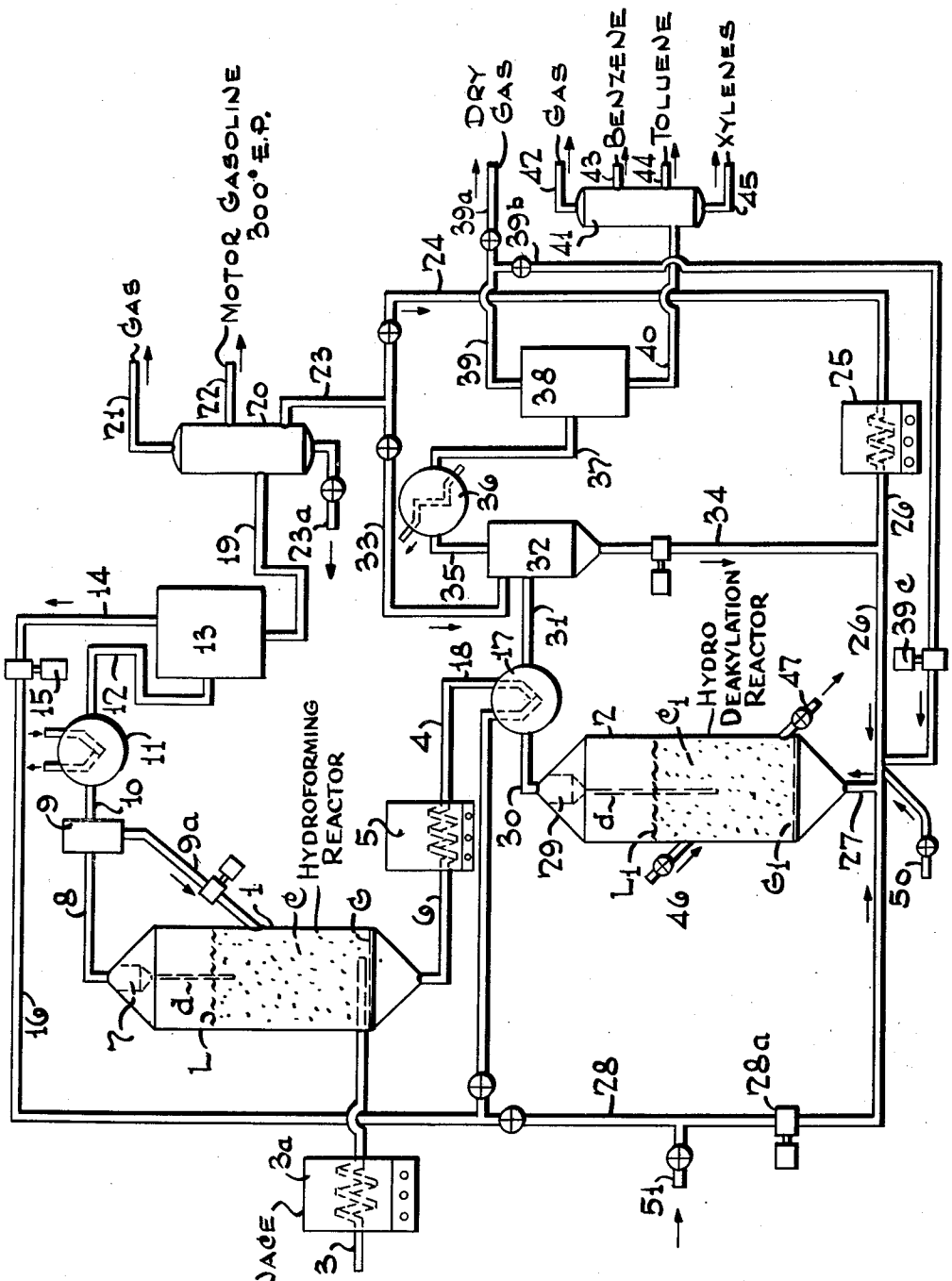
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REFORMING FOLLOWED BY HYDRODEALKYLATION

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REFORMING FOLLOWED BY HYDRODEALKYLATION

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The present invention relates to improvements in hydrodealkylation of hydrocarbons and in particular it relates to improvements in the performance of this process employing the fluid solids technique.

Heretofore and prior to the present invention, it was old to hydroform naphthas to convert the naphthas therein contained to aromatics and at the same time to cause some isomerization of normal hydrocarbons to form branched chain paraffinic hydrocarbons. This type of operation is carried out, at least commercially, in the presence of fixed beds of catalyst. Furthermore, in this type of operation the feed stock was not only one which contained appreciable quantities of naphthenic hydrocarbons but also boiled within a limited range, namely, 200°–360° F. One aspect of the present invention involves the use as a feed of a higher boiling material which in one phase of the process is hydroformed and the higher boiling portions of the hydroformate product are dealkylated to form aromatics of lower boiling range.

One object of the present invention, therefore, is to produce relatively low boiling aromatics, such as benzene, toluene, and various xylene isomers from a relatively high boiling naphthenic naphtha.

Another object of the present invention is to produce gasolines of increased volatility from light gas oils, which gasolines possess a high octane rating.

Another object of the present invention is to carry out the hydrodealkylation process under substantially isothermic conditions.

Another object of the present invention is to carry out the hydrodealkylation of products from a hydroforming operation in a system which is substantially self-sufficient as regards hydrogen requirements for the hydroforming step or phase.

It is pointed out that hydroforming is an operation conducted at elevated temperatures and pressures in the presence of added hydrogen and a solid contact material wherein the feed stock is a hydrocarbon oil containing substantial quantities of naphthenic hydrocarbons which are converted to the corresponding aromatics by dehydrogenation. Usually the hydroforming operation is accompanied by some isomerization of straight chain paraffins present and isomerization of alkylated 5-carbon naphthenic ring compounds such as ethylcyclopentane, to a 6-carbon ring such as methylcyclohexane.

To the accomplishment of the foregoing and related ends, a hydrocarbon oil is subjected first to a hydroforming operation in the presence of a bed of fluidized hydroforming catalyst and then to a hydrodealkylation step in the presence of a fluidized bed of powdered material in a manner more fully described hereinafter.

In the accompanying drawing there is shown diagrammatically the essential elements of a suitable apparatus in which a preferred modification of the present invention may be carried into effect.

Referring in detail to the drawing, 1 represents a hydroforming zone containing a fluidized bed of catalyst and 2 represents a vessel in which hydrodealkylation of

alkylated aromatics is carried out in the presence of a fluidized bed of powdered inert material, such as sand, pumice, silica, coke, etc., or active cracking materials as activated alumina, silica, alumina-silica or acid treated clays may be employed with heavier or higher boiling feed stocks. A naphthenic naphtha boiling within the range of from, say, 250°–450° F. enters the present system through line 3, is charged to a furnace 3*a* where it is vaporized and heated to a temperature of about 1000° F. and thereafter charged into the hydroforming vessel 1 which contains, as previously indicated, a fluidized bed C of powdered hydroforming catalyst. This catalyst powder ranges in size from about 100 to 400 mesh or any other suitable size adapted for fluidization, and the gasiform material moves through the bed at a superficial velocity of from about 0.2 to 0.7 ft. per second. As usual, the vessel containing the fluidized bed of catalyst is provided with a foraminous member G which acts as a gas distributing means for hydrogen-containing gas, which is fed from line 4 to furnace 5 where it is heated to a temperature of 1150° F. or thereabouts, and thereafter charged via line 6 into the bottom of the reactor vessel 1 where it passes upwardly through the foraminous member or grid G into contact with the bed of catalyst C. In connection with the oil feed, it is to be noted, as shown in the drawing, that the feed oil is fed to a point above the grid G. Under conditions more fully set forth hereinafter, the desired conversion takes place and the product issues from the dense fluidized bed of catalyst which has an upper level at L into a disengaging space disposed between L and the upper portion of the reactor. In this disengaging space there is a light phase suspension of catalyst in gasiform material which decreases in concentration towards the top of the reactor, for it is characteristic of this type of technique that the main bulk of the catalyst be separated from gasiform material within the reactor. As is conventional, there is disposed in the upper portion of the reactor, one or more "cyclone" separators 7 through which the gasiform material about to issue from the reactor is forced for the purpose of removing entrained catalyst, which removed catalyst is returned to the dense phase bed C by one or more dip pipes *d*. The gasiform material finally emerges from the reactor through line 8.

With respect to the catalyst in bed C, it is pointed out that this may be any conventional reformer catalyst such as a VI group metal oxide carried on a suitable spacing agent, or it may be a precious metal catalyst such as platinum or palladium carried on a spacing agent. In the first class of catalysts are included molybdenum oxide or chromium oxide carried on activated alumina. In the second class of catalysts mentioned, the carrier may be also alumina associated with a minor amount of silica. In both cases, the catalyst may have associated therewith a relatively small amount of hydrogen fluoride. The present combination may be either of the so-called regenerative type or it may be the non-regenerative type. In the case where the catalyst requires regeneration, the catalyst may be withdrawn either continuously or periodically and treated with air or other regeneration gas in conventional apparatus not shown.

Referring again to the product in line 8 issuing from reactor 1, the same is first fed to a conventional scrubbing means 9 where it is treated with, say, an oil to scrub out the last traces of catalyst which may still persist in the vapors and the oil slurry thus obtained may be returned to the bed of catalyst in reactor 1 via line 9*a*. The scrubbed vapors from 9 are charged via line 10 to a cooler 11 wherein the normally liquid constituents are condensed and the product is then charged via line 12 into a separator 13. From separator 13 a hydrogen rich gas is withdrawn overhead via line 14 and pumped in pump 15 through

line 16 through heat exchanger 17 to line 18 and thence to line 4 for return to vessel 1, as previously indicated.

Referring again to separator 13, the liquid product is withdrawn therefrom through line 19 and charged to a fractionating column 20. From fractionating column 20, a light hydrocarbon fraction is withdrawn overhead through line 21 and this fraction may be utilized for blending into a motor gasoline, or otherwise disposed of. A second intermediate fraction is taken off still 20 through line 22 and this fraction comprises the motor gasoline fraction boiling between the light ends, which are taken off at line 21, and at 300° F.; the heavier material boiling from 300° F. to, say, about 450° F. is withdrawn from the bottom side stream of still 20 through line 23. Higher boiling polymer products, if any, are removed through line 23*a* from bottom of still 20 and are disposed of as fuel oil or otherwise utilized. The material in line 23 contains almost exclusively C_8 to C_{11} alkylated aromatics, and it is one of the main purposes of this invention, as previously stated, to dealkylate these aromatics in the presence of hydrogen to form benzene, toluene and xylenes. This product is withdrawn, as stated, through line 23, thence passed through valved line 24 and charged to furnace 25 where it is heated to a temperature of about 800° F. or whatever temperature is required to control the temperature in reactor 2, but in any case, at a temperature below that prevailing in reactor 2, which it has been noted is a reactor in which the hydrodealkylation reaction occurs, and thereafter withdrawn from the heater 25 through line 26 and charged to line 27 leading into the bottom of reactor 2. Hydrogen-containing gases from line 16 are withdrawn therefrom through valved line 28 and compressor 28*a* and also charged into line 27. The mixture of oil vapors and hydrogen gas passes into the reactor 2 and upwardly through a grid or other foraminous member G_1 into contact with the fluidized bed of powdered material C_1, which has an upper dense phase level at L_1. As usual, the superficial velocity of the gasiform material is maintained so as to form the powdered material into a dense fluidized bed. This velocity is of the order of .2–1.7 ft. per second where the powdered maaterial has a particle size of 100–400 mesh.

Under conditions of temperature, pressure and residence time or feed rate set forth hereinafter, the reaction in vessel 2 occurs and the product passes through to a disengaging space in reactor 2 positioned between L_1 and the top of the reactor. As usual, one or more "cyclone" separators 29 are disposed in the upper portion of the reactor for the purpose of separating entrained powdered material from the gasiform material about to issue from the reactor, and this separated powdered material is returned to reactor via one or more dip pipes *d*. The crude product is withdrawn from the reactor through line 30 and caused to flow in heat exchange relationship with the hydrogen-containing gas in heat exchanger 17 previously mentioned, and thereafter it is withdrawn from the heat exchanger 17 through line 31 and charged to scrubber 32 where it is treated with a portion of the heavy ends in line 23, which heavy ends pass from line 23 into line 33 near the top of said scrubber 32, the purpose of the scrubbing being to remove entrained particles of solid powdered material. The slurry of oil and powdered material is withdrawn from scrubber 32 through line 34 and charged to line 26 for return to reactor 2. The scrubbed product is withdrawn from scrubber 32 through line 35, condensed in a cooler 36, withdrawn from the condenser through line 37 and charged to a separator 38. From separator 38, a portion of the gas is withdrawn overhead through line 39 and rejected in part through line 39*a* from the present system while the remainder is recirculated to reactor 2 through line 39*b*, compressor 39*c* and lines 26 and 27. The liquid product is withdrawn from separator 38 through line 40 and charged to a finishing still 41. From finishing still 41, four fractions are recovered as follows: through line 42 hydrocarbon gases are recovered, through line 43, a benzene fraction is recovered, through line 44, a toluene fraction is recovered, and finally, through line 45, a mixture of xylene isomers and heavy higher boiling aromatics are recovered. These aromatic fractions have a purity of 95–100% as above recovered and without further purification.

Referring to reactor 2, a small percentage of feed in line 27 is converted to carbon in the reactor. When this amounts to 5–25% of solids content in the reactor, a portion is withdrawn through line 47 and fresh inert material, such as sand is added through line 46 to restore the inventory in reactor 2. The carbon may be burned from the material withdrawn through line 47 so that the carbon-free solids may be added through line 46, but the method and technique of this carbon burning is not a part of this invention.

To explain the present invention, the following further information is set forth representing typical operating conditions for obtaining the indicated results:

Conditions in reactor 1

	Preferred	Range
Feed temperature, ° F	950	850–1,100
Pressure, p. s. i.	200	150–500
Temperature, ° F., in reactor	900	850–975
Space velocity, lbs. feed/hr./lb. catalyst	0.25	0.15–0.8
Recycle gas, C. F./Bbl.	3,000	2,000–6,000
Catalyst—10% molybdena on activated alumina.		

Feed stock to reactor 1

°API	48.2
Anil pt	129
I. B. P., °F	284
10%	298
50%	324
90%	379
F. B. P	412
CFRR octane number	39.2
Aromatics, vol. percent	14.6
Naphthenes vol. percent	46.1
Paraffins	39.3

Product inspection—reactor 1

Liquid yield, C_4–EP, vol. percent feed	85
CFRR octane number	95
Aromatics, vol. percent	63
Naphthenes	10
Paraffins	27
C_4–300° fraction, vol. percent of feed	45
300°+ fraction, feed to reactor 2, vol. percent of feed	40
Hydrogen production, C. F./Bbl. of feed	900

Conditions in reactor 2

	Preferred	Range
Feed Temperature, ° F	800	500–1,000
Pressure, p. s. i.	600	200–750
Temperature, ° F	1,350	1,000–1,400
Contact time, sec.	9	3–15
Gas rate, C. F./Bbl.	4,000	2,000–7,000

Feed to reactor 2

300–450° F. fraction from reactor 1

Aromatic content:

C_7 aromatics	volume percent 5
C_8 aromatics	do 15
C_9 aromatics	do 40
C_{10} aromatics	do 20
C_{11} aromatics	do 10
Paraffins	10

Products from reactor 2

Liquid yield, 80 vol. percent of feed to reactor 2
Benzene yield, 24% of product of reactor 2
Toluene yield, 30% of product of reactor 2
Xylene yield, 44% of product of reactor 2

In the hydrodealkylation reaction in reactor 2 about 1500 s. c. f. of hydrogen per barrel of feed is consumed in the highly exothermic reaction of removing substantially all of the side chains from the aromatic rings and the addition of hydrogen to form the dealkylated aromatic ring and resultant paraffin products. The exothermic heat of this reaction is in the order of 500 B. t. u. per pound of liquid feed. It is obvious that if the feed mixture was brought to the initial reaction temperature of about 1200° F. as in the conventional fired tube reactor, a "run-away" reaction would occur, the exothermic heat causing a temperature rise of about 500° F., or to 1700° F., if cooling were not used. On the other hand, in the fluidized bed of solids here used, the feed mixture thereto need not be brought to 1200° F., but rather can be introduced at a temperature lower than the reaction temperature, say, 800°–900° F., and the exothermic heat of reaction is used, aided by the turbulence in the bed, to heat the feed to reaction temperature. Thus, the temperature in reactor 2 is controlled by varying the preheat temperature of the feed.

The invention is not limited to the precise details set forth above. Naturally occurring heavy aromatic type hydrocarbons as kerosene extracts, heating oil extracts, catalytically cracked heating oil fractions and the like may be introduced through line 50 to mix with the high boiling hydroformate in line 26 to enter reactor 2 through line 27 Of course, high boiling hydroformates from other sources may be used and hydrogen rich gases from other hydroformers, say, one operating on lower boiling stocks, or from other sources may be fed into line 28 via line 51 to add to or enrich the hydrogen-containing gas in that line.

With respect to the catalyst that may be employed, it is pointed out that in addition to molybdenum oxide, chromium oxide, nickel sulfide, or tungsten sulfide, or any of a number of oxides or sulfides of metals of groups IV, V, VI, VII and VIII of the periodic system. These catalysts are usually supported on a base or spacing agent and the most commonly used base is alumina, either of the gel type or precipitated alumina. For example, a modified alumina, made by heat treating hydrated aluminum oxide, has been used as a support or extending agent for the active reforming catalysts mentioned above. Thus, a good catalyst for reforming or hydroforming is one containing about 10% molybdenum oxide supported on an alumina base. However, alumina in its various forms is not heat-stable, particularly at regeneration temperatures which are of the order of 1100°–1400° F. At these temperatures alumina is definitely impaired by prolonged heating, and this impairment is reflected in the loss of activity of the catalyst composition of which the alumina is the support or spacing agent.

With respect to the hydrogen concentration in the recycle gas, it may be of the order of 60–75% hydrogen although, of course, purer hydrogen may be employed.

It will be understood that the alkylated aromatics which are hydrodealkylated according to the present process may be from any source. In other words, these alkylated aromatics may be recovered, for example, from thermal reforming of heavy naphthas, or from any source where these heavy aromatics would be present. One of the main features of the present invention is to provide equipment which will be useful in carrying out the hydrodealkylation, and as hereinbefore pointed out one of the important aspects of the present invention involves providing a system which supplies hydrogen necessary in the hydrodealkylation process. Specifically, the present invention defines the hydrogen necessary for the hydrodealkylation by hydroforming naphthenic naphtha, which hydroforming

operation results in a net production of hydrogen over and above that necessary for the hydroforming operation, and this excess hydrogen may be utilized in the hydrodealkylation step of the present combination. Another important aspect of the present invention resides in the fact that the catalyst in the hydroforming zone and the powdered solids in the hydrodealkylation zone are in the form of fluidized beds which means that the respective beds of powdered material are maintained at substantially uniform temperatures throughout. This is very important with respect to the hydroforming operation, which because it is a highly endothermic reaction, has heretobefore been carried out in fixed beds of catalyst through which severe temperature drops occurred. To counteract this temperature drop through the beds in prior practice, it was necessary to preheat the feed to temperatures at which there was imminent danger of causing thermal cracking of said feed. The present technique permits much lower preheat of the feed to the hydroforming zone and consequently reduces thermal cracking in the preheating furnaces.

Numerous modifications of the present invention will be obvious to those who are skilled in the present art without departing from the spirit of the invention.

What is claimed is:

1. The method of producing high octane gasoline and aromatics of high purity which comprises subjecting a naphtha containing naphthenes which are predominantly C_9–C_{11} hydrocarbons and boiling substantially within the range of 250°–450° F. to a hydroforming operation in the presence of a fluidized bed of hydroforming catalyst, recovering a hydroformed product from the hydroforming step, recovering a gas rich in hydrogen from the said hydroforming step separating a motor gasoline fraction from said hydroformed product, recovering high boiling alkylated aromatics from said hydroformed product, preheating said aromatics to a temperature of from about 800°–900° F. and thereafter subjecting said aromatics to hydrodealkylation in the presence of a fluidized bed of powdered inert non-catalytic material and in the presence of added hydrogen recovered from the said hydroforming step and recovering therefrom benzene, toluene and xylene isomers.

2. The method set forth in claim 1 in which the catalyst is a VI group metal oxide carried on alumina base.

3. The method set forth in claim 1 in which the powdered material is sand.

4. The method of producing high octane gasoline and aromatics which comprises subjecting a naphtha containing naphthenes which are predominantly C_9–C_{11} hydrocarbons having an end boiling point above the gasoline boiling range to the influence of heat and pressure in the presence of a fluidized bed of a hydroforming catalyst in a hydroforming zone, feeding a hydrogen-containing gas to said hydroforming zone, permitting the reactants to remain resident in the reaction zone for a sufficient period of time to effect the desired conversion, withdrawing the product from the hydroforming reaction zone, recovering a hydrogen-containing gas from the product withdrawn from the hydroforming reaction zone, separating for product a hydroformate boiling substantially within the motor gasoline boiling range, recovering a residual product containing high boiling alkyl aromatics, preheating said residual product to a temperature of from about 800°–900° F. and thereafter subjecting said residual material at hydrodealkylation temperatures and pressures to contact with a powdered inert non-catalytic material in the form of a fluidized bed and added hydrogen recovered from the said product withdrawn from the hydroforming reaction zone for a sufficient period of time to effect dealkylation of said residual material and recovering an aromatic product containing benzene, toluene and xylene.

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