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onderwerp:

Hydrogenation of Benzene to Cyclohexane

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"Never let your schooling interfere with your education"     Mark Twain

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April 29, 1982
Summary

This FVO describes the catalytic hydrogenation of benzene to cyclohexane with a Pt/Al₂O₃ catalyst. The process is designed for a production capacity of 100,000 mton per year. The conversion for this process is almost complete. The overall selectivity is more than 99.8% calculated on benzene. The operating conditions in the multi-bed reactor of 100 C and 6 atm make this a vapor phase reaction.

A second part of this paper is an inventarisation of some commercially available processes. Based on this comparison study, a FVO has been made.
Contents

I Introduction

II Inventarization of Processes for the Hydrogenation of Benzene
   1. Hydrogenation of Benzene
   2. Thermodynamics and Kinetic Data
   3. Liquid phase Hydrogenation
   4. Gas phase Hydrogenation
   5. The Catalyst
   6. Overview of Existing Processes
   7. Economics
   8. Conclusion

III Design Considerations
   1. Capacity of Factory
   2. The Catalyst
   3. Specifications of Raw Material
   4. Specifications of End Product

IV Description of Process Flow Sheet

V Calculations for the Design
   1. The Catalyst Volume
   2. The Reactor Volume
   3. Pressure drop over the Reactor
   4. Heat Exchangers
   5. Compressors and Pumps
   6. Liquid-gas Separator

VI Safety and Health

VII Conclusion

VIII Notation

Appendix 1
Appendix 2
Appendix 3
Appendix 3A
Appendix 4
Appendix 5
Appendix 6
Appendix 7
References
I. Introduction

Cyclohexane is very important due to its use as a raw material for the manufacturing of nylon, and as a solvent for various fats, oils, waxes, etc. (1).

There are two different ways to produce cyclohexane. About 70% of all cyclohexane is obtained by the hydrogenation of benzene. The remaining 30% is recovered as natural cyclohexane by special fractionation and/or isomerization processes (2). The first route produces cyclohexane of the highest purity, is the most important in industry, and will be used in this paper for the design of a FVO.
II. Inventarization of Processes for the Hydrogenation of Benzene.

II.1. Hydrogenation of Benzene

Since Sabatier developed the first hydrogenation process for benzene in 1898, it has become the most important route to produce cyclohexane (3).

The main objective of this part of the paper is to compare technological and economical aspects of the most important commercial processes available. Based on this study an existing or a new process will be chosen for design and reactor calculations.

II.2. Thermodynamics and Kinetic Data

The catalytic hydrogenation of benzene to cyclohexane is a very exothermic reaction (ΔH° = -51.2 kcal/mole) (4). The operating conditions are not critical and can be taken in the conventional ranges. For example the pressure between 1 and 50 atm, and the temperature between 50 and 400 °C (5). However, to avoid undesirable by-products (methylcyclopentane, benzene isomerization products), an unacceptable high equilibrium benzene content and hydrocracking, the temperature should be kept under 230 °C.

Depending on these operating conditions, the process can be carried out either in liquid or mixed liquid-vapor phase, or in vapor phase, in the presence of a fixed bed of catalyst or a dispersed catalyst.

Because of the equilibrium of the reaction:

\[ \text{Benzene} + 3H_2 \rightarrow \text{Cyclohexane} \]
the conversion of benzene is greater at lower temperature and at higher pressure. Therefore most commercial processes operate at 200°C and 40 atm, in liquid phase (6,7,8,9,10), having a conversion of more than 99%. However, in the last couple of years some gas phase processes were developed, operating at 400-600°C and 20-30 atm (11,12). Also claiming a conversion of more than 99% and reporting no significant by-product formation. These processes use very special catalysts. Especially these last gas phase processes are very interesting, but unfortunately not much information is available.

The kinetics of liquid phase hydrogenation have been studied extensively (13,14,15). Not much is published on the vapor phase reactions (16,17). Because of the trend (11,12) towards gas phase processes, it would be interesting to compare the advantages and disadvantages of gas and liquid phase processes.

II.3. Liquid phase Hydrogenation

Most commercial processes developed in the late 60's are liquid phase processes. The operating conditions are temp. around 200°C and pressure around 40 atm. Each process claiming a specific catalyst.

The advantages are:

(1) Reactor volume is small
(2) Temp. control is easy
(3) Liquids are easier to pump
(4) Allows high-order of flexibility in capacity

Some of the disadvantages are:

(1) It is hard to keep the catalyst in suspension in all parts of the liquid. Therefore there is a possibility of local hot spots, introducing reverse-reaction and start of hydrocracking.
(2) The higher pressures require more expensive equipment.

II.4. Gas Phase Hydrogenation

As said before, the newer processes available are characterized by lower pressures between 1 and 25 atm. Some use high temp. (400-600 C), others lower temp. between 150 and 250 C. They all claim specific catalysts bringing about a conversion of benzene of more than 99%.

The advantages are:

1. Easier for continuous operation
2. There is always a good contact with catalyst
3. Less change of a temp. run away, and less hold-up, which can lead to explosive temp.
4. Lower operating pressures require less expensive equipment.

The disadvantages are:

1. Require larger reactor
2. Theoretically at lower pressure there should be lower conversion, which means recirculation. This turns out to be no problem in industrial processes.
3. These processes need high excess of hydrogen (12:1-20:1).

II.5. The Catalyst

The most important hydrogenation catalysts used are Ramsey nickel, or nickel, platinum or palladium, preferably on a support such as alumina, silica, kieselguhr, or inorganic oxides, alone or in combinations. Some processes use a catalyst slurry (4).

The use of a nickel-containing catalyst could be a disadvantage, because of the fact that nickel is sensitive to sulfurous compounds, possibly contained in the benzene concentrate. On the other hand nickel is the least expensive catalyst (1).
The selectivity of all these catalysts is very high (more than 99.8%). Only very small amounts of by-products (i.e., CP) may be produced, which can be minimized through use of suitable operating conditions.

The amount of catalyst in the reactor(s) will depend on the quality of the feed stocks.

The life of the different catalysts have been reported in literature anywhere between 1 and 7 years.

II.6. Overview of existing processes

The commercially available processes mainly differ in the way they remove the high exothermic heat of reaction. Simplified they can be divided into two categories:

(1) Processes employing indirect water cooling in the reactor(s). (IFP-process, HA-84, ARCO-process, and DSM-process).

(2) Processes recycling portion of feed or product to the reactor to assist in controlling the reactor temp. (Aerosat-process, Hyndra-process, and Houdry-process).

A short description and flow sheet of each process will follow below.

Institute Francais du Petrole (6). Figure 1.

Hydrogenation is almost completely achieved in a liquid phase reactor. Heat in excess is removed in an exchanger where low pressure steam is produced. A small catalytic pot acts as finishing reactor. After condensation, the reactor effluent is flashed in HP separator. A stabilizer removes hydrogen-rich gas. Practically stoichiometric yields of cyclohexane from benzene are obtained.
Benzene and hydrogen are preheated to reaction temperatures (200 °C) by exchanging first with reactor effluent and then with steam. The reactants flow through a fixed bed of precious metal catalyst which completely hydrogenates the benzene to cyclohexane. The reaction temp. is efficiently controlled by using the high heat release to generate steam. The entire hydrogenation is effected in a single reactor. The reactor effluent is exchanged, cooled and flashed at system pressure. A portion of the separator vapors is used as hydrogen recycle gas. The stabilizer bottoms is the high purity cyclohexane product.

Hydrar by Universal Oil Products Co.(8). Figure 3.

Benzene feed, recycle cyclohexane and fresh and recycle hydrogen are brought to reaction temp. and charged to the reactor. The reactor effluent, after exchanging heat with the feed, is charged to the separator. A portion of the cyclohexane from the separator is recycled to the reactor to assist in the control of the reaction temp. Product cyclohexane is flashed and/or stabilized to remove light hydrocarbons.

DSM by Stamicarbon B.V.(11). Figure 4.

At a pressure of 25 to 30 atm and a temp. of about 400 °C, benzene is almost completely converted to cyclohexane with an overall efficiency better than 99%. A noble metal catalyst is used. Only a minor quantity of by-product is formed, further purification of the cyclohexane is not necessary.
A preheated mixture of benzene and hydrogen is catalytically hydrogenated in the vapor phase over a special noble metal catalyst to produce essentially complete conversion. The specially designed reactor assures complete benzene conversion by providing plug flow and also eliminates the need to recycle cyclohexane for heat control by generating steam instead. The reactor effluent exchanges heat with the feed then is cooled before entering the liquid-gas separator.

Fresh feed benzene is mixed with recyclohexane, make-up hydrogen and recycle hydrogen, and charged to the reactor. The product cyclohexane flows to the stabilizer to remove light hydrocarbon gases. Product cyclohexane is cooled and sent to storage.

Benzene, hydrogen and cyclohexane product are heated to reaction temp. by exchange with reactor effluent. The exothermic heat of reaction is removed or controlled by heat exchange to feed and recycle streams. The liquid cyclohexane product is further purified by stripping of the light gases.

II.7. Economics

Because cyclohexane and benzene sell for about the same price on a volume basis, the expansion in weight through hydrogenation provides a narrow margin for profit. There is every incentive to minimize direct costs as well as capital load (indirect costs). Therefore a tight, easily operable, and yet safe design is required.
A comparison between the above described processes will be made based on the (scarce) information provided in the sited references. It will not be possible to calculate the investment and manufacturing costs, because of the differences in plant capacities and the date of information available. Figures are calculated for process utilities, based on a capacity of 100,000 mton per year.

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<tr>
<td>Houdry</td>
<td>25.8</td>
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<td>30</td>
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</table>

Table 1: Process utilities, based on 100,000 mton cyclohexane per year.

No conclusion can be drawn for the direct costs based on the results in table 1. These results vary widely, depending on design rather than gas or liquid phase process.

Since there are no figures on investment costs, in general can be said that material and equipment for gas phase processes will be slightly cheaper than for liquid phase processes, caused by lower operating pressures.
II.8. Conclusion

Considering the above information, a vapor phase process, similar to that of ARCO's will be used for process design and reactor calculations.

The vapor phase process is chosen for several reasons. First, there is a recent trend in industry toward these type of processes (DSM, Shell, ESSO). Eventhough these processes seem to become increasingly important, not much information is available.

Further, the most important advantage of a vapor phase process is the reduced risk for temperature runaways, causing explosions. The temp. is easier to control in a liquid phase reactor, but once the temp. goes up, it will go so fast, that it is impossible to stop it. When the temp. gets above 230 C, the reverse reaction will produce hydrogen. The hydrogen at that temp. will initiate hydrocracking, causing even higher temperatures, producing more hydrogen, etc. In the gas phase, this temp. run away will go so much slower, that it can be controlled.

Thirdly, the new gas phase processes are so advanced, that even at lower pressures, the conversion of benzene is more than 99.8%. This implies that separation of benzene out of the product stream is not necessary.

The multi-bed reactor is designed in such way, that the temperature of each doesn't exceed 210 C. This is achieved by removing the heat of reaction by injecting cold cyclohexane in between the beds.

Of course this process has some disadvantages. A larger reactor volume will be necessary. Also an excess of hydrogen and cyclohexane will be required, but can be recycled.

All these considerations lead to the design of a simple and easy to operate, but yet safe and efficient process.
III. Design Considerations

III.1. Capacity of Factory

The capacity of the factory will be 100,000 mton cyclohexane per year. Based on 330 steam days, this will require 3.26 kg/s of benzene to produce 3.50 kg/s cyclohexane.

III.2. The Catalyst

The catalyst, Pt/Al₂O₃, described by Aben (16), is used for this design. It is reasonable to assume, that this catalyst has an extremely high selectivity of more than 99.8%. Cyclohexane will be the unique product. Neither intermediate nor by-products will be formed.

III.3. Specifications of Raw Material

Hydrogen: will be pure.
Benzene: will be obtained commercially, containing less than 1 ppm unpurities.

III.4. Specifications of End Product

High purity cyclohexane will be produced, having a benzene content of less than 50 ppm.
IV. Description of Process Flow Sheet

The process will be described using flow sheet of figure 8.

Fresh benzene (1) together with make-up (3) and recycle (14) hydrogen are preheated to reaction temperature (100°C) by exchanging with reactor effluent in the feed-product exchanger H1.

The exothermic heat of reaction is removed by injecting cold (30°C) cyclohexane (7,8,9) in between the beds of the specially designed multi-bed reactor (R1).

One third of the effluent from the reactor is cooled to 90°C by exchanging with the feed. The remaining stream of effluent is also cooled to 90°C in heat exchanger H3, parallel to H1. The two streams come together and are cooled to 30°C in heat exchanger H4.

Subsequently the total cooled effluent is separated into hydrogen gas and liquid cyclohexane in a liquid-gas separator drum (V1).

The excess hydrogen gas is recycled to the feed stream.

A portion of the cyclohexane is recycled to be injected in between the reactor beds. The other portion of the cyclohexane is sent to storage.
PROCESSHEMA VAN CYCLOHEXAANPRODUCTIE VIA BENZEEN HYDROGENATIE


Marian G. Korteknecht
Fabriekseverontwerp No. 2535
April 1992
V. Calculations for the Design

V.1. The Catalyst Volume

The design of the reactor for the hydrogenation of benzene in the gas phase is based on the kinetic information provided by Aben (16).

For a production of 100,000 mton cyclohexane per year, 7.8 m³ catalyst Pt/Al₂O₃ is required. This calculation (appendix 2) is based on the given LHSV for Pt/Al₂O₃ under the following assumptions:

1. LHSV is based on a constant temperature of 100°C.
2. Linear extrapolation can be used to get a 100% conversion.

These assumptions have been made realizing that in reality there will be a temperature increase over the reactor. Also, there will be a diffusion limitation for higher conversions. The first effect will require less catalyst, because the reaction rate increases at higher temperature. The diffusion limitation will require more catalyst. The impact of each effect, however, is unknown.

V.2. The Reactor Volume

The large heat of reaction is a problem. Especially since the temperature may not exceed 230°C, to prevent undesired by-products. To achieve a temperature below 230°C, a multi-bed reactor is designed, cooled by injecting cold cyclohexane in between the beds.

The calculations are based on the fact that the reaction rate constant is independent of the hydrocarbons (16):
Therefore we can assume that the conversion is a linear function of the temperature:

\[ \xi(\%) = 100 \left( \frac{1}{1 + b_p^{1/2}} \right) \]

The outlet temperature of 530°C is the temperature under adiabatic conditions and 100% conversion, calculated by trial and error (appendix 3).

In order that the temperature (with safety margin) doesn't exceed 210°C in the reactor, we need 4 catalyst beds. The results of the calculations are summarized in table 2.

**V.3: Pressure drop over the Reactor**

For calculating the total pressure drop over the reactor, the expression of Ergun (19) is used for each bed. The result is a total pressure drop of 1.3 atm (appendix 4).

<table>
<thead>
<tr>
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<th>bed 2</th>
<th>bed 3</th>
<th>bed 4</th>
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<td>100</td>
<td>100</td>
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<td>210</td>
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<td>( \xi ) (%)</td>
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<td>26</td>
<td>26</td>
<td>23</td>
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</table>

Table 2: Calculations for reactor beds.
V.4. Heat Exchangers

There are a total of four heat exchangers in this process, which will be described below.

H1: Feed-Product Exchanger:

In this heat exchanger the feed stream is preheated from 30 to 100°C with part of the reactor effluent (222.2 mole/s). The other part of the product stream is cooled down in heat exchanger H3. Both parts are cooled down from 150 to 90°C.

Using data from appendix 5 and 6, the required surface area for this heat exchanger is:

\[
\begin{align*}
T_{\text{ln}} &= 54.9 \, ^\circ \text{C} \\
U &= 602 \, \text{cm}^2/\text{W} \\
A &= 83.4 \, \text{m}^2 \\
L &= 1061.4 \, \text{m}^3 (d_1 = 0.025 \, \text{m}) \\
Q &= 2755.2 \, \text{kW}
\end{align*}
\]

H2: Cooling of Recycle Hydrogen:

This heat exchanger is necessary to cool down the recycle hydrogen stream from 35 to 30°C. This stream is slightly heated by compressor 2. Need 2.69 kg/s cool water of 20°C to accomplish the cooling.

\[
\begin{align*}
T_{\text{ln}} &= 16.4 \, ^\circ \text{C} \\
U &= 845 \, \text{cm}^2/\text{W} \\
Q &= 200.8 \, \text{kW} \\
A &= 14.5 \, \text{m}^2 \\
\dot{m}_{\text{H}_2o} &= 2.69 \, \text{kg/s}
\end{align*}
\]
H3: Cooling of Product stream:

This heat exchanger has to cool down the other part of the reactor effluent from 150 to 90 °C. Cool water of 40 °C (from H4) generating 134 °C steam is used for cooling.

\[
T_{in} = 19.1 \, ^{\circ}C \\
U = 845 \, \text{Cm}^2/\text{W} \\
Q = 6434.5 \, \text{kW} \\
A = 398.7 \, \text{m}^2 \\
\phi_{h_2o} = 2.67 \, \text{kg/s}
\]

H4: Additional Product stream cooler:

This heat exchanger cools down the product stream from 90 to 30 °C, using 20 °C cool water.

\[
T_{in} = 18.2 \, ^{\circ}C \\
U = 845 \, \text{Cm}^2/\text{W} \\
Q = 1491.8 \, \text{kW} \\
A = 97 \, \text{m}^2 \\
\phi_{h_2o} = 20.0 \, \text{kg/s}
\]
V.5. **Compressors**

A couple of compressors are necessary to bring hydrogen (both recycle and make up) at the right operating pressure. Assumed is that hydrogen is an ideal gas. The adiabatic discharge temperature is 

\[ T_2 = T_1 \left( \frac{P_2}{P_1} \right)^{\frac{k}{k-1}} \]

(\( k = 1.4 \) for 2 atm gases)

- **C1:**
  - \( p_1 = 1 \text{ atm} \)
  - \( p_2 = 6 \text{ atm} \)
  - \( T_1 = 18 \text{ C} \)
  - \( T_2 = 30 \text{ C} \)

- **C2:**
  - \( p_1 = 3.4 \text{ atm} \)
  - \( p_2 = 6 \text{ atm} \)
  - \( T_1 = 30 \text{ C} \)
  - \( T_2 = 35 \text{ C} \)

**Pumps**

The fresh benzene and the recycle cyclohexane require regular centrifugal pumps to bring the liquid to operating pressure, and to pump it around in the system. In general, pumps do not generate that much heat (24), that they significantly heat the liquids. Therefore, this part is neglected in the calculations.
Finally, the stream of hydrogen gas and liquid cyclohexane needs to be separated. Since the solubility of hydrogen gas in the cyclohexane is so low (appendix 7), stripping will not be necessary. A regular L/G separator drum will be sufficient. The volume stream of liquid is about 1.2 m$^3$/s and that of the gas is 2.9 m$^3$/s. Therefore, the L/G drum needs to be at least 4.1 m$^3$ in volume.
VI. Safety and Health (25)

The threshold limit value (TLV) for cyclohexane is 1050 mg/m$^3$. With prolonged exposure at 1050 mg/m$^3$ and more, cyclohexane may cause irritation to eyes and skin. At high concentration, it is an anesthetic and narcosis may occur. Overall, cyclohexane is not dangerous to your health.

The opposite is true for benzene. This is a poisonous substance with acute and chronic toxic effects. The TLV is 3.2 mg/m$^3$ (in USA). The short term effects of inhalation, ingestion, or skin contact of benzene are immediately apparent. However, the effects of chronic exposure to lower levels is not. In several tests, benzene is found to be a very serious carcinogenic compound, having caused deaths in the past. All exposures (malfunctions, maintenance) should be avoided.

Hydrogen gas is not considered toxic, but it can cause suffocation by exclusion of air. The main danger lies in its extreme flammability with oxygen or air. Since hydrogen is odorless and colorless, it is not easily detectable. Therefore precautions should be taken to avoid leaks.
VII. Conclusion

This FVO turns out to be a rather simple, but nevertheless realistic picture of a process for the hydrogenation of benzene to cyclohexane. Only the cooling of the product stream could have been solved a little more elegant.

However, the purpose of this FVO, to get an overall feeling for and exercise in design and calculation of a chemical process, is achieved.

If there would have been more time, certain parts (economics, other than pure feed streams) could have been studied in more detail.
### Massa-en Warmtebalans

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- **C 1**
- **P 1**
- **H 1**
- **R 1**
- **H 3**
- **Cool Water**

*Legend:*
- **M**: Massa (kg)
- **Q**: Warmte (kJ/h)
Màssa in kg/s
Warmte in kW

Fabrieksvoorontwerp
No:
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**Totaal:**

| Hydrogen       | 3.250 | 17.97 |
| Benzene        | 3.250 | 17.97 |

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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Totaal:**

| Hydrogen       | 13.961 | 80.83 |
| Benzene        | 4.830  | 27.97 |
| Cyclohexane    | 4.654  | 26.94 |

M in kg/s
Q in kW
<table>
<thead>
<tr>
<th>Componenten</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.917</td>
<td>1670.89</td>
<td>0.642</td>
<td>1169.66</td>
<td>0.917</td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>17.464</td>
<td>9820.48</td>
<td>13.961</td>
<td>80.83</td>
<td>12.222</td>
</tr>
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</table>

**Totaal:**

<table>
<thead>
<tr>
<th>11</th>
<th>12</th>
<th>13</th>
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</thead>
<tbody>
<tr>
<td>18.381</td>
<td>11491.37</td>
<td>13.961</td>
<td>80.83</td>
<td>12.864</td>
</tr>
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</table>

<table>
<thead>
<tr>
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<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.642</td>
<td>607.82</td>
<td>0.917</td>
<td>860.29</td>
<td>0.275</td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>12.222</td>
<td>1001.47</td>
<td>17.464</td>
<td>1430.97</td>
<td>5.242</td>
</tr>
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</table>

**Totaal:**

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<th>17</th>
<th>18</th>
<th>19</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.864</td>
<td>1609.29</td>
<td>18.381</td>
<td>2299.26</td>
<td>5.517</td>
</tr>
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</table>

**Stroom/Componenten staat**

- M in kg/s
- Q in kW
<table>
<thead>
<tr>
<th>Componenten</th>
<th>21</th>
<th>22</th>
<th>23</th>
<th>H2 a</th>
<th>H2 b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.917</td>
<td>17.464</td>
<td>3.50</td>
<td>2.69</td>
<td>2.69</td>
</tr>
<tr>
<td>Benzene</td>
<td>66.75</td>
<td>101.11</td>
<td>20.28</td>
<td>-24.96</td>
<td>175.92</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Totaal:**

<table>
<thead>
<tr>
<th>M in kg/s</th>
<th>Q in kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.917</td>
<td>66.75</td>
</tr>
<tr>
<td>17.464</td>
<td>101.11</td>
</tr>
<tr>
<td>3.50</td>
<td>20.28</td>
</tr>
<tr>
<td>2.69</td>
<td>-24.96</td>
</tr>
<tr>
<td>2.69</td>
<td>175.92</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Componenten</th>
<th>H3 c</th>
<th>H3 d</th>
<th>H4 e</th>
<th>H4 f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>2.67</td>
<td>2.67</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>174.28</td>
<td>6608.54</td>
<td>-189.29</td>
<td>1308.31</td>
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</table>

**Totaal:**

<table>
<thead>
<tr>
<th>M in kg/s</th>
<th>Q in kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.67</td>
<td>174.28</td>
</tr>
<tr>
<td>2.67</td>
<td>6608.54</td>
</tr>
<tr>
<td>20.0</td>
<td>-189.29</td>
</tr>
<tr>
<td>20.0</td>
<td>1308.31</td>
</tr>
</tbody>
</table>

*Stroom/Componenten staat*
### VIII. Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>surface area</td>
<td>m²</td>
</tr>
<tr>
<td>(C_p)</td>
<td>specific heat</td>
<td>cal/mole.C</td>
</tr>
<tr>
<td>d</td>
<td>diameter</td>
<td>m</td>
</tr>
<tr>
<td>(d_p)</td>
<td>diameter of particle</td>
<td>m</td>
</tr>
<tr>
<td>(E_a)</td>
<td>activation energy</td>
<td>kcal/mole</td>
</tr>
<tr>
<td>(\Delta G_f)</td>
<td>standard free energy</td>
<td>kcal/mole</td>
</tr>
<tr>
<td>H</td>
<td>Henry coefficient</td>
<td></td>
</tr>
<tr>
<td>(\Delta H_r)</td>
<td>heat of reaction</td>
<td>kcal/mole</td>
</tr>
<tr>
<td>(\Delta H_f)</td>
<td>heat of formation</td>
<td>kcal/mole</td>
</tr>
<tr>
<td>(\Delta H_v)</td>
<td>heat of evaporation</td>
<td>kcal/mole</td>
</tr>
<tr>
<td>H</td>
<td>enthalpy</td>
<td>cal</td>
</tr>
<tr>
<td>k</td>
<td>reaction rate constant</td>
<td>kmole/m³/s</td>
</tr>
<tr>
<td>L</td>
<td>length of reactor</td>
<td>m</td>
</tr>
<tr>
<td>(M_{\text{wt}})</td>
<td>molecular weight</td>
<td>kg/mole</td>
</tr>
<tr>
<td>pp</td>
<td>vapor pressure</td>
<td>atm</td>
</tr>
<tr>
<td>p</td>
<td>partial pressure</td>
<td>atm</td>
</tr>
<tr>
<td>Q</td>
<td>heat transfer rate</td>
<td>cal/s</td>
</tr>
<tr>
<td>R</td>
<td>heat transfer coefficient</td>
<td>C.m²/W</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
<td>°C</td>
</tr>
<tr>
<td>U</td>
<td>overall heat transfer coeff.</td>
<td>W/m²°C</td>
</tr>
<tr>
<td>v</td>
<td>volumetric flow rate</td>
<td>m³/s</td>
</tr>
<tr>
<td>(v)</td>
<td>velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>V</td>
<td>volume</td>
<td>m³</td>
</tr>
<tr>
<td>x</td>
<td>mole fraction</td>
<td></td>
</tr>
</tbody>
</table>

### Greek symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\varepsilon)</td>
<td>porosity or fraction voids in s packed bed</td>
<td></td>
</tr>
<tr>
<td>(\rho)</td>
<td>density</td>
<td>kg/m³</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>dynamic viscosity</td>
<td>N.s/m²</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>heat conductivity coefficient</td>
<td>W/m°C</td>
</tr>
<tr>
<td>(\phi)</td>
<td>flow</td>
<td>m³/s</td>
</tr>
<tr>
<td>(\xi)</td>
<td>conversion</td>
<td></td>
</tr>
</tbody>
</table>
figure 1. Cyclohexane—INSTITUT FRANCAIS DU PETROLE

figure 2. Cyclohexane—HYDRORESEARCH RESEARCH, INC.

figure 3. Hydrar—UNIVERSAL OIL PRODUCTS CO.
figure 4. Cyclohexane (DSM) — STAMICARBON B.V.


figure 6. Cyclohexane — ARCO Technology Inc.
figure 7. **Arosat—THE LUMMUS CO.**
### Appendix 1: Physical Properties

<table>
<thead>
<tr>
<th></th>
<th>M_{Wt}</th>
<th>T_{b}</th>
<th>ρ</th>
<th>η</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>2.02</td>
<td>-252.37</td>
<td>89.9</td>
<td>0.11 \times 10^{-3}</td>
</tr>
<tr>
<td>BZ</td>
<td>78.12</td>
<td>80.1</td>
<td>878.6</td>
<td>0.15 \times 10^{-3}</td>
</tr>
<tr>
<td>CH</td>
<td>84.16</td>
<td>80.74</td>
<td>778.5</td>
<td>0.14 \times 10^{-3}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>ΔH\text{f}^0</th>
<th>ΔH\text{v}</th>
<th>ΔG\text{f}^0</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0</td>
<td>7.3</td>
<td>0</td>
</tr>
<tr>
<td>BZ</td>
<td>19.82</td>
<td>7.35</td>
<td>30.09</td>
</tr>
<tr>
<td>CH</td>
<td>-29.19</td>
<td>7.85</td>
<td>6.39</td>
</tr>
</tbody>
</table>

(kcal/mole)

\[ \Delta H_{298}^{\circ} = (\Delta H_{f}^{\circ})_p - (\Delta H_{f}^{\circ})_r = -29.19 - (0 + 19.82) = -49.01 \text{ kcal/mole} \]

<table>
<thead>
<tr>
<th></th>
<th>λ</th>
<th>β</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>6.947</td>
<td>-0.200</td>
<td>0.481</td>
</tr>
<tr>
<td>BZ</td>
<td>-0.409</td>
<td>77.621</td>
<td>-26.429</td>
</tr>
<tr>
<td>CH</td>
<td>0.213</td>
<td>83.714</td>
<td>-24.512</td>
</tr>
<tr>
<td>H₂O</td>
<td>7.219</td>
<td>2.374</td>
<td>0.267</td>
</tr>
</tbody>
</table>

\[ C_p = \alpha + \beta \times 10^{-3} \times T + \gamma \times 10^{-6} \times T^2 \text{ (cal/gmole.K)} \]
Appendix 2: Calculation of the Catalyst Volume

Given: LHSV = 40 ml.h^{-1}.ml^{-1} (4.3m\% conversion)  
\[ \rho = 0.879 \text{ um} \]  
BZ: 11736 kg/s = 150.5 kmole/h

Activity: 40 ml/h BZ/1 ml cat (4.3\% conv.)  
0.45 ml/h BZ/23.3 ml cat (100 \% conv.)

To convert: 150.5 kmole/h BZ:

\[
\text{cat. Vol.} = \frac{150.5 \times 10^3}{0.45} \times 23.3 = 7.8 \text{ m}^3
\]
Appendix 3: Calculation of amount of cyclohexane to be injected in between the catalyst beds.

Energy to heat 1 mole CH from 30 to 100 C:

\[ \Delta H_{CH} = H^{100} - H^{30} + H_v \]

\[ \Delta H_{CH} = 1906.2 - 115.8 + 7350 = 9.54 \text{ kcal/mole} \]

BED #1:

583.8 mole H₂
41.7 mole BZ
→ 100 C

26% conv.

100 C

551.4 mole H₂
30.9 mole BZ
10.8 mole CH

→ 210 C

\[ H^{210} = 913.9 \text{ kcal} \]
\[ H^{100} = 359.6 \text{ kcal} \]

\[ \Delta H_p = 913.9 - 359.6 = 554.3 \text{ kcal that needs to be removed by CH-injection.} \]

Therefore need: \( \frac{554.3}{9.54} = 57.5 \text{ mole CH} \)
BED #2:

- 551.4 mole H₂
- 30.9 mole BZ
- 10.8 mole CH (57.5 mole CH)

\[ H^{210} = 878.9 \text{ kcal} \]
\[ H^{100} = 345.1 \text{ kcal} \]
\[ \Delta H_p = 878.9 - 345.1 = 533.8 \]

Need: \[ \frac{533.8}{9.54} = 55.4 \text{ mole CH} \]

BED #3:

- 519.0 mole H₂
- 20.1 mole BZ
- 21.6 mole CH (112.9 mole CH)

\[ H^{210} = 843.9 \text{ kcal} \]
\[ H^{100} = 330.6 \text{ kcal} \]
\[ \Delta H_p = 513.3 \text{ kcal} \]

Need: \[ \frac{513.3}{9.54} = 53.3 \text{ mole CH} \]
The outlet temperature of the reactor is a lot lower than 210 °C, because of the cooling effect of the recycling CH in the product stream.
Appendix 3A: Calculation of $C_p$ and $H$'s

$$C_p = \alpha \Delta T + \frac{A}{2} (T^2 - T_0^2) + \frac{Y}{3} (T^3 - T_0^3)$$

Heat of reaction at $T_2$:

$$\Delta H_{r,2} = \Delta H_{r,1} + (H_2 - H_1)_p - (H_2 - H_1)_r$$

Enthalpy:

$$H_t = (\zeta m C_p)_t$$

Table 3A: $C_p$ for different temperatures.

<table>
<thead>
<tr>
<th>$T$ (°C) (K)</th>
<th>$H_2$</th>
<th>BZ</th>
<th>CH</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 (303)</td>
<td>34.65</td>
<td>102.6</td>
<td>115.8</td>
</tr>
<tr>
<td>35 (308)</td>
<td>132.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 (313)</td>
<td>381.3</td>
<td>1189.45</td>
<td></td>
</tr>
<tr>
<td>60 (323)</td>
<td>450.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80 (333)</td>
<td>520.1</td>
<td>1689.3</td>
<td>1906.2</td>
</tr>
<tr>
<td>100 (363)</td>
<td>667.3</td>
<td>3396.8</td>
<td></td>
</tr>
<tr>
<td>120 (393)</td>
<td>936.8</td>
<td>3712.3</td>
<td></td>
</tr>
<tr>
<td>140 (423)</td>
<td>1075.8</td>
<td>4362.1</td>
<td></td>
</tr>
<tr>
<td>160 (453)</td>
<td>1146.3</td>
<td>4696.2</td>
<td></td>
</tr>
<tr>
<td>180 (483)</td>
<td>1284.6</td>
<td>5382.7</td>
<td></td>
</tr>
<tr>
<td>200 (513)</td>
<td>2613.3</td>
<td></td>
<td>13046.7</td>
</tr>
<tr>
<td>300 (603)</td>
<td>3313.8</td>
<td></td>
<td>17837.2</td>
</tr>
<tr>
<td>400 (703)</td>
<td>3473.5</td>
<td></td>
<td>19107.9</td>
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<td>500 (803)</td>
<td>3535.5</td>
<td></td>
<td>19155.9</td>
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<tr>
<td>600 (903)</td>
<td>3602.4</td>
<td></td>
<td>19884.9</td>
</tr>
<tr>
<td>700 (1003)</td>
<td>3673.5</td>
<td></td>
<td>20407.3</td>
</tr>
<tr>
<td>800 (1103)</td>
<td>4029.6</td>
<td></td>
<td>23085.8</td>
</tr>
<tr>
<td>900 (1203)</td>
<td>4748.9</td>
<td></td>
<td>28456.1</td>
</tr>
</tbody>
</table>
Trial and error method for calculating reactor outlet temperature.

Feed stream : 583.8 mole H₂ and 41.7 mole D₂
Product stream: 457.9 mole H₂ and 41.7 mole C₂H

Table 38: Enthalpy of Feed and Product streams in kcal/gmole.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>H_H₂</th>
<th>H_D₂</th>
<th>H_Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>303.6</td>
<td>70.4</td>
<td>374.0</td>
</tr>
<tr>
<td>400</td>
<td>1196.6</td>
<td>544.0</td>
<td>1740.6</td>
</tr>
<tr>
<td>500</td>
<td>1519.7</td>
<td>743.8</td>
<td>2263.5</td>
</tr>
<tr>
<td>525</td>
<td>1590.5</td>
<td>796.8</td>
<td>2387.3</td>
</tr>
<tr>
<td>530</td>
<td>1618.9</td>
<td>798.8</td>
<td>2417.7</td>
</tr>
<tr>
<td>540</td>
<td>1649.5</td>
<td>829.2</td>
<td>2478.7</td>
</tr>
<tr>
<td>550</td>
<td>1682.1</td>
<td>851.0</td>
<td>2533.1</td>
</tr>
<tr>
<td>600</td>
<td>1845.2</td>
<td>962.7</td>
<td>2807.9</td>
</tr>
</tbody>
</table>

ΔH₂⁰⁹⁸ = -49.01 kcal/gmole

For adiabatic reaction:

ΔH_p - ΔH_r - ΔH₂⁰⁹⁸ = 2417.7 -374.0 -(41.7*49.01) = 0

The reactor outlet temperature is 530 °C.
Appendix 4: Calculation of pressure drop over the beds

Using the equation of Ergun (19):

$$\Delta P = \left( \frac{d \nu^2}{4 \rho} \right) \left( \frac{1 - \varepsilon}{\varepsilon^3} \right) \left( \frac{170 \eta}{\rho v_0 d \rho} \right) \left( 1 - \varepsilon \right) + 1.75$$

Where: $$\varepsilon = 0.43$$
$$\rho = 1.8 \text{ kg/m}^3$$
$$\eta = 0.11 \times 10^{-3} \text{ Ns/m}^2$$
$$d = 0.004 \text{ m}$$
$$\Phi_V = \frac{22.4}{2.5} \text{ m}^3/\text{s} = 2.3 \text{ m}^3/\text{s}$$ (example)

<table>
<thead>
<tr>
<th>Table 4: pressure drop over each catalyst bed in atm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_{\text{cat}} ) (m(^3))</td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>( d_r ) (m)</td>
</tr>
<tr>
<td>( A ) (m(^2))</td>
</tr>
<tr>
<td>( L ) (m)</td>
</tr>
<tr>
<td>( \Phi_V ) (m(^3)/s)</td>
</tr>
<tr>
<td>( v_o ) (m/s)</td>
</tr>
<tr>
<td>( \Delta P ) (atm)</td>
</tr>
</tbody>
</table>

The total pressure drop over the reactor \( \Delta P = 1.3 \text{ atm} \)

The pressure drop over a valve and heat exchanger are assumed to be 0.9 and 0.1 atm respectively.
Appendix 5: Calculation of Heat Exchangers

H1: Feed-Product Exchanger:

Feed: 583.8 mole $H_2$ and 41.7 mole $BZ$

$T_{in} = 30^\circ C$, $H^{30} = 24.5$ kcal/s
$T_{out} = 100^\circ C$, $H^{100} = 374.0$ kcal/s

$H_v = 306.5$ kcal/s

$\Delta H = (H^{100} - H^{30}) + H_v = 656$ kcal/s = 2755.2 kW

needed for heating the feed stream.

Prod: 458.7 mole $H_2$ and 41.7 mole $CH$

$T_{in} = 150^\circ C$, $H^{150} = 1104.0$ kcal/s
$T_{out} = 90^\circ C$, $H^{90} = 574.4$ kcal/s

$H_v = 1632.0$ kcal/s

$\Delta H = 2188.6$ kcal/s to be removed by feed stream.

Using therefore: $\frac{656.0}{2188.6} = 0.30 \times 2188.6 = 200.0$ mole Prod.

Other part (i.e. 466.6 mole) has to be cooled in another exchanger (H3).

H2: Cooling of recycle Hydrogen:

$H_2$: 458.7 mole/s

$T_{in} = 35^\circ C$, $H^{35} = 63.7$ kcal/s
$T_{out} = 30^\circ C$, $H^{30} = 15.9$ kcal/s

$\Delta H = 47.8$ kcal/s = 200.8 kW to be removed by $H_2O$

$H_2O$: For 1 mole:

$T_{in} = 20^\circ C$, $H^{20} = 139.7$ cal/mole
$T_{out} = 60^\circ C$, $H^{60} = 279.3$ cal/mole

$\Delta H = 0.32$ kcal/mole = 1.34 kJ/mole $H_2O$

Therefore need: $\frac{200.8}{1.34} = 149.7$ mole/s = 2.59 kg/s $H_2O$

to cool down the recycle hydrogen stream.
H3: Cooling of Product Stream:
Prod: 321.3 mole H₂ and 145.5 mole CH

\[
T_{\text{in}} = 150^\circ C \quad H^{150} = 772.8 \text{ kcal/s}
\]
\[
T_{\text{out}} = 90^\circ C \quad H^{90} = 383.2 \text{ kcal/s}
\]
\[
H_v = 1142.4 \text{ kcal/s}
\]
\[
\Delta H = 1532.0 \text{ kcal/s} = 6434.5 \text{ kW to be removed.}
\]

H₂O: For 1 mole:

\[
T_{\text{in}} = 60^\circ C \quad H^{60} = 279.8 \text{ cal/mole.s}
\]
\[
T_{\text{out}} = 134^\circ C \quad H^{134} = 890.0 \text{ cal/mole.s}
\]
\[
H_v = 9720 \text{ cal/mole.s}
\]
\[
\Delta H = 10.33 \text{ kcal/mole} = 43.4 \text{ kJ/mole}
\]

Therefore need: \[
\frac{6434.5}{43.3} = 148.7 \text{ mole/s} = 2.67 \text{ kg/s H₂O}
\]

H₄: Additional Product Stream Cooler:

Prod: 458.7 mole H₂ and 41.7 mole CH

\[
T_{\text{in}} = 90^\circ C \quad H^{90} = 383.2 \text{ kcal/s}
\]
\[
T_{\text{out}} = 30^\circ C \quad H^{30} = 28.0 \text{ kcal/s}
\]
\[
\Delta H = 355.2 \text{ kcal/s} = 1491.8 \text{ kW to be removed.}
\]

H₂O: For 1 mole:

\[
T_{\text{in}} = 20^\circ C \quad H^{20} = 279.8 \text{ cal/mole.s}
\]
\[
T_{\text{out}} = 60^\circ C \quad H^{60} = -39.2 \text{ cal/mole.s}
\]
\[
\Delta H = 319 \text{ cal/mole.s} = 1.34 \text{ kJ/mole.s}
\]

Therefore need: \[
\frac{1491.8}{1.34} = 1113.3 \text{ mole/s} = 20.0 \text{ kg/s H₂O}
\]
Appendix 6: Overall Heat Transfer Coefficient

Using the following equations (19, 20):

\[
U = \left( \frac{d_u}{d_i} R_u + \frac{d_u}{d_i} R_v + \frac{d_u}{d_i} \ln \frac{d_u}{d_i} + R_v + R_i \right)^{-1}
\]

\[
Nu = 0.023 \cdot Re^{0.8} \cdot Pr^{0.40}
\]

For the feed-product exchanger:
(assuming that both streams are primarily H₂ gas)

\[
R_v = 0.1 \cdot 10^{-3} \text{ Cm}^2/\text{W} \quad \text{(dirt)}
\]
\[
R_u = 6.1 \cdot 10^{-4} \text{ Cm}^2/\text{W} \quad \text{(feed → pipe)}
\]
\[
R_i = 7.3 \cdot 10^{-4} \text{ Cm}^2/\text{W} \quad \text{(prod → pipe)}
\]
\[
d_u = 0.025 \text{ m}
\]
\[
d_i = 0.020 \text{ m}
\]
\[
\lambda = 50 \text{ W/m°C} \quad \text{(pipe)}
\]

Results in: \( U = 602 \text{ W/m}^2\text{C} \)

For the other heat exchangers:

\[
R_v = 0.1 \cdot 10^{-3} \text{ Cm}^2/\text{W} \quad \text{(dirt)}
\]
\[
R_u = 1.4 \cdot 10^{-4} \text{ Cm}^2/\text{W} \quad \text{(water → pipe)}
\]
\[
R_i = 7.3 \cdot 10^{-4} \text{ Cm}^2/\text{W} \quad \text{(prod → pipe)}
\]
\[
d_u = 0.025 \text{ m}
\]
\[
d_i = 0.020 \text{ m}
\]
\[
\lambda = 50 \text{ W/m°C}
\]

Results in: \( U = 845 \text{ W/m}^2\text{C} \)
Appendix 7: **Liquid-gas Separator.**

To decide what type of separator will be used, we need to check the following:

1. How much hydrogen gas will dissolve in cyclohexane?

   The solubility of gases in liquid is defined by Henry's Law (20):
   \[ H = \frac{P_a}{x_a} \]

   Where: \( H = 8.2 \times 10^4 \) atm/mole fraction (Henry's coeff.)
   \( P_{H_2} = 3.5 \) atm

   And: \( x_{H_2} = 4.2 \times 10^{-5} \) is the mole fraction of \( H_2 \) in the liquid phase.

   The maximum that can dissolve in 13.96 kg/s CH is:
   \[ \frac{4.2 \times 10^{-5}}{1 - 4.2 \times 10^{-5}} \times \frac{2}{84} \times 13.96 = 2.1 \times 10^{-5} \text{ kg/s } H_2 \]

2. How much CH will be in hydrogen gas?

   For calculating this amount, the partial and vapor pressures are used at 30°C.

   \( P_{\text{tot}} = 3.5 \) atm

   \( P_{\text{CH}} = (1/12) \times 3.5 = 0.29 \) atm

   \( P_{H_2} = (11/12) \times 3.5 = 3.21 \) atm

   At 30°C (26):

   \( p_{\text{CH}} = 1.1 \) psia

   \( p_{\text{tot}} = (1 + 3.5) \times 14 = 63 \) psia

   \( p_{H_2} = 63 - 1.1 = 61.9 \) psia

   Than: \( \frac{1.1}{61.9} = 0.018\% \) of CH will go with \( H_2 \) gas.

   This amount is so small that it can be neglected.
## Tabel voor 1 kg verzadigde stoom bij gegeven druk

<table>
<thead>
<tr>
<th>Druk in bar</th>
<th>Temperatuur in °C</th>
<th>Enthalpie in kJ/kg</th>
<th>Verdampingswarmte in kJ/kg</th>
<th>Volume in m³/kg</th>
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</table>

*In deze tabel zijn tussen () aangegeven de drukwaarden overeenkomende met die, welke gebruikt zijn voor gegevens bij oververteerde stoom betreffende volume (tabel 3), enthalpie (tabel 4) en entropie (tabel 5). De drukken en temperaturen zijn hierbij gekozen uit de tegenwoordig meest gewerkte gebieden.*
References


(3) Sabatier I., Ind. Eng. Chem. 18, 1926, pp 1005-8


(21) VDI-Warmeatlas, VDI - Verlag, Dusseldorf, 1974.


General References


THE HYDROGENATION OF BENZENE OVER SUPPORTED PLATINUM, PALLADIUM AND NICKEL CATALYSTS

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Koninklijke/Shell-Laboratorium, Amsterdam, The Netherlands (Shell Research N.V.)

Abstract

The activity for the hydrogenation of benzene has been studied for supported platinum, palladium and nickel at a function of particle size and carrier. Metal crystallite sizes varied between 10 and 200 Å and silica-alumina, silica-alumina and silica-magnesia were used as supports. It has been found that the activity per exposed metal atom is independent of the metal crystallite size or of the support used. The hydrogenation activities per exposed metal atom at a temperature of 100 °C and a hydrogen pressure of 3.6 atm are ranked as follows: \( k_{Pt} : k_{Ni} : k_{Pd} = 18 : 7 : 1 \).

It is further shown that the activation energies observed experimentally for the various catalysts at a given set of conditions are predicted with a high degree of accuracy with the aid of the theory of absolute reaction rates, based on a reasonable estimate of the number of exposed metal atoms per hydrogenation site.

1. Introduction

The influence of metal dispersion and the carrier on the intrinsic catalytic activity of supported metals is a controversial subject in the literature. Nikolajenko et al. [1] do not find any effect of metal particle size over a wide range of sizes in a study of the hydrogenation of benzene over magnesia-supported nickel. Swift et al. [2] report a particle size and a carrier effect for the dehydrogenation of cyclohexane over silica and alumina-supported nickel. According to Hill and Selwood [3] smaller nickel particles are less active per unit metal surface area than larger ones for the hydrogenation of benzene. Dorling and Moss [4] discriminate between the intrinsic activities of platinum particles smaller and larger than 50 Å for the hydrogenation of benzene. Yates et al. [5] do not observe a particle-size effect of silica-supported nickel in the hydrodeinsertion of ethane, whereas Carter et al. [6] report a substantial influence when the nickel particles are silica-alumina supported. Tavlor et al. [7] show a considerable carrier effect in the hydrogenolysis of ethane over nickel on silica, alumina and silica-alumina. In studying the activity of platinum catalysts for the hydrogenation of cyclopropane, Boudart et al. [8] find that "the difference between the highly dispersed samples and the others (sintered, less dispersed, foil) was a modest twofold change in specific activity".

The present paper deals with the activity of supported platinum, nickel and palladium catalysts with metal crystallite sizes varying from 10 to 200 Å in the hydrogenation of benzene. In one case palladium black with a particle size of 400 Å was included in the investigation. Crystallite sizes
were determined by means of hydrogen chemisorption, which technique had been specially adapted to palladium. Silica, alumina, silica-alumina and silica-magnesia were used as supports.

2. Experimental part

Materials

Benzene was obtained from Union Chimique Belge. Its analysis indicated:
residue on evaporation < 0.0005 %
sulfur content < 1 ppmw
water content < 0.02 %

Before the benzene feed was introduced into the reactor, it was passed over a mixture of reduced copper catalyst (BTS catalyst from BASF) and Linde 5A molecular sieves to remove possible trace amounts of oxygen and water. Electrolytic hydrogen was dried prior to use over Linde 5A molecular sieves.

Silica, alumina, silica-magnesia and silica-alumina were used as catalyst supports. Their physical properties are as follows:

<table>
<thead>
<tr>
<th>Support/source</th>
<th>Surface area, m²/g</th>
<th>Pore volume, ml/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃/UOP</td>
<td>181</td>
<td>0.73</td>
</tr>
<tr>
<td>SiO₂/Davison</td>
<td>293</td>
<td>1.02</td>
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<tr>
<td>SiO₂·MgO/Davison</td>
<td>475</td>
<td>0.46</td>
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<tr>
<td>SiO₂·Al₂O₃/Ketjen</td>
<td>525</td>
<td>0.78</td>
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</table>

Platinum catalysts were made by impregnation with an aqueous solution of chloroplatinic acid. Then they were dried at 120 °C for three hours and subsequently calcined at 500 °C in air for three hours. As alumina-supported platinum preparations we used commercially available reforming catalysts. By subjecting them to a reduction treatment in hydrogen at various severities (300—800 °C), samples were obtained in which platinum particles were sintered to various degrees.

Palladium catalysts were prepared either by impregnating the carrier with an aqueous solution of H₂PdCl₄ or by ion exchange with Pd(NH₃)₄(HO)₂ [9]. Then they were dried at 120 °C for 3 hours and subsequently calcined at 500 °C in air for three hours. Palladium black was made according to Willstätter [10]. Palladium catalysts with a lower specific metal surface area were prepared from the more highly dispersed samples via high-temperature sintering in hydrogen (500—800 °C). Nickel catalysts were obtained by impregnating the carrier with an aqueous solution of nickel nitrate and dried at 120 °C for three hours. Then they were either calcined in air at 500 °C for 3 hours and subsequently reduced in hydrogen at 400 °C or directly reduced at 220—300 °C.
**Procedure**

The metal surface areas of supported Pt, Pd and Ni were determined by hydrogen chemisorption. The measurements were carried out in a conventional static sorption apparatus [11]. Prior to the adsorption proper the samples were reduced in hydrogen at 400 °C and atmospheric pressure for one hour and then evacuated (10⁻⁶ Torr) at 400 °C for sixteen hours. The way in which the subsequent adsorption measurements were carried out depended on the metal under investigation. Platinum-containing samples were cooled down to −78 °C and the amount of hydrogen was determined which adsorbed at −78 °C at 10 Torr pressure [12]. Palladium catalysts were cooled down to 70 °C and the amount of hydrogen was measured which was taken up by the sample at this temperature and a pressure of 1 Torr [9]. With the nickel-containing samples hydrogen was introduced at a pressure of 10 Torr, while the sample was cooled down from 400 °C to −78 °C [11].

Hydrogenation experiments with benzene were conducted in a flow system using 1 to 2 ml of catalyst of 0.1−0.2 mm particle size. In order to avoid temperature rises the catalysts were occasionally diluted with the bare support of the same particle size.

In all cases the hydrogenation activity was determined of those samples which had previously been subjected to the hydrogen chemisorption measurements. After the reactor had been loaded, the catalysts were pretreated: platinum and palladium-containing catalysts were reduced in atmospheric hydrogen at 100 °C for two hours and nickel catalysts in atmospheric hydrogen at 400 °C for two hours.

Unless stated otherwise, the reaction conditions were as follows:

<table>
<thead>
<tr>
<th>Feed:</th>
<th>benzene</th>
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<tbody>
<tr>
<td>Temperature:</td>
<td>100 °C</td>
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<tr>
<td>Benzene partial pressure:</td>
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<tr>
<td>Hydrogen partial pressure:</td>
<td>5.6 atm</td>
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</tbody>
</table>

3. Results and discussion

**Kinetics of benzene hydrogenation**

The data in Table 1 show that at the prevailing conditions the hydrogenation of benzene is of zero order in the hydrocarbon over Pt, Pd and Ni catalysts. The effect of hydrogen pressure can be described as resulting from a Langmuir-type adsorption, as illustrated in Fig. 1.

\[
\text{Hence, } k = k_0 \theta = k_0 \frac{b \rho_{H_2}}{1 + b \rho_{H_2}}
\]

(1)

where \( b \) is the adsorption coefficient for molecular hydrogen and \( \theta \) the fraction of the surface covered.
Fig. 1. Effect of hydrogen partial pressure on benzene hydrogenation activity

Table 1
Hydrogenation of benzene is zero order in hydrocarbon
Conditions: temperature: 100°C, hydrogen partial pressure: 5.6 atm

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Benzene partial pressure, atm</th>
<th>LHSV, ml·ml⁻¹·h⁻¹</th>
<th>Conversion, σ₄₅°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Al₂O₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>40</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>40</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>40</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>4</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>4</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>5</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>Ni/SiO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.30</td>
<td>5</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>0.40</td>
<td>5</td>
<td>15.8</td>
<td></td>
</tr>
</tbody>
</table>

Effect of metal dispersion and carrier on activity

Figures 2a and 2b show that there exists a linear relationship between the hydrogenation activity per mg atom of metal and the atomic hydrogen/metal ratio as determined by hydrogen chemisorption. Since one
relationship between atomic hydrogen. Since one

on activity

5.6 atm

Fig. 2. Relationship between metal dispersion and benzene hydrogenation activity
hydrogen atom is adsorbed per exposed metal atom [9, 11, 12, 13, 14] it follows that the hydrogenation activity per exposed metal atom is independent of the metal crystallite size or of the support used. In the supported catalysts the metal crystallite sizes varied from 10 to 200 Å. Palladium black, which also fits the palladium line, had a particle size of about 400 Å.

The data further show that the hydrogenation activities per exposed metal atom of Pt, Ni and Pd at the prevailing conditions of 100 °C and a hydrogen pressure of 5.6 atm are ranked as follows: $k_{\text{Pt}} : k_{\text{Ni}} : k_{\text{Pd}} = 18 : 7 : 1$.

**Absolute reaction rates**

The rate expression for the hydrogenation of benzene over Pt, Pd and Ni is given by

$$k = k_0 \frac{b_{\text{H}_2}}{1 + b_{\text{H}_2}}$$  \hspace{1cm} (1)

The temperature dependence of the rate constant $k$ (i.e. the apparent activation energy, $E_{\text{app}}$) was found experimentally (see Fig. 3). It was
then of interest to determine whether this experimental value agreed with that calculated on the basis of the theory of absolute reaction rates from expression (1). For this purpose we needed to know the temperature dependence of \( b \) (i.e. the heat of adsorption for hydrogen for the various metals). This dependence was measured for a silica-supported palladium catalyst. The results are presented in Fig. 4. It was found that

\[
\Delta H_{ad} = -8.4 \text{ kcal/mole}
\]

\[
\Delta S_{p=1} = -29.2 \text{ cal.mole}^{-1} \cdot \text{deg.}^{-1}
\]

where

\[
b = e^{-\frac{\Delta H_{ad}}{RT}} e^{\frac{\Delta S_{p=1}}{R}}
\]

(2)

It is gratifying to note that the change in standard entropy as found experimentally approximates very closely the translational entropy of gaseous hydrogen at 100 °C and 1 atm, viz. -30 cal.mole\(^{-1}\).deg.\(^{-1}\).

Substitution of the value of \( b \) for platinum and nickel as derived from Fig. 1 and of \( \Delta S_{p=1} = -29.2 \text{ cal.mole}^{-1} \cdot \text{deg.}^{-1} \) into expression (2) yields \( \Delta H_{ad} \). The results are listed in Table 2.

![Fig. 4. Effect of temperature on the adsorption coefficient \( b \) for hydrogen](image-url)
We now proceed as follows. By differentiating (1) with respect to \((RT)^{-1}\) we obtain:

\[
E_{\text{app.}} = E_0 + (1 - \theta)\Delta H_{\text{ad}}
\]

where \(E_0\) is the activation energy referring to the reaction between adsorbed benzene and adsorbed hydrogen. Expression (1) can now be rewritten as

\[
A \exp \left[ -\frac{E_{\text{app.}}}{RT} \right] = A_0 \exp \left[ -\frac{E_0}{RT} \right] A_1 \exp \left[ -(1 - \theta)\frac{\Delta H_{\text{ad}}}{RT} \right]
\]

The pre-exponential factor \(A_1\) can be computed from

\[
A_1 = \theta \exp \left[ (1 - \theta)\frac{\Delta H_{\text{ad}}}{RT} \right]
\]

If \(k\) and hence also \(k_0\), is expressed in molecules per site per second, then

\[
A_0 = \frac{kT}{h} \exp \left[ \frac{\Delta S^*}{R} \right]
\]

where \(k\) and \(h\) are the Boltzmann and Planck constants, respectively. \(\Delta S^*\) is the activation entropy of the reaction between adsorbed benzene and adsorbed hydrogen and is therefore to a large approximation equal to zero \((\Delta S^* = 0)\).

It then follows that \(\ln A = \ln \frac{kT}{h} + \ln A_1\).

In order to express the reaction rate constant in molecules per site per second we need to have an estimate of the number of exposed metal atoms per site. Since there is ample evidence in the literature \([15, 16, 17]\) that at the prevailing conditions benzene is adsorbed "flatwise" on the metal surface, it has been assumed that 5-10 metal atoms are involved in one hydrogenation site.

The apparent activation energy can then be computed from

\[
E_{\text{app.}} = RT (\ln A - \ln k)
\]

The results of our calculations are given in Table 3.

It is seen that the activation energies observed experimentally at a given set of conditions can actually be predicted with a high degree of accuracy with the aid of the theory of absolute reaction rates, based on a reasonable estimate of the number of metal atoms per active site. It is shown that the difference in hydrogenation activity between Pt and Pd at 100 °C and 5.6 atm \(H_2\) is largely due to the difference in \(E_0\), i.e. the activation energy of the hydrogenation proper.

### Table 2

Heats of adsorption of hydrogen \(\Delta H_{\text{ad}}\)
in the hydrogenation of benzene

<table>
<thead>
<tr>
<th>Metal</th>
<th>(\Delta H_{\text{ad}}) (kal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>-9.3</td>
</tr>
<tr>
<td>Ni</td>
<td>-9.1</td>
</tr>
<tr>
<td>Pd</td>
<td>-8.4</td>
</tr>
</tbody>
</table>

402
\[ k = \frac{k_B}{1 + b_{PH}} \]

subject to \((RT)^{-1}\)

(3)

been adsorbed and rewritten as

\[ \frac{\Delta H_{ad}}{RT} \]

(4)

second, then Planck constant

\[ 1 - \frac{\Delta H_{ad}}{RT} \]

between large approximations

per site per metal atoms based on a large degree of involvement in one moment

(16, 17) that involved in one

(10, 11) platininum 20.7 20.1 14.5 13±1

number of metal atoms per site)

References

Benzene can be converted to cyclohexane of high purity by the HA-84 process. Here are yield and cost data for the process.

Stanford Field, Hydrocarbon Research, Inc.
Trenton, N. J.

Milton H. Dalson, Sinclair Research, Inc.
Harvey, Ill.

The increased demand for nylon in the past few years has focused the attention of the petrochemical industry on cyclohexane. The HA-84 process is a new commercially proven method for catalytically reacting benzene with hydrogen to produce high purity cyclohexane. This catalytic process was jointly developed by Sinclair Research, Inc. and Engelhard Industries and is available through Hydrocarbon Research, Inc. This article presents the economics of utilizing the HA-84 process to produce cyclohexane.

Fig. 1—The investment and operating costs associated with a cyclohexane recycle stream are eliminated.
ECONOMICS OF MAKING CYCLOHEXANE . . .

Process Description. The schematic flow diagram of a typical HA-84 unit is shown in Fig. 1. Fresh feed benzene together with make-up and recycle hydrogen is preheated to reaction temperatures by exchanging first with reactor effluent and then with steam. The reactants flow through a fixed bed of precious metal catalyst which completely hydrogenates the benzene to cyclohexane.

A distinctive feature of the process is the catalyst. It has been specifically formulated to maintain high hydrogenation activity at low temperatures and to completely inhibit the side reaction in which cyclohexane is isomerized to methylcyclopentane.

After reaching a given preheat temperature, this hydrogenation reaction becomes autocatalytic and rapidly evolves heat amounting to approximately 1,100 Btu per pound of benzene; the concomitant chemical hydrogen consumption is 4,500 scf per barrel of benzene. The reaction temperature is efficiently controlled by using the high heat release to generate steam. Over-all process utility requirements are minimized by receiving a credit for the exported steam.

Although the HA-84 process requires an additional investment for steam generation facilities, the investment and operating costs associated with a cyclohexane recycle stream are eliminated since there is no recycling of cyclohexane for heat control. Further, the efficient control of the exothermic reaction permits the entire hydrogenation to be effected in a single reactor; whereas if cyclohexane were recycled, it would be necessary to mitigate the harmful effects of backmixing caused by the recycle, by using a multistage reaction system.

The reactor effluent is exchanged, cooled and flashed at system pressure. A portion of the separator vapors is used as hydrogen recycle gas. The excess gas is vented at system pressure. A portion of the separator vapors from the system. Recovery of the cyclohexane in the vent gas is normally justified and may be achieved by an adsorption system. The separator liquid is stabilized to remove light hydrocarbons introduced with the fresh feed hydrogen stream. The stabilizer bottoms is the high purity cyclohexane product. Rerun facilities are dependent on the purity of the benzene charged and are not normally required.

One commercial plant has been in successful operation for over two years. The unit is located at the Atlantic-Richfield refinery in Watson, California and has a capacity of 1,000 barrels per day of cyclohexane. During the two-year period, the catalyst has shown no significant evidence of activity decline while maintaining a consistent output of high purity cyclohexane.

Cyclohexane Yield and Purity. The HA-84 process hydrogenates benzene to produce cyclohexane in yields that are virtually 100 percent of theoretical on a reactor outlet basis. Theoretical yields are 107.7 wt % and 121.7 vol % of the benzene charged with a chemical hydrogen consumption of 4,500 scf per barrel of benzene charged.

The material balance shown in Table 1 for an HA-84 unit charging 1,245 bpsd of benzene to produce 1,500 bpsd of cyclohexane assumes a recovered product yield that is 99.0% of theoretical.

A salient feature of the HA-84 process is the ability of the catalyst to completely hydrogenate the benzene without promoting side reactions. The purity of the cyclohexane product then becomes directly related to the purity of the benzene being charged. Table 2 assumes a hypothetical benzene charge stock and shows the resulting cyclohexane product. The n-hexane and methylcyclopentane contaminants in the feed are unaffected by reaction conditions, while toluene is hydrogenated to methylcyclohexane. On the basis of the benzene and cyclohexane charged, the process can produce a cyclohexane product that is 99.9995% pure. The only detectable impurity would be 3 ppm of benzene. The current commercial operation is producing cyclohexane having a 99.9% purity.

The HDA Hydrodealkylation process for converting toluene into benzene, produces a benzene product that contains cyclohexane as the main contaminant.

<table>
<thead>
<tr>
<th>Potential Composition, mol%</th>
<th>HDA Product</th>
<th>HA-84 Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.06</td>
<td>99.99</td>
</tr>
<tr>
<td>Benzene</td>
<td>99.93</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

If the HDA benzene were charged to an HA-84 unit, a cyclohexane product having a purity of 99.99% would be possible.

Investments and Manufacturing Costs. Investment figures presented in Table 3 are based on the erected
battery limits U.S. Gulf Coast plants (1966) which include the complete reaction system, hydrogen recycling, gas separation, product stabilization, initial catalyst charge and fully paid royalty. These investments range from $1,200 to $600 per daily barrel of cyclohexane for plants ranging in size from 500 bpsd to 3000 bpsd, respectively.

Manufacturing costs in the United States are calculated to be 2.38 cents per gallon of cyclohexane for a plant producing 500 bpsd of cyclohexane. As the capacity of the plant is increased to 3000 bpsd of cyclohexane, manufacturing costs diminish to 0.91 cents per gallon of cyclohexane (Table 3 and Fig. 2). The utilities and their costs bases are presented in Table 4. The manufacturing costs shown do not include raw material costs.

Based on commercial experience, HA-84 unit onstream efficiency can be expected to be 350 stream days per year. The commercial unit at the AtlanticRichfield refinery has been onstream about two years with no indication that the catalyst has lost any activity. The cost calculations have assumed operating labor of one man per shift although experience with integrated petrochemical units indicates that the labor requirement can be less. Only routine maintenance is required.

Flexibility can exist in the manufacturing costs of a plant that is built larger than the current demand. Initially the plant will operate at partial capacity. As the market for cyclohexane develops, the throughput is increased until it finally reaches the design capacity.

Suppose an HA-84 unit were built costing $1,192,000 to produce 1500 bpsd of cyclohexane at design capacity, the manufacturing costs would be 2.47 cents per gallon of cyclohexane if the plant were run initially at 50 percent of capacity. As the demand for cyclohexane increased and production was raised to 75 percent of capacity, manufacturing costs would decline to 1.67 cents per gallon of cyclohexane; still further expansion to 100 percent of capacity would trim costs to 1.27 cents per gallon of cyclohexane (Table 5 and Fig. 3). With hydrogen and fuel gas at fuel value of 20 cents per 1 million Btu, benzene at 23.0 cents per gallon and cyclohexane at 24.7 cents per gallon, calculations indicate that this plant could run at 50 percent of capacity and still generate a net profit before taxes of 2.65 cents per gallon of cyclohexane produced.

Process Utilities. The HA-84 reaction system has been specifically designed to recover the large quantity of heat released during the hydrogenation reaction. The heat of reaction of about 1,100 Btu per pound of benzene is used to generate steam. For a plant producing 1,000 bpsd of cyclohexane, there would be net export from the site of 3,800 pounds per hour of steam. Using the utility values shown in Table 4, the credit for steam production at the rate of 40 cents per 1,000 pounds reduces the cost of utilities to a negligible 0.02 cents per gallon of cyclohexane manufactured.

Base Case Profitability of 23.2 Percent. A hypothetical case was chosen in which an HA-84 unit producing 1,500 bpsd of cyclohexane was to be erected for $1 million and complete construction occurred during the first year. The investment credit of 7 percent which

![Fig. 2—Larger units give lower manufacturing costs.](image1)

![Fig. 3—Costs for a 1500 bpsd cyclohexane unit.](image2)

### TABLE 3—Investments and Manufacturing Costs

<table>
<thead>
<tr>
<th>Cyclohexane Production, bpsd</th>
<th>500</th>
<th>1,000</th>
<th>1,500</th>
<th>2,000</th>
<th>3,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimated Investment $</td>
<td>600,000</td>
<td>920,000</td>
<td>1,192,000</td>
<td>1,422,000</td>
<td>1,830,000</td>
</tr>
<tr>
<td>Manufacturing Costs $/gal. CH/yr.</td>
<td>8.16</td>
<td>6.30</td>
<td>5.41</td>
<td>4.84</td>
<td>4.15</td>
</tr>
<tr>
<td>Utilities</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Catalyst</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Operating Labor, Overhead, Supervision</td>
<td>1.02</td>
<td>0.51</td>
<td>0.34</td>
<td>0.26</td>
<td>0.17</td>
</tr>
<tr>
<td>Maintenance, Insurance, Taxes</td>
<td>0.47</td>
<td>0.31</td>
<td>0.27</td>
<td>0.25</td>
<td>0.21</td>
</tr>
<tr>
<td>Interest and Depreciation</td>
<td>0.88</td>
<td>0.59</td>
<td>0.53</td>
<td>0.49</td>
<td>0.49</td>
</tr>
<tr>
<td>Total</td>
<td>2.38</td>
<td>1.57</td>
<td>1.27</td>
<td>1.11</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Notes: 1. Estimated investment is on-site erected cost, U.S. Gulf Coast basis, including engineering, contractor’s expenses and fee, initial catalyst charge, and fully paid royalties.
2. Operating labor at one man per shift or $30,000 per year; overhead, supervision and fringe benefits at 10% of operating labor.
3. Maintenance, insurance and taxes at 0% of investment per year.
4. Interest and depreciation at 13% of investment per year.

May 1967, Vol. 46, No. 5
ECONOMICS OF MAKING CYCLOHEXANE ...  

TABLE 4—Process Utilities  

<table>
<thead>
<tr>
<th></th>
<th>Cents per Gallon of Cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Per 1000 bpd</td>
<td></td>
</tr>
<tr>
<td>Power</td>
<td>0.12</td>
</tr>
<tr>
<td>Cooling Water (AT-36°F)</td>
<td>0.03</td>
</tr>
<tr>
<td>Net Steam Generation</td>
<td>0.13 (credit)</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
</tr>
</tbody>
</table>

Notes: 1. 85% purity hydrogen available at 100°F and 500 psig  
2. Benzene available at 100°F and 0 psig  
3. Cooling water at 85°F  
4. Steam generated at 100 psig  
5. (a) Power at 0.0 cents per kwh  
(b) Cooling water at 8 cents per 1 million Btu  
(c) Steam at 40 cents per 1,000 pounds  

TABLE 5—Effect of Reduced Throughput on Manufacturing Costs  
(Design Capacity: 1,500 bpd of Cyclohexane)  

<table>
<thead>
<tr>
<th>Percent of Design Capacity</th>
<th>Manufacturing Costs Cents per Gallon of Cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Utilities</td>
<td>0.02</td>
</tr>
<tr>
<td>Catalyst</td>
<td>0.05</td>
</tr>
<tr>
<td>Operating &amp; Overhead, Supervision</td>
<td>0.04</td>
</tr>
<tr>
<td>Maintenance, Insurance, Taxes</td>
<td>0.04</td>
</tr>
<tr>
<td>Interest and Depreciation</td>
<td>1.18</td>
</tr>
<tr>
<td>Total</td>
<td>2.47</td>
</tr>
</tbody>
</table>

Cyclohexane Production and Price... The production of cyclohexane in the United States during the 1960-1965 period has had a dramatic increase from 87 to 280 million gallons per year (Fig. A). The rapid growth rate of 26.4 percent per year is expected to decrease to a still quite substantial 13 percent per year for the period from 1965 to 1970. The projected demand in 1970 would be about 500 million gallons per year. The estimated use pattern in 1970 is expected to be about 50 percent for nylon and most of the remainder for export. Approximately 25 percent of the cyclohexane for general nylon use is expected to be used in the manufacture of nylon 66. The remaining portion for nylon is expected to take the route through caprolactam to nylon 6 (Fig. B).

Cyclohexane has demanded an increasingly greater portion of benzene production with a rise from 19 percent in 1960 to 35 percent in 1965. Forecasts indicate that in 1970, cyclohexane manufacture will be about 43 percent of benzene production. It is reasonable to assume that the prices of these materials will become more closely related. It has been theorized that prices decline as production increases, ostensibly because the newer facilities has been suspended by the U.S. government at this time was not taken as a credit. As the second year began, the plant went on stream and ran at an average of 50 percent of capacity for that year. A charge of $842,000 was made for working capital and capitalized royalty during the second year. Although benzene is presently selling for about 27.0 cents per gallon, by the year 1970 the increased production rate is expected to decrease the price by about 4.0 cents per gallon. Benzene was valued at 23.0 cents per gallon, while cyclohexane was being sold for 24.7 cents per gallon. The latter price is based on an average incremental advantage of 1.7 cents per gallon for cyclohexane over benzene during the last ten years. The raw material hydrogen stream entering the plant and the fuel gas product were given fuel values at 20 cents per 1 million Btu.

As cyclohexane demand expanded, it was assumed that the plant would run at 75 percent capacity during the third year and, finally would reach full capacity during the fourth year. Thereafter the plant was assumed to run at 100 percent throughput for the remainder of the 20-year project life. Depreciation was taken at the rate of 10 percent per
year, assuming a 10 percent salvage value, and occurred in the accounting from the second to the eleventh years, inclusive.

On the basis of these assumptions, an attractive after-tax profitability (sometimes called profitability index) of 23.2 percent was calculated (Table 6). A decrease in
cyclohexane price to the same price as benzene of 23.0 cents per gallon reduced the after-tax profitability to a still attractive 14.6 percent. It may be that an after-tax profitability of about 15 percent will be the controlling factor in determining future cyclohexane prices.

**Payout and Price Differential Factor.** A general method for calculating payout can be simplified to a straight-line formula such as the following example for a 1500 bpsd cyclohexane production rate:

\[
(PO)^{-1} = 0.0961 \left( CH - \frac{B}{1.205} \right) - 0.0953
\]

Where:

- \((PO)^{-1}\) = reciprocal payout years or cash flow: investment
- \(CH\) = cyclohexane price in cents per gallon
- \(B\) = benzene price in cents per gallon

It is evident that the payout is related to the cyclohexane price, minus the benzene price divided by the fractional recovered volumetric yield of cyclohexane from benzene. For simplicity this difference has been called the price differential factor. The foregoing formula assumes the material balance of Table 1 with hydrogen entering the unit and vent gas leaving the process having a fuel value of 20 cents per 1 million Btu.

The estimation of payouts as prices and plant sizes are varied is facilitated by the graphical solution presented in Fig. 4. It can be seen that the effect of changing fresh feed hydrogen from fuel value at 20 cents per 1 million Btu to 20 cents per 1,000 scf can be a substantial increase in payout time. However, the change in payout due to changes in hydrogen price diminishes as the price differential factor is increased. That is, the effect of hydrogen value on payout time is lessened as the spread between the prices of cyclohexane and benzene becomes greater. This graph assumes that the plant will be run at 100 percent of capacity immediately and continuously; it is therefore a rather simplified but representative picture of the entire concept.

Original presentation was before the API Division of Refining, Los Angeles, May 17, 1967.

**ACKNOWLEDGMENT**

The authors wish to extend their gratitude to the management and staff of Sinclair Research, Engelhard Industries and Hydrocarbon Research for their assistance and cooperation in the preparation of this publication.

**LITERATURE CITED**

Reactive balances

De hydrogencatie van benzeen is ofwel in benzeen.
De door Abten gevonden reacche snelheid vgl. is:

\[ R = \frac{6\text{PH}_2}{1+\text{PH}_2} \]

\( R \) is dus alleen afhankelijk van \( T \) (via \( \beta \)) en \( \text{PH}_2 \).
Donk de zeer grote overmaat \( \text{H}_2 \) (14x) heen de \( \text{PH}_2 \)
hydren de reactie nauwelijks af (per bed minder dan 0.5%) en wordt daaronder als constant verondersteld.
\( R \) is dusdanig alleen afhankelijk van \( T \).

Om nu een temp. profiel over de reactor te krijgen,
kan de volgende, van de warmtebalans afgeleide, vgl.
worden gebruikt:

\[ \frac{dT}{dTs} = -\frac{6\text{H}_2}{\beta \text{CP}} \frac{6\text{PH}_2}{1+\text{PH}_2} \]

\[ T_s = \frac{V_s \text{cat}}{\phi \text{DZ}} \]

\( \phi = \frac{\text{CP}}{6\text{H}_2} \cdot \frac{dT}{R} = dT_s \)

Aangemoen wacht dat \( \phi \) en \( \text{CP} \) per bed constant zijn bij
een gem.tempt. vlh bed (155°C)

Berekening \( \beta \)

1.2 moedelen \( \text{DZ} \)

\[ \frac{\text{atomen Pt} - 5}{\text{m}^3 \text{kat} - 5} \]

\[ \frac{5\times1.2 \times \frac{1}{2} \text{kmol DZ}}{\frac{1}{5} \times 195 \times 100 \times 0.5 \times 10^6 \text{m}^3 \text{kat} - 5} = 615.4 \]

\[ 1.9 \text{ Pt atomen} \]

\[ 0.5 \text{ mV kat} \]

\[ 190 \text{ Pt at. kat} \]
### A. Tussenbed koeling

\[
\int dT_s = \int_{0}^{480} \frac{\dot{q} \, dT}{\dot{q} H_s} = \int_{0}^{480} \frac{\dot{q} \, dT}{\dot{q} H_s} = \frac{\dot{q}}{\dot{q} H_s} \]

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
T & \xi & \rho & \dot{q} & \phi & \Psi \\
\hline
100 & 373 & 0.117 & 242.2 & 0 & \\
125 & 398 & 0.053 & 139.8 & 0.075 & 0.046 \\
150 & 423 & 0.026 & 77.6 & 0.133 & 0.049 \\
175 & 448 & 0.017 & 44.3 & 0.192 & 0.137 \\
200 & 473 & 0.008 & 26.2 & 0.562 & 0.300 \\
210 & 483 & 0.007 & 23.0 & 0.662 & 0.578 \\
\hline
\end{array}
\]

\(\phi_{\Psi 0} = 4.52\) \(\phi_{\Psi 0} = 3.25\) \(\phi_{\Psi 0} = 2.03\)

(Ver 5 exposed Pt atomen) \(V_{\text{sat}} = 5.0 \text{ m}^3\) \(V_{\text{sat}} = 2.2 \text{ m}^3\) \(V_{\text{sat}} = 1.4 \text{ m}^3\)

### Totaal

7.2 m³ bed. nodig

Opmerking: Opvallend is dat \(\xi\) en dus \(\rho\) epe eend met toenemende Temp. Zijt chemische reactie over in diffuse? De opeenvolgende beelden worden steeds kleiner, wat logisch is, geven ze steeds minder BZ aanwezig en ongetemd niet te maken. (Verdundings-effect?) Juiste reactordimensionen worden nog bepaald, als deze berekeningen juist zijn?

(No te op het 10 Pt atomen zitten, dan is er minder bed) nodig.
A. Tussenbed Koeling: Berekening $\phi_{b_2}$

$P_{b_2} = 5.6$ atm
$\phi_{b_2} = 4.92$ kg/s
$T = 100^\circ$

$P_{b_2} = 5.58$ atm
$\phi_{b_2} = 4.92$ kg/s
$T = 210^\circ$

$P_{b_2} = 5.52$ atm
$\phi_{b_2} = 4.92$ kg/s
$T = 130^\circ$

$P_{b_2} = 5.50$ atm
$\phi_{b_2} = 4.92$ kg/s
Toelichting + verklaring  Tussenbed koeleing

Deze bed een iets lagere conversie. Dit is te verklaren
uit het feit dat er weinig warmtecapaciteit van weleere 3 met
H_2 en 1 mol BB slechts 1 mol CH in de plaats komt.
De vijfomdenende reactie warmte kan de afdage in warmte-
capaciteit niet heelmaal wannderen. Daarom loopt de
temp. iets sneller naar zijn max. toelaatbare 210 toe.

By gebruik van tussenbed koeleing zijn 4 bedden nodig,
tereyme by CH-injektie 3 kunnen voldoen. Drie een
moet tussenhids waden gebeld om mengel weer op 100°
te bragen, tereyme by CH-injektie niet gebeld moet wade
op met stoom. Samn dit de 3 warmteinwelaars uitz. Daen
plaat wel tegen over dat de vordig de productstoom meer
tot 143° kan afwelen, zodat additionele koeleing noodzakelyk
is. By tussenbed koeleing wordt product stoom afgebeld
tot 84°C en vordig opgewaamd tot 85°C. Deze moet
dan weer waden opgewaamd waden tot 100°, wat met de
vijfomdenende stroom v. tussenbed koeleing kan waden gedaan

KOELEING van product stoom met vordig:

product: 458,3 mol H_2
4,1 mol CH

vordig: 583,8 mol CH
41,7 mol B2

H_{210} = 860,2 kcal
H_{ch} = 289,4 kcal

\frac{H_{210}}{898,4} = \frac{H_{ch}}{592,4}

A = 2,409
A = \frac{2,409}{602 \times 84,6} = 0,392 m^2

\begin{array}{c}
30 \\
85
\end{array}
\begin{array}{c}
84 \\
210
\end{array}

\frac{A}{210} = \frac{125 - 54}{54} \times 84
**B. INJECTIE MET Koud CH**

Het kromme profiel wacht op derdele manier als A, behalve,
alleen neemt de $P_{CH}$ per bed af door de verdunning met CH.

**BED #1**

$P_{CH} = 5.59$ atm; $C_P = 8.342$; $\frac{C_{CP}}{a_{CH}} = 0.074$; $\Phi_{CH}^{H_2} = 4.52 \ m^3$

<table>
<thead>
<tr>
<th>$T$</th>
<th>$b$</th>
<th>$R$</th>
<th>$T_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>393</td>
<td>0.117</td>
<td>243.2</td>
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<tr>
<td>125</td>
<td>398</td>
<td>0.053</td>
<td>140.6</td>
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<tr>
<td>150</td>
<td>423</td>
<td>0.016</td>
<td>78.1</td>
</tr>
<tr>
<td>175</td>
<td>488</td>
<td>0.014</td>
<td>44.6</td>
</tr>
<tr>
<td>200</td>
<td>473</td>
<td>0.009</td>
<td>26.3</td>
</tr>
<tr>
<td>210</td>
<td>483</td>
<td>0.007</td>
<td>23.2</td>
</tr>
</tbody>
</table>

$V_{kat} = 4.52 \times 0.656 = 3.0 \ m^3$

**BED #2**

$P_{CH} = 5.03$ atm; $C_P = 10.845$; $\frac{C_{CP}}{a_{H_2}} = 0.044$; $\Phi_{H_2}^{H_2} = 2.34 \ m^3$

<table>
<thead>
<tr>
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<th>$R$</th>
<th>$T_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>393</td>
<td>0.117</td>
<td>227.8</td>
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<tr>
<td>125</td>
<td>398</td>
<td>0.053</td>
<td>129.4</td>
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<tr>
<td>150</td>
<td>423</td>
<td>0.026</td>
<td>71.1</td>
</tr>
<tr>
<td>175</td>
<td>449</td>
<td>0.014</td>
<td>40.5</td>
</tr>
<tr>
<td>200</td>
<td>473</td>
<td>0.008</td>
<td>23.8</td>
</tr>
<tr>
<td>210</td>
<td>483</td>
<td>0.007</td>
<td>20.9</td>
</tr>
</tbody>
</table>

$V_{kat} = 2.34 \times 0.945 = 2.2 \ m^3$

**BED #3**

$P_{CH} = 4.52$ atm; $C_P = 13.319$; $\frac{C_{CP}}{a_{H_2}} = 0.055$; $\Phi_{H_2}^{H_2} = 1.07 \ m^3$

<table>
<thead>
<tr>
<th>$T$</th>
<th>$b$</th>
<th>$R$</th>
<th>$T_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>139</td>
<td>412</td>
<td>0.036</td>
<td>96.0</td>
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<tr>
<td>150</td>
<td>423</td>
<td>0.026</td>
<td>64.7</td>
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<tr>
<td>175</td>
<td>449</td>
<td>0.014</td>
<td>36.6</td>
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<tr>
<td>200</td>
<td>473</td>
<td>0.008</td>
<td>21.5</td>
</tr>
<tr>
<td>210</td>
<td>483</td>
<td>0.007</td>
<td>18.9</td>
</tr>
</tbody>
</table>

$V_{kat} = 1.07 \times 1.142 = 1.2 \ m^3$

Totaal $6.4 \ m^3$ het nodig bij deze reactie. Minder dan nodig
dan bij tweede bed hoewel… Doen verdunning? Of roque efficiency
dan maar 3 bedden?
B. CH- INJECTIE : BEREKENING \( q_{B2} \)

\[ \begin{align*}
q_{B2} &= 5.6 \text{ kJ/m}^3 \\
\Phi_{h,m} &= 4.92 \text{ kJ} / \text{m}^3
\end{align*} \]

\[ \begin{align*}
\phi_{h} &= 5.58 \text{ atm} \\
\phi_{h,m} &= 4.92 \text{ kJ} / \text{m}^3
\end{align*} \]

\[ \begin{align*}
\phi_{h} &= 5.58 \text{ atm} \\
\phi_{h,m} &= 4.92 \text{ kJ} / \text{m}^3
\end{align*} \]

\[ \begin{align*}
H_{10} &= 381.6 \text{ kcal} \\
\Delta H_{L, q_{B2}} &= 573.3 \\
H_{210} &= 954.9 \text{ kcal} \\
H_{10u} &= 366.1 \text{ kcal}
\end{align*} \]

KOELING: \( q_{B2} = 366.1 \text{ kcal} \)

\[ \begin{align*}
\text{CH} &= \frac{587.9}{9.8} = 60.0 \text{ mol CH}
\end{align*} \]

\[ \begin{align*}
H_{10} &= 492.2 \text{ kcal} \\
\Delta H_{L, q_{B2}} &= 798.2 \\
H_{210} &= 1290.8 \text{ kcal} \\
H_{189} &= 744.5
\end{align*} \]

KOELING: \( 1290.8 - 744.5 = 546.3 \text{ kcal} \)

\[ \begin{align*}
\text{CH} &= \frac{546.3}{9.8} = 55.8 \text{ mol CH}
\end{align*} \]

\[ \begin{align*}
\text{H}_{189} &= 938.9 \text{ kcal} \\
\Delta H_{L, q_{B2}} &= 631.3 \\
H_{210} &= 1608.6 \text{ kcal}
\end{align*} \]
**Toelichting + verklaring**

**CH: opwarmen van 1 mol CH van 30 → 100°C:**

\[ \text{H}_\text{CH}^{100} = +2102.1 \text{ kcal} \]

\[ \text{H}_\text{CH}^{298} = -116.6 \text{ kcal} \]

\[ \text{H}_\text{v} = 7860 \text{ kcal} \]

\[ \text{q} = 835.3 \rightarrow 9.8 \text{ kcal/mol CH weder} \]

\[ b_2: \] De conversie van benzine neemt per bed toe. Dit is ook terug te wijzen aan verdunning door injectie van CH. De geinjecteerde CH met zijn warmtecapaciteit kan een deel van de warmteabsorbeer. Door de verdunning neemt de \[ \text{P}_\text{H}_2 \] van \[ \text{H}_2 \] af. Dit van een verlaging van de reactie, dus lagere conversie. Dit effect wordt echter minder overtroffen dan het eerste.

**KOELING van product door met vordering**

**Product:** 458.7 mol \[ \text{H}_2 \]

157.5 mol \[ \text{CH} \]

\[ \text{H}_\text{v210} = 1604.6 \text{ kcal} \]

\[ \text{H}_\text{v298} = 948.3 \]

\[ 660.3 \text{ kcal} = 2773 \text{ kcal} \]

663.6 kcal weder om van 30 → 100°C 19 kcal warrme.

**Vordering:** 583.8 mol \[ \text{H}_2 \]

41.3 mol \[ \text{B}_2 \]

\[ \text{H}_\text{v298} = \]

\[ \text{H}_\text{v30} = \]

\[ 2973 \text{ kcal} \]

\[ A = \frac{2773}{602 \times 111.5} = 41.3 \text{ m}^2 \text{ Koel opp.} \]