

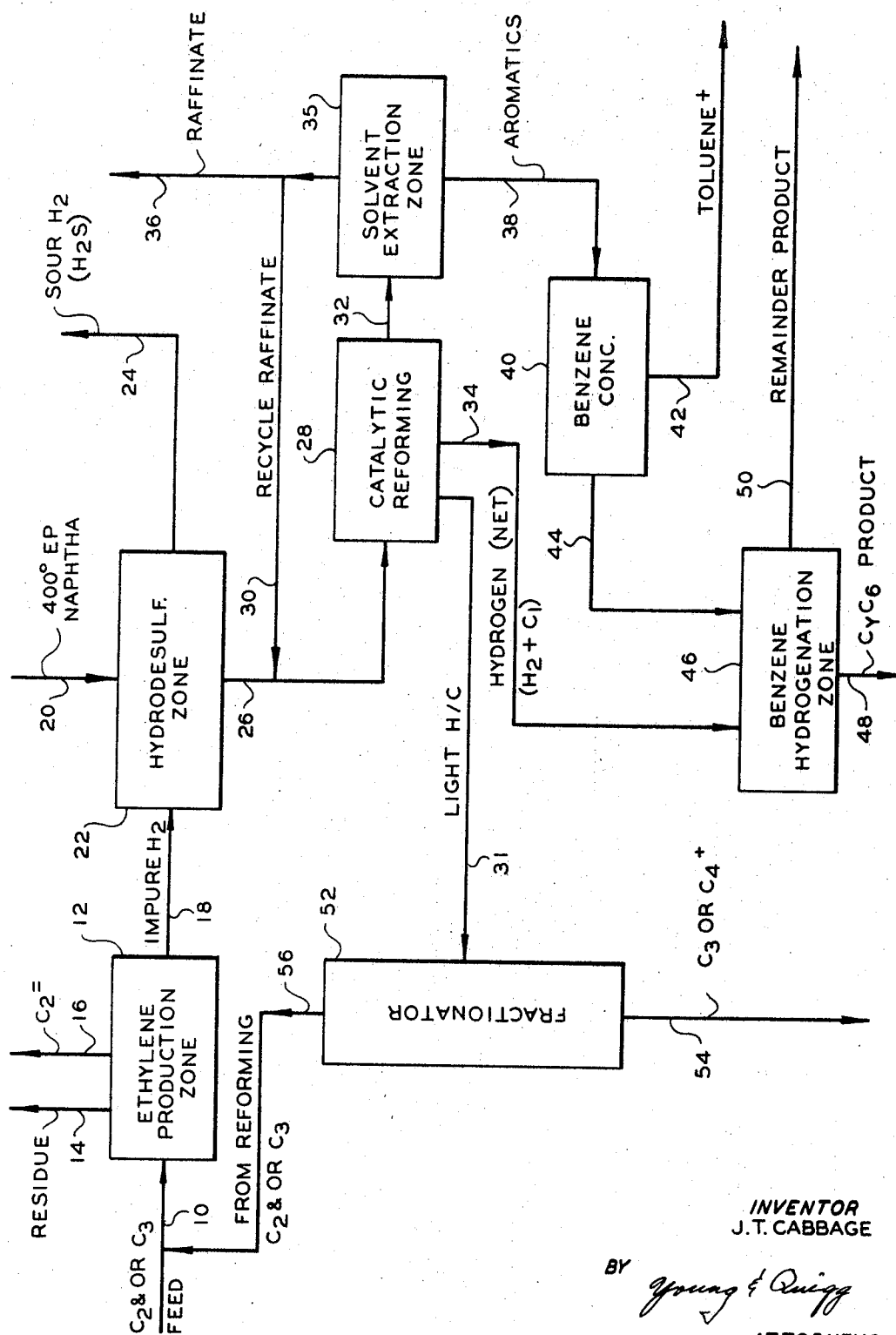
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J. T. CABBAGE

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HYDROCARBON CONVERSION PROCESS

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INVENTOR
J. T. CABBAGE

BY

Young & Quigg

ATTORNEYS

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HYDROCARBON CONVERSION PROCESS

John T. Cabbage, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

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This invention relates to an improved process for the conversion of hydrocarbons to more useful product streams.

In the petroleum industry various available hydrocarbon streams are utilized to produce more desirable hydrocarbon product streams. To illustrate, in one petroleum refinery a 400° F. end point naphtha is hydrodesulfurized in admixture with hydrogen in contact with a hydrodesulfurization catalyst (cobalt molybdate) and the desulfurized naphtha is passed to a catalytic reforming zone containing a suitable reforming catalyst (platinum-alumina). The reformate is separated into a light hydrocarbon stream (C₅ and lighter) and an aromatic-rich stream, the latter being solvent extracted to recover a principally aromatic stream of benzene, toluene and heavier, and the raffinate being recycled to the reforming zone. The aromatic-rich stream is separated into a benzene concentrate and a toluene and heavier stream, the benzene concentrate being hydrogenated in a hydrogenation zone in admixture with hydrogen in contact with a nickel hydrogenating catalyst (nickel on kieselguhr) to produce cyclohexane as a product of the process.

It requires a relatively pure hydrogen stream free of CO in the hydrogenation zone because of the susceptibility of nickel to poisoning by CO. A CO-free stream of H₂ is produced as an effluent from the reforming zone but this stream must be divided between the benzene hydrogenation zone and the naphtha hydrodesulfurization zone to which it is passed in a once-through operation because of the sour condition of the hydrogen off-gas (high concentration of H₂S therein). Cyclohexane production in this type of operation is greatly curtailed by the lack of a larger volume hydrogen-rich stream free of CO.

This invention is concerned with the more efficient utilization of refinery streams, particularly hydrogen-rich streams produced in refinery operations.

Accordingly, it is an object of the invention to provide an improved hydrocarbon conversion process which effects more efficient utilization of available hydrocarbon streams produced by different refinery operations. Another object is to provide a hydrocarbon conversion operation which is more economical in the use of available hydrocarbon streams from normal conversion operations. A further object is to provide a refinery process which increases the production of cyclohexane from a naphtha stream. Other objects of the invention will become apparent to one skilled in the art upon consideration of the accompanying disclosure.

A broad aspect of the invention as applied to simultaneous hydrodesulfurization of the naphtha stream, catalytic reforming of the naphtha stream to produce an aromatic-rich stream, solvent extracting the latter stream to separate an aromatics stream and a lighter raffinate, separating a benzene concentrate from the toluene and heavier aromatics, and hydrogenating the benzene concentrate over a nickel hydrogenation catalyst to produce cyclohexane, comprises passing all of the relatively pure (CO-free) hydrogen stream from the catalytic reforming zone as the hydrogen feed to the benzene hydrogenation zone which avoids poisoning of the nickel catalyst, dehydrogenating ethane and/or propane to produce ethylene and an impure H₂-rich stream, and passing the impure hydrogen-rich stream produced in the ethylene production zone to the hydrodesulfurization zone which can tolerate

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the impurities in this stream (CO). An additional aspect of the invention comprises separating the C₂-C₅ hydrocarbon produced in the reforming zone into a light stream and a heavier stream, and passing the light stream as feed to the ethylene production zone.

The invention is best understood by reference to the accompanying schematic drawing which is a process flow or arrangement of apparatus in accordance with the invention.

Referring to the drawing, a suitable feed for the production of ethylene is passed through line 10 into ethylene production zone 12 for thermal cracking and dehydrogenation to ethylene. The feed in line 10 may consist essentially of ethane, propane, or a mixture of these hydrocarbons. A residual material is recovered through line 14, an ethylene-rich stream through line 16, and an impure hydrogen stream containing CO through line 18.

A naphtha stream, such as one having a 400° F. end point, is fed through line 20 into hydrodesulfurization zone 22 and is hydrodesulfurized therein in admixture with the impure hydrogen stream from line 18 in contact with a suitable hydrodesulfurization catalyst such as cobalt molybdate on alumina. A sour H₂ gas is recovered through line 24 and the desulfurized naphtha is recovered through line 26 and passed into catalytic reforming zone 28 in admixture with recycle raffinate from line 30. The reforming in zone 28 is effected in contact with a conventional reforming catalyst, such as platinum on alumina which may or may not have been fluorinated. The reformate in zone 28 is separated into a light hydrocarbon stream containing principally C₂-C₅ hydrocarbons which are passed through line 31 to further treatment described below, an aromatic-rich stream which is passed through line 32 into solvent extraction zone 35, and a hydrogen-rich stream substantially free of CO which is recovered through line 34. Solvent extraction zone 35, which utilizes any suitable liquid solvent for aromatics, produces a raffinate in line 36 relatively free of aromatics a portion of which is recycled through line 30 to the reforming zone and an aromatics-rich stream in line 38 which is passed to benzene concentration zone 40. An effluent toluene-and-heavier stream is recovered through line 42 from benzene concentration zone 40 and a separate benzene-rich stream is passed through line 44 into benzene hydrogenation zone 46 along with the relatively pure hydrogen stream from line 34. Zone 46 is provided with a nickel catalyst which is preferably deposited on a solid porous support such as a kieselguhr or silica gel. The cyclohexane produced in zone 46 is recovered as a product of the process through line 48 and residual hydrocarbons are recovered through line 50 following their separation from the cyclohexane.

The C₂-C₅ hydrocarbon stream from line 31 is passed into a separation zone 52 for separation and recovery of a heavier fraction through line 54 and a lighter fraction through line 56, the latter being passed to ethylene production zone 12 via line 10 in admixture with the feed to this zone. When the feed in line 10 is principally ethane, separation zone 52 is operated substantially as a deethanizer. When the feed in line 10 is a mixture of ethane and propane, as it well may be, separation zone 52 is operated so as to take overhead substantially all of the ethane and propane in the stream from line 31, the C₄'s and C₅'s and heavier being recovered through line 54.

The various hydrocarbon conversion and separation zones referred to and shown in the drawing are operated in conventional manner, each of these steps being commonly practiced in petroleum refineries. The conditions of operation in the various conversion and separation zones are not a part of the invention, and specific details of these operations need not be delineated herein. The invention is in the sequence of and relationship between the various steps in the complete process. Thus, by adding

ethylene production to the combination, the impure hydrogen stream in line 18 can be utilized in hydrodesulfurization zone 22 in contact with a cobalt molybdate catalyst, as well as other hydrodesulfurization catalysts, without appreciable detriment to the catalyst. However, this stream cannot be utilized in benzene hydrogenation zone 46 because of the presence therein of CO in a concentration highly detrimental to the nickel catalyst therein. By utilizing all of the CO-free hydrogen stream from line 34 in benzene hydrogenation zone 46 instead of a portion thereof in hydrodesulfurization zone 22, the poisoning of the nickel catalyst in the hydrogenation zone is avoided and all of the hydrogen stream in line 34 is fed to benzene hydrogenation zone 46 along with all of the benzene concentrate from line 44 to greatly increase cyclohexane production. In addition, the process makes specific use of the ethane and/or propane from line 31 in the ethylene production zone 12, thereby materially increasing ethylene yield and the cooperation between the various operational steps in the unitary process.

To further illustrate the invention, one set of conditions representing plant operation of the invention are presented in the example below. The data in the example are merely illustrative and are not to be interpreted as unnecessarily limiting the invention.

EXAMPLE

Flow rates:		
Ethane feed (line 10)	b./d.	3,300
Reformer feed (line 26)	b./d.	16,000
"Impure" hydrogen (line 18)	m.s.c.f./d.	6,000
Hydrogen	volume percent.	86.6
Methane	do.	9.1
Ethylene	do.	3.2
Ethane	do.	0.9
Carbon monoxide	do.	0.2
H ₂ S	p.p.m.	1
CO ₂	p.p.m.	12
Cyclohexane product (line 48) (99.5% pure)	b./d.	1,800
"Pure" hydrogen (line 34)	m.s.c.f./d.	8,000
Hydrogen	volume percent.	85.5
Methane	do.	6.1
Ethane	do.	3.1
Propane (plus)	do.	5.3
Carbon monoxide	do.	None
H ₂ S	do.	Trace
Ethane to charge (line 56)	b./d.	200
Toluene product (line 42)	b./d.	200

Unit operations	Temp. ° F.	Pressure, p.s.i.g.
Ethylene production zone	1,500	10
Hydrodesulfurization zone	650	400
Reforming zone	925	500
Solvent extraction zone	250	135
Benzene hydrogenation zone	400	500

Certain modifications of the invention will become apparent to those skilled in the art and the illustrative details disclosed are not to be construed as imposing unnecessary limitations on the invention.

I claim:

1. A process comprising the steps of:

- (1) dehydrogenating a feed stream of ethane, propane, or a mixture thereof to produce an ethylene stream as a product of the process and an impure stream rich in H₂ containing a minor concentration of CO;
- (2) hydrodesulfurizing a naphtha-rich stream in admixture with the impure H₂-rich stream of step (1) in contact with a catalyst immune to CO poisoning to

produce a substantially sulfur-free, naphtha-rich stream;

- (3) catalytically reforming the resulting naphtha-rich stream of step (2) to produce a substantially CO-free H₂ stream, an aromatics-rich stream, and a lighter C₂-C₅ stream;

- (4) solvent-extracting the aromatics-rich stream of step (3) to separately recover a principally aromatics stream and a raffinate stream of principally non-aromatics;

- (5) separating the aromatics stream of step (4) into a principally benzene stream and a toluene and heavier stream as a product of the process; and

- (6) hydrogenating the benzene stream of step (5) in admixture with the CO-free H₂ stream of step (3) in contact with a nickel hydrogenation catalyst to produce a cyclohexane stream as a product of the process.

2. The process of claim 1 including the steps of:

- (7) separating the C₂-C₅ stream of step (3) into a lighter stream containing at least ethane and a heavier stream as a product of the process; and

- (8) passing the lighter stream of step (7) to step (1) as a portion of the feed thereto.

3. The process of claim 1 wherein the catalyst in step (2) comprises essentially cobalt molybdate, the catalyst of step (3) comprises essentially a supported platinum catalyst, and the catalyst of step (6) comprises essentially nickel supported on silica.

4. The process of claim 1 wherein the feed stream of step (1) is principally ethane, the feed stream of step (2) is a 400° F. end-point naphtha, and the lighter stream of step (7) is principally ethane.

5. The process of claim 4 wherein the catalyst in step (2) comprises essentially cobalt molybdate, the catalyst of step (3) comprises essentially a supported platinum catalyst, and the catalyst of step (6) comprises essentially nickel supported on silica.

6. The process of claim 2 wherein the catalyst in step (2) comprises essentially cobalt molybdate, the catalyst of step (3) comprises essentially a supported platinum catalyst, and the catalyst of step (6) comprises essentially nickel supported on silica.

7. The process of claim 2 wherein the feed stream of step (1) is principally ethane, the feed stream of step (2) is a 400° F. end-point naphtha, and the lighter stream of step (7) is principally ethane.

References Cited

UNITED STATES PATENTS

3,012,961	12/1961	Weisz	260—667
3,070,637	12/1962	Honeycutt	208—96
3,108,946	10/1963	Makin	260—667
3,227,768	1/1966	Cole	260—667
3,234,121	2/1966	Machaneu	260—667
3,253,047	5/1966	Belinger	260—667
3,274,275	9/1966	Hutto et al.	260—667
3,347,779	10/1967	Grocacudaal	260—667

60 DELBERT E. GANTZ, *Primary Examiner.*

VERONICA O'KEEFE, *Assistant Examiner.*

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