



TOGETHER
for a sustainable future

OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.



TOGETHER
for a sustainable future

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as “developed”, “industrialized” and “developing” are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org



003661



Distribution
LIMITED

ID/WG.123/13
7 June 1972

Original: ENGLISH

United Nations Industrial Development Organization

Expert Group Meeting on Transfer of Know-how
in Production and Use of Catalysts

Bucharest, Romania, 26 - 30 June 1972

**RESEARCH RELATED TO THE DEVELOPMENT
AND MANUFACTURE OF COMMERCIAL CATALYSTS^{1/}**

by

Ion Ghejan

ROMANIAN RESEARCH AND DESIGN INSTITUTE
FOR PETROLEUM REFINING
Ploiesti Romania

^{1/} The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the Secretariat of UNIDO. This document has been reproduced without formal editing.

We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards, even though the best possible copy was used for preparing the master fiche.

The production of commercial catalysts has been greatly developed in the last twenty years. Although the use of catalyst has not penetrated uniformly in the chemical industry, still the stage has been reached where a large part of the chemical industry and especially the petrochemical one, have adopted the catalytic procedures for the fabrication of a large assortment of products.

It is worth mentioning that the oil processing industry, long considered as a conservative industry as regards the engineering processes applied, has adopted the catalytic processing procedures to such an extent that it can be said that at present it is almost completely centred on catalytic action.

Acknowledging the importance of commercial catalysis, it is not surprising that more and more people who desire efficiency, have chosen catalytic action as a means of improving the production of material goods. It seems that, to date, one problem has not been sufficiently elucidated and, that is how much human and material efforts is to be invested in the catalysis field.

There are some people who affirm that special care is required in committing oneself to the use of commercial catalyst due to the low rate of success in this field on a world-wide scale. In addition, it has been clearly demonstrated that the most important achievements have been obtained by strongly developed countries which could afford very expenditures that could later be redeemed either from the high volume of production obtained as a result of this commitment or by sale of licences and documentation. It would seem that they are right.

Others consider that by permanently contemplating the industrial potential difference between the large and small countries, sooner or later the difference would increase and the dependency on the achievements of others would be even more emphasized. Moreover, it will not even be possible to estimate at a legitimate value a certain achievement as there will be no actual possibility of comparing the new solutions. Their conclusion is that such problems should be studied more extensively in order to keep up with general progress. It would seem that they are very right.

However, by analysing the two points of view, it can be seen that even though the first point of view reduces effort at present, it very probably shall increase in the future, when, being obliged to modernize production, it shall be necessary to pay to the one who offers the new solution, a part of the expenses incurred by same for finding and developing the solution.

It is very probable that less would be paid for this purpose than would be spent by us to develop the same solution, but we would not gain the experience had by those who developed the new solution. For this reason, in most cases of this kind, even our intellectual training remains behind industrial development instead of being ahead of it.

Although we consider the second point of view as more reasonable, it must be taken into account that, no matter how high the enthusiasm might be of those who desire to introduce technical progress in production, effort should be estimated as function of anticipated economical effects, effects which must be sufficiently high for the human and material effort to be profitable. It is true that profitableness must also be regarded from an improvement working conception angle, development of scientific and technical activity level, which, in the final analysis, significantly increases staff competence and opens new horizons for the improvement of production. Even so, as

we are not discussing a didactic activity, it is not timely to over-emphasize this aspect but to acknowledge its part in promoting technical progress.

However, it is doubtful whether the economical effect would be favorable at a high effort and low production or low production value, especially when the quality of production develops rapidly.

Production of catalysts, especially those that require special preparation, is not an exception to the rules shown above. It seems, however, that there is a certain peculiarity and namely, that there are very few cases when processes are offered regarding the manufacture of catalysts.

Explanations could, of course, be found for this situation. One of these may be that at present there is a relatively small number of catalyst producers in the world, who are either large companies, or who are more or less using licences belonging to large companies. Generally speaking, the production capacities of these companies are large and it seems that the sales ensure a substantial profit. For this reason, the processes are not disclosed and probably also for the fact that they must be sufficiently versatile to easily assimilate, in fabrication, the new types of catalysts with improved performances. It could even be assumed that in certain cases the cost of research work to improve the performances of a catalyst would be much higher than the investments required to put into practice the new fabrication variant of a catalyst.

It is true that in the case of low tonnage catalyst production, there is a flexibility of the units partly due to the fact that certain phases of fabrication are achieved under a discontinuous process, a system that shall probably be less economical to apply in case production is increased.

Although the use of discontinuous processes somewhat allows the correction of some parameters resulting from errors in the development tests, this possibility should not be extensively used as a completely different catalyst could be obtained in the commercial unit than that which was considered when the process was confirmed. Generally, for this reason, development engineering must

affirm its contribution to research work regarding the elaboration of the catalysts, more so since the production of catalysts includes a relatively large number of phases, each one being strongly different as to type and complexity.

We must not lose sight of the fact that in most cases catalyst is probably fabricated to replace imported catalyst, operating conditions of which have been optimized by the supplier. In spite of appearances, the small performance differences of some of the catalysts fabricated by us may have strong effects in production, especially when production based on the respective catalyst has a high value.

Due to these reasons, the studies carried out for the elaboration of a commercial catalyst shall not have a practical value outside of the organic bond between the catalyst and the process for which it is intended. This is the reason for which the catalyst performances should not be estimated at the level of possibilities but at the level of necessities. In other words, the fact that a certain catalyst has given in a test unit, say an arbitrary pilot, good results or even better ones than those obtained in a commercial unit with an imported catalyst that is to be replaced, must be considered as a simple information. A more convincing test would be to simulate the phenomena of a commercial plant which would give a more realistic estimation of the catalyst's behaviour at a commercial level.

Although much progress has been made in this direction, from a scientific point of view, there are very few cases where, based on laboratory or even pilot test, the performance of the catalyst in an industrial plant can be precisely predicted. For this reason we believe that it is more prudent to consider the elaboration of a catalyst as concluded when a complete industrial charge has been experimented, with respect to quality and product yield performance obtained as well as period of service and regeneration possibilities.

Generally there are two aspects met in the elaboration of a catalyst :

Under the first aspect the catalyst, referring to a reaction or a specific process, is not sufficiently known neither as regards its fabrication nor service in the catalytic process. In this situation, research effort and risk are great.

Under the second aspect, the catalyst, especially its service, is known but the cost of the catalyst and eventually of the licence for using it, is not convenient for which reason it is preferable to elaborate one's own catalyst. In this case the situation is not complicated as there are catalysts and industrial processes which confirm the sure possibilities of elaborating variants of the procedure.

In this case research effort shall be less but there is a risk of solving the problem with a difference pertaining to quality as related to the catalyst used as a model, taking into account the fact that the party who has elaborated the first catalyst, being in an advanced stage, shall have the possibility of improving it thus ensuring first place in the technico-economical efficiency classification.

Although small and average countries prefer to approach problems pertaining to case II. in order to increase the chances to industrialise the research results, the complexity of the researchers' assignments is not greatly reduced, on the contrary only the preliminary stages are cut down.

Therefore, the problems are not greatly simplified from a organisational or technical point of view, personnel and research means at a corresponding level being required, as well as a simultaneous approach to the matter by the customer and designer as well as equipment manufacturer.

Table 1 shows typical stages required for preparing a solid industrial catalyst /5/, suggesting many possibilities by combining the work elements. The stages may be featured for each type of catalyst function or the process requirements. Thus, in

Table 2, several aspects are shown related to the preparation of an industrial catalyst for catalytic reforming. Although each stage of catalyst elaboration may be distinctly studied, it is absolutely necessary to take into account the existing interdependence between the various stages so that the effect of any modification in the procedure of preparing and testing of catalysts may be precisely established. Many times, on an industrial scale, a catalyst may be taken out of competition due to a difference of yield in the basic product on only 1-2%.

This statement may appear to be exaggerated. But if we look at an example things will become clear. Let us consider the manufacture of a reforming catalyst for a capacity of 2 million tons/year reformed gasoline with octane number 90. At a yield reduction of 2% for the same quality in the case of introducing the new catalyst, efficiency reduction shall be 20 mil. ton/year, figure that results from the difference in value between the gasoline of quality shown and gases reculted to the detriment of gasoline yield.

Improvement of this situation requires not only additional expenses incurred mostly on an industrial level but extra time as well in order to eliminate deficiencies found. Therefore, it results that the problem regarding the elaboration of a catalyst can be considered final only after the catalyst elaborated has been industrially experimented and thus after the process using it has been optimized.

Thus, it is very important that all concerned (researchers, designers, equipment manufacturers and customer) in solving these problems must coordinate their efforts.

Several examples regarding the fabrication of a catalyst, using active alumina as a support, obtained by the precipitation procedure, shall indicate certain aspects in connection with the above.

TABLE I

STAGES RELATED TO PREPARATION OF AN
INORGANIC CATALYST

Mature of catalytic constituents	Method of chemical elaboration and separation from reaction medium	Shaping	Thermal treatments	Special Chemical treatments	Regenerating and reactivating possibilities
<ul style="list-style-type: none"> -In the form of elements or combinations -Crystallized products, non-crystalline, gels, solutions -Used as such or supported 	<ul style="list-style-type: none"> -Precipitation, coprecipitation with temperature -Condition, concentration, time, pH. -Solid-solid reactions -Separation, interchange washing, transport. -Aqueous, under conditions specified by medium, pH, temperature, time. 	<ul style="list-style-type: none"> - Forcing - Tablets - Atomization 	<ul style="list-style-type: none"> -In atmosphere controlled by: air, inert gas, reducers, etc., with temperature and time control. 	<ul style="list-style-type: none"> -To increase certain special features. Can be done by treating with Cl₂, H₂, O₂, H₂, H₂O, etc. 	<ul style="list-style-type: none"> -To rebuild spent catalyst activity. The methods may be very varied.

TABLE 2
PROBLEMS IN RELATION WITH FABRICATIONS OF A CATALYST
FOR GASOLINE REFORMING AND ACETALIZATION

<p>Aspects related to the elaboration stages of a catalyst</p>	<p>measuring surface area and corresponding purity</p>	<p>Platinum dispersion Crystal stability</p>	<p>activity of test reactions to establish supporting qualities.</p>
<p>nature of aluminas used as a support and preparation procedure Alumina activation procedure</p>	<p>adsorption methods (BET etc.) and impurity dosage Arbitrary method of selective adsorption</p>	<p>CO, H₂, etc. chemisorption X-ray diffraction Electronic microscopy</p>	<p>activity of test reactions for hydrogenation and dehydrogenation.</p>
<p>special support treatments for acid treatment (Cr₂O₃, SiO₂) in view of catalyst finishing.</p>	<p>determination between hydrogenation-dehydrogenation balance and acid one Specification of acid centre nature.</p>	<p>Gas adsorptions measurable by: -colourimetry -thermo-gravimetry -I.R. and -special vibrations</p>	<p>activity for dehydrogenation and isomerization reactions. activity under special conditions for the control of catalyst stability.</p>
<p>physico-chemical properties required</p>	<p>measurements of catalyst properties</p>	<p>Catalytic properties of major interest</p>	

a. Precipitation of aluminium hydroxide gel from an aluminium salt solution

Usually the hydrogel is filtered but filtrability is very weak. Generally, at least 2 filtrations are required, one for the formed precipitate and the other or others, for the washed precipitate. In sizing the filtering equipment, suspension filtrability for each filtering operation must be taken into account as filtrability changes during the gel washing phases. It has been determined experimentally that filtering rates are reduced 3-4 times by the washing operations. However, certain preliminary preparations of the suspension may increase by several times the filtering efficiency, thus reducing investment costs. These must be utilized.

Another example, also for the alumina gel precipitation phase, can demonstrate what could happen if a designer would not respect an indication resulting from research work. Two reactants, one with basic and the other with acid properties, and rates in the order of 100/l, are contacted to obtain alumina hydrates. The importance of the pH, being known as well as contacting mode and temperature upon the catalytic support quality that is to be obtained, contacting practically at random is, nevertheless, allowed, and in order not to exceed the reaction temperature, action is taken upon the rate of one of the reactants instead of acting upon the cooling equipment. Keeping in mind the above considerations, unrepeatability of the hydrate properties and then of the catalytic supports, "is ensured".

In figures 1 and 2 is shown the effect of pH and reaction temperature upon the structural properties of the alumina hydrates /6,7/. It is observed that the existing differentiations in the hydrate properties are sensitive even at slight variations of the parameters shown, effecting at later stages the support or catalyst structure.

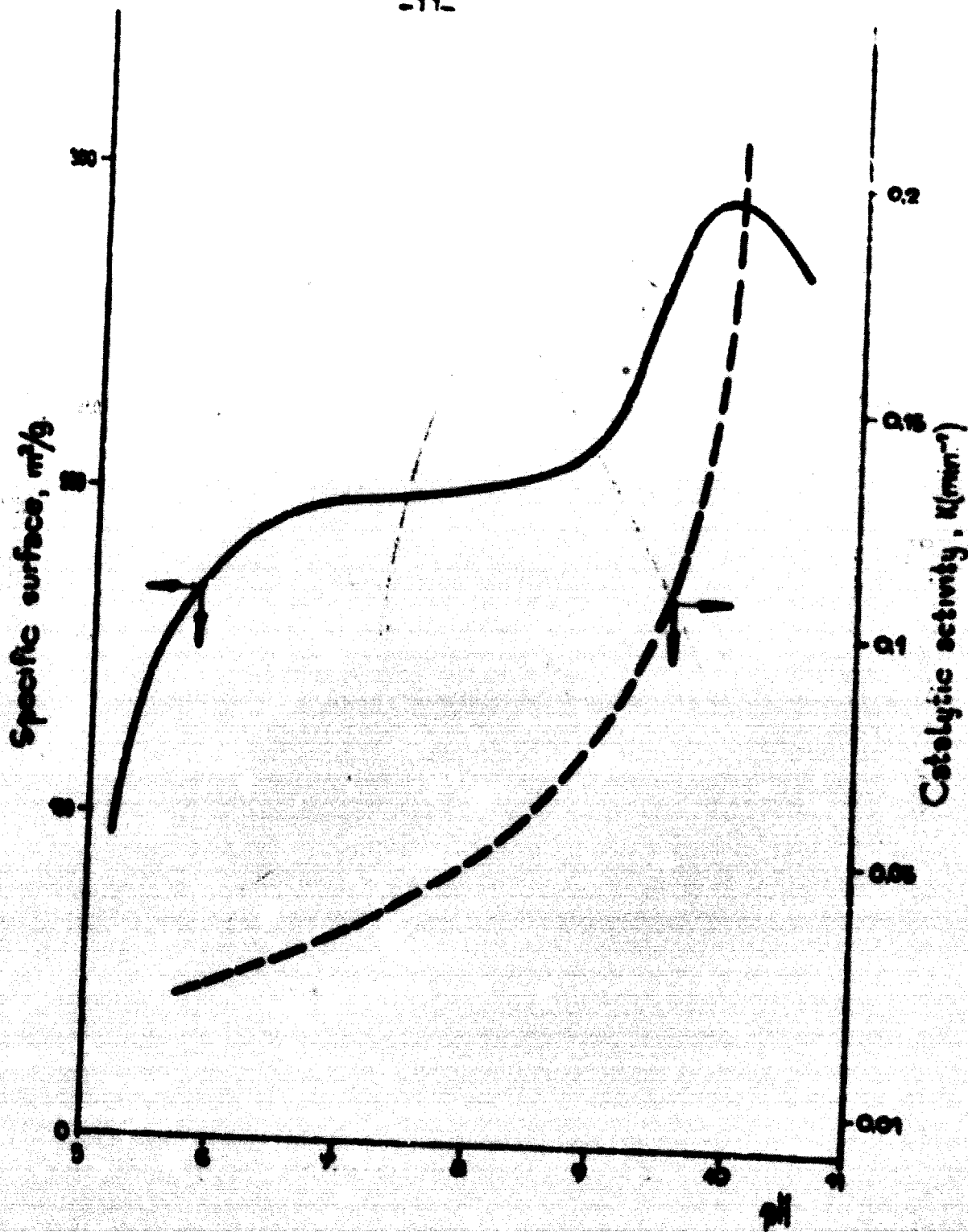


FIG. 1 - THE INFLUENCE OF PRECIPITATION pH ON THE SPECIFIC SURFACE AREA AND THE CATALYTIC ACTIVITY OF THE ACTIVATED ALUMINA IN THE REACTION OF HYDROGEN BURNING.

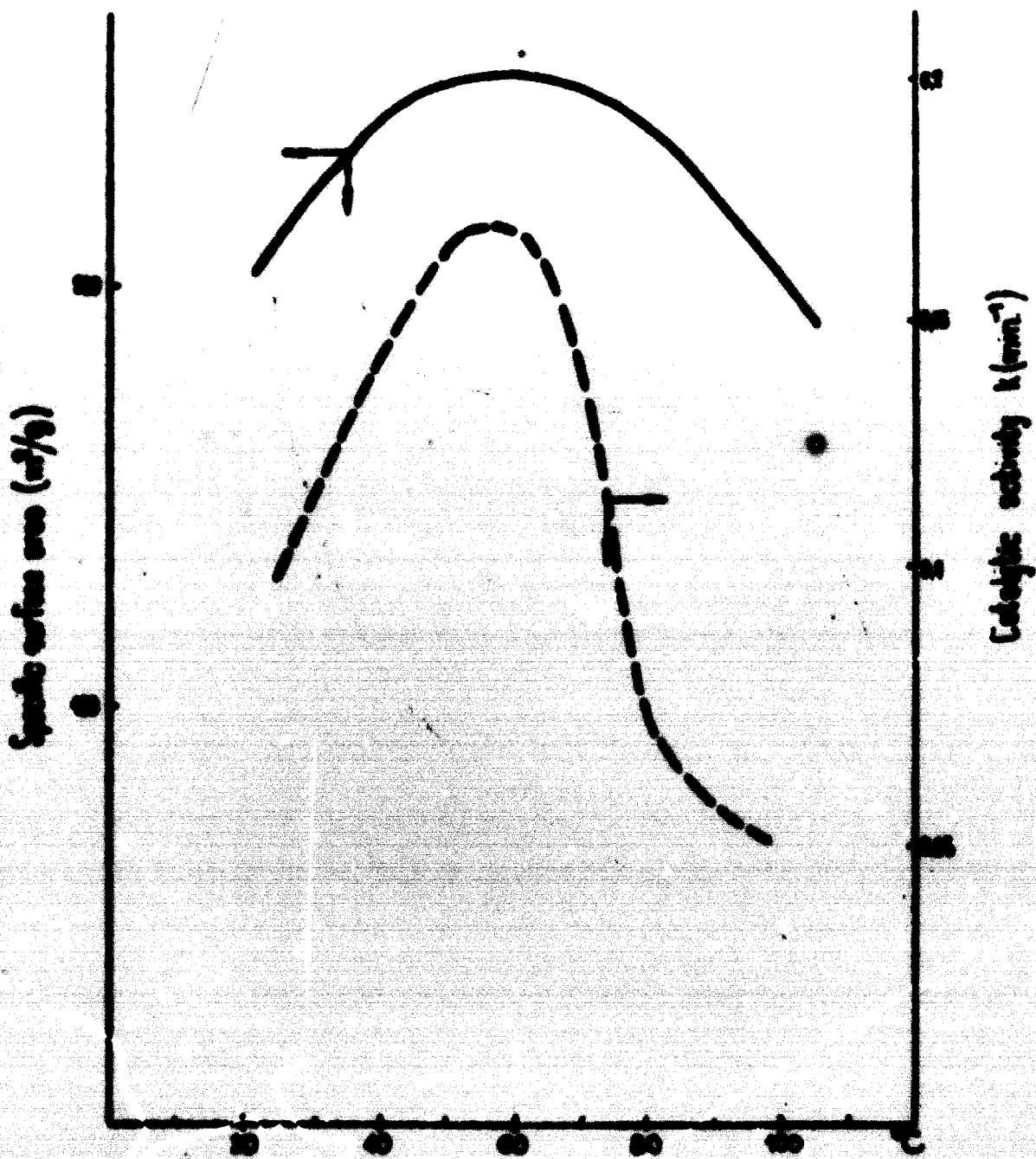


Fig. 2 - THE INFLUENCE OF PREPARATION TEMPERATURE ON THE SPECIFIC SURFACE AND THE CATALYTIC ACTIVITY OF THE OBTAINED MATERIALS OF THE REACTION OF HYDROGENAL NITROGENATION.

A suitable automation of the precipitation phase must not be considered in this case as a reduction of manpower but as a key element in the achievement of the process.

In addition, the control instrument must be placed in the weakest point of the operation and not some place where it shall detect average values of the parameters required. In other words, it seems that chemical engineering has a very important contribution more so as the chemical reaction is practically instantaneous and the reaction products are solids and solutions with a strong reciprocal influence.

Another example :

b) obtaining hydrated alumina by eliminating inter-particle liquid is another phase in the preparation of catalyst which impresses strongly its character upon the constitutive and structural properties of the catalyst.

It is known that, in most cases, function of the precipitation conditions, tri- and mono-hydrates are obtained which, in the dehydrating treatments, successively pass through a series of species in α -alumina (?). Transformation procedure is a function of initial structure, temperature, drying medium, calcination, etc. It is sufficient to present only one variant of such a transformation in order to see the importance of control which is also required at this stage. Table 3 shows the decomposition stages of aluminum hydrates by heating in dry air (c). It can be observed that although the final decomposition structure of any hydrate is alpha-alumina, the intermediate stages depend upon the initial hydrate structure as well as the temperature at which the transformation occurred. As regards the gamma and eta forms, more frequently employed as catalytic supports, it is observed that these require that the initial structure be either trihydrates or alpha-monohydrates but in no case beta-monohydrates which lead directly to the alpha form. It is understood that in

TABLE I
TRANSFORMATION POINTS OF SOME AMMONIUM BORATES

Alpha-trihydrate	$\frac{140^\circ}{260^\circ}$	Alpha-monohydrate	$\frac{280^\circ}{320^\circ}$	Gamma	$\frac{500^\circ}{550^\circ}$	Kappa	$\frac{1020^\circ}{1120^\circ}$	Theta	$\frac{1150^\circ}{1180^\circ}$	Alpha
Beta-trihydrate	$\frac{140^\circ}{240^\circ}$	Alpha-monohydrate	$\frac{250^\circ}{350^\circ}$	Eta	$\frac{500^\circ}{550^\circ}$			Theta	$\frac{1180^\circ}{1250^\circ}$	Alpha
		Alpha-monohydrate	$\frac{400^\circ}{450^\circ}$	Gamma	$\frac{850^\circ}{1050^\circ}$	Delta	$\frac{1080^\circ}{1120^\circ}$	Theta	$\frac{1150^\circ}{1200^\circ}$	Alpha
		Beta-monohydrate	$\frac{400^\circ}{450^\circ}$		$\frac{400^\circ}{450^\circ}$					Alpha

- Transformation conditions : One hour heating in dry air
- Top figures : temperature at which the following phase begins its formation (%)
- Lower figures : temperature at which transformation is complete (%)

some cases alpha-alumina is the one required but it is known that only in cases when special structural properties are not requested as a catalytic support.

In order to have a complete picture regarding the influence of the hydrate initial structure upon the structural properties of the catalytic support, the evolution of the alumina's specific area obtained by the decomposition of alpha-trihydrate and alpha-monohydrate function of temperature and dehydrating medium (B) are shown in figure 5. It can be observed that while the specific area of the alpha-monohydrate practically does not undergo any modification up to 400°C, the specific area of alpha-trihydrate undergoes a maximum modification in the interval shown.

In tables 4 and 5 are shown also other structural modifications of the above mentioned hydrates, indicating essential differences between the behaviour of mono- and trihydrates (B).

From the above it can be seen that, function of the properties desired for the catalytic support, it is absolutely necessary that the procedure, for obtaining hydrogels, respectively, hydrate or hydrates, must be clearly outlined and repeatable in all details.

In the first place, it is the researcher's duty to make up a research schedule which would permit the development of the process up to establishing the parameters for the industrial plant. The parameters developed in the laboratory must be considered only as a preliminary phase which would prove the feasibility of such a product but not the manner in which it shall be obtained on an industrial scale. Arbitrary repetition of the process on a pilot scale shall not give more information. On the contrary, in many cases, the pilot units are so constructed that more problems are raised by these ^{they} ~~units~~ are required to solve and, at the end, the industrial plant is designed without having the necessary data in spite of having a process pilot unit.

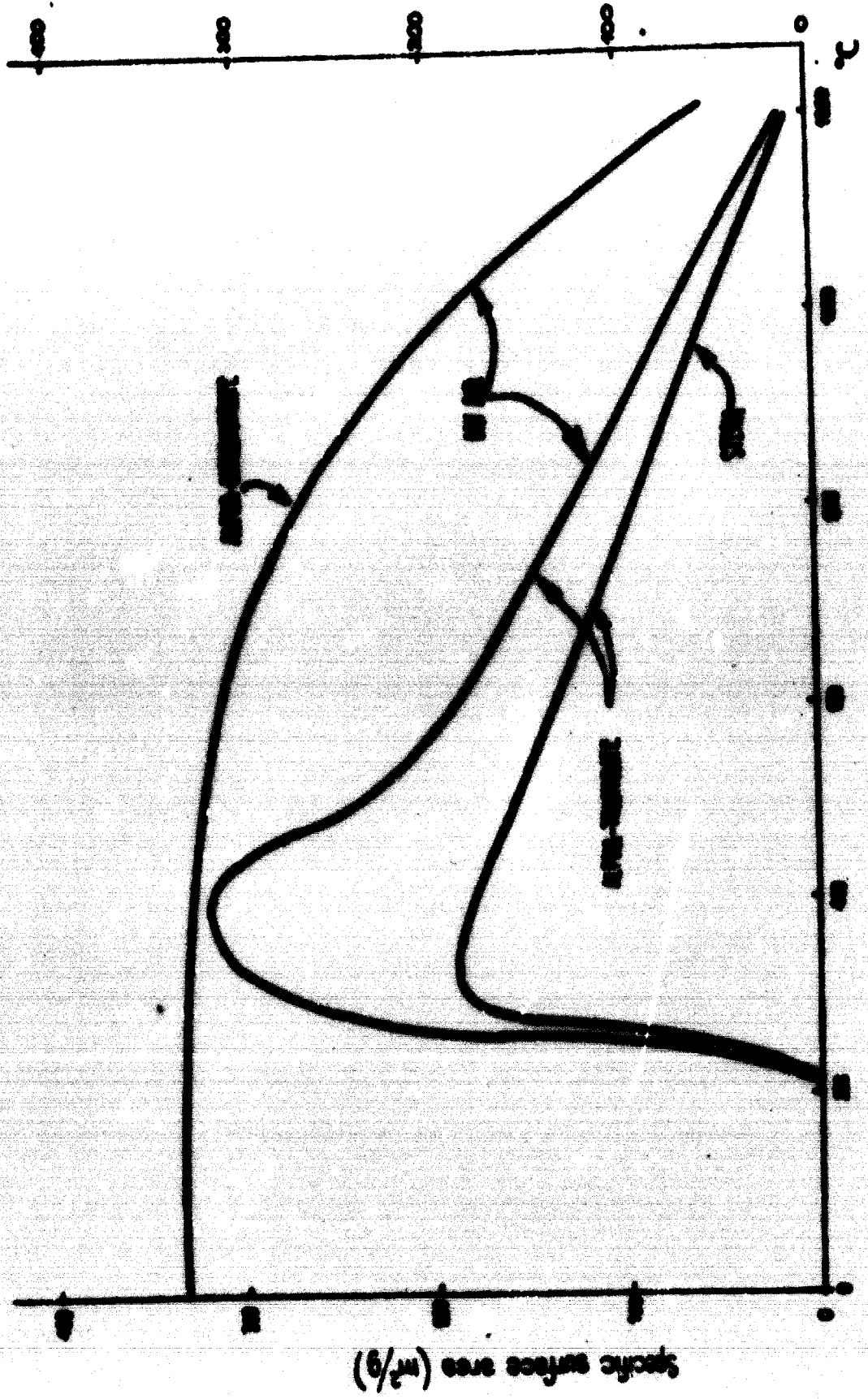


FIG. 3.- EFFECT OF TEMPERATURE ON THE SPECIFIC SURFACE AREA OF THE SAMPLE.

TABLE 4

ALPHA-RADIOLYTIC TRANSFORMATIONS

Characteristic	Chamber temperature					
	2000°	2050°	2080°	2100°	2500°	4000°
H ₂ O/Al ₂ O ₃ Ratio	3.0	2.5	2.0	1.5	1.0	0.1
Density, with He, g/ml	2.4	2.4	2.4	2.5	2.6	3.0
Density, with H ₂ , g/ml	2.3	1.9	1.7	1.6	1.6	1.9
Pore volume, ml/g	0.025	0.114	0.175	0.222	0.248	0.203
Specific area, m ² /g	negligible	5	50	125	250	225
Pore radius, Å	...	400	70	36	20	18

TABLE 5
ALPHA-ALUMINA OXIDATION TRANSDUCATION

Characteristics	Chamber temperature	255°C	355°C	450°C
H ₂ O/Al ₂ O ₃ Ratio	1.5	1.0	0.5	0.1
density, with H ₂ O, μ/ml	2.4	2.4	2.4	2.5
density, with H ₂ O, G/ml	0.9	0.8	0.6	0.65
Pore volume, ml/g	0.71	0.85	0.63	0.79
Specific area, m ² /g	310	310	310	285
core radius, μ	41	54	74	59

c) Integration of active components and catalyst finishing

Due to the numerous problems related to preparation of the support, in many cases, the researchers are tempted to limit their attention to the subsequent phases of active component integration and catalyst finishing. In the cases in which the proportion of the active components as related to the support is high, this aspect is less important, it seems that the situation changes when the active component concentration is low, as in this case, interdependence between the support and active components plays a decisive part upon the catalyst performances.

As an example bifunctional catalyst may be considered with platinum or platinum associated with other elements where the active metal content is in the order of 0.2-0.6%.

When using the impregnating method, complications arise in extrapolating laboratory results to an industrial scale, especially due to the strong adsorbant properties of the support resulting in an uneven distribution of the platinum in the catalyst. The adsorption and diffusion phenomena as well as intergranular flow must be thoroughly studied in order to design and size the proper equipment. There is no information given in literature regarding impregnation process engineering. Moreover, this problem must be solved in direct connection with the type of support and catalyst finishing method (forcing, tableting, atomization).

Usually, in order to ensure an even impregnation, a so-called competitor is used which is in fact another solute, which, in certain concentration, reduces the relative capacity of platinum compound adsorption on the support surface, promoting the penetration of the platinum compound into the granule depth. Determination of adsorption constants on the given support, for the platinum compound as well as for the competitor solute (acid, salt, etc.) represents the first step in elaborating the data required for designing the industrial equipment.

In figure 4 is shown the influence of several competitors upon the activity of a platinum catalyst in a cyclohexane dehydrogenation reaction to benzene /9/.

It has been ascertained that the effect of the competitors depends on their nature as well as the content of the active component, in this case platinum. They can stimulate or inhibit the catalyst activity, which, of course, necessitates only a severe selection of the competitor but also checking, in time, the catalyst's behaviour. Under any circumstances compounds which could potentially endanger the catalyst stability must be avoided, even though, apparently, they present certain advantages.

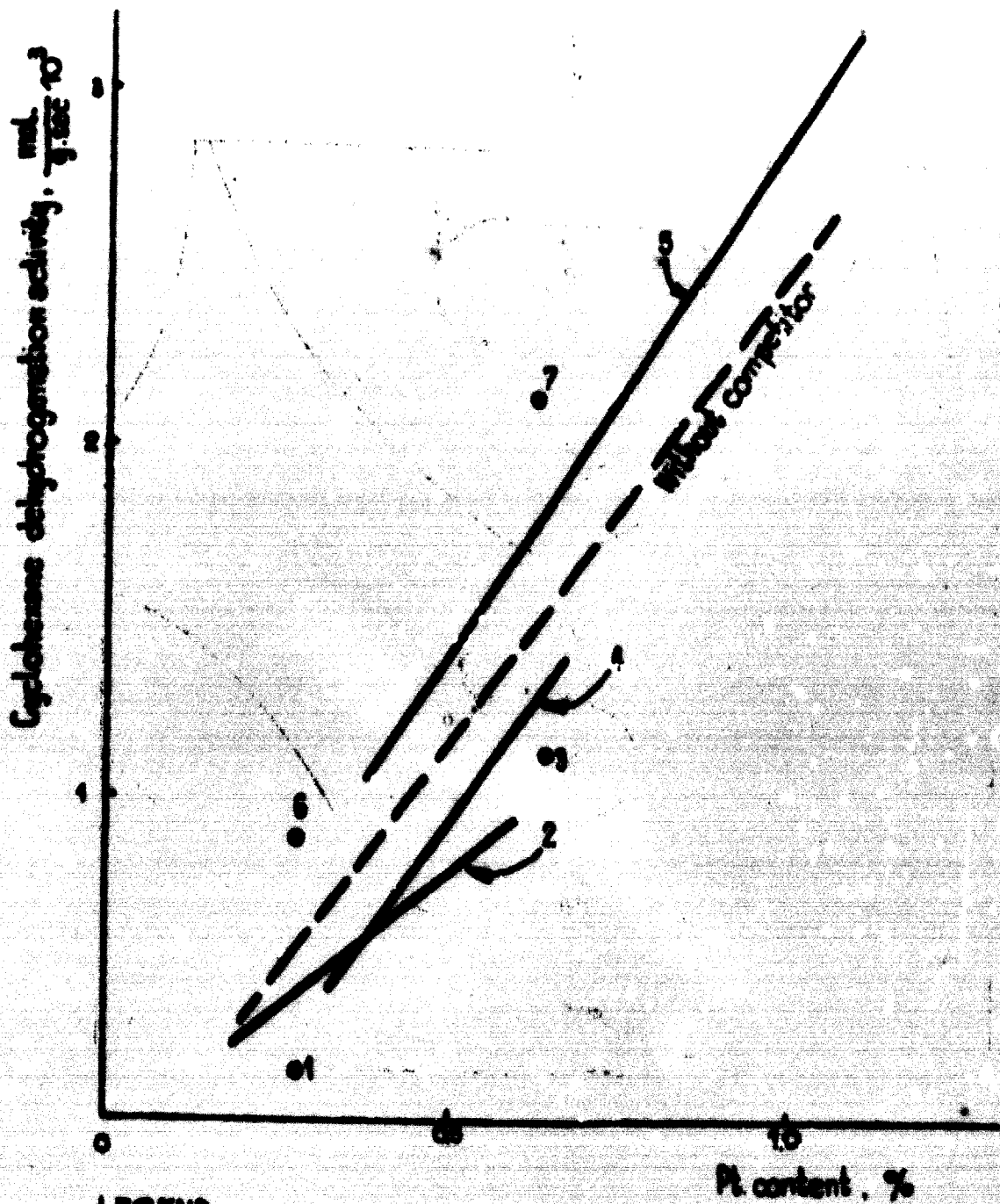
Thus in the example quoted it is shown that sodium nitrate can also be a good competitor although it is known that alkaline elements are not desired in the platinum type catalysts for gasoline reforming.

A premature conclusion in this respect may be very detrimental to the catalyst performances during operation, for which reason, in the elaboration of any industrial catalyst, a long testing period is absolutely necessary.

Nevertheless, it would mean loss of time and waste of material effort to recommend for such tests catalyst which showed "certain promising symptoms" on the pretext that we desire to be efficient and to shorten research time.

The above conclusions are, of course, also valid for tableted catalysts. In this case impregnation is done before the tableting operation in certain grained powder. Although the problems related to the absorption of active components is simplified, other complications arise due to the use of additives before as well as during the tableting operation, which, in some cases, influences, in a large measure, the catalyst properties.

As an example, in figure 5, is shown schematically the relative distribution of the density in the mass of a well elaborated cylindrical tablet /10/. It has been ascertained that the distribution of density varies considerably depending on the



- LEGEND:
- | | |
|-----------------------------------|--------------------------------------|
| 1. HNO ₃ | 5. Al(NO ₃) ₃ |
| 2. HCl | 6. Ni(NO ₃) ₂ |
| 3. NH ₄ Cl | 7. NH ₄ NO ₃ |
| 4. H ₂ SO ₄ | ----- without competitor. |

FIG. 4. THE INFLUENCE OF IMPREGNATING COMPETITORS ON THE CYCLOHEXANE DEHYDROGENATION ACTIVITY OF A PLATINUM CATALYST.

DIRECTION OF COMPRESSION

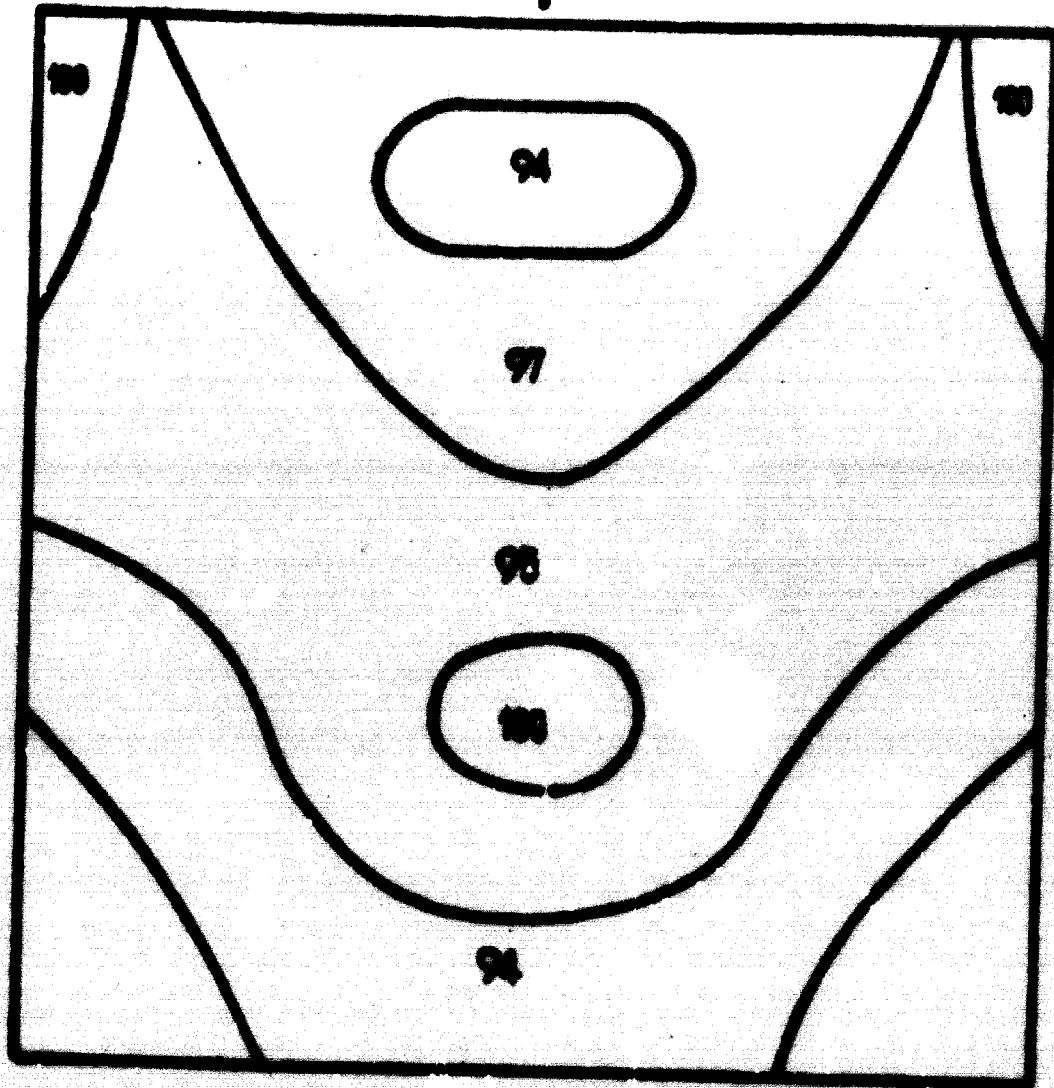


FIG. 5.- DISTRIBUTION PATTERN OF CATALYST DENSITY WITHIN THE PELLETS. (RELATIVE UNITS)

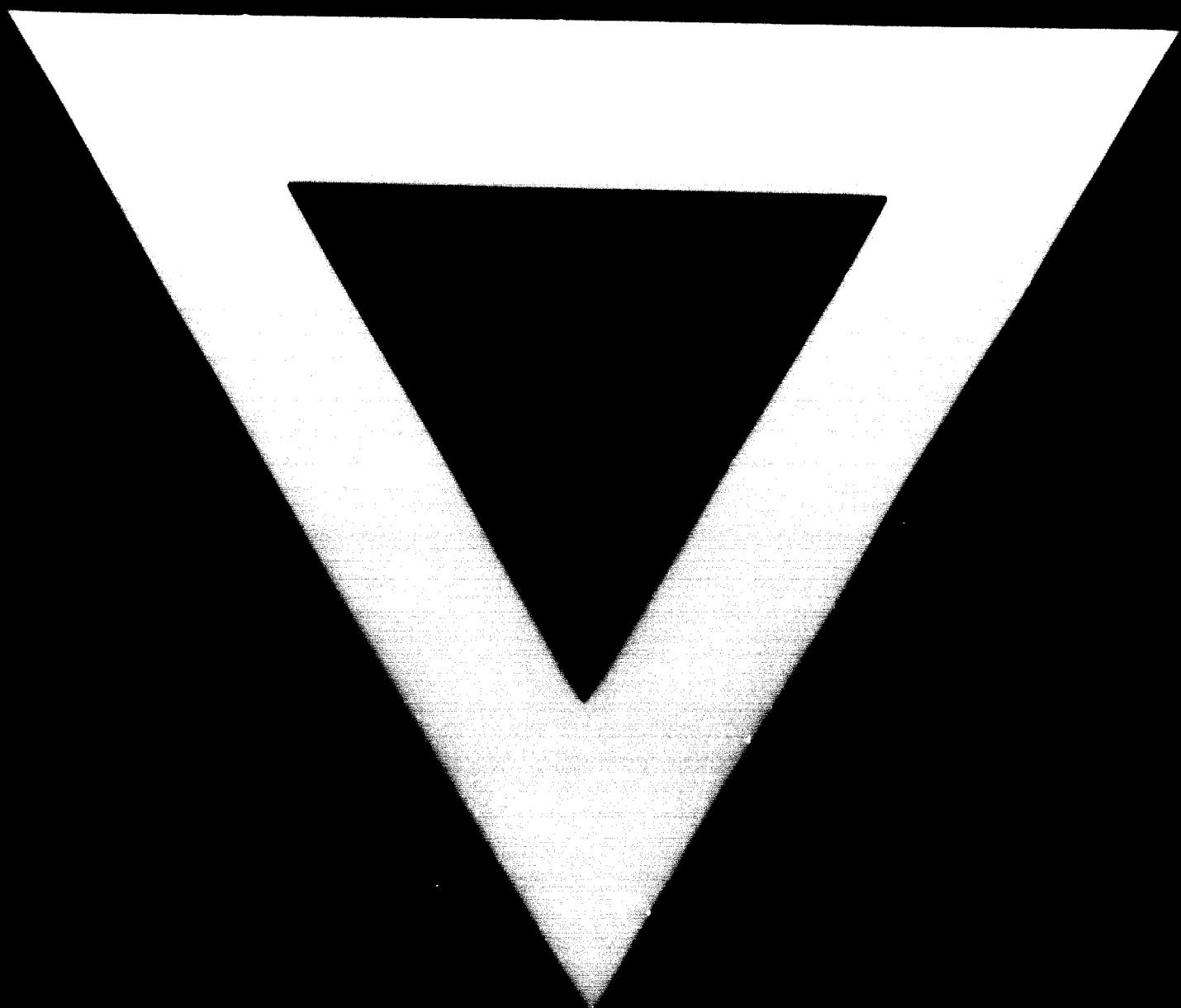
preparation of the granular material to be tableted as well as on the type of tablet and tableting machine.

Thus, the tableting machine shall not be selected simply by comparing the prices quoted in various offers, but adaptation of the machine characteristics to the catalyst elaboration concept shall be taken into consideration, for which reason the type of machine must be selected by the researcher and not the designer.

The few aspects given in this paper were selected from industrial practices as well as specialized literature. The purpose of this paper was to emphasize certain problems not fully approached to date and which must be the object of future studies in view of fabricating a catalyst that would fulfill up-to-date requirements.

REFERENCES

1. Haensel, VI - Chemistry and Industry, April 8, 1967
2. De Boer - Proceedings of the IInd International Congress of Catalysis, Paris, 1960.
3. Boreseev - Proceedings of the IIIrd International Congress of Catalysis, Amsterdam, 1964.
4. Haensel, VI - Proceedings of the III-rd Symposium on Catalysis, Alberto, Canada, 19-22 October 1969
5. Johnson, M, Hooi, J. - Journal of Catalysis, 10, 1968
6. Rödel, von K., Sonntag, H. - Zeitschrift für anorganische und allgemeine Chemie, Band 343, 1966
7. Ala Nicolescu, Maria Grăia and I.V.Nicolescu - Chemical Journal, vol. 10, December 1965.
8. Newsome, J.W., Heiser, H.W., Russell, A.S., Stumpf, H.C. - Technical report "Alumina Properties" Aluminum Co. of America, Pittsburgh, 1960.
9. Russel Mastman - Industrial and Engineering Chemistry, vol. 51, No. 8, August 1959.
10. Treina, F., Pernicon, N - Proceedings of the Xth International Congress on Industrial Catalysis, Milano, May 19-21, 1969.



16. 7. 74

