purification circuit. Its main parameters are: reaction temperature, hydrogen pressure, hydrogen consumption, charge rate and type of catalyst employed. The optimum process conditions have been evaluated within certain limits from the experimental data obtained with loop "Castone" and loop "63". Figures 8-23 demonstrate how the variation of each parameter influences the deoxygenation, the dechlorination and the desulphuration efficiencies of the run.

4.1. Reaction temperature

The reaction temperature (figures 8-10) is near to the ORGEL circuit operation temperature and has been varied from 300-400°C. A raise of the average run temperature from 300 to 350°C caused a remarkable increase of the overall efficiencies, while further augmentations up to 400°C did not have such a significant effect. The optimum run temperature has been found around 350°C, especially for executions with loop "63".

4.2. Hydrogen pressure

The hydrogen pressure has been varied from 10-15 atm. in loop "Gastone" and from 15-30 atm. in loop "63" experiments. Deoxygenation shows a strong pressure dependency (see figure 11). Nevertheless, at 15 atm. the efficiency already reaches 90-95% and the further gain at 30 atm. is only 1-2% more, so that 15 atm. have been considered sufficient in practice. Dechlorination is not dependent from H₂-pressure, at least in the considered range from 10-30 atm., as is obvious from figure 12. Only few values have been available for desulphuration (figure 13), demonstrating however a strong pressure dependence and confirming that more than 15 atm. are necessary for a successful sulphur removal.

4.3. Hydrogen consumption

For the technical application of the MINOX process the knowledge of the hydrogen consumption is very important. Because of the high costs for hydrogen gas, it could be a limiting parameter and it should be tried to find out the minimum possible rather than the optimum consumption.

The hydrogen flow rate has been varied from 2,0-0,1 mol H₂/mol feed. Figures 14-16 show that there is a noteworthy dependency on the hydrogen flow in all runs executed in loop "Gastone", whereas the loop "63" experiments have been successful also at the minimum flow rate of 0,1 mol H₂/mol feed. This is valid for oxygen and chlorine removal. Desulphuration has been tried in

the lab-scale loop "Gastone" exclusively, however with the same tendency. The difference of the results obtained with the two loops is due to a better hydrogen gas distribution within the bigger column and larger tubings of loop "63". The columns have been operated in downflow direction, the hydrogen gas being introduced directly at the upper column entrance. The use of a minimum hydrogen flow - e.g. 0,1 mol H₂/mol feed - will be applicable in practice if a thorough distribution of the gas in the column guarantees intensive contacts with the catalyst surface.

4.4. Charge rate

Figures 17-19 demonstrate the dependency on the charge rate, calculated as LHSV (= liquid-hourly-space-velocity). For oxygen and chlorine removal LHSV = 4,5 - corresponding to contact times of about 2-3 minutes - could be considered as an optimum if catalyst NC-4a is used and especially for treatments at 350°C and 15 atm. H₂-pressure. At higher temperatures and pressures, eg. 400°C / 30 atm., also LHSV = 8 would be acceptable. This is also confirmed by figure 17 b, which shows the oxygen uptake in g O₂/g catalyst/hour depending on the charge rate. The experiments cited have been run with about 10.000 ppm oxygen contained in the coolant. Desulphuration, however, needs much longer contact times (LHSV ≪ 4,5).

The column stand-time was good. There was no drop of efficiencies at the end of the successful eight hour runs and only about 10% diminution estimated during an one week experiment at LHSV = 4,5, using Grenoble spent coolant containing 10% high polymers.

4.5. Catalysts

Among the eight preselected catalysts enlisted in table 2, the most effective had to be chosen according to the results of autoclave and loop experiments. It has been stated that for deoxygenation in the autoclave at 4 hours contact time the precious metal catalysts (Pd,Pt) gave the best results, while in column operations, where contact times are reduced to several minutes, the CoMo- and NiMo-catalysts have been much more effective. The CoMo-catalysts have proved to be the best also for desulphuration in autoclave and column and for dechlorination. This is confirmed by the results in tables 5,6 and 8 and by the figures 20-22, where the deoxygenation, dechlorination and desulphuration efficiencies obtained with different catalysts are posed against the time of each run. The influence of the specific catalyst surface on the deoxygenation efficiency is demonstrated in figure 23, showing maximum efficiencies with surface areas over $180 \text{ m}^2/\text{g}$. The most efficient CoMo-catalyst has a specific surface area of $250 \text{ m}^2/\text{g}$.

Activation of the CoMo- and NiMo-catalysts by a $\text{H}_2 \text{ S}$ - pretreatment supports the starting activity but makes no difference in the overall results in comparison with not pretreated catalysts. On the contrary, it has been found that the sulphur from the pretreatment covered about 20% of the specific surface, reducing the pore volume and blocking preferably the micro-pores. Therefore, the only recommended pretreatment is preheating the catalyst for one hour at a temperature corresponding to the operation temperature, directly before filling in the column or preferably in situ.

5. CATALYST SURFACE REACTIONS

5.1. Hydrogenation

The coolant composition has been controlled before and after each experiment by gaschromatographic analyses in order to detect isomerization, polymerization and hydrogenation effects caused by the catalytic contacts. In general, no remarkable changes of the OM-2 coolant composition have been observed, except for slight hydrogenations. 1-3% of (partially) hydrogenated terphenyls have been formed during some of the autoclave runs under the standard conditions employed (see figure 6). During the column performances traces of hydrogenated terphenyls appeared only in the loop "63" experiments. The hydrogenation rates augmented up to 0,5-1,0% after applying H₂-pressures over 15 atm. or very low charge rates (LHSV = 1) or when using precious metal catalysts (Pt,Pd). All coolants - OM-2, OM-D and HB-40-demonstrated the same behaviour, although it was difficult to distinguish in HB-40 the slight hydrogenation effects caused by the treatment.

5.2. Cracking and coke formation

Cracking of high polymers (HB) occurred when spent coolant mixtures were used. In the 8 hr. loop experiments with 6-8% initial HB - content under MLNOX standard conditions, average cracking rates in the coolant of 50-80 mg HB/g cat./hr. have been calculated.

The organic residues deposited on the catalyst surface during the runs have been estimated quantitatively by fractional thermogravimetric analyses (see chapter 2.5.). These deposits are composed mainly of adsorbed high polymers (HB) and carbonaceous cracking residues (coke). In the course of the 8 hr. experiments with pure OM-2 coolant, the adsorption rate was 5-8 mg HB/g cat./hr. corresponding to 0,02-0,03 mg HB/m² specific surface/hr.. No coke has been formed, whereas in the experiments with spent coolant mixtures containing initially 6-8% HB, the total deposition rate was up to 20 mg/g cat./hr. (= 0,08 mg/m² spec.surf./hr.), including 3 mg/g cat./hr. of coke.

The dependence of the total deposition rates on the initial HB-content in the coolant, the charge rate and the average run temperature is given in figures 24-26. The HB adsorption and coke formation on the catalyst surface augment considerably with increasing initial HB-content and run temperature and with decreasing charge rates.

5.3. Thermal regeneration

As the MINOX treatment of spent coolants is accompanied by HB adsorption and coke forming processes on the catalyst surface, an easily and quickly practicable regeneration method is wanted in order to maintain the full catalyst activity over a long time period. The catalyst regeneration possibilities have been studied and it has been found that the in situ thermal regeneration gave the best results in any respect. Three examples of thermal regeneration of catalysts used in the MINOX experiments are given underneath.

a) During a 44 hours spent coolant treatment under MINOX standard conditions (15 atm. $H_2/300^\circ C/LHSV=4,5/0,4$ mol H_2/mol charge/CoMo-cat./11% HB initially ...) the total deposition of HB and coke on the catalyst surface was 10%w of the catalyst weight. This deposit occupied 20% of the catalyst specific surface and 10% of its pore volume and caused an efficiency drop of about 10% for deoxygenation and 6% for dechlorination.

Thermogravimetric analyses of the used catalyst showed that - besides terphenyl - there was only HB and no coke deposited on the surface during the run. For regeneration it was, therefore, sufficient to heat the catalyst 1 hr. at $450^\circ C$. The regain of the specific surface in the course of the thermal regeneration can be seen in figure 27, where the results of the specific surface measurements of the used and not used catalysts are confronted in dependence on the treatment temperatures. The values in table 9 also show the regain of the pore volume and the average pore radius, which remains slightly diminished.

b) Figure 28 demonstrates the regeneration of a CoMo-catalyst which had been pretreated with H_2S and used in a spent coolant (8% HB) treatment. The sulphur adsorbed by the pretreatment covered about 20% of the specific surface. Another 20% of the specific surface have been occupied by HB-deposition during the run (corresponding to 11%w of cat.wt.). Complete regeneration was possible at $450^{\circ}C$. Also the sulphur remaining from the pretreatment vaporized from the catalyst surface during the regeneration procedure.

c) If there is also coke besides the HB deposited on the catalyst surface, the regeneration temperature must be raised up to $550-600^{\circ}C$ in order to burn up the carbonaceous residues completely. The reaction can be promoted by airflow through the column, but the temperature should not exceed $650^{\circ}C$ because of beginning lattice shrinkage and irreversible specific surface diminution. Figure 29 shows the regeneration of a coke bearing Pt-catalyst, which had been used in a spent coolant treatment under almost hydrocracking conditions. The total deposition after an 8 hrs. run was 9%w (of cat.wt.) HB and coke, occupying 30% of the specific surface.

6. CONCLUSIONS

a) MINOX, a catalytic deoxygenation process for irradiated organic reactor coolants, is proposed "in-pile" as a continuously operated liquid-phase column hydrotreatment.

b) MINOX standard conditions elaborated are:

hydrogen pressure - 15 atm.

reaction temperature - 350°C

hydrogen consumption - 0,1-0,4 mol H₂/mol feed

charge rate - 4,5 LHSV

catalyst - CoO.MoO₃ on γ -Al₂O₃,

1,5 mm ϕ extrudates, 250 m²/g
spec.surf.

c) The process has been applied with good success to OM-2, OM-D and HB-40 coolants.

d) Deoxygenation efficiencies of 95-98% have been obtained, preferably for oxygen-containing organic compounds of the phenylic, carbonylic and carboxylic types.

e) Besides, the activity of the process for chlorine removal is very effective. Dechlorination was possible as far as 0,07 ppm.

f) Sulphur removal has been found incomplete. Sulphur-free coolants are recommended.

g) Side-reactions of the process as isomerisation, polymerization and hydrogenation were not observed or can be avoided by proper choice of the reaction conditions.

h) Cracking of high polymers occurs to a certain degree when spent coolant mixtures are treated, but this is considered rather an advantage.

i) Activation of the catalyst is recommended by in situ preheating at the operation temperature.

k) Catalyst regeneration is possible by an in situ thermal treatment, at 450°C if only HB is adsorbed, at 500-600°C if coke is deposited on the catalyst surface.

l) Technical application of the MINOX process had been proposed for the ESSOR reactor at the J.N.R.C. Ispra/Italy. Installation scheme and short description are given in the appendix.

7. References

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Acknowledgement

The authors thank Mrs. A.Zovini, Miss E.Barberis and Messrs. A.Dealbertis and G.Ojoli for their collaboration in preparation and execution of this work.

Table 1 - Composition, analyses and some physical properties of OM-2, OM-D and HB-4o coolants

a) <u>Composition (%)</u> :	OM-2	OM-D	HB-4o
ϕ_2	1	23,8	o,0
o - ϕ_3	15	57,8	18,1
m - ϕ_3	8o	18,1	< o,5
p - ϕ_3	4	o,3	< o,5
ϕ_3 - H	-	-	> 81,o

b) <u>Physical properties</u>	OM-2	OM-D	HB-4o
Molecular weight	23o	~ 2oo	235 - 24o
Melting range (°C)	64 - 79	15 - 25	- 25
Normal boiling point (°C)	356	298	34o
Flash point (°C)	147	142	174
Fire point (°C)	166	155	18o
Auto-ignition point (°C)	53o	535	374
Density (g/cm ³)	12o°C = 1,oo	25°C = 1,07	2o°C = 1,0
Viscosity (c P)	12o°C = 3	25°C = 44	25°C = 5o

c) <u>Total contents (ppm) of</u>	OM-2	OM-D ^{x)}	HB-4o
oxygen	2oo - 3oo	~ 8oo	~ 25o
chlorine	1 - 5	~ 1	~ o,3
sulphur	< 3 - 16o	< 2	< 2

x) OM-D from ESSOR MK-5 primary system

Values for a) and b) taken from (2o,21,22)

Table 2 - Catalysts used for the elaboration of the MINOX process.

Reference no. ^{xx)}	Active elements	Support	Activation	Shape	Diameter mm	B.E.T. measurements ^{x)}			Thermogravimetry Total weight loss 20 - 1000 °C
						Specific surface m ² /g	Pore volume cm ³ /g	Medium pore size Å	
NC - 2	Pt	γ -Al ₂ O ₃	-	extruded	1,5	187	0,34	36	16,6 %
NC - 3	Pd	γ -Al ₂ O ₃	-	extruded	1,5	182			15,9
NC - 7	Pd	γ -Al ₂ O ₃	-	pellets	3,0	91			6,7
NC - 14	Pd	γ -Al ₂ O ₃	-	spheres	4 - 6	251	0,34	27	13,1
NC - 15	Pd	α -Al ₂ O ₃	-	spheres	4 - 6	20			0,0
NC - 4a	CoO.MoO ₃	γ -Al ₂ O ₃	-	extruded	1,5	247	0,36	30	13,3
NC - 4b	CoO.MoO ₃	γ -Al ₂ O ₃	H ₂ S	extruded	1,5	199	0,32	44	16,8
NC - 5	CoO.MoO ₃	γ -Al ₂ O ₃	-	extruded	3,0	225	0,39	34	12,4
NC - 8	NiO.MoO ₃	γ -Al ₂ O ₃	-	extruded	3,0	183	0,32	37	13,4

^{x)} samples pretreated 1 hr at 120 °C

^{xx)} manufacturers : KETJEN N.V. (NC-4,5,8), DEGUSSA (NC-2,3,14,15), JOHNSON-MATTHEY (NC-7)

Table 3 - Chemical analyses of some catalysts used for the MINOX process.

(Values in weight percentages)

Element	NC - 2	NC - 3	NC - 4	NC - 5 ^{x)}	NC - 8 ^{x)}
Pt	0,45%	-	-	-	-
Pd	-	0,42	-	-	-
CoO	-	-	3,60	4	-
NiO	-	-	-	-	5
MoO ₃	-	-	12,00	12	12
Fe ₂ O ₃	0,07	0,07	0,08	0,1	0,1
Al ₂ O ₃	87,90	88,40	78,40	80	80
SiO ₂	0,12	0,18	0,66	1,3	1,3

x) average values given by the producer

Table 4 - Deoxygenation of some oxygen-containing model compounds at 300 °C, 40 atm. H₂-p, 10 %w Pd-catalyst(NC-3), 0,5 kg charge and 4 hrs contact time in the autoclave.

Charge	Oxygen added (ppm)	Oxygen content(ppm)		Efficiency (%)
		Before	After	
OM-2 +				
..... a) benzophenone	880	1035 ± 150	220 ± 40	79
..... b) mixture of o- and p-hydroxydiphenyl	1000	1290 ± 150	215 ± 30	83
..... c) 2.5-diphenyl-1.4-benzoquinone	1000	1050 ± 70	250 ± 90	76
..... d) 9-anthracenecarboxaldehyde	780	1010 ± 50	205 ± 20	80
..... e) benzanthrone	1000	1400 ± 100	500 ± 60	64
..... f) diphenylene oxide	800	935 ± 50	845 ± 80	< 10

Table 5 a - Conditions of the experiments executed in the loop "Gastone".

Experiment no.	Coolant	Oxygen model compound	Catalyst no.	H ₂ -pressure (atm.)	LHSV	average temperature (°C)	mol H ₂ /mol feed
G - 9	OM-2	-	NC - 4b	15	4,5	284 ± 5	1,0
G - 1	"	benzophenone	"	15	1,0	346	0,4
G - 12	"	"	"	15	4,5	304	0,4
G - 24	"	"	"	15	4,5	335	0,1
G - 10	"	"	"	15	4,5	299	0,4
G - 11	"	"	"	15	12,0	294	0,4
G - 13	"	"	"	15	8,0	282	0,4
G - 14	"	"	"	15	4,5	287	0,2
G - 15	"	"	"	15	4,5	345	0,4
G - 18	"	"	"	10	4,5	338	0,4
G - 22	"	"	NC - 4a	15	4,5	332	0,4
G - 32	"	"	"	15	4,5	388	0,4
G - 33	"	"	"	15	4,5	338	0,1
G - 35	"	"	"	15	8,0	336	0,2-0,4
G - 38	"	"	"	15	12,0	327	0,4
G - 30	"	"	" 1)	15	4,5	343	0,4
G - 37	"	"	" 2)	15	4,5	338	0,4
G - 23	"	"	NC - 5b	15	4,5	331	0,4
G - 34	"	"	NC - 5a	15	4,5	338	0,4
G - 17	"	"	NC - 8b	15	4,5	343	0,4
G - 20	"	"	"	15	4,5	328	0,4
G - 21	"	"	NC - 8a	15	4,5	324	0,4
G - 16	"	"	NC - 14	15	4,5	339	0,4
G - 25	"	diphenylene oxide + anthraquinone	NC - 4b	15	4,5	335	0,4
G - 26	"	9-anthracene carboxaldehyde + benzanthrone	"	15	4,5	330	0,4
G - 29	Grenoble spent coolant	-	NC - 4a	15	4,5	338	0,4

1) 2) regenerated catalysts

Table 5 b : Results of the experiments executed in loop "Gastone".

Experiment no.	Oxygen content		Deoxygenation efficiency (%)	Chlorine content		Dechlorination efficiency (%)	Sulphur content		Desulphuration efficiency (%)	Hydrogenated terphenyl (%)
	initial (ppm)	final (ppm)		initial (ppm)	final (ppm)		initial (ppm)	final (ppm)		
G - 9	305	199	34,8	-	-	- ¹⁾	84	58	31,0	0
G - 1	1325	196	85,2	-	-	-	94	23	75,2	1 - 3
G - 12	1235	221	82,1	1,6	0,49	69,0	85	26	59,4	0
G - 24	1470	271	81,6	18,3	0,32	98,2	145	105	27,6	0
G - 10	12500	4490	64,1	5,4	1,34	75,2	-	-	-	0
G - 11	-	-	-	3,3	0,66	80,0	47	47	0,0	0
G - 13	9755	4374	55,2	21,5	2,31	89,3	77	69	10	0
G - 14	10350	3171	69,4	22,0	1,83	91,7	71	60	15	0
G - 15	9880	866	91,2	20,5	0,79	96,1	74	52	30	0
G - 18	11000	2187	80,1	28,0	1,10	96,1	73	64	12,3	0
G - 22	11230	960	91,5	21,5	0,26	98,8	93	64	31,5	0
G - 32	15570	1430	90,8	24,0	0,30	98,7	80	53	33,7	0
G - 33	10050	3734	62,8	35,0	1,92	94,5	-	-	-	0
G - 35	9860	3828	61,2	25,0	2,50	90,0	-	-	-	0
G - 38	9750	4407	54,8	24,3	4,50	81,5	-	-	-	0
G - 30	12680	2078	83,6	12,2	0,89	92,7	115	84	27,0	0
G - 37	11630	1830	84,3	24,8	1,22	95,1	-	-	-	0
G - 23	11650	2450	79,0	24,6	1,44	94,1	105	63	40,0	0
G - 34	10310	1890	81,7	30,0	1,29	95,7	85	71	16,5	0
G - 17	1430	438	69,4	15,8	0,45	97,2	104	64	38,5	0
G - 20	10250	2576	74,9	39,2	0,42	98,9	96	75	22,4	0
G - 21	10300	2630	74,5	25,5	0,87	96,6	77	50	35,1	0
G - 16	10400	8225	20,9	18,0	11,8	34,5	80	73	8,8	0,5
G - 25	2020	1134	43,9	-	-	-	200	75	62,5	-
G - 26	2000	888	55,6	22,0	1,23	94,4	175	83	52,5	-
G - 29	323	272	15,8	1,08	0,28	74,1	-	-	-	1,0

¹⁾ not estimated

Time of each run: 8 hrs., except G-29 (37 hrs.)

Table 6 a - Conditions of the experiments executed in loop "63".

Experiment no.	Coolant	Oxygen model compound	Catalyst no.	H ₂ -pressure (atm.)	LHSV	average temperature (°C)	mol H ₂ /mol feed
L - 4	OM-2	benzophenone	NC - 4b	30	4,5	367 ± 5	0,4
L - 2	"	"	NC - 4a	30	4,5	336	0,4
L - 3	"	"	"	15	4,5	350	0,1
L - 5	"	"	"	15	4,5	354	0,4
L - 6	"	"	"	20	4,5	368	0,4
L - 7	OM-D	"	"	15	4,5	327	0,4
L - 8	"	"	"	30	4,5	308	0,4
L - 17	HB-40	"	"	15	4,5	330	0,4
L - 18	"	"	"	30	4,5	347	0,4
L - 11	OM-2 + spent coolant	"	"	15	4,5	363	0,4
L - 12	" "	"	"	30	4,5	379	0,4
L - 13	" "	"	"	30	4,5	402	0,4
L - 14	" "	"	"	30	2,5	381	0,4
L - 15	" "	"	"	30	2,5	370	2,0
L - 16	" "	"	NC - 2	30	4,5	397	0,4

Time of each run: 8 hrs.

Table 6 b - Results of the experiments executed in loop "63".

Experiment no.	Oxygen content		Deoxygenation efficiency (%)	Chlorine content		Dechlorination efficiency (%)	Hydrogenated terphenyl (%)	Highboiler content (TGA)	
	initial (ppm)	final (ppm)		initial (ppm)	final (ppm)			initial (%)	final (%)
L - 4	10317	333	96,8	22,1	0,08	99,6	0,3 - 0,5	-	-
L - 2	9410	208	97,8	23,1	0,07	99,7	0,5	-	-
L - 3	9731	381	96,1	19,7	0,10	99,5	traces	-	-
L - 5	10005	280	97,2	17,2	0,12	99,3	traces	-	-
L - 6	10430	237	97,7	21,0	0,18	99,1	0,5	-	-
L - 7	8860	609	93,1	16,5	0,19	98,9	-	-	-
L - 8	9670	445	95,4	-	-	-	-	-	-
L - 17	11150	292	97,4	10,0	0,12	98,8	-	-	-
L - 18	10250	363	96,5	15,2	0,22	98,6	-	-	-
L - 11	9600	480	95,0	20,4	0,16	99,2	traces	7,9	4,2
L - 12	11800	461	96,1	19,5	0,19	99,0	0,1 - 0,5	7,5	6,5
L - 13	10050	397	96,1	21,0	0,18	99,1	traces	7,4	5,9
L - 14	10033	285	97,2	19,1	0,16	99,2	traces	7,5	3,5
L - 15	10100	250	97,5	20,4	0,14	99,3	traces	7,6	3,4
L - 16	9520	851	91,1	22,5	0,76	96,6	traces	6,4	5,3

Table 7 - Deoxygenation of virgin and Grenoble irradiated OM-2 at 300 °C, 40 atm.H₂-p, 10 %w catalyst, 0,5 kg charge and 4 hrs. contact time in the autoclave.

Charge	Catalyst	Oxygen content (ppm)	
		Before	After
Virgin OM-2	NC - 4b	245 ± 25	210 ± 40
Spent coolant (Grenoble)	NC - 3	a) 490 ± 60	220 ± 30
		b) 345 ± 50	145 ± 25

Table 8 - Desulphuration at 300 °C, 40 atm.H₂-p, 10 %w catalyst, 0,5 kg charge and 4 hrs. contact-time in the autoclave.
Charge : OM-2 + 1 %w benzophenone.

Catalyst no.	Sulphur content (ppm)		Efficiency (%)
	Before	After	
NC - 7	124	64	48
NC - 2	144	74	49
NC - 3	110	40	64
NC - 4a	130	21	84
NC - 4b	158	24	85

Table 9 - B.E.T. measurements of used and not used CoMo-catalyst after thermal treatment

Thermal treatment	Catalyst NC-4a			Catalyst NC-4a used in experiment G-29/30		
	Ss (m ² /g)	Vp (cm ³ /g)	Rm (Å)	Ss (m ² /g)	Vp (cm ³ /g)	Rm (Å)
120°C	247	0,36	29,5	172	0,25	29,1
270	252	0,37	30,0	201	0,34	29,6
450	260	0,43	32,1	260	0,38	29,2
600	264	0,39	32,3	261	0,38	29,2
800	142	0,16	22,5	-	-	-

--- Ss = specific surface, Vp = pore volume, Rm = average pore radius ---

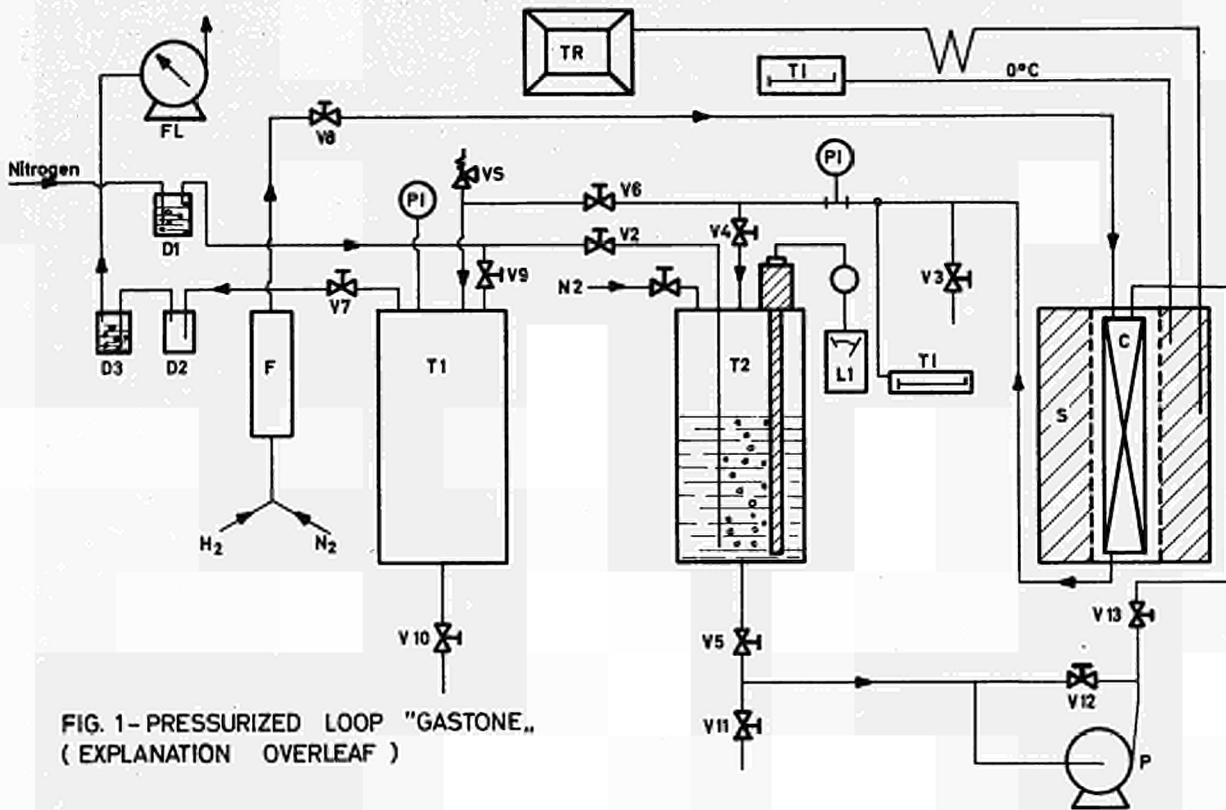


FIG. 1- PRESSURIZED LOOP "GASTONE,,
(EXPLANATION OVERLEAF)

EXPLANATION PRESSURISED LOOP (FIG 1)

- | | | |
|----------|---|-----------------------|
| FL | : | flowmeter |
| D1-D2-D3 | : | wash bottles |
| F | : | filter |
| V | : | valves |
| V.S. | : | security valves |
| T 1 | : | tank no. 1 |
| T 2 | : | tank no. 2 |
| PI | : | manometer |
| LI | : | feed rate control |
| TI | : | temperature indicator |
| TR | : | temperature recorder |
| S | : | furnace |
| P | : | metering pump |
| C | : | column |

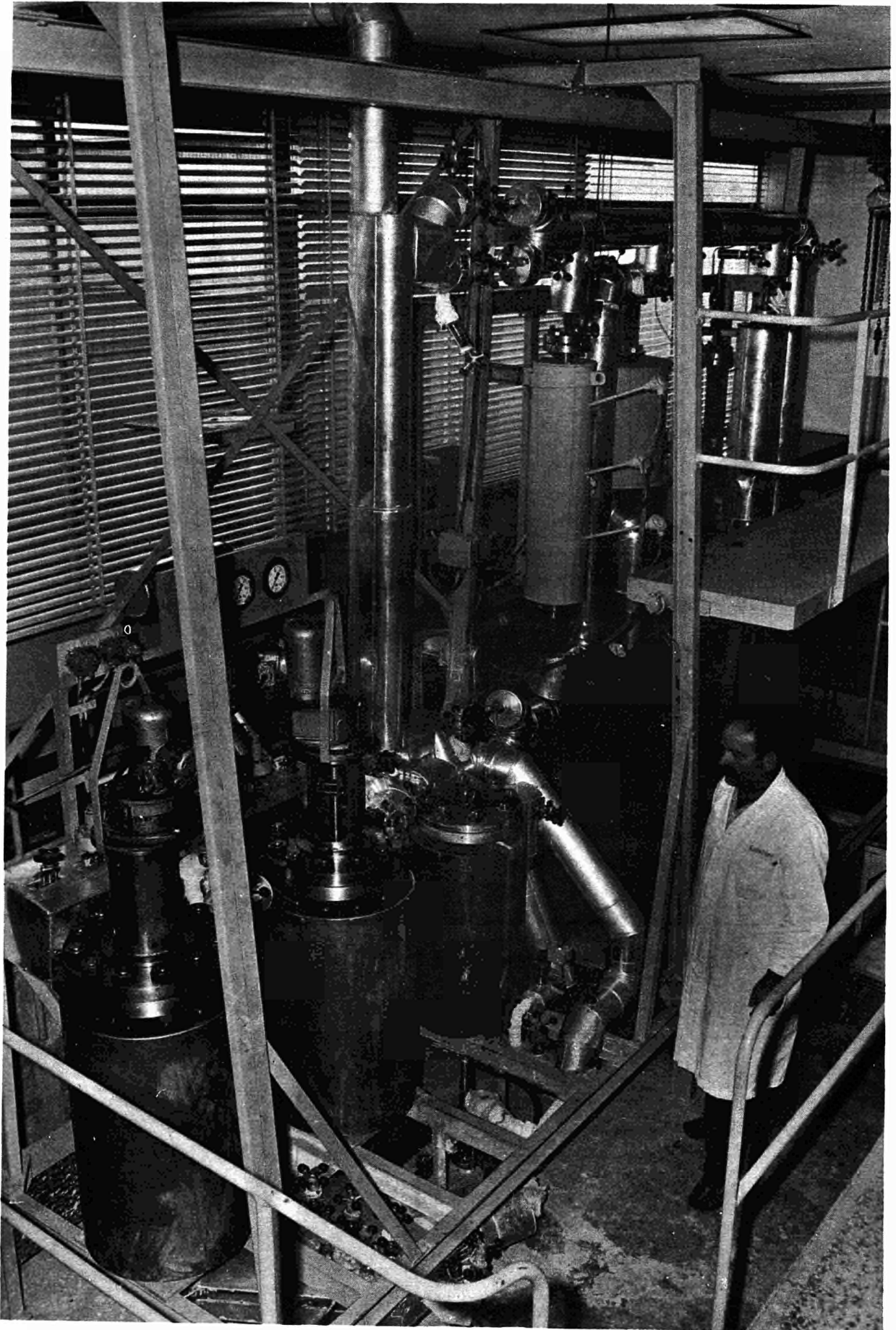


Fig. 2 - Semi-technical pressurized loop "63" .

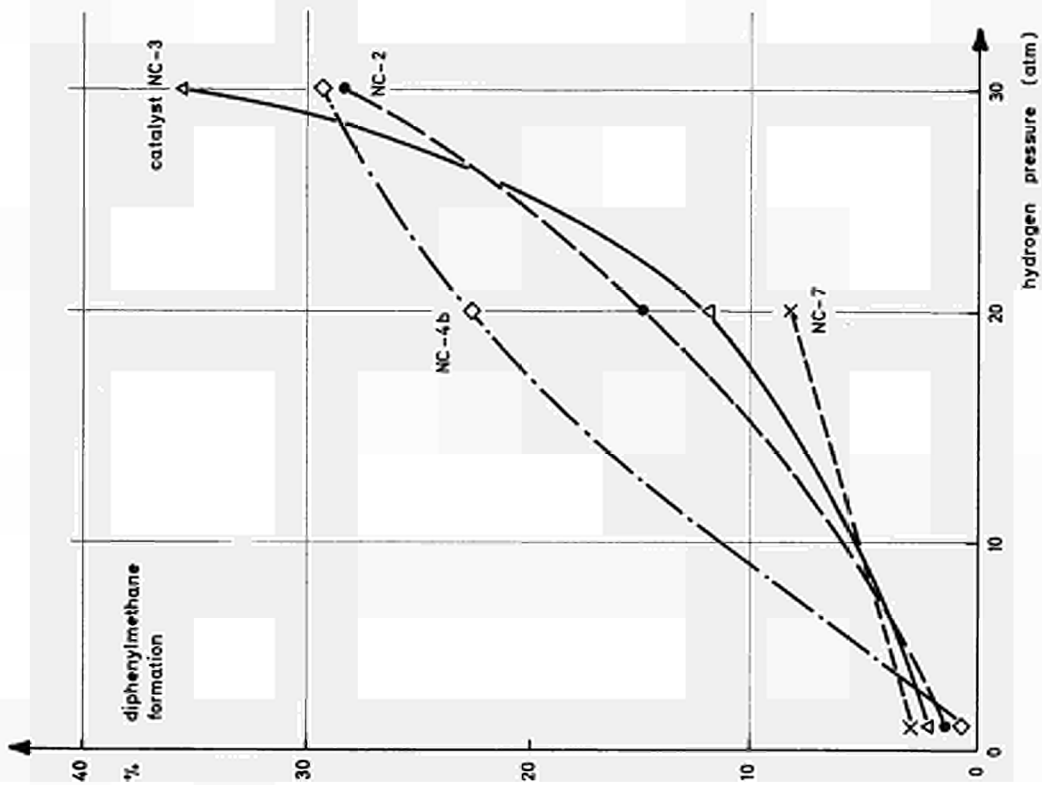
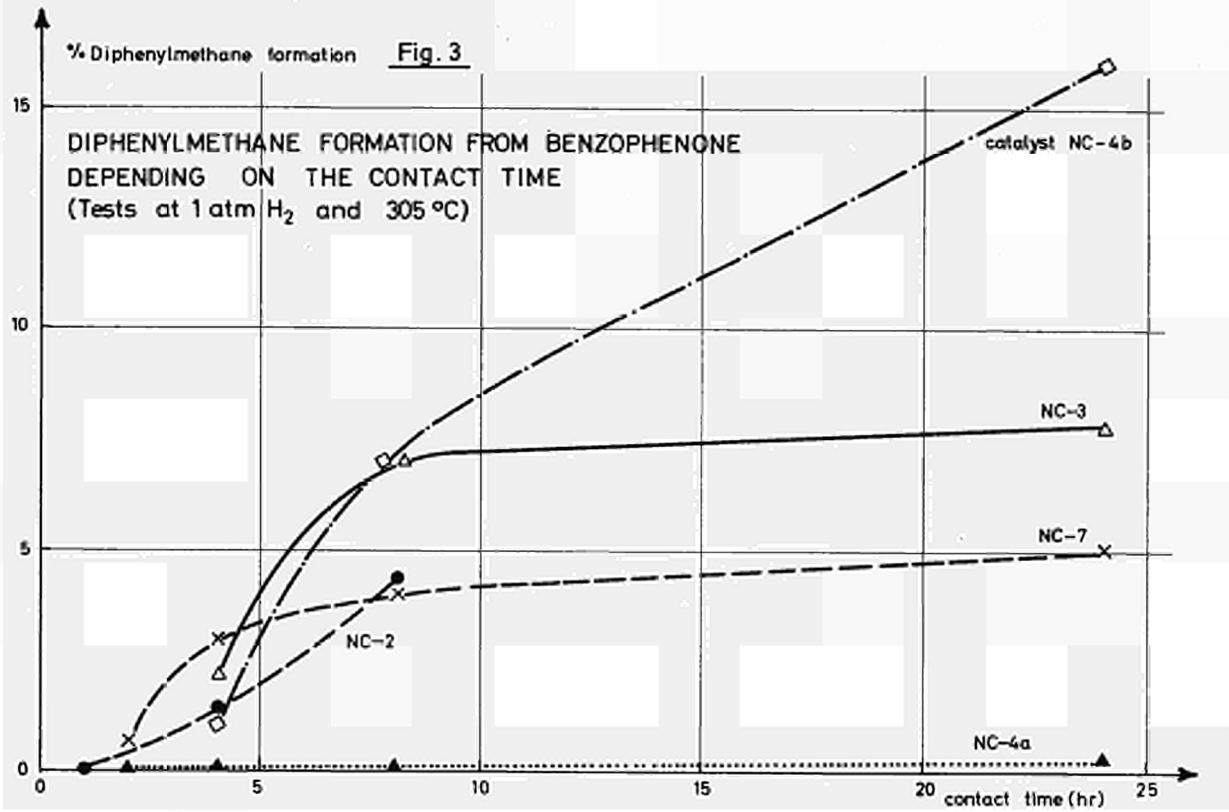


FIG. 4 - DIPHENYLMETHANE FORMATION FROM BENZOPHENONE DEPENDING ON THE HYDROGEN PRESSURE - (Tests at 305 °C and 4 hrs. contact time in the autoclave)

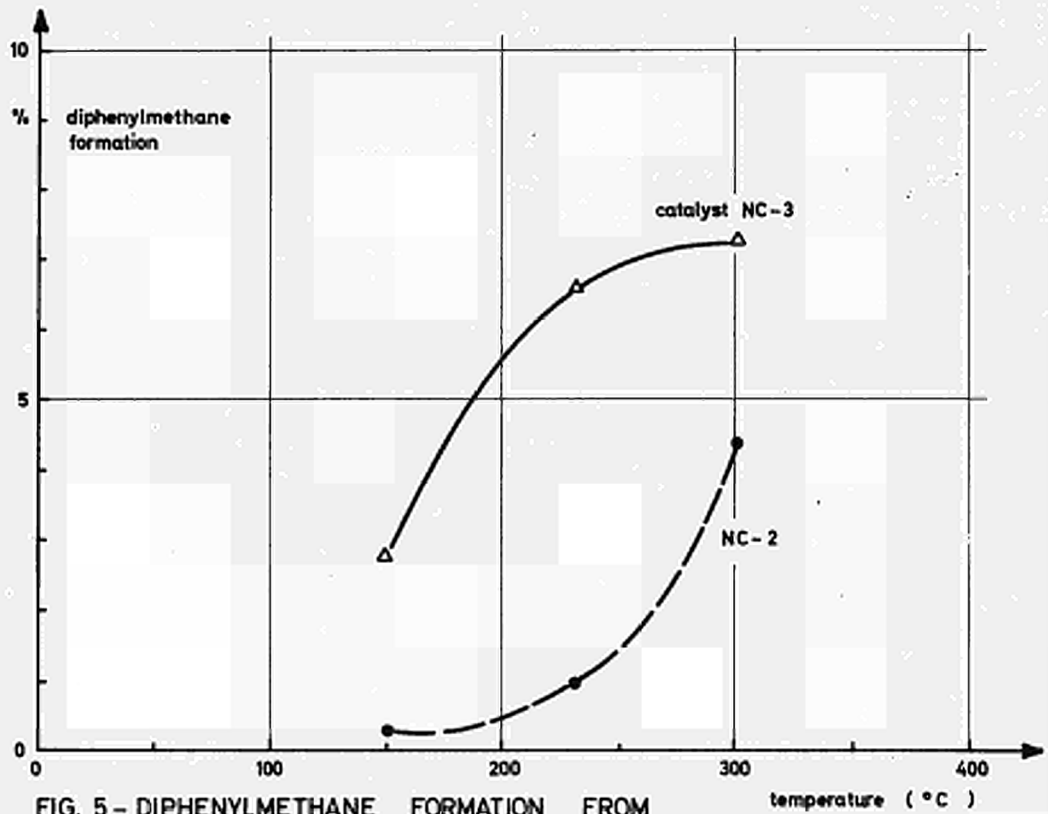


FIG. 5 - DIPHENYLMETHANE FORMATION FROM BENZOPHENONE DEPENDING ON THE REACTION TEMPERATURE (Tests at 1 atm H₂ and 8 hrs contact time)

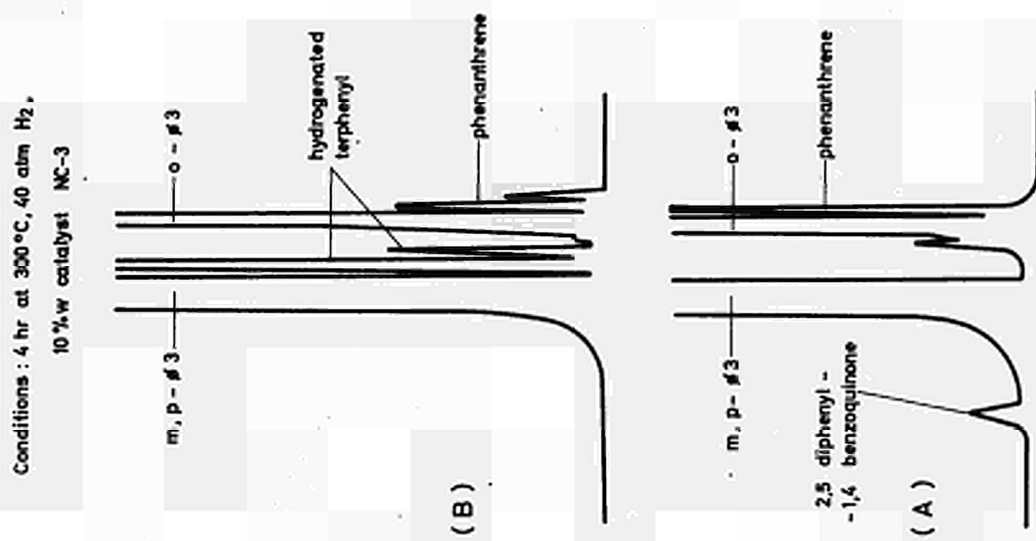


FIG. 6 - GASCHROMATOGRAMS OF OM-2 + 1% 2,5 DIPHENYL-1,4 BENZOQUINONE BEFORE (A) AND AFTER (B) TREATMENT IN THE AUTOCLAVE

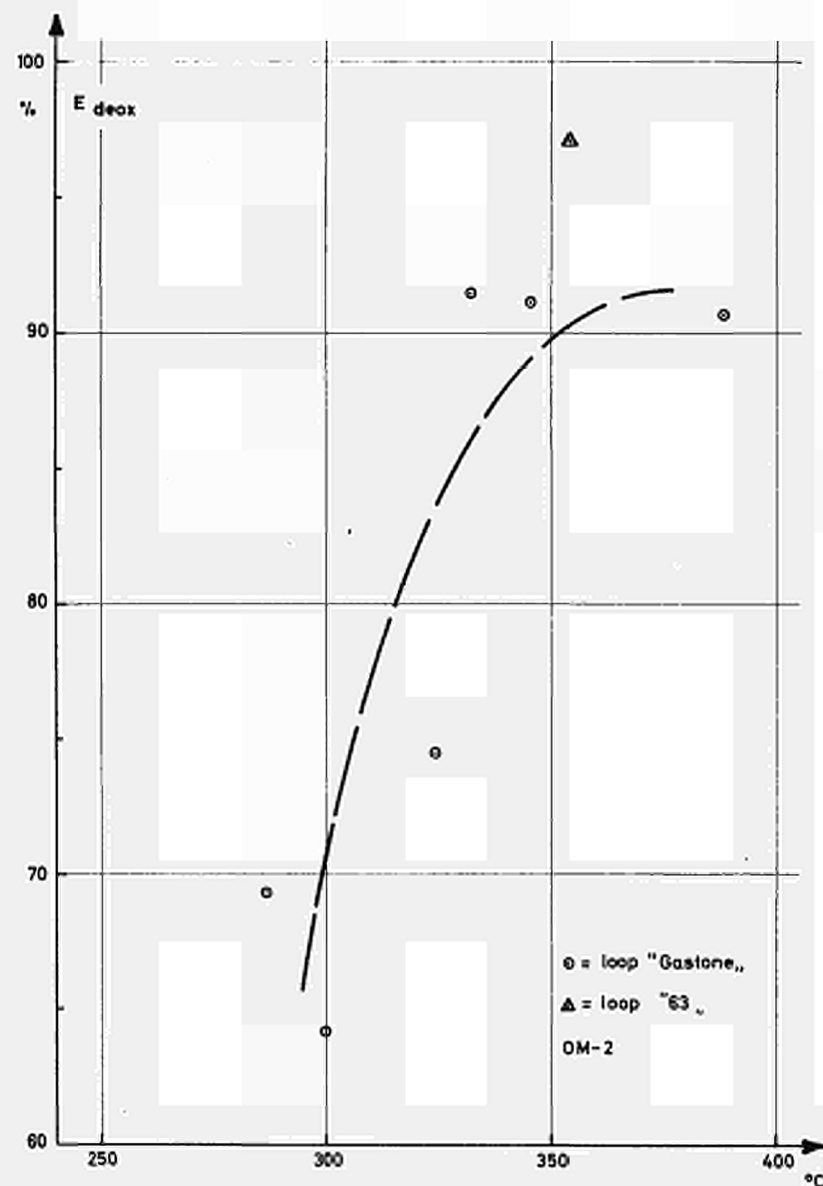


FIG. 8 - DEOXYGENATION DEPENDING ON THE AVERAGE RUN TEMPERATURE

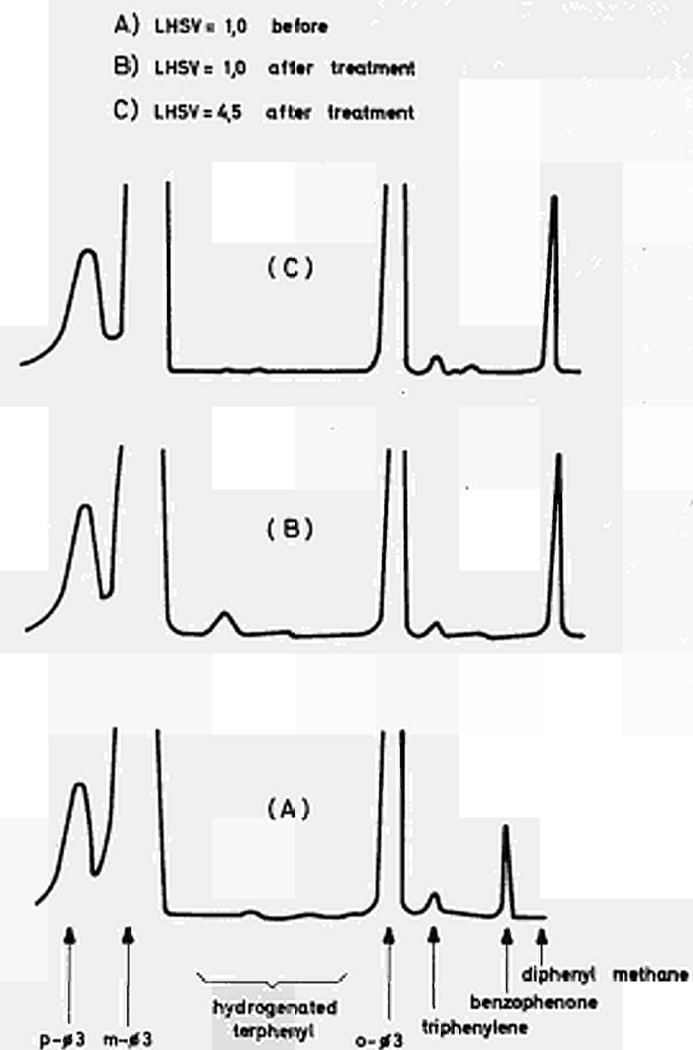


FIG. 7 - GASCHROMATOGRAMS OF OM-2 + 1% w BENZOPHENONE BEFORE AND AFTER COLUMN TREATMENT

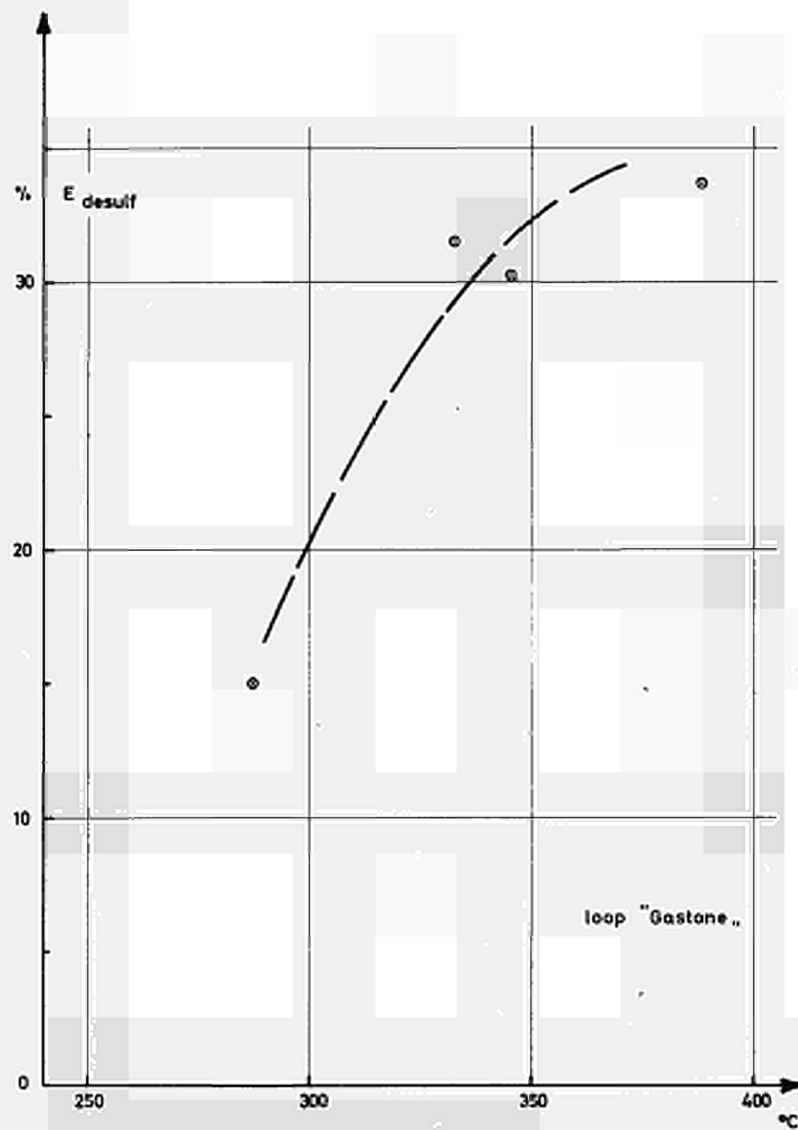


FIG. 10 - DESULPHURATION DEPENDING ON THE AVERAGE RUN TEMPERATURE

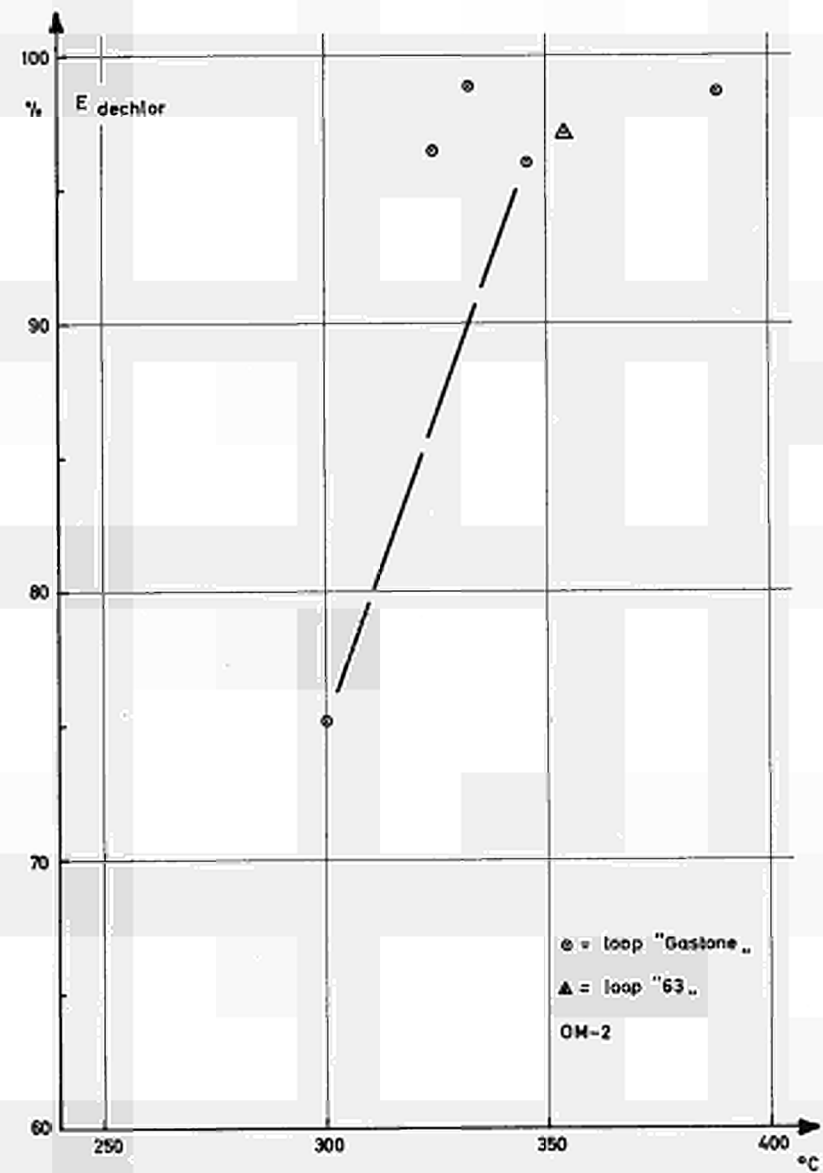


FIG. 9 - DECHLORINATION DEPENDING ON THE AVERAGE RUN TEMPERATURE

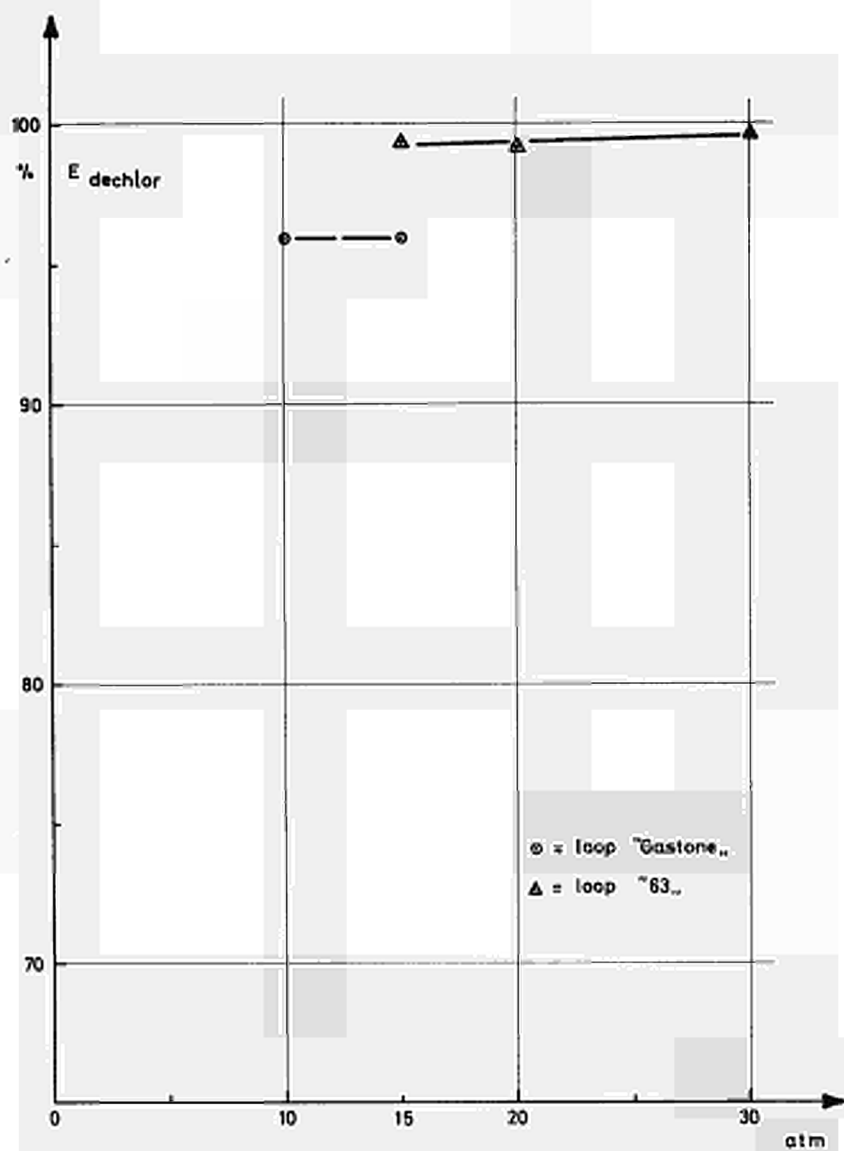


FIG. 12 - DECHLORINATION DEPENDING ON THE H₂-PRESSURE

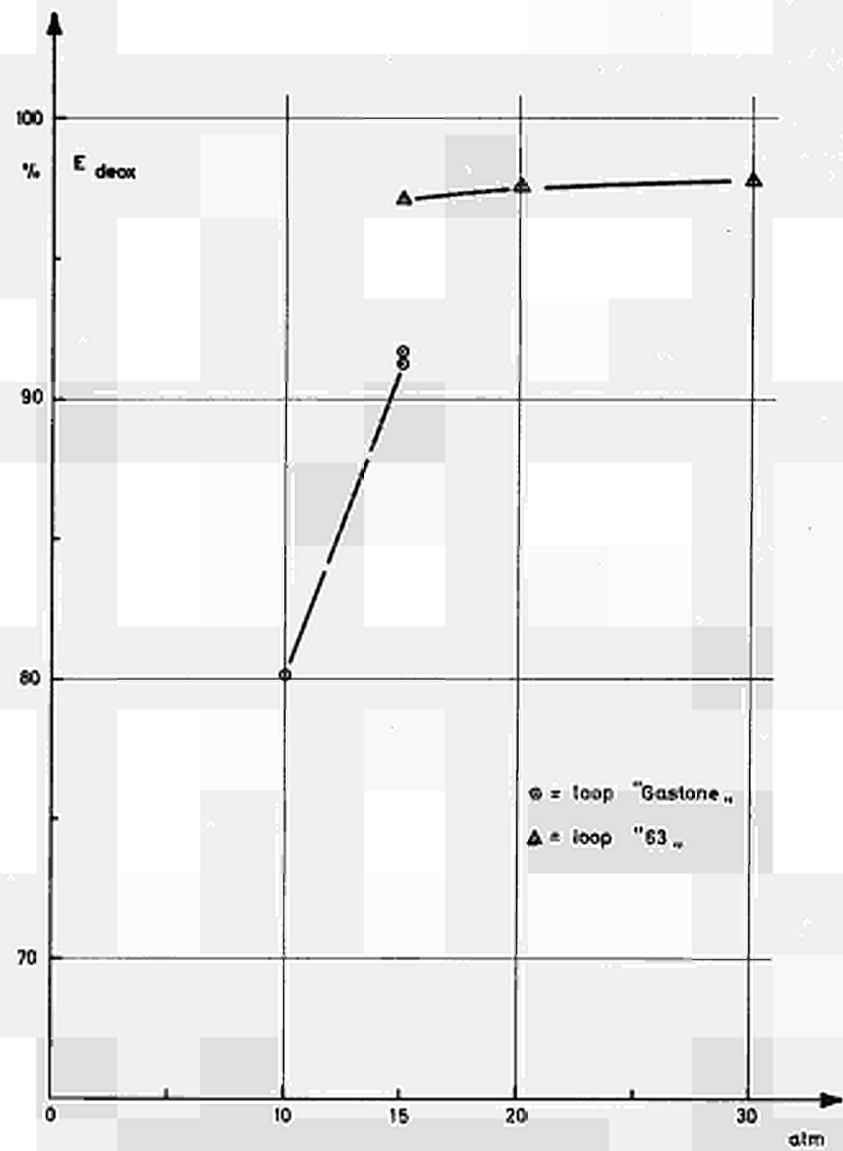


FIG. 11 - DEOXYGENATION DEPENDING ON THE H₂-PRESSURE

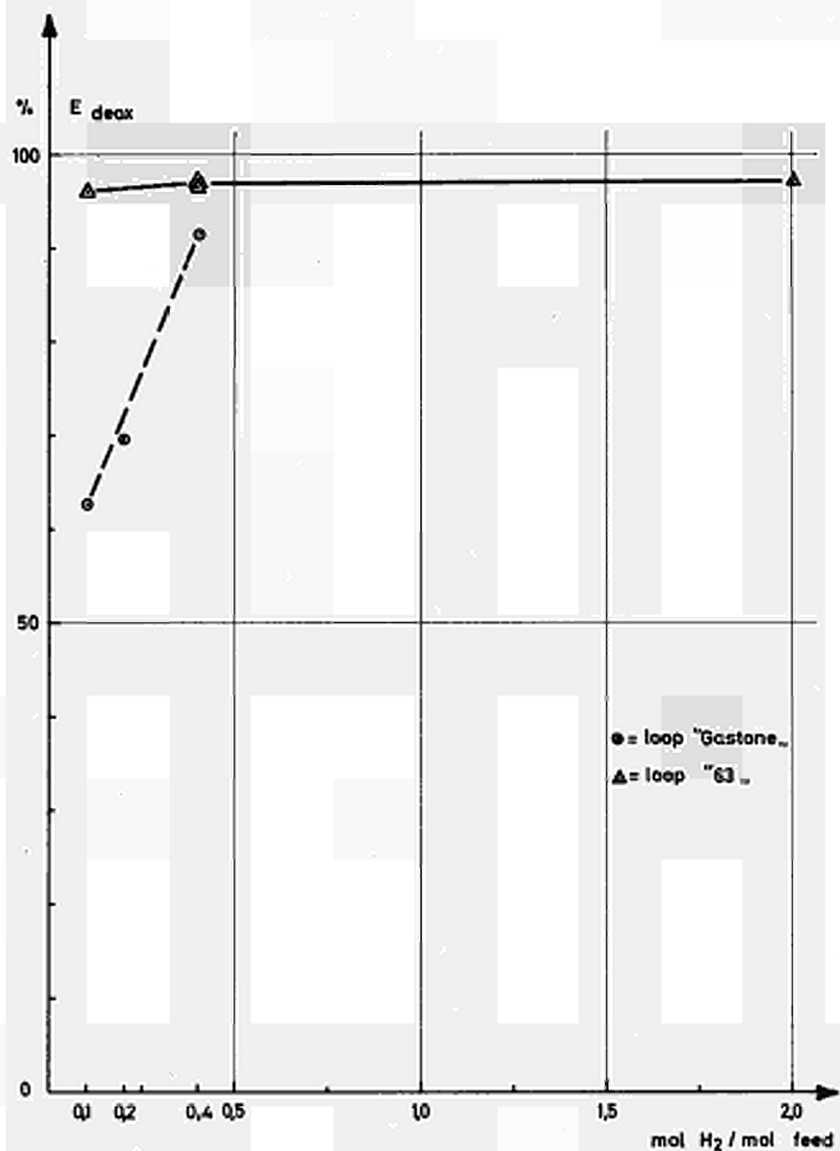


FIG. 14 - DEOXYGENATION DEPENDING ON THE H_2 -FLOW

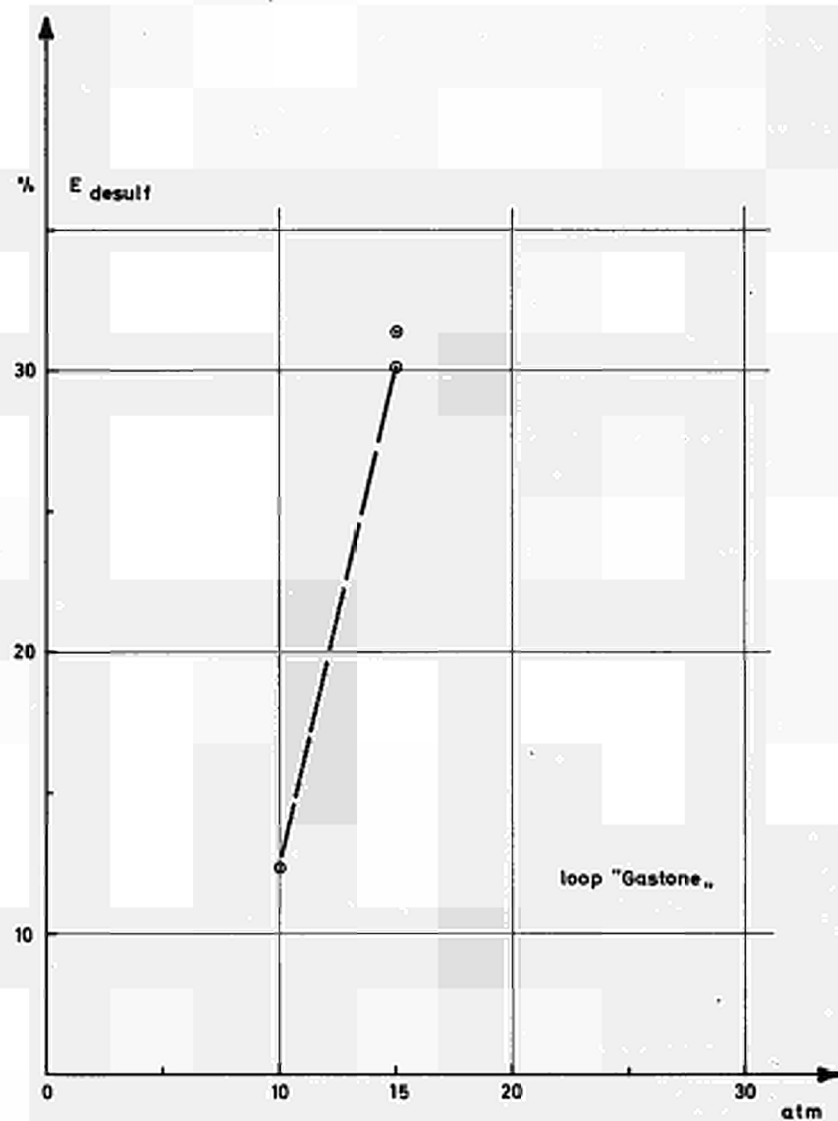


FIG. 13 - DESULPHURATION DEPENDING ON THE H_2 -PRESSURE

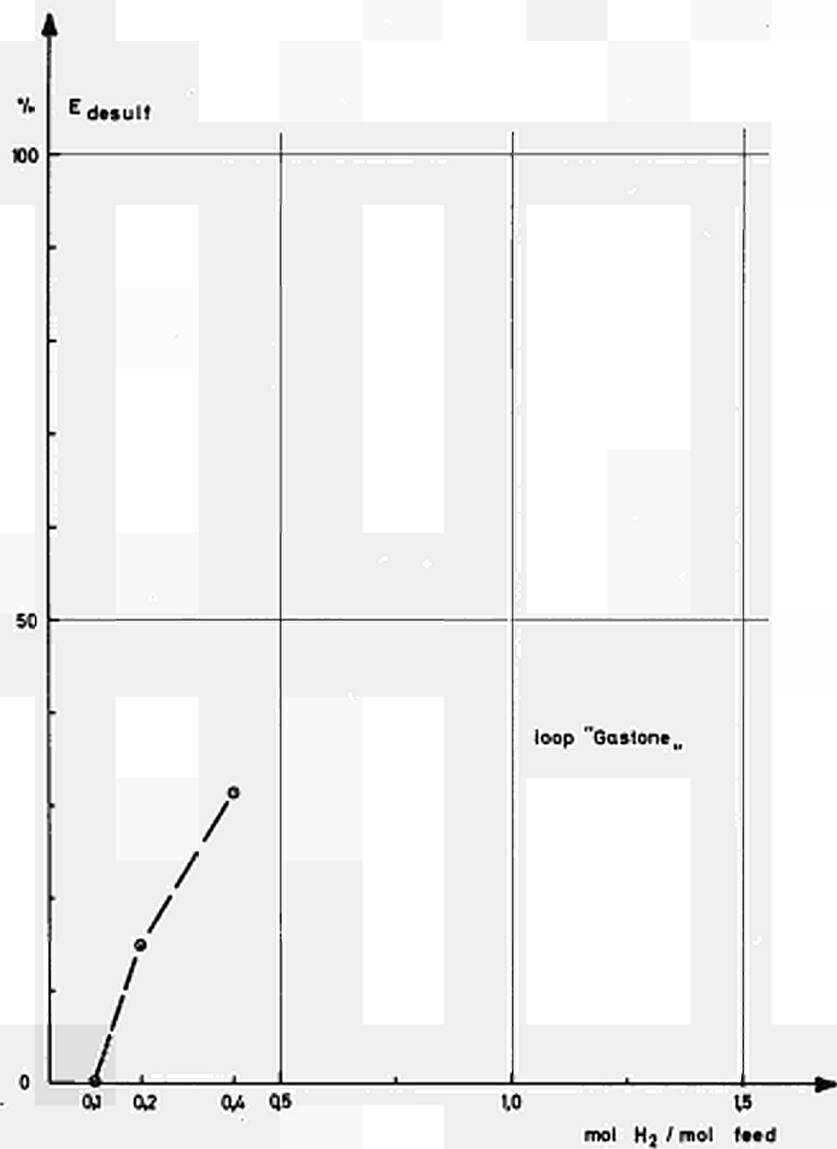


FIG. 16-DESULPHURATION DEPENDING ON THE H_2 -FLOW

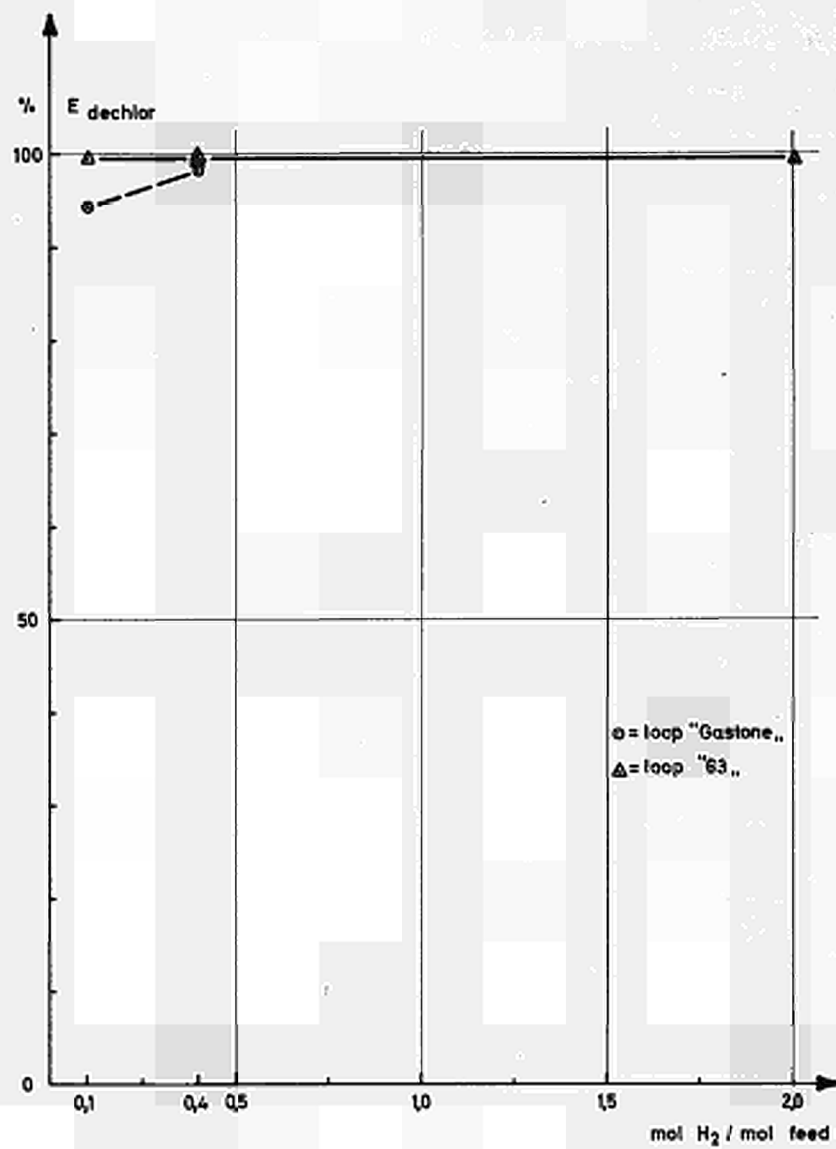


FIG. 15-DECHLORINATION DEPENDING ON THE H_2 -FLOW

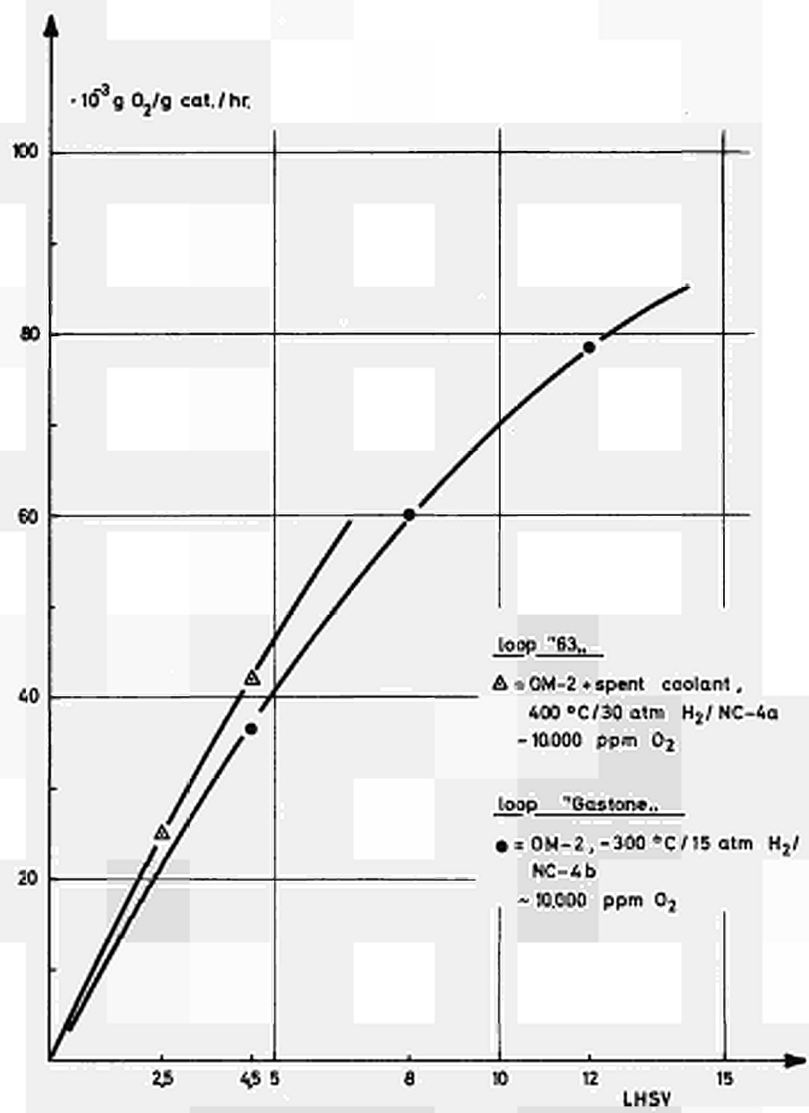


FIG. 17 b - OXYGEN UPTAKE BY CoMo - CATALYSTS
 DEPENDING ON THE CHARGE RATE

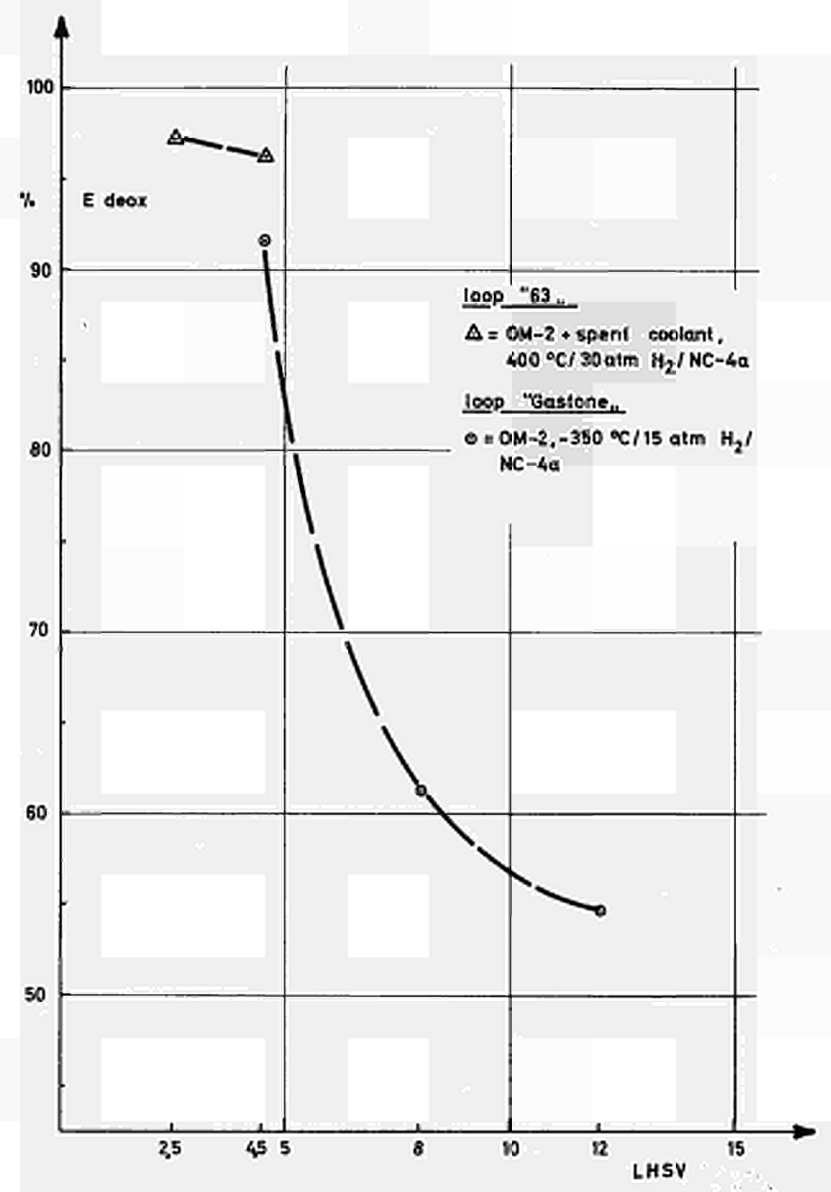


FIG. 17 a - DEOXYGENATION DEPENDING ON THE CHARGE RATE

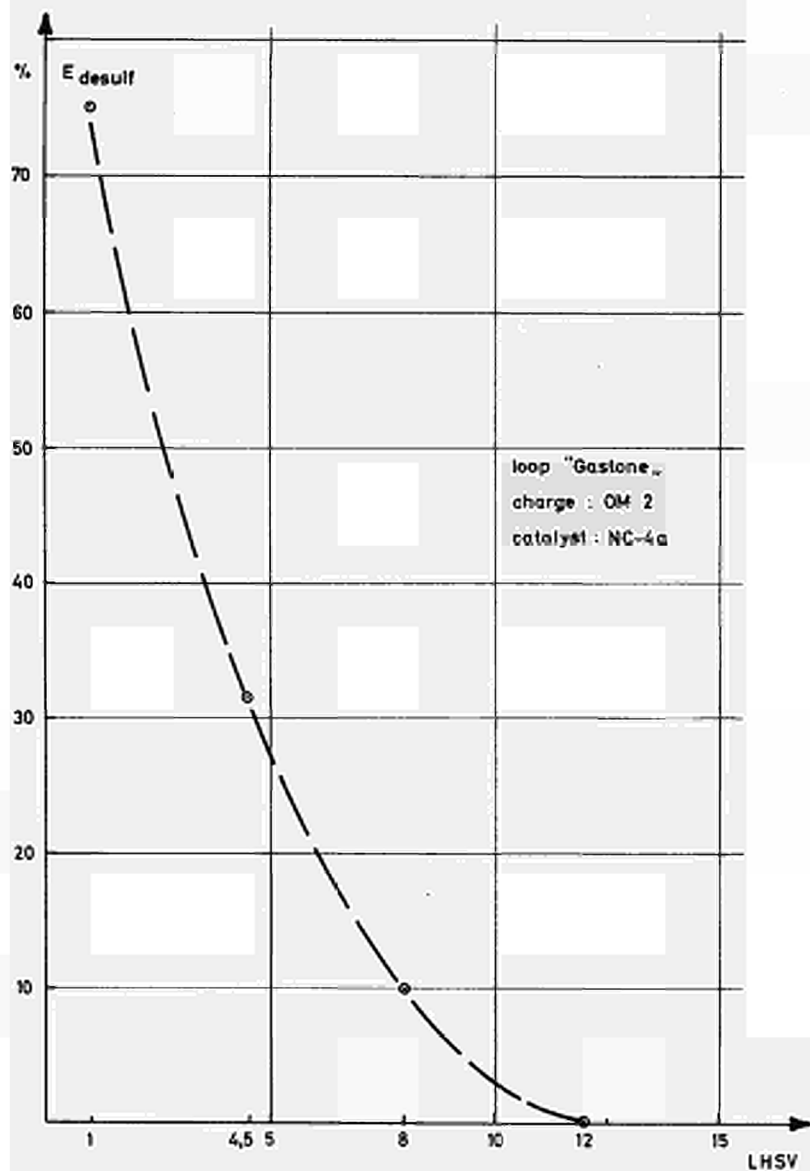


FIG.19-DESULPHURATION DEPENDING ON THE CHARGE RATE

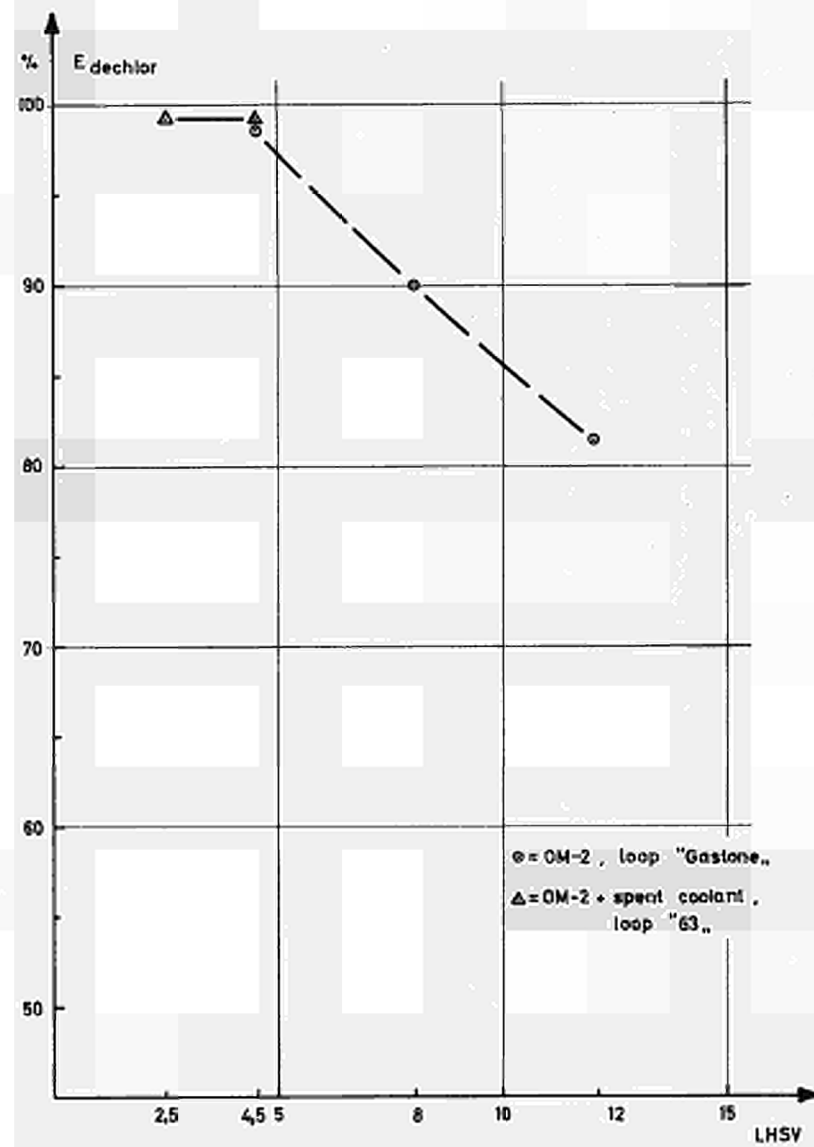


FIG.18 -DECHLORINATION DEPENDING ON THE CHARGE RATE

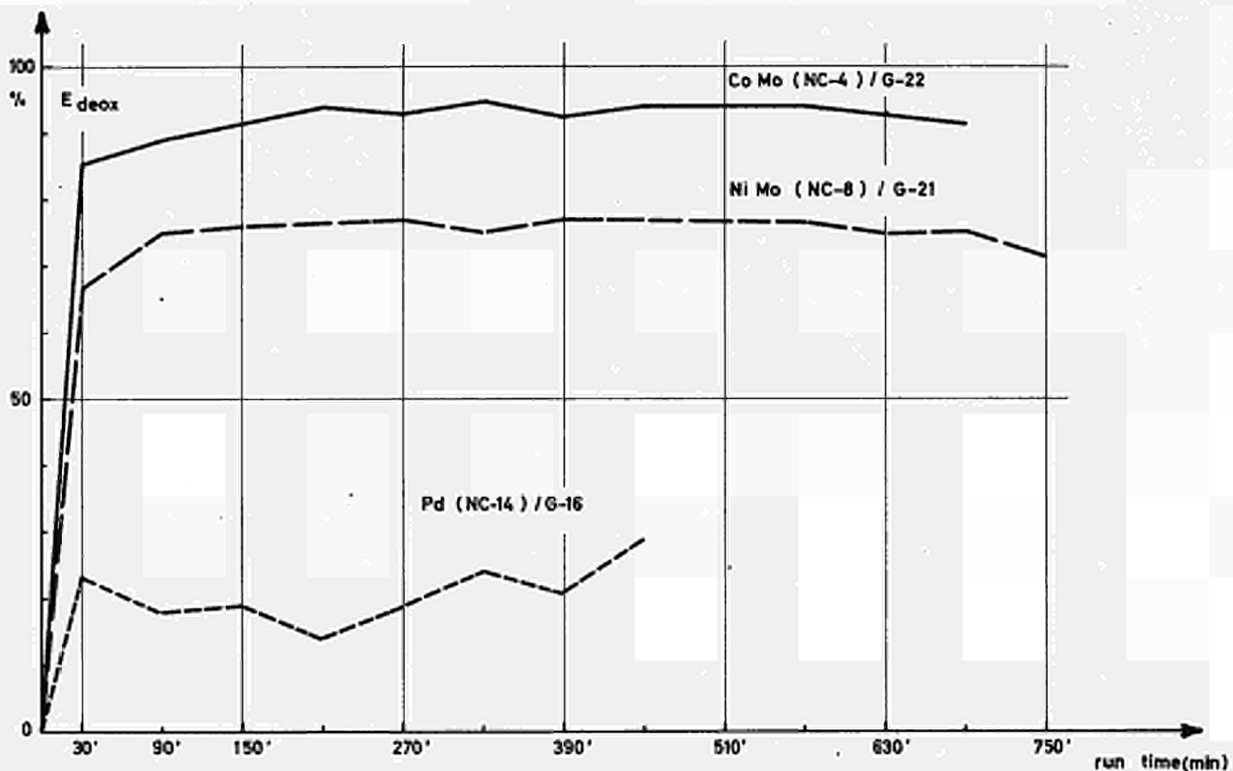


FIG. 20 - DEOXYGENATION EFFICIENCIES OBTAINED WITH DIFFERENT CATALYSTS
POSED AGAINST THE TIME OF EACH RUN

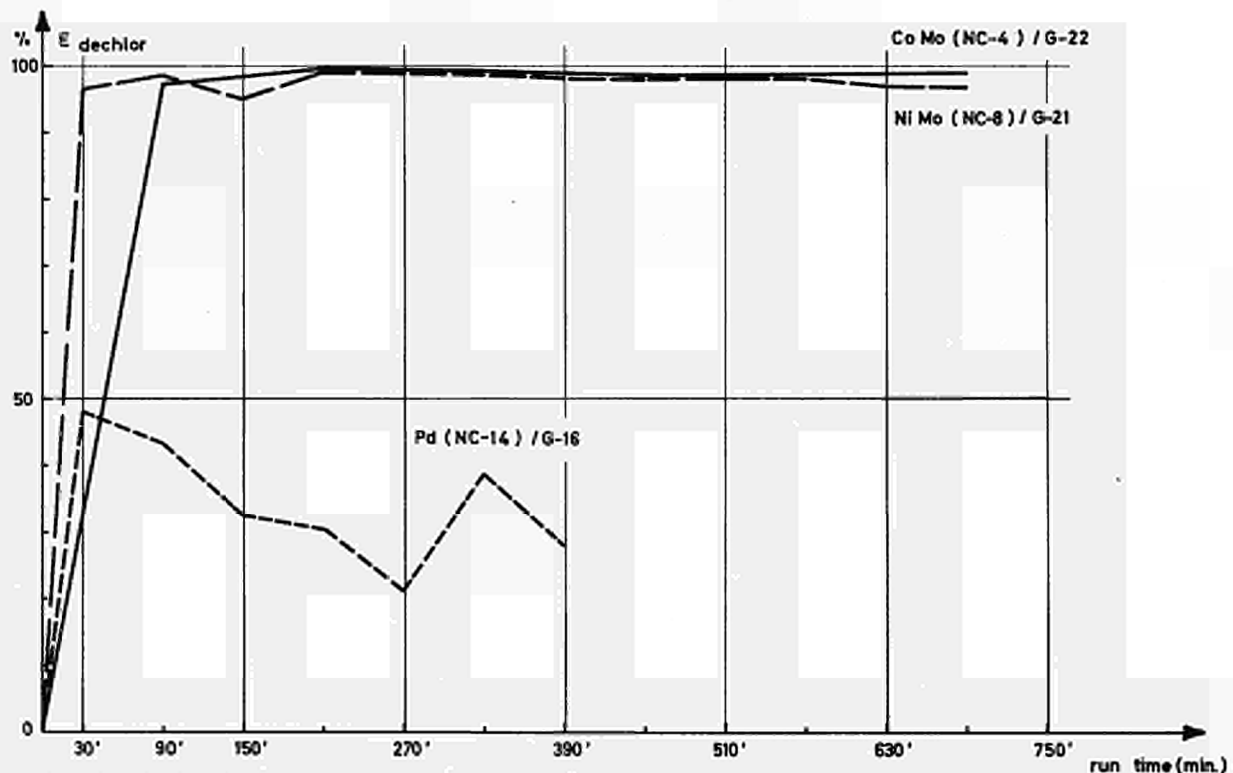


FIG. 21 - DECHLORINATION EFFICIENCIES OBTAINED WITH DIFFERENT CATALYSTS
POSED AGAINST THE TIME OF EACH RUN

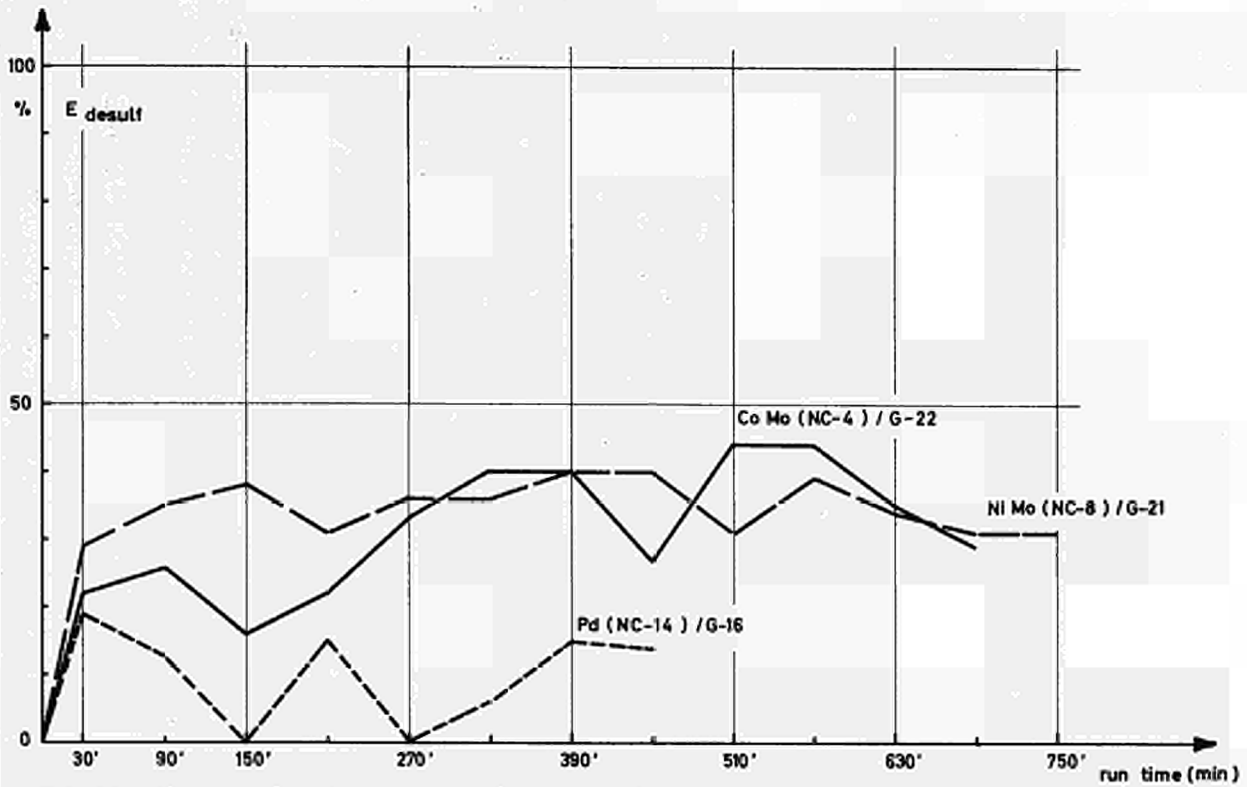


FIG. 22 - DESULPHURATION EFFICIENCIES OBTAINED WITH DIFFERENT CATALYSTS POSED AGAINST THE TIME OF EACH RUN

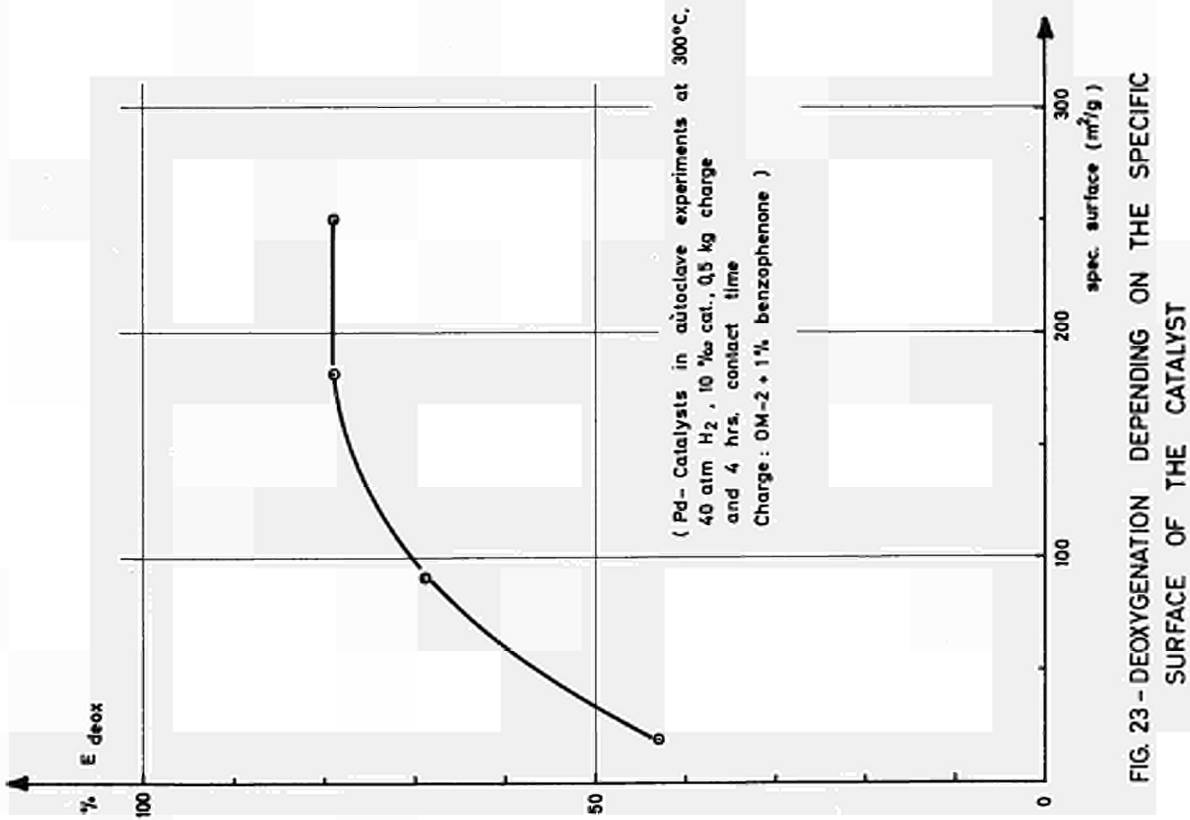


FIG. 23 - DEOXYGENATION DEPENDING ON THE SPECIFIC SURFACE OF THE CATALYST

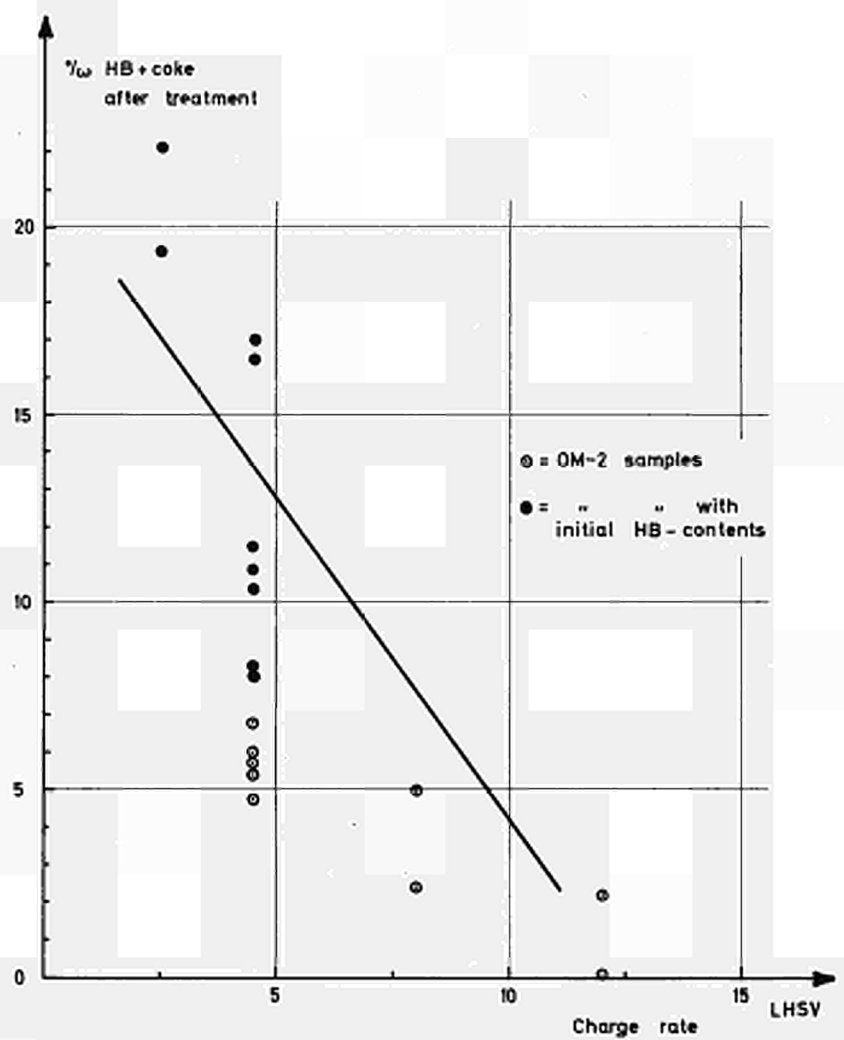


FIG. 25 - HB-ADSORPTION AND COKE FORMATION ON THE CATALYST SURFACE DURING COLUMN TREATMENT DEPENDING ON THE CHARGE RATE (8 hrs.)

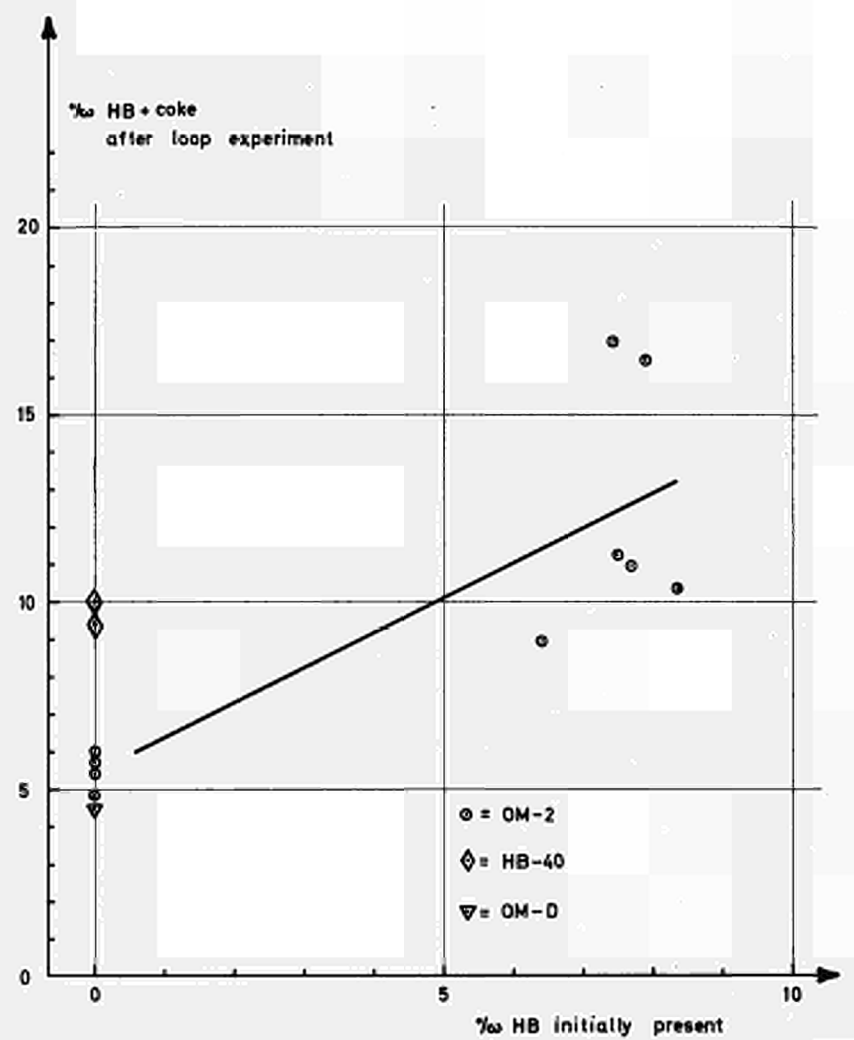


FIG. 24 - ADSORPTION AND COKE FORMATION ON THE CATALYST SURFACE DURING COLUMN TREATMENT DEPENDING ON THE HB-CONTENT INITIALLY PRESENT IN THE COOLANT (8 hrs.)

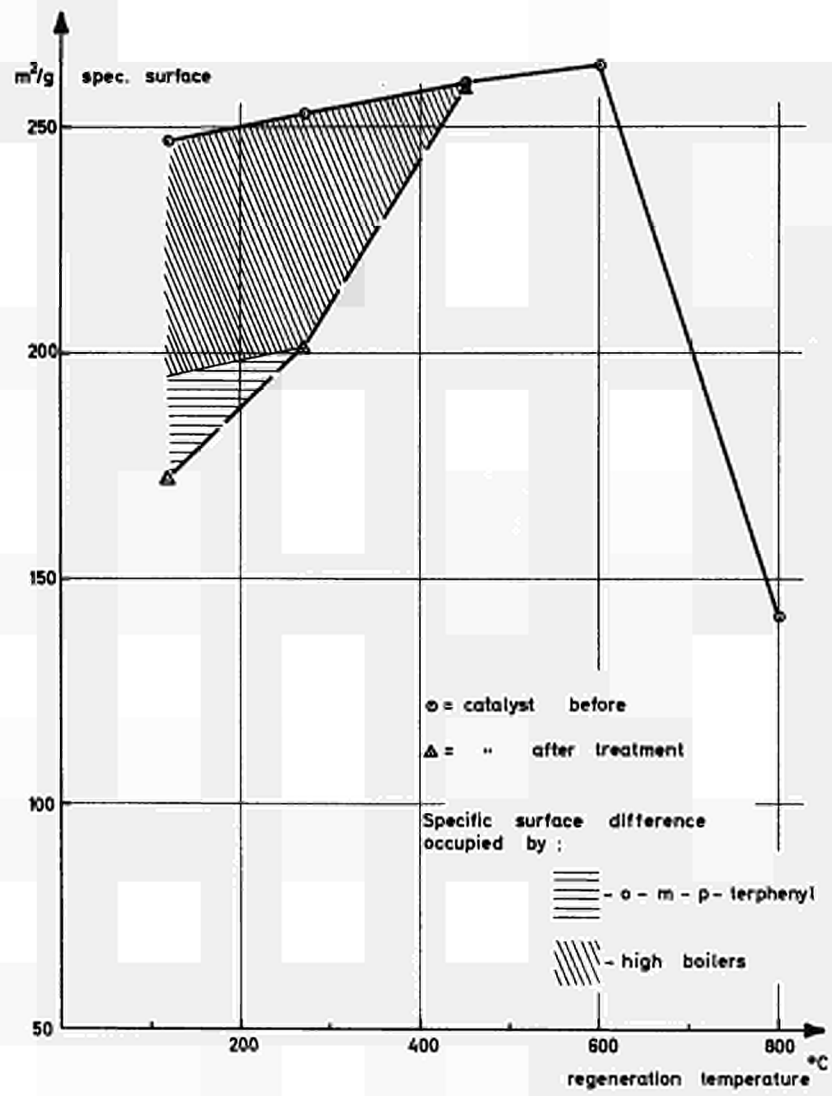


FIG. 27 - EFFECTS OF THERMAL REGENERATION OF USED CATALYSTS - a) CoMo-catalyst (NC-4a) used in 44 hrs. loop experiment G-29/30

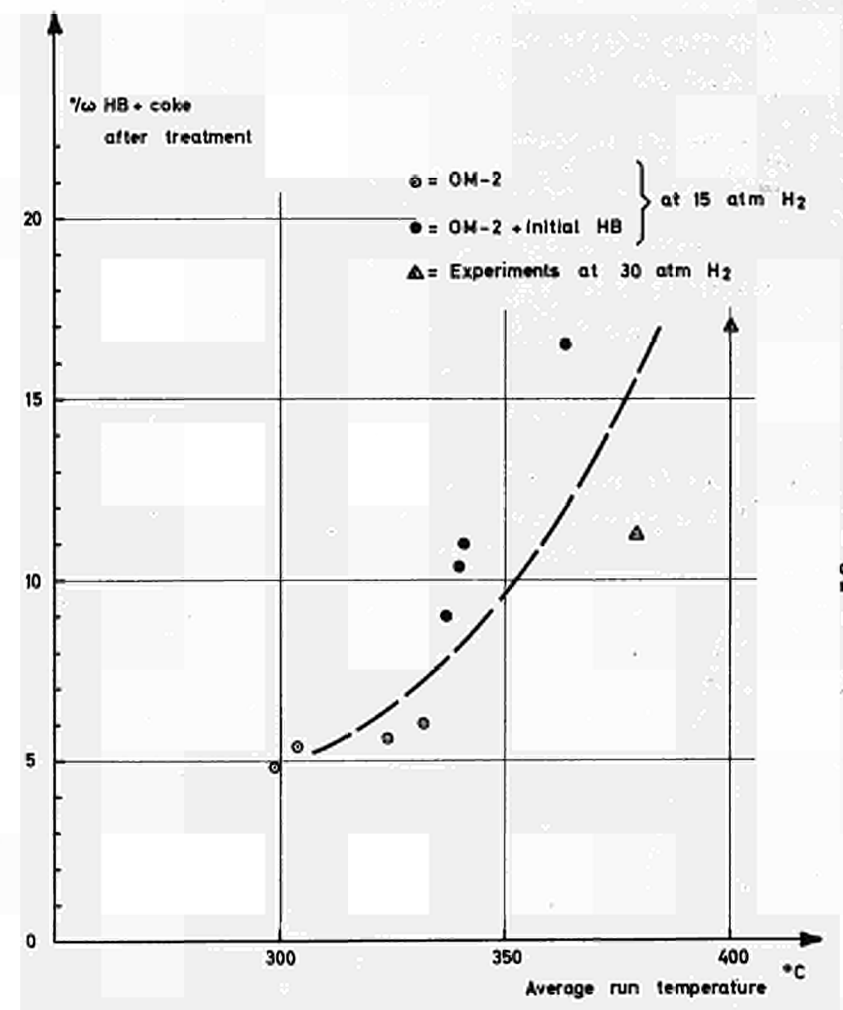


FIG. 26 - HB-ADSORPTION AND COKE FORMATION ON THE CATALYST SURFACE DURING COLUMN TREATMENT DEPENDING ON THE AVERAGE RUN TEMPERATURE (8 hrs.)

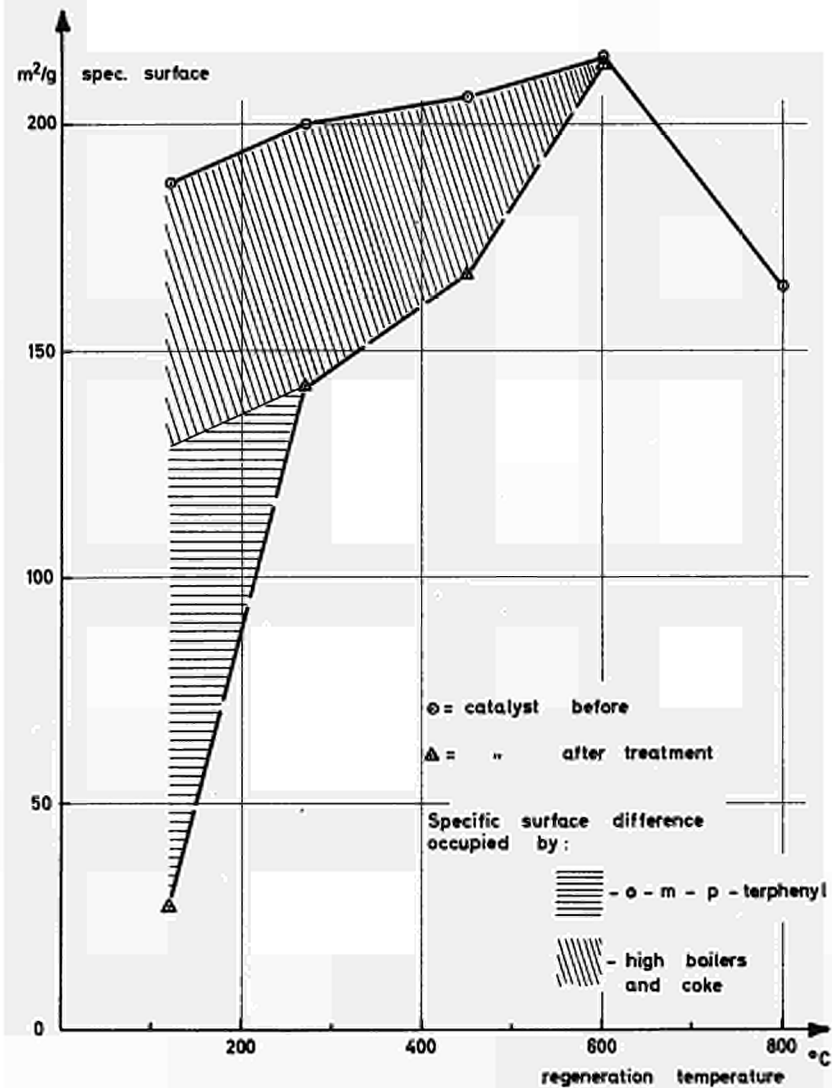


FIG. 29 - EFFECTS OF THERMAL REGENERATION OF USED CATALYST - c) Pt-catalyst (NC-2) used in 8 hrs. loop experiment L-16

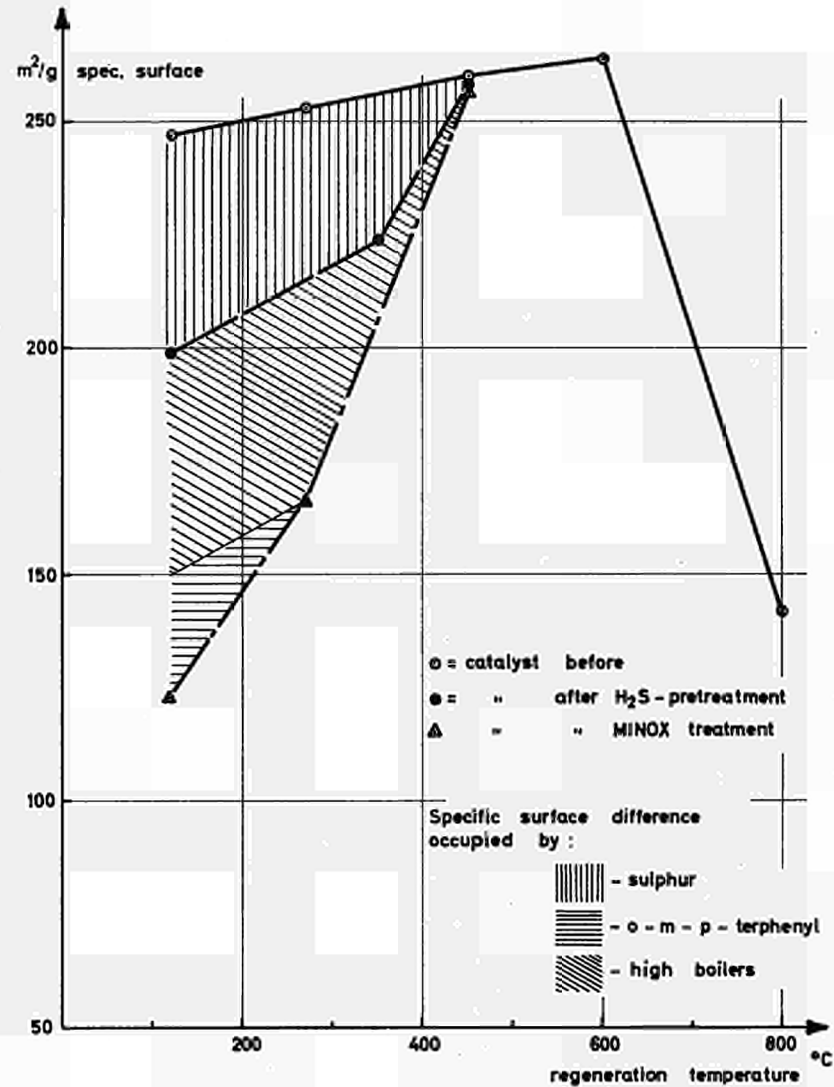


FIG. 28 - EFFECTS OF THERMAL REGENERATION OF USED CATALYSTS - b) Sulphur activated CoMo-catalyst (NC-4b) used in 8 hrs. loop experiment G-27

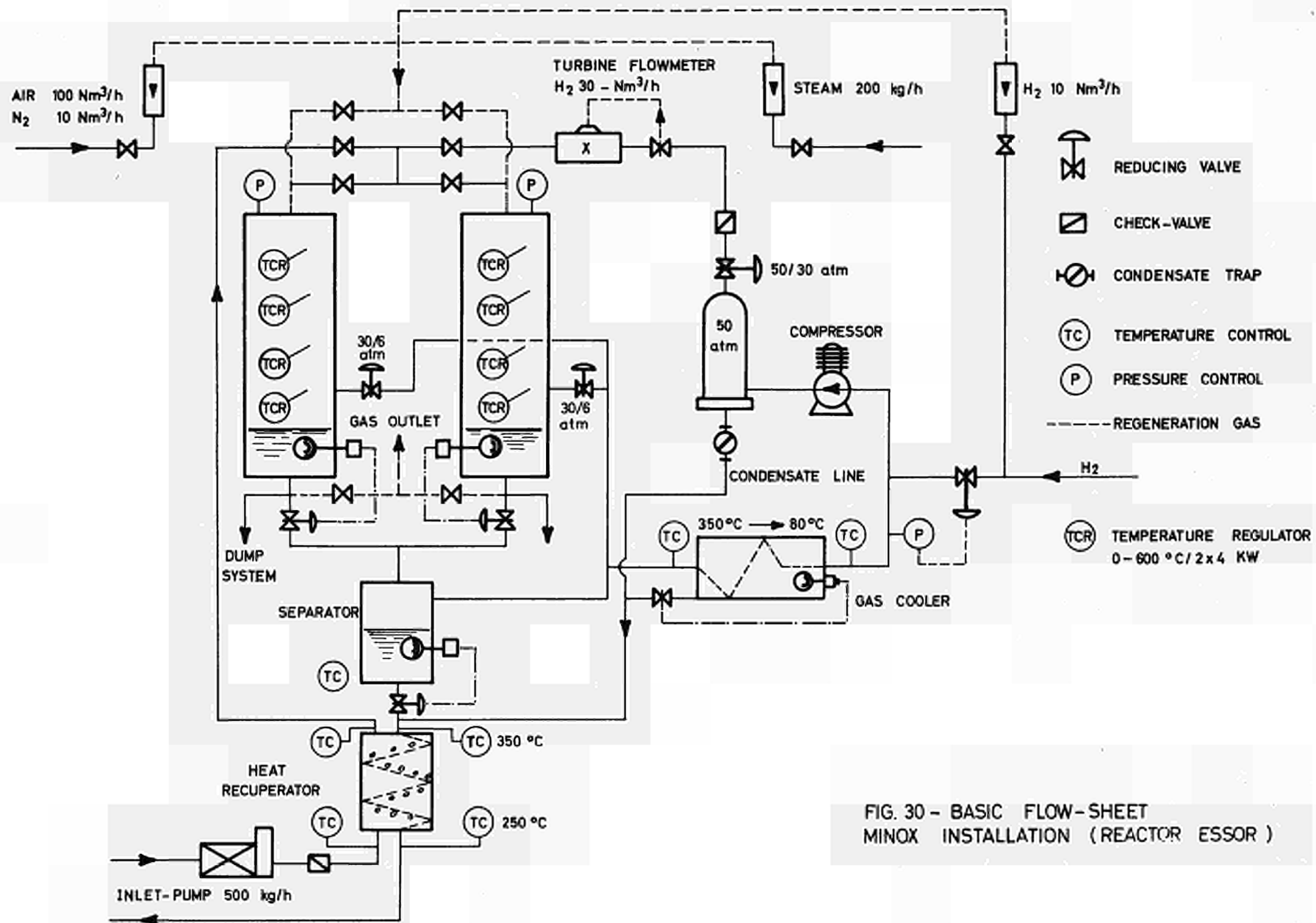


FIG. 30 - BASIC FLOW-SHEET
MINOX INSTALLATION (REACTOR ESSOR)

APPENDIX:

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Project - MINOX PLANT MK-5 (Reactor - Essor)

Minox is a fixed bed catalytic hydro-deoxygenation process. The installation has been designed for coolant throughput of $500 \text{ kg}\cdot\text{h}^{-1}$. The general outline of plant and process items is given below.

1.) Inlet pump:

May be either a centrifugal or a direct displacement pump. It should be able to pump a flow of $500 \text{ kg}\cdot\text{h}^{-1}$ at 10 to 30 atm. total pressure.

2.) Heat recuperator:

The maximum admissible temperature in the degasifier will be about 250°C , with tertiary eutectic OM-D used as a coolant. To be able to operate Minox at 350°C a heat recuperator is installed, which consists of a countercurrent heat exchanger in which the incoming and leaving fluids are used as primary and secondary fluids. The duty of this heat exchanger should be:

Flow: (primary and secondary) $500 \text{ kg}\cdot\text{h}^{-1}$
Heat load: $30,000 \text{ Kcal/h}$

3.) Catalyst beds:

There are two columns on the design because of in situ catalyst regeneration, changing and experimental purposes. The particulars of each column are:

Diameter:	65 cm
Effective catalyst height:	180 cm
Catalyst content:	600 liter
Working temperature and pressure:	$350^\circ\text{C}/30 \text{ atm.}$
Regeneration temperature and pressure:	$600^\circ\text{C}/1 \text{ atm.}$
External heating:	32 KW (corresponding with a column heating velocity of $2-3^\circ\text{C}/\text{min}$)

Thermocouples:	4
Nominal throughput:	Liquid 500 kg.h ⁻¹ Gas 30 Nm ³ .h ⁻¹

The bottom of the column is a liquid/gas separator with a level contact. The pressure is decreased after the column to the system-pressure of 6 atm.

4.) The liquid-separator:

The liquid entering at 30 atm., leaves at 6 atm. Duty:

Pressure:	6 atm.
Temperature:	350°C
Liquid flow:	500 kg/h
Gas flow:	30,000 Nm ³ /h H ₂

5.) Hydrogen recirculation system:

To minimise the hydrogen consumption of the process the bulk of the hydrogen will be recycled. To this end the gas from the liquid/gas separator will be passed through a gas-cooler in which the gas has to be cooled down to 80°C.

The cooled gas can be recompressed from 6 to 50 atm. by a compressor. Duties of the compressor are:

Feed gas temperature:	100°C
Flow rate:	30 Nm ³ .h ⁻¹
Inlet pressure:	6 atm.
Discharge pressure:	50 atm.

During cooling and recompression a certain amount of vaporized coolant will be separated as a liquid. These condensables will both be discharged with the main fluid stream to the degasifier.

The recycle gas, compressed to 50 atm., is passed through a reducing valve which stabilises the column pressure at 30 atm.

The gas flow will be regulated by a valve commanded by a turbine flow meter. Conditions:

Temperature:	150°C
Nominal flow:	30 Nm ³ .h ⁻¹
Pressure:	30 atm.
Gas:	Hydrogen

Make-up hydrogen supply will be introduced at the low pressure side of the system by means of a reducing valve to the compressor inlet, which ensures a steady compressor inlet pressure at 6 atm.

N.B. It must be noted that the lay-out of the hydrogen recirculation system has not been based upon practical experience in our laboratories, since no practical work on this subject has been carried out.

6.) Regeneration:

The regeneration of the catalyst beds will be carried out in situ. To this end the column has to be heated to 550°C, hydrogen is removed by nitrogen sweeping and air passed through in downflow.

The temperature of the catalyst bed during the regeneration is regulated by the addition of low pressure steam to the regeneration gas.

After all the adherent coke has been burnt off, nitrogen sweeping takes place, followed by hydrogen reactivation of the catalyst at ~200°C. The complete regeneration cycle will be carried out at atmospheric pressure. Relevant data:

Air flow rate:	100 Nm ³ /h ⁻¹
Steam flow rate:	200 kg.h ⁻¹
Nitrogen flow rate:	10 Nm ³ .h ⁻¹
Hydrogen flow rate:	10 Nm ³ .h ⁻¹

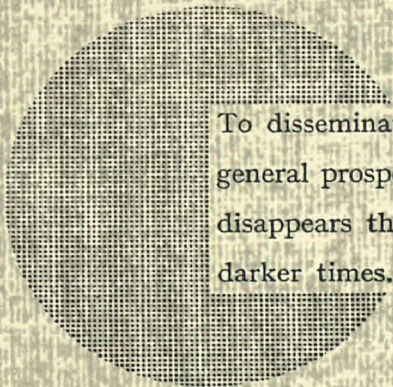
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Alfred Nobel

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