

May 5, 1959

K. K. KEARBY ET AL
HYDROCRACKING OF GAS OILS

2,885,346

Filed March 17, 1953

8 Sheets-Sheet 1

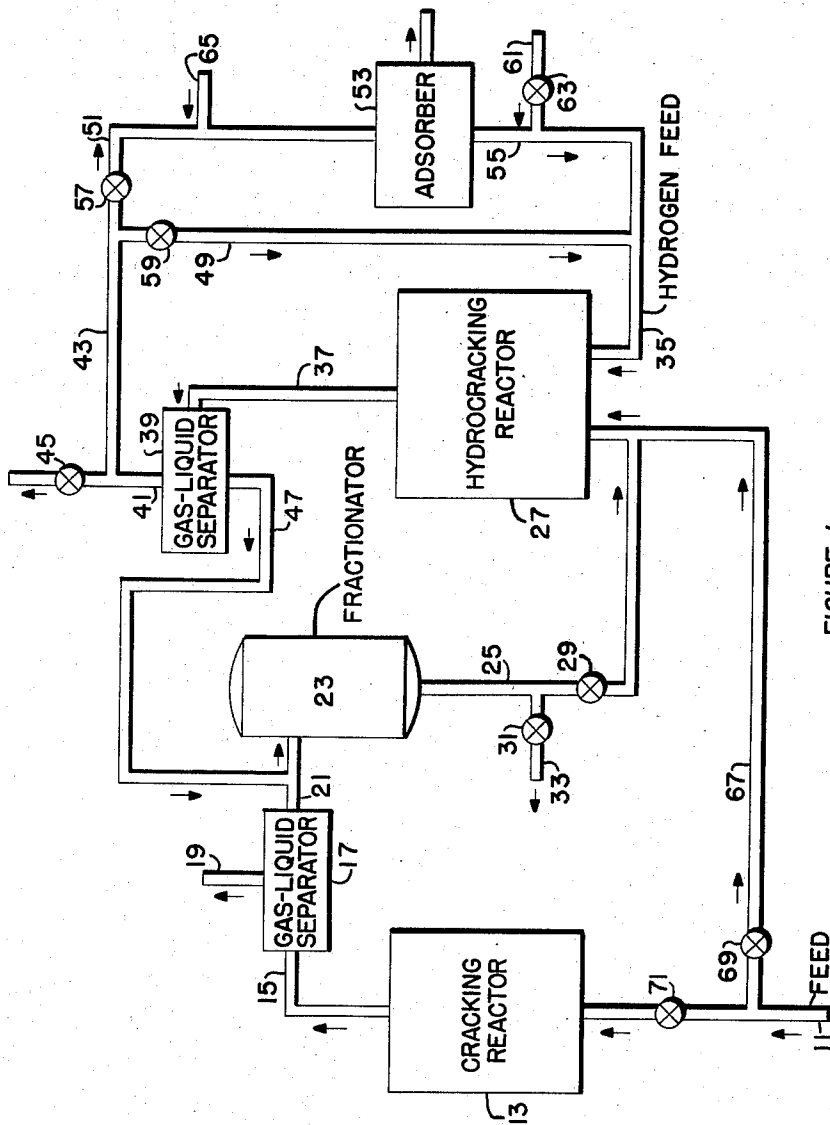


FIGURE-1

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8 Sheets-Sheet 2

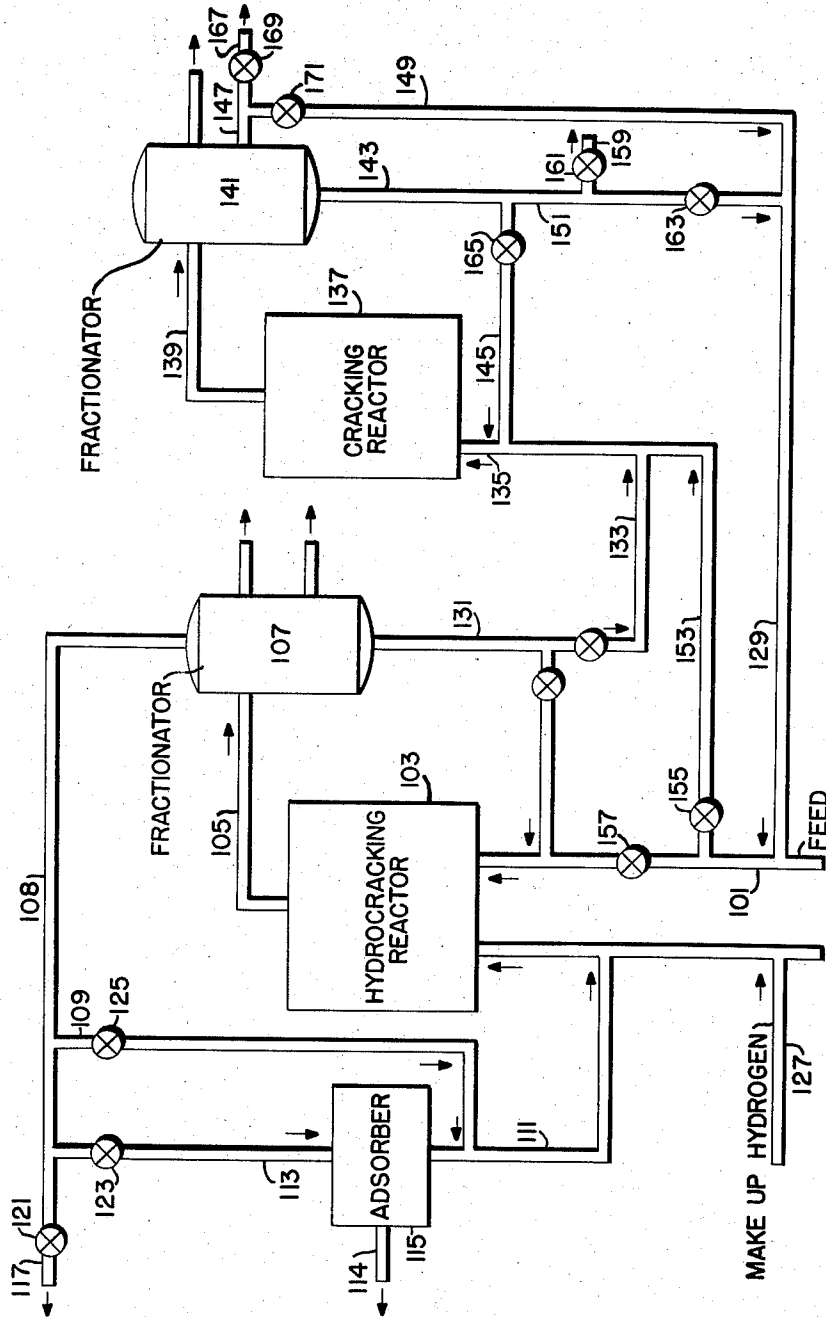


FIGURE-2

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8 Sheets-Sheet 3

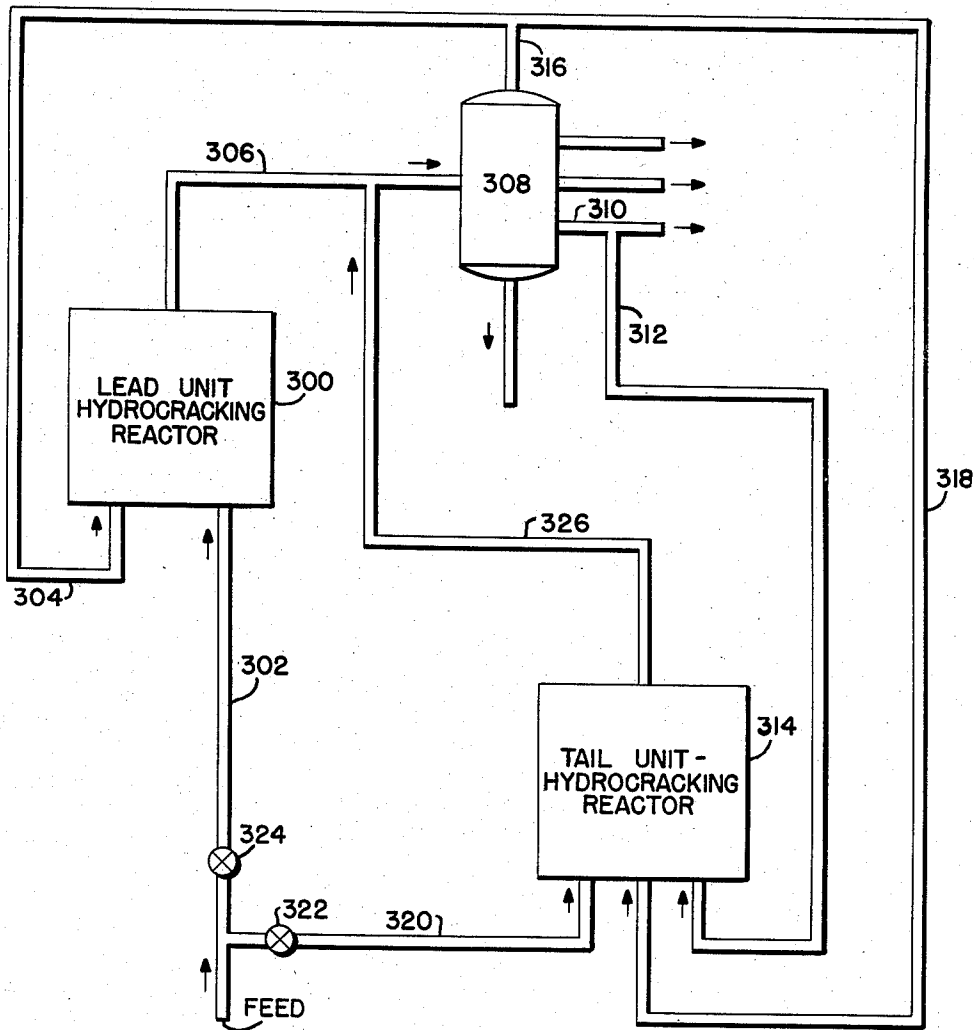


FIGURE-3

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8 Sheets-Sheet 4

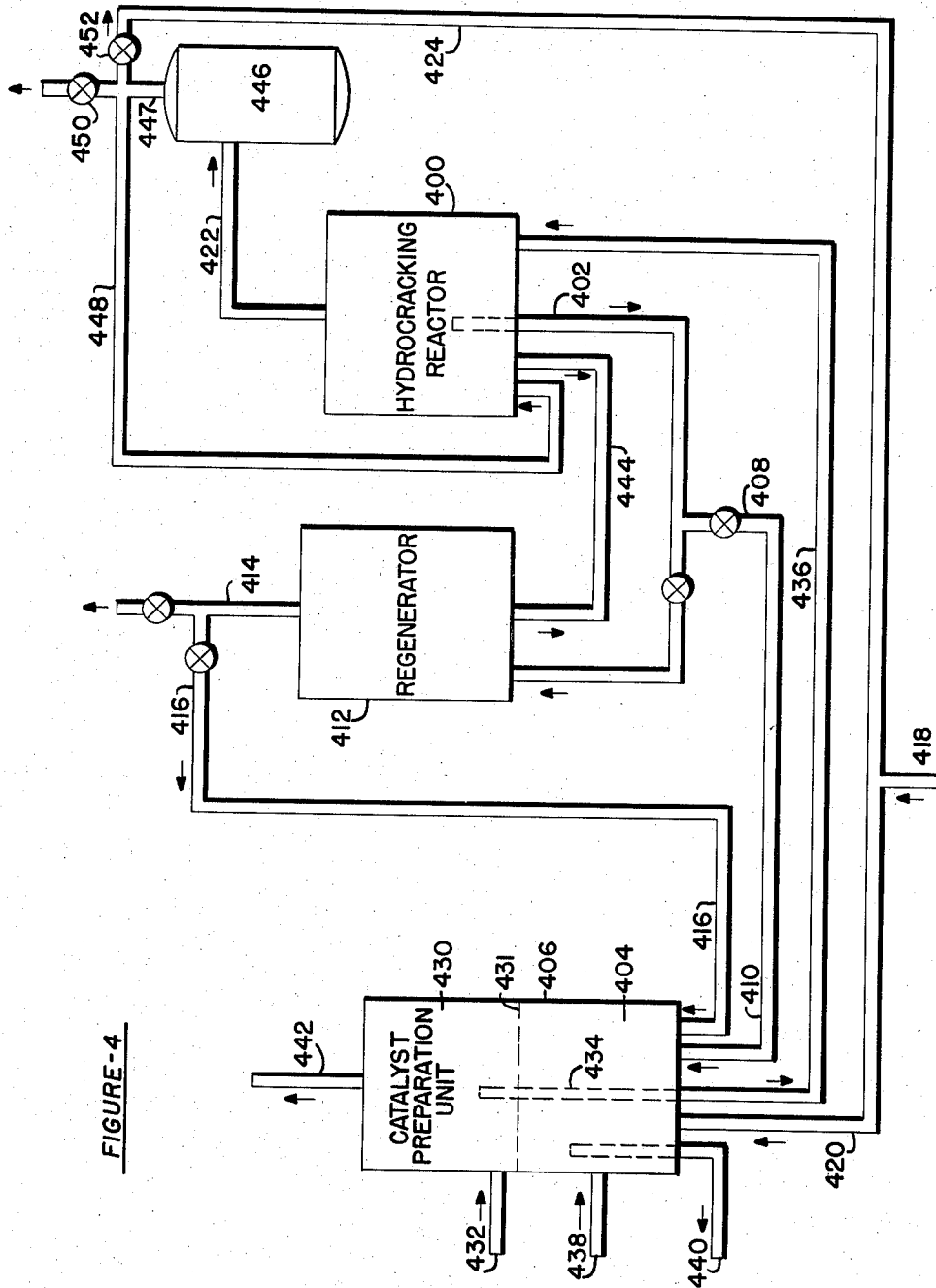


FIGURE-4

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8 Sheets-Sheet 5

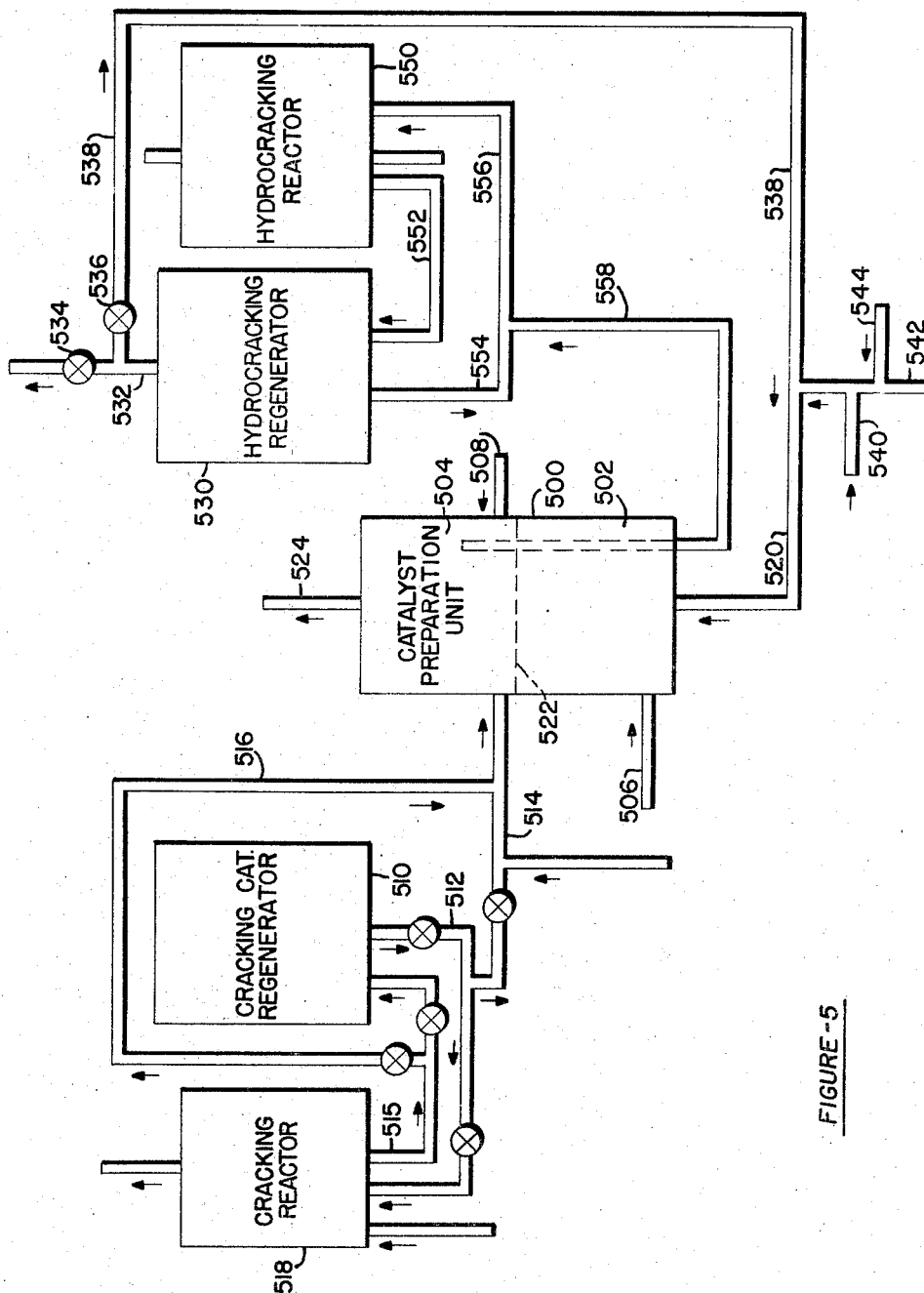


FIGURE -5

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8 Sheets-Sheet 6

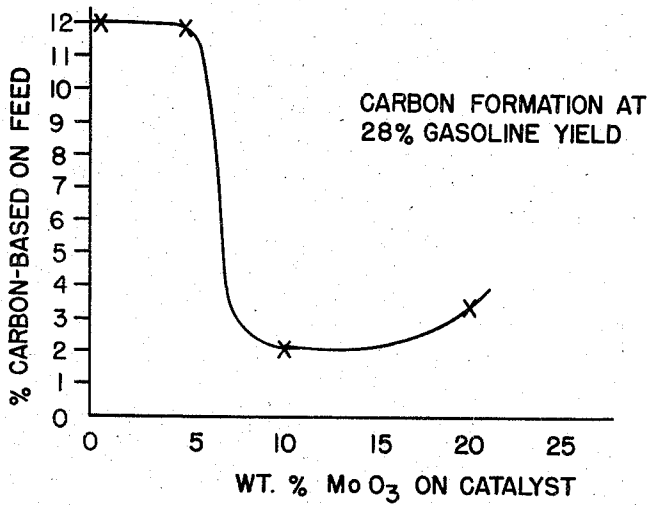


FIGURE-6

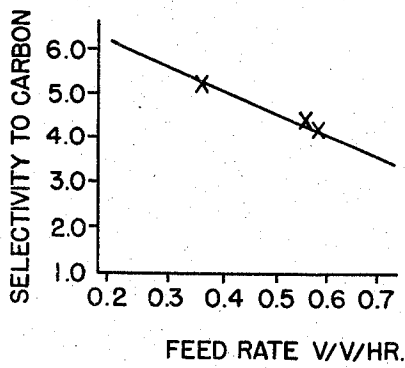


FIGURE-7

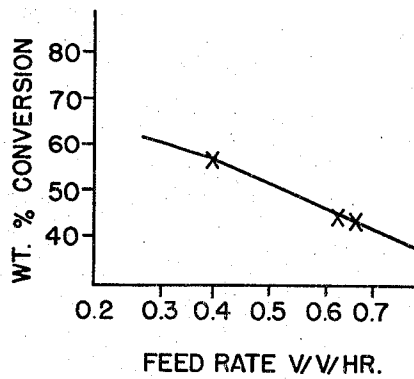


FIGURE-8

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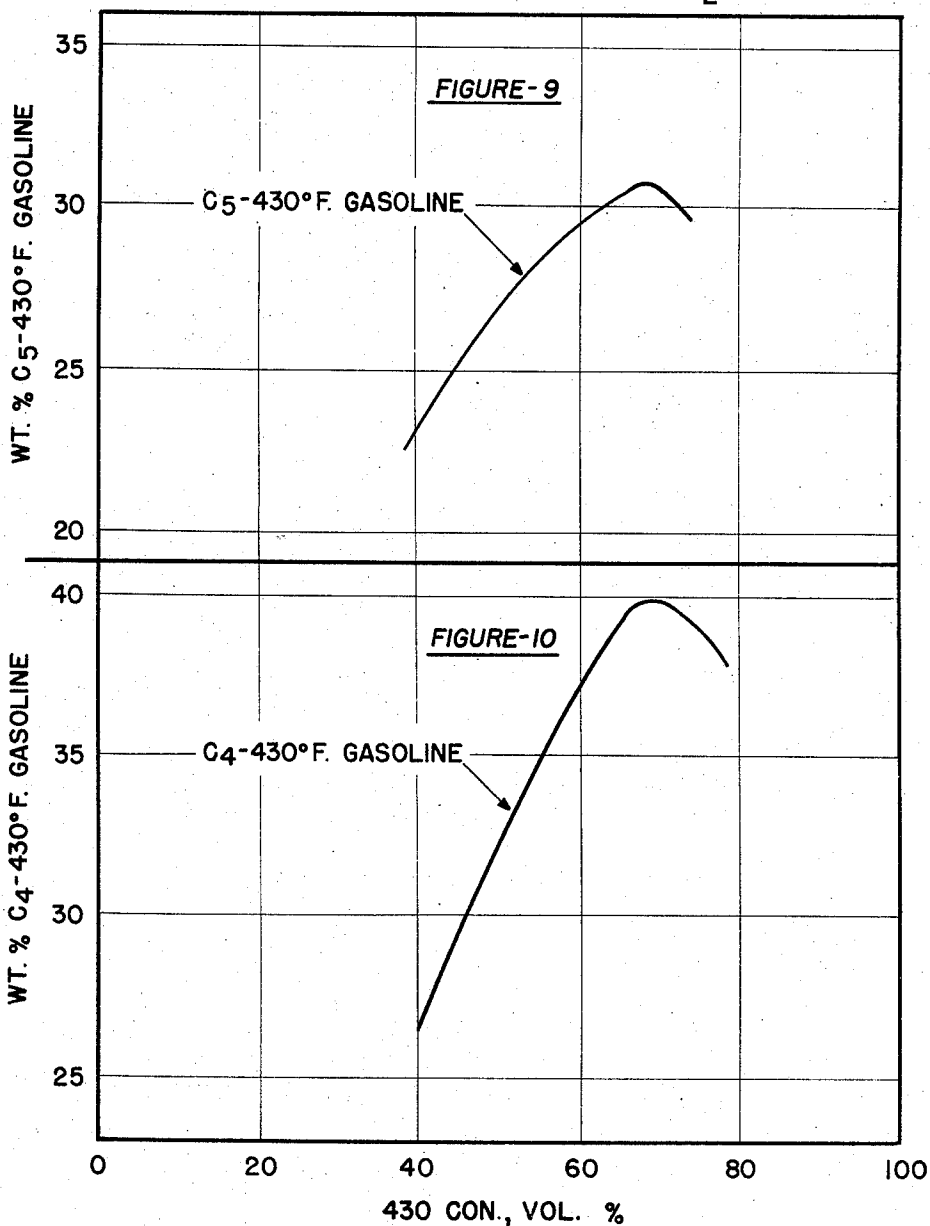
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HYDROCRACKING OF E.T.L.G.O.
100-500 psig; 1000-1070°F.; 3000-5000 CF H₂/Bbl. OIL



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HYDROCRACKING OF GAS OILS

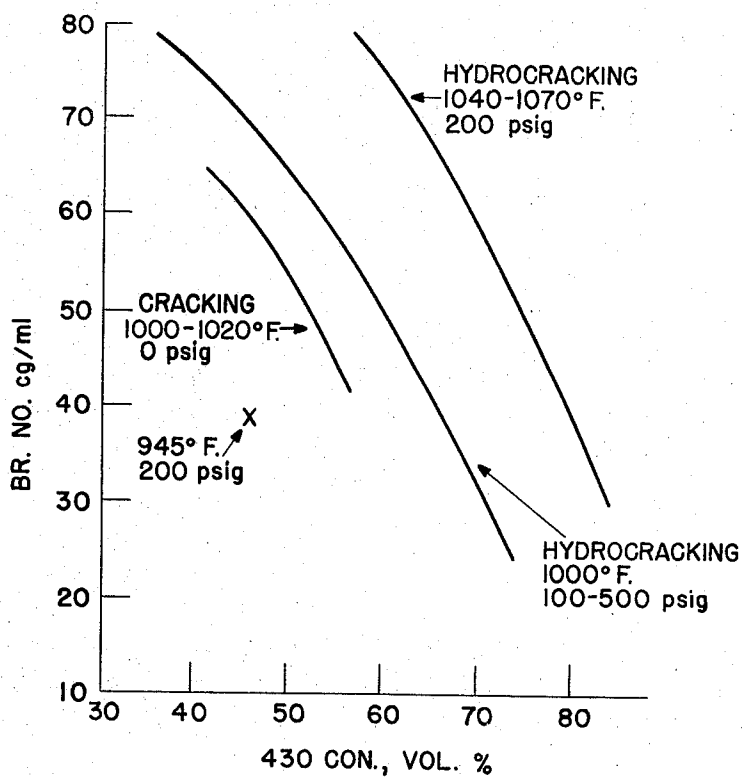
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FIGURE-II

EFFECT OF OPERATING VARIABLES ON OLEFINICITY



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HYDROCRACKING OF GAS OILS

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Application March 17, 1953, Serial No. 343,919

7 Claims. (Cl. 208—79)

The present invention relates to a new and improved hydrocracking process for hydrocarbons such as gas oils and other petroleum fractions heavier than naphtha. This process is designed to obtain high quality fuels of gasoline boiling range. The invention relates further to a process which secures good yields of high quality fuels accompanied by reduced production of coke and certain other degradation products as compared with more conventional refining operations. The invention is particularly applicable to hydrocarbon feed stocks of the general type mentioned above having high contents of naphthenes. It is not necessarily limited to the highly naphthenic stocks, however.

Gasoline, as the term is commonly used to define motor fuels, is commonly produced from petroleum by the following principal processes:

(1) By simple distillation or topping, which produces a "virgin" gasoline usually of rather highly saturated type, good volatility range, but rather low octane number. The products are largely non-branched paraffins in chemical composition.

(2) Thermal cracking of gas oils and heavier petroleum fractions to produce moderately branched olefinic motor fuels of reasonably good octane number.

(3) Catalytic cracking of gas oils and other petroleum fractions heavier than naphtha. These cracked products are usually rather highly unsaturated and of good octane number.

(4) Special synthesizing or reforming processes, usually applied to naphthas and lighter fractions, such as alkylation, isomerization, polymerization and aromatization, to obtain motor fuels of highly branched paraffinic type. These are frequently of relatively very high octane value.

Commercial motor fuels are usually obtained by blending together suitable proportions of two or more of the above products, adding special modifiers such as tetraethyl lead, etc., where desirable.

Of the foregoing, the catalytic cracking processes have received by far the greatest emphasis in recent years. By subjecting gas oil fractions of the 400° to 800° F. boiling range, for example, to catalytic cracking operations, motor fuel constituents of very good quality (high octane number) may be produced at moderate cost. Some of the special synthesizing or reforming techniques mentioned above are used to produce particular ingredients for special requirements (e.g. constituents for aviation fuels) but catalytic cracking has been used more widely for general fuels because of its efficiency and economy.

Under some conditions, however, catalytic cracking is not a preferable process. Modern cracking systems operating at or near atmospheric pressures require large and expensive apparatus and they tend to produce rather large proportions of coke and other degradation products. Moreover, cracking catalysts are easily poisoned and rendered ineffective by some commonly occurring elements. This requires constant or frequent catalyst replacement, resulting in high catalyst costs. Thus, with certain types of oils containing substantial proportions of certain

catalyst poisoning constituents, cracking catalysts are rapidly rendered ineffective. Also, catalytic cracking is not as effective in upgrading certain kinds of feed stocks, for example some of those of high naphthenes content, as in some other stocks.

In the prior art a number of suggestions have been for made combining the general functions of catalytic cracking of gas oils with hydrogenation or aromatization, using feed stocks of various types. Thus, it has been suggested that conventional cracking catalysts of the silica or alumina type might be modified by adding thereto hydrogenation or dehydrogenation catalysts of known types. Other prior art has suggested modifying alumina or silica catalysts by mixing or impregnating them with various salts and other catalytically active materials including, for example, the chlorides, oxides, sulfides, etc., or molybdenum and of various other metals. The use of an improved catalyst of this general type is one feature of the present invention.

In particular, however, the invention is based on the discovery that certain petroleum fractions which have been difficult to convert efficiently to motor fuels may be more effectively converted than hitherto by a careful and particular choice of operating conditions, catalyst, etc. For example, a gas oil fraction of 400 to 800° F. initial and final boiling points may be treated according to the present invention to produce motor fuels of exceptionally high quality. At the same time the process of this invention is accompanied by the production of remarkably small quantities of carbon or coke and by low production of certain other light end products, especially of C₄ and C₅ hydrocarbons. For example, a gas oil feed having the boiling range mentioned above and containing substantial proportions of naphthenes may be subjected to hydrocracking treatment in the presence of a special type of catalyst described below. Moderate pressures, preferably between 150 and 350 p.s.i.g. may be used and the gas oil fraction is converted in the presence of substantial proportions of hydrogen gas which is passed through the process at the rate of 3000 to 10,000 cubic feet (at standard atmospheric pressure and temperature) for each barrel of feed.

From this process a good yield of motor fuel of high octane number is obtained, quite contrary to experience with somewhat related prior art process. Normally a gas oil product, hydrogenated under pressure, would be expected to produce motor fuel of substantially lower octane number than a regular catalytic cracking process. In other words, hydrogenation under pressure would be expected from experience in the prior art to produce a substantially saturated and relatively unbranched fuel product.

A catalyst which is particularly effective and which is presently preferred for the present invention consists of a conventional silica-alumina cracking catalyst, preferably predominating in silica, e.g. an 87% silica-13% alumina catalyst of well-known type, to which is added from 8 to 16% preferably around 10 to 12% by weight, based on the total catalyst composition, of molybdenum oxide.

When such a combination catalyst is used in the process described below to simultaneously crack and hydrogenate or to "hydrocrack" a light gas oil, not only is a motor fuel of particularly high octane number obtained but it is obtained in very good yields. At the same time a very small amount of carbon or coke is produced. The amount of coke may be less than 1% of the feed when fluid-solids technique is employed. With other conversion procedures, coke may reach about 2% but even this is less than might be expected.

The essence of the present invention, therefore, is the discovery that a higher octane gasoline can be produced

with minimum coke formation in a single cracking-hydroforming operation, i.e. by cracking with a combination catalyst in the presence of hydrogen and under moderate pressure. The temperature range employed in this process is somewhat higher than in most of the prior art, i.e. about 970° to 1100° F., preferably between 1000° and 1070° F.

Catalysts suitable for this invention are satisfactorily prepared from conventional silica-alumina cracking catalysts or from catalysts of this general type but of reduced cracking activity. Thus, they may be prepared from used cracking silica-alumina catalysts which have been already subjected to conventional catalytic cracking operations and have lost some of their activity. Much less satisfactory catalysts are prepared from conventional cracking catalysts which contain MgO and SiO₂ as their active components. The silica-alumina type catalysts are preferably impregnated with a conventional hydrogenating component, preferably molybdenum oxide. Catalysts of the type required for the present invention are somewhat costly but fortunately their costly molybdenum content may be reclaimed by volatilizing molybdena from the used catalyst and depositing this ingredient either on a fresh base or on used cracking catalyst of the desired range of activity. The used cracking catalyst, when it is chosen, is preferably of the specific type mentioned above and widely employed in catalytic cracking of gas oils. It consists of about 87% SiO₂ and 13% Al₂O₃ by weight. The hydrocracking catalyst product prepared therefrom by addition of molybdena is preferably regenerated after use in a conventional manner. Air is used to burn the coke off the catalyst and also to oxidize any molybdenum or molybdenum oxides, etc., adhering thereto. If additional heat is needed to carry out the regeneration a tail gas from a conventional catalytic cracking reactor may be introduced and burned with the coke on the catalyst, a suitable oxidation gas, usually air, being introduced in appropriate proportions. The specific manner preferred for reactivating the catalysts or impregnating them with molybdena is described in greater detail below but briefly the molybdenum oxide or equivalent is led into the regenerator where a stream of the catalyst is being regenerated and is added to the base catalyst there. The invention will be more fully understood by reference to specific embodiments which are illustrated graphically in the attached drawings.

Figure 1 is a diagrammatic view of a cracking and dehydrogenating or hydrocracking system embodying the present invention;

Figure 2 illustrates diagrammatically another system embodying the general features of the invention;

Figure 3 shows a multiple reactor hydrocracking process according to the present invention which results in high yields of high octane number gasoline with a minimum degradation to carbon and fuel gas;

Figure 4 shows diagrammatically a hydrocracking system including a unit for activating or reactivating conventionally used cracking catalyst to make it suitable for purposes of the present invention;

Figure 5 shows another modified system;

Figure 6 is a graph showing the relation of carbon formation to the hydrogenating catalyst component of the hydrocracking catalyst;

Figure 7 shows graphically the relation between feed rate and selectivity to carbon in a hydrocracking process carried out at 1,000 °F. under a pressure of 100 p.s.i.g.;

Figure 8 shows the relation between the feed rate and the percentage of conversion of a gas oil to high grade gasoline under the same hydrocracking conditions as Figure 7;

Figures 9 and 10 show graphically the relation between total conversion and yields of C₄-430° F. and C₅-430° F. gasoline;

Figure 11 shows graphically the effect of process variables and conversion levels on the olefinicity of products.

Before proceeding to a detailed description of the various systems and modifications shown in the drawings, it may be noted that carbon formation apparently can be minimized during cracking by (1) decreasing the transfer of hydrogen and minimizing dehydrogenation reactions of the coke precursors; (2) hydrogenation of coke precursors, and (3) decreasing catalyst activity to permit the use of higher cracking temperatures. All of these objectives are obtained in some degree by hydrocracking over a catalyst of the type described above, particularly an alumina or silica-alumina catalyst carrying the optimum percentage of dehydrogenating catalyst, the latter preferably being MoO₃. The MoO₃ appears to decrease hydrogen transfer activity and in the presence of relatively high pressures of hydrogen appears to hydrogenate the coke or carbon precursors. As a result of these facts it appears that at least 30 to 40% less carbon may be obtained in hydrocracking as compared with conventional catalytic cracking to obtain the same yield of C₆⁺ gasoline. The process also produces a gasoline containing more olefins and less aromatics.

In addition to producing less carbon the process of the present invention produces significantly less proportions of C₄ and C₅ gases. However, the process tends to produce more dry gas (C₁ to C₃) than does catalytic cracking under similar conditions. This tendency to produce more of the dry gases and less C₄ and C₅ fractions may be reversed by treating the catalyst with small amounts of H₂O or HF and this is an additional feature of the invention. The process therefore is flexible and can be adapted to situations where production of the lighter hydrocarbons (C₃ and below) is desirable, e.g. where liquified or high pressure gas is in good demand.

A catalyst composed of about 87 parts by weight SiO₂ and 13 parts Al₂O₃ (a silica-alumina catalyst) and 10 parts MoO₃ was used in most of the experiments described below. However, the MoO₃ or equivalent dehydrogenation component may be varied somewhat in most cases. It may be added by merely mixing the dry ingredients together or by preparing a solution of ammonium molybdate, impregnating the silica-alumina catalyst with this solution, and drying and calcining. Alternatively the MoO₃ may be sublimed to coat the cracking catalyst. Other methods known to those skilled in the art may also be used.

In broader respects the silica-alumina component usually should comprise from 84 to 92 parts by weight of the total catalyst combined with 8 to 16 parts of the hydrogenation catalyst. The latter may be promoted, if desired, by treatment with zinc oxide, phosphoric acid or phosphates, sulfides, calcium oxide, cobalt oxide, magnesium oxide, conventional halogen compounds, or even by small quantities of potassium oxide. Such promotion is well known in the art. The cracking component of the catalyst also may be promoted with phosphoric acid, boria, hydrogen fluoride or other fluorides or other halogens. For high sulfur feed stock special advantages may be obtained by using equivalent quantities of cobalt-molybdate or zinc-molybdate as the hydrogenation catalyst in place of the molybdena.

The process of this invention is primarily designed for cracking gas oils but it also may be used to advantage in cracking other fractions such as petroleum residues, waxes, cycle stocks, kerosenes and other middle distillates. Synthetic feed stocks of appropriate grade may be used such as those formed by hydrocarbon synthesis as well as the products of visbreaking and catalytic polyforming. The process may be used also for liquid phase as well as vapor phase hydrocracking, although it is applicable primarily to the latter. The process is useful in conjunction with hydroforming systems where an excess of hydrogen is produced. It may thus be used to obtain a desirable balance in refinery operations that could not be secured with conventional cracking processes and apparatus.

In general, it is preferred to use the fluids solids technique for hydrocracking, treating the feed stock in the vapor phase as is well known in the catalytic cracking art. The invention will be described in detail particularly with respect to the fluid catalyst process but it will be understood that fixed bed and moving bed catalysts of other conventional types may be employed.

In preparing the hydrocracking catalysts used in the present invention various methods may be used. Molybdena may be added as molybdena blue, by carbonyl decomposition, or it may be added as the naphthenate or ammonium molybdate. With some feed stocks and in some types of operations it is advantageous to prepare the aluminum oxide component of the catalyst in carbonic acid solutions.

In operating the hydrocracking process, improved selectivity to high octane number fuel and/or to C₄ and C₅ compounds may be obtained by adding small amounts of acids such as HF, HCl, acetic acid, naphthenic acids, etc. The process, therefore, is of special advantage for producing aviation fuel.

Hydrocracking catalysts appear to be less susceptible to loss of activity and selectivity caused by high aromatic feed stocks than are conventional cracking catalysts. In some cases the hydrocracking catalysts used in the present invention appear to be benefited by recycling aromatic streams or by pretreating the catalyst with aromatics such as benzene and toluene.

Referring now to Fig. 1 a system is disclosed wherein a suitable feed stock such as a gas oil, preferably a virgin gas oil, is fed through line 11 to a conventional cracking unit 13. The products from the cracker are passed through line 15 into a gas-liquid separator 17. Gaseous products are removed from a separator through line 19 and the liquid products are taken through line 21 into a fractionator 23. The cycle oil fraction from the fractionator, which may be all or part of the 430° F. product is then led from the bottom of the fractionator through line 25 to a hydrocracking unit 27. Valves 29 and 31 may be provided for withdrawing a portion of this product through line 33 if desired.

In the hydrocracking unit the oil is subjected to a temperature of 750 to 1100° F., preferably between 1035 and 1070° F. The hydrocracking operation is carried out at 100 to 500 p.s.i. pressure, preferably about 150-350 p.s.i.g. Most prior art processes have required higher pressures. Hydrogen rich gas is supplied through line 35 at the rate of about 500 to 10,000 cubic feet of hydrogen, preferably at least 3000 cubic feet, on an atmospheric pressure basis, per barrel of oil fed to the hydrocracking unit. The catalyst preferred contains about 10% MoO₃ on a silica-alumina (87-13) base as described above. The hydrogen may be supplied from external sources or may be recycled as will be pointed out below. The gaseous products from the hydrocracking unit are taken overhead through a line 37 to a gas-liquid separator 39. Dry gases from the separator are removed through line 41 and may be recycled through line 43 or drawn off through valve 45. The liquid products from the separator are withdrawn through line 47 and passed into fractionator 23. Although shown as one fractionating unit a number of fractionators may be used and the products from the cracking reactor 13 and the hydrocracking reactor 27 may be led to separate fractionators if desired.

The dry gases from separator 39 contain considerable hydrogen and are partially or completely recycled to the hydrocracking unit, either through lines 49 and 35 or through lines 51, adsorber 53 and lines 55 and 35. As is well known, an adsorber serves to concentrate the hydrogen content of the recycled gas. The adsorber unit may utilize the fluid char adsorption process or may use oil adsorption or low temperature adsorption processes. Appropriate valves 57 and 59 are provided to control the flow or to by-pass the adsorber as desired. Addi-

tional hydrogen is sometimes needed from extraneous sources and such may be introduced through line 61 by opening valve 63. Extraneous hydrogen may also be introduced through line 65 ahead of the adsorber to improve adsorber operation under some conditions.

A convenient source of extraneous make-up hydrogen is the tail gas from a hydroforming unit of known type. The tail gas from the cracking unit 13 may be used, however, after enrichment by a suitable adsorption process. With some feed stocks no enrichment of hydrogen may be required. In other cases the make-up hydrogen can be manufactured in a converter from natural gas or other conventional sources.

Under some conditions it may be desirable to introduce fresh feed to the hydrocracker along with the cycle oil from line 25. In this case the fresh feed may be introduced from its supply through line 67 connected to line 11 and controlled by valves 69 and 71.

In one modification of the invention all or part of the fresh feed is passed over a hydrocracking catalyst in the presence of hydrogen at a temperature in the range of 500° to 750° F. before passing the feed to the cracker. This conditions the feed by removing cracking catalyst poisons such as nickel, vanadium, iron, sulfur, etc.

It will be understood that gases other than hydrogen produced by the hydrocracker may be suitably utilized in various ways. The C₂ to C₅ olefins contained therein can be concentrated or passed directly to a polymerization unit. This reduces or eliminates compression costs as compared with gases from an atmospheric pressure fluid cracking unit.

Referring now to Fig. 2, fresh feed, for example, one which contains a substantial proportion of naphthenic stock, is introduced through incoming feed line 101 into a hydrocracking unit 103 operating under the same general conditions of temperature, hydrogen pressure and catalyst as that shown in Fig. 1. The product of the hydrocracker is removed overhead through a line 105 to a fractionator 107. It may be fractionated via knock-out drums and fractionation columns. Part or all of the gas product from the fractionator may be recycled through lines 108, 109, and 111 or alternatively through lines 108, 113 and adsorber 115 for hydrogen enrichment as in Fig. 1. Part of the product gases may be withdrawn from the system through lines 117 and 119, suitable valves 121, 123 and 125 being provided.

Ordinarily the hydrocracker is operated under conditions of low overhead or net gas production so that no net hydrogen is consumed. Under more severe operating conditions, as in Fig. 1, make-up hydrogen may be required and this can be added through line 127. Alternatively the tail gas from cracking unit to be described may also be recycled through line 129. A hydrogen donor may be utilized but this forms no part of the present invention.

The 430° F. stream from the bottom of fractionator 107 is led through lines 131, 133, 135 into a cracking unit 137 which is of conventional type, preferably utilizing the fluidized solids technique. Here the feed is cracked and the cracked products are led via line 139 to fractionator 141, a knock-out system being included in line 139 if desired. From the fractionator, cycle oil is sent back to the cracking unit via lines 143, 145 and 135. Fractionators 107 and 141 may be combined in a single unit if desired. Regenerators for cracking and/or hydrocracking catalysts may be used but are not shown.

The aromatic and olefinic constituents of the final products may be controlled by recycling part of the products from the fractionator 141 (or 107) through lines 147, 149 and 129 to the hydrocracking unit. In some cases it is convenient to recycle some of the heavy fractions of the cycle oil back to the hydrocracker and this may be done through lines 143, 151 and 129. The hydrocracker is able to crack these streams with less carbon formation than is

obtained in conventional cracking. This is an important aspect of the invention.

In some cases it may be desirable to introduce some fresh feed directly into the cracking unit. Line 153, controlled by valves 155 and 157, is provided for this purpose. Heavy bottoms from the fractionator 141 can also be withdrawn through line 159 under the control of valves 161, 163 and 165. Likewise the products of line 147 may be withdrawn from the system through line 167 controlled by valves 169 and 171 instead of being recycled.

The combination cracking and hydrocracking process of Fig. 2 is especially applicable to high nitrogen and high sulfur feed stocks. The hydrocracking step lowers their nitrogen and sulfur contents. This permits the use of a sulfur sensitive catalyst in the cracking unit.

The hydrocracking operation of Fig. 2 is carried out preferably at 150-350 p.s.i.g. and at 1035-1060° F. using 3,000 to 10,000 cu. ft. of hydrogen gas recycle per barrel of oil. When hydrogen enrichment is carried out by the fluid char adsorption process, the adsorption is carried out in the pressure range of 100-500 p.s.i.g. at a temperature of 150-200° F. A char circulation rate of 0.25-1 lb./cu. ft. of tail gas is most satisfactory.

In some cases feed stocks contain compounds that are difficult to crack and do not give the best operation in the units or systems described above. If the hydrocracking process is operated under conditions severe enough to crack these refractory compounds some of those compounds which are cracked more easily break down to gas with excessive coke formation. According to the present invention this difficulty may be overcome by the use of a multiple hydrocracking reacting system in which the lead reactor or plurality of reactors are operated under mild conditions and the subsequent reactors under severe conditions. Such a system is illustrated in Fig. 3.

In the system of Fig. 3 the product from a lead or first reactor is separated (or the separator may be bypassed) and the cycle oil boiling about 430° F. is sent on to a subsequent or tail reactor. Thus, the feed enters reactor unit 300 through a line 302 along with hydrogen gas which is recycled through a line 304. The product of this first reactor is carried overhead via line 306 to a knock-out drum and/or a fractionating column indicated diagrammatically at 308. The recycled fraction is then led through lines 310 and 312 to the second or tail reactor 314 along with recycled gas from the fractionator fed through lines 316 and 318. In some cases it is advantageous to add some fresh feed to the second reactor through a line 320, valves 322 and 324 being provided for proportioning the feed to the separate reactors. The products from tail reactor 314 are taken overhead through line 326 into line 306 and into the knock-out drum and fractionator. Obviously separate drums and/or fractionators may be used for the separate reactors if desired and this is often of advantage when the entire process is operated at substantially one pressure. However, if the two reactor units are operated at different pressures, as is sometimes desirable, it may be preferable to keep the liquid gas separating equipment separate for the different stages. This minimizes the need for compressing the recycled gas in one case or the other.

The hydrocracking reactor units may be operated so as to either produce or consume net hydrogen. Where net hydrogen is consumed in the operation it is necessary to supply make-up hydrogen. This may be obtained either from other reactor units operating under different conditions or from an extraneous source, such as a hydroformer.

The lead reactor units are operated under conditions previously specified, i.e. preferably at 100 to 500 p.s.i.g. or more specifically 100 to 350 p.s.i.g. and at a temperature ranging between about 1000 and 1060° F. with 3000 to 10,000 cubic feet of hydrogen gas per barrel of oil.

The tail reactors may be operated at much higher pres-

ures in some cases, for example at pressures up to 5,000 p.s.i.g. and at temperatures of 970 to 1100° F. A hydrogen recycle rate between 1,000 to 15,000 cubic feet per barrel of oil may be used in extreme cases. As in the case of the lead reactors various hydrocracking catalysts may be used. It is desirable, however, to activate the catalysts for the tail reactor by addition of halogen, for example by treatment with HF, NH₄F or HCl. In addition to the hydrocracking catalysts mentioned above excellent catalysts for the second stage are, for example, silica alumina compositions, e.g. of 87SiO₂/13Al₂O₃ with or without halide promotion and without molybdenum oxide, catalysts based on HF treated clays with HF promotion, etc. When catalysts of the same composition are used both in the lead and the tail reactors a common regenerator, not shown in Fig. 4, may be used. Otherwise separate regenerators may be required.

As previously described, it may be desirable to recover the molybdenum oxide from spent catalyst since losses of this expensive catalyst ingredient frequently are considerable. For example, in a 20,000 barrel per day fluid cracking catalyst plant it is common practice to reject about 1.5 tons of catalyst each day. This amounts to a loss of over 45 tons of molybdenum oxide per year. According to the present invention this molybdena may be recovered in situ by leading off a side stream of coked catalyst to a separate vessel where the molybdena is evaporated and stripped off at a temperature of 1300 to 2,000° F. A system for carrying out a hydrocracking operation and recovering the expensive molybdena ingredient is illustrated in Fig. 4.

As shown in this figure hydrocracking is carried out in a reactor 400 from which used catalyst is removed through a line 402. This catalyst is fluidized and introduced into a used catalyst zone 404 of a catalyst preparation unit 406 through lines 408 and 410. Gas from the regenerator 412 is supplied through lines 414 and 416 for fluidization. The advantage of using this gas from the regenerator is that it normally contains appreciable quantities of MoO₃ lost from the catalyst during regeneration as well as containing some steam. This steam aids in stripping the molybdena from the used catalyst.

The temperature in zone 404 is maintained between 1300 and 2,000° F., preferably 1400 to 1600° F., by introducing excess air via lines 418 and 420. This air is used in burning the coke off the catalyst as well as in oxidizing the molybdena. If additional heat is needed tail gas may be drawn from the reactor through lines 422, 424 and 420 (via a stripper or fractionator described below). Auxiliary fuel such as gas, torch oil, or coke may be used if needed. This gas or other auxiliary fuel is then burned with the coke on the catalyst in the catalyst preparation unit.

The volatilized molybdena is carried from the zone 404 into an upper zone 430 of the preparation unit 406. The two zones are separated by a grid 431. Here the molybdena is deposited on a new catalyst base which is introduced through line 432 from any suitable source. The renewed catalyst is then removed via line 434 and 436, through which it is returned to the reactor 400 for use.

If pretreatment of the catalyst, such as calcination, for example, is desired this may be carried out in situ in the catalyst preparation unit 404, 430 by introducing hydroformer tail gas or air via line 420. Alternatively, the prepared catalyst may be transferred to separate vessels for the calcination or pretreatment step. Make-up molybdena may be added to zone 404 through a line 438. Rejected base catalyst may be withdrawn through line 440. It will be understood that the catalytic solids are preferably fluidized and appropriate fluidizing means, draw-off means, standpipes, grids and distributors, etc., will be used as needed. These are well known in the art and need not be described in detail.

In a modification of this invention, Fig. 4, the gas

stream rich in molybdena may be led directly back to the reactor or regenerator by so directing line 442 to connect, for example, with a line 444. In this case a stream of make-up base catalyst would be added to the reactor or regenerator. Regenerated catalyst from the regenerator is returned to the reactor through line 444. Hydrogen rich gas may be recycled from the stripper or fractionator 446 through a line 447, 448, appropriate valves 450 and 452 being provided for directing the gas from the latter unit as desired.

Other modifications within the scope of the invention are the use of catalyst preparation zones, the use of either purified or commercial grade molybdena to make up for losses and the design of the molybdena recovery section as either a fluid roaster rotary kiln or a Herreshoff furnace, etc. The volatilizing gas for recovering molybdena may be any inert gas and more molybdena may be added if needed.

As pointed out above, there are a number of advantages in submitting high boiling distillates to hydrocracking over a catalyst which comprises a cracking catalyst base carrying an active molybdena component. One major advantage is the marked reduction in coke formation. For example, hydrocracking a light gas oil over a catalyst having a composition of 90% $(87\text{SiO}_2 \cdot 13\text{Al}_2\text{O}_3)$ /10% MoO_3 composition actually produced a 99 research octane number gasoline with only 0.9% by weight of carbon based on the feed. A conventional cracking process using the same feed stock over the base catalyst with no molybdena content to obtain the same gasoline yield and octane number produced 3.9% of carbon by weight. Catalysts of this type are useful not only in catalytic cracking of gas oils but also in catalytic reforming of naphthas.

Although catalysts of the type just described have excellent selectivity for motor fuel production when prepared from fresh or steam treated cracking catalyst base there are a number of economic advantages in preparing the catalyst, either for hydrocracking or for naphtha reforming, from used cracking catalyst. Moreover, with some feed stocks this method of preparation results in a better distribution of products.

The hydrocracking catalyst made from used cracking catalyst can be prepared by conventional methods as described above. However, where refineries have cracking and naphtha reforming reactor units, especially those of the fluid solids catalyst type, a preferred method of catalyst preparation is shown schematically in Fig. 5.

The catalyst preparation unit in this modification may consist of one vessel 500 have two zones 502 and 504. In the lower zone molybdena is fluidized while in the upper zone a cracking catalyst is fluidized. Fresh molybdena may be fed in through line 506 and fresh base catalyst through line 508 when desired. Fluidizing, distributing, draw-off means, etc., may be provided as is well known. In general, however, regenerated used cracking catalyst is led from a regenerator unit 510 through lines 512 and 514 into zone 504 of the catalyst preparation unit. This unit is maintained preferably at a temperature of between 1,000° to 1300° F. by the hot freshly regenerated catalyst. Temperatures as high as 1500° F. are permissible in this zone. Heat may be controlled in zone 504 by recirculating unregenerated or partially regenerated catalyst via lines 515, 516 and 514 directly from catalytic cracking reactor 518. This unregenerated catalyst, coated to some extent with coke, may be burned in situ to supply the additional heat which may be required under some conditions. Air for burning such coke or carbon may be introduced either through the base catalyst supply line 508 or through a line 520 leading from a hydrocracking or reforming unit shown at the right of Fig. 5.

The lower fluidized molybdena zone 502 is maintained preferably at a temperature of 1400° to 1600° F. although lower or higher temperatures may be used. The

molybdena preferably is both fluidized and volatilized by a gas stream entering through line 520 and suitable grid or distributing means, not shown. This stream carries the molybdena into the base catalyst zone 504 through a suitable partition grid 522 where the molybdena is combined with the fluidized cracking catalyst base. An exit gas line 524 carries the overhead gas to a molybdena recovery system (not shown) where entrained molybdena can be recovered before the gas is rejected from the system.

Although the gas used for volatilizing the molybdena may be inert, it is advantageous to use gases taken off overhead from a hydrocracking regenerator unit as shown diagrammatically at 530. These gases pass through a line 532 under control of valves 534 and 536 into line 538 and thence into line 520 previously mentioned. Such gases contain MoO_3 which is normally lost during regeneration. They also contain some steam. The steam aids in volatilizing the molybdena in zone 502. Additional steam, air, or inert gas may be added via lines 540, 542 and 544, as desired.

It is often convenient to add a tail gas from the cracking or hydrocracking unit together with some air from lines 540, 520. This mixture of tail gas and air burns in zone 502 and thus helps to maintain the desired high temperature of the molybdena.

It will be understood that the hydrocracking reactor 550 is operated such that catalyst is passed through line 552 to the regenerator 530 and returned through lines 554, 556. Newly prepared catalyst from the preparation unit 500 may be fed into the hydrocracking line 556 through a line 558 as will be obvious.

The operation of the cracking reactor and regenerator 518 and 510 is conventional and need not be further described.

As indicated above, an important feature of the present invention is the discovery that optimum operating conditions may be obtained by a careful selection and control of catalysts as well as of feed rates, temperatures and pressures. Fig. 6 shows the remarkable reduction in carbon formation at a 28% gasoline yield when cracking gas oil of a conventional quality. As will be noted, the carbon content based on the feed was over 12% when a straight cracking catalyst was used and this dropped to a very low level near 2%, when about 8 to 10% by weight of molybdena was added to the catalyst. As the molybdena content exceeded about 16% there was an appreciable rise in the carbon formation, the C_5 to 460° F. gasoline yield being kept constant.

As shown in Fig. 7 the process shows a decreasing selectivity to carbon as the feed rate is increased. Fig. 8 shows a corresponding conversion (catalyst activity) decrease as the feed rate is increased. Hence, the factors of carbon formation and conversion must be balanced to obtain optimum operating conditions. The feed rate selected will vary with feed stock, with catalyst, and with operating conditions. For the feed stock, catalyst and conditions shown above, the optimum appears to be between about 0.5 to 1.0 v./v./hr.

As stated above, an optimum temperature should be selected so that neither excessive gas nor carbon is produced and so that gasoline of desired octane value is obtained. Too low temperatures of operation give low octane number gasolines, low olefinicity in gasoline and more carbon. Data are shown in the table below and in Figures 9, 10, and 11. Preferably the temperature is between 1035° and 1070° F. The preferred pressure is between 150 and 350 p.s.i.g., about 200 p.s.i.g. being desirable. The preferred hydrogen recycle rate is at least 4,000 cubic feet per barrel of oil, with about 10,000 as maximum.

A comparison was made between two catalyst bases (a) one of 65% SiO_2 and 35% MgO and (b) one of 87% SiO_2 and 13% Al_2O_3 . Each of these was treated

to add thereto 10% by weight of molybdenum oxide. Both were used to hydrocrack a light gas oil of 490° to 700° F. boiling range. The pressure used was 200 p.s.i.g., temperature 1000° F., and a hydrogen feed rate of 3000 cubic feet (standard conditions) per barrel of oil. Results are indicated in Table I.

Table I

Catalyst	90(a)-10 MoO ₃	90(b)-10 MoO ₃
430 Conversion, Vol. Percent.....	50	50
Yields, Wt. Percent:		
C ₅ -430° F. Gasoline.....	27	27
Carbon.....	1.6	1.5
Dry Gas.....	14	14
C ₄ 's.....	6	5
Research octane number of C ₅ + Gasoline.....	86	91

It was found that at 50% conversion level, an increase in operating temperature from 1000° to 1050° F. raised the octane number from an average of 90 to an average of 92, other conditions being as indicated above.

Hydrocracking of gas oils over the catalyst of Table I produces about 1-2% more C₅+ gasoline and about 2-5% more C₆+ gasoline than does catalytic cracking to the same conversion level at 1000°-1020° F. in the same unit at atmospheric pressure. However, the hydrocracking process produces about half as much C₄'s and C₅'s and about 3% more dry gas than does high temperature catalytic cracking. At about a 50% conversion level, the hydrocracking C₅-430° F. gasoline had a 93 octane number as compared to 95 for the catalytically cracked gasoline.

A further study was made to compare hydrocracking of an East Texas light gas oil (490°-700° F. boiling range) with the same catalyst and hydrogen feed as used for the data of Table I, a temperature of 1000 to 1020° F. Pressures of 200 p.s.i.g. were used for hydrocracking and atmospheric pressure for conventional catalytic cracking. Results are shown in Table II.

Table II

430 Conversion, Vol. Percent. Process.....	46 Hydro- cracking 200	46 Cracking 0	53.5 Hydro- cracking 200	53.5 Cracking 0
Pressure.....				
Yields, Wt. Percent:				
C ₅ -430° F. Gasoline.....	25.8	24.8	28.2	25.6
C ₆ -430° F. Gasoline.....	21.5	19.4	24.0	18.6
Carbon.....	1.2	1.2	1.6	1.6
Dry Gas.....	13.0	10.6	16.0	12.6
C ₄ 's.....	3.0	8.7	6.0	12.4
C ₅ 's.....	3.0	5.4	4.0	7.0
Research octane number of C ₅ -430 Gasoline.....	93	95	93	95

When hydrocracking and cracking were carried out, as in Table II to obtain identical yields of C₆+ gasoline (19%), the hydrocracking produced 1% or less of carbon whereas catalytic cracking produced 1.4%—an increase of at least 40%.

Referring to Fig. 11, a marked increase in olefinicity was obtained by hydrocracking as compared with ordinary cracking with standard 87 silica-13 alumina type catalyst. Within conversion ranges of 40 to 60%, the bromine number of the cracked product (1000-1020° F.) ranged between about 40 and 65 as compared with about 50 to 75 for the hydrocracking product at the same temperature at 200 p.s.i.g. Other hydrocracking pressures as low as 100 and as high as 500 p.s.i.g. fell substantially on the same curve. With cracking under pressure of 200 p.s.i.g. the temperature had to be reduced to 945 to keep the conversion level below 50%. A bromine number of about 39 was obtained (point X) suggesting that cracking under pressure may tend to

reduce olefinicity. Upon increasing hydrocracking temperature to 1040° F. (at 200 p.s.i.g.) the bromine number was increased considerably further in a series of runs over various conversion ranges. Further increases in temperature to 1050 and 1070° F. did not appreciably change the bromine numbers, the data falling substantially on the same upper curve.

What is claimed is:

1. A process of cracking mineral oil fractions boiling above the gasoline range to produce motor fuel of high octane number with low carbon production which comprises subjecting said fractions to contact with a cracking catalyst containing a major proportion of silica, a minor proportion of a refractory metal oxide selected from the group consisting of alumina and magnesia and from 8 to 16% of molybdenum oxide at a temperature of 1000 to 1100° F. and a pressure of 150 to 300 pounds' pressure per square inch and in the presence of hydrogen gas supplied at the rate of 3000 to 10,000 cubic feet under standard conditions per barrel of feed.

2. A process of cracking mineral oil fractions boiling between about 400 and 800° F. and of high naphthenes content to produce motor fuel of high octane number which comprises feeding said fractions in contact with a finely divided fluidized solid catalyst containing 84 to 92% by weight of alumina-silica cracking catalyst containing a major proportion of silica and 8 to 16% of molybdenum oxide, said operations being conducted at a pressure of 150 to 300 p.s.i.g. at a temperature of 1000 to 1100° F. in the presence of hydrogen supplied at the rate of 3000 to 10,000 cubic feet per barrel of feed.

3. Process according to claim 2 wherein the operating temperature is between 1035 and 1070° F.

4. Process according to claim 2 wherein the pressure is about 200 p.s.i.g.

5. A process according to claim 2 wherein the proportion of molybdenum oxide is about 10% of the total catalyst.

6. The process of cracking petroleum oil which comprises feeding a gas oil of high naphthenes content and boiling range between 400 and 800° F. to a hydrocracking reactor in the presence of finely divided solid catalyst comprising an alumina-silica cracking catalyst containing a major proportion of silica containing 8 to 16% by weight of molybdenum oxide, said reactor being operated at a pressure of about 150-300 p.s.i.g. and a temperature of 1035° to 1070° F., feeding hydrogen gas along with said oil and catalyst at a rate of about 4,000 cubic feet per barrel of gas oil, simultaneously subjecting a naphtha to a hydroforming operation in the presence of a hydrogenation catalyst, and utilizing the hydrogen from the hydroforming operation to supply hydrogen for the hydrocracking operation.

7. The process which comprises hydrocracking a gas oil over a silica-alumina base cracking catalyst containing a major proportion of silica which contains 8 to 16% by weight of molybdenum oxide, to produce liquid hydrocarbons of the motor fuel boiling range and of octane number at least 90 plus gaseous hydrocarbons in which molybdenum oxide is entrained, conveying the gases with entrained molybdenum oxide to a zone containing fluidized base catalyst and there reimpregnating the base catalyst with said entrained molybdenum oxide, and returning the reimpregnated catalyst to the hydrocracking step.

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