

BAG No. 3520

BAD SACHSA

12. BUTANE

DEHYDROGENATION

12.
7. November 1939 Dr. Hz/M.

Nat. Dehydrierung

A k t e n n o t i z

Betr.: Versuchsergebnisse bei Butandehydrierung /
Besprechung mit Herrn Dr. Rudorfer.

Zur anliegenden Zusammenstellung der Versuchsergebnisse führte Herr Dr. Rudorfer folgendes aus:

Die Umsatz- und Ausbeuteangaben basieren auf sorgfältigen technischen Analysen. Stockanalysen sind noch in Bearbeitung, doch dürften die Abweichungen der technischen Analysen hiervon nur unwesentlich sein. +)

Der von Herrn Dr. Rudorfer verwendete Kontakt besteht aus Chromoxyd auf Aluminiumgel (Dr. Stoewener). Er wurde von Herrn Dr. Rudorfer selbst hergestellt und enthält nur etwa 3 % Cr_2O_3 . Das Chromoxyd wird in Form von Kaliumbichromat auf das Aluminiumgel gebracht. Die Anwesenheit von Kalium ist nach Herrn Dr. Rudorfer von besonderem Vorteil. Im Verlauf der Arbeiten wurde als neue Erkenntnis festgestellt, dass es von wesentlicher Bedeutung für die Dehydrierung ist, wenn die Kontakttemperatur merklich niedriger als die Temperatur des Gases ist. Wählt man Versuchsanordnungen, die diese Bedingungen einzuhalten gestatten, so lassen sich nach den Beobachtungen von Herrn Dr. Rudorfer sogar mit wesentlich schlechteren Kontakten hohe Leistungen und hohe Selektivität erzielen. Vorgenannte Erkenntnis ist Gegenstand einer Patentanmeldung. Es ist zur Zeit die Aufgabe, ihr noch eine zweckmässige technische Ausgestaltung zu geben.

Da aus den bisherigen Versuchen zu erkennen ist, dass die Versuchsergebnisse beim Arbeiten mit grösseren Kontaktmengen günstiger werden, ist es wünschenswert, Versuche in grösserem Masstab durchführen zu können. Es steht die Frage zur Diskussion, wo solche grösseren Versuche am besten vorgenommen werden sollen.

BÜRO SPARTE I

Anlage.

Hofmeier

D.a. Herrn Dr. Rudorfer ✓
Herrn Dr. Ringer, Berlin. ✓

+) Eine bereits durchgeführte Stockanalyse war in völliger Übereinstimmung mit der technischen Analyse.

Versuchsergebnisse bei Butandehydratierung

Kontakttemperatur 510° bei Beginn, 540° bei Ende jedes einzelnen Versuches
 Gastemperatur = 580°

Normal-Butan: (z.B. eine Temperatursteigerung von 510 - 540 über 4 h)

Durchsatz	Umsatz	Ausbeute	Selektivität	Zeit	Bemerkungen
1 : 500	35 %	93 %	98 %	8 h	1 l Kontakt 1-5 x reg.
1 : 500	37-38 %	93 %	98 %	2-3 h	" " "
1 : 1000	35 %	93 %	98 %	4 h	42 l Kontakt 15 x reg. 50 Std. Laufzeit
1 : 1000	30 %	93 %	98 %	6 h	" " "
1 : 1000	25-28 %	93 %	98 %	4-6 h	25 ccm Kontakt
1 : 2000	~ 24 %	<i>Erndtline by Chlorin</i>	95-96 %	3 h	13 ccm Kontakt
1 : 4000	~18-20%	<i>best. bei vollständiger Butan-Umwandl.</i>	~ 90-95 %	2-3 h	7 ccm Kontakt

Iso-Butan:

1 : 500	35-36 %	~ 92 %	~ 98 %	8 h	1/4 l Kontakt ~12 x reg.
1 : 500	45-50 %	~ 92 %	~ 98 %	3 h	" " "
1 : 1000	25-30 %		95-96 %	4-6 h	25 ccm Kontakt

Die Kontakte wurden stets über Nacht mit 7 % O₂ enthaltenden N₂ regeneriert, wobei die Temperatur scheinbar keine Rolle spielt.

Die Regen.-Temperatur betrug gewöhnlich 510°, jedoch wurden auch mit Temperaturen von 640-700° dieselben Ergebnisse erzielt.

Catalytic

MEMORANDUM

for Standard Oil

hlu

7794

September 14, 1939

Catalytic Dehydrogenation

DD 112.1

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Data which have been obtained by the Standard Oil Company of Louisiana on catalytic dehydrogenation of C₃ and C₄ hydrocarbons were summarized for representatives of I.G., Indiana and the M. W. Kellogg Companies.

It was pointed out that initial investigations involved the study of various catalytic materials and that a catalyst consisting of 4% Cr₂O₃ supported on activated alumina was found to be very satisfactory. This material was used as a standard for evaluating dehydrogenation results and catalysts. The fact that all process data had been obtained with this catalyst at temperatures ranging between 1000 and 1050°F was mentioned and the data were presented as follows:

A. LABORATORY WORK

1. Quartz Reactors, 1" I.D. and 200 cc capacity, atm. pressure.

Dehydrogenation of isobutane, normal butane and field butane was studied at feed rates up to 1000 V/V/hour. At 350 V/V and conversions as high as 40% per pass dehydrogenation selectivity (mols butylenes produced per 100 mols butane reacting) was of the order of 85 to 90% for feed cycles of 6 to 12 hours. At 1000 V/V/hr. and conversions up to 35%, dehydrogenation selectivities ranged between 85 and 90%. Conversions of the order of 55 to 60% resulted in selectivities of about 70%.

2. All-Metal Unit

An all-metal unit was designed to operate with 1" I.D. reactors (wall thickness 1/4") containing 100 cc of catalyst. The top section of the reaction chamber was packed with quartz chips and used as a preheat zone. Investigations with this unit involved the study of (a) the effect of pressure, (b) materials for reactor construction, and (c) catalyst life.

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- (a) Results with an Ascoloy-55 Reactor
(26-30% Cr, 1% Mn, 0.6% Ni and the rest iron)

Dehydrogenation of isobutane at feed rates ranging between 350 and 1750 V/V/hr. and pressures up to 60 lbs./sq.in.g.a. were studied. At atmospheric pressure, 350 V/V/hr. and 40% conversion a selectivity of 90% was obtained which checked results obtained with the quartz reactors. Operation at 1750 V/V/hr. and atmospheric pressure resulted in selectivities of the order of 90% at conversions up to 26% per pass. At 0, 20, and 60 lbs./sq.in.g.a., 25 to 27% conversion and feed rates of 1000 and 1750 V/V/hr., selectivities with respect to the above pressures were of the order of 90%, 85% and 75%. The rate of coke formation and decrease in selectivity increased at pressures above 30 lbs.

Feed cycles up to 36 hours at 350 V/V/hr. showed no appreciable decrease in conversion with time on feed.

The relationship of coke formation, time on stream and percent conversion was illustrated with Figure I.

- (b) Results with an NCT-3 Reactor
(20% Ni, 25% Cr, 0.15% C, 54.85% Fe)

(1) Operation with isobutane at 1000 and 1750 V/V/hr. employing pressures of 0, 30 and 60 lbs./sq.in.g.a. checked results obtained with the Ascoloy-55 reactor inasmuch as elevated operating pressures decreased selectivity and increased coke formation. Up to 30 lbs. pressure results were considered satisfactory. Above 30 lbs. the effect of pressure on selectivity and coke formation was appreciably greater.

Operation, most of which was at 30 lbs. pressure and 1000 V/V/hr. was continued for an on stream period of 1200* hours or a total time of 1500 hours (21% plant down time) without decreasing appreciably the dehydrogenation selectivity. The rate of temperature increase required to maintain constant conversion amounted to 1.6°F per stream day. This indicated that a

* Actually obtained - method of estimation does not apply to this figure.

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catalyst life of at least 1000 to 1200 hours on stream is a safe figure. Catalyst life is estimated by using the spread between the temperature required for a given conversion with fresh catalyst and 1100°F (apparent maximum temperature at which satisfactory selectivity can be obtained at the same conversion) and the average rate of temperature increase required to maintain constant conversion.

Operation at 1000 V/V, 30 lbs./sq.in.ga. and 25% conversion will permit on stream periods up to 18 hours without loss in catalyst activity.

Elimination of the hydrogen reduction period which ordinarily precedes the feed cycle resulted in a decrease in conversion which amounted to a maximum of about 2% based on the feed. However, the necessity of employing the hydrogen period is questionable. This would depend upon the plant economic picture.

(2) Dehydrogenation of normal butane showed about the same results as those obtained with isobutane with respect to selectivity and temperature-conversion relationship. Coke deposition was higher with normal butane. The following relative coke figures were used for illustration:

Feed Rate - 1000 V/V/Hour
% Conversion - 25%
Pressure - 30 lbs./sq.in.ga.

Feed	Carbon-lbs./1000 cu.ft. Reacting
Isobutane	0.768
Normal Butane	1.060

The catalyst life obtainable with isobutane is also predicted for normal butane.

- (c) Results with a Duronze Reactor
(97% Cu, 2.75 to 3% Si, and 0.17% Fe)

Dehydrogenation of isobutane at 350 V/V/hr. and atmospheric pressure showed high selectivities

* Conversion as mols of butane destroyed per 100 mols butane fed.

and very low carbon formation. An abnormal loss in catalytic activity occurred. Following these runs it was found that the reactor had scaled to an extent which was sufficient to poison the catalyst with copper.

(d) Results with a KA_2S Reactor

The use of KA_2S resulted in low selectivity, high carbon formation and abnormal loss in catalytic activity. The catalyst was poisoned by iron which was attributed to scaling of the reactor.

(e) Dehydrogenation of Propane

Propane was dehydrogenated with standard catalyst in a Duronze reactor at atmospheric pressure and feed rates of 350 and 2000 V/V/hour. Representative data were presented as follows:

Feed Rate, V/V/Hr.	350	2000
% Conv./Pass	28	19
% Selectivity	91	98
Temperature, °F	1022	1078

(f) The suitability of the various metals for reactor construction was summarized as follows:

(1) Duronze - lowest carbon formation but scales.

(2) Ascoloy - second lowest carbon formation but unsuitable from an engineering standpoint due to embrittlement when cooled.

(3) Quartz - third lowest carbon formation.

(4) NCT_3 - fourth lowest carbon formation, suitable from both process and engineering viewpoints.

(5) KA_2S - highest carbon formation and scales.

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B. LARGE SCALE WORK

1. First Investigation

Initial large scale investigations were carried out feeding field butane over 2-4 mesh standard catalyst (4% Cr₂O₃ supported on Al₂O₃). The feed was analyzed as follows:

Mol %	C ₃ H ₈	8.7
" "	I-C ₄ H ₁₀	23.2
" "	N-C ₄ H ₁₀	67.3
" "	C ₅	0.6

The reactor was a 3-5/8" I.D. Ascoloy-55 tube containing 1.3 cu. ft. of catalyst (20' packed section). The preheater coil was fabricated from 3/4" carbon steel pipe. All preheating was done by direct firing. The flue gas from the preheat section was passed thru an auxiliary furnace, where additional heat was supplied, and then to the reactor section to maintain the desired temperature level in the catalyst. The flow with reference to flue gas and feed was countercurrent in both sections.

Feed rates of the order of 350 V/V/hr. were employed at substantially atmospheric pressure (about 4# pressure drop thru catalyst). This study covered an on stream time of 327 hours or a total time of 473 hours (including flushing and regeneration time). ~~Results checked laboratory data with respect to temperature-conversion relationship and selectivity.~~

2. Second Investigation

The second large scale investigation was carried on on commercial isobutane at feed rates of the order of 1000 V/V/hr., 20 lbs. reactor outlet pressure, 35 lbs. reactor inlet pressure and 3 hour feed cycles. A 3-1/2 NCT-3 tube containing 1.3 cu. ft. of 2-4 mesh standard catalyst was used for this work. Arrangements were made whereby both vertical and radial temperature gradients could be studied. The preheater coil was standard 3/4" 4-6% chrome pipe. Heat was supplied to both the preheat and reactor section by direct firing. Initial results from study were in agreement with data obtained from laboratory with respect to conversion and selectivity. However, iron scale was deposited on the catalyst and abnormal loss in catalytic activity and increased coke formation resulted. The following was used for illustrating typical temperature gradients:

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Location	-----Temperatures-----		
	Wall	Between Wall & Cat.	Center of Cat.
47-1/2" from top	1097	1046	1025
43" from bottom	1094	1064	1067

A filter has been installed between the preheater and reactor to prevent catalyst contamination. Operation has not been resumed since this installation.

C. REGENERATION OF CATALYST

Most regeneration data were obtained by once-thru operation with a mixture of either inert gas (90% N₂, 10% CO₂) or cylinder nitrogen and air which contained 1% oxygen. The maximum temperature was 1350°F. Regeneration rates of the order of 3000 V/V/hr. were employed for most of the work. However, during the first large scale investigation rates of 400 to 700 V/V/hr. were employed.

All of the oxygen entering the reactor is consumed until carbon removal has been completed. If the amount of carbon on the catalyst is known, the time required for regeneration can be calculated.

~~The use of steam as a regeneration gas diluent was studied. Following the use of steam, dehydrogenation selectivity decreased and carbon formation increased. However, when removed from the reaction chamber, the catalyst showed an iron deposit which was apparently introduced with the regeneration gas. Due to this condition the effect of steam as a reactivation gas diluent cannot be accurately evaluated at present.~~

D. CATALYST DEVELOPMENT

1. Catalyst Supports

Various materials such as magnesia, silica gel, Kaolin, pumice, bauxite and activated alumina were evaluated as supports for chromic oxide. Activated alumina showed the best results and silica gel was the next best support. Bauxite was fair but the iron content was too high.

2. Active Ingredients

Chromium, nickel, iron, molybdenum, vanadium and tin oxides supported on activated alumina (prepared by impregnation) were investigated. Vanadium oxide on silica

gel was also studied. The chromic oxide catalyst showed the highest activity. Vanadium oxide supported on either activated alumina or silica gel was the next best catalyst. A mixture consisting of 2% nickel oxide and 2% chromic oxide supported on activated alumina was a good dehydrogenation catalyst, and its activity appeared to be less sensitive to high temperatures.

3. Effect of Method of Preparation on Ratio of Components

Various combinations of chromic oxide and activated alumina, prepared both by impregnation and coprecipitation, were tested. Coke formation increased with an increase in chromic oxide content. This was illustrated by Figure 2.

The catalysts which were prepared by impregnating the activated alumina with a solution of the active ingredient showed a higher level of activity than those prepared by coprecipitating the components. Optimum chromic oxide contents appeared to be 25% for impregnated catalysts and 40 to 60% where coprecipitation was employed. This was illustrated with Figure 3.

4. Compounds Used as a Source of Chromic Oxide

The following chromium compounds were used in preparing chromic oxide-alumina catalysts:

- (1) Chromium nitrate
- (2) Chromic acid
- (3) Ammonium dichromate

Catalysts prepared with these compounds were of about equal activity.

5. Effect of Catalyst Form

Chromic oxide-alumina catalysts in lump form from 2 to 15 mesh and in pill form showed the same activity.

E. GENERAL DISCUSSIONS

1. Polymerization

I.G. reported that they had noted the accumulation of polymer after the reactor during dehydrogenation work. Baton Rouge reported that polymerization had never been observed in their dehydrogenation work.

2. Effect of Water on Activity

Baton Rouge reported that moisture in the feed caused a temporary loss in catalytic activity. Although the maximum amount that can be tolerated is not well defined, it was pointed out that at atmospheric temperature, isobutane accumulates a sufficient amount of moisture from a wet test meter to reduce the activity of the catalyst by about 50%. Isobutane with a moisture content of 0.03 to 0.04% did not cause inactivation.

I.G. reported that they found that isobutane could tolerate a moisture content of 0.03% whereas the limit for normal butane was practically nil.

3. Effect of Feed Rate on Butylene Production

~~Baton Rouge reported that by increasing the feed rate from 350 to 2000 V/V/hr. the butylene per unit of catalyst consumed could be increased by about 500%.~~

4. Effect of Conversion per Pass on Butylene Production

Baton Rouge reported that by increasing the percent conversion per pass butylene production could be increased. However, 25 to 30% conversion was recommended due to (a) increased rate of coke formation, and (b) ~~a possible decrease in catalyst life due to the higher temperatures required at higher conversions.~~

5. Effect of Temperature on Catalytic Activity

Baton Rouge results showed that at temperatures above 1600°F the activity of the standard catalyst was permanently impaired. A maximum temperature level of 1350°F was considered safe.

F I.G. DATA

The I.G. mentioned that besides the 100 cc catalyst testing units they had available two 25 liter units which were equipped to carry out moving or fixed bed operation. There was a 100 liter unit which had just been completed for stationary catalyst operation and a 600 liter unit which had been used in the old work on moving catalyst.

The I.G. investigation of the dehydrogenation of isobutane has been nearly completed. The catalyst which they used for this operation consisted of 94% Al_2O_3 , 5% Cr_2O_3 and 1% Kaolin. The method of manufacture of this catalyst consisted of mixing together 3.8 kg. of powdered technical aluminum hydroxide, 26 grams of Kaolin, 178 grams of ammonium bichromate, 450 grams of water and 315 grams of 65% nitric acid. The batch was mixed together in a simplex mixer to a stiff paste for about one hours' time and then extruded and dried at 450°C . When the catalyst was used for moving bed operation it was formed into 6-7 mm balls by using a machine similar to that used in the manufacture of hard candy. This machine was capable of producing 80,000 bbls./hour. It should be mentioned that the I.G. found the pressure drop when using ball-formed catalyst was one-fourth of that found when using granular catalyst and that the pressure drop when using pills was somewhere between the two. The I.G. presented some data which is attached in Table I which have been obtained in their 100 cc quartz units when dehydrogenating isobutane. The catalyst used was No. 1850 and was identical with that described above. An examination of the table indicates that the results obtained are very similar to those which Development reported for their standard catalyst. The work had been carried somewhat further than Development's in that space velocities of 2000 to 2500 V/V/hr. had been employed. It was noticeable that at these high space velocities that even at temperatures as high as $570-600^\circ\text{C}$ the conversions were low and the selectivity somewhat impaired.

In regard to the dehydrogenating of normal butane the I.G. have found that low V/V's were impractical due to the fact that the catalyst activity dropped off rapidly. At V/V's of 500 to 1000, or even 2000, satisfactory dehydrogenation of normal butane could be obtained. The optimum temperature for the dehydrogenation of normal butane appeared to be about 25°C lower than that for isobutane. These results were preliminary and might be subject to change when further investigations are carried out. The I.G. were interested in the relative rates of dehydrogenation of the iso and normal butane inasmuch as in a recycle system containing both of these materials it was felt that the concentration of isobutane might build up to an undesirable extent due to the fact that a higher temperature would be required for dehydrogenating this material. Development mentioned that this had been considered but they did not feel that the difference in temperature was quite as great as the 25°C mentioned by the I.G. They also felt that no trouble would be found from a slight buildup in the concentration of isobutane in the recycle system.

In order to demonstrate that there was a difference between the behavior of iso and normal butane upon dehydrogenation the I.G. mentioned that a silica chromium catalyst which was prepared from the mixed gels (molal ratio 1:0.25 to 1:2) would

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successfully dehydrogenate normal butane but was much less effective on isobutane. It was pointed out that both the I.G. and Development lacked good data on the relative dehydrogenation rates of iso and normal butane.

The I.G. had found evidence of isomerization of iso to normal butane and vice versa when dehydrogenating over their alumina chromium catalyst. This seemed to be of interest to them although the extent of isomerization was small. Development had also noticed a certain amount of isomerization. However, the extent was so small that it did not seem of interest and, in addition, there was some question as to the accuracy of its determination by gas analyses.

The I.G. have done considerable work on a search for suitable materials to construct heat exchanger and reaction tubes for catalytic dehydrogenation plants. In carrying out this work the method had been to test the coking tendency of turnings of the various metals when exposed to isobutane in quartz tubes at 550-600°C with a contact time of 1 minute or more. The metals tested were Sicromal 8, 9, 10 and 12, KA₂S, NCT-3, manganese copper (containing 2-3% silicon) and FF30 (containing 30% chromium and less than 0.3% nickel). All of the metals tested proved satisfactory with the exception that the KA₂S did indicate a higher coking tendency. Additional tests were carried out by passing isobutane thru tubes of Sicromal 8, 9 and 10 for long periods of time. It was found that the tubes were entirely clean up to 500 hours but at the 516th hour carbon formation started and they plugged the tubes. The I.G. felt that iron carbide formation might be responsible for this difficulty. The tubes were then cleaned by blowing with air and were again satisfactory for 500 hours' operation. The 600 liter oven at Leuna had tubes constructed of FF30 and were satisfactory for an operation of one year without coke formation. After the expiration of the year the tubes started to form coke rapidly and it was concluded that the iron-chromium alloy was forming coke. It was the general conclusion of the I.G. that Sicromal 8 or 9, which were the lowest alloy steels tested, would be satisfactory for the construction of heat exchanger tubes and for reactor tubes. The analysis of Sicromal 8 was given as 6% chromium, 1% silicon and 0.5 - 1% aluminum. Mr. Murphree pointed out that further tests on dehydrogenation in the presence of catalyst with this type of tube should be carried out in order to determine definitely whether the tube metal would affect the catalyst activity. The I.G. mentioned that some work along this line had been carried out but that their investigations were not yet complete.

In regard to catalytic dehydrogenation furnace design Development explained that two types of furnaces have been developed. When low space velocities were used and low heat inputs to the tubes were possible, use was made of a close grouping of tubes in a forced draft convection type of furnace where-in flue gas circulation was carried out. The second type of furnace which had been designed for use with higher thruputs was designed similar to the hydrogen production furnace with which the I.G. are familiar. The I.G. had developed a furnace for the dehydrogenation operation which was similar in construction to a water tube boiler. There was an inlet drum at the top and an outlet drum at the bottom. Between the two were 15 rows of four 60 mm tubes each containing the catalyst. Flue gases from a furnace enter the reaction bank of tubes at the top between 900 and 1000°C with a velocity of 3-4 meters per second. As heat was extracted from the gases their velocity was increased on passing downward in a zigzag fashion so that at the outlet where the temperature of the gas was 630-650° the velocity reached 15 meters per second, thereby increasing the convection coefficient. As a result, the overall coefficient of heat transfer could be adjusted so that the heat is distributed as required for the reaction. A single oven of this variety would contain 2 cubic meters of catalyst and appeared to be of an economic type of design. Regeneration was to be carried out using inert gas and air with a concentration of oxygen between 3 and 5%.

Previous work had been carried out on a moving bed operation using a charcoal catalyst. In this operation the conversion was in the range 16-17% and the charcoal was held in the apparatus between 100 to 120 hours. The I.G. had little interest at the present time in this type of dehydrogenation because of the fact that much better yields were obtained with the alumina-chromium type of catalyst. In the operation of this apparatus 25-30% of the charcoal was reduced to fines due to the grinding action of the inlet and outlet catalyst mechanism. There was no objection to this inasmuch as the charcoal was cheap and not regenerated. When synthetic catalyst was substituted for charcoal in this type of apparatus trouble was experienced with the valves inasmuch as the harder pieces of synthetic catalyst caused rapid wear on the mechanism. When using charcoal catalyst a regulation star feeder type of valve was used. There was later developed for synthetic catalyst a valve similar to that shown in the sketch below.

The principle upon which it works is that the leading edge of the valve cuts thru the catalyst in a zone which is not entirely filled with catalyst due to the fact that the angle of repose of the catalyst prevents it from entirely filling the area. Inasmuch as the chromium alumina type of catalyst has a sufficient length of life to be used in a stationary catalyst type of equipment, the use of a moving catalyst has been abandoned.

The I.G. presented some curves indicating the effect of conversion on steam, fuel, power, cooling water and catalyst cost. All these costs showed a lowering at the higher conversion. Not shown was the corresponding curve showing the increase in cost of feed stock due to loss in selectivity at the higher conversions. This curve would, of course, increase with the higher conversions. It was the I.G.'s feeling that the optimum point was at 30% conversion which they felt should be obtained at about 1000 V/V.

Previous work by Development showed that substantial savings in plant cost could be obtained by the use of higher feed rates and higher pressures. Increasing the feed rate from 350 to 1000 V/V/hr. (along with an increase from atmospheric to 25# operating pressure) cut plant cost about 25% when obtaining a 25% conversion in both cases.

Development stated that their figures showed that recovery of the C₄ hydrocarbons from the cracked gases could be carried out more cheaply at 300# than at 100# when using oil scrubbing. Development's figures on the cost of coke removal equipment were incomplete inasmuch as they had been based on the use of steam and air which had since been shown to be of questionable utility.

Mr. Murphree outlined Development's program for future work. This included a better demonstration of dehydrogenation under moderate pressures, say 15-30 pounds. An effort was to be made to check the effect of tube size and to obtain data on heat transfer of tubes packed with catalyst. For this purpose temperature measurements within the catalyst mass were to be carried out. The metals of construction were also to be tested and calorized tubes were to be looked into. It was felt that this work should be carried out on the dehydrogenation of normal butane inasmuch as the difference in yields between catalytic and thermal dehydrogenation of this feed stock was greater than that for isobutane.

TABLE I
I.G. RESULTS ON DEHYDROGENATION

Unit Size - 100 cc

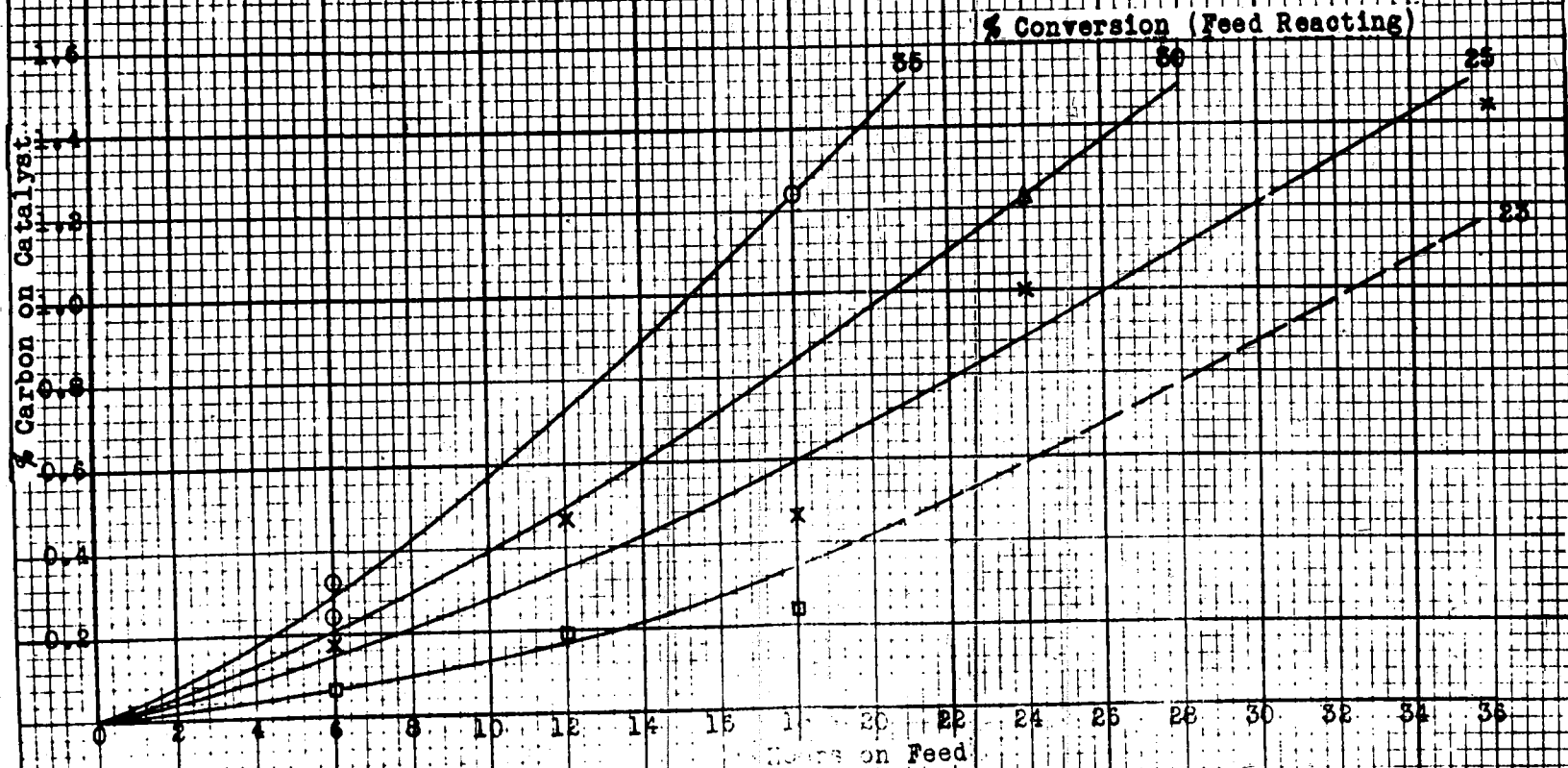
Feed Stock - Isobutane

Catalyst #1850, Al₂O₃-94%, Cr₂O₃-5%, Clay-1%

<u>V/V/Hr.</u>	<u>Cycle Length Hours</u>	<u>Temperature °C</u>	<u>Conv. %</u>	<u>Selectivity</u>	<u>Total Run</u>
300	4.5	560-575	40	89	-
	6.0	580-600	40	86.7	-
	19.0	565-575	35.7	87.2	-
	15.5	580-600	37.1	85.9	100
1000	7	575-590	25.0	88.0	-
	11	570-575	24.7	89.9	-
	6	560-575	23.5	89.4	-
	17	565-575	22.3	90.8	100
1000	4	590-600	35.5	90.5	-
	11	540-600	37.0	90.9	-
	19	570-600	28.0	87.5	-
	6	600	32.2	88.5	100
2000	6	575-600	19	88.0	-
	19	570-600	13	87.0	-
2500	6) 580-600	26.0	88.4	30
	8		20.0	87.0	100
	20		18.0	87.5	50

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FIGURE 1
 DEHYDROGENATION OF COMMERCIAL ISOBUTANE
 (95% ISO-C₄H₁₀, 5% N-C₄H₁₀) OVER STANDARD
 CATALYST AT 350 V./V./HOUR - ASCOLOY REACTOR



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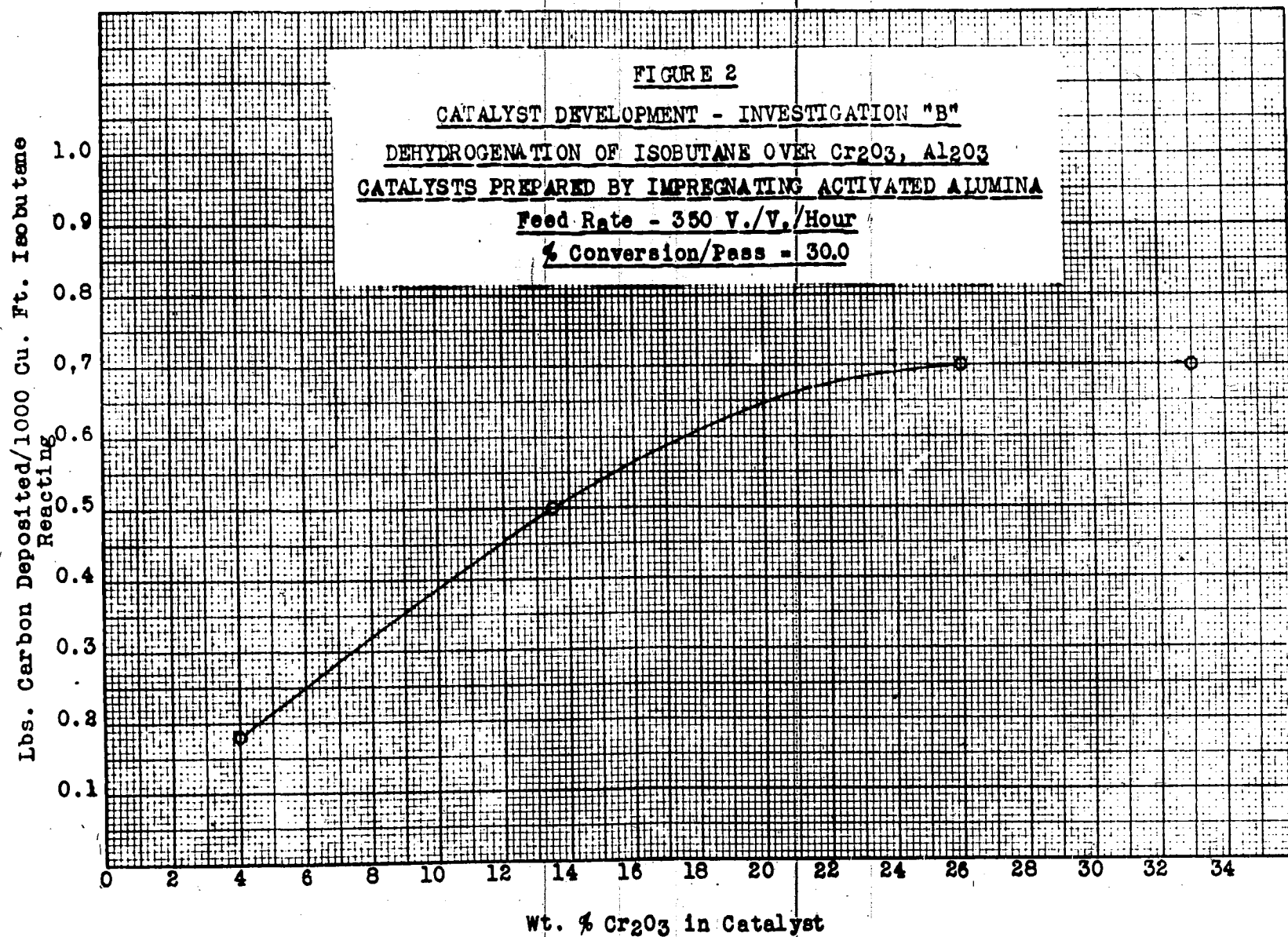


FIGURE 3

RELATIONSHIP OF PERCENT Cr_2O_3 AND DEHYDROGENATION ACTIVITY
FOR Cr_2O_3 - Al_2O_3 - CAT. MIXTS - DETERMINED WITH C. P. ISOBUTANE
AT 350 V./V./HR. AND 975 °F. BLOCK TEMPERATURE

