

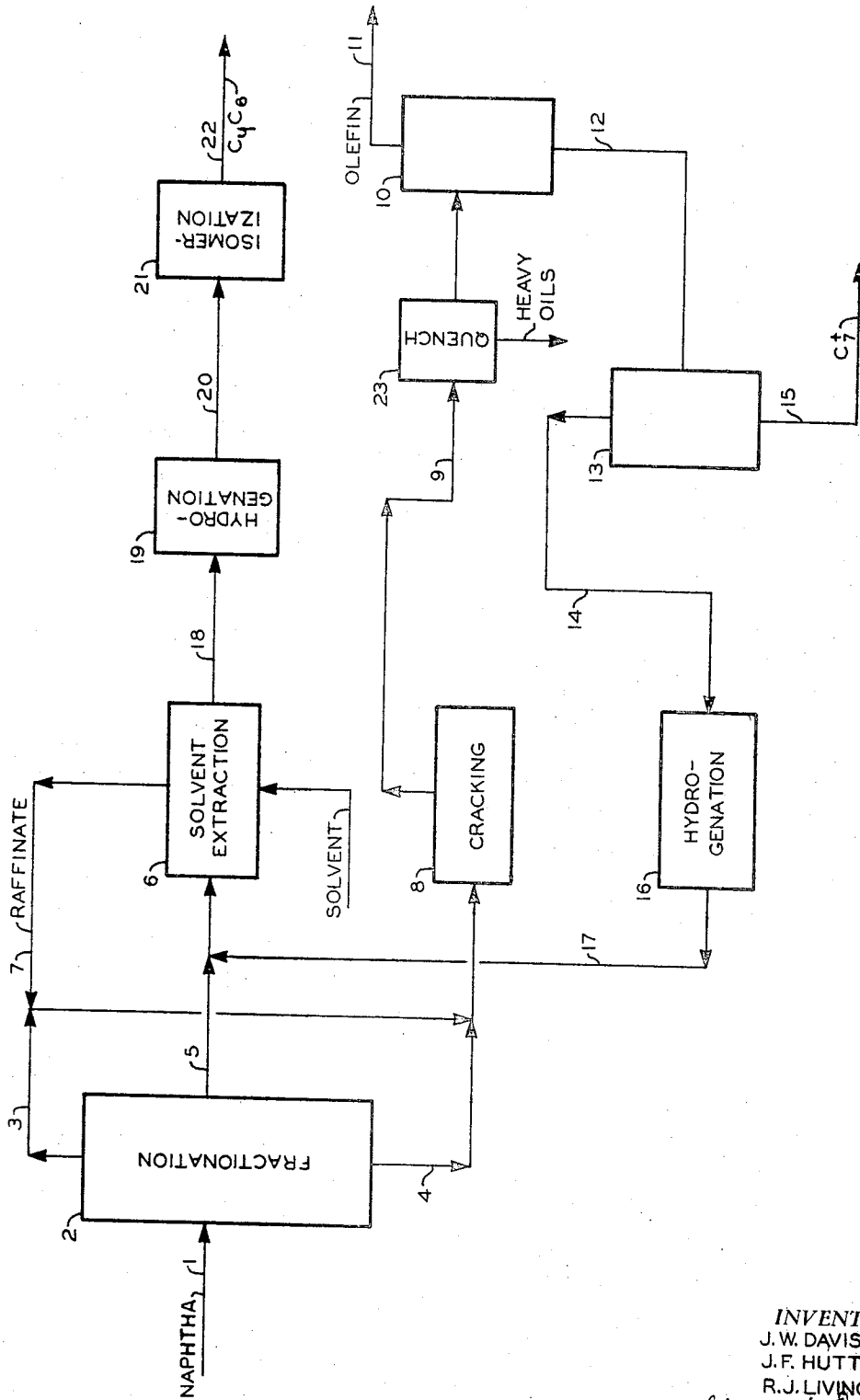
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PRODUCTION OF CYCLOHEXANE FROM NAPHTHA

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## 3,406,217 PRODUCTION OF CYCLOHEXANE FROM NAPHTHA

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### ABSTRACT OF THE DISCLOSURE

A process of producing cyclohexane from a petroleum naphtha stream wherein the naphtha stream is fractionated in a distillation zone to form an overhead fraction containing  $C_5$ 's and lighter, an intermediate fraction containing benzene, methylcyclopentane, and cyclohexane, and a bottom fraction containing  $C_7$ 's and heavier. The bottom fraction is passed to a cracking zone wherein a benzene-containing stream is formed which is then combined with the intermediate fraction from the distillation zone. The resulting combined stream is then passed through an extraction zone wherein paraffinic hydrocarbons are removed therefrom. The effluent from the extraction zone is passed through a benzene hydrogenation zone wherein benzene is hydrogenated to cyclohexane, and the effluent from the benzene hydrogenation zone is passed through an isomerization zone wherein methylcyclopentane is converted to cyclohexane. A pure cyclohexane stream is removed from the isomerization zone.

This invention relates to the production of cyclohexane from naphtha. In one of its aspects, it relates to a process for the production of cyclohexane from a naphtha containing stream, the process comprising fractionating the naphtha stream to recover an overhead portion, a bottoms portion, and an intermediate stream containing hydrocarbons boiling in the benzene range; cracking the bottoms portion from the fractionator to produce an olefin-containing stream, a stream boiling in the gasoline range, and a benzene boiling range stream; combining the benzene boiling range stream with the intermediate stream from the fractionator, from which combined stream can be obtained a high quality cyclohexane product. In another of its aspects, the invention relates to a process for producing cyclohexane from naphtha as hereinbefore described wherein the combined stream of benzene-forming hydrocarbons is passed to a solvent extraction zone for removal of paraffins, and the remaining benzene boiling range stream is hydrogenated to produce cyclohexane from benzene and a resulting stream is isomerized to produce cyclohexane from methylcyclopentane. In another of its aspects, the invention relates to a process for the production of cyclohexane from naphtha as hereinbefore described wherein the overhead portion from the fractionator and the paraffin containing raffinate phase from the solvent extraction step are combined with the bottoms from the fractionator prior to the cracking step. In a still further aspect, the invention relates to an apparatus for carrying out the aforementioned processes.

Naphtha, which is readily obtained from certain crude oils, is cracked to produce olefins and diolefins in the  $C_2$  to  $C_5$  range and paraffins boiling in the gasoline range. It is known that the naphtha also contains a small fraction of benzene and other hydrocarbons boiling in the benzene range. However, heretofore it has been uneconomical to recover these hydrocarbons from naphtha. With increasing quantities of naphtha being cracked, and with increasing demand for cyclohexane which is used as an intermediate in the production of nylon, it has now been found economically feasible to recover a benzene fraction from crude naphtha.

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We have now discovered that cyclohexane can be produced from a naphtha fraction by removing the heart cut of naphtha prior to cracking, combining a cracked naphtha product fraction containing benzene and cyclohexane with the heart cut from the naphtha fraction and treating the products to produce a high quality cyclohexane.

By various aspects of this invention, one or more of the following, or other, objects can be obtained.

It is an object of this invention to provide a process and apparatus for the maximum recovery of cyclohexane from crude naphtha fraction.

It is a still further object of this invention to provide a process and apparatus for the maximum production of cyclohexane wherein olefins and diolefins are simultaneously produced with increased efficiency.

Other aspects, objects, and the several advantages of this invention are apparent to one skilled in the art from a study of this disclosure, the drawing and the appended claims.

According to the invention, cyclohexane is recovered as a product of the process from a naphtha containing stream. The naphtha containing stream is fractionated and the heart cut containing hydrocarbons boiling in the benzene range are removed. The heart cut from the fractionator is treated in a solvent extraction zone to remove paraffins therefrom, and is passed to a benzene hydrogenator to produce cyclohexane from benzene and then to an isomerization step wherein methylcyclopentane is converted to cyclohexane.

According to one embodiment of the invention, the heavy product from the fractionator is cracked to produce an olefin and diolefin containing stream, a benzene containing stream, and a gasoline boiling range stream. The benzene containing stream can be admixed with the heart cut from the fractionator. In another embodiment of the invention, the overhead from the fractionator and the raffinate from the solvent extraction zone are combined and admixed with the bottoms from the fractionator prior to the cracking step.

The invention will now be described with reference to the accompanying drawing which shows an embodiment of the invention.

A naphtha stream passes through line 1 into fractionator 2 which separates the naphtha into a heavy bottom fraction which is removed through line 4, an overhead fraction containing  $C_5$  and lighter hydrocarbons, and a heart cut containing hydrocarbons boiling in the benzene boiling range. The overhead fraction is removed through line 3 and the benzene boiling range fraction is removed through line 5 and passed to a solvent extraction zone 6 wherein a solvent such as methylcarbitol is used as a solvent. Suitable conditions in fractionator 2 are a top temperature of 210 to 250° F., a bottom temperature of 250 to 300° F., and a pressure of 55 to 65 p.s.i.a. The paraffin containing raffinate from the solvent extraction zone 6 is removed through line 7 and combined with the overhead from fractionator 2 in line 3. The combined streams are further combined with the bottoms from fractionator 2 in line 4 and passed to cracking zone 8. Cracking zone 8 can be any conventional cracking reactor such as a catalytic cracker or thermal cracker. The effluent from the cracking reactor 8 passes through line 9 and is quenched in 23 to remove heavy ends. The effluent from 23 is passed to fractionator 10 wherein olefins and diolefins are removed through line 11 and heavier boiling hydrocarbons are passed through line 12 to fractionator 13 wherein gasoline boiling range hydrocarbons and heavier hydrocarbons are removed through line 15 and a benzene containing fraction is removed through line 14. Suitable operating conditions for the fractionator 10 are a top temperature of

25 to 50° F., bottom temperature of 200 to 250° F., and 100 to 150 p.s.i.a. Suitable operating conditions for fractionator 13 are a top temperature of 150 to 200° F., bottom temperature of 250 to 400° F., and a pressure of 50 to 75 p.s.i.a. The benzene containing stream in line 14 is passed to a mild hydrogenation zone 16 wherein unsaturated compounds such as olefins, diolefins and acetylenes are converted to saturated compounds. The effluent from hydrogenation zone 16 is passed through line 17 and combined with the benzene boiling range stream in line 5. The effluent from the solvent extraction zone 6 is passed through line 18 to hydrogenation zone 19 wherein benzene is converted to cyclohexane. In hydrogenation zone 19, benzene is contacted with hydrogen in the presence of a hydrogenation catalyst such as nickel at a temperature in the range of 350° F. to 500° F. A benzene free hydrocarbon effluent is withdrawn from hydrogenation zone 19 via conduit 20 and passed to liquid isomerization zone 21 wherein methylcyclopentane within the feed mixture is isomerized to cyclohexane by contacting the feed with a conventional isomerization catalyst such as HCl promoted aluminum halide complex-type catalyst. When employing an aluminum halide complex-type catalyst, the temperature and pressure of the isomerization zone is preferably maintained typically in the range of 100° F. to 160° F. and in the range of 100 to 250 p.s.i.a., respectively. The isomerization zone effluent is removed through line 22 and the cyclohexane is removed from the impurities by conventional means, not shown.

Thus, according to the invention, cyclohexane is efficiently produced from a naphtha fraction. Further, because the benzene boiling fraction has been removed from the naphtha, a greater percentage of paraffins are passed to the cracking zone. This yields an improved amount of olefins from the cracking zone. Thus, the process, while producing cyclohexane, also increases the yield of olefins from the naphtha fraction.

As a specific example of how this invention works, the following table giving a material balance for the operation as described in the drawing is shown. The units given are pounds per hour.

TABLE

|                    | Stream number                |          |           |                |                          |                           |
|--------------------|------------------------------|----------|-----------|----------------|--------------------------|---------------------------|
|                    | 1<br>Prefractionator<br>feed | 3<br>OHD | 4<br>BTMS | 5<br>Side-Draw | 7<br>Paraffin<br>Recycle | 9<br>Cracking<br>effluent |
| Ethane and lighter | 214                          | 214      |           |                |                          | 1,429                     |
| Propylene          | 2                            | 2        |           |                |                          | 454                       |
| Propane            | 108                          | 106      |           | 2              | 2                        | 24                        |
| Butenes            | 64                           | 64       |           |                | 6                        | 256                       |
| Butanes            | 194                          | 193      |           | 1              | 3                        | 13                        |
| Pentanes           | 214                          | 210      |           | 4              | 8                        | 21                        |
| Hexanes            | 386                          | 304      |           | 82             | 84                       | 14                        |
| Methylcyclopentane | 324                          | 1        |           | 323            | 10                       | 11                        |
| Benzene            | 96                           |          |           | 96             | 9                        | 206                       |
| Cyclohexane        | 252                          |          | 1         | 251            | 8                        | 9                         |
| Heptanes           | 624                          |          | 308       | 316            | 373                      | 172                       |
| Octanes            | 558                          |          | 555       | 3              | 3                        | 131                       |
| Heavier            | 546                          |          | 546       |                |                          | 270                       |
| Total, lb./hr.     | 2,582                        | 1,094    | 1,410     | 1,078          | 506                      | 3,010                     |

|                    | Stream number            |                             |                        |                                   |               |                                 |
|--------------------|--------------------------|-----------------------------|------------------------|-----------------------------------|---------------|---------------------------------|
|                    | 12<br>2nd Fract.<br>feed | 14<br>Hydro-treater<br>feed | 15<br>Heavy<br>product | 17<br>Hydro effluent<br>(recycle) | 18<br>Extract | 20<br>Hydrogenation<br>effluent |
| Ethane and lighter |                          |                             |                        |                                   |               |                                 |
| Propylene          |                          |                             |                        |                                   |               |                                 |
| Propane            |                          |                             |                        |                                   |               |                                 |
| Butenes            | 6                        | 6                           |                        | 6                                 |               |                                 |
| Butanes            | 2                        | 2                           |                        | 2                                 |               |                                 |
| Pentanes           | 4                        | 4                           |                        | 4                                 |               |                                 |
| Hexanes            | 2                        | 2                           |                        | 2                                 |               |                                 |
| Methylcyclopentane | 8                        | 8                           |                        | 8                                 | 321           | 321                             |
| Benzene            | 194                      | 194                         |                        | 194                               | 281           |                                 |
| Cyclohexane        | 9                        | 9                           |                        | 9                                 | 262           | 555                             |
| Heptanes           | 172                      | 65                          | 107                    | 65                                | 8             | 8                               |
| Octanes            | 131                      |                             | 131                    |                                   |               |                                 |
| Heavier            | 270                      |                             | 270                    |                                   |               |                                 |
| Total, lb./hr.     | 798                      | 290                         | 508                    | 290                               | 860           | 884                             |

Reasonable variation and modification are possible within the scope of the foregoing disclosure, the drawing and the appended claims to the invention, the essence of which is that there has been provided a process and apparatus for the production of cyclohexane from a naphtha fraction by removing the heart cut from the naphtha fraction, removing the paraffinic material from the heart cut, cracking the remaining naphtha fraction to produce olefins and gasoline boiling range hydrocarbons, and a benzene boiling range hydrocarbon fraction, and combining the benzene boiling range hydrocarbons with the heart cut of the naphtha.

We claim:

1. A process for producing cyclohexane from a petroleum naphtha fraction containing benzene, methylcyclopentane, cyclohexane, and paraffinic hydrocarbons containing from 1 to at least 8 carbon atoms comprising:

- passing said naphtha fraction to a distillation zone;
- removing an intermediate fraction containing benzene, methylcyclopentane, and cyclohexane, an overhead fraction containing pentanes and lighter paraffinic hydrocarbons, and a bottom fraction containing heptanes and heavier paraffinic hydrocarbons from said distillation zone;
- passing said bottom fraction to a cracking zone wherein at least a portion thereof is transformed to benzene, olefins, and diolefins;
- separating a benzene-containing stream from said cracking zone and combining said benzene-containing stream with said intermediate fraction;
- removing paraffin constituents from the combined stream of step (d) to form a benzene-hydrogenation feed stream;
- passing said benzene-hydrogenation feed stream through a benzene-hydrogenation zone wherein benzene is converted to cyclohexane;
- passing the effluent from the benzene-hydrogenation zone through an isomerization zone wherein methylcyclopentane is converted to cyclohexane; and
- removing cyclohexane from said isomerization zone.

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2. The process of claim 1 wherein said paraffinic constituents are removed in step (e) by solvent extraction.

3. A process according to claim 1 wherein said overhead from said distillation zone is combined with said bottoms prior to said cracking step.

4. A process according to claim 2 wherein paraffinic raffinate from said solvent extraction zone is combined with said bottoms from said distillation zone prior to said cracking step.

5. A process according to claim 2 wherein said overhead from said distillation zone and said paraffinic raffinate from said solvent extraction zone are combined with said bottoms from said distillation zone prior to said cracking step.

6. The process of claim 1 wherein step (d) comprises quenching the effluent from said cracking zone; passing the quenched effluent to a second distillation zone wherein olefins and diolefins are removed as overhead and a heavier fraction containing benzene is removed from the bottom thereof; passing said heavier fraction to a third distillation zone wherein a benzene-boiling range fraction containing

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benzene, olefins, and diolefins is removed as overhead and a stream containing heptanes and heavier hydrocarbons is removed from the bottom thereof; passing said benzene boiling range fraction through a mild hydrogenation zone wherein olefins and diolefins contained therein are converted to saturated compounds; removing said benzene-containing stream from said mild hydrogenation zone.

7. A process according to claim 2 wherein said solvent is methylcarbitol.

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