Leuna Works - March 16, 1944.

THE CATALYTIC DEHYDROGENATION OF PROPANE TO PROPYLENE

Laboratory Experiments.

The experiments for the determination of the optimum reaction conditions and for testing the catalysts were carried out in electrically-heated quartz tubes of a length of 3.3 feet and a diameter of 0.59 inches, having a catalyst volume of 1.67 cubic inches. The temperature was measured at three points in the catalyst layer and was kept constant throughout the entire test period.

In order to obtain satisfactory conversion, the temperature for the dehydrogenation of propane must be kept about 20 to 40°F. higher than for the dehydrogenation of butane but this is not accompanied by losses in the yield because of the higher thermal stability of the propane. The optimal reaction temperature lies at 1,040 - 1,112°F.

Since the dehydrogenation reaction results in an increase in volume due to hydrogen formation, the reaction proceeds better if the pressure is kept low. For technical reasons, however, it is not feasible to work at pressures below atmospheric.

Comparative experiments on the dehydrogenation of butane and propane gave analogous results with respect to catalyst activity. Catalysts which were found to be the most satisfactory for butane were also found best for propane and vice versa. Consequently, the same catalysts which were used for the dehydrogenation of butane have been used for propane and the development of a special propane catalyst was unnecessary. Consequently, at present, a catalyst is used consisting of 90% alumina (90% activated alumina and 10% precipitated alumina), 8% Cr_2O_3 and 2% K_2O. It is assumed that improvements which will be found in the future with respect to improvement of the activity for butane dehydrogenation will also be applicable to the dehydrogenation of propane.

The most advantageous space velocity lies between 500 and 1,000 volumes of gas (standard conditions) per volume of catalyst per hour. It is not advisable to go to lower space velocities because this would tend to increase the reaction space, whereas space velocities above 1,000 are not advantageous because the amount of heat to be introduced per unit area of the reactor wall becomes too large. This results in excessively high wall temperatures which usually leads to losses in yield due to cracking. The conversion also decreases very rapidly with shortening of the residence time. Which space velocity between 500 and 1,000 should be chosen depends on the conversion desired and the quality of the catalyst used.

Due to the high reaction temperatures, it cannot be avoided that the catalyst activity decreases already after a few hours because of carbon deposition so that the catalyst must be continuously regenerated. Since carbon deposition is essentially a function of the operating temperature, the length of the operating period between regenerations depends on the operating temperature. Up to a temperature of 1,040°F., operating periods of 6 to 8 hours can be maintained, whereas above 1,040°F. only 4 to 6 hours of operation are practicable without too large a decrease in the conversion as compared to the maximum obtained during the initial operating period.

Whereas hydrocarbons lower than C_3 behave practically as inert gases, the presence of higher hydrocarbons should be avoided since they may be the cause of increased carbon deposition. 1% - 2% C_4 have no noticeable detrimental effects. It is very important that the propane feed is as dry as possible because small amounts of water vapor noticeably decrease the conversion obtained. The water concentration in the feed gas must not exceed 0.02 to 0.03% by weight. This would indicate the desirability of using a solid catalyst bed since a moving catalyst which is regenerated in a separate unit always takes up moisture from the atmosphere.

The following results were obtained with plant catalyst 6448 at 1,076°F. a space velocity of 1,000:1 and an operating period of 4 hours over a total of 850 hours of dehydrogenation. The experiment shows that under the reaction conditions given, propane dehydrogenation is carried out with satisfactory results even with a less active catalyst.

Table 1

	% Conversion (% by vol.)	% Yield (% by vol.)	% Carbon deposit based on propane reacted
After 50 hours	30		1.5
" 200 "	27	92	0.9
" 500 "	23	93	0.6
" 800 "	21	89	0.4
Average	22-23	92	0.8
Catalyst consumption about 0.3% by wt. based on propylene made.			

A second experiment was made with an especially active catalyst which, however, has not been in commercial production as yet. The catalyst 4548 is the same as the previously-used catalyst 6448, except that it contains 2% more Cr_2O_3. Due to the increased activity of the catalyst, the reaction temperatures could be lower than in the first experiment. The results obtained are shown in the following table:

Table 2

	1004°F.	1040°F.	1058°F.	1076°F.	Average
% Conversion (by vol.)	24	30	27	30	28
% Yield (by vol.)	96	96	96	95	about 96
% Carbon deposit based on propane reacted	0.7	0.5-0.6	0.6	0.6	0.6
Hours of dehydrogenation	40	204	304	60	

The catalyst was still active at the end of the experiment.

The attached diagrams which show the course of the reaction in relation to the most important reaction conditions are based on data obtained with a catalyst of average activity lying between the activity of catalyst 4548 and catalyst 6448. The results refer to a period in which the catalyst had already been used for some time.

Figure 1 shows the change in conversion over an 8-hour period. Curve 1 gives the approximate condition with a catalyst operated under normal conditions (gradual increase of temperature according to change in conversion). Curve 2 shows the change in conversion which takes place when the temperature is raised too rapidly. The catalyst in that case is too active and deposits too much carbon which results in a rapid decrease in the conversion at the end of the operating period. The induction period which is always observed may have its cause in traces of water which are formed during regeneration and by the reduction of the higher chromium oxide in the course of the regeneration. The relation of the average conversion to the space velocity is shown in Figure 2, whereas Figure 3 shows yield and carbon deposit as functions of the operating temperature. The following table shows the composition of the reactor exit gas expressed in volume percent at a conversion of about 22% and a yield of 94%; the data are based on Stock analyses:

Inlet Gas	Exit Gas
C_3H_8 - over 99%	H_2 - 17%
	CH_4 - 0.2%
	C_2H_6 - 1.0%
	C_2H_4 - 0.5%
	C_3H_8 - 64.5%
	C_3H_6 - 17%

Pilot Plant Experiments.

The pilot plant experiments were carried out in a gas-heated Sicromal-8 tube of 2.76 inch diameter and a length of 14.8 feet using a solid-bed catalyst. The temperature of the fuel gas was measured and also the temperature of 6 measuring points inside the catalyst layer. The temperature increased from the reactor inlet to the outlet. The point of highest temperature in the catalyst bed was assumed to represent the reaction temperature. Figure 4 shows the course of the temperature within the catalyst layer at a reaction temperature of 1,058°F. The flow of product and fuel gas was parallel.

The propane was brought to the reaction temperature by means of a gas-heated preheater. However, the heat losses on the comparatively long way from the preheater outlet to the reactor inlet were so high that the reactor inlet temperature was only 842 to 860° so that the gas reached the reaction temperature proper only at the end of the first third of the catalyst bed which resulted in incomplete utilization of the catalyst. The catalyst volume was 0.5 cubic feet. The propane used in the experiments came partly from the butane dehydrogenation unit and had been separated from the C_4 hydrocarbons by laboratory distillation and partly from the hydrogenation unit; the latter was freed from olefins by washing with sulphuric acid followed by distillation. Special drying of the propane was not necessary since the pseudoazeotrope of propane and water was taken over as a preliminary out during distillation.

The following reaction conditions were used; Temperature - 1,040°F., which was raised according to the conversion obtained; Through-put - 424 cubic feet of propane per hour, corresponding to a space velocity of 801:1; Length of operating period - 6 to 8 hours. The results obtained are given in the following table;

Table 3

	1040°F.	1058°F.	1076°F.	Average
% Conversion (by vol.)	23.5	22.0	22	22
% Yield (by vol.)	91.5	92	91	91
% Carbon deposit based on propane reacted	2.0	2.5	3	3.0
Hours of dehydrogenation	189	43	130	362 total hours
Average length of operating period (hours)	8	6	6	

A temporary reduction of the space velocity to 600:1 resulted in an increase in conversion by 6%. The catalyst was still active at the end of the experiment. As compared to the first laboratory experiment which was carried out with the same catalyst, the carbon separation in the pilot plant run was higher, and the yield and conversion was lower; the space velocity was also lower. The decreased yield is due to the higher wall temperatures which result from the larger cross-section of the tube and this circumstance is also responsible for the increase in carbon deposited. The material of the reactor may also have a certain effect. The lower conversion is explained by the lower gas inlet temperature which actually utilizes only about two-thirds of the catalyst.

Table 3 indicates that at the beginning of the experiment operating periods of 8 hours could be maintained which later had to be reduced to 6 hours because of the increased carbon deposition caused by the rise in temperature.

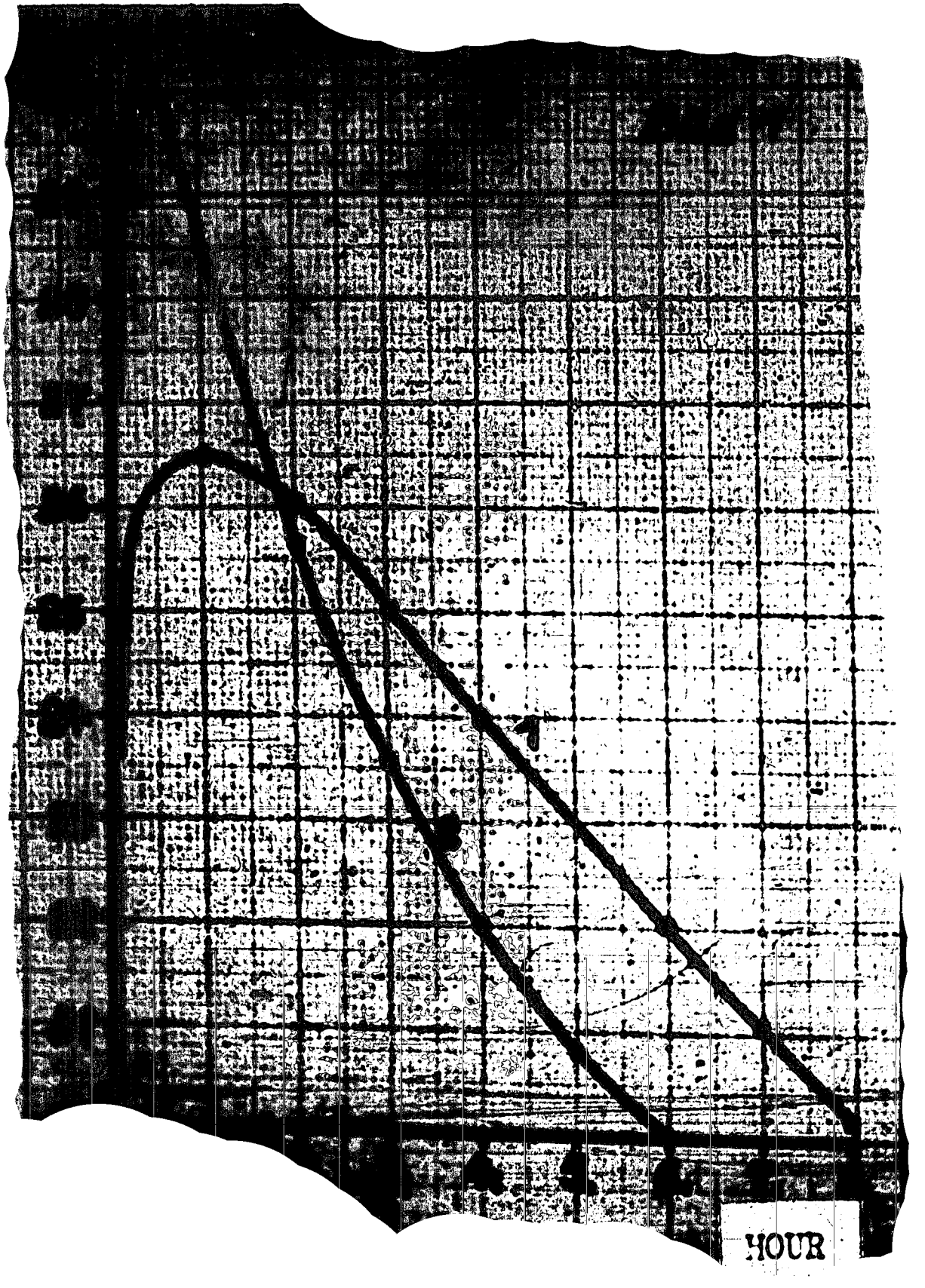
The regeneration of the catalyst was carried out at atmospheric pressure with a mixture of air and nitrogen. Care was taken that the regeneration temperature did in no case exceed the temperature of the preceding operating period. One thousand sixty (1,060) cubic feet of gas per hour were used for regeneration and the pressure at the reactor inlet was 48.6 - 51.5 psia., whereas the pressure at the reactor outlet was 14.7 psia., which corresponds to a pressure loss of 33.8 to 36.8 psi.

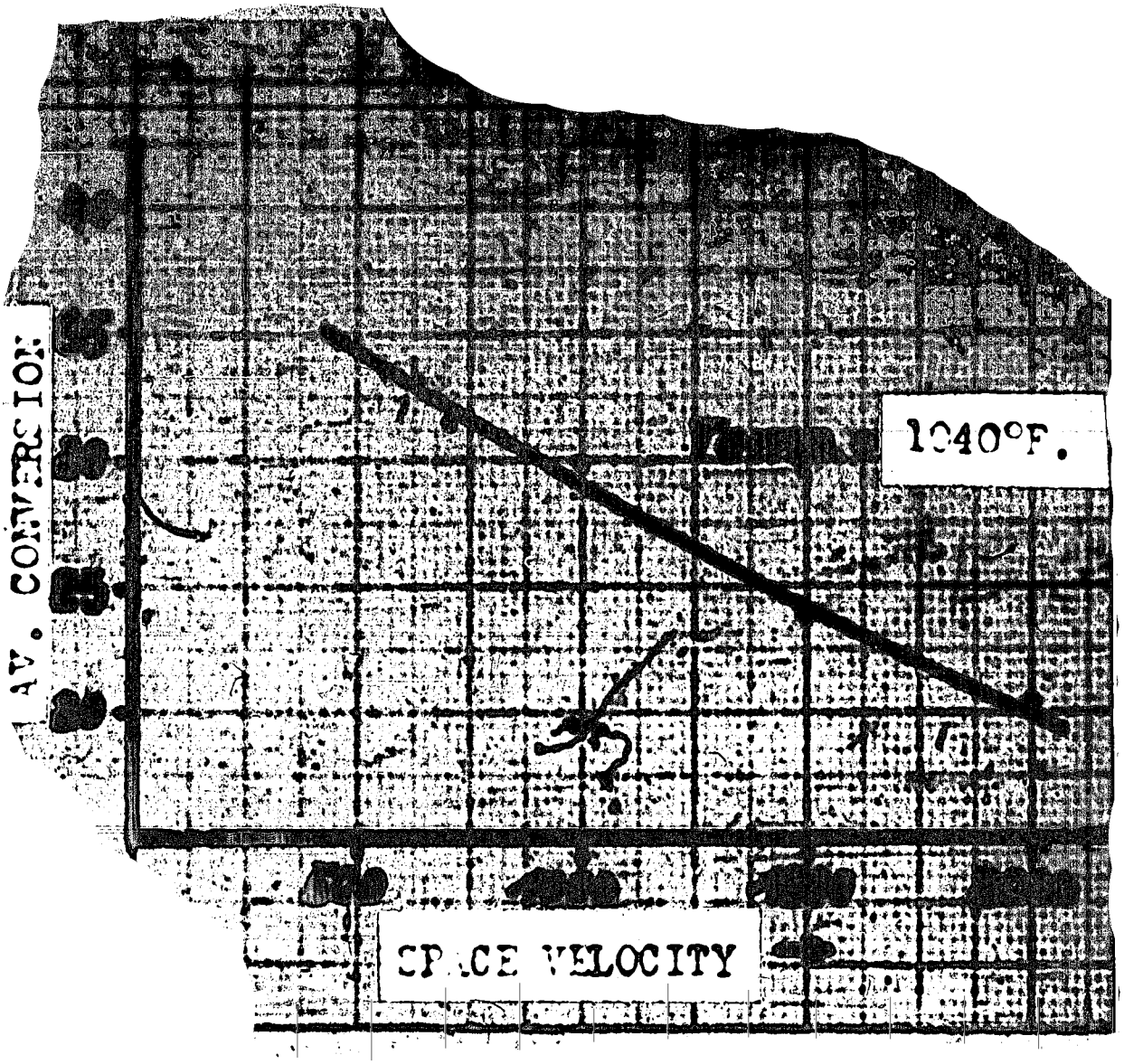
The reactor temperature was lowered to 878°F. (measured in the catalyst bed) prior to regeneration. The oxygen content in the regeneration gas amounted to 2% during the first two-thirds of the experiment and was kept constant during the entire regeneration period. During the last 100 hours of dehydrogenation the oxygen content in the regeneration gas was only 1 to 1.5% because of the higher carbon deposit which had to be maintained in order to keep the temperatures at the desired level. Towards the end of the regeneration period the oxygen content was increased to 2%. After reaching the end of the regeneration period the reactor was heated to the temperature of the subsequent operating period while the gas flow (2% oxygen) was maintained in order to assure complete regeneration of the catalyst. The ratio of reaction to regeneration time, including heating, amounted to 2:1.

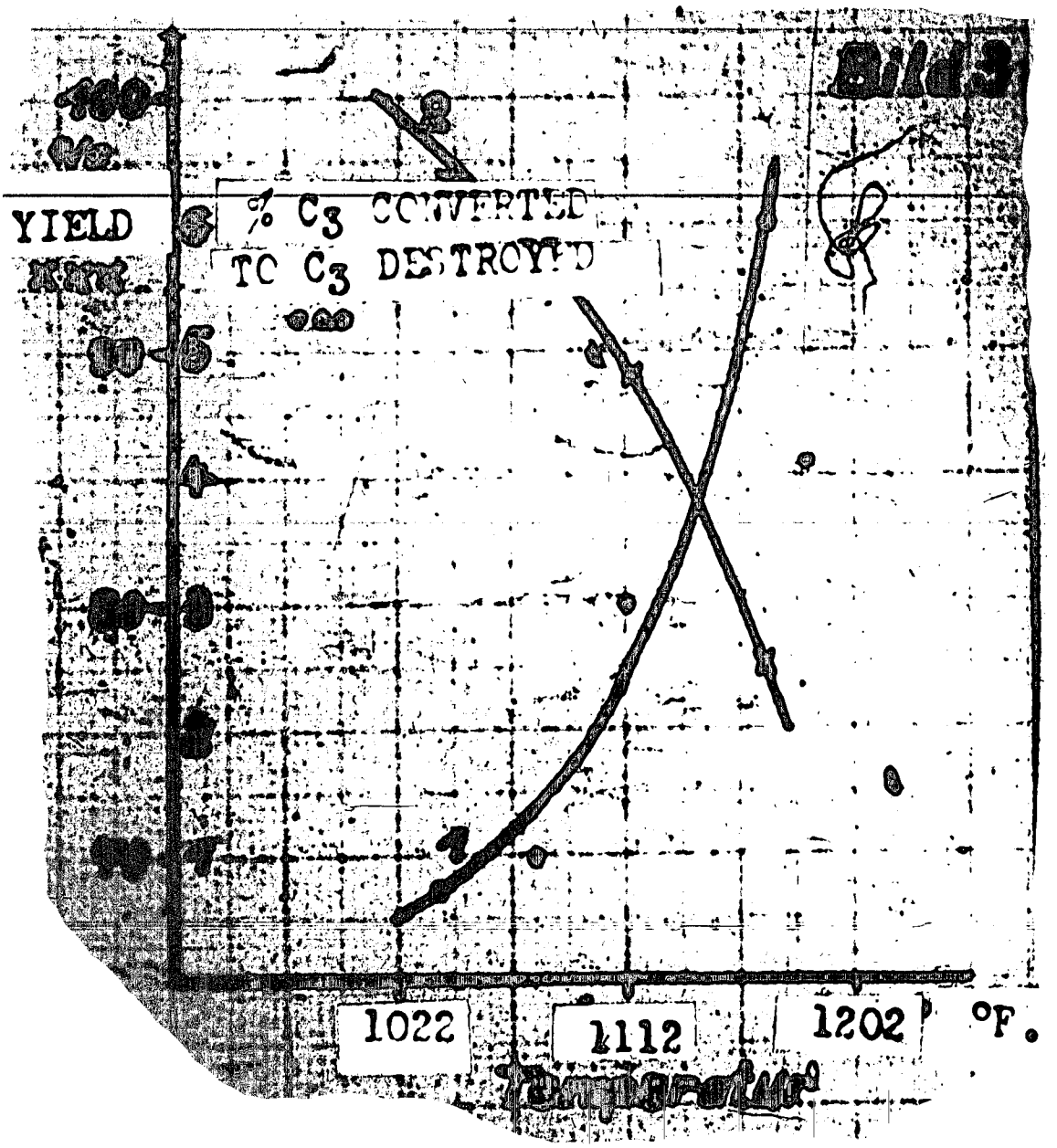
Due to the lack of feed-stock and help, the experiments had to be discontinued. The Sicromal-8 tube did not show any corrosion at the end of the experiments.

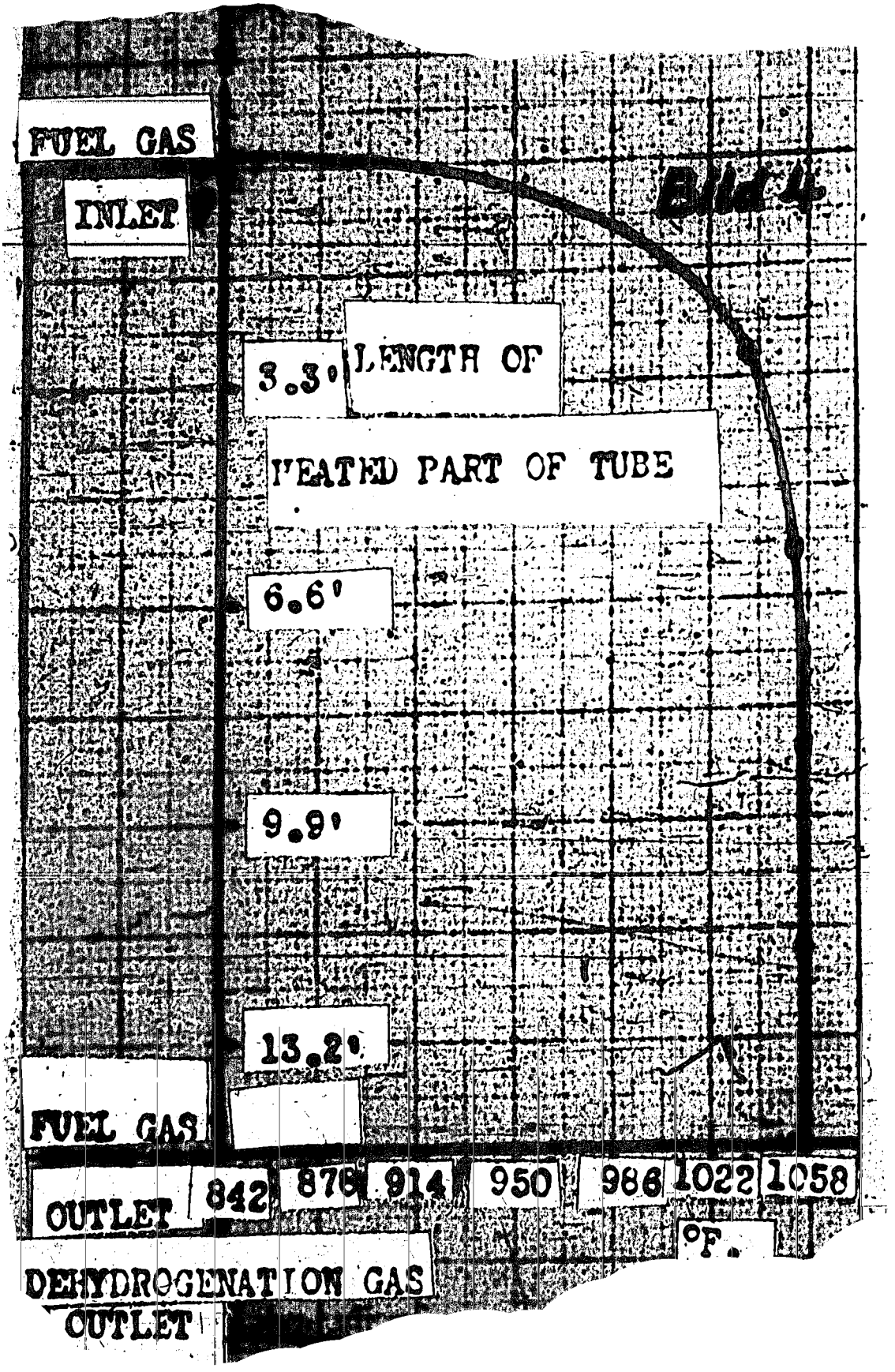
The experiments show that the dehydrogenation of propane takes place under almost the same reaction conditions and with about the same results as the dehydrogenation of butane. The yield is about 2 to 3% higher and the conversion about 2 to 4% lower. The same considerations must be applied to both processes with respect to design, with the modification that for a satisfactory conversion in the dehydrogenation of propane, only the solid-bed process is of practical importance. The dehydrogenation of propane is simpler as compared to the dehydrogenation of butane insofar that the mixture of propane and propylene can be separated by distillation. This permits to operate with a somewhat lower conversion.

The catalysts used in these experiments were those prepared for a moving catalyst process. For their manufacture it was important that besides activity they should have high mechanical strength and high resistance to attrition. Since in a solid-bed process the activity of the catalyst is the predominant factor, the preparation of an active catalyst for the dehydrogenation of propane should be simpler and it should be easier to improve its activity.


% CONVERSION
HOUR


AV. CONVERSION
1040°F.
CE VELOCITY


YIELD
% C_3 CONVERTED
TO C_3 DESTROYED
1022
1112
1202
°F.


FUEL GAS
INLET
3.3'
LENGTH OF
HEATED PART OF TUBE
6.6'
9.9'
13.2'
FUEL GAS
OUTLET
842
876
914
950
986
1022
1058
°F.
DEHYDROGENATION GAS
OUTLET