

THE CATALYTIC DEHYDROGENATION OF
BUTANE IN FLUIDIZED BEDS

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Sergio Bracale

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N O T I C E

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BUTANE IN FLUIDIZED BEDS

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Date Approved by Chairman

May 28, 1958

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SUMMARY

The purpose of this study was to obtain experimental data on the dehydrogenation reactions of n-butane to butylenes and butadiene in a fluidized bed reactor, employing a standard chromia-alumina catalyst.

The experimental reactor used was made from a stainless steel tube having a length of 30 inches and an internal diameter of 1.93 inches. The fluidized solid particles were obtained by grinding a dehydrogenation catalyst which was in the form of cylindrical pellets of 1/8" x 1/8". A screened portion of the product so obtained, passing 25 and retained on 45 U. S. Sieve Series, was used in all dehydrogenation runs. This catalyst, Cr. 0205 T, lot 101, was supplied by the Harshaw Chemical Co., and had an approximate composition of 20 per cent Cr_2O_3 and 80 per cent Al_2O_3 .

The two variables investigated in this research were reaction temperature and space velocity. Three selected reaction temperatures, i. e., 450, 475, and 500° C, were used. For every temperature experimented with, several different space velocities were used, varying from the minimum values required to start the fluidization to the maximum values permitted by the particular batch fluidization system.

The reacting feed was composed of a mixture of nitrogen, as a diluent, and 99 per cent pure n-butane at a partial pressure of approximately 0.18 atmosphere. The total pressure in the reactor was about one atmosphere for all runs.

The results obtained indicate that at low space velocities (i. e., close to the minimum values to start the fluidization), the butane conversion and carbon deposition is very high, while the selectivities to desired products are poor. At the highest space velocities used, both selectivities and conversion are satisfactory, and carbon deposition is low.

As a general trend, the selectivity decreases and the carbon deposition increases as the conversion levels increase. For a fixed space velocity, the butane conversion increases and total selectivity decreases with increasing temperature from 450° C. to 500° C. On the basis of the results obtained it appears evident that the catalyst used had a very high activity for both carbon deposition and selectivity to butylenes and butadiene.

In conclusion, it may be stated that the butane dehydrogenation in a fluidized bed reactor should be practical. In fact, the great activity of the catalyst used, for both selectivity and carbon deposition, could be favorable because it permits the adoption of working temperatures about 100° C. below those used in fixed bed operations.

CHAPTER I

INTRODUCTION

Methods of making olefins had been available for several years as a result of intensive research carried out by the petroleum industry in the period 1930 to 1940. However, these processes were too costly to be competitive during that time. The demand for gaseous olefins was adequately met by the large quantities that became available as a by-product of catalytic cracking.

Rapid development of commercial processes for the manufacture of butylenes and butadiene resulted from the requirement of the wartime synthetic rubber program. In fact, during the war the requirement of olefins for alkylate and gasoline, and diolefins for synthetic rubber led to the installation of numerous dehydrogenation plants. Just prior to World War II, the petroleum industry was beginning to install plants to produce butadiene by the high-temperature thermal cracking of naphthas and gas oil. The yields to butadiene by thermal cracking process, were only 2 to 5 per cent on feed. At the outset of World War II, the use of thermal cracking under the U. S. Synthetic Rubber program was expanded to some extent in order to provide so-called "quickie" butadiene.

Only a small portion of the capacity developed under the Synthetic Rubber Program utilized butane as a feed stock. The comparatively expensive process of converting ethyl-alcohol into butadiene was also used extensively. However, the largest share of the butadiene program was allocated to a new butene dehydrogenation process which became well known as the "Jersey Process" because it had been developed by the Standard Oil Development Company, a subsidiary of Standard Oil Co. of New Jersey. The German process of making butadiene from acetylene was not adopted in the U. S.

At present, the large and increasing demand for butylenes for alkylate, polymer gasoline, and tetramer for the detergent industry has tended to put butylenes in short supply for the manufacture of butadiene by those who do not have a captive source of butylenes. Because of its cheapness and availability as a result of petroleum refining and natural gas operations, butane has become the logical raw material for the production of butadiene and for the production of butylenes should the present demands exceed the supply.

In general, when butane is employed as the starting material, it is first dehydrogenated to butene and then to butadiene in a subsequent step, although the complete conversion can be made in a single catalyst unit. All commercial dehydrogenation processes are carried out in fixed bed reactors which require catalyst regeneration (1, 2, 3, 4, 5, 6, 7, 8, 9, 10). Consequently, there is still a great incentive for development of an

efficient high-yield, continuous, one-step, dehydrogenation process to produce butenes and butadiene from butane.

It is well known that the fixed bed technics, generally, have three major disadvantages:

(1) In the case of highly endothermic or of a highly exothermic reaction, it is difficult to transfer heat into or out the catalyst bed fast enough to prevent large temperature gradients within the catalyst bed or even within the catalyst pellets themselves. In such cases, it is very difficult to obtain and maintain an "isothermal" bed.

(2) When the rate of diffusion through the pores of the catalyst pellets is slow compared with the reaction rate, it is not possible to utilize the total surface area of the catalyst because the minimum pellet size is limited by the allowable pressure drop through the bed.

(3) When the catalyst life is short, and the catalyst needs periodic regenerations, the expense of taking the fixed-bed reactor out of service and regenerating catalyst may upset the economics of the process.

The use of a fluidized bed reactor may eliminate all the disadvantages of a fixed bed reactor and at the same time present other favorable features.

In the fluidized bed reactor the catalyst bed is in the form of a fine powder which is suspended by the upward motion of the reacting gases passing through the bed. The constant motion of the catalyst particles serves to prevent any temperature gradients within the bed even where

there is a large heat of reaction. Therefore, a very close approach to an "isothermal" bed may be attained and local points of temperature deviation may be virtually eliminated.

The fluidized bed reactor also offers a means of overcoming the second disadvantage of the fixed bed reactor. The particles in a fluidized bed are much smaller than could be tolerated in a fixed bed reactor and therefore offer a greater surface area immediately available for reaction. In addition, the third disadvantage is also eliminated because the use of fluidized bed technics renders the operation continuous.

The purpose of this experimental work has been to obtain preliminary information about the possibility of carrying out in only one step the dehydrogenation of butane to butylenes and butadiene in a fluidized bed reactor, employing a commercial chromia-alumina catalyst.

Generally, in order to arrive at the optimum process specifications for a catalytic reactor, knowledge is necessary regarding the effect of the process variables on both conversion and product distribution. The important variables substantially include temperature, pressure, pressure drop, the presence of diluent on the feed, feed rate, and, in particular, in a fluidized bed reactor all the parameters that, directly or indirectly, affect the course of reactions. These parameters include degree of voids, uniformity of fluidized bed, height of fluidized bed, and diameter of solid particles. Direct experimental investigation of all the possibly important

variables in such a system frequently requires pilot plant operations extending over many years.

The present investigation deals only with a preliminary step of this complex study; i.e., it was proposed to obtain, from a limited number of experimental runs, an idea of total conversion and selectivity of butane dehydrogenation to butylenes and butadiene achieved in a fluidized bed reactor.

Previous Work

A. Fluid bed reactors. —To date no experimental investigations on the catalytic dehydrogenation of butane in fluidized bed reactor have been reported in the literature.

However, Riedel has written (11) that: "Universal Oil Products Co., for example, anticipates that such a process will be available in the reasonable future. UOP states that the wide range of conversions possible with this unit permits operation at the conversion level which provides the optimum balance between feed costs and operating costs for a particular manufacturer. UOP has not given any figures on selectivity, but high over-all yields of butylenes and butadiene are obtained. Operating efficiency and catalyst stability are both high."

B. Fixed bed reactors. —A large amount of experimental work about the catalytic dehydrogenation of paraffins to olefins or diclefins for fixed bed reactors has been reported. Since from 1919 investigators have been

interested in the catalytic dehydrogenation of paraffins to olefins, but until 1930 no really satisfactory catalyst was found.

The choice of chromia catalyst by Frey and Huppke (12) for their studies of the equilibria involved in these reactions was a major factor in the development of a satisfactory catalyst. Their work showed that equilibrium could be closely approached in dehydrogenations to form ethylene, propylene, isobuthylene and butenes. Frey and Huppke showed that selective dehydrogenations could be obtained at suitable conditions, but excessive temperatures or contact time caused cracking reactions to occur.

Alumina, itself, has only mild activity, which is greatly enhanced by small amounts of chromium oxide. Burgin and Groll (13) showed that as little as 2 per cent chromium resulted in a marked improvement, and 15 per cent resulted in further improvement. Alumina-chromia compositions ranging from as low as 3 per cent to as high as 60 per cent Cr_2O_3 are effective catalysts for dehydrogenation of paraffins to olefins. Early studies by the Universal Oil Co. (14) used a catalyst containing only 3 to 4 per cent Cr_2O_3 . A publication by Howard (15) indicates that the Kellogg Co. considered 90 Al_2O_3 - 10 Cr_2O_3 a suitable composition. The Phillips Co. has indicated that their commercial process was improved by increasing the Cr_2O_3 content of the catalyst. (16). The improved composition may be the 17 to 19 per cent Cr_2O_3 catalyst described as a "commercial catalyst" by Pitzer (17). Rietz and al. (1) claimed advantages for a

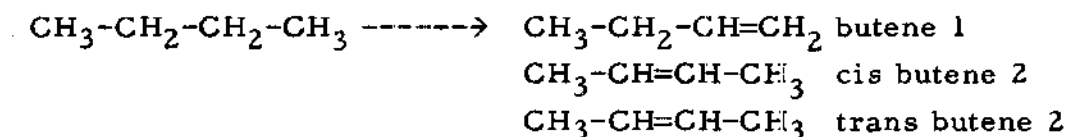
75 $\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3$ catalyst, made by coprecipitation rather than by impregnation of active alumina.

The various modifications reported above are only a few of those studied for basic chromia-alumina system. In addition, many other systems have been studied, yet chromia and alumina still constitute the best known catalyst for converting butane to either butenes or butadiene. Compositions containing about 20 per cent Cr_2O_3 are in most general use today.

Dodd and Watson (18) have published results of a study of the kinetics of butane dehydrogenation in a fixed bed reactor using a commercial catalyst supplied by the Phillips Petroleum Co. as representative of that used in their commercial butane dehydrogenation. It was in the form of 1/8" per 1/8" cylindrical pellets. Part of their results are graphically shown in Figure 1 for an isothermal, isobaric reactor at 1060° F. and 1 atmosphere. From this diagram, it is interesting to note that butene production increased with increased catalyst-feed ratio until a maximum is reached, beyond which butene production is lost.

General Thermodynamic Considerations

The dehydrogenation of n-butane has been studied by a large number of investigators. The problem is complicated, due to the fact that three isomeric n-butylenes are possible:



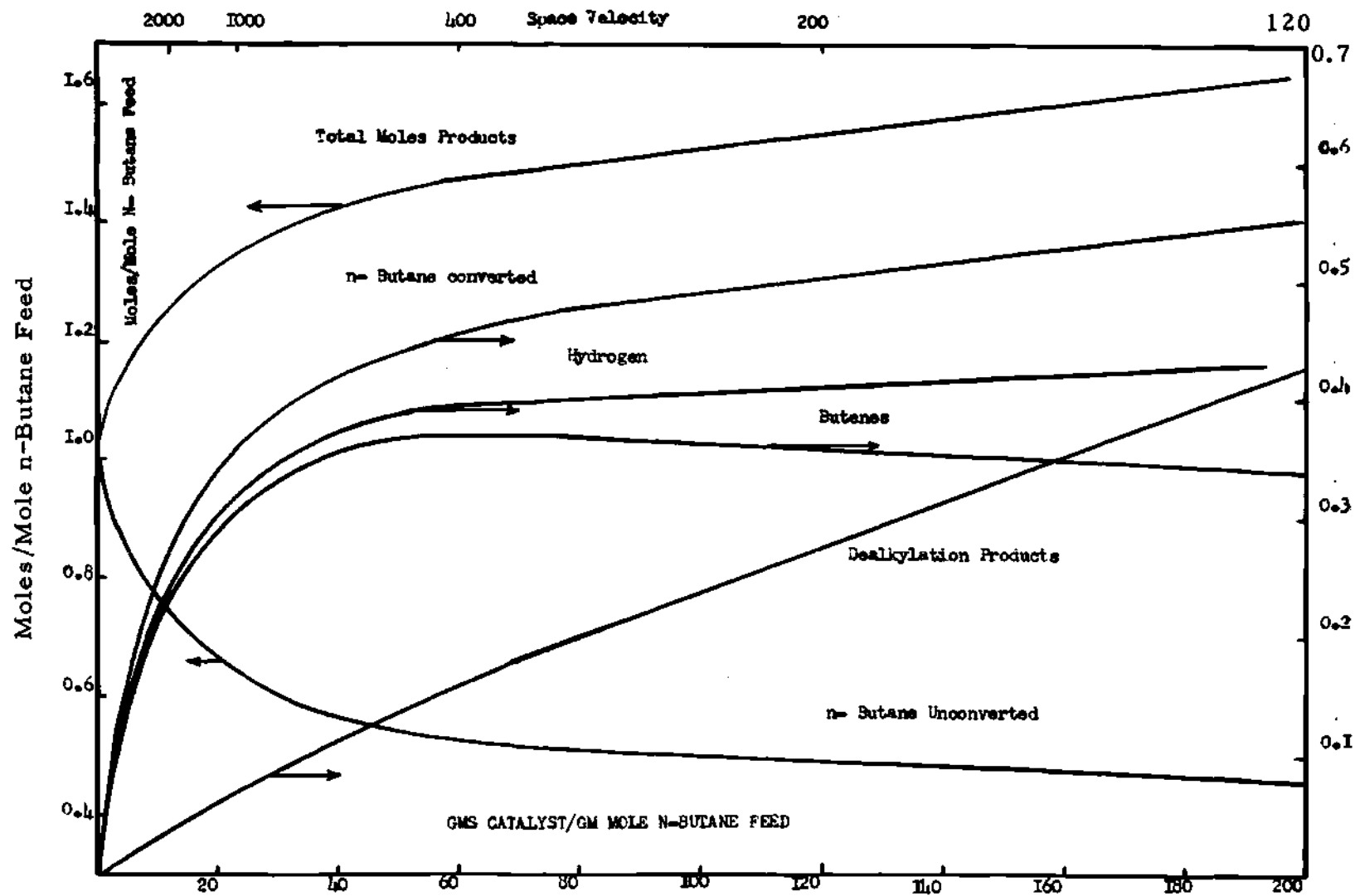


Figure 1. Catalytic Dehydrogenation of n-Butane at 1.0 Atmosphere and 1060° F.

The standard state free energies of formation from graphite and hydrogen are given in table 1 for the main compound involved (19, 20, 21).

The heat of dehydrogenation varies only slightly with the temperature and, at 800° K the standard state heats of reaction are:

| | ΔH_{800}° | (heat absorbed) |
|---|--------------------------|-----------------|
| n-Butane -----> Butene-1 + H ₂ | 31,420 | Cal. /gr. mol. |
| n-Butane -----> cis butene-2 + H ₂ | 28,200 | " " |
| n-Butane -----> trans butene-2 + H ₂ | 27,700 | " " |
| cis-butene-2 --> butadiene 1,3 + H ₂ | 30,200 | " " |

Both dehydrogenations are highly endothermic and approximately 30,000 cal. per mole, or 1000 B. T. U. per lb. of butene or butadiene produced must be supplied.

Equilibrium data at 1.0 and 0.167 atmospheres pressure for the simultaneous formation of mixed normal butenes and 1.3 butadiene from n-butane are shown in Figure 2. It is evident that the extent of dehydrogenation at equilibrium in the reactions mentioned above increases with increasing temperature and decreasing pressure.

The principal reactions in the catalytic processing of butane over chromia-alumina catalyst is the direct catalytic dehydrogenation to butenes. Secondary catalytic dehydrogenation to butadiene takes place. These reactions occur largely as a result of the presence of the catalyst and are presumed to take place on its surface (15). Some additional dehydrogenation occurs through uncatalyzed pyrolysis in the void spaces

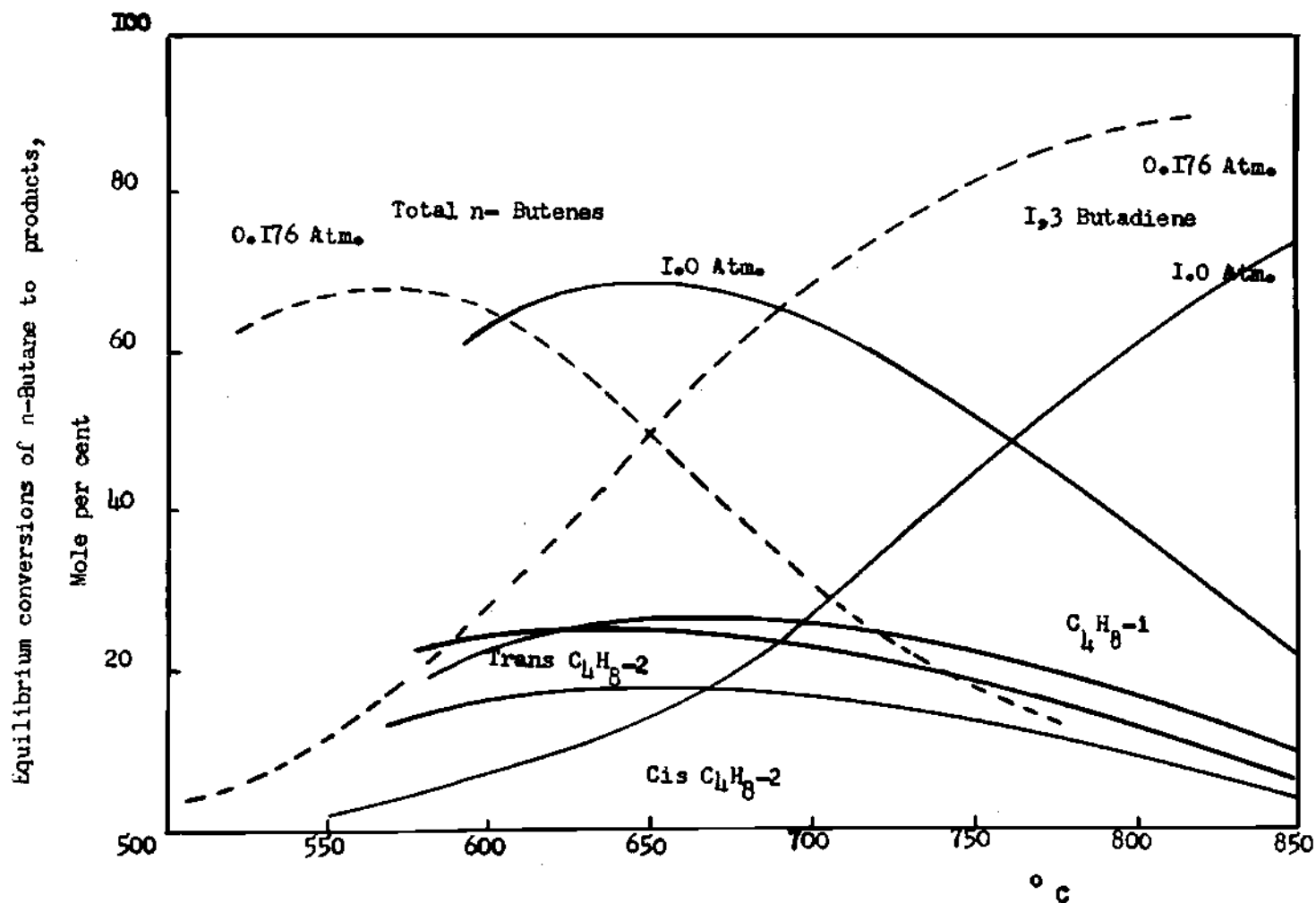


Figure 2. Equilibrium between Paraffin, Olefins, and Diolefins ($n\text{-Butane} \rightleftharpoons n\text{-Butenes} \rightleftharpoons 1, 3 \text{ Butadiene}$)

of the catalyst bed and in the preheater and transfer spaces at the inlet and outlet of the reactor.

In addition to these principal reactions, there are important side reactions which result in the destruction of butane, butenes or butadiene to form undesired products. These reactions may be classified as dealkylation (or "cracking") and the polymerization. They may occur either through catalytic action or as a result of uncatalyzed pyrolysis in the preheater and transfer spaces.

The dealkylative reactions are:

(a) The dealkylation of butane to form methane, ethane, and ethylene.

(b) The dealkylation of butenes to form methane, ethane, propane, ethylene, propylene and carbon.

(c) The dealkylation of butadiene to form hydrogen, methane, ethylene, acetylene and carbon.

There are many other reactions which probably occur to limited extent but which are negligible under the conditions ordinarily encountered in the dehydrogenation of butane. Examples of such reactions are the polymerization of butenes and of butadiene.

In such a complex system it is not possible to make a complete thermodynamic study for all the reactions considered above. Thus the

conversions and selectivities* shown in the diagram of Figure 2 represent a maximum not obtained in practice.

*Conversion is defined as that fraction of the key or limiting reactant in the feed which reacts by any means. Thus, percentage conversion is the percentage of the key reactant in the feed which is converted into other products. The selectivity of the reaction is the percentage ratio of the moles of desired product formed per mole of converted key reactant to the number of moles which would have resulted if there were no undesired side reactions.

CHAPTER II

EXPERIMENTAL METHODS

Experimental Apparatus. --A flow diagram of the experimental apparatus, as finally arranged in this research, is shown in Figure 3. Cylinders of nitrogen and 99 per cent n-butane, and a laboratory air supply line furnished the fluidizing agent, which was measured by means of two flowmeters: one for nitrogen or air, and the other for n-butane. After measurement of the flow rates, the gases passed to the preheater. From the preheater the hot gases were sent directly to the reactor. After the passage through the reactor, the gases produced were cooled at room temperature, by means of a water cooled heat exchanger. After cooling, the gases were transferred to the gas holder.

Two taps were located in transfer lines in order to get gas samples: one at the reactor inlet, and the other following the heat exchanger.

The most important part of the experimental apparatus is the reactor. Figure 4 shows a diagram of the fluidized bed reactor. This reactor was constructed from a stainless steel tube with a 1.93 in. I. D., and a length of 30 in. To the bottom of the reactor is flanged a plate containing a porous stainless steel disc. The disc distributes the inlet gases across the bed. The reactor also contains two pressure taps, one at the bottom near the porous plate, and the other near the top. This

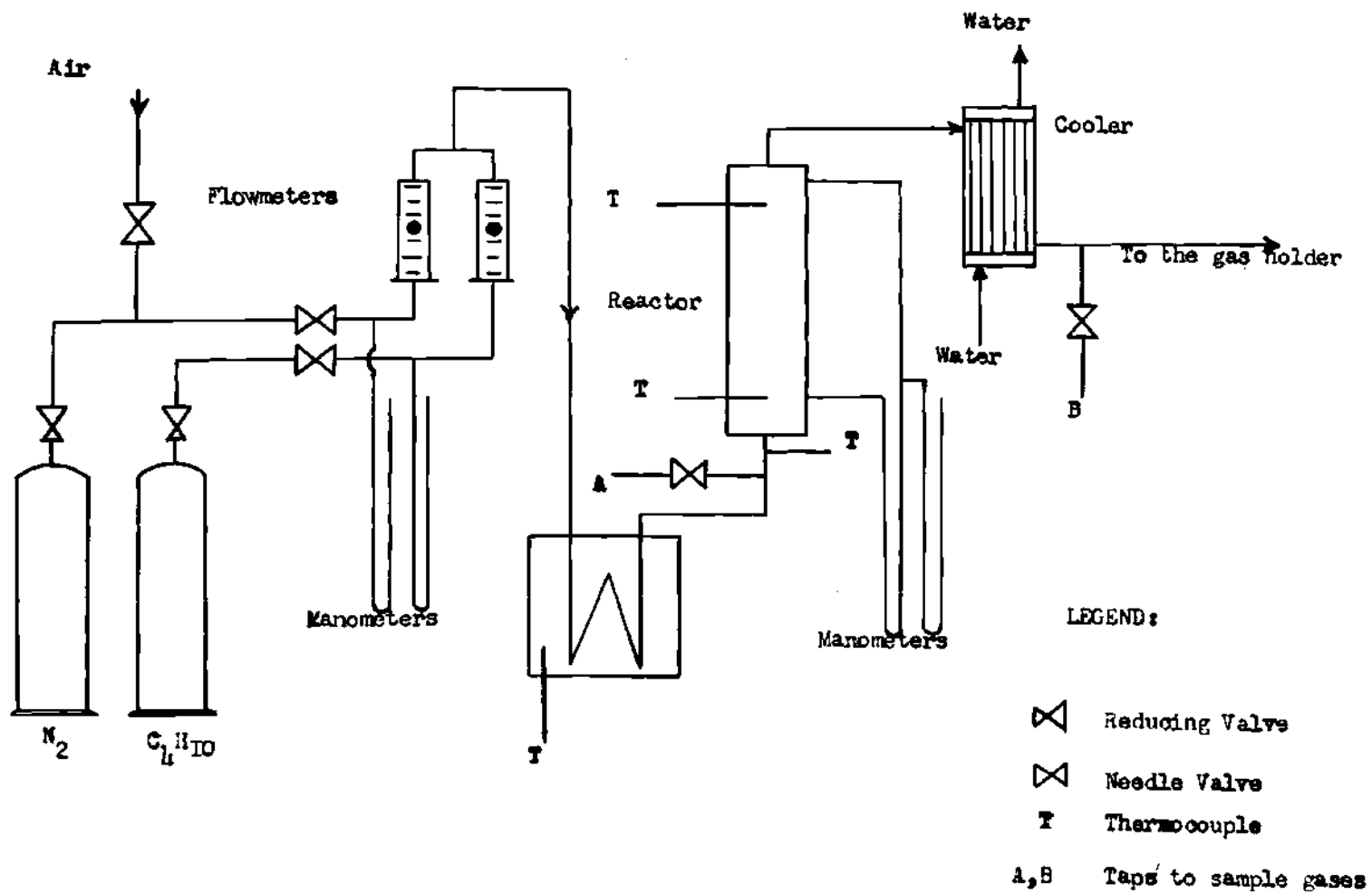


Figure 3. Diagram of Equipment

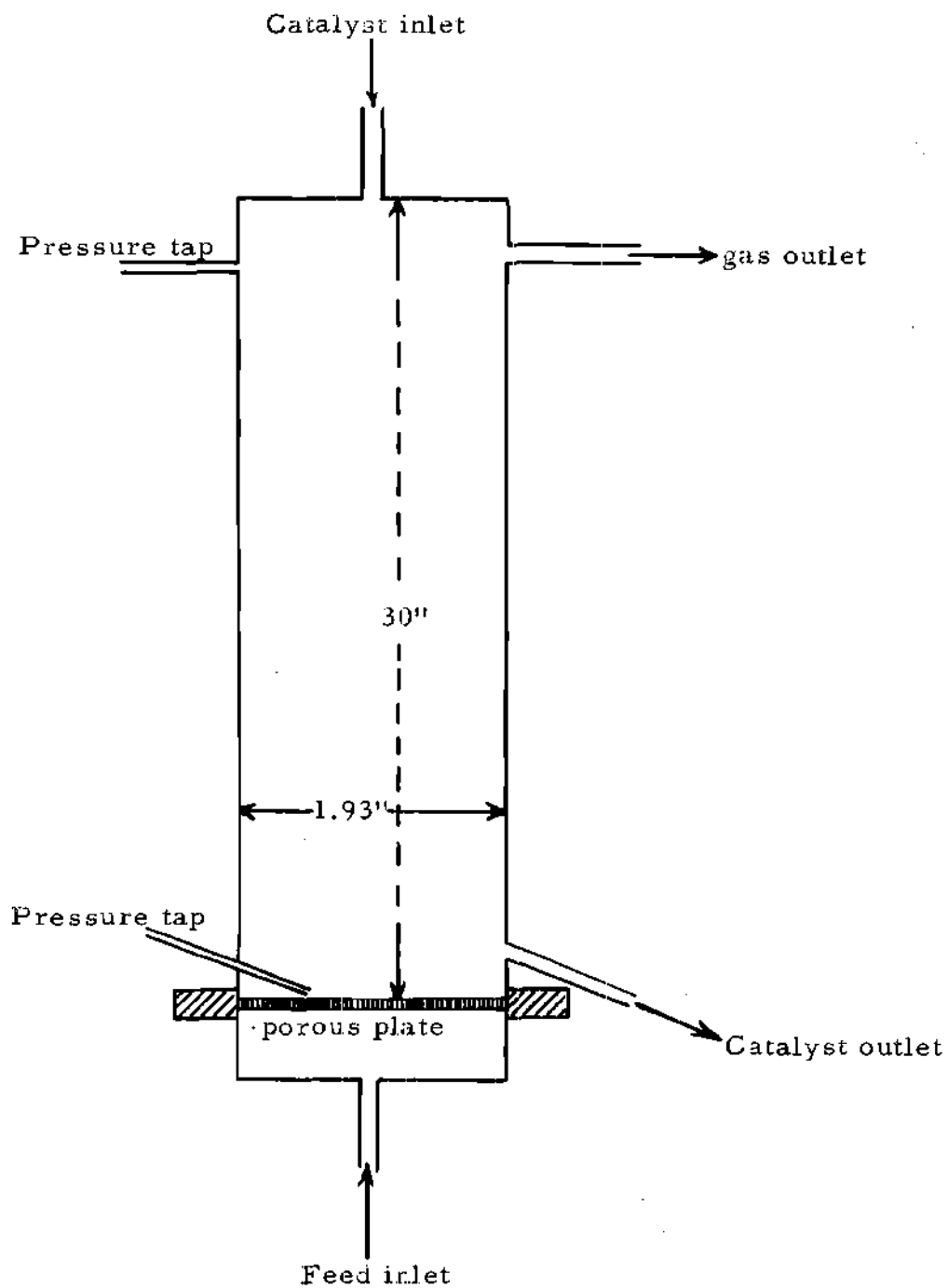


Figure 4. Diagram of Experimental Reactor

allowed pressure drop and total static pressure measurements to be made on the reactor. There are three additional taps: two at the top, one for the gas outlet, and one for putting the catalyst in the reactor; the third is near the bottom, and is used for removal of the catalyst.

Temperatures were measured by means of chromel-alumel thermocouples, located at critical points. These points were: (1) reactor inlet, below the porous plate, (2) catalyst bed, at a point about two inches above the porous plate, and (3) at the top of the reactor.

The lower part of the reactor is wound with 16 gauge nichrome wire to a height of 20 in. By means of this heater, it is possible to preheat the reaction zone and the catalyst to the desired temperature, and to furnish the heat for the reactions during the runs. The heat input is controlled by means of a variable resistance. The reactor is also thermally insulated with magnesia to minimize the heat losses. The preheater was constituted by a stainless steel coil placed in an electric furnace.

Experimental Procedure. —As has been previously stated, the dehydrogenation reactions of the hydrocarbons are promoted by low pressure, or in the case of diluent by low partial pressure of the reacting hydrocarbon.

In this experimental work, it was preferred to use the latter solution, i. e., to carry out the dehydrogenation reactions with the use of diluent in order to simplify the apparatus and procedure. For the same reason it was decided to use a batch fluidized system with no recycle of the solid phase.

Prior to a set of runs, the required amount of catalyst was charged to the reactor, and the various heaters were adjusted to bring the reactor to the desired temperatures. During this period, the catalytic bed was fluidized with an air current, preheated to the reaction temperature and at approximately the flow rate of reacting mixture to be used during the runs.* When the catalytic bed reached the desired temperature, the air flow was interrupted and nitrogen was used as fluidizing agent. After some minutes, when all transfer lines and the reactor itself were purged of air, the butane flow was started in the desired quantity. The flow rates of air, nitrogen, and butane were controlled by manually operated needle valves. The temperatures were also controlled manually and measured by means of a potentiometer.

Each run was approximately 4 — 5 minutes. The gas samples of feed and products from the gas holder were usually taken by means of aspirator bottles filled with water and analyzed by a Perkin Elmer chromatographic analyzer which gave a complete gas analysis on the hydrogen free basis. This procedure was developed from preliminary experiments to give reproducible results.

Catalyst.—In all the dehydrogenation runs, a commercial chromia-alumina catalyst, C₂-0205 T, lot no. 101, supplied by the Harshaw

*It is evident that in this operation, the air regenerates, if necessary, the catalyst, by burning up the carbonaceous deposit formed during previous processings.

Chemical Company, was used. The catalyst had a particle density of 1.07 gr./CC. The fluidized solid particles were obtained by grinding cylindrical 1/8" x 1/8" catalyst pellets. The fraction used was that which has passed by a No. 25 and was held on a No. 45 U. S. Sieve.

CHAPTER III

EXPERIMENTAL CONDITIONS

Fluidizing Velocities. --In order to check the operability of the fluidized bed technic, a series of runs was made at three different reactor temperatures and different space velocities and at an approximately fixed partial pressure of reacting n-butane.

The choice of the space velocities used in all the runs was related to the particular fluidizing agent used and to the physical and geometric characteristics of the dehydrogenation catalyst, i. e., specific gravity and sphericity. It is well known that it is always difficult, and often impossible, to predict theoretically the value of fluid velocity necessary to start the fluidization. In this case, the problem was complicated by the irregular shape of the catalytic particles, and, due to the cracking and dehydrogenation reaction, the fluidizing gas was constituted by a mixture of nitrogen, light hydrocarbons and hydrogen.

For the above reasons, the minimum fluidizing velocities were evaluated experimentally at the three different temperatures used in the dehydrogenation runs, i. e., 450, 475, and 500° C. This was accomplished by visual examination of the float in the flowmeters during dehydrogenation runs. In fact, when the catalytic bed, at the temperature

of the experiment, was in a fluidized state, it was possible to observe fluctuations of the float in the flowmeters, which became more intense as the velocity of the fluidizing gas increased. Also, the manometer measuring the pressure drop across the bed began to fluctuate intensely at fluidizing velocities. By decreasing progressively and slowly the total flow rate, a point was reached in which no more float movements or pressure drop fluctuations were observed. In this condition, the catalytic bed was assumed to be in an incipient fluidization state and the corresponding superficial gas velocity was determined.

In Table 2 are listed corresponding minimum fluidizing velocities for the three different reactor temperatures. These minimum fluidizing velocities determine the lower limit for experimental fluidizing runs. These values are in close agreement with those calculated by means of recommended formula (22, 23, 24).

Experimental Data.—As stated in the preceding paragraph, several runs were made at three selected temperatures, i. e., at 450, 475, 500° C. For each of these temperatures, different space velocities* were used, varying from the minimum values required to start the fluidization to the maximum values permitted for batch fluidization of the system.

*A convenient unit for expressing a relationship between feed rate and catalytic bed volume in a flow process is the space velocity, which is defined as the volume of feed, measured at standard conditions, per unit time, per unit volume of catalytic bed. This unit has the dimension of reciprocal time.

The butane partial pressure in the feed mixture, composed of nitrogen and butane, was in all runs about 0.18 atmosphere. The quantity of catalyst used in every dehydrogenation experiment was about 540 grms., and the ratio L/D , i. e., the ratio of minimum bed height to the reactor internal diameter was 8. At very high fluidizing gas velocities, greater than twice the minimum value, the ratio L/D increased to about 12, due to the expansion of the bed.

The length of each run was about five minutes. The temperature of fluidized bed was kept almost constant, there being only 4 or 5 degrees centigrade change.

The data collected are summarized in Tables 3, 4, and 5. Hourly gaseous space velocities, referred to the reactor conditions, varied from 1,300 and 3,500 l/hr. Consequently the ratio of the actual fluidizing gas velocity to the minimum fluidizing velocity changed between 1 and 3.

Feed and yields composition, in volume per cent for all runs are given in Tables 3-B, 4-B, and 5-B. The feed compositions are referred to the feed sampled after the preheating furnace, below the porous plate in the reactor. The yields compositions are referred to the reactor products collected in the gas holder.

In Figure 5 are reported the experimental values of conversion and total selectivity, expressed in mole per cent, as a function of space velocity and temperatures.

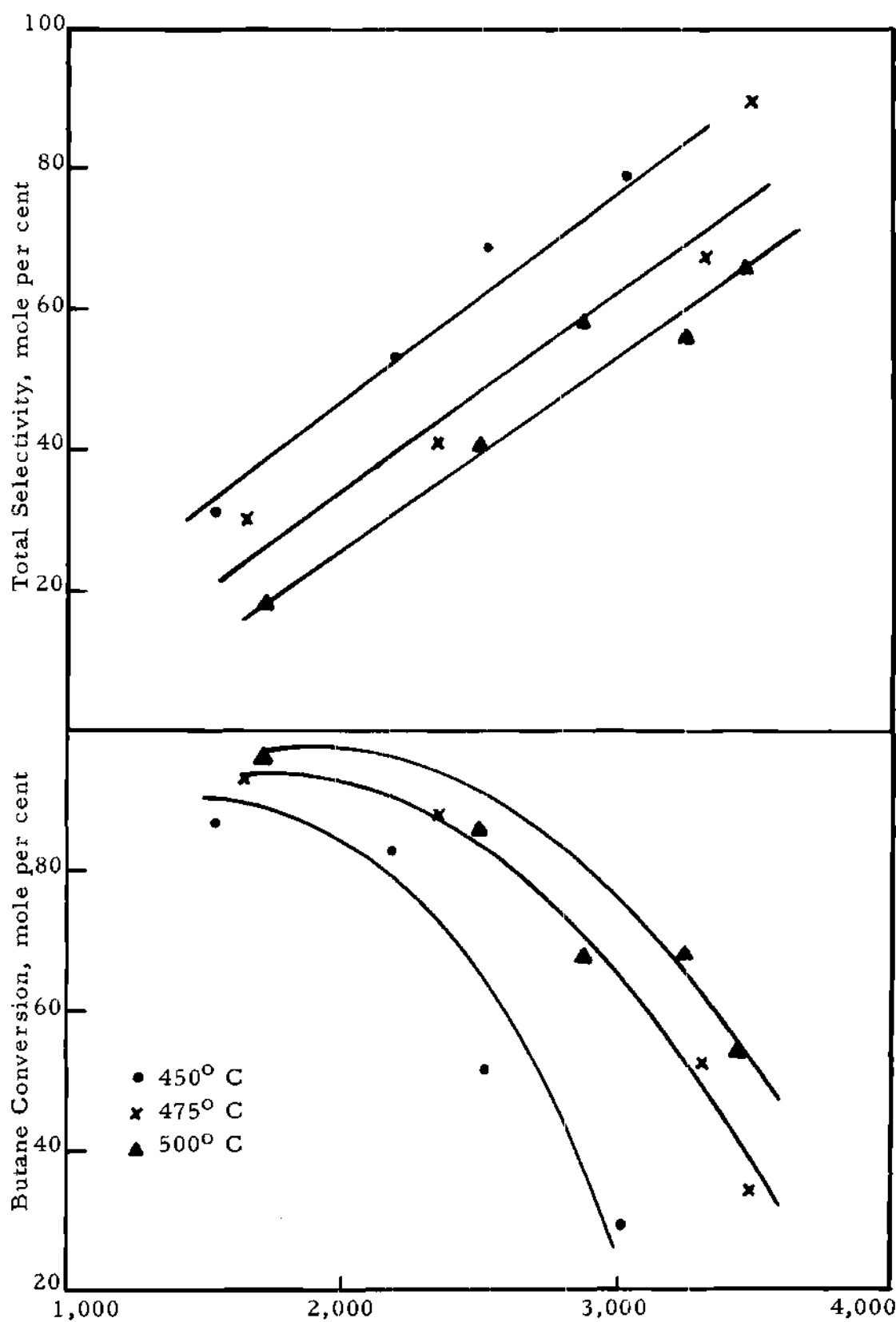


Figure 5. Butane Conversion and Selectivity as a Function of Space Velocity

Discussion of Results. — The results indicate that operating conditions have a marked effect on product distribution. For a given temperature, the superficial gas velocity, which affects both the residence time of reacting feed mixture and the characteristic of fluidization, influences greatly both conversion and selectivity.

At low space velocities, close to the minimum values to start the fluidization, the butane conversion per cent is very high, selectivity to desired products, i. e., butylenes and butadiene, is very poor, and carbon deposition is high.

The selectivities decrease as the conversion levels increase, and the carbon depositions increase as the conversion levels increase.

It appears evident, from the diagram of Figure 5, that for a fixed space velocity, the butane conversion increases and total selectivities decrease with increasing temperature from 450 to 500° C.

Only at higher space velocities used for each temperature are the carbon deposits reasonably low, and both selectivity and conversion per cent satisfactory. At space velocities of about 3,500 l/hr., conversions varied from 30 to 55 per cent, the corresponding selectivities varied from 89 to 67 per cent, and the carbon deposition varied from 0.5 to 22 per cent.

It is not possible to make a direct comparison between the experimental results obtained in this present work, and the data available in the literature, because of the different experimental conditions (i. e.,

chemical composition and particle dimension of the dehydrogenation catalyst, temperature, space velocity, and partial pressure of butane). On the other hand it is always possible to draw some qualitative considerations.

It appears evident that the order of magnitude of the butane per cent conversions and selectivity, for the greater space velocities, is compatible with that referred to in the fixed bed operations at temperatures between 575 and 600° C. For example, Dodd and Watson found that for temperatures of 570° C., total pressure of butane of one atmosphere and for space velocities ranging between 1,230 and 6,160 l/hr. (measured at reactor conditions), the conversions were varying from 31 to 48 mole per cent, and the selectivities from 97 to 76 mole per cent. The carbon deposition was about 1 or 2 per cent. (18).

To have found, in this experimental work, conversions and selectivities not too far from those found by Dodd and Watson, even if the temperatures are considerably less, indicates that the catalyst used in fluidized bed experiments is very active with regard to the dehydrogenation and cracking reactions.

For the lowest values of space velocities used, the catalyst acts as a very active cracking catalyst. This particular behavior could be explained by the fact that the catalyst used in this work had an average size much less than the catalyst size used in fixed bed operations. Dodd and Watson, in fact, used a catalyst in the form of 1/8" x 1/8" cylindrical pellets.

CHAPTER IV

CONCLUSIONS

No detailed comparison of the results of this report can be made with data of other investigators, because of the completely different experimental conditions.

With regard to the particular experimental setup and procedure, the following conclusions can be drawn:

(1) The experimental results indicate that the dehydrogenation of n-butane in a fluidized bed is practical. In fact, the great activity of the dehydrogenation catalyst used, for both selectivity to desired product and to carbon deposition, could be very favorable because it would permit the adoption of working temperature 100° centigrade or more below those used in fixed bed operations.

(2) Selectivity increases and conversion and carbon depositions decrease with increased space velocities.

(3) Selectivity decreases and conversion and carbon depositions increase with increasing temperatures.

CHAPTER V

RECOMMENDATIONS

It appears evident that the present investigation needs to be expanded to include a wider range of information. Some items which should be included in a proposal for further study are:

- (1) Effect of ratio L/D.
- (2) Effect of particle sizes.
- (3) Characteristics of different dehydrogenation catalysts.
- (4) Effect of increased space velocity.
- (5) Effect of wider range of temperatures.
- (6) Effect of butane partial pressure.

APPENDIX

Table 1. Free Energy of Formation, Cal/Gr. mole

| Temp., °K. | 298 | 400 | 600 | 800 | 1000 |
|----------------|--------|--------|--------|--------|--------|
| n-Butane | 3,600 | 5,600 | 24,700 | 44,500 | 64,500 |
| Butene-1 | 17,700 | 23,800 | 36,700 | 50,100 | 63,700 |
| cis-Butene 2 | 16,200 | 22,500 | 35,800 | 49,700 | 64,100 |
| trans-Butene-2 | 15,400 | 21,700 | 35,000 | 48,900 | 63,100 |
| Butadiene 1,3 | 36,600 | 40,000 | 47,600 | 55,600 | 63,900 |

Table 2. Minimum Fluidizing Velocities

| Temp., °C. | 450 | 475 | 500 |
|--|-------|-------|-------|
| Minimum fluidizing velocity, ft./sec. | 0.458 | 0.429 | 0.414 |

Table 3, A. Experimental Data at 450° C.

| Run No. | 23 | 24 | 25 | 26 |
|--|-------|-------|-------|-------|
| Weight of catalyst, grms. | 540 | 540 | 540 | 540 |
| Butane partial pressure, atm. | 0.188 | 0.176 | 0.170 | 0.17 |
| Total Flow* rate, cf/min. | 0.248 | 0.355 | 0.406 | 0.484 |
| Space velocity [†] 1/hr. | 1,528 | 2,191 | 2,507 | 3,027 |
| Fluidizing gas [†] velocity, ft./sec. | 0.534 | 0.766 | 0.876 | 1.057 |
| Ratio of the actual to the minimum fluidizing velocity | 1.16 | 1.67 | 1.91 | 2.31 |

*Measured at 0° C. and 760 mm.

†At reactor conditions. Volume of catalyst is bed volume at minimum of fluidization.

Table 3, B. Experimental Data at 450° C.

| Run No. | 23 | 24 | 25 | 26 |
|---|-------|-------|-------|-------|
| Feed Composition, | | | | |
| Vol. per cent: | | | | |
| N ₂ | 80.71 | 82.97 | 82.47 | 82.97 |
| CH ₄ | - | - | - | - |
| C ₂ H ₆ | 0.08 | 0.19 | - | - |
| C ₂ H ₄ | - | - | 0.36 | - |
| C ₃ H ₈ | 0.31 | 0.13 | 0.36 | 0.09 |
| C ₃ H ₆ | 0.12 | - | - | - |
| n-C ₄ H ₁₀ | 18.79 | 17.59 | 17.07 | 16.93 |
| C ₄ H ₈ , C ₄ H ₆ | - | - | - | - |
| Product Composition, | | | | |
| Vol. per cent: | | | | |
| N ₂ | 83.76 | 79.52 | 81.30 | 81.87 |
| CH ₄ | 2.74 | 3.83 | 1.51 | 1.59 |
| C ₂ H ₆ | 3.61 | 3.34 | 1.46 | 0.82 |
| C ₂ H ₄ | 0.49 | 0.94 | 0.63 | 0.28 |
| C ₃ H ₈ | 0.71 | 0.83 | 0.42 | 0.20 |
| C ₃ H ₆ | 1.00 | 1.33 | 0.55 | 0.23 |
| n-C ₄ H ₁₀ | 2.60 | 2.81 | 8.13 | 9.64 |
| C ₄ H ₈ | 4.90 | 6.74 | 5.69 | 5.27 |
| C ₄ H ₆ | 0.22 | 0.67 | 0.31 | 0.33 |
| Butane Conversion*, | | | | |
| mole per cent | 36.67 | 83.34 | 51.73 | 30.54 |
| Reacted Butane*, | | | | |
| to carbon, * mole per cent | 48.14 | 15.26 | 5.12 | 3.55 |
| Butylenes and Butadiene | | | | |
| selectivity, * mole per cent | 30.51 | 52.52 | 69.90 | 79.07 |
| Butadiene selectivity*, | | | | |
| mole per cent | 1.38 | 4.75 | 3.55 | 4.65 |

*Based on nitrogen balance only.

Table 4, A. Experimental Results at 475° C.

| Run No. | 17 | 18 | 20 | 28 |
|--|-------|-------|-------|-------|
| Weight of catalyst, grms. | 540 | 540 | 540 | 540 |
| Butane partial pressure, atm. | 0.184 | 0.189 | 0.180 | 0.195 |
| Total Flow rate, * cf/min. | 0.253 | 0.365 | 0.508 | 0.540 |
| Space velocity, † 1/hr. | 1,636 | 2,361 | 3,287 | 3,491 |
| Fluidizing gas [†] velocity, ft./sec. | 0.572 | 0.824 | 1.12 | 1.22 |
| Ratio of the actual to the minimum fluidizing velocity | 1.33 | 1.92 | 2.62 | 2.84 |

*Measured at 0° C. and 760 mm.

†At reactor conditions. Volume of catalyst is bed volume at minimum of fluidization.

Table 4, B. Experimental Data at 475° C.

| Run No. | 17 | 18 | 20 | 28 |
|---|-------|-------|-------|-------|
| Feed Composition, | | | | |
| Vol. per cent: | | | | |
| N ₂ | 81.06 | 80.60 | 81.67 | 80.22 |
| CH ₄ | - | - | - | - |
| C ₂ H ₆ | - | 0.10 | - | - |
| C ₂ H ₄ | 0.29 | 0.23 | 0.19 | - |
| C ₃ H ₈ | 0.22 | 0.18 | 0.10 | 0.21 |
| C ₃ H ₆ | - | - | - | 0.09 |
| n-C ₄ H ₁₀ | 18.42 | 18.89 | 18.03 | 19.48 |
| C ₄ H ₈ , C ₄ H ₆ | - | - | - | - |
| Product Composition, | | | | |
| Vol. per cent: | | | | |
| N ₂ | 87.01 | 81.26 | 82.04 | 79.24 |
| CH ₄ | 2.70 | 3.99 | 2.28 | 0.95 |
| C ₂ H ₆ | 0.49 | 3.25 | 0.78 | 0.57 |
| C ₂ H ₄ | 0.62 | 0.26 | 0.31 | 0.35 |
| C ₃ H ₈ | 0.81 | 0.62 | 0.29 | 0.16 |
| C ₃ H ₆ | 1.46 | 1.48 | 0.43 | 0.16 |
| n-C ₄ H ₁₀ | 1.40 | 2.25 | 8.43 | 12.87 |
| C ₄ H ₈ | 5.03 | 6.41 | 6.05 | 5.47 |
| C ₄ H ₆ | 0.47 | 0.47 | 0.38 | 0.22 |
| Butane Conversion, | | | | |
| mole per cent | | | | |
| | 92.94 | 88.8 | 53.46 | 33.16 |
| Reacted Butane* | | | | |
| to carbon, mole per cent | | | | |
| | 55.89 | 40.26 | 18.49 | 0.31 |
| Butylenes and Butadiene | | | | |
| selectivity, mole per cent | | | | |
| | 29.90 | 41.34 | 66.36 | 89.16 |
| Butadiene selectivity, | | | | |
| mole per cent | | | | |
| | 2.55 | 2.76 | 3.92 | 3.44 |

*Based on nitrogen balance only.

Table 5, A. Experimental Data at 500° C.

| Run No. | 16 | 15 | 14 | 31 | 13 |
|--|-------|-------|-------|-------|-------|
| Weight of catalyst, grms. | 540 | 540 | 540 | 540 | 540 |
| Butane partial pressure, atm. | 0.20 | 0.183 | 0.183 | 0.175 | 0.188 |
| Total Flow rate, * cf/min. | 0.254 | 0.374 | 0.434 | 0.483 | 0.517 |
| Space velocity, † 1/hr. | 1,695 | 2,491 | 2,896 | 3,220 | 3,441 |
| Fluidizing gas velocity, ft./sec | 0.59 | 0.87 | 0.97 | 1.13 | 1.14 |
| Ratio of the actual to the minimum fluidizing velocity | 1.42 | 2.10 | 2.34 | 2.72 | 2.75 |

*Measured at 0° C. and 760 mm.

†At reactor conditions. Volume of catalyst is bed volume at minimum of fluidization.

Table 5, B. Experimental Data at 500° C.

| Run No. | 16 | 15 | 14 | 31 | 13 |
|---|-------|-------|-------|-------|-------|
| Feed Composition, | | | | | |
| Vol. per cent: | | | | | |
| N ₂ | 79.03 | 81.33 | 81.34 | 82.21 | 82.20 |
| CH ₄ | - | - | - | - | - |
| C ₂ H ₆ | 0.09 | - | 0.07 | - | - |
| C ₂ H ₄ | 0.14 | 0.21 | 0.15 | 0.21 | 0.24 |
| C ₃ H ₈ | 0.14 | 0.11 | 0.13 | 0.08 | 0.11 |
| C ₃ H ₆ | 0.07 | - | - | - | - |
| n-C ₄ H ₁₀ | 20.51 | 18.36 | 18.32 | 17.50 | 17.46 |
| C ₄ H ₈ , C ₄ H ₆ | - | - | - | - | - |
| Product Composition, | | | | | |
| Vol. per cent: | | | | | |
| N ₂ | 83.24 | 83.76 | 82.32 | 82.73 | 82.66 |
| CH ₄ | 4.58 | 2.81 | 2.35 | 1.96 | 1.26 |
| C ₂ H ₆ | 4.94 | 2.49 | 0.98 | 1.36 | 0.80 |
| C ₂ H ₄ | 0.38 | 0.11 | 0.17 | 0.38 | 0.17 |
| C ₃ H ₈ | 0.75 | 0.50 | 0.25 | 0.45 | 0.22 |
| C ₃ H ₆ | 1.44 | 0.89 | 0.52 | 0.63 | 0.46 |
| n-C ₄ H ₁₀ | 0.89 | 2.61 | 5.76 | 5.63 | 7.90 |
| C ₄ H ₈ | 3.35 | 6.25 | 7.02 | 6.64 | 5.90 |
| C ₄ H ₆ | 0.41 | 0.58 | 0.63 | 0.23 | 0.61 |
| Butane Conversion*, | | | | | |
| mole per cent | | | | | |
| | 95.88 | 86.16 | 68.34 | 68.05 | 54.98 |
| Reacted Butane* | | | | | |
| to carbon, mole per cent | | | | | |
| | 56.43 | 43.67 | 28.43 | 25.90 | 21.21 |
| Butylenes and Butadiene | | | | | |
| selectivity, * mole per cent | | | | | |
| | 18.15 | 41.90 | 60.38 | 56.76 | 67.50 |
| Butadiene selectivity*, | | | | | |
| mole per cent | | | | | |
| | 1.98 | 3.06 | 4.97 | 1.93 | 6.31 |

*Based on nitrogen balance only.

BIBLIOGRAPHY

1. Rietz, C. H., Pelican, T. L., and V. I. Komarewsky, "Catalytic Dehydrogenation of Natural Gas Hydrocarbons", The Oil and Gas Journal, July 15, 1944, p. 67.
2. Reidel, J. C., "Phillips Petrochemical", The Oil and Gas Journal, January 12, 1953, p. 84.
3. Beesley, E., and B. Whipp, "Butane Dehydrogenation at Billingham," Symposium Society of Chemical Industry and Institute of Petroleum, at London, March 2, 1953; Chemistry and Industry, August 10, 1953, p. 50.
4. Lassiat, R. C., and F. D. Parker, "Butane Dehydrogenation by the Houdry Process," The Oil and Gas Journal, November 18, 1944, p. 229.
5. Hornaday, G. F., and J. J. Cicalese, "Houdry Dehydrogenation Process," Petroleum Refiner, December 1956, p. 173.
6. Brack, W. J., and M. R. Beychok, "First Postwar Butadiene Plant," The Oil and Gas Journal, June 10, 1957, p. 82.
7. Russell, R. P., Murphree, E. V., and W. C. Asbury, "Production of Butadiene by Dehydrogenation of N-Butylenes," Transactions American Institute of Chemical Engineers, 42, (1946), p. 1.
8. Nicholson, E. W., Moise, J. E., Segura, M. A., and C. E. Kleiker, "Butene Dehydrogenation," Industrial and Engineering Chemistry, 41, (1949), p. 646.
9. Kearby, K. K., "Catalytic Dehydrogenation of Butenes," Ind. Eng. Chem., 42, (1950), p. 295.
10. Watson, K. M., and L. H. Beckberger, "Catalytic Dehydrogenation of Normal Butenes to Butadiene in Presence of Steam," Chem. Engr. Progress, 44, (1948), p. 229.
11. Reidel, J. C., "Butane Dehydrogenation Today," Oil and Gas Journal, December 9, 1957, p. 114.

12. Frey, E. F. and W. F. Uppke, "Equilibrium Dehydrogenation of Ethane, Propane, and the Butanes," Ind. Eng. Chem., 25, (1933), p. 54; U. S. Patent 2,098,958, (1937).
13. Burgin, J., and H. Groll, U. S. Patent 2,184,234-5, (1939); 2,217,865 (1940) and 2,270,165 (1942).
14. Grosse, A. V., and Ipatieff, V. N., "Catalytic Dehydrogenation of Gaseous Paraffins," Ind. Eng. Chem., 32, (1940) p. 268.
15. Howard, E. W., University of Illinois, Bulletin 48, No. 29, Circular 61 (1950).
16. Hanson, G. H., and H. L. Hays, "Phillips Butane Dehydrogenation Process," Chem. Engr. Progress, 44, (1948), p. 431.
17. Pitzer, E. W., U. S. Patent 2,586,377, (1952).
18. Dodd, R. H., and K. M. Watson, "Dehydrogenation of Butane," Trans. A. I. Ch. E., 42, (1946), p. 263.
19. Aston, J. G., Szasy, G. I., and F. G. Brickedde, Pennsylvania State College, paper presented by office of Rubber Directory, 1943.
20. "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, March 31, 1947.
21. Gilliland, E. R., "Chemicals for Synthetic Rubber," Science of Petroleum, Oxford University Press, vol. V, part II (1953), p. 32, p. 41.
22. Lewis, W. K., Gilliland, E. R. and W. C. Bauer, "Characteristics of Fluidized Particles," Ind. Eng. Chem., 41, 1104, (1949).
23. Morse, R. D., "Fluidization of Granular Solids," Ind. Eng. Chem., 41, 1117, (1949).
24. Wilhelm, R. H., Kwauk, M., "Fluidization of Solid Particles," Chem. Engr. Progress, 44, 201, (1948).

