United States Patent

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[73] Assignee Phillips Petroleum Company

[54] **PRODUCTION OF NAPHTHA FEEDSTOCK FROM CRUDE OIL**
7 Claims, 1 Drawing Fig.

[52] U.S. Cl. 208/80, 208/70, 208/93
[51] Int. Cl. C10g 39/00
[50] Field of Search 208/78, 80, 92, 93, 94, 69, 70

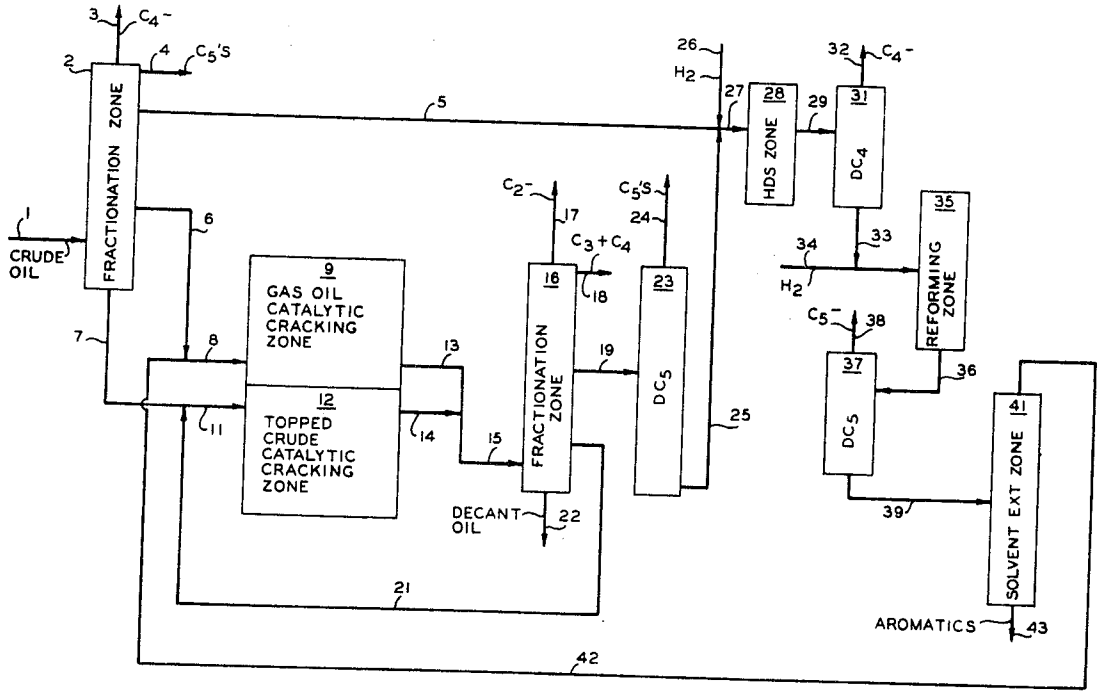
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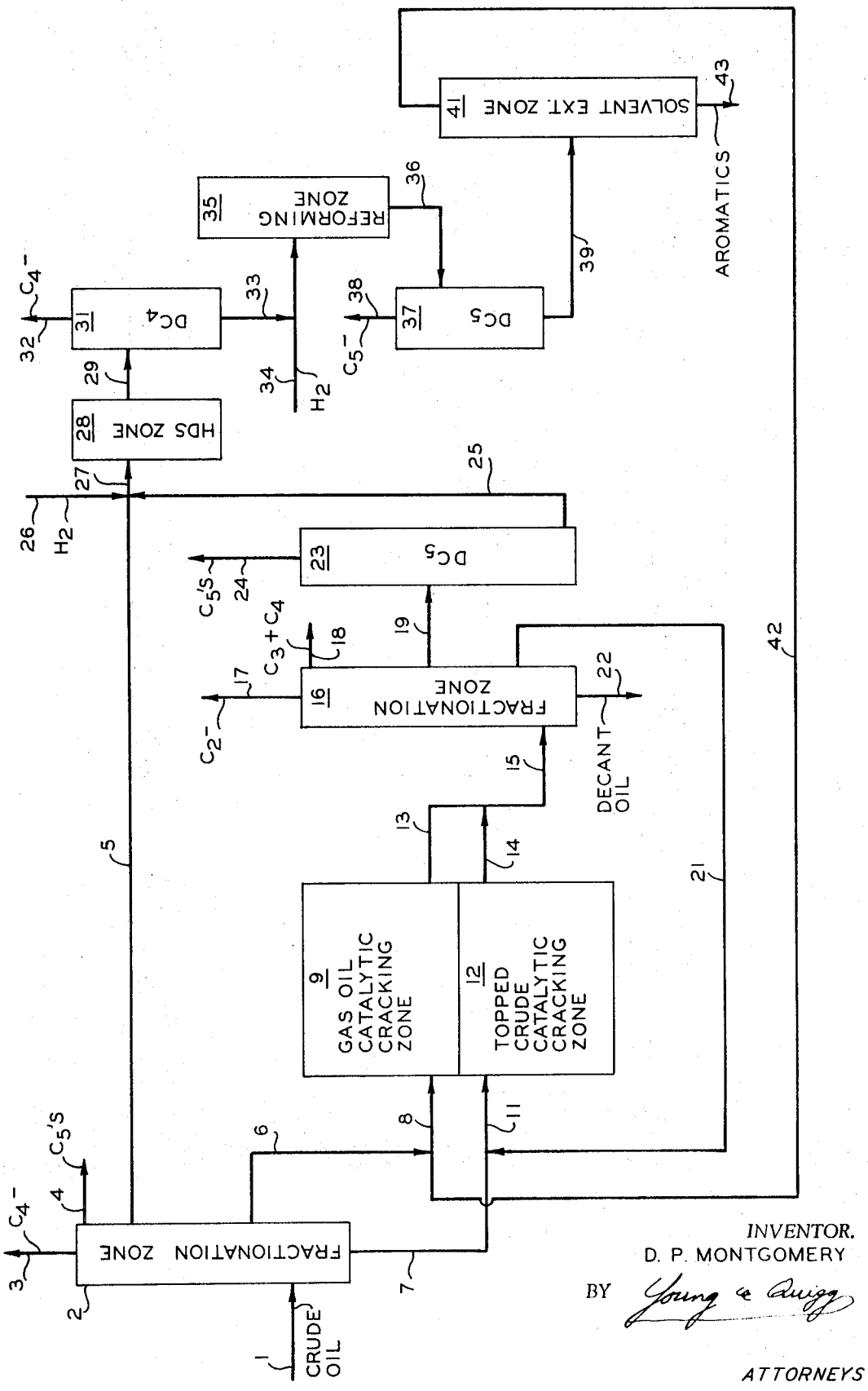
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ABSTRACT: A process for improved production of aromatics-rich naphtha from crude oils: crude oil is fractionated to produce a virgin naphtha, gas oil is combined with paraffinic raffinate and cracked, and bottoms which is combined with fractionator cycle oil and cracked. Products of cracking are combined and fractionated into cracked naphtha, cycle oil, and decant oil. The naphtha cuts are combined, hydrodesulfurized, reformed, and separated into paraffinic raffinate and the aromatics-rich extract naphtha as product.





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PRODUCTION OF NAPHTHA FEEDSTOCK FROM CRUDE OIL

This invention relates to a process for improved conversion of crude oils into naphtha. It further relates to a process for the improved production of aromatics-rich naphtha from crude oil stocks.

BACKGROUND OF THE INVENTION

Petrochemical plants are technically complex and face an increasing demand for petrochemical productions and for the myriad of products made from petrochemicals, such as polymers and fibers. Petrochemical refinery economics are equally complex and reflect an intrarelationship of myriad costs and production factors, product production capabilities, product values, and product demands, and hence saleabilities. Many values vary with passing time and changing economic conditions. Versatility is a necessity.

Economics would certainly be more favorable within the petrocomplexity should a way be found to process crude oil stocks to produce greater proportions of aromatics-rich naphtha, and lesser amounts of other components of lesser value.

An effective way to convert crude oil stocks to improved proportions of aromatics-rich naphtha is precisely what I have discovered. My process employs a minimum of steps, produces a minimum of side products both in number and quantity, while resulting in a desirably higher proportion of aromatics-rich naphtha.

It is an object of my invention to improve the aromatics-rich naphtha yield of crude oils.

Other aspects, objects, and the several distinctive advantages of my invention will be apparent to one skilled in the art from the following description and from the appended claims as well as the drawing.

BRIEF STATEMENT OF THE INVENTION

The process scheme which I have discovered and developed can be observed more clearly by reference to my drawing attached. The drawing shows the essentials of my process. The crude oil feedstock is first fractionated by thermal distillation in a crude still to recover the virgin naphtha of up to about 350° F. boiling point. The remainder of the crude, i.e., that boiling above about 350° F., is subjected to cracking processes. That portion of the crude from the naphtha end point up to around 600° F. is combined with a paraffinic raffinate derived from the extractive end-step of my process, and the combined stream is cracked in a gas oil or clean oil cracking unit. The heavier residual material from the crude oil fractionation, that with an initial boiling point of about 600° F., is combined with a cycle oil obtained from fractionation of the combined products of cracking, and this second combined stream is cracked in a topped crude or dirty oil cracking unit. The effluents from the cracking units are combined, thermally distilled in a fractionator to recover a second naphtha stream, i.e., the cracked naphtha; the cycle oil, and a small amount of carbon black oil equivalent to a decant oil recovered in cracking.

The two naphtha streams so produced are combined, hydrodesulfurized, reformed, and extractively separated into a paraffin raffinate for recycle to the gas oil cracking unit, and the desired aromatics-rich naphtha fraction as product, and which can be subjected to further conventional separations and processing.

This approach, the recycle and dehydrocyclization of the aromatics-free and substantially naphthenics-free paraffin raffinate in the gas oil cracker coupled with the severe cracking conditions tending toward aromatics and other cyclics formation in the topped crude cracker, results in the increased ultimate production of the desired aromatics-rich naphtha as the end product of my process.

Any low boiling components produced or separated in the process in the various stages can be utilized in a variety of ways, such as for fuel in various processes within the petrocomplexity, or for use in making alkylate, or in water gas shift steps for production of hydrogen, and the like.

DETAILED DISCUSSION OF INVENTION AND DRAWING

Referring, now, to my drawing in more detail, the crude oil feedstock **1** is brought to the crude still **2** and subjected to thermal distillation. The crude still **2** is operated so as to produce a limited number of effluent product streams: an overhead **3** of C_4 and lighter components; a C_5 stream **4** of mixed C_5 components; the virgin naphtha cut **5** comprising those components of the crude oil from C_6 up to about 350° F.; a gas oil cut **6** of those components boiling above the cutoff point of the virgin naphtha stream on up to about 600° F.; and a bottoms **7** or topped crude or residuum comprising everything else, i.e., all components boiling above the gas oil cutoff of about 600° F. on up to the end point of the particular crude.

The gas oil stream **6** of about 350° to 600° F. is combined with a paraffin raffinate **42** derived from the solvent extraction zone **41** to form a first combined feed stream **8** as the feed to one of two catalytic cracking units, the gas oil or clean oil cracking unit **9**.

The bottoms or residuum **7** is combined with a cycle oil **21**, derived from the fractionator **16** following the cracking steps, to form a second combined stream **11** as feed to the second of the two cracking units, the topped crude cracking unit **12**.

These cracking units, **9** and **12**, typically will be fluid catalytic cracking units wherein the respective feeds are catalytically cracked so that a substantial proportion of the feedstocks are converted to components of reduced molecular size, and particularly in the case of the gas oil fluid catalytic cracker, operation is such that paraffinic components tend to form cyclic products, i.e., aromatics and aromatics precursors.

The effluent **13** from gas oil cracking unit **9** is combined with effluent **14** from topped crude cracking unit **12** to form a combined feed **15** to a fractionation zone **16** for thermal distillation. Fractionator **16** produces an overhead stream **17** of very light material of C_2 and lighter which can be utilized as a source of ethylene, for plant fuel requirements, or for hydrogen production; a stream **18** of mixed C_3 and C_4 components, both paraffinic and olefinic, which can be utilized for alkylation and the like; a stream **19** comprising C_5's on up to about 375° F. boiling point as the cracked naphtha stream; a cycle oil stream **21**, usually in practice taken separately as light and heavy cycle oils, which is combined with the bottoms or residuum stream **7** from the crude oil still **2** to form the second combined feed **11** to the topped crude cracking unit **12**; and a relatively small amount of high BMCI (Bureau of Mines Correlation Index) decant oil **22** useful as a valuable carbon black feedstock oil.

The cracked naphtha stream **19** can be combined directly with the virgin naphtha stream **5** and sent to hydrodesulfurization **28**. More usually, stream **19** is first conducted to a depentanizer **23** where the mixed C_5's are removed as an overhead **24** leaving the bottoms stream **25** as a C_6 on up to 375° F. cracked naphtha stream.

The depentanized cracked naphtha stream **25** is combined with the virgin naphtha stream **5** together with added hydrogen **26** to form combined feed **27** to hydrodesulfurization zone **28**. Of course, the hydrogen **26** can be added in part directly to the hydrodesulfurizer **28** if desired. Conditions in the hydrodesulfurization unit **28** result in formation of minor amounts of C_4 and C_5 and lighter components. The effluent **29** from hydrodesulfurization **28** normally is conducted to a debutanizer **31** for removal of C_4 and lighter components as overhead **32**, leaving the debutanizer bottoms **33** consisting of C_5 and heavier components.

Additional hydrogen **34** is added to the C_5 and heavier stream **33** for feeding to reforming zone **35** wherein cyclization, dehydrocyclization, and isomerization of hydrocarbon molecules occurs to produce additional aromatic hydrocarbons.

Product effluent 36 from the reforming unit 35 is taken to a second depentanizer 37 where C_5 and lighter components added to or formed in reformer 35 are removed as an overhead 38 leaving the bottoms 39 as C_6 and higher boiling components for final treatment in solvent extraction zone 41. The solvent extraction process 41 separates the feed stream 39 into a paraffinic naphtha recycle stream 42 of C_6 to 375° F. paraffins, and the desired aromatics-rich naphtha stream 43 as the product of the process.

The recycle stream 42 of paraffinic naphtha is brought back to rejoin the gas oil stream 6 as a part of the first combined feed stream 8 to the gas oil cracking unit 9 for cyclization, dehydrocyclization, and cracking, to form additional aromatics product which can be recovered by the further processing through my process as I have described.

The product of my process, stream 43, is an aromatics-rich naphtha stream high in BTX, i.e., high in benzene, toluene, and xylenes together with some C_9^+aromatics. This aromatics-rich stream 43 can be further separated in a separator zone not shown, such as in a fractionator, crystallization zone, etc., as known in the art, into separate benzene, toluene, o-, m-, and p-xylene streams, and heavier C_9's plus stream, each useful in various chemical plant requirements.

EXAMPLES OF MY PROCESS

The examples following illustrate the effectiveness and uniqueness of the process of my invention.

EXAMPLE I

The process of my invention is illustrated by the following material balance showing the result of a feed of 50,000 barrels of a crude oil charge, a Tiajuana Medium Crude, the process, and the yield results of aromatics-rich naphtha.

Stream	Component	Barrels/Day
1	Crude oil input to crude still 2	50,000
Crude Oil Still 2		
3	C_4 and lighter)	
4	C_5's)	1,000
5	C_6 to 350° F. virgin naphtha	3,500
6	350° to 600° F. virgin gas oil	9,500
7	600° F. initial boiling point topped crude	36,000
8 (6+42)	First combined feed stream to gas oil cracker 9	21,550
11 (7+21) 21)	Second combined feed stream to topped crude cracker 12	47,700
From Fractionator 16		
21	Cycle oil to topped crude cracking	11,700
22	Decant oil	1,800
Depentanizer 23		
25	$C_6$to 375° F.	27,250
Debutanizer 31		
33	C_5^+ bottoms to reformer	31,200
Depentanizer 37		
39	C_6^+ bottoms to extraction 41	28,400
Solvent Extraction 41		
42	Paraffinic raffinate to gas oil cracker	12,050
43	Aromatics, BTX and C_9^+, product	16,350

My process reduces yield of paraffinic naphtha to zero, since the raffinate 42 is recycled to extinction within my process.

EXAMPLE II

To demonstrate clearly that the paraffinic raffinate is dehydrocyclicized in a fluid catalyst cracking unit as we have discussed above, a separate run was made using specifically a C_6^+paraffinic naphtha of about 350° F. end point. This feed was produced by reforming, e.g. platforming, a virgin low end-point naphtha which had been solvent extracted by the Udex process so as to remove any aromatics. This stream was converted in a fluid catalytic cracking unit under conditions of 900° F., 0.49 WHSV, 10 p.s.i.g., using 16 pounds of steam per barrel of hydrocarbon feed, and using a molecular sieve type of cracking catalyst, Filtrol 800 supplied by the Filtrol Corporation. After the aromatics-free fraction was subjected to cracking as per conditions listed, the resulting stream composition was as follows:

H_2, SCF/BBL* of feed	100
H_2-C_2, SCF/BBL* of feed	156

	Wt.%	Vol.%
H_2	0.22	—
C_1	0.39	—
$C_2^=$	0.70	1.25
C_2	0.34	0.64
$C_3^=$	2.57	3.46
C_3	4.71	6.51
$C_4^=$	1.55	1.73
iC_4	7.31	9.10
nC_4 & C_5's	0.96	1.15
C_6^+ Liq.	79.20	77.47
BTX content	—	10.6
Coke	2.05	—

*Standard cubic feet per barrel.

This run illustrates that a paraffinic naphtha (aromatics-free naphtha) stream can be converted in a fluid catalyst cracking unit to yield appreciable quantities of BTX. Hence, the overall effectiveness of my process wherein the paraffinic raffinate separated from my process end-step is cycled to the gas oil cracker as a part of the feed thereto.

DISCUSSION OF PROCESS STEPS

In my process, the crude oil initially is subjected to thermal distillation in the crude still operated with a bottom temperature of from about 600° to 690° F., a pressure of 0 to about 20 p.s.i.g., more preferably near 5 p.s.i.g. The topped crude yield or bottoms stream will vary with the crude of course, and may range from 10,000 to as much as 45,000 barrels per day based on a feed of 50,000 barrels per day. Gas oil yield will similarly range from 5,000 to about 30,000 barrels per day on the same basis. The virgin naphtha yield will range from perhaps 1,000 to as much as 30,000 barrels per day again depending upon the type of crude.

The gas oil cracking unit normally will be a fluid catalytic cracker and will be used to crack both the gas oil fraction as well as the paraffin raffinate recycle from the solvent extraction zone. Typically, in a fluid catalytic cracking operation, a finely divided particulate catalyst is heated to a high temperature in a regeneration zone, brought into admixture with the hydrocarbon feedstock, the admixture then conducted to a reaction zone where the cracking takes place, though a major portion cracking may occur in the conduits on the way to the cracking or reaction zone, and products of cracking are separated in a separation zone with the products taken to a fractionator, and spent catalyst returning to the regeneration zone.

In a fluid catalytic cracker, the particulate catalyst tends to accumulate coke which is a combination of carbon and carbonaceous residues. The accumulation of coke tends to reduce the activity of the particulate catalyst. The catalyst is regenerated by subjecting it to a periodic treatment at elevated temperatures, such as from about 1,050° to 1,250° F., in the presence of an oxygen-containing gas. The air supply to the regeneration zone normally acts as the fluidizing gas as well as the source of oxygen for coke burnoff, with products of combustion therefrom exiting as a flue gas, and the then regenerated catalyst being returned into admixture with additional hydrocarbon feedstock.

A fluid catalytic cracker can operate with a separate reactor and a separate regenerator, or these can be combined into a single unit such as a reactor section above a regenerator section, or vice versa. The details of such fluid catalytic cracking units are not shown in my drawing in order to avoid complex-

ing my drawing and possibly obscuring essentials of the process of my invention.

The gas oil cracking unit typically will operate at from about 900° to about 975° F., preferably near 950° F., with a pressure ranging from about 5 to about 25 p.s.i.g., with a catalyst-to-oil weight ratio of from about 3 to about 12, preferably near 4. A finely divided particulate catalyst is used, particularly the natural and synthetic zeolites known as molecular sieves, such as the commercial catalyst under the name Filtrol 800 which is a molecular sieve type cracking catalyst supplied by Filtrol Corporation. The gas oil unit will receive a virgin gas oil feed of from about 5,000 to about 30,000 barrels per day, together with from about 6,000 to about 20,000 barrels per day of the C_6 to 375° F. paraffinic raffinate recycled from the solvent extraction zone as end-step of my process.

The other fluid catalyst cracking unit, the topped crude cracking unit, typically will operate under conditions similar to those described above for the gas oil unit. Feed will range from about 10,000 to about 45,000 barrels of topped crude bottoms, together with from about 5,000 to 20,000 barrels per day of recycle oil from the fractionator, again based on an input of 50,000 barrels per day of crude into my process.

The products from both fluid catalyst cracking units are combined for feed to a fractionator operated to thermally distill the feed to produce the cuts as described. The fractionator will operate at pressures of from about 0 to 25 p.s.i.g. and with a bottom temperature of from about 600° to 725° F.

As feed to the hydrodesulfurizer, the virgin naphtha feed will range from about 1,000 to about 30,000 barrels per day, and the cracked naphtha feed from about 10,000 to about 40,000 barrels per day. The hydrodesulfurizer will operate at a temperature ranging from about 550° to 750° F., preferably near 600° F., with a pressure ranging from about 50 to 600 p.s.i.g., more preferably near 600 p.s.i.g.; a hydrogen-to-hydrocarbon mole ratio of from about 4 to 10, preferably near 7. A useful catalyst can be a sulfided cobalt-molybdenum on alumina, such as Cyanamid HDS–2obtained from American Cyanamid Company.

Product stream from hydrodesulfurization is debutanized, and the C_5 and above then admixed with additional hydrogen and brought to the reforming zone. Hydrogen requirement is usually of the order of 4 to 10 moles of hydrogen per mole of hydrocarbon feed, preferably near 7. Conditions in the reforming zone will include a temperature of from about 900° to 980° F., preferably near 950° F., a pressure of from about 400 to 700 p.s.i.g., preferably near 600 p.s.i.g. A useful catalyst is a platinum on alumina catalyst, such as UOP R–11 obtained from Universal Oil Products Company.

In the solvent extraction end-step of my process, the total hydrocarbon feed will be in the range of 20,000 to 45,000 barrels per day, with the zone operating at a temperature of from about 100° to 350° F., preferably near 280° F.; under a pressure from about 2 to about 200 p.s.i.g., preferably near 90 p.s.i.g.; and with a solvent-to-oil ratio of from about 1 to about 8, preferably near 3. A preferred solvent is glycol, though any suitable solvent such as sulfolane, dimethylformamide, and the like, can be utilized.

In the foregoing discussions I have disclosed my process, described it in detail as to the accompanying flow sheet, have shown how to practice each step, and shown the effectiveness of my process to increase aromatics production from crude oils.

Reasonable variations and modifications of my invention are possible within the scope of my disclosure without departing from the spirit and scope thereof as disclosed in the specification hereinabove and the claims hereinafter, together with my drawing attached.

What is claimed is:

1. A process for the increased production of aromatics-rich naphtha from crude oil which comprises:

a. thermally distilling a crude oil feedstock and thereby producing streams comprising a virgin naphtha stream, a gas oil stream, and a bottoms stream,
b. cracking at least a portion of said bottoms stream,
c. cracking at least a portion of said gas oil stream,
d. combining the products of said cracking steps (b) and (c),
e. fractionating said combined cracked products thereby producing a cracked naphtha stream, at least one cycle oil stream, and a decant oil stream,
f. feeding said cycle oil stream to said cracking step (b),
g. combining said virgin naphtha stream from said step (a) and said cracked naphtha stream from said step (e),
h. reforming the combined stream from step (g),
i. separating the products of said reforming step (h) under solvent extraction conditions into a substantially paraffins-containing stream and a substantially aromatics-containing stream, and
j. returning said paraffins-containing stream to said cracking step (c).

2. A process according to claim 1 wherein step (g) is followed by hydrodesulfurization wherein minor amounts of sulfur-containing compounds contained in said combined naphtha stream are substantially removed, and wherein the hydrodesulfurized naphtha stream is substantially debutanized prior to said reforming said (h).

3. A process according to claim 2 wherein said step (a) said virgin naphtha stream comprises from about C_6 to about 350° F., said gas oil stream comprises from about 350° F. to about 600° F., and said bottoms stream comprises from about 600° F. to end point; and wherein in said step (g) said cracked naphtha stream comprises from about C_6 to about 375° F.

4. A process according to claim 3 wherein further is produced in said step (a) at least one light overhead stream consisting essentially of straight run products of about C_5 and lighter; and wherein further in said fractionating step (e) is produced a second light overhead stream consisting essentially of products of cracking of about C_4 and lighter.

5. A process according to claim 4 wherein said cracked naphtha stream is substantially depentanized prior to said hydrodesulfurization step, and wherein said products of said reforming step (h) are substantially depentanized prior to said separating step (i).

6. A process according to claim 5 wherein said catalytic cracking conditions in said step (b) and step (c) are fluid catalytic cracking conditions and include a solid particulate molecular sieve catalyst, a temperature of from about 900° to about 978° F., a pressure of from about 5 to about 25 p.s.i.g., and a catalyst-to-oil ratio of from about 3 to about 12;

wherein said hydrodesulfurizer includes conditions of a temperature of from about 550° to about 750° F., a pressure of from about 50 to about 600 p.s.i.g., a hydrogen to hydrocarbon mole ratio of from about 4 to about 10, and using a sulfided cobalt molybdenum on alumina catalyst;

wherein said reforming step (h) includes reforming conditions of a temperature of from about 900° to about 980° F., a pressure of from about 400 to about 700 p.s.i.g., and a platinum on alumina catalyst;

and wherein said separating step (i) solvent extraction conditions include a temperature of from about 100° to about 350° F., a pressure of from about 2 to about 200 p.s.i.g., and a solvent-to-oil ratio of from about 1 to about 8.

7. A process according to claim 6 wherein said step (j) is followed by:

fractionating said substantially aromatics-containing stream and thereby producing a lower boiling stream consisting essentially of benzene, toluene, and xylene, and a higher boiling stream consisting essentially of C_9^+ aromatic hydrocarbons.

* * * * *

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,617,494 Dated: Nov. 2, 1971

It is certified that error appears in the above-identified patent and that sa: Letters Patent are hereby corrected as shown below:

Claim 6, Col. 6, line 48, "978°F." should be --- 975°F. ---.

Signed and sealed this 16th day of May 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents