Leuna Works - February 14, 1944

REPORT ON THE DRYING OF DEHYDROGENATION CATALYST. (BUTANE DEHYDROGENATION).

It has been found during the operation of the alkylation plant that sulfuric acid consumption is dependent on the dehydrogenation temperature during dehydrogenation of n-butane to butylene, since the butadiene concentration in the butylenes is increased when the dehydrogenation temperature is raised. Lowering of the dehydrogenation temperature was made possible by changing the reactors with respect to distribution of flue gas and catalyst and by shortening the active life of the catalyst. Laboratory investigations which had been carried out several years ago have shown that a moisture concentration exceeding 0.1% by vol. in the butane has a detrimental effect on the dehydrogenation. Continuous analytical control of the purity of the n-butane used as feed stock for the dehydrogenation unit always indicated values of 0.03 - 0.05% by volume of moisture which are far below the limit of permissible concentration. However, a second possibility of moisture entering the dehydrogenation gas had to be considered.

The highly active catalyst could pick up moisture at 1 point during its moving cycle and release the moisture during dehydrogenation. It has been observed in pilot plant experiments that the dehydrogenation catalyst picked up moisture on the way from the regenerator to the reactor and that subsequently the conversion was decreased to a considerable extent.

Independent from this finding, moisture determinations have been carried out in the plant at various points of the catalyst cycle. From the results of these determinations it was concluded that the catalyst absorbs, on the average, 0.7% moisture in the regenerator. From this value it can be calculated that under operating conditions the moisture content of the dehydrogenation gas in the dehydrogenation step will rise to 0.25 - 0.3% by volume, due to the moisture given off by the catalyst and picked up by the butane which thereby reaches a moisture content above the permissible limit.

Figure 1 shows the moisture content of the catalyst in the various stages of its cycle. The catalyst containing a carbon deposit leaves the reactor almost dry and does not pick up any moisture while in the conveyor on the way to the regenerator since its absorptive capacity has been considerably lowered by the carbon deposit. The regenerated catalyst leaves the regenerator with a moisture content of about 0.7% by weight and picks up in the conveyor an additional 0.1% by weight. The absorption of moisture by the catalyst in the regenerator is due to the moisture concentration of about 5% in the recycled regeneration gas which is caused by the admixture of fuel gas and by the combustion of hydrocarbon compounds present in the carbon deposit. In a small-scale experiment it could be confirmed that dry regenerated catalyst on treatment with nitrogen containing about 5% by volume of moisture picked up about 0.7% moisture at the average regenerator temperature of 797°F. Furthermore, it can be concluded from the results of the experiments on catalyst drying that at the dehydrogenation temperature and at a space velocity of 900, the catalyst is almost completely dry which means that it had to release its moisture to the butane gas. The absorptive capacity of the regenerated catalyst is indicated by the fact that the moisture content of a catalyst sample after storage in the air for 24 hours rises from 0.7 to 6.3% by weight.

Soon after starting the alkylation unit, it was found that high dehydrogenation temperatures must be avoided in order to keep sulfuric acid consumption

down. Using lower conversions and lower dehydrogenation temperatures led to a decrease in the amount of carbon deposited on the catalyst; the regeneration of the catalyst, therefore, could only be carried out by the addition of larger amounts of fuel gas. This led to operating conditions which increased the moisture content of the regeneration gas. It was subsequently attempted to detect the calculated moisture concentration of 0.25 - 0.3% by vol. in the reaction gas of the dehydrogenation unit. However, water determinations by the magnesium nitride method made on dehydrogenated butane always gave values below 0.1% by vol.

In small-scale experiments it was found that only 30 - 40% of the original moisture content could be detected in nitrogen containing about 0.6% by volume of moisture, when the moist nitrogen, together with 10% of butylene, was passed over the dehydrogenation catalyst at 932 - 1,022°F. The subject method for the determination of water, therefore, always gives low values in the presence of olefins or diolefins.

The following laboratory tests were carried out in order to obtain design data for a drying plant:

Several preliminary tests were made for drying the catalyst by passing nitrogen at higher temperatures over it and the results obtained are given in Figure 2. They indicate that at a low nitrogen space velocity very high temperatures are required for complete drying. With the small amount of catalyst (50 cc.), of a moisture content of about 0.7% by weight, measurement of the high experimental temperatures was not very accurate. The drying time required was 1 hour or, including the heating time, 1.5 hours; in the drying experiments under vacuum, the drying time itself was 1/2 hour and the heating time 1 hour. Drying of the catalyst in the plant can only be carried out at temperatures below 932°F. in order to avoid damage to the catalyst by heating it above the dehydrogenation temperature. According to the results of preliminary tests, considerably higher space velocities are required.

Drying of the catalyst was subsequently tried in reactors of 100 cc. catalyst capacity and the effects of nitrogen space velocity, temperature, time, and moisture content of the drying gas were investigated. The effects of the moisture content of the catalyst on the drying conditions have not been investigated since only the drying of regenerated plant catalyst with a moisture content of 0.7% by weight was of interest and only this catalyst was used in all experiments. The test was continued for 2 hours, which includes 1/2 hour of heating time, since this corresponds to a drying time which could be used in the plant. Figure 3 shows the results of experiments on the effect of temperature and space velocity of nitrogen on drying of the catalyst; it can be seen that at 932°F. a space velocity of 600 volumes of nitrogen per volume of catalyst per hour must be maintained in order to dry the catalyst completely in 2 hours.

The effect of the moisture content in the nitrogen used for drying is shown in Figure 4; these experiments were carried out under the same conditions as listed above. It is seen that the moisture content of the nitrogen must not exceed 0.1% by vol. in order to obtain complete drying under the conditions chosen. The effect of the drying time at 932°F, and a space velocity of 600 can be seen in Figure 5, according to which 65% of the water present can be driven out after 1 hour, including 1/2 hour heating time, whereas 2 hours are required to obtain complete dryness. The 2 experiments were carried out in order to remove the entire amount of water present in the catalyst. They indicate that after the removal of the adsorbed water at 932°F., still more water is released from the catalyst by heating to 1,112 - 1,472°F.; the latter quantity of water must be considered as chemically bound or water of hydration and amounts to only about 0.2% by weight.

In another experiment the temperature was raised to 2,372°F., which led to the well-known rose color of the catalyst, but no more water was released. The water of hydration, therefore, is given off at 1,112 - 1,472°F. and should be distinguished, in this connection, from the adsorbed water.

The following experiments were carried out in order to study the effect of catalyst drying on the conversion in the dehydrogenation of n-butane in the plant.

1. Nitrogen was introduced into the regenerator below the pocket valve arrangement in order to dry the catalyst during movement through the pocket valves. Even after shutting off the cooling water for the pocket valves, no drying effect was obtained since the catalyst was cooled by the nitrogen from the reactor temperature of 795°F. to 572°F. at a space velocity of 300 - 400 volumes of nitrogen. According to the laboratory tests under these conditions no drying of the catalyst can be expected. The improved drying effect obtained in other experiments by increasing the space velocity was balanced by increased cooling of the catalyst.

2. The upper catalyst hopper of one reactor was provided with a tail gas line in order to heat the catalyst in the upper hopper to 842°F. and this was accomplished by using part of the preheated butane. The high pressure drop through the catalyst in the hopper prevented the application of sufficiently large quantities of butane.

3. Catalyst drying by means of nitrogen in a reactor was successful. The operation can be visualized from the attached drawing. Instead of the usual transfer period during which the regenerated catalyst is passed to the reactor by means of conveyor 1 and, simultaneously, the used catalyst is transferred to the regenerator by conveyor 2, 2 moving periods are introduced. In the first period the regenerated catalyst is passed into the dryer and the used catalyst is passed to the regenerator from the reactor as usual. In the second period the dried catalyst from the dryer is transported to the conveyor 2 by means of conveyor 1 using a simple switching arrangement and is then introduced in the reactor. This process for catalyst drying should only be considered as temporary solution; it has the following disadvantages:
   a. The dried catalyst leaves the dryer-dehydrogenation reactor cold because of cooling in the pocket valve arrangement and again picks up moisture while in the conveyor (approximately 0.1% by weight).
   b. Catalyst and nitrogen used for drying flow in parallel. The nitrogen leaves the dryer with about 0.6% by volume of moisture (calculated as well as determined analytically in plant tests) and the catalyst, therefore, is not completely dry; it contains still 0.2 - 0.3% by weight of water.
   c. When 2 reactors are used with 1 dryer, the residence time of the catalyst in the reactor is doubled, even when the dryer is operated as fast as possible.
   d. The process requires additional capacity for reactors.

In the experimental runs the dryer was operated with 35,314 cu. ft. of nitrogen per hour and a temperature of 977°F.; this corresponds to a space velocity of 1,400 volumes per volume of catalyst per hour. The residence time of the catalyst in the dryer was 2.5 hours. The effect of catalyst drying on the reactor is shown in Figure 6.

The first period of the experiment corresponded to the operating condition of the reactor without catalyst drying. In the second period the dehydrogenation temperature could be lowered by about 30° by preliminary drying of the catalyst. At the same time, the conversion rose from 17.5 to 20%. When the dehydrogenation temperature was raised again by 20°F., the conversion further increased to 22.5%. The fourth experimental period was a repetition of the second, yielding the same result, and the process was consequently operated under these conditions. When a second reactor was used with the same dryer, the same favorable effect of catalyst drying on conversion was observed as with the first reactor.

On the basis of these experimental results, the entire dehydrogenation unit has been operated in the way described for several weeks. 4 reactors with 2 dryers and 2 regenerators are operated; 2 reactors are always connected with 1 dryer and 1 regenerator. 80,628 - 88,000 cu. ft. of nitrogen per hour are required. The operation of the drying process in the plant led, on the average, to a lowering of the temperature by 30 - 40°F. in the reactor. At conversions of 18 - 20%, the dehydrogenation yield increased from 70 - 75% to 80 - 86% at the low catalyst temperature. The acid consumption in the plant decreased from 45 to 20%. The results are shown in Figure 7.

The effect of catalyst drying on the operation of the dehydrogenation unit and acid consumption in the alkylation unit was confirmed by shutting down and restarting the drying unit. This solution of the problem of catalyst drying can only be considered as temporary. It is planned to install a drying unit in the dehydrogenation plant. Each reactor shall be equipped with 1 drying oven arranged above the catalyst hopper. Nitrogen is circulated by means of a blower which feeds all dryers.

FIGURE 1

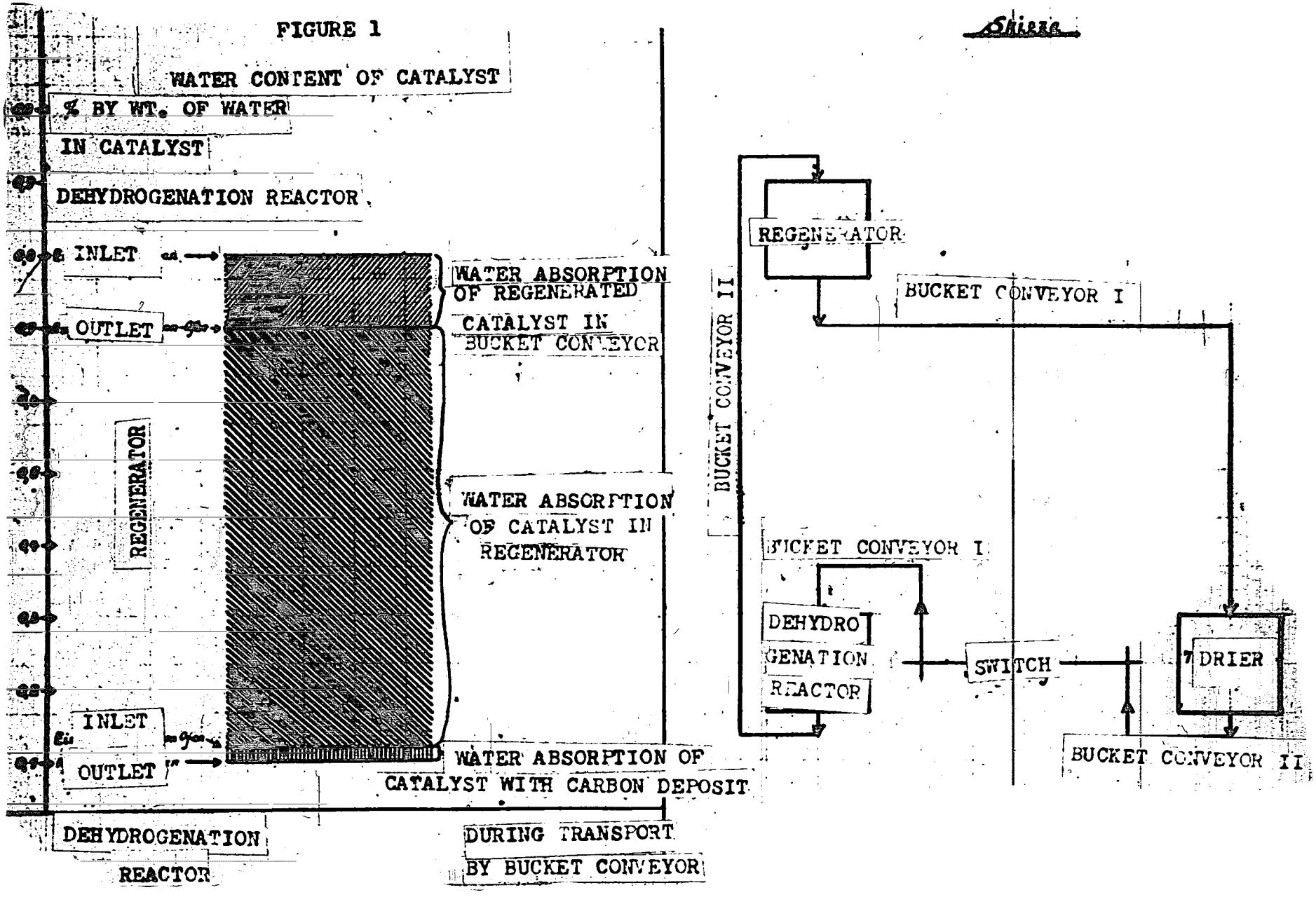
WATER CONTENT OF CATALYST
% BY WT. OF WATER IN CATALYST
DEHYDROGENATION REACTOR
INLET
OUTLET
REGENERATOR
INLET
OUTLET
WATER ABSORPTION OF REGENERATED CATALYST IN BUCKET CONVEYOR
WATER ABSORPTION OF CATALYST IN REGENERATOR
WATER ABSORPTION OF CATALYST WITH CARBON DEPOSIT DURING TRANSPORT BY BUCKET CONVEYOR
DEHYDROGENATION REACTOR
REGENERATOR
BUCKET CONVEYOR I
BUCKET CONVEYOR II
BUCKET CONVEYOR I
DEHYDRO GENATION REACTOR
SWITCH
DRIER
BUCKET CONVEYOR II

FIGURE 2

DRYING TESTS

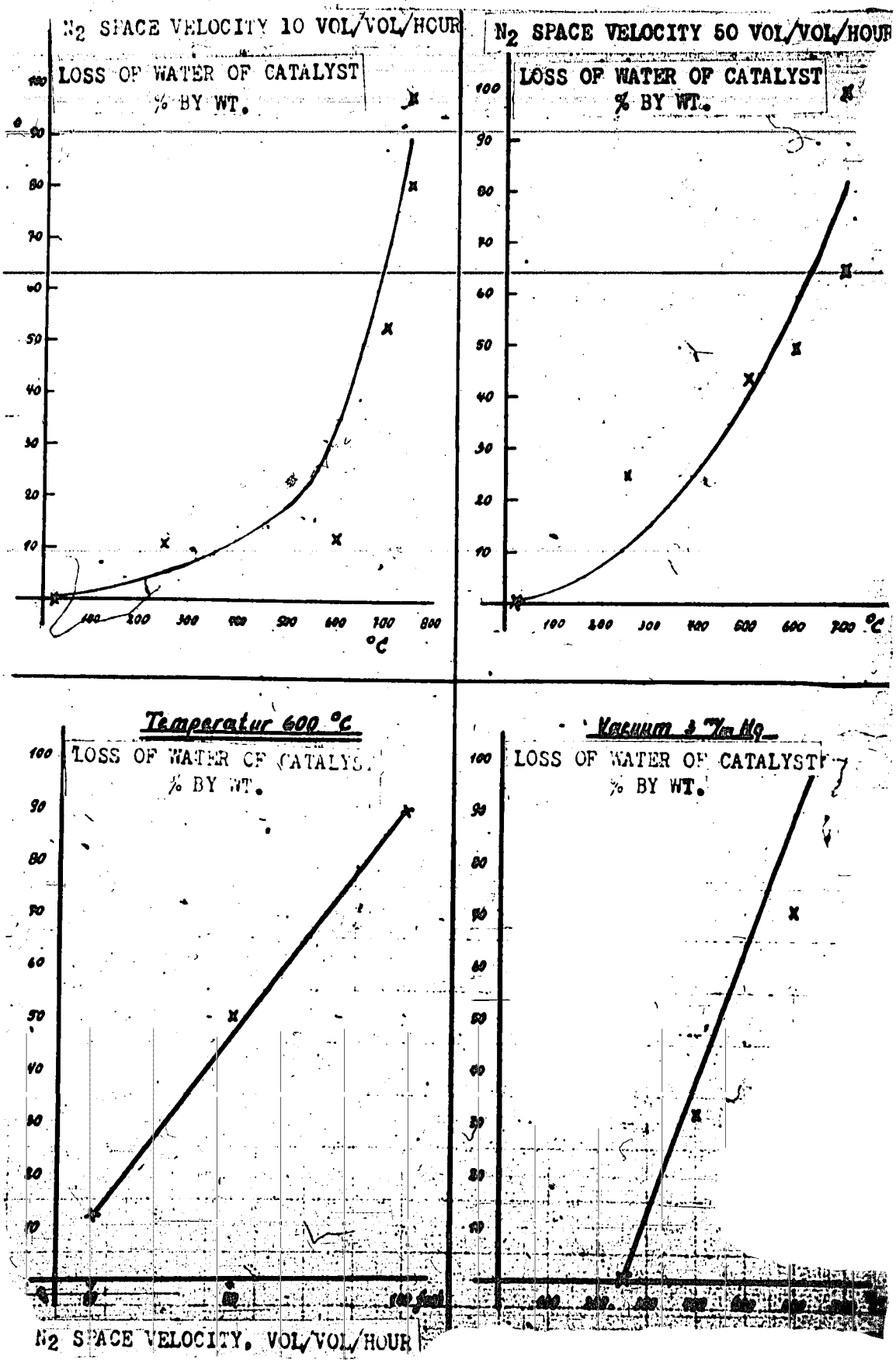

FIGURE 3

DRYING TESTS

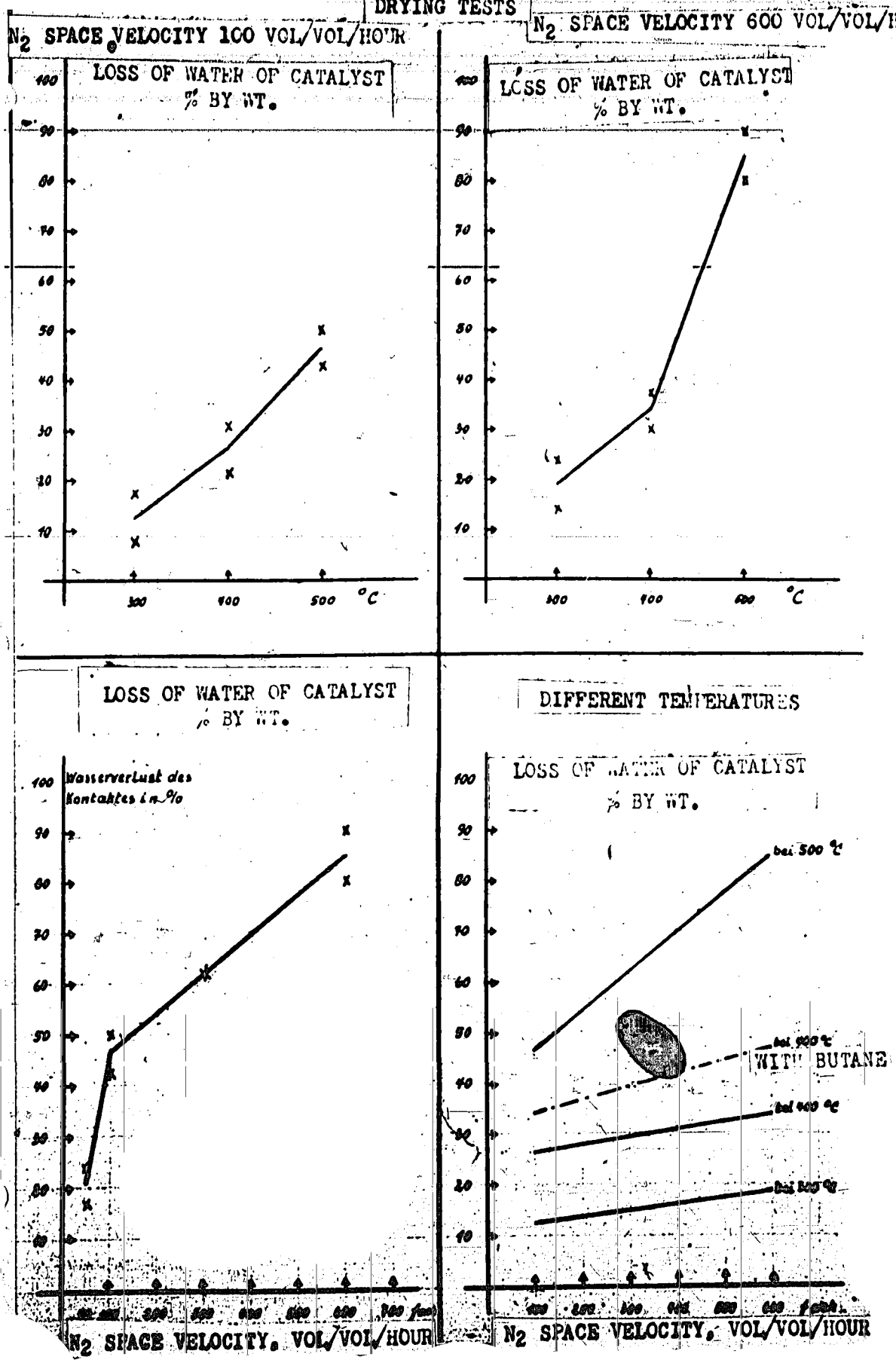

FIGURE 4

DRYING TESTS

MOISTURE CONTENT IN NITROGEN FOR DRYING

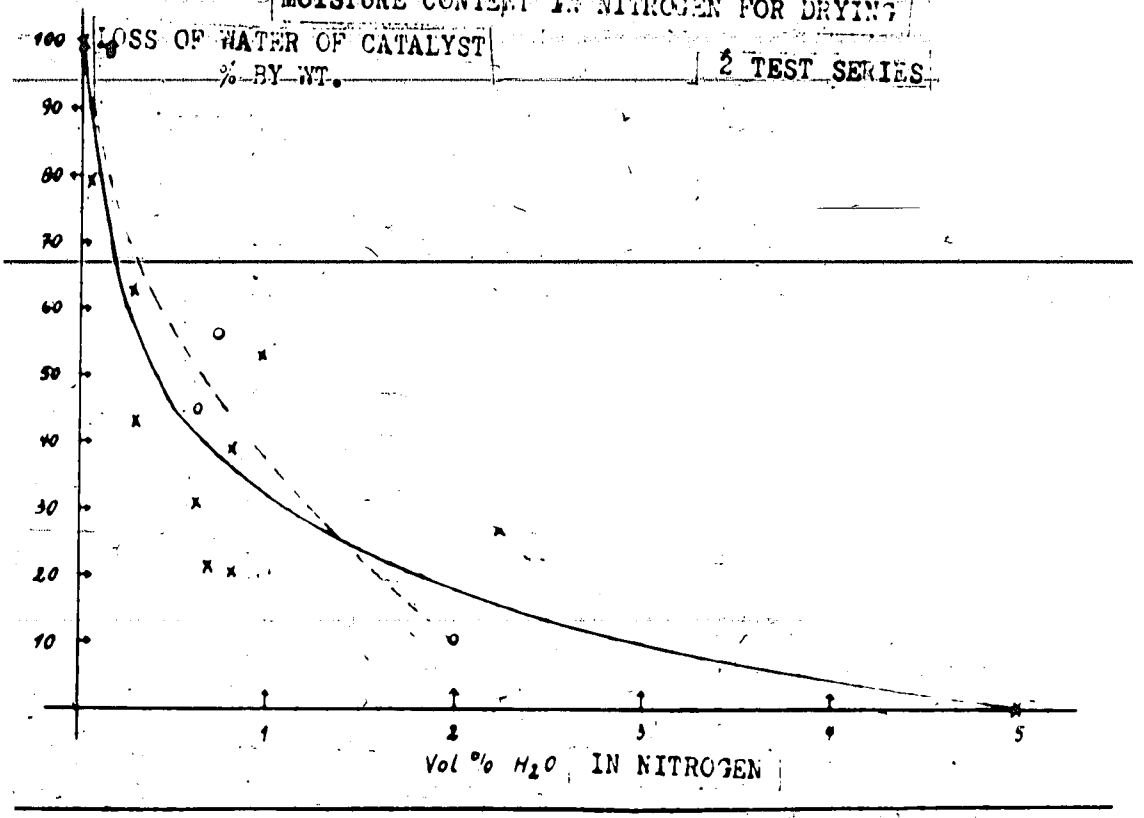

FIGURE 5

ADSORBED WATER AND WATER OF HYDRATION

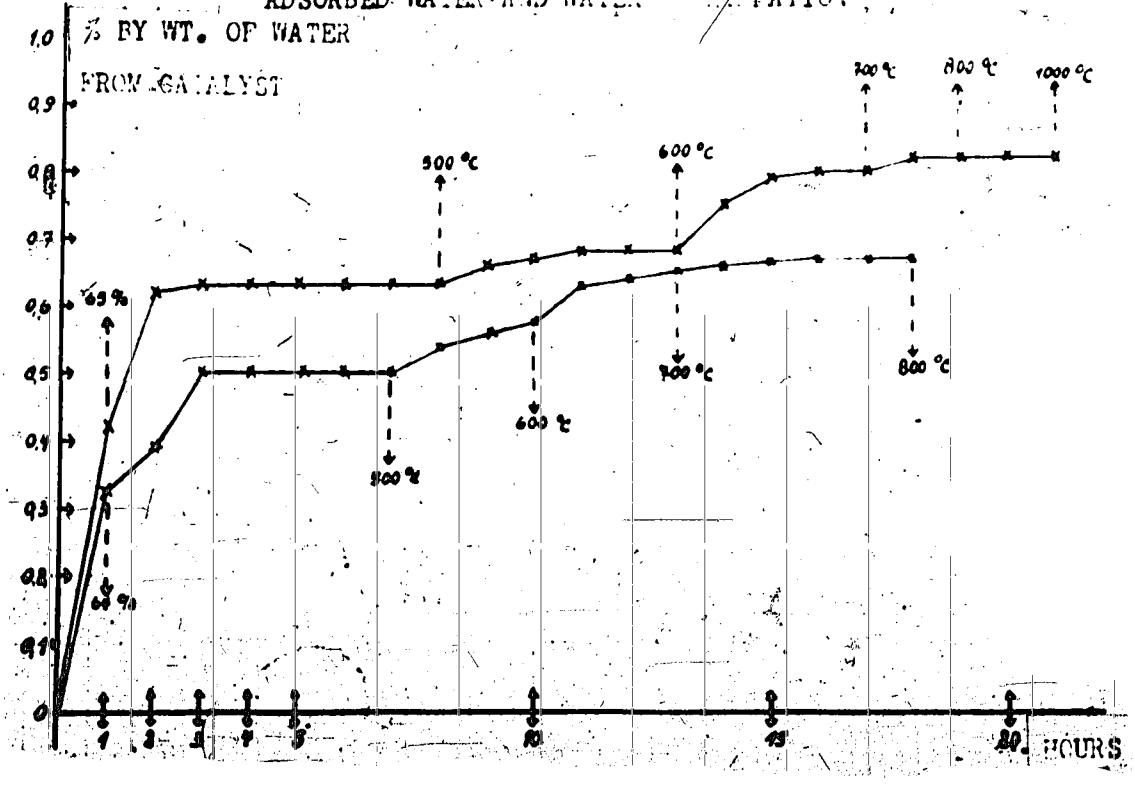

FIGURE 6

EFFECT OF CATALYST DRING IN PLANT TEST RUNS

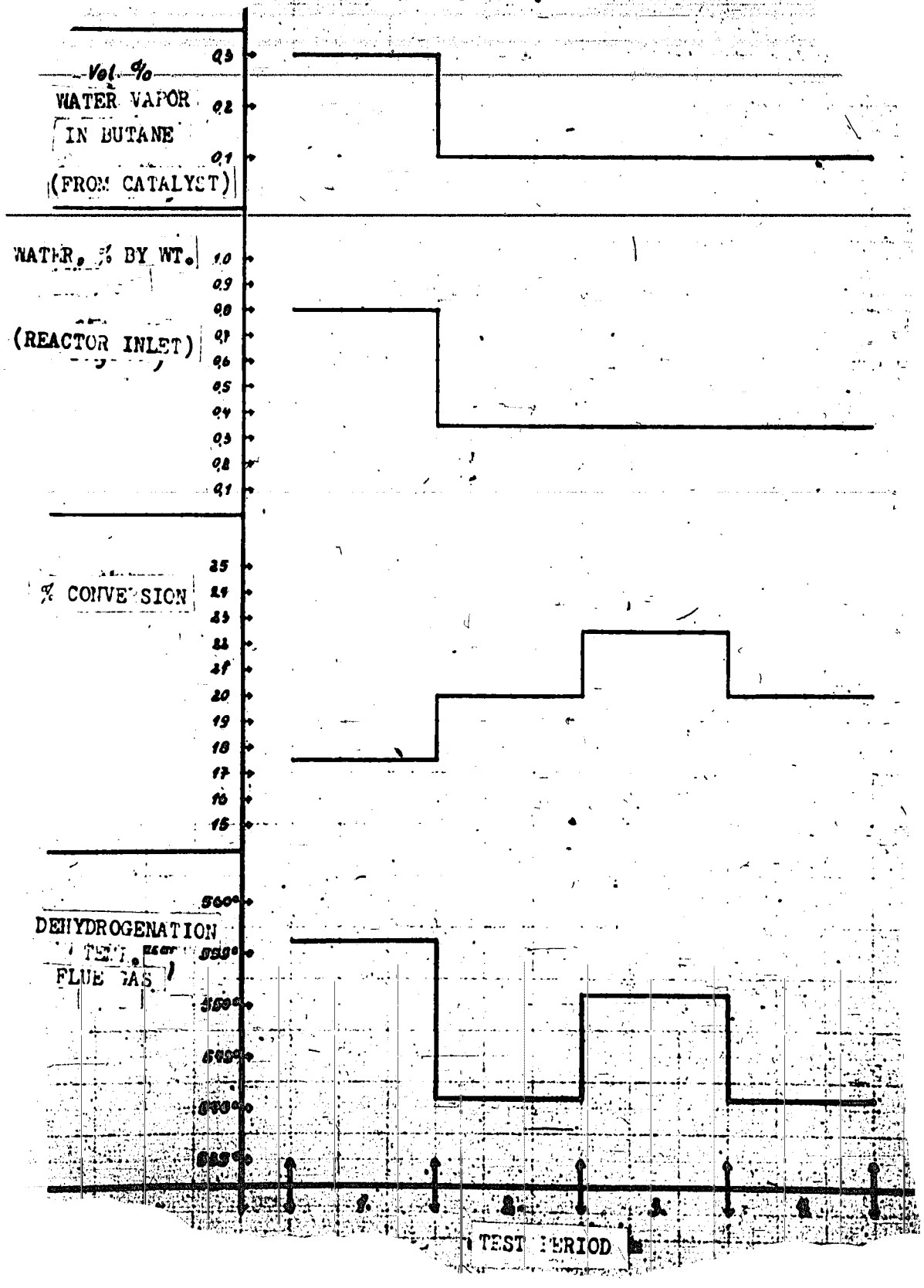

FIGURE 7

EFFECT OF CATALYST DRYING ON PLANT OPERATIONS