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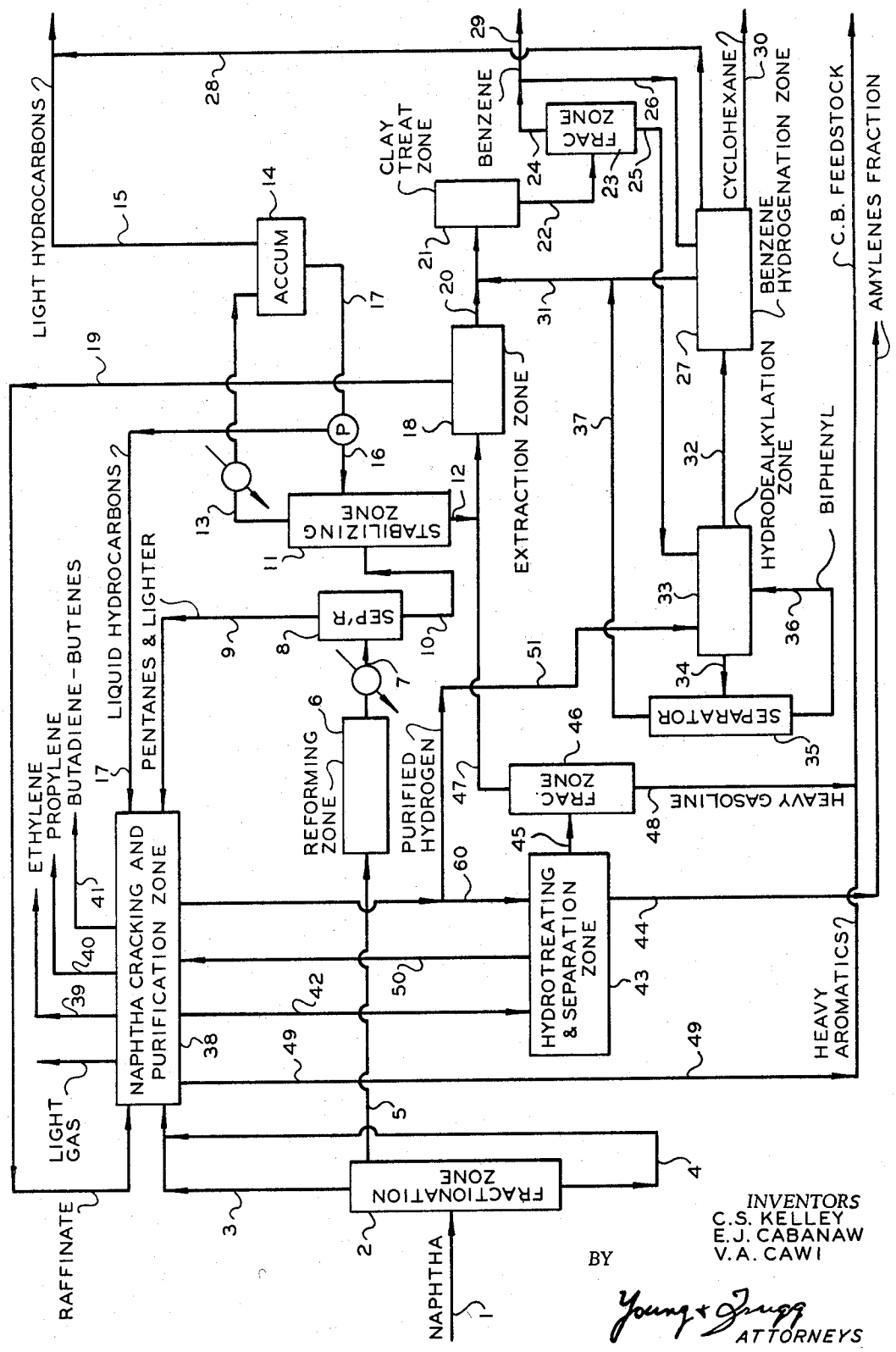

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FRACTIONATION AND CONVERSION OF A NAPHTHA FRACTION

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ABSTRACT OF THE DISCLOSURE

Heart cut naphtha such as that produced by fractionating crude naphtha is reformed and the aromatic constituents are purified by extraction of paraffins and clay treated with subsequent recovery or hydrogenation of benzene and hydrodealkylation of heavier aromatics. The light and heavy naphthas produced in the original fractionation, as well as reformed off gas and paraffinic material recovered from reformate extraction, are cracked to produce hydrogen, olefins, gasoline hydrocarbon, and heavier gas oil, the gasoline range hydrocarbon being hydrotreated to convert a part thereof to aromatics which can be added to the feed to the extraction step, the heavy gas oils being employed as feedstock for carbon black production.

A considerable degree of interrelation between hydrocarbon refining process steps derives from the usually complicated nature of feedstocks processed and the variant kind and characteristics of products produced by such operations. It is, of course, desirable to utilize each feed component in a manner that will best contribute to the nature and quality of the desired products. As a result, where more complex feedstocks are employed or where a broader spectrum of products is desired, the nature and interrelation of the process steps required to effect the desired conversions becomes more complicated. In an effort to improve the utilization of hydrocarbon feedstocks and the quality of products produced therefrom, we have discovered a new and useful combination of hydrocarbon processing operations uniquely integrated to effect this purpose.

It is therefore one object of this invention to provide a process for converting hydrocarbons more efficiently. It is another object of this invention to provide an integrated series of processing operations for more effectively utilizing hydrocarbon feedstocks. It is yet another object of this invention to provide an improved co-ordinated hydrocarbon refining process. It is yet another object of this invention to provide an improved integrated process for upgrading crude hydrocarbon naphtha.

In accordance with one embodiment of this invention, crude hydrocarbon naphtha is fractionated to produce a heart cut which is in turn subjected to reforming to increase the aromatic content thereof. The aromatics are then purified by solvent extraction, clay treated and fractionated after which benzene can be recovered as product or partially hydrogenated to produce cyclohexane, the heavier aromatics being hydrodealkylated and recycled.

Further in accordance with this invention, the light and heavy naphtha produced in the initial crude naphtha fractionation can be subjected to a cracking operation along with the paraffinic raffinate from the reformate extraction zone. Lighter hydrocarbons, e.g., C_5's, and lower recovered from the reformate product can also be passed to the naphtha cracking zone wherein are produced olefins, hydrogen, gasoline range hydrocarbons and heavier gas oils.

Further in accordance with this invention, these gasoline range hydrocarbons can be hydrotreated, e.g., hydrogenated, and fractionated to produce lighter hydrocarbons as recycled to the cracking operation, an intermediate boiling fraction enriched in aromatics, e.g., benzene which can be extracted along with the above-noted reformate, and heavy gas oil fraction which can be combined with the gas oil recovered directly from the naphtha cracker as feedstock for carbon black production.

Further in accordance with this invention, hydrogen produced in the naphtha cracking operation can be passed to the hydrotreating, hydrodealkylating, and benzene hydrogenation steps as desired.

The invention can be better understood by reference to the drawing, which is intended only to be a schematic illustration of one embodiment of the concept of this invention. The description includes examples, flow rates, and operating conditions which can be employed.

Straight run naphtha comprising, for example, a mixture of hydrocarbons boiling from about 80 to about 410° F. is passed at a rate of 17,580 b./d. by way of pipe **1** to fractionator **2** from which light naphtha, primarily C_5 hydrocarbons, is removed by way of pipe **3** as overhead at 2,022 b./d.; 10,144 b./d. heavier naphtha boiling from 240–410° F. is removed as bottoms product by way of pipe **4** and 5,414 b./d. of a heart fraction, boiling from 120–240° F., being substantially enriched in C_6 hydrocarbons, for example, methylcyclopentane, cyclohexane, and close boiling paraffinic materials is removed by way of pipe **5** and passed to reformer **6** wherein at least a portion thereof is converted to additional aromatic material. The reformate thus produced is passed by way of pipe **7** to a suitable separation zone, for example, flash vessel **8**, from which hydrogen-rich gas is removed as overhead by way of pipe **9** at a rate of 9,142 M s.c.f./d. and passed to naphtha cracking zone **38**. C_6 and heavier materials comprising aromatic and paraffinic hydrocarbons are removed as bottoms product from separator **8** and are passed to fractionator **11** by way of pipe **10** wherein C_5 and lighter hydrocarbons are removed as overhead product by way of pipe **13** and accumulated in receiving vessel **14** from which C_5 and lighter materials are removed at a rate of 286 b./d. as overhead by way of pipe **15**, recycled hydrocarbon substantially reduced in C_5 and lighter content being returned to fractionator **11** by way of pipe **16**. As desired, a portion (1814 b./d.) of this more volatile hydrocarbon fraction being substantially reduced in C_5 and lighter hydrocarbons can be passed to naphtha cracking zone **38** by way of pipe **17**, as illustrated in the drawing. C_6 and heavier hydrocarbons being substantially free of C_5 and lighter materials are removed at a rate of 3062 b./d. as bottoms product from fractionator **11** and passed by way of line **12** to extraction zone **18** from which paraffinic hydrocarbons (2475 b./d.) are removed as raffinate by way of pipe **19** and passed to naphtha cracking zone **38**. Aromatic materials (3504 b./d.) being substantially reduced in paraffinic content are removed as extract phase by way of pipe **20**, passed to clay treating zone **21** and are fed to fractionator **23** through pipe **22** from which there are recovered an overhead product comprising primarily benzene (3002 b./d.) by way of pipe **24** and a heavier aromatics bottoms product (2387 b./d.) by way of pipe **25**.

As desired, a portion (1360 b./d.) of the benzene overhead from fractionator **23** may be passed by way of pipe **26** to hydrogenation **27** wherein benzene is hydrogenated to cyclohexane. About 1608 b./d. of cyclohexane product is removed by way of pipe **30** while C_5 and lighter hydrocarbons present in the benzene feed and produced in hydrogenation zone **27** are removed as overhead by way of pipe **28** at a rate of 8021 M s.c.f./d. and can be combined with the hydrocarbon gas exiting the system by way of pipe **15**. Unconverted benzene can be separated

from the hydrogenation product and recycled to clay treating zone **21** by way of pipe **31**. Product benzene (1642 b./d.) can be recovered by way of pipe **29**.

The heavier aromatics bottoms products from fractionator **23** is passed by way of pipe **25** to hydrodealkylation zone **33** wherein a portion thereof is converted to benzene. The hydrodealkylation product (1848 b./d.) containing the benzene thus produced is passed to fractionator **35** by way of pipe **34** from which benzene is recovered as overhead product and passed by way of pipe **37** to clay treating zone **21**. Recycle feed to the clay treater by way of pipes **31** and **37** amounts to 1885 b./d. Bottoms product (69 b./d.) containing C_7 and higher aromatics, in particular, biphenyl, is recycled to hydrodealkylation by way of pipe **36**. Excess hydrogen recovered from hydrodealkylation can be passed by way of pipe **32** to benzene hydrogenation zone **27** as the hydrogen source for cyclohexane production.

The light and heavy naphthas recovered from fractionator **2** by way of pipes **3** and **4**, respectively, along with lighter hydrocarbons introduced by way of pipes **9** and **17** and paraffinic material from extraction zone **18**, are cracked in naphtha cracking zone **38** to produce lighter olefinic hydrocarbons, gasoline range hydrocarbons, and heavy aromatic gas oil.

In the presently preferred embodiment of this invention, hydrocarbons fed to cracking zone **38** are converted to, for example, ethylene, propylene, butenes and butadienes. The product can be fractionated to recover 1,096,000 lb./d. of ethylene by way of pipe **39**, 3226 b./d. of propylene by way of pipe **40**, and 1627 b./d. of a C_4 fraction (butadiene and butylene) being recovered by way of pipe **41**.

A heavy aromatics fraction (643 b./d.) is recovered by way of pipe **49** as feed for carbon black production. A pyrolysis gasoline fraction (4229 b./d.) is removed by way of pipe **42** and passed to hydrotreating zone **43**. Hydrogen (3414 M s.c.f./d.) produced in cracking zone **38** and purified in the hydrogen purification zone can be recovered and passed by way of pipe **60** to provide hydrogen to hydrotreating zone **43**. A portion of this recovered hydrogen may also be passed by way of pipe **51** to hydrodealklation zone **33**, the remainder being passed by way of pipe **32** to benzene hydrogenation zone **27**.

Lighter hydrocarbons fed to hydrotreating zone with the gasoline range hydrocarbon by way of pipe **42** as well as lighter hydrocarbons produced in the hydrotreating zone for example, hydrocarbons having 5 or less carbon atoms, are recovered as off gas and passed at a rate of 1494 M s.c.f./d. by way of pipe **50** to hydrogen purification unit located in the naphtha cracking zone **38**. A portion (about 758 b./d.) of these lighter hydrocarbons, primarily amylenes, can also be recovered as product by way of pipe **44**. The remainder of the hydrotreating effluent is passed by way of pipe **45** to fractionation zone **46** from which about 2917 b./d. of an overhead product comprising primarily C_6 hydrocarbons containing paraffinic and aromatic materials is passed by way of pipe **47** to extraction zone **18**. About 333 b./d. of a heavy gasoline fraction is removed as bottoms product by way of pipe **48** and further processed. For example, it is presently preferred that this material be combined with the heavier gasoline fraction removed from naphtha cracking zone **38** by way of pipe **49** and passed in combination therewith as feed for carbon black production.

The hydrogenation, hydrodealkylation, solvent extraction, clay treating, reforming, hydrotreating and cracking operations can be any of those known in the prior art which would be chosen by one skilled in the art. For example, the hydrogenation process can be a catalytic process employing a nickel on kieselguhr-type catalyst. The hydrodealkylation reaction can be thermal or catalytic (e.g., Hydeal), using a chromia-alumina type catalyst. The solvent extraction can be carried out using diethylene or triethylene glycol or sulfolane as solvent.

Ethylene is a major product of naphtha cracking. Separated ethane can also be recycled and cracked to ethylene as desired. Other olefins produced include propylene, butylene, butadiene, etc. Other products include hydrogen, methane, pyrolysis gasoline, and heavy aromatic oil. Naphtha and ethane can be preheated by waste heat, mixed with steam, and charged to reaction coils in the fire box. Reaction pressure is preferably slightly above atmospheric, and the temperature is typically in the range of 1450–1650° F. Exact conditions depend upon products desired, as is known in the art. This naphtha cracking zone has conventional separation facilities including fractionation towers, caustic washers for H_2S and CO_2 removal, and water washing facilities to remove caustic from treated products. These separations are well known in the art and are not detailed herein.

The catalytic reforming can employ conventional catalysts such as platinum on alumina type reforming catalysts in one or more fixed beds in series. Suitable processes known in the art are, for example, Platforming, Houdriforming, and Powerforming. This operation converts part of the heart cut naphtha, e.g., hexanes and heptanes to benzene and toluene, plus an excess of hydrogen which can be used in other processes as described. In addition, lighter hydrocarbons (C_3 to C_5, carbon hydrocarbons) are produced as well as fuel gas (C_2 and C_1 hydrocarbons).

The hydrotreating process **43** preferably comprises a two-step operation in which the pyrolysis gasoline **42** from naphtha cracking is treated to convert at least a portion of the diolefins therein to linear and cyclic olefins; the motor fuel constituents being fractionated from the product. In the first step raw pyrolysis gasoline **42** and hydrogen **60** are passed over a conventional catalyst known in the art, for example, cobalt-molybdenum type catalysts to convert diolefins to monoolefins. The reaction products are fractionated to yield fuel gas **50**, an amylenes concentrate **44**, a heart cut comprising benzene, toluene, hexenes, and heptenes; a high octane gasoline and residual aromatics and polymers. In the second step, the heart cut is contacted over a conventional nickel on kieselguhr hydrogenation catalyst to convert hexanes and heptenes to paraffins and naphthenes. The hydrogenated heart cut **47** is then passed to aromatic extraction zone **18** for recovery of benzene and toluene.

The thermal hydrodealkylation process **33** is well known in the art. Herein, in one reactor, toluene and xylenes **25** are converted to benzene in the presence of hydrogen **51**. Hydrogen is consumed, and the main by-products are methane and biphenyl. The biphenyl is separated and recycled **36** preferably to a separate biphenyl reactor wherein it is converted into additional benzene in the presence of hydrogen. 14,560,000 standard cubic feet per day of hydrogen **51** can be charged to hydrodealkylation zone **33**.

TYPICAL CONDITIONS

	Temperature, ° F.	Pressure, p.s.i.g.
Naphtha cracking (38)	1550	10
Reforming (6)	1000	250
Hydrotreating (43):		
(Stage I)	350	400
(Stage II)	750	400
Solvent extraction (18)	150	50
Hydrodealkylation (33)	1400	500
Benzene hydrogenation (27)	400	400

These above-mentioned individual processes per se are well known in the art.

We claim:

1. A method of converting hydrocarbon naphtha which comprises

(a) fractionating said naptha to produce an overhead rich in light naphtha, a bottoms product rich in heavy naphtha and a heart cut having a substantially reduced concentration of said light and heavy naphtha and having a substantially increased concentration of C_6 hydrocarbons, including methylcyclopentane and cyclohexane,

(b) reforming said heart cut to convert at least a portion thereof to aromatic hydrocarbons,

(c) fractionating said reformate to produce a fraction having a substantially reduced concentration of lighter hydrocarbons,

(d) solvent extracting said fraction to produce a paraffin rich raffinate and an aromatic rich extract, and clay treating said extract,

(e) fractionating the thus clay treated extract to produce a concentrated benzene overhead and a bottoms product being substantially reduced in benzene concentration,

(f) cracking said light hydrocarbons of step (c) to convert at least a portion thereof to olefin hydrocarbons, hydrogen, gasoline range hydrocarbons and heavier gasoline hydrocarbons,

(g) hydrotreating said gasoline range hydrocarbons to hydrogenate at least a part thereof, and

(h) hydrodealkylating said bottoms product from step (e) to convert at least a portion thereof to additional benzene.

2. The method of claim 1 further comprising

(I) passing at least a portion of said light hydrocarbon removed from said reformate to said cracking step,

(II) passing said paraffin rich raffinite to said cracking step,

(III) hydrogenating at least a portion of said benzene overhead from step (e) to produce cyclohexane,

(IV) fractionating the hydrodealkylated product of step (h) to produce a benezene rich overhead and a benzene lean bottoms product and recycling said bottoms product.

3. The method of claim 2 further comprising

(A) passing unconverted benezene from said hydrogenating step to said clay treating step,

(B) passing said benzene rich overhead from said hydrodealkylating step to said clay treating step,

(C) passing hydrogen from said hydrodealkylation step to said benzene hydrogenating step (III), and

(D) fractionating dehydrogenated product of step (g) to remove heavy gasoline as bottoms product and passing the remainder of said overhead products to said extraction step.

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