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HF CONVERSION OF HYDROCARBONS

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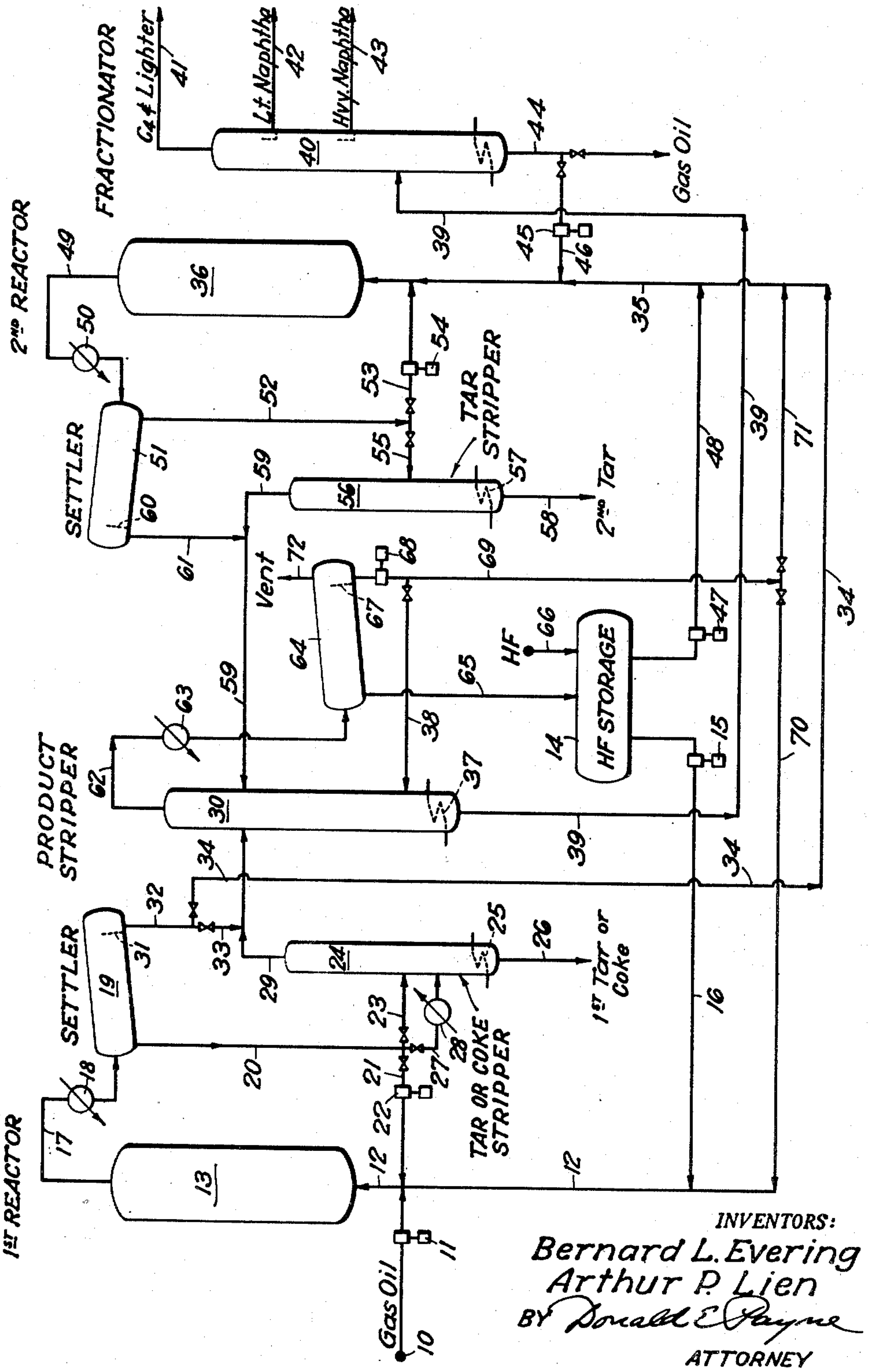

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HF CONVERSION OF HYDROCARBONS

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8 Claims. (Cl. 196—52)

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This invention relates to the conversion of hydrocarbons by use of a hydrogen fluoride catalyst and it pertains more particularly to the conversion of high boiling hydrocarbons for the production of hydrocarbons in the gasoline and/or Diesel fuel boiling range and one or more valuable tars. In its more specific aspects the invention relates to a combination process wherein one step involves the separation of substantially HF- insoluble polycyclic aromatic hydrocarbons such as alkyl naphthalenes from saturated hydrocarbons by a process which involves intermolecular chemical condensation of said aromatic hydrocarbons to produce HF-soluble polynuclear aromatic hydrocarbons which are extracted from said saturated hydrocarbons. The chemical condensation and the extraction steps are performed in a medium consisting essentially of liquid anhydrous hydrogen fluoride which functions as a catalyst in the chemical reaction and as a solvent in the extraction operation. Also, the invention may eliminate sulfur at the higher temperatures by splitting out H_2S from the organic sulfur compounds to form unsaturated hydrocarbons, although some of the organic sulfur compounds may be simply extracted by the hydrogen fluoride. The chemical condensation per se is claimed in copending application Ser. No 135,166, filed December 27, 1949, as a continuation in part of copending application Ser. No. 760,061, which was filed on even date hereof and in which condensation by combined use of HF and BF_3 is claimed.

An object of the invention is to provide a method and means for improving the cracking susceptibility of gas oils, residual charging stocks and/or any hydrocarbons which are higher boiling than gasoline and which contain chemically condensable aromatics and sulfur compounds. A further object is to convert such charging stocks into valuable products with lower operating and investment costs than have heretofore been required. A further object is to obtain good yields of high quality gasoline and/or Diesel fuel components from a given charging stock while at the same time obtaining more useful by-products than have heretofore been obtainable. Another object is to produce from such operations two radically different types of tars: (1) a condensed aromatic tar and (2) a viscous highly olefinic oil having unique and valuable properties and suitable for use as a drying oil and/or a component of coating materials, and plastic compositions. Other objects will be apparent as the detailed description of the invention proceeds.

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In practicing our invention we employ a multistage operation wherein the incoming charging stock is first contacted under mild operating conditions for the purpose of condensing and/or removing chemically condensable aromatics (and sulfur compounds) as an aromatic tar in high specific gravity while effecting only a slight amount of cracking so that a gas oil is produced which is substantially free from sulfur and condensable aromatics and which contains only a small amount, preferably less than 5%, of hydrocarbons of the gasoline boiling range. The gas oil from this first stage, either before or after removal of gasoline boiling range components, is then contacted with hydrogen fluoride under cracking conditions in a second stage to produce gas, gasoline (and/or Diesel fuel) and an entirely different type of tar than is produced in the first stage. A portion of the tar from the second reaction stage may be recycled thereto for increasing gasoline yields and rate of conversion while another portion of the tar from the second stage is separated from catalyst to yield a valuable by-product having unique drying properties. These and other features of the invention will be more clearly apparent from the following detailed description of a specific example thereof read in conjunction with the accompanying drawing which is a schematic flow diagram of a system for converting an East Texas gas oil into gas, gasoline, a valuable olefinic tar and a tar comprising principally condensed ring polynuclear aromatic hydrocarbons.

While any aromatic and sulfur-containing charging stock may be employed, such charging stock should preferably be higher boiling than gasoline and the preferred charge is a gas oil or reduced crude containing chemically condensable aromatic hydrocarbons. The invention will be described as applied to the conversion of a 37° API gravity East Texas gas oil which is introduced into the system from source **10** by pump **11** and charge line **12** to first reactor **13**. Hydrogen fluoride is introduced from storage tank **14** by pump **15** and lines **16** and **12** to said first reactor in such amounts that the total charge entering the first reactor will contain about 10 to 200%, preferably 15 to 50% hydrogen fluoride by volume based on gas oil charged. Reactor **13** is maintained at a conversion or condensing temperature in the range of 200 to 375° F., preferably about 250 to 330° F. by preheating the gas oil charge or supplying heat to the reactor in any other known manner. First reactor **13** is operated under a pressure sufficient to maintain liquid phase conversion conditions, i. e. within a range of about 250 to 1000 p. s. i., or preferably about 500 to 800 p. s. i. The time of contact in the reactor should be relatively long, usually within the range of about 20 to 200 minutes (the lower temperatures requiring longer contact times); with efficient contacting means for securing intimate contact, the time at 330° F. may be about an hour. Aromatic condensation without excessive cracking is dependent on several variables. When the HF concentration is high the contact time and temperature used will be relatively low. Conversely higher temperatures and longer contact times will be used at lower HF concentrations. The conditions should be such as to effect condensation of condensable aromatics and removal of sulfur so that the hydrogen-fluoride insoluble material will be chiefly a paraffinic gas oil, substantially free from condensable aromatics and sulfur and containing only a small amount, preferably less than 5%, of gasoline-boiling-range hydrocarbons, including benzene and methylbenzenes.

The reactor itself may be a stirred autoclave, a packed or unpacked tower with or without mixing orifices, a circulating system of the type commonly employed for effecting sulfuric acid alkylation, or any other effective contacting means. Since no invention is claimed in the contacting means per se it will not be described in further detail.

The effluent from the first reactor is withdrawn by line **17** through a cooler **18** (although such cooler may not be necessary) and introduced into settler **19** which may operate at substantially conversion pressure but at a temperature sufficiently low to insure the separation of the hydrogen fluoride phase as a lower layer, e. g. a temperature in the range of about 100 to 250° F. It should be understood that more than one settler may be employed and that separation may first be effected at substantially reaction temperature and the hydrogen fluoride phase from this high temperature separation may be subsequently separated at a lower temperature. The separated hydrogen fluoride layer is withdrawn from the settler by line **20** and a portion of it may be recycled by line **21** and pump **22** to reactor inlet line **12** in order to decrease the amount of hydrogen fluoride that must be supplied from storage tank **14** and to maintain in reactor **13** about 25 to 50% or more, preferably at least about 30% by weight of tar (hydrogen fluoride soluble hydrocarbons) based on the hydrogen fluoride in the reactor. At the beginning of the operation all of the hydrogen fluoride-tar material withdrawn through line **20** may thus be recycled to the reactor for the dual purpose of improving the catalyst effectiveness in the reactor and for degrading said tar and obtaining maximum yields of hydrogen fluoride-insoluble hydrocarbons such as gas oil therefrom. When desired equilibrium conditions are reached and there is for example about 40% by weight of tar in reactor **13** based on hydrogen fluoride therein, a sufficient amount of the liquid withdrawn through line **20** is introduced through pressure reducing valve **23** into tar stripper **24** to maintain the substantially constant amount of tar in the reactor and to remove any excess tar.

The excess tar may be simply stripped of hydrogen fluoride by heating means **25** in the base of a conventional stripping tower so that a first tar is removed by line **26** which tar may be characterized by a specific gravity of about .98 and an iodine number of about 200 more or less. The conversion in reactor **13** effects a condensation and removal of most of the aromatic compounds as well as sulfur compounds so that the tar removed through line **26** will contain large amounts of condensed aromatics and sulfur. Such tar may be subjected to a coking operation for obtaining additional low boiling hydrocarbons; the coking may be effected in the presence of hydrogen fluoride by passing liquid withdrawn from line **20** through line **27** and heater **28** (which may be a series of coils to provide the necessary holding time) and then flashed into tar or coke stripper **24** for hydrogen fluoride removal. If such a coking operation is employed, butane or other gas may be introduced at the base of tower **24** for stripping and removing hydrogen fluoride from coke particles and for providing a supporting and fluidizing medium so that the solids may be removed in fluidized condition through line **26**. In either case the hydrogen fluoride and any light hydrocarbons which may be associated therewith are withdrawn overhead from the tar stripper through line **29** to product stripper **30**.

The hydrocarbon phase in settler **19** flows over baffle **31** and is withdrawn through line **32**. The material thus withdrawn consists chiefly of substantially aromatic-free gas oil and perhaps a small amount of gasoline-boiling-range components containing dissolved hydrogen fluoride. The withdrawn stream of these materials may be introduced by lines **33** and **29** to product stripper **30** or may be introduced by lines **34** and **35** to second reactor **36**. If it is introduced into the product stripper **30** via lines **33** and **29** the dissolved hydrogen fluoride is removed therefrom by heater **37** and/or stripping gas introduced through line **38** and the hydrogen fluoride-free products are withdrawn by line **39** to fractionating system diagrammatically illustrated by tower **40**, wherein a normally gaseous stream containing butanes is withdrawn through line **41**, a light naphtha stream through line **42**, a heavy naphtha stream through line **43** and a gas oil stream through line **44**. The gas oil stream or at least a substantial portion thereof may then be returned by pump **45** and lines **46** and **35** to second reactor **36**. Thus in either type of operation a substantially aromatic-free gas oil produced in first reactor **13** is subsequently charged to second reactor **36**. The substantially aromatic-free gas oil produced in our process or a fraction thereof is useful per se as a superior Diesel fuel. Also such gas oil is particularly suitable as a charging stock for catalytic cracking with solid catalysts of the silica alumina or silica magnesia type in the systems and under the conditions generally known to the art in fixed bed (Houdry), moving bed (Thermofor Catalytic Cracking) or powdered catalyst (Fluid) processes; this particular gas oil is not only remarkably amenable to such cracking processes but it can be processed with less carbon deposition than would otherwise be obtained. This subject matter is claimed in our copending application Ser. No. 168,112, filed July 14, 1950, as a continuation-in-part of the present application and also as a continuation-in-part of our copending application Ser. No. 718,038, filed December 23, 1946.

We control the amount of gasoline boiling range non-condensable aromatics introduced into the second reactor by passing through line **33** controlled amounts of the stream from line **32** to stripper **30** and thence by line **39** to fractionator **40** where any mononuclear aromatics of gasoline boiling range, formed by scission of side chains from aromatic nuclei in the first reactor, are removed as a part of the naphtha stream. The remainder of the stream in line **32** is sent directly by lines **34** and **35** to the second reactor. This proportioning of the stream in line **32** keeps the amount of aromatics, which tend to inhibit cracking in the second reactor, at a desirably low figure, that is, about 0.05 to 5% or less.

Hydrogen fluoride is withdrawn from storage tank **14** and introduced by pump **47** and line **48** to line **35** and second reactor **36**, the amount of hydrogen fluoride thus introduced being such that the total stream entering the second reactor contains about 10% to 400%, preferably about 50% to 200% by volume based on total gas oil (or gas oil plus gasoline) charged thereto. The second reactor may be of the same type as the first reactor, although it may be somewhat smaller in size. Conversion conditions in the second reactor **36** may be more severe than those in the first reactor **13**, particularly if aromatics such as benzene of the gasoline boiling range are included in the charge. The temperature in reactor **36** should be in the range of 250° to 500° F., preferably 300° to 400° or about 350° F. The time of contact should be relatively short, i. e. within the range of about 2 to 60 minutes, preferably 2 to 20 minutes, for example about 5 to 15 minutes. The weight space velocity may be about .5 to 5 or preferably about 1 to 2 parts by weight of oil charged per hour per part of hydrogen fluoride in the conversion zone. The reaction is primarily cracking and hydrogen transfer for production of isobutane, gasoline, and/or Diesel fuel and a valuable tar.

The product stream leaves the second reactor through line **49** and passes through cooler **50** to settler **51** wherein a hydrogen fluoride-tar phase separates out as a lower layer and is withdrawn through line **52**. At the beginning of the operation, all of the liquid withdrawn through line **52** may be recycled by line **53** and pump **54** to line **35** and reactor **36** until the total amount of tar in the second reactor is within the range of about 15% to 40%, or preferably about 25%, by weight based on the hydrogen fluoride contained in the second reactor. Thereafter, the amount of material recycled through line **53** is just sufficient to maintain the tar ratio in the reactor substantially constant, and the excess tar is introduced by line **55** to tar stripper **56** which is provided with a suitable heater **57** for removing the hydrogen fluoride. This tar stripper **56** like tar stripper **24** may be operated at a temperature in the range of 350 to 550° F. and at a relatively low pressure of the order of about 5 to 50 pounds per square inch gage. An alternative method of operation, designed to increase the yield and improve the drying oil properties of the tar, is to operate the second reactor on a once-through basis with respect to tar.

The substantially hydrogen fluoride-free second tar withdrawn through line **58** is quite different in character from the first tar withdrawn through line **26**. The second tar may have a specific gravity of approximately .90 to .94 and an iodine number of about 250 to 350 or more. It does not contain appreciable amounts of condensed aromatics or sulfur, but is a highly unsaturated polyene material having drying properties and is useful in the preparation of paints, coating materials, and the manufacture of synthetic plastics and resins.

The overhead from tar stripper **56** is passed by line **59** to product stripper **30**. The upper hydrocarbon layer from settler **51** passes over baffle **60** and is withdrawn through line **61** to line **59** and product stripper **30**. The product stripper **30** is operated under such conditions that substantially all of the HF is removed overhead as a butane azeotrope, the overhead stream passing through line **62** and cooler **63** to separator **64** which may operate at condenser water temperature, preferably below 100° F. The relatively pure hydrogen fluoride which separates out as a lower layer is introduced by line **65** into storage tank **14**, any required makeup hydrogen fluoride being introduced through line **66**.

Butane (chiefly isobutane) flows over baffle **67** and is withdrawn by pump **68**. A part of this butane may be introduced at a low point in stripper **30** by line **38** as hereinabove described. The rest of the withdrawn butane stream may pass by line **69**, line **70**, and line **12** to first reactor **13** in order to facilitate tar degradation. At least a portion of the butane may be passed by lines **69**, **71**, and **35** into second reactor **36** wherein it may serve to prevent excessive gas production. Should it be required to vent any gases lighter than butane from the system, such gases may be removed from the top of settler **64** through line **72**; if and when such venting is necessary the vented gases may be scrubbed with tar, e. g. from line **26**, in order to remove the last traces of hydrogen fluoride from the vented gases and the hydrogen fluoride-containing tar may then be returned to first reactor **13**.

In the example hereinabove described, it will be noted that hydrocarbons from both tar strippers and from at least one of the product settlers are all introduced into one and the same stripper **30** and the butanes may be returned if desired from settler **64** to first reactor **13**. An alternative procedure is to operate settler **19** at a sufficiently low temperature and pressure so that at least a portion of the overhead from tower **30** may be introduced into settler **19**. Similarly by operating settler **51** at sufficiently low temperature and pressure, at least a portion of the overhead from product stripper **30** may be introduced thereto. An advantage of the system illustrated in the drawing is that settlers **19** and **51** may be operated at substantially conversion pressure, thus minimizing, if not entirely eliminating, the pumping required for recycle through lines **20** and **52** respectively. The system illustrated in the drawing also provides for the removal of net butane production from the base of product stripper **30** since the azeotropic distillation of hydrogen fluoride from products in stripper **30** will permit the removal of the net butane production with the bottoms stream while substantially all the hydrogen fluoride is taken overhead as a butane azeotrope.

While we have described a specific example of the invention in considerable detail, it should be understood that the invention is not limited to the specific system or conditions therein described since many alternative arrangements and operating conditions will be readily apparent from the above description to those skilled in the art. Promoters such as boron trifluoride may be employed to enhance the activity of the catalyst and such promoters are particularly desirable when it is desired to effect the cracking of naphthenes. Engineering details such as valves, pumps, heat exchangers, etc. have been largely omitted from the schematic drawings and conventional refining methods are to be employed for fractionation and stripping where such operations are schematically illustrated in the drawings.

We claim:

1. The method of obtaining valuable products from a hydrocarbon charging stock which is higher boiling than gasoline and which contains substantial amounts of polycyclic aromatics which are insoluble in hydrogen fluoride but which are condensable in the presence of hydrogen fluoride into higher molecular weight hydrogen fluoride soluble hydrocarbons with liberation of hydrogen, which method comprises treating said charging stock with a catalyst consisting essentially of hydrogen fluoride in a first conversion zone under conditions for effecting intermolecular chemical condensation of said polycyclic aromatic hydrocarbons into hydrogen fluoride-soluble condensed aromatics of higher molecular weight with simultaneous liberation of hydrogen, separating the condensed polycyclic aromatics and the hydrogen fluoride in which they are dissolved from hydrogen fluoride-insoluble hydrocarbons consisting essentially of a gas oil which is relatively free from condensable aromatics, subsequently contacting said gas oil with a catalyst consisting essentially of hydrogen fluoride under conditions for converting said gas oil into hydrocarbons of the gasoline boiling range and a high boiling, highly olefinic, hydrogen-fluoride soluble product, substantially free from condensed aromatics, separating the olefinic product and the hydrogen fluoride in which it is dissolved from hydrocarbon products insoluble in hydrogen fluoride and separately removing hydrogen fluoride associated, respectively, with the condensed polycyclic aromatic material, the highly olefinic product and the hydrocarbon products insoluble in hydrogen fluoride.

2. The method of claim 1 wherein a small amount, but less than 5%, of hydrocarbons of the gasoline boiling range is produced as well as gas oil in the first conversion zone, which includes the further step of separating said gasoline boiling range hydrocarbons from said gas oil before said gas oil is introduced into said second conversion zone.

3. The method of claim 1 which includes the step of introducing directly into the second conversion zone substantially all of the hydrogen fluoride insoluble products from the first conversion zone.

4. The method of treating a hydrocarbon charging stock which is higher boiling than gasoline and which contains substantial amounts of polycyclic aromatics which are insoluble in hydrogen fluoride but which are condensable in the presence of hydrogen fluoride into higher molecular weight hydrogen fluoride soluble hydrocarbons with liberation of hydrogen, which method comprises reacting said charging stock in a first conversion zone under aromatic condensation conditions at a temperature in the range of 200 to 375° F. at a pressure sufficient to maintain liquid phase conversion conditions and in the range of 250 to 1000 pounds per square inch and for a time of contact within the range of 20 to 200 minutes while introducing about 10 to 300% by volume of hydrogen fluoride per volume of hydrocarbon introduced into said first conversion zone; separating hydrogen fluoride and tar from products including a gas oil portion leaving the first conversion zone; subsequently contacting at least the gas oil portion of said products with a catalyst consisting essentially of hydrogen fluoride in a second conversion zone under cracking conditions including a temperature in the range of 250 to 500° F., a pressure sufficient to maintain liquid phase conversion conditions, a catalyst-to-oil weight ratio in the range of .5:1 to 5:1 and a contact time in the range of 2 to 60 minutes; separating a second tar from hydrogen fluoride insoluble products produced in the second conversion zone; separately stripping the two removed tars, and stripping at least the hydrogen fluoride insoluble products from the second conversion zone in order to remove hydrogen fluoride therefrom; and recovering hydrocarbons of the gasoline boiling range from stripped products.

5. The method of converting a high boiling hydrocarbon charging stock containing chemically condensable polycyclic aromatics chiefly into three main products, namely, a high specific gravity tar, a lower specific gravity high boiling highly olefinic product substantially free from condensed aromatics, and gasoline boiling range hydrocarbons, which method comprises treating said charging stock with a catalyst consisting essentially of hydrogen fluoride under conditions for effecting condensation of condensable aromatics into higher molecular weight hydrocarbons with liberation of hydrogen, separating from the reaction products a hydrogen fluoride layer containing said condensed aromatics from a hydrogen fluoride insoluble fraction, stripping hydrogen fluoride from said condensed aromatics and returning said hydrogen fluoride to the system, mixing additional catalyst consisting essentially of hydrogen fluoride with the hydrogen fluoride insoluble layer and contacting said mixture at a temperature of at least about 300° F., at a pressure sufficient to maintain liquid phase conversion conditions with a hydrogen fluoride-to-oil weight ratio of about .5:1 to 5:1 for a period of about 2 to 20 minutes to effect a conversion into low boiling paraffinic hydrocarbons and high boiling olefinic hydrocarbons, the latter being associated with the hydrogen fluoride, separating the paraffinic hydrocarbons from the hydrogen fluoride-olefinic hydrocarbon mixture, removing hydrogen fluoride from the latter to produce a high boiling highly olefinic product substantially free from hydrogen fluoride and stripping hydrogen fluoride from the paraffinic hydrocarbons.

6. The method of obtaining valuable products from a hydrocarbon charging stock which is higher boiling than gasoline and which contains substantial amounts of polycyclic aromatics which are insoluble in hydrogen fluoride but which are condensable in the presence of hydrogen fluoride into higher molecular weight hydrocarbons with liberation of hydrogen, which method comprises treating said charging stock with a catalyst consisting essentially of hydrogen fluoride in a first conversion zone under conditions for effecting intermolecular chemical condensation of said polycyclic aromatic hydrocarbons into hydrogen fluoride-soluble condensed aromatic compounds of higher molecular weight with simultaneous liberation of hydrogen, separating the condensed aromatic compounds, together with the hydrogen fluoride in which they are dissolved, from hydrogen fluoride-insoluble hydrocarbons consisting essentially of a gas oil which is relatively free from condensable aromatics, subsequently contacting said gas oil with a cracking catalyst which consists essentially of hydrogen fluoride under conditions for effecting as the predominant reaction a conversion of said gas oil into hydrocarbons of the gasoline boiling

range and separating said last named hydrocarbons from higher boiling and lower boiling components.

7. The method of claim 6 wherein the first conversion zone is maintained at a temperature in the range of about 200° F. to 375° F., under a pressure in the range of about 250 to 1000 pounds per square inch and for a time of contact in the range of about 20 to 200 minutes with an amount of hydrogen fluoride in the range of about 10 to 300 volume per cent based on stock charged.

8. The method of claim 6 wherein the gas oil contains about .05 to 5 per cent of aromatics.

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