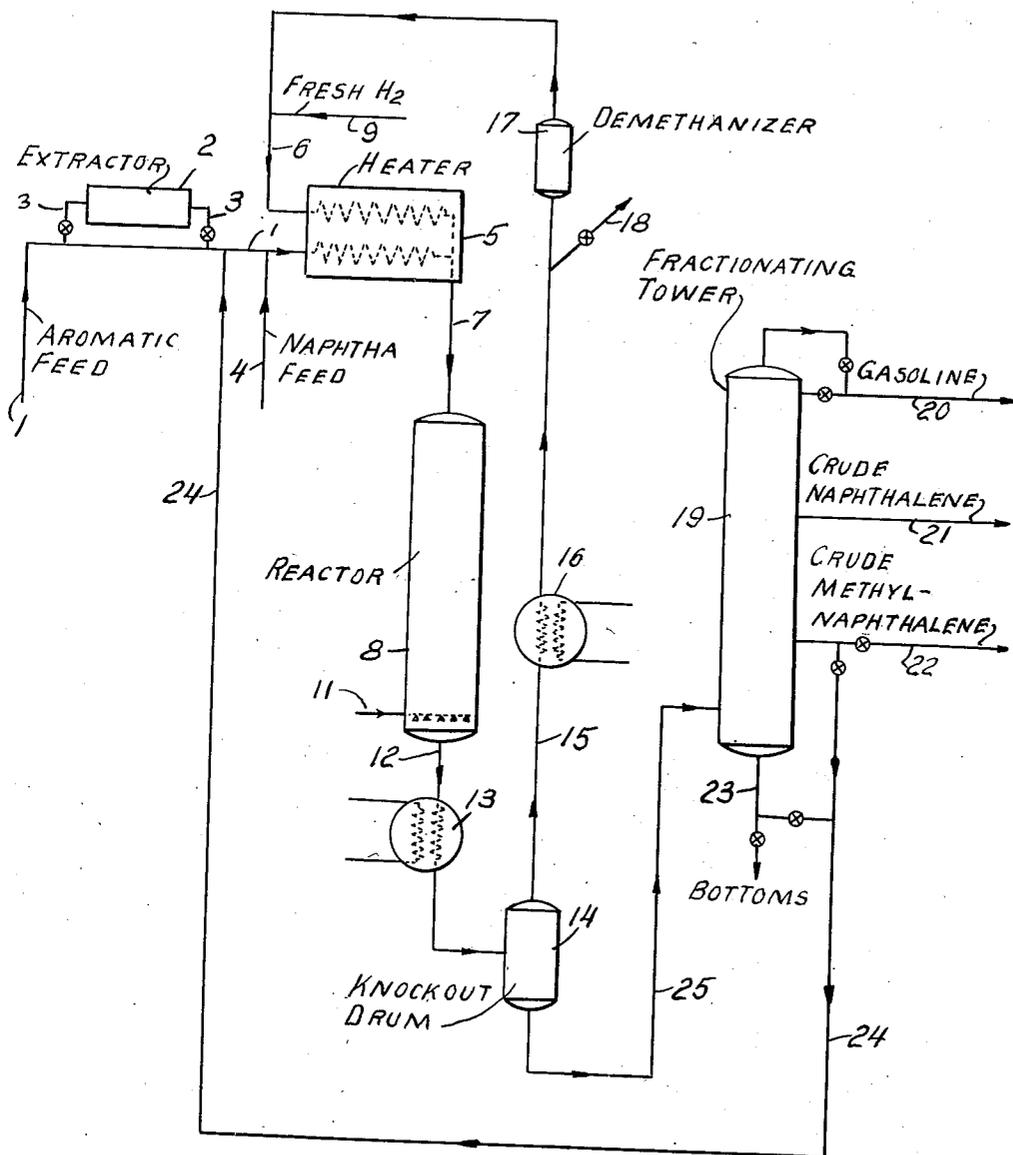


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B. S. FRIEDMAN
COMBINATION CRACKING PROCESS FOR PRODUCING
AROMATICS FROM PETROLEUM
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INVENTOR
BERNARD S. FRIEDMAN
BY
Adams, Forward & McLean
ATTORNEYS

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COMBINATION CRACKING PROCESS FOR PRODUCING AROMATICS FROM PETROLEUM

Bernard S. Friedman, Chicago, Ill., assignor to Sinclair Refining Company, New York, N. Y., a corporation of Maine

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My invention relates to the simultaneous production of naphthalene and low molecular weight, gasoline range-boiling hydrocarbons from mixtures of hydrocarbon fractions rich in alkylated fused-ring aromatics, especially cycle oils, and light petroleum distillate fractions, such as naphthas, by conversion in the presence of a hydroforming catalyst.

Conventional cracking operations to prepare useful petroleum products such as gasoline from heavier hydrocarbon fractions is essentially an incomplete process when the total conversion to useful products is considered. In particular, cycle stock, or relatively refractory hydrocarbons boiling in the gas oil range, accumulates in vast quantities. As a result, a difficult problem is presented in handling these cycle stocks to further improve the commercial aspects of cracking operations. Continued recycling of such fractions in the system for additional conversion becomes uneconomical because of their general refractory character. On the other hand, as useful products cycle stocks have extremely limited utility. For instance, as heating oils these hydrocarbons have low or negligible value while their ignition quality is too poor for practical use as diesel fuels.

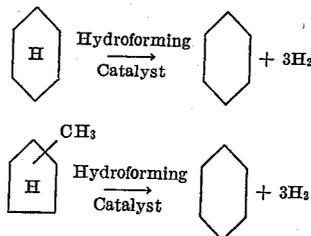
Cycle stocks are characterized by a high content of alkylated fused-ring aromatic compounds, particularly alkylated naphthalenes such as the methyl naphthalenes. Although these materials have limited present market value and cannot be individually separated, naphthalene itself has a definite market value if prepared at low cost. In copending applications of L. H. Beckberger, Serial Nos. 161,211, now U. S. Patent No. 2,674,635 and 161,212, now U. S. Patent No. 2,653,176, there is disclosed and claimed the production of naphthalene in substantial yields from these fractions rich in alkylated fused-ring aromatics by conversion in the presence of hydrogen. Application Serial No. 161,211, U. S. Patent 2,674,635, describes a process wherein the aromatic-rich fraction is thermally converted in the presence of hydrogen from extraneous sources or by use of recycle gases. In application Serial No. 161,212, U. S. Patent 2,653,176, the conversion of similar fractions is described over a water gas-active, steam-insensitive catalyst using hydrogen from similar sources and employing steam as an in situ source of hydrogen as a result of the water gas reaction. In each case it is necessary to provide hydrogen in some form to effect the conversion.

I have found that when hydrocarbon fractions rich in alkylated fused-ring aromatics are converted in the presence of a light petroleum distillate fraction and a hydroforming catalyst, it is not necessary to add extraneous hydrogen to produce naphthalene; and, in addition to the production of considerable quantities of naphthalene, attractive yields of useful low molecular weight, gasoline range-boiling hydrocarbon fractions are also prepared in my process. Essentially, I react the aromatic-rich fraction with a light petroleum distillate, advantageously rich in cycloparaffins, such as cyclohexane, in the presence of a hydroforming catalyst at a temperature in the range approximating 900° to 1100° F. and at a pressure between about 50 to 1500 p. s. i. g. The reaction is carried out at these temperatures and pressures for a period of time sufficient to effect conversion to the desired products, although generally the holding time will vary between several minutes to one or more hours. The reaction mixture may, for instance, comprise a 50/50 volume blend of a cycle stock from a cracking operation and a straight-run naph-

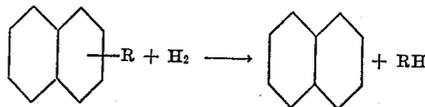
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tha boiling between 300°-400° F. Suitable hydroforming catalysts include such metals or metal oxides as molybdena, chromia, tungsten, nickel, cobalt and the like either alone or in combination, and advantageously supported on carriers such as alumina, thoria, zinc oxide and the like. I particularly prefer 5 to 10% of molybdena supported on activated alumina. Although extraneous hydrogen is not added to the reaction, it is generally necessary to initiate the process by the addition of a small amount of a hydrogen-rich gas, and, advantageously, the tail gases, rich in hydrogen, from the reaction itself may be recycled to maintain an excess of hydrogen in the reaction, advantageously from about 1 to 10 moles of hydrogen per mole of feed.

Although my invention is not based upon any particular theory, I believe that simultaneously conducting the reforming reaction in the presence of the dealkylation reaction results in the hydrogen produced by one of the reactions (reforming) being consumed by the other (dealkylation). That is, the cycloparaffinic components of the light distillate (e. g. straight run naphtha) react over a hydroforming catalyst to liberate hydrogen, these cycloparaffinic, e. g., naphthenic components, being converted to benzenoid aromatics as represented generally by the following equations:



while the alkylated fused-ring aromatic compounds, say in a cycle stock, consume the available hydrogen to form naphthalene as follows:



Although the process according to my invention is especially adaptable to petroleum cycle stocks, which are readily available at low cost and in considerable quantities, other sources of alkylated fused-ring aromatics may be employed. In general, these cycle oils and other similar fractions contain large proportions of compounds with polycyclic aromatic nuclei attached to which are such groups as methyl, ethyl, propyl (or higher) radicals as well as cycloalkyl, e. g. cyclohexyl, and aryl radicals. In particular, I contemplate using hydrocarbon fractions essentially consisting of alkyl, polyalkyl, aryl or polyaryl naphthalene derivatives or any oil containing these derivatives in appreciable amounts. I especially prefer cycle stocks derived from cracking operations such as those boiling in the range of 400°-600° F. Coal tar fractions of similar boiling ranges can also be used. However, certain other heavier fractions rich in alkylated fused-ring aromatics such as derivatives of anthracene and phenanthrene are useful. Pure or highly concentrated naphthalene derivatives are not essential since any non-aromatic constituents in the charge will be hydrocracked to lower boiling hydrocarbon liquids and gases from which the naphthalene and gasoline is removed by distillation. In addition, the presence of non-aromatics and alkylbenzenes in the feed result in the production of benzene, toluene, and xylenes, as well as useful hydrocarbon gases, particularly butane. Cycle oils of relatively low aromatic concentration may be initially treated or prepared prior to reaction. For example, solvent extraction with a selective solvent of the nature of furfural or sulfur dioxide, will effect separation from non-aromatic constituents present in undesirable amounts.

For blending with the alkylated fused-ring aromatic-rich fractions, any petroleum stock that may be reformed to liberate and make available hydrogen is satisfactory. In particular, I use light virgin fractions rich in cyclo-

paraffins such as cyclohexanes, for example a light distillate fraction such as a straight run 300°-400° F. naphtha. The naphtha fraction is so blended with the alkylated fused-ring aromatic fraction that preferably an excess of hydrogen is made available for the accompanying dealkylation reaction.

The reaction is carried out in the presence of a hydroforming catalyst, advantageously a catalyst comprising 5 to 10% of molybdenum oxide supported on activated alumina. However, the selection of a suitable hydroforming catalyst affords considerable latitude. For instance, the catalyst may include unsupported molybdena, chromia, tungsten, cobalt, nickel, etc., alone or in combination. These materials are advantageously supported, say, on alumina, thoria, zinc oxide or the like. Although these materials tend to promote the dealkylation reaction as well, in the absence of a virgin light distillate in the feed, liquid yields are low and coke make is very high.

The reaction is conducted at elevated temperatures in the range of about 900° to 1100° F. Above the upper limit of 1100° F. the yield of liquid products becomes unattractive, while below 900° F. the formation of naphthalene and gasolines fall off. I have found that reaction temperatures of about 950° to 1050° F. are particularly advantageous. The reaction pressures afford considerable latitude in operation, and are in the range approximating 50 to 1500 p. s. i. g. I prefer a pressure of about 500 p. s. i. g.

The holding time of the hydrogen feed in the reaction zone is varied according to the reaction conditions and feed stocks in order to effect the desired conversion. Generally the holding time will vary from several minutes to one or more hours. Advantageously the holding period is short, below about thirty minutes.

Hydrogen or hydrogen-rich gases are required to initiate the reaction. Although it is not necessary to add hydrogen thereafter, I prefer to add the tail gases from the effluent non-condensable gases of the reaction which are rich in hydrogen and which may be augmented where necessary by adding substantially pure hydrogen so that hydrogen is maintained in excess during the reaction at all stages of contacting. The reforming operation on virgin stocks generally produces enough hydrogen so that the overall reaction is in approximate material balance, and, in addition, the side cracking reactions on the cycle stocks may produce additional substantial increments of hydrogen which assist the reaction although insufficient alone to direct the overall reaction of the cycle stocks toward dealkylation. The hydrogen is advantageously maintained in molar ratio to the hydrocarbon feed of about 1 to 10, calculated as pure H₂ to feed oil. Below a 1:1 ratio the product yields are relatively low while a molar ratio above 10:1 is wasteful of hydrogen. I prefer to maintain a molar ratio of about 3 to 10.

The following example is intended to more clearly illustrate my invention.

A 50:50 blend by volume of a fraction containing over 99% methyl-naphthalenes and a 300°-400° F. boiling straight run naphtha analyzing as follows:

Gravity, °A. P. I. -----	49.5
IBP, °F. -----	311
10, °F. -----	323
50, °F. -----	340
90, °F. -----	363
E. P., °F. -----	413
Olefins, weight percent -----	0.0
Aromatic, weight percent -----	10.0
Naphthalene, weight percent -----	0.0
Methyl-naphthalene, weight percent -----	0.0

was introduced into a reactor vessel packed with a molybdenum oxide-activated alumina supported catalyst. Hydrogen was introduced in a mole ratio to hydrocarbon feed of 1.2 to 1 to simulate tailgas recycling. The reaction was carried out at a temperature reaching a peak of 1022° F. and at a pressure of 400 p. s. i. g. 72.5% liquid reaction products were obtained as based on the charge, 10.5% of gas products and 17.0% of coke. Fractionation of the liquid products showed the following components by weight:

	Percent
IBP-400° F. -----	32.8
400°-460° F. -----	9.5
460°-480° F. -----	51.8
Bottoms -----	5.9

The liquid products analyzed 64.4% of gasoline by weight on the naphtha in the feed and 13.9% of naphthalene, 73.2% of methyl-naphthalene, and 8.6% of bottoms, by weight on the methyl-naphthalene fraction in the feed.

5 The gaseous products analyzed as follows by mole percent:

H ₂ -----	17.5
C ₁ -----	36.9
C ₂ -----	21.2
C ₃ -----	12.7
C ₄ -----	3.2
Others -----	8.5

15 The accompanying drawing is a flow diagram illustrating somewhat schematically a continuous process according to my invention.

A petroleum fraction rich in alkylated fused-ring aromatics, a cycle oil boiling in the range 400°-600° F. from a cracking operation, is introduced by line 1. Extraction zone 2 is provided, accessible by line 3, if it is necessary to improve the quality of the feed oil to be treated, for example by extraction with a selective solvent such as furfural or sulfur dioxide. A light distillate fraction, a 300°-400° F. straight run naphtha, is introduced by line 4 and blended with the cycle oil by passing into line 1, for instance as a 50/50 volumetric blend with the cycle oil. The feed oil blend is then heated in heating zone 5 and passed into the reaction zone 8 by line 7. Although the reaction is self-sufficient in hydrogen once commenced, it is necessary to initially introduce a small quantity of hydrogen or of a hydrogen-rich gas through line 6, and fresh hydrogen can also be introduced by line 9 whenever necessary. Both the feed oil mixture and hydrogen gases are preheated to an elevated temperature in the heater 5, say to 400° to 600° F., and mixed together when they are passed by line 7 to the reaction zone 8. Reaction zone 8 is packed with a hydroforming catalyst material, advantageously 5 to 10% of a molybdenum oxide supported on activated alumina. The reaction is carried out at a temperature in the range of about 900° to 1100° F. at a pressure between about 50 to 1500 p. s. i. g. A temperature between about 950° to 1050° F. at a pressure around 500 p. s. i. g. is preferred for good yield. The hydrocarbon feed is held in the reaction zone for a period of time sufficient to effect conversion, say from several minutes to an hour or more, although thirty minutes or so is usually satisfactory. Hydrogen is introduced in regulated amounts between about 1 to 10 moles per mole of feed and is advantageously maintained at this concentration throughout the reaction. A water quench 11 is provided in the reaction zone so that thermal conditions may be regulated during reaction and for cooling of the hot effluent vapors. The effluent products from the reaction are taken off by line 12 and passed through cooling zone 13, advantageously a waste heat boiler, where they are cooled to about 300° to 400° F. The products are then passed through liquid separation zone 14, a knockout drum, where the non-condensable gases are separated from the liquid at line 15. The non-condensable or tail gases, rich in hydrogen, are cooled in cooling zone 16 and passed to demethanizer 17, e. g. an oil scrubber, by line 15. Any amount of these gases may be bled out by line 18. After the methane has been removed the hydrogen-rich gases are recycled back to the reaction zone as desired. The liquid separated from knockout drum 14 is introduced into fractionating zone 19 by line 25 for separation into useful constituents. From fractionating zone 19, the gasoline range-boiling constituents are removed as overhead by line 20, tar as bottoms by line 23, a crude methyl-naphthalene fraction by line 22 and a crude naphthalene fraction by line 21. The gasoline and naphthalene fractions are passed to storage or may be redistilled for additional purity. Crude methyl-naphthalene and the bottoms may be recycled as desired by line 24 to be admixed with the feed stock.

I claim:

1. The method of simultaneously preparing lower fused-ring aromatic compounds and gasoline boiling-range hydrocarbons which comprises passing a mixture of a light petroleum distillate fraction and a hydrocarbon fraction rich in alkylated fused-ring aromatic compounds into a reaction zone in the presence of a hydroforming catalyst supported on a carrier selected from the group consisting of alumina, thoria and zinc oxide, maintaining

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the reaction zone at a temperature in the range approximating 900 to 1100° F. and at a pressure between about 50 to 1500 p. s. i. g. for a period of time sufficient to effect conversion, and separating the lower-boiling fused-ring compounds and gasoline boiling-range hydrocarbons from the effluent reaction products.

2. The method of simultaneously preparing naphthalene and gasoline boiling-range hydrocarbons which comprises passing a mixture of naphtha and a petroleum cycle stock rich in alkylated naphthalenes into a reaction zone in the presence of a hydroforming catalyst supported on a carrier selected from the group consisting of alumina, thoria and zinc oxide, maintaining the reaction zone at a temperature in the range approximating 900 to 1100° F. and at a pressure between about 50 to 1500 p. s. i. g. for a period of time sufficient to effect conversion, separating the tail gases from the effluent reaction products and recycling said gases to the reaction zone, and fractionally distilling the liquid reaction products to separate the naphthalene and gasoline boiling-range hydrocarbons therefrom.

3. The method of simultaneously preparing lower fused-ring aromatic compounds and gasoline boiling-range hydrocarbons which comprises passing a mixture of a light petroleum distillate fraction and a hydrocarbon fraction rich in alkylated fused-ring aromatic compounds into a reaction zone in the presence of hydroforming catalysts selected from the group consisting of molybdena, chromia, tungsten, nickel and cobalt, maintaining the reaction zone at a temperature in the range approximating 900° to 1100° F. and at a pressure between 50 and 1500 p. s. i. g. for a period of time sufficient to effect conversion, and separating the lower boiling fused-ring compounds and gasoline boiling-range hydrocarbons from the effluent reaction products.

4. The method according to claim 3 wherein the tail gases are separated from the effluent reaction products and are recycled to the reaction zone.

5. The method according to claim 3 in which the hydroforming catalyst is supported on a carrier selected from the group consisting of alumina, thoria and zinc oxide.

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6. The method according to claim 1 in which the hydroforming catalyst consists essentially of 5 to 10 per cent molybdena supported on activated alumina.

7. The method of simultaneously preparing naphthalene and gasoline boiling-range hydrocarbons which comprises passing a mixture of a naphtha and a petroleum cycle stock rich in alkylated naphthalenes into a reaction zone in the presence of hydroforming catalysts selected from the group consisting of molybdena, chromia, tungsten, nickel and cobalt, maintaining the reaction zone at a temperature in the range approximating 900° to 1100° F. and at a pressure between 50 and 1500 p. s. i. g. for a period of time sufficient to effect conversion, and separating naphthalene and gasoline boiling-range hydrocarbons from the effluent reaction products.

8. The method of simultaneously preparing naphthalene and gasoline boiling-range hydrocarbons which comprises passing a mixture of naphtha and a petroleum cycle stock rich in alkylated naphthalenes into a reaction zone in the presence of a hydroforming catalyst supported on a carrier selected from the group consisting of alumina, thoria and zinc oxide, maintaining the reaction zone at a temperature in the range approximating 900 to 1100° F. and at a pressure between about 50 to 1500 p. s. i. g. for a period of time sufficient to effect conversion, and fractionally distilling the liquid reaction products to separate the naphthalene and gasoline boiling-range hydrocarbons therefrom.

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