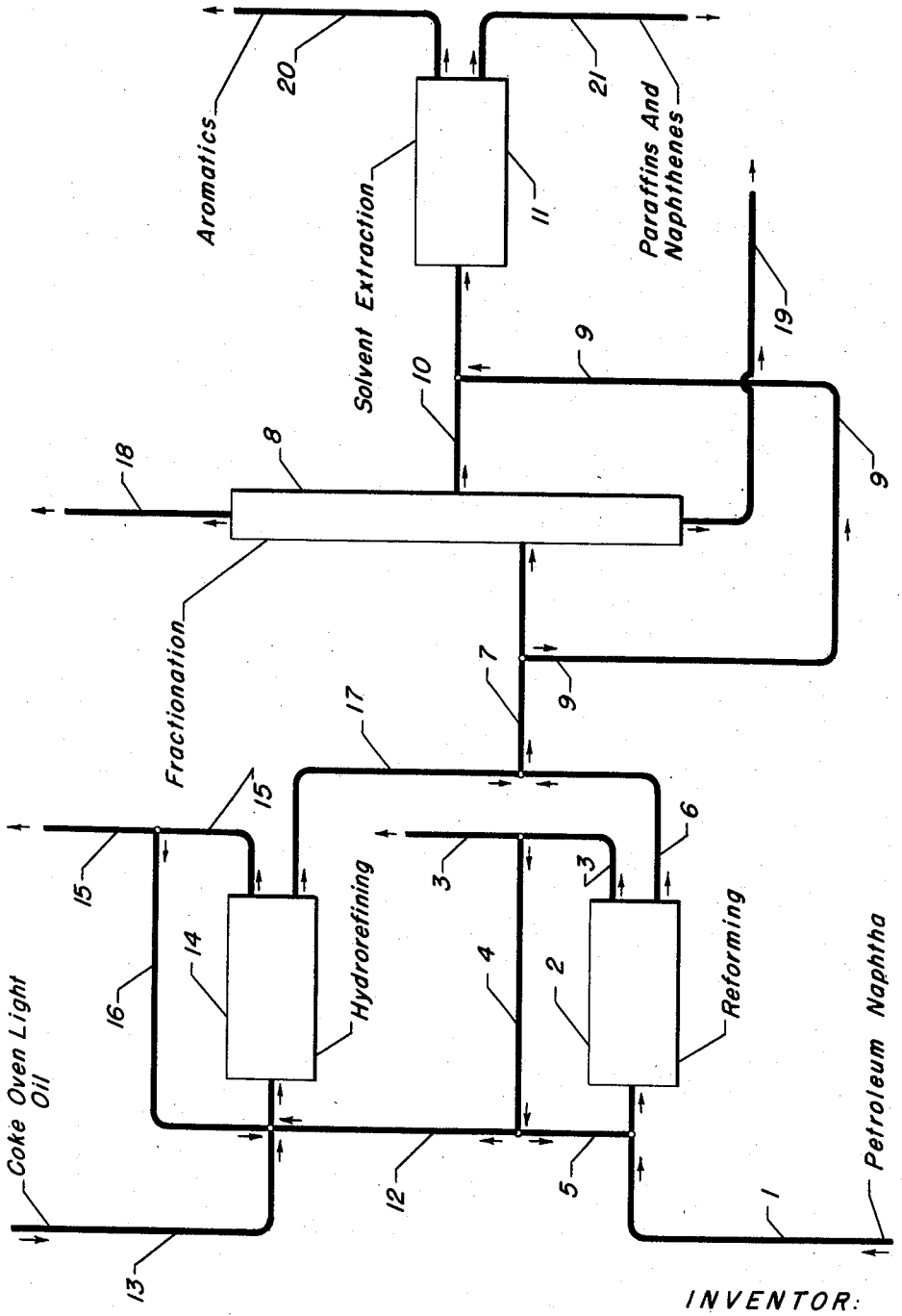
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PRODUCTION AND RECOVERY OF AROMATIC HYDROCARBONS

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PRODUCTION AND RECOVERY OF AROMATIC HYDROCARBONS

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This invention relates to a novel combination process for the production and recovery of aromatic hydrocarbons from coke oven light oils and petroleum naphtha.

Coke oven light oils and other distillates of similar boiling range from coal predominate in aromatic hydrocarbons but also contain paraffins and/or naphthenes as well as sulfur compounds and other non-hydrocarbon impurities. Because of the latter impurities, the coke oven light oils can not be separated by solvent extraction to produce aromatic hydrocarbons which meet nitration grade specifications. However, the coke oven light oil may be subjected to refining in the presence of hydrogen in order to remove or convert the impurities to forms in which they are easily removed, following which satisfactory aromatic hydrocarbon fractions may be recovered by solvent extraction.

As mentioned above, the refining of the coke oven light oil must be effected in the presence of hydrogen. While coke oven gas is available at the steel plants, the coke oven gas apparently is not of sufficient purity to permit its satisfactory use as the source of hydrogen for refining the coke oven light oils. While the hydrogen may be purchased in cylinders or otherwise, the cost of the hydrogen is excessive and it would be uneconomical to refine the coke oven light oils with such hydrogen.

I propose a novel combination process in which a petroleum naphtha is subjected to reforming under conditions to produce aromatics and to yield a net production of hydrogen, the greater portion of the hydrogen so produced being utilized in the hydrorefining of coke oven light oil. The resultant effluent products from both steps of the process are commingled and subjected to solvent extraction to separate and recover aromatic hydrocarbons. By the novel combination process herein proposed, the aromatic hydrocarbons will meet nitration grade or more severe specifications. This combination process not only produces additional aromatics in the reforming step, but also makes available an inexpensive source of hydrogen, thereby providing a means by which coke oven light oils may be economically treated to produce pure aromatic hydrocarbon fractions.

The invention is further explained with reference to the accompanying diagrammatic flow drawing which illustrates a preferred embodiment of the invention.

Referring to the drawing, a petroleum naphtha is directed by way of line 1 to reforming zone 2. The charge to reforming may comprise either a full boiling range gasoline fraction or a selected fraction thereof. In a preferred embodiment, the naphtha comprises a selected fraction of gasoline having an initial boiling point within the range of from about 150° to bout 250° F. and an end boiling point within the range of from about 250° to about 375° F. The reforming step of the process is effected in the presence of a catalyst and under conditions to yield a net production of hydrogen. A particularly preferred catalyst is the catalyst now known as "Platforming" catalyst, which catalyst comprises a composite of alumina, from about 0.1 to about 3% by weight

of platinum and from about 0.1 to about 3% by weight of combined halogen. Other platinum containing catalysts include composites of alumina and platinum; silica, alumina and platinum; silica, magnesia and platinum, etc. The reforming treatment generally is effected at a temperature of from about 800° to about 1100° F. and a pressure of from about 50 to 1000 and preferably 200 to 500 pounds per square inch or more.

The reforming step may be effected in any suitable manner. A preferred method comprises a fixed bed type of operation in which a bed of catalyst is disposed in one or more reaction zones and the charge, at the desired temperature and pressure, is passed therethrough. Other methods include the fluidized type of operation, the fluidized-fixed bed type, the moving bed type in which the reactants are passed either concurrently or countercurrently to a moving bed of catalyst, etc.

Following the reforming operation, the effluent products are cooled and separated into a gaseous fraction and a liquid fraction. The gaseous fraction comprises principally hydrogen and is withdrawn by way of line 3. Although a portion of the hydrogen may be removed from the process through the extension of line 3, at least a portion is directed by way of line 4, to be returned in part by way of lines 5 and 1 to reforming zone 2 for further use therein. Another portion of the hydrogen fraction is used in the hydrorefining of the coke oven light oil in a manner to be hereinafter set forth in detail.

The liquid effluent products of reforming are withdrawn from zone 2 through line 6 and are directed by way of line 7 either to fractionator 8 or by way of lines 9 and 10 to solvent extraction zone 11.

As hereinbefore set forth, a portion of the hydrogen fraction being directed through line 4 is passed through line 12 and utilized in the hydrorefining of coke oven light oil introduced into the process through line 13. The hydrogen and coke oven light oil are directed into hydrorefining zone 14 and therein subjected to treatment in the presence of a suitable catalyst. A particularly preferred catalyst comprises a composite of alumina, molybdenum compound and cobalt compound, the cobalt and molybdenum components each comprising from about 1 to about 15% by weight of the final catalyst. Generally the catalyst comprises alumina, molybdenum oxide and cobalt oixde or it may comprise alumina, molybdenum sulfide and cobalt sulfide. Other catalysts include silica-alumina-molybdenum oxide-cobalt oxide, silica-magnesia-molybdenum oxide-cobalt oxide, alumina-magnesia-molybdenum oxide-cobalt oxide, etc. Still other catalysts include composites of alumina-nickel sulfide-tungsten sulfide, silica-alumina-tungsten sulfide-nickel sulfide, etc.

The hydrorefining generally is effected at a temperature of from about 600° to about 800° F. and at a pressure of from about 50 to 1500 pounds per square inch or more.

As hereinbefore set forth, hydrogen from the reforming operation is utilized in the hydrorefining step of the process. In general, it will require the reforming of from about 0.25 to about 0.40 volume of petroleum naphtha in order to satisfactorily hydrorefine one volume of coke oven light oil. However, it is understood that larger amounts of petroleum naphtha may be subjected to reforming in accordance with the present invention in order to insure that sufficient hydrogen will be available for use in the hydrorefining step of the process as well as for recycling to the reforming step of the process in order to maintain in the latter a hydrogen to hydrocarbon mol ratio within the range of from about 1:1 to about 10:1.

The hydrorefining step of the process may be effected in any suitable manner. A preferred method is the fixed

bed type of operation. Other methods include the fluidized system, the fixed bed-fluidized type, the moving bed type, etc.

While both the reforming and hydrorefining steps of the process are shown diagrammatically in the drawing, it is understood that one or both may comprise one or a plurality of reaction zones, heat exchangers, coolers and/or receivers.

The effluent products of hydrorefining are separated into a gaseous fraction and a liquid fraction. The gaseous fraction is withdrawn from zone 14 through line 15 and may be removed from the process through an extension of this line or recycled, all or in part, by way of lines 16 and 13 to zone 14. The liquid effluent products from zone 14 are withdrawn through line 17 and are directed either through line 7 to fractionator 8 or through lines 9 and 10 to solvent extraction zone 11.

In one embodiment, the effluent products from both reforming zones are passed to solvent extraction zone 11 or in another embodiment are directed by way of line 7 to fractionation zone 8. In fractionator 8, constituents boiling below benzene are withdrawn from the upper portion of zone 8 by way of line 18, while constituents boiling above the highest boiling aromatic desired are withdrawn from the lower portion of zone 8 through line 19. When employed, zone 8 generally will be utilized to separate a concentrate containing benzene toluene and xylene. In another embodiment, zone 8 may be operated to separate a benzene cut, a toluene cut, or a xylene cut, or a benzene-toluene cut or a toluene-xylene cut.

Regardless of the particular operation of zone 8 or whether this zone is employed, the aromatic fraction is directed through line 10 to solvent extraction zone 11. In zone 11, the charge is subjected to solvent extraction in order to separate aromatics from non-aromatic hydrocarbons. Any suitable solvent may be employed in this step of the process and preferably comprises a glycol solvent including ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, dibutylene glycol, etc., or mixtures thereof. Other solvents include alcohols and phenols, ethers, nitriles, esters, etc. It generally is preferred to utilize water or other anti-solvent in order to increase the selectivity of the solvent, and this is particularly true in connection with the glycol solvents. The solvent extraction may be effected at any suitable temperature which may range from atmospheric to 400° F. or more at pressures from atmospheric to 300 pounds or more, the conditions being selected to maintain liquid phase in the extraction zone. The aromatic hydrocarbons are withdrawn from zone 11 through line 20, and the non-aromatics are withdrawn therefrom through line 21. While solvent extraction zone 11 is illustrated in block form, it is understood that the solvent extraction preferably includes an extraction zone and a stripping zone, the latter being employed to separate the aromatics from the solvent, the solvent being recycled for further use within the process.

The aromatic hydrocarbons recovered by the novel combination process of the present invention will meet nitration grade specifications in many cases. However, in other cases it is desirable to pass the aromatic fraction over clay or other suitable adsorbent, generally at moderate temperatures which will be below about 500° F. and under sufficient pressure to maintain liquid phase, in order to insure the purity of the aromatic fraction.

When the aromatic hydrocarbons recovered from the solvent extraction zone comprise a mixture of aromatics, they may be readily separated by conventional fractionation into separate benzene, toluene and xylene cuts. This fractionation may be effected either before or after clay treating when the latter is employed.

As mentioned above, the drawing is purely diagrammatic. It is understood that suitable heaters, reaction zones, heat exchangers, coolers, fractionating zones, solvent stripping zones, pumps, valves and similar appurtenances will be provided as required.

The following example is introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

Example

1000 barrels per day of Pennsylvania straight run naphtha is subjected to reforming in the presence of a catalyst comprising alumina. 0.5% by weight of platinum and 0.6% by weight of combined halogen at a temperature of 900° F. and a pressure of 400 pounds per square inch. The products from the reforming reactor are cooled and passed into a receiver, from which a hydrogen containing stream and a liquid effluent product stream are separately withdrawn. A portion of the hydrogen stream is recycled to the reforming step and another portion is supplied to a hydrorefining step. In the hydrorefining step, 3000 barrels per day of coke oven light oil comprising about 70% by volume of benzene, about 18% by volume of toluene and about 4% by volume of xylene, is subjected to hydrorefining in the presence of the hydrogen supplied from the reforming operation and in the presence of a catalyst comprising alumina, about 8% by weight of molybdenum oxide and about 3% by weight of cobalt oxide. The hydrorefining is effected at a temperature of 750° F. and a pressure of 800 pounds per square inch. The effluent products from the hydrorefining are separated into a gaseous fraction and a liquid fraction.

The liquid fractions from the reforming and hydrorefining steps are combined and subjected to solvent extraction in the presence of a diethylene glycol-water solvent to separate an aromatic fraction. The aromatic fraction thus recovered is subjected to clay treating at 400° F. and 250 pounds and then to fractionation in order to separate and recover a benzene fraction, a toluene fraction, and a xylene fraction. The benzene and toluene fractions will meet nitration grade specifications.

I claim as my invention:

1. A combination process for the production and recovery of aromatic hydrocarbons which comprises subjecting a petroleum fraction boiling in the gasoline range to reforming under conditions to yield a net production of hydrogen, separating from the effluent products a hydrogen fraction and a liquid fraction, subjecting coke oven light oil derived from coal and containing non-hydrocarbon impurities to hydrorefining in the presence of a portion of said hydrogen fraction to remove said impurities, separating from the effluent products a gaseous fraction and a liquid fraction, combining the last mentioned liquid fraction with the first mentioned liquid fraction, and subjecting the mixture to solvent extraction to separate an aromatic hydrocarbon fraction, and recovering said aromatic hydrocarbon fraction.

2. A combination process for the production and recovery of aromatic hydrocarbons which comprises subjecting a petroleum fraction boiling in the gasoline range to reforming in the presence of hydrogen under conditions to yield a net production of hydrogen, separating from the effluent products a hydrogen fraction and a liquid fraction, recycling a portion of the hydrogen fraction to said reforming, subjecting coke oven light oil derived from coal and containing non-hydrocarbon impurities to hydrorefining in the presence of a second portion of said hydrogen fraction to remove said impurities, separating from the effluent products a gas fraction and a liquid fraction, combining the last mentioned liquid fraction with the first mentioned liquid fraction, and subjecting the mixture to solvent extraction to separate an aromatic hydrocarbon fraction, and recovering said aromatic hydrocarbon fraction.

3. A combination process for the production and recovery of aromatic hydrocarbons which comprises subjecting a petroleum naphtha to reforming in the presence

of hydrogen and a platinum containing catalyst under conditions to yield a net production of hydrogen, separating from the effluent products a hydrogen fraction and a liquid fraction, recycling a portion of the hydrogen fraction to said reforming, subjecting coke over light oil derived from coal and containing non-hydrocarbon impurities to hydrorefining in the presence of a second portion of said hydrogen fraction and an alumina-molybdenum oxide-cobalt oxide catalyst to remove said impurities, separating from the effluent products a gas fraction and a liquid fraction, combining the last mentioned liquid fraction with the first mentioned liquid fraction, and subjecting the mixture to extraction with a glycol solvent to separate an aromatic hydrocarbon fraction, and recovering said aromatic hydrocarbon fraction.

4. A combination process for the production and recovery of aromatic hydrocarbons which comprises subjecting a petroleum naphtha to reforming at a temperature of from about 800° to about 1100° F. in the presence of hydrogen and a platinum containing catalyst under conditions to yield a net production of hydrogen, separating from the effluent products a hydrogen fraction and a

liquid fraction, recycling a portion of the hydrogen fraction to said reforming, subjecting coke oven light oil derived from coal and containing non-hydrocarbon impurities to hydrorefining at a temperature of from about 600° to about 800° F. in the presence of a second portion of said hydrogen fraction and an alumina-molybdenum sulfide-cobalt sulfide catalyst to remove said impurities, separating from the effluent products a gas fraction and a liquid fraction, combining the last mentioned liquid fraction with the first mentioned liquid fraction, and subjecting the mixture to extraction with a glycol solvent to separate an aromatic hydrocarbon fraction, and recovering said aromatic hydrocarbon fraction.

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