

Leuna Works - January 2, 1945.

EXPERIMENTS ON THE REMOVAL OF BUTADIENE FROM THE BUTANE  
DEHYDROGENATION GASES BY MEANS OF SELECTIVE HYDROGENATION

In order to reduce the acid consumption in sulphuric acid alkylation which is caused by the presence of diolefins, mainly of butadiene, in the butylene feed, experiments were made to remove the diolefins by selective hydrogenation.

While laboratory experiments were successful, both at atmospheric pressure and at a pressure of 147 psi., large-scale experiments which were only carried out at atmospheric pressure gave much less satisfactory results.

Laboratory Experiments.

The exit gas from the butane dehydrogenation reactor was processed in a laboratory apparatus consisting of a quartz tube with a capacity of 15.2 - 18.3 cubic inches. The first experiments were made with catalyst 4788 which is a chromium-nickel catalyst, used for the selective hydrogenation of  $C_2H_2$  in ethylene in the plant.

The dehydrogenation gas contains 15 to 20%  $C_4H_8$ , 0.5 to 1.5%  $C_4H_6$  and 15 to 20%  $H_2$  and was hydrogenated without the addition of fresh hydrogen. The experiments were made in the temperature range from 302 - 572°F. at space velocities from 1,000 to 5,000 volumes of gas per volume of catalyst per hour. The results are shown in the attached tables. Table 1 gives the results obtained with gas washed with 10% NaOH solution, whereas the results given in Table 2 are obtained without caustic washing. The data indicate that the diolefins are hydrogenated to olefins and that only traces of the olefins have reacted. Tests in a special alkylation apparatus indicated that the acid consumption decreased from 25 to 30% for the untreated dehydrogenation gas to 15 to 20% after selective hydrogenation.

Table 3 shows the effect on acid consumption by hydrogenation under various conditions using catalyst 4788.

Test results with the commercial hydrogenation catalyst 3076 ( $WS_2.2NiS$ ) which is not sensitive to sulphur compounds are shown in Table 4. The particular catalyst used had been previously in plant service for several months (hydrogenation of heavy gas oil from Fischer-Tropsch synthesis).

Good results were also obtained with catalyst 7846 ( $WS_2.2NiS$  on an alumina carrier) and catalyst 7058 ( $MoS_2.2NiS$ ) among others.

Raising the hydrogen concentration of the dehydrogenation gas to 50% by the addition of fresh hydrogen also gave favorable results.

The results of hydrogenation tests at a pressure slightly above atmospheric are given in Table 5 for several catalysts.

All laboratory results indicate that butadiene in the butane dehydrogenation gas can be selectively hydrogenated at atmospheric and slightly elevated pressure. The olefins are practically not changed under these conditions.

### Plant Experiments.

On the basis of the laboratory results, experiments were carried out on a technical scale using catalysts 3076 and 4788. The experiments were made at atmospheric pressure, temperatures of 356 - 392°F. and space velocities of 1,000 to 4,000 volumes per volume of catalyst per hour. No satisfactory results were obtained under these conditions and only when the temperature was raised to 482 - 572°F. hydrogenation of butadiene was obtained, provided the space velocity was sufficiently low.

The dehydrogenation gas from the reactor was freed from dust and passed into a steam-heated preheater from where it flowed to two reactors connected in parallel. The dimensions of the reactors were as follows:

|                    | <u>Reactor 1</u> | <u>Reactor 2</u> |
|--------------------|------------------|------------------|
| Diameter           | 2.3 feet         | 2.6 feet         |
| Height             | 7.2 "            | 7.4 "            |
| Catalyst Bed       | 4.5 "            | 3.9 "            |
| Volume of Catalyst | 17.7 cu. ft.     | 17.7 cu. ft.     |

The reactor was not heated but insulated against radiation losses. In cases where higher temperatures were desired, the steam-heated preheater was replaced by a gas-heated preheater.

All experiments were practically without success, with the exception of the experiment in which freshly-reduced catalyst 3076 was used at 570°F. and a space velocity of 500 volumes of gas per volume of catalyst per hour. The expected decrease in acid consumption in the alkylation was not reached because only part of the dehydrogenation gases could be passed through the experimental unit. The activity of the catalyst in the successful experiment decreased, however, considerably after 20 days. The results of the tests in the large-scale unit are given in Table 6.

It might be possible to prolong the activity of a catalyst by a preliminary purification of the dehydrogenation gas by means of coke filters. Because of air attacks no large-scale experiments under pressure could be made.

Table 1

| Space Velocity<br>Vol/Vol/hour | Pressure<br>psig. | Reactor Temp.<br>°F. |                |                | Analyses        |                 |                |                |
|--------------------------------|-------------------|----------------------|----------------|----------------|-----------------|-----------------|----------------|----------------|
|                                |                   | top                  | center         | bottom         | Olefins         |                 | Diolefins      |                |
|                                |                   |                      |                |                | feed            | product         | feed           | product        |
| 2000                           | 0                 | 266                  | 446            | 482            | 9.8             | 9.4             | 0.7            | 0.2            |
| 3000                           | 0                 | 239                  | 401            | 500            | 12.3            | 12.0            | 0.5            | 0.2            |
| <del>3600</del>                | <del>0</del>      | <del>230</del>       | <del>392</del> | <del>491</del> | <del>14.4</del> | <del>14.2</del> | <del>0.7</del> | <del>0.4</del> |
| 4700                           | 0                 | 212                  | 383            | 473            | 16.8            | 17.1            | 0.8            | 0.1            |
| 3000                           | 0                 | 266                  | 473            | 572            | 17.2            | 17.5            | 1.1            | 0.1            |

Table 2

| Space Velocity<br>Vol/Vol/hour | Pressure<br>psig. | Reactor Temp.<br>°F. |        |        | Analyses |         |           |         |
|--------------------------------|-------------------|----------------------|--------|--------|----------|---------|-----------|---------|
|                                |                   | top                  | center | bottom | Olefins  |         | Diolefins |         |
|                                |                   |                      |        |        | feed     | product | feed      | product |
| 2000                           | 0                 | 347                  | 572    | 662    | 12.6     | 12.2    | 0.4       | 0.1     |
| 3000                           | 0                 | 248                  | 446    | 581    | 13.4     | 13.5    | 0.9       | 0.3     |
| 4600                           | 0                 | 266                  | 527    | 662    | 14.4     | 15.0    | 0.4       | 0.1     |
| 4500                           | 0                 | 320                  | 536    | 662    | 11.2     | 11.0    | 0.3       | 0.0     |

Table 3

| Catalyst | Temp.<br>°F. | Space Velocity<br>Vol/Vol/hour | Pressure<br>psig. | Caustic Wash | Acid Consumption<br>lbs. acid/bbl. alkylate |                  |
|----------|--------------|--------------------------------|-------------------|--------------|---|------------------|
|          |              |                                |                   |              | before<br>hydrog.                           | after<br>hydrog. |
| 4788     | 482          | 2000                           | 0                 | no           | 73.6  | 58.5             |
| 4788     | 482          | 2000                           | 0                 | yes          | 76.2  | 42.7             |
| 4788     | 572          | 3000                           | 0                 | yes          | 76.2  | 39.8             |
| 4788     | 572          | 3000                           | 0                 | yes          | 76.2  | 35.6             |
| 4788     | 572          | 3000                           | 0                 | no           | 76.2  | 39.3             |
| 4788     | 572          | 3000                           | 0                 | no           | 76.2  | 30.7             |
| 4788     | 572          | 4000                           | 0                 | no           | 90.9  | 54.5             |

Table 4

| Catalyst                | Space Velocity<br>Vol/Vol/hour | Temp.<br>OF. | Pressure<br>psig. | % Olefins<br>feed product | % Diolefins<br>feed product | Acid Consumption<br>lbs. acid/bbl. alkylate<br>feed product |
|-------------------------|--------------------------------|--------------|-------------------|---------------------------|-----------------------------|---|
| 3076                    | 2000                           | 302          | 0                 | 17.6                      | 17.6                        | 90.9  |
| "                       | 4000                           | 392          | 0                 | 17.8                      | 17.8                        | 92.4  |
| "                       | 4000                           | 482          | 0                 | 16.6                      | 16.0                        | 92.4  |
| "                       | 4000                           | 572          | 0                 | 17.6                      | 17.3                        | 92.4  |
| "                       | 6000                           | 572          | 0                 | 20.2                      | 20.0                        | 106.8   |
| 3076 Freshly<br>reduced | 4000                           | 392          | 0                 | 14.0                      | 14.0                        | 127.2   |
| "                       | 4000                           | 392          | 0                 | 14.6                      | 14.2                        | 130.0   |
| "                       | 4000                           | 392          | 0                 | 14.2                      | 13.8                        | 122.6   |
| "                       | 4000                           | 572          | 0                 | 14.6                      | 14.2                        | 122.6   |

Table 5

| Catalyst                | Space Velocity<br>Vol/Vol/hour | Temp.<br>OF. | Pressure<br>psig. | % Olefins<br>feed product | % Diolefins<br>feed product | Acid Consumption<br>lbs. acid/bbl. alkylate<br>feed product |
|-------------------------|--------------------------------|--------------|-------------------|---------------------------|-----------------------------|---|
| 3076                    | 3000                           | 392          | 117.5             | 16.0                      | 14.8                        | 92.4  |
| used                    | 4000                           | 482          | 117.5             | 14.2                      | 14.0                        | 92.4  |
| in plant                | 6000                           | 482          | 117.5             | 16.6                      | 15.4                        | 92.4  |
| "                       | 6000                           | 572          | 117.5             | 15.2                      | 14.8                        | 106.8   |
| "                       | 8000                           | 572          | 117.5             | 13.8                      | 13.8                        | 106.8   |
| 3076 Freshly<br>reduced | 4000                           | 572          | 117.5             | 16.2                      | 15.0                        | 129.0   |
| 7846                    | 2000                           | 572          | 117.5             | 14.4                      | 13.4                        | 110.5   |
| 7058                    | 2000                           | 572          | 117.5             | 13.5                      | 13.2                        | 135.0   |

Table-6

| Catalyst       | Space Velocity<br>Vol/Vol/hour | Temp. of  |           | Feed<br>% Olefin | Product<br>% Olefin | Acid Consumption<br>lbs. acid/bbl. alkylate<br>feed product | Reactor Filling |           |           |  |
|----------------|--------------------------------|-----------|-----------|------------------|---------------------|---|-----------------|-----------|-----------|--|
|                |                                | Reactor 1 | Reactor 2 |                  |                     |   |                 |           |           |  |
| 4788           | 1000                           | 356       | 356       | 14.0-16.0        | 0.5-0.9             | 14.0-16.0   | 0.3-0.6         | 73.6-86.0 | unchanged | both reactors filled with<br>17.6 cu. ft. of 4788 each   |
| 3076           | 2000-4000                      | 366       | 366       | 14.0-16.0        | 0.9-1.1             | 14.0-15.0   | 0.5-0.9         | 73.6      | "         | reactor 1, 17.6 cu. ft.<br>3076 from Kogasxin<br>reactor, reactor 2, 21.2<br>cu. ft. of 3076 from plant. |
| 4788)<br>3076) | 3000-4000                      | 347       | 347       | 14.0-15.0        | 0.4-0.9             | 14.0-15.0   | 0.4-0.7         | 103       | "         | reactor 1, 21.2 cu. ft. 4788<br>reactor 2, 33.6 cu. ft. 3076   |
| 3076           | 460                            | 320       | 347       | 14.0-15.0        | 0.8-1.0             | 14.0-16.0   | 0.6             | 122.8     | "         | reactor 2, 26.6 cu. ft. 3076<br>freshly reduced.   |
|                | 1330                           | 356       | 356       |                  |                     | 14.0-16.0   | 0.25            |           |           |  |
|                | 2670                           | 356       |           |                  |                     | 14.0-16.0   | 0.9             |           |           |  |
| 4788)<br>3076) | 2500                           | 471-482   | 471-473   | 15.1-15.8        | 0.5                 | 16.0-15.4   | 0.25-0.5        | 44.2      | "         | reactor 1, 21.2 cu. ft. 4788<br>reactor 2, 33.6 cu. ft. 3076   |
|                |                                | 478-486   | 482-489   | 15.2             | 0.5                 | 16.2-15.4   | 0.25            |           |           |  |
|                |                                | 536-545   | 536-550   | 15.2-15.8        | 0.5                 | 16.2-15.6   | 0.25            |           |           |  |
|                |                                | 572-581   | 572-594   | 17.0-17.2        | 0.5                 | 16.6-16.8   | 0.25            |           |           |  |
| 4788)          | 2600                           | 559-561   | 559       | 16.0             | 0.7                 | 15.6  | 0.6             | 44.2      | "         | reactor 1, 21.2 cu. ft. 4788   |
| 3076)          | 3000                           | 576-590   | 576-579   | 15.6             | 0.7                 | 15.4  | 0.5             | 44.2      | "         | reactor 2, 33.6 cu. ft. 3076   |
|                | 1000                           | 572       | 575-586   | 15.6             | 0.5-0.7             | 15.4  | 0.25            | 44.2      | "         |  |
|                | 500                            | 572       | 572-594   | 15.0             | 0.5-0.7             | 14.5  | 0.35            | 44.2      | "         |  |
|                | 250                            | 572       | 572-626   | 14.0             | 0.5                 | 13.0  | 0.35            | 44.2      | "         |  |
| 3076           | 2500                           | 482-518   | 482       | 13.4             | 0.75                | 13.0  | 0.2             | 110       | "         | reactor 1, 24.7 cu. ft. 3076<br>(0.16") Freshly reduced  |
|                | 1500                           | 572-579   | 572-579   | 14.9             | 0.9                 | 14.0  | 0.6             | 135       | "         | reactor 2, 33.6 cu. ft. old<br>3076.   |
|                | 1500                           | 572-590   | 572-590   |                  |                     |   |                 |           | 110.5     |  |