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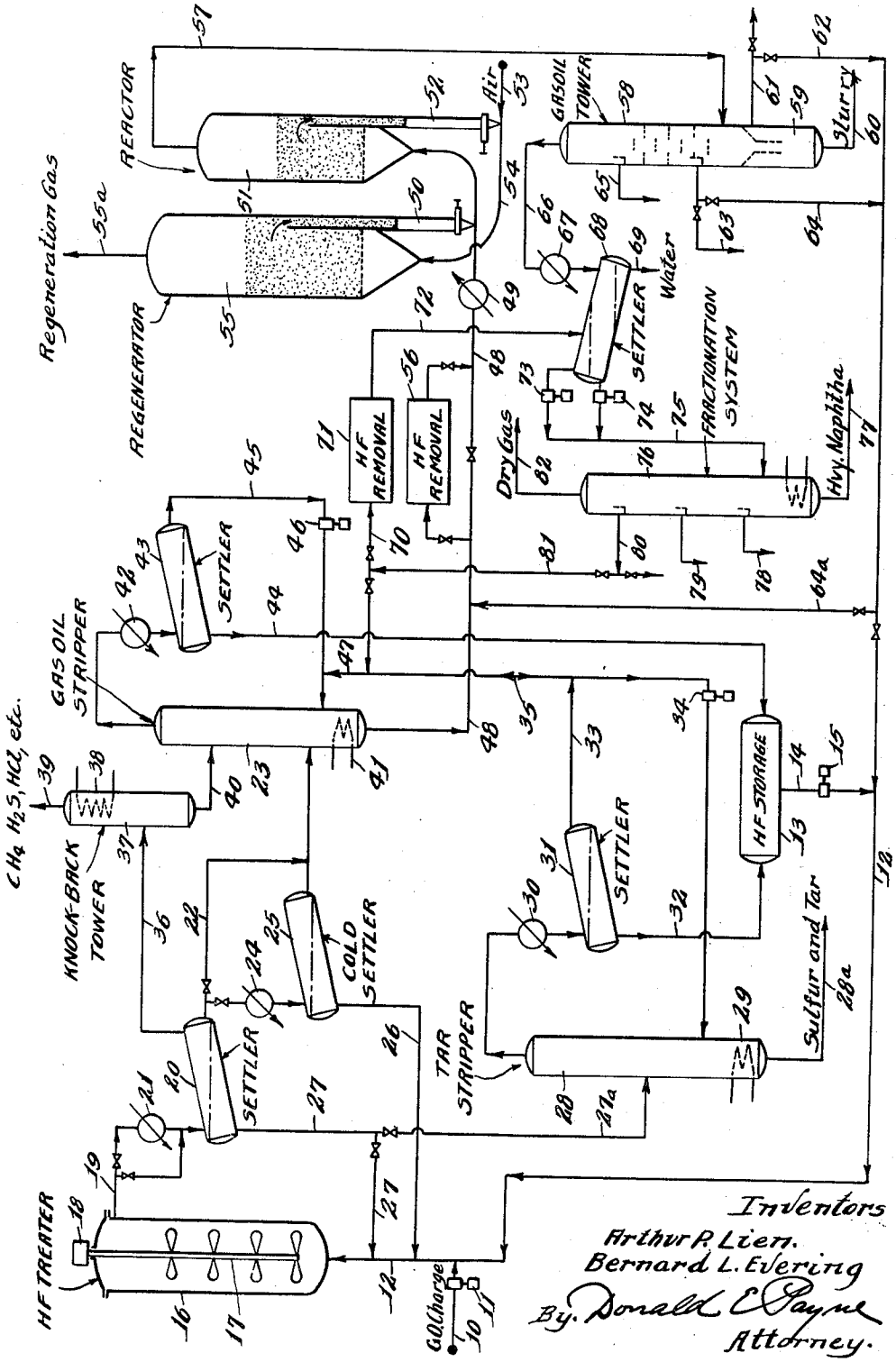

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COMBINATION HF TREATING CATALYTIC CRACKING PROCESS

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This invention relates to a process of producing high quality motor fuel from heavier-than-gasoline hydrocarbons by a new and improved combination of HF treating and catalytic cracking and it pertains more particularly to processes wherein the catalytic cracking is effected by silica alumina type catalysts. This is a continuation-in-part of our copending application Ser. No. 718,038, now U. S. 2,525,812, and also Ser. No. 760,062, now U. S. 2,525,811.

An object of the invention is to provide a method and means for obtaining maximum yields of high quality motor fuel from catalytic cracking charging stocks containing large amounts of sulfur compounds, objectionable polycyclic hydrocarbons, and/or other components which are not efficiently handled by catalytic cracking processes and/or which may be detrimental in catalytic cracking systems. A further object is to improve the effectiveness and efficiency of catalytic cracking systems employing silica alumina type catalysts, i. e. to obtain increased motor fuel production, decreased coke formation and superior product quality. A still further object is to provide a process wherein the catalyst used in the second step is promoted in situ by traces of treating agent employed in the first step so that the expense of removing such traces of treating agent is largely avoided so that the combination of steps produces results heretofore unobtainable in the art. Other objects will be apparent as the detailed description of the invention proceeds.

Briefly, the invention contemplates the production of high quality motor fuel from heavier-than-gasoline charging stocks which have heretofore presented serious problems to the refining industry. For example, a West Texas gas oil may contain 2 to 3% of sulfur and when such gas oil is charged to a conventional catalytic cracking process the finished gasoline will contain about .3% sulfur and the catalytic gas oil about 1½ to 2% of sulfur. By giving gas oil a preliminary treatment with HF and then subjecting it to substantially the same conditions of catalytic cracking, we obtain a marked and substantial increase in gasoline production per pass and a marked improvement in gasoline quality, the gasoline containing only about one-tenth as much sulfur and being characterized by a higher A. P. I. gravity, a lower bromine number, and a greatly increased responsiveness to lead tetraethyl. In spite of treating losses in the initial step the overall yield of gasoline may be as high as the yield that would be obtained from untreated charging stock. The effective catalytic cracking capacity is markedly increased. The treating step itself eliminates sulfur and other undesirable components and it may produce a utilizable by-product tar from material which would otherwise be deposited as coke on the catalyst in the cracking step. Furthermore, the treating step may remove organic and/or inorganic material from the charge that would otherwise contaminate or deactivate the catalyst and lead to lower conversion, undesirable product distribution, excessive gas and coke formation, etc.

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The initial step of the process is a light treatment with HF, i. e. a treatment under such mild conditions as to avoid any substantial amount of cracking but which is sufficient to eliminate the bulk of the sulfur and other undesirable components in the gas oil. A low temperature treatment is described and claimed in U. S. 2,525,812. In the present invention, the initial treatment is mild by virtue of the correlation of the time of contact, temperature and amount of HF which is preferably in the range of about 5 to 50% by weight, although amounts may be as high as 200 to 300% by weight. The temperature should be above 150° F. and may be as high as 400° F. or more so that at least some of the sulfur can be removed as H_2S.

The high temperature treating step results in intermolecular chemical condensation of certain of the aromatic hydrocarbons to produce HF-soluble polynuclear aromatic hydrocarbons which are extracted from saturated hydrocarbons, the HF serving both as a catalyst in the chemical reaction and as a solvent for effecting the extraction. Many gas oils and other hydrocarbon charging stocks which are higher boiling than gasoline contain 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 (note U. S. 2,525,810 and 2,525,809).

The treated charging stock, which may be of the distillate fuel or gas oil boiling range and which preferably contains not more than about 5% of hydrocarbons of the gasoline boiling range, may be separated from gases or low boiling components as well as from the bulk of HF (extract phase) in a settling zone wherein the undesirable polycyclic hydrocarbons and sulfur compounds associated therewith are withdrawn in the bottom HF layer and the gases, including

liberated hydrogen and H_2S, are taken overhead. The dissolved HF in the treated charge may be removed by a simple stripping operation and the charge, which contains only traces of HF, is then directly introduced into a catalytic cracking reactor containing a solid catalyst of the silica alumina type and operated under conditions for converting the charge to motor fuel. By the expression "silica alumina type" we mean to include the so-called clay type or natural catalyst such as acid treated montmorillonite clay, synthetic or gel type silica alumina catalysts, silica magnesia catalysts, silica alumina magnesia catalysts, catalysts prepared from blast furnace slag, etc., either in the presence or absence of additional catalyst components and/or activators. In other words, the cracking catalysts may be of the type referred to by Webb and Ehrhardt in "Properties of Cracking Catalysts," Petroleum Processing, January 1947.

Traces of HF remaining from the initial treatment of our charging stock may effect an in situ activation of the cracking catalyst so that the yield per pass of gasoline is substantially increased. At any rate, the net result of our combined process is the production of remarkably high quality gasoline of low sulfur content, an increase in the capacity of the cracking unit, the substantial elimination of the expense of defluorinating and a net increase in production of valuable by-product materials, the increase in gasoline production made possible by the treating step substantially balancing "losses" due to by-product removal in the treating step.

The invention will be more clearly understood from the following description read in conjunction with the accompanying drawing which is a schematic flow diagram illustrating a practical application of our invention.

While the invention is applicable to any heavier-than-gasoline hydrocarbon charging stock, up to and including reduced crudes, which contains components such as large amounts of sulfur, condensable aromatics, etc., which are deleterious to or are ineffectively handled in a catalytic cracking system, it will be described in connection with the treatment of a heavy, high sulfur gas oil. Such high sulfur gas oil charging stock is introduced through line **10** by pump **11** to line **12** where it meets HF from storage tank **13**, line **14** and pump **15**. Knot hole mixers or other mixing means may be employed for attaining intimate contact of the two streams in line **12** and/or said intimate contact may be obtained in treating chamber **16** by mechanical stirrer **17** driven by motor **18**. Instead of a stirred reactor, we may employ a packed or unpacked tower with mixing orifices, a circulating system of the type commonly employed for effecting sulfuric acid alkylation or any other effective contacting means. Instead of the illustrated concurrent flow through the reactor, the HF may be introduced at the top thereof while the charge is introduced at the base, such countercurrent treatment being particularly desirable in towers where the treating is to be effected in a countercurrent manner and the separation is effected in the tower itself, the treated material being in that case taken overhead while the HF and impurities are withdrawn from the base of the tower. In the system illustrated in the drawing, a mixture of HF and treated charging stock is withdrawn from vessel **16** by line **19** to settler **20**, a cooler **21** being employed if the treating is at very high temperature.

The treating should be effected under relatively mild conditions so that sulfur and/or other undesirable components may be removed from the charging stock without materially changing its boiling range, i. e. without effecting substantial amounts of cracking. By effecting the treatment at a temperature in the range of 150° to 400° F. or more, at least a part of the sulfur compounds are converted into H_2S in the treating step. The preferred temperature of treatment is in the range of 200 to 375° F. with best results being obtained at temperatures of about 250° to 330° F. The treating is effected 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. At the highest treating temperatures the time of contact should be sufficiently short, substantially less than 10 minutes, and/or the amount of HF should be sufficiently low, e. g. 5 to 50 volume per cent HF, so that no substantial cracking of the charging stock takes place. At temperatures of the order of 200 to 330° F., 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). An hour's contact time at 330° F. is adequate. The treating conditions should in any case be such as to effect condensation of condensable aromatics with removal of sulfur so that hydrogen fluoride-insoluble material will be chiefly a parafinic 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 methyl benzenes.

If settler **20** is operated at cooling water temperature, the treated hydrocarbons which separate as an upper layer may be withdrawn directly through line **22** to gas oil stripper **23**. Settler **20** may, however, operate at a higher temperature in the range of about 100 to 250° F. and in such cases the treated gas oil may be withdrawn through cooler **24** and cold settler **25** for throwing out additional amounts of HF which may then be recycled directly by line **26**, thereby diminishing the load on the stripper tower **23**.

The HF layer from settler **20** is withdrawn from line **27** and a part of it may be recycled to treater **16** via line **12**. At the beginning of the treating operation all of the hydrogen fluoride soluble tarry material withdrawn from the settlers **20** and **25** may thus be recycled to the reactor for the dual purpose of improving the catalyst effectiveness in the reactor and for degrading the tar dissolved therein and obtaining maximum yields of hydrogen fluoride-insoluble hydrocarbons, such as gas oil therefrom. When equilibrium conditions are established, there may be for example about 40% by weight of HF-soluble tar in reactor **16** based on hydrogen fluoride therein.

The net production of tar (condensed aromatics, sulfur compounds, etc. which are soluble in HF) is withdrawn in HF solution through line **27***a* to tar stripper **28** which is provided at its base with conventional heater or reboiler **29**. The tar and sulfur adducts with HF are decomposed by heating to 250–500° F. The overhead from this stripper is passed through condenser **30** to settler **31** in which the HF separates out as a lower liquid and is withdrawn through line **32** to storage tank **13**. The upper layer in settler **31** consists chiefly of light hydrocarbons and it may be recycled through line **33** by pump **34** to serve as a stripping oil in tower **28** by virtue of

azeotrope formation with HF, any deficiency or excess of light hydrocarbons being supplied to or removed from this circulating system through line 35.

Tar and sulfur compounds are withdrawn from the base of the stripper through line 28a and such tar may be utilized per se as a by-product or it may be subjected to coking or cracking to form additional amounts of gasoline.

The H_2S produced in the HF treating step is removed along with other gases from the top of settler 20 through line 36 to knock back tower 37 which is provided with cooling, scrubbing or reflux means 38 so that methane, H_2S, HCl (from desalting) and other fixed gases may be vented through line 39 while HF and condensible hydrocarbons are returned by line 40 to stripper 23.

Stripper 23 is provided with a suitable heater or reboiler 41 at its base and overhead from this stripper passes through condenser 42 to settler 43. Liquid HF accumulates in the bottom of this settler and is withdrawn through line 44 to storage tank 13. A light hydrocarbon is withdrawn from the upper part of the settler through line 45 and recycled by pump 46 to serve as a stripping gas in tower 23, any excess or deficiency of such light hydrocarbons being removed from or supplied to the system through line 47.

The stripped gas oil leaving the base of stripper 23 through line 48 may pass through a preheater 49, then pick up hot regenerated catalyst from the base of standpipe 50 and carry this catalyst into reactor 51. Spent catalyst from reactor 51 passes downwardly through standpipe 52, is picked up by air introduced in line 53 and conveyed thereby in line 54 to regenerator 55, regeneration gases being vented through line 55a. The fluid type catalytic cracking system thus briefly and diagrammatically represented is now well known to those skilled in the art and requires no detailed description. The catalyst-to-oil ratios employed may be in the range of 2:1 to 20:1 on a weight basis, the cracking temperature may be in the range of about 800 to 1000° F., e. g. about 900° F. and the weight space velocity may be in the range of about 0.2 to 20 pounds of oil charged per hour per pound of catalyst in the reactor. In other words, the cracking conditions may be approximately the same as those heretofore employed for conventional gas oil stocks although somewhat smaller amounts of catalyst cr higher throughputs may be obtained by virtue of the promoting effect of the residual amounts of HF which are introduced into the cracking system with the treated gas oil. While the fluid type catalytic cracking system has been illustrated in the drawing it should be understood that the invention is equally applicable to fixed bed systems and to moving bed systems. The catalyst itself is of the silica alumina type and may be either conventional Super Filtrol or a synthetic silica alumina catalyst of any type known to the art.

Apparently Super Filtrol and other silica alumina type cracking catalysts generally are markedly improved in their activity by treatment with HF, which perhaps results in the formation of aluminum fluosilicate. In our process this activation of the catalyst is particularly effective because it is produced in situ. The traces of HF remaining in the treated gas oil are thus effectively removed therefrom in the cracking operation and at the same time the effectiveness of the catalyst is increased so that higher conversions per pass are obtained with smaller amounts of carbon deposition on the catalyst. Usually the amount of HF introduced is so small that the make-up catalyst requirements in the cracking step are sufficient to take care of it. It some cases, however, it may be necessary or desirable to pass a portion of the treated gas oil through bauxite chambers or other HF removal means 56 (note U. S. Patent 2,391,149). Our invention minimizes the required HF removal and may entirely eliminate it.

The products from catalytic cracking reactor 51 pass by line 57 to tower 58 which may be provided with a settling section 59 at its base so that catalyst slurry may be returned through line 60 to the stream entering the reactor and decanted oil may be withdrawn through line 61 and either removed from the system or recycled through lines 62 and 12 to the HF treating step. Heavy gas oil may be withdrawn as a side stream through line 63, recycled by lines 64 and 12 to the HF treating step, and/or recycled by lines 64 and 64a to the catalytic cracking step. Cycle gas oil from this process is usually in most respects superior to the untreated original gas oil charge but if all of it is recycled through line 64a, a buildup in sulfur compounds or aromatics might result; at least a part of the gas oil stream should usually therefore either be withdrawn through line 63 or recycled through line 12 to the treating step in order to prevent any buildup of sulfur compounds or aromatics in the catalytic cracking step. A light gas oil stream may be withdrawn through line 65 and it likewise may be recycled either to the HF treating step or to the catalytic cracking step. Gasoline and lighter components are taken overhead through line 66 and condenser 67 to settler 68 from which any water from diluent steam in the cracking step or otherwise accumulated in the system may be withdrawn through 69. Any gasoline produced in the HF treating or tar cracking and taken overhead from strippers 23 or 28 may be passed via lines 35 or 47 through line 70, HF removal chambers 71 and line 72 to separator 68. Gases from this separator are compressed by compressor 73, liquid hydrocarbons are pumped by pump 74, and the combined stream is passed through line 75 to superatmospheric pressure fractionation system diagrammatically illustrated by tower 76 from which heavy naphtha is withdrawn through line 77, and one or more lighter naphtha streams through lines 78 and 79. A C_4 or C_3–C_4 stream may be withdrawn through line 80 and such butane or propane-butane mixtures may be introduced by line 81 and line 70 to supply any deficiency of stripping gas for towers 23 and 28 respectively. Dry gas is removed from the system through line 82. In actual practice of course a conventional absorber and stripper system may be employed instead of a simple tower but since this fractionation step per se forms no part of the claimed invention it will not be described in further detail.

From the above description it will be seen that we have accomplished the objects of our invention. The mild HF treating step removes sulfur compounds and/or polycyclic aromatics which are not readily amenable to cracking and makes possible the recovery of tar and sulfur compounds as utilizable by-products. This particular method of pretreating the catalytic cracking charging stock (coupled perhaps with traces of HF left in the treated charging stock) results in greatly increased cracking yields, substantially less carbon formation on the catalyst and an

improved cracked gasoline which is less olefinic, more amenable to improvement by lead tetraethyl and which contains only about one-tenth as much sulfur as would be obtained by the cracking of the same stock without the initial treating step. The catalytic cracking apparently concentrates the sulfur compounds in the cycle gas oil so that when this gas oil is recycled to the HF treating step still further amounts of sulfur can be eliminated from the system and kept out of the final gasoline products. In fact, gas oils produced by catalytic or thermal cracking (such as continuous pressure still gas oil, coke still gas oil, vis breaker gas oil, etc.) are particularly suitable as original charging stocks to our process because such gas oils usually contain large amounts of aromatics which are originally insoluble in HF but which are condensible to form HF-soluble polycyclic aromatics with liberation of hydrogen. Our process thus eliminates from such catalytic cracking charging stocks the components which are most detrimental and deleterious (polycyclic aromatics and sulfur compounds) with minimum treating losses and maximum ultimate production of high quality gasoline. The butane or propane-butane hydrocarbons produced in the catalytic cracking step serve as stripping gases and form HF azeotropes which facilitate HF removal from the treated gas oil and the tar respectively. Thus this new and improved unitary combination accomplishes results which have heretofore been unattainable in the cracking of low grade charging stocks and particularly those containing large amounts of sulfur.

While we have described in detail a specific example of our invention, many alternative modifications, procedures and operating conditions will be apparent from the above description to those skilled in the art. When salt bearing reduced crudes are employed the process will offer the additional advantage of salt removal. While hydrogen is liberated in the aromatic condensation reaction, it is not necessarily present in the off gases, since it may be consumed by reacting with sulfur compounds or by saturating olefins. No specific details as to structural materials and general safety precautions have been recited herein since those skilled in the art are familiar with the handling of HF in view of its commercial utilization in effecting alkylation.

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 at a temperature above 150° F. but not substantially above 400° F. 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 having a substantially reduced content of condensable aromatics, subsequently contacting said gas oil with a solid siliceous cracking catalyst under catalytic cracking conditions for converting said gas oil into hydrocarbons of the gasoline boiling range.

2. 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 at a temperature above 200° F. but not substantially above 375° F. under conditions for effecting intermolecular chemical condensation of said polycyclic aromatic hydrocarbons into hydrogen fluoride with the soluble condensed aromatic compounds of higher molecular weight with simultaneous liberation of hydrogen, separating the condensed aromatic compounds, together with 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 solid siliceous catalytic cracking catalyst 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.

3. The method of claim 2 wherein the first conversion zone is maintained under a pressure in the range of 250 to 1000 pounds per square inch and for a time of contact in the range of about 10 to 200 minutes with an amount of hydrogen fluoride in the range of about 10 to 200 volume per cent based on stock charged.

4. The method of claim 2 wherein the charging stock also contains substantial amounts of sulfur compounds, which method includes the further step of converting at least a part of the sulfur compounds to H_2S in the treating step and separating H_2S from liquid products.

5. The method of claim 2 which includes the step of recycling at least a part of said higher boiling components to the treating step.

6. The method of claim 2 wherein the original charging stock is a hydrocarbon fraction of the gas oil boiling range produced as a by-product in a cracking operation.

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