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2 Sheets-Sheet 1

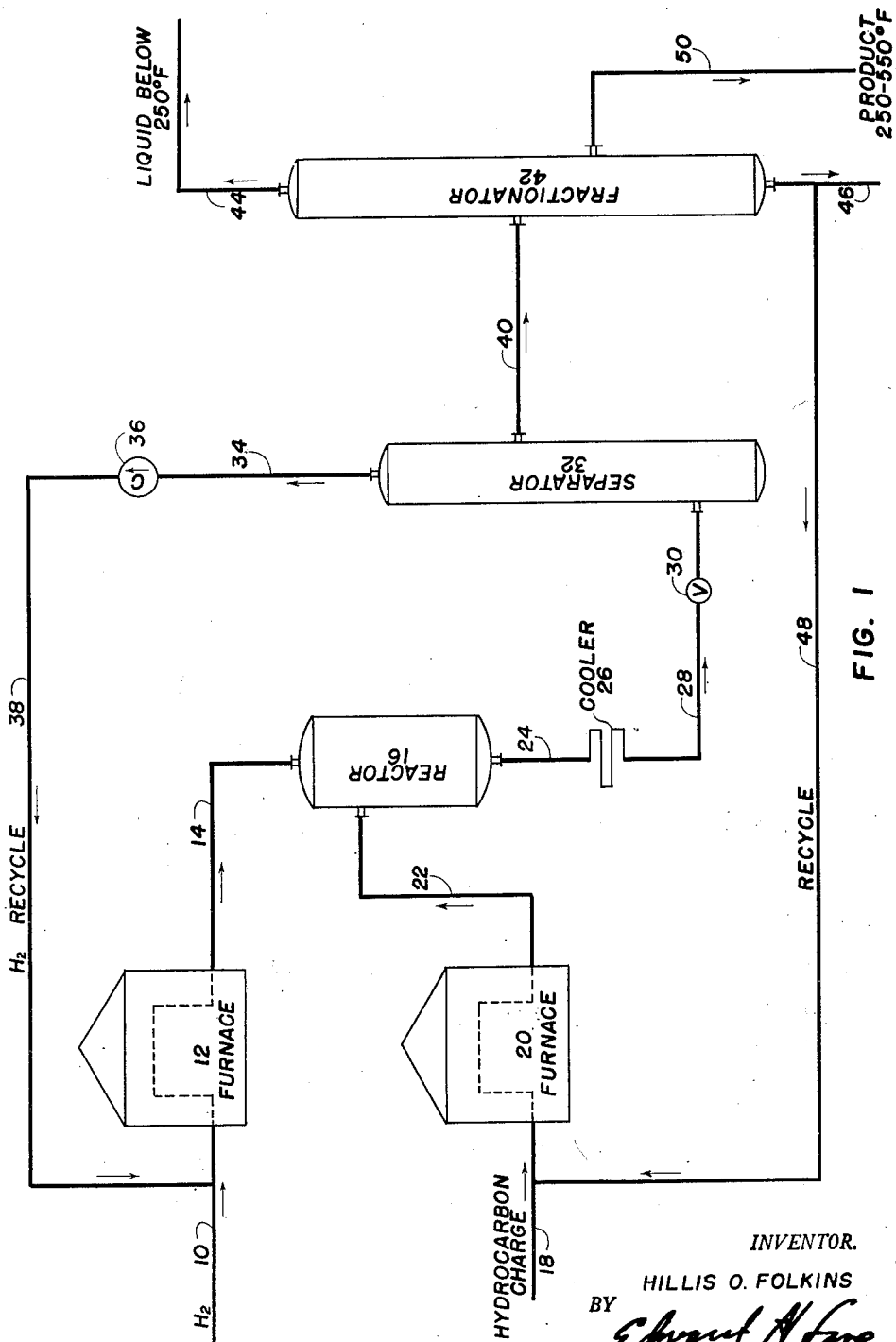


FIG. 1

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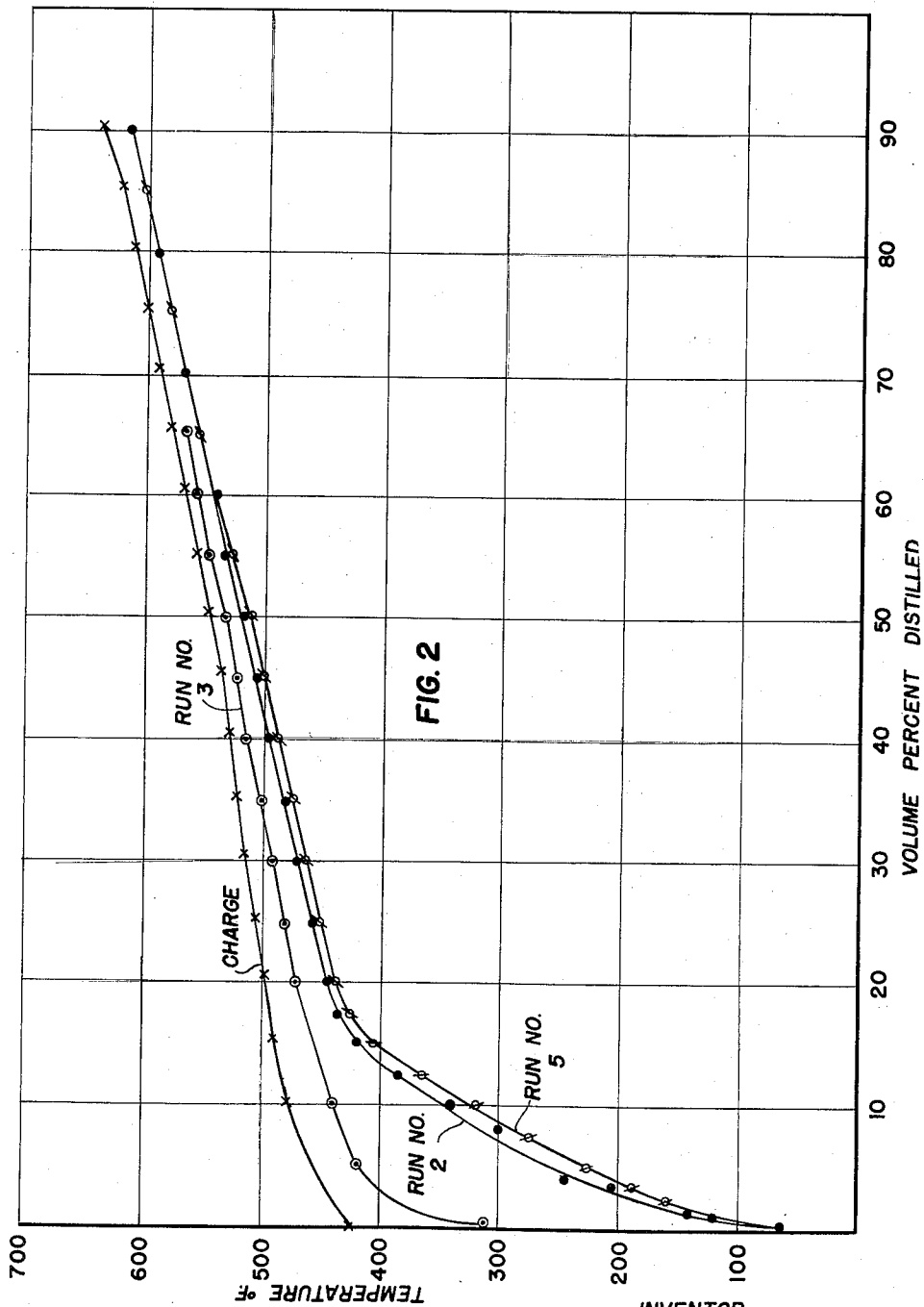
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1

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PRODUCTION OF JET FUEL HYDROCARBONS

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3 Claims. (Cl. 208—59)

This invention relates to a process and particular catalyst compositions for the production of hydrocarbons boiling in the range of about 250° to 550° F. and having desirable properties for use as jet fuels.

The development of jet engines has called for higher grade fuels, which trend is illustrated by the various grades of jet fuel already evolved. Jet fuel specifications for JP-1, JP-3, JP-4, JP-5 and referee fuels have been established by the N.A.C.A. Subcommittee on Aircraft Fuels. These specifications, as described in the Oil & Gas Journal of October 6, 1952, volume 51, No. 22, page 96, include as the more important qualifications, flammability, low-temperature fluidity, proper volatility, stability and good odor, and non-corrosiveness to polysulfide-type synthetic rubber parts used in the present fuel systems. Regarding volatility, the military has established that at an atmospheric temperature of 100° F., the minimum 10% A.S.T.M. distillation temperature should be approximately 350° F. Military operations require starting of engines and operations at atmospheric temperatures of -65° F. or lower. At the same time, the engines must operate at high temperatures under conditions where vapor locking, slugging and changes in fuel temperature may occur during flight. Similarly, engine deposits should be at a minimum to prevent decreased performance, poor acceleration characteristics and starter spark-plug fouling. Fuels which meet these various specifications are necessarily a compromise of certain qualifications in view of maximum availability from present resources.

It has been found in accordance with this invention that heavy petroleum fractions such as reduced crudes, gas oils, or catalytic cycle stocks or mixtures thereof may be converted into substantial yields of hydrocarbons meeting the jet fuel qualifications and boiling in the range of 250-550° F. The process is carried out with a minimum of disproportionation to gases or hydrocarbons in the low gasoline boiling range, and with a minimum of coke formation, by selective hydrocracking at temperatures between about 675 and 875° F., pressures of 500-1500 p.s.i.g., liquid hourly space velocities of 0.5 to 10, and hydrogen-to-hydrocarbon mol ratios of 2 to 10. The type of catalyst found to be necessary to obtain the selective conversion to a predominance of material boiling in the range of 250-550° F. contains a metal or metal compound, such as an oxide, having a high activity for hydrogenation reactions deposited on or combined with an acidic-type catalytic support which has cracking activity. The metals and/or metal oxides useful for this purpose are those of tungsten, molybdenum, chromium, cobalt and nickel, alone or in combination on the cracking support. Since some of these active metal components, such as nickel, will be present (under process conditions) as the metal and others, such as molybdenum and tungsten will be present as the oxides, the concentrations of the active components will be expressed in terms of the metal content. It is to be understood,

2

however, that in the case of some components such as those containing molybdenum and tungsten, the oxides will be the form in which the components are present under process conditions.

5 Examples of supports are silica-alumina, silica-magnesia, silica-alumina-zirconia and alumina-boria. However, as will be demonstrated, catalysts comprising a particular ratio of nickel and cobalt on silica-alumina, and nickel and tungsten on silica-alumina, are superior in their selectivity for this purpose, especially on silica-
10 alumina supports containing 5-50% alumina.

Another aspect of the invention comprises the application of a two-stage treatment to such feed hydrocarbons with the catalysts aforementioned wherein the conditions
15 in the first stage are controlled to within 800-875° F. and space velocities of 3 or above, preferably about 3 to 10, to promote selective cracking as opposed to hydrogenation, and the conditions in the second stage to which the first products are immediately transferred
20 are controlled to 675° to 725° F. to promote hydrogenation as opposed to cracking.

Accordingly, a primary object of this invention is to provide a process for the production of hydrocarbon fractions boiling in the range of about 250°-550° F.
25 from heavier hydrocarbons, which products are characterized by their high flash points, low pour points and low contents of olefins and aromatics.

Another object of the invention is to provide a certain range of reaction conditions and a catalyst to bring about the selective hydrocracking of heavier hydrocarbons in a manner such that a major part of the product boils in the range of about 250-550° F., and, quite unexpectedly, the amount of C₅ to C₇ hydrocarbons boiling below 250°
30 F. is at a minimum.

Still another object of the invention is to convert heavy petroleum fractions of the class of gas oils, reduced crudes and catalytic cycle stocks into increased yields of clean burning, high-flash, low-pour fractions of low aromatic and olefin content, boiling in the range of 250-
40 550° F., which qualify as high-temperature fuels for use in jet engines and the like, by hydrocracking under controlled conditions of 675-875° F. with pressures of hydrogen not exceeding 1500 p.s.i.g., liquid hourly space velocities of 0.5 to 10, preferably 0.5 to 5.0, and hydrogen mol ratios of 2 to 10, in the presence of a nickel-cobalt-silica-alumina or nickel-tungsten-silica-alumina catalyst having both cracking and hydrogenation activity.

A further object of the invention is to provide a two-stage catalytic process in accordance with the foregoing in which the first stage is controlled at 825-875° F. to promote cracking, and the second stage is controlled at 675-725° F. to promote hydrogenation and yield products boiling in the range of about 250-550° F. which
50 qualify as superior jet fuels.

These and other objects of the invention will appear in whole or in part as the description of the invention proceeds.

The invention is illustrated in part by the drawings wherein,

60 Figure 1 is a flow diagram of one form of apparatus to be used in carrying out the invention,

Figure 2 is a graph showing the relationship of the distillation characteristics of the products produced by the experiments represented in the specification.

65 In carrying out the process, the catalyst is usually employed in a fixed bed reactor. Catalysts are generally pre-formed and may be in the shape of 1/8" or 3/16" pellets. The reactants, hydrogen and hydrocarbon feed, are preheated and charged to the reactor in the usual manner.

70 The operation is started by introducing a stream of hydrogen, or other suitable gaseous heat-transfer medium,

and the catalyst is pretreated from one to several hours at reaction temperatures in the stream of hydrogen or hydrogen-rich gas before the hydrocarbon material is charged to the reactor. Alternately, if the catalyst has been previously reduced, the reaction system may be brought to operating reaction temperatures by circulating hydrocarbon charge with the hydrogen under process conditions of hydrogen-to-hydrocarbon ratios. The effluent from the reactor, consisting of the liquid product and hydrogen-rich gas, is cooled and passed to a flash separator from which the recycle hydrogen, or hydrogen-rich gas passes overhead and is recompressed for recycling to the reactor. The liquid product, depending upon the charge stock and the operating conditions, may be utilized as recovered or may be passed to a fractionating tower where the minor fraction boiling under 250° F. is distilled overhead to be used as a component in gasoline blending. The fraction boiling above 550° F. may be drawn from the bottom of this tower and used as heavy fuel, or it may be recycled to the reactor for ultimate conversion to the desired product.

Although by judicious choice of reaction conditions over the range specified high yields (55–65%) of the product boiling in the range of 250–550° F. can be realized in the presence of these catalysts, it is sometimes preferable to conduct the process in two stages.

In the first stage the material is passed over a catalyst bed at temperatures in the range of 825–875° F. and at liquid hourly space velocities of 3 or greater to promote controlled cracking and mild hydrogenation, as well as to achieve more effective desulfurization. The effluent from the first stage then passes to a larger catalyst bed in the second stage where temperatures are maintained at a lower level in the range of 675–725° F. Preferred liquid volume hourly space velocities in the second stages are in the range of 0.5 to 3. Hydrogen-to-hydrocarbon mole ratios in both stages are maintained in the range of 2–10. Thus the two-stage operation differs from the first in that two reactors and two temperatures are employed. Other process conditions and sequence of operations are the same.

The use of the two-stage operation is preferred for processing stocks which contain a high content of aromatics, and for sulfur removal, because it permits somewhat greater desulfurization in the first stage and greater overall hydrogenation of ring compounds.

Referring to Figure 1, briefly the process is carried out as follows: Hydrogen is introduced at line 10 and is heated to reaction temperature in furnace 12. The preheated hydrogen flows through line 14 into the top of reactor 16, which may be any of the various known types of catalytic reactors. Hydrocarbon charge is introduced by line 18 into furnace 20 and proceeds via line 22 into reactor 16. In furnace 20 the charge is brought to reaction temperature. Instead of using two furnaces, a common furnace for both the hydrogen and the charge may be used with separate coils therein for the two reactants. Reaction products leave reactor 16 via line 24 and pass into cooler 26. From cooler 26 they pass via line 28 through pressure-control valve 30 into separator 32. In separator 32, the excess hydrogen is taken off through line 34, passed through compressor 36 for recycle via line 38 into line 10. The remaining reaction products pass through line 40 into fractionator 42 wherein liquid products boiling below 250° F. are taken off at line 44; the bottoms are drawn off at line 46, or recycled via line 48; and the 250–550° F. product, qualifying as a jet fuel, is taken off at line 50.

It has already been suggested in the art that the general combination of a hydrogenation catalyst and a cracking component be used in hydrocracking processes. Gas oils, crude oils, topped crudes and many other hydrocarbon fractions and mixtures have been subjected to these various catalysts under a wide range of conditions,

up to over 1200° F. and pressures up to 1300 p.s.i.g. for the production of motor fuels boiling up to 400° F., or slightly above. These end-products qualify as motor fuel components and do not have the properties of high flash point, low pour point, low freezing point, prescribed volatility and low content of aromatics required for the various jet engines in prominence today. The prior art processes of hydrocracking are in general directed to the production of high-octane gasolines through the use of wide variations in conditions with various catalysts. The present invention is based on the discovery of reaction conditions under which the hydrogenating and cracking activities of the composite catalyst unexpectedly complement each other to substantially exclude the production of C₅ to C₇ hydrocarbons, and produce a predominance of hydrocarbons boiling above 250° F. to about 550° F.

Furthermore, it has been found that as the temperature of hydrocracking approaches 875° F., the space velocity should be increased from about 0.5 to the range of 5–10 to maintain the high selectivity and obtain at the same time an optimum conversion per pass. For example, it has been found that the production of gaseous material and light gasoline fractions boiling below 250° F. is practically eliminated if reaction conditions are maintained at about 750° F. +10° F., 700 p.s.i.g., and 1.5 LVHSV, while still converting as much as 55 to 60 percent of the feed to the desirable hydrocarbons boiling between about 250° F. and 550° F. which have the best qualities for jet engines.

In order to demonstrate the invention, a comparison is made of the product distribution obtained by ordinary fluid catalytic cracking processes and refinery test runs with a series of experiments using different catalysts and different conditions wherein the effect of selective cracking in accordance with this invention, as far as the boiling range of the products is concerned, is shown. The product distribution obtained during ordinary fluid catalytic cracking is shown in Table I and is taken from "Advances in Catalysis," volume 6, page 410, by R. V. Shankland, published by Academic Press (1954). The original data shown therein are from Murphree, "Advances in Chem. Series," 5, 30 (1951).

TABLE I

Product distribution in fluid catalytic cracking with silica-alumina catalyst

[Advances in Catalysis, vol. VI, page 410]

Temperature, °F.	850	900	950	1,000
Conversion, Vol. percent	55.0	55.0	55.0	55.0
Product Distribution:				
C ₃ and Lighter, wt. percent	4.4	5.5	6.9	8.5
Butanes, Vol. percent	6.6	6.0	5.4	4.3
Butylenes, Vol. percent	3.9	5.3	7.2	9.5
Gasoline, C ₅ -400° F., Vol. percent	43.3	42.1	40.6	39.0
Gas Oil, Wt. percent	45.0	45.0	45.0	45.0
Carbon, Wt. percent	5.8	4.7	3.8	3.2
Gasoline, O.N.:				
Research, clear	93.8	95.2	96.5	97.5
Research, +2 cc. TEL/gal	98.1	98.9	99.9	100.5
Motor, clear	82.0	82.1	82.1	82.5

From the original article referred to above it appears that the feed used in the experiments shown in Table I had the following characteristics: API gravity, 26.8°; TBP, 20% at 529° F., 50% at 735° F., and 80% at 908° F.

Present day refinery test runs are shown in Table II following, which compare very favorably with the results shown by Shankland and Murphree.

It is to be observed that in these ordinary cracking processes as shown in Tables I and II, considerable amounts of coke and gaseous hydrocarbons are formed as well as gasoline and gas oil fractions. These products do not qualify as jet fuels. To show that the process of this invention produces negligible amounts of coke and gaseous hydrocarbons, and selectively converts the higher

5
TABLE II

Material balance data for fluid catalytic cracking

	Pounds/ Day	Wt. per- cent on Fresh Feed	B.p.s.d.	Vol. per- cent on Fresh Feed
Fresh Feed.....	2,142,636		6,975	
Gas.....	56,479	2.64	866 (M s.c.f./d.)	
"B-B".....	252,319	11.78	1,306	18.72
Stabilized Gasoline.....	775,865	36.21	2,994	42.92
Light Distillate.....	557,317	26.01	1,828	26.20
Heavy Distillate.....	333,180	15.55	1,070	15.34
Decanted Oil.....	82,268	3.84	250	3.58
Coke.....	85,152	3.97	42.6 (Tons)	
Recovery.....	2,142,580			
		100.00		

		Properties of Feed Stock and Gasoline prod.	
		Feed Stock	Gasoline
Grav.....	29.5		59.4
IBP, ° F.....	455		104
5%.....	505		120
10%.....	530		130
30%.....	656		158
50%.....	770		204
70%.....	872		273
90%.....	990		356
EP.....	1,030		422
Rec.....	98		99
F-1 O.N.....	(clear)		92.6
	+1.5 cc. TEL.....		96
Sulfur.....	Wt. percent 0.246		0.010

NOTE.—Conversion = 54.0 vol. percent.

boiling constituents in the feed to increased yields of material boiling in the approximate range of 250–550° F., reference is made to Tables III and IV following.

TABLE III

Run No.	Catalyst	Temp., ° F.	Press. (p.s.i.g.)	LVHSV	H ₂ /HC (mol.)	Liq. Rec. (wt. per- cent)	° API	S, Wt. percent	RI, N _D ²⁰
1.....	2.5% Ni + 3.75% Co on Silica-alu- mina (13%)	750	700	1.49	3.36	99.4	36.4	0.01	1.4743
2.....	do.	751	700	1.53	4.89	100.2	36.0	0.05	1.4741
3.....	2.4% Co + 6.2% Mo on H-41 alumina.	701	700	1.60	4.71	99.7	32.2	0.05	1.4838
4.....	5% Ni + 10% Mo on H-41 alumina.	746	700	1.97	5.06	100.6	32.2	0.03	1.4857
5.....	10% NiWO ₄ on silica-alumina (25%)	752	700	1.49	5.03	100.1	33.8	0.01	1.4800
		754	700	1.52	4.92	99.9	36.2	0.06	1.4746

In run No. 5 the catalyst composition may be expressed as 1.9% nickel and 6.0% tungsten present as the metal on a support comprising 75% silica and 25% alumina. The H-41 alumina used in run Nos. 3 and 4 is not an acidic-type cracking catalyst as defined herein.

The feed material used in the experiments of Table III was a cycle stock from a fluid catalytic cracking operation, and had the following characteristics: Gravity API°, 30.5; IBP, 436° F.; EP, 629° F.; mol wt., 200; aniline point, 129.6; CR (wt. percent), 0.00; bromine No., 11.3; color, NPA, +1½; ref. index, n_D²⁰ 1.4947; specific dispersion, 200.9; mol. ref., 0.3347; and sulfur (wt. percent), 0.22. The feed material was obtained from a refinery fluid catalytic cracking unit.

Table IV following shows the product distribution obtained from certain of the runs made in Table III.

The experiments, the results of which are presented in Tables III and IV, were carried out in a laboratory pressure utilizing a fixed bed reactor containing 200 milliliters of pelleted catalyst. The reactor was constructed from a heavy-wall, one-inch internal diameter, stainless steel tube, and was inserted in an electrically heated

6
TABLE IV

Products from processing cycle stock

Run No.	Charge	1	2	3	5
Product (wt percent of chg.)— Distillation (TBP) Vol. Per- cent:	(100)	99.4	100.2	99.7	99.9
80° F.....		2.2			
100.....		2.5	0.5		0.8
140.....		3.2	1.4		1.5
180.....		4.2	2.2		3.0
220.....		5.5	3.5		4.6
260.....		7.5	5.0		6.5
300.....		9.8	7.2	0.4	8.6
340.....		12.5	10.0	1.0	10.8
380.....		15.0	12.0	2.2	13.0
420.....		21.0	15.0	5.0	16.4
460.....	5.1	32.0	25.0	16.0	25.5
500.....	11.0	46.0	42.0	34.0	42.5
540.....	46.0	61.0	58.0	55.0	60.5
550.....		65.0	62.0	57.5	65.0
580.....	65.5		74.0		75.0
600.....			83.0		84.0
618.....			90.0		
620.....	85.0				
638.....	90.5				
617.....					90
574.....		75.0			
571.....				67.5	

¹ Distillation terminated.

aluminum-bronze block furnace. The hydrocarbon charge was fed to the reactor by means of a small piston-type pump. Hydrogen, purified by a De-Oxo unit and a dryer, was metered by a rotameter to the reactor. Reaction conditions were as follows: Temperature, 750° F.; pressure, 700 p.s.i.g.; liquid volume hourly space velocity, 1.5; and hydrogen/hydrocarbon mole ratios of around 3 to 5. The products from the reactor were cooled and the pressure was reduced to atmospheric whereupon separation of liquid product from recycle hydrogen was carried out in a separating tower. In these runs hydrogen was not recycled, but the process of my invention includes operation with recycle hydrogen. In starting the experi-

ments, the catalyst was raised to temperature in the presence of hydrogen, and a flow of hydrogen was maintained over the catalyst for one hour at reaction temperatures prior to the introduction of the hydrocarbon charge.

It is apparent from these experiments that runs 1 and 2, using a nickel-cobalt-silica-alumina catalyst, produce a large percentage of product boiling under 500° F. and only a small amount of product boiling below 250° F. The high liquid recoveries show that the amount of dry gas produced was negligible. However, run No. 3 using a catalyst consisting of 2.4% cobalt and 6.2% molybdenum on H-41 alumina, shows in contrast very little activity for selectively cracking the charge. These experiments also show that a major amount of the sulfur present in the charge is removed by treatment in accordance with this invention. This is important to meet the non-corrosive properties required of JP-4 and JP-5 fuel specifications. Furthermore, the resulting products are, for all practical purposes, olefin-free and the aromatic content is substantially reduced. These characteristics contribute toward the product stability essential for jet fuels.

Similarly, in Table III it is seen from run 4 that a catalyst composed of 5% nickel plus 10% molybdenum on H-41 alumina (contains 5% silica) is far inferior in selective activity to our preferred catalysts (runs 1, 2 and 5).

The results of these experiments are shown graphically in Figure 2 wherein the abscissa represents the volume percent distilled and the ordinate represents the temperature in ° F. The increase in the fraction boiling between 250° to 550° F. is apparent from this comparative relationship of the distillation characteristics of the products obtained in run numbers 2, 3 and 5.

The preferred catalyst compositions comprise the combination of nickel and cobalt or the combination of nickel and tungsten as the hydrogenation components on an acidic-type cracking support or carrier. The combined amounts of metal (and/or metal oxides) preferred are in the range of 4-15 weight percent. Where active components such as nickel are employed in combination with other metals, or metal oxides, they should be present in lower concentrations than the other component, in this instance the cobalt or tungsten, and a range of 0.5 to 5 percent by weight of nickel is preferred. Concentrations of nickel higher than 5 percent will result in excessive hydrocracking and coke deposition. Although the role of the cobalt is not definitely established, it is believed to act as a stabilizer for the nickel and thus decreases the rate of catalyst degeneration which leads to increased catalyst life and longer on-stream periods between regenerations. The combined amounts of metal, or metal and metal oxide, hydrogenation component present in the reduced state of the catalyst is in the range of 2 to 20 weight percent and preferably in the range of 4 to 15 weight percent. Within this concentration range it has been found that adequate activity is attained without degenerative cracking which higher concentrations of metals will promote.

The acidic-type supports used in the preparation of the catalysts of this invention include those compositions which have found use in catalytic cracking hydrocarbons in the general temperature range of 800 to 1000° F., at atmospheric pressure, and at space velocities between about 0.5 to 5.0 v./hr./v. and catalyst/oil ratios of 1.5 to 30, which are the general catalytic cracking conditions. Such supports include silica-alumina, silica-magnesia, silica-alumina-zirconia and alumina-boria having micro-porous structures with surface areas of about 100 square meters/gm. or above. In many cases the surface areas of these acidic-type supports are in excess of 300 square meters per gm. The preferred acidic-type support is one which contains about 50 to 95% of silica or in combination with 5 to 50% alumina. Specific examples of these silica-alumina supports comprise compositions containing 97 weight percent of silica and 13 weight percent of alumina, 83 weight percent silica and 17 weight percent alumina, and 75 weight percent silica with 25 weight percent alumina. Other carriers may include silica-alumina-zirconia supports containing around 5 to 10% alumina and 5 to 10% zirconia, and silica-magnesia supports with around 15 to 35% magnesia. Similarly, activated clays such as those derived from montmorillonite or halloysite may be employed. Activated aluminas containing only small amounts of silica to impart acidic properties may be employed, although their activity for the present purposes may be reduced. Included in this category are H-41-type aluminas produced by the Alumina Company of America and also activated and purified bauxites.

In preparing the catalysts of this invention, the acidic-type support is impregnated with an aqueous solution of a water-soluble salt of the metal hydrogenation component. Such metal salts as acetates, chlorates, chlorides, nitrates, iodides, and sulfates may be used. The two-metal hydrogenation catalysts may be prepared by simultaneous impregnation with the metal salts thereof,

or impregnation may take place in sequential steps. Before impregnation with the hydrogenation component, the acidic-type support may be given a pretreatment with mineral acids such as hydrochloric acid or hydrofluoric acid. In accordance with this invention, sufficient amounts of the hydrogenation component, that is the metal or metal oxides of tungsten, molybdenum, chromium, cobalt and nickel, are incorporated in the catalyst to give, after calcination and reduction, a catalyst composition containing from about 2 to 20 weight percent of the combined amounts of metal or metal and metal oxide. The weight percents given are on the basis of the weight of the entire catalyst mass. Preferably about 4 to 15 weight percent of the combined amounts of metal as above defined are used because within this concentration range it has been found that adequate activity is attained without the presence of degenerative cracking where active components, such as the nickel, are employed in combination with the other metals listed or the metal oxides. The nickel should be present in lower concentrations than the other component and a range of about 0.5 to 5% is preferred for this purpose.

After impregnation of the acidic support with one or both of the metal salts, the solid material is separated from the excess aqueous solution and dried in an oven at 100° C. for about 8 to 24 hours. Following this, the mass is decomposed and activated, preferably in a stream of hydrogen, by gradual heating to 950 to 1000° F. over a period of about 4 to 8 hours, and preferably conditioning the hydrogen at 950 to 1000° F. for several hours just prior to use. If the catalyst is to be used in a fixed bed operation, it is generally desirable to pellet, extrude, or otherwise form the catalyst before activation.

As an alternate method of preparation, the support may be impregnated with a suitable salt solution of nickel and cobalt, or nickel and tungsten, and the metals fixed thereon as insoluble compounds by precipitation within the pores of the catalyst support through the addition of a suitable precipitant. For example, the support may be impregnated with the nitrates of the metals and the metals co-precipitated as carbonates by the addition of ammonium carbonate as the precipitant. The resulting material is then freed of excess solution, dried and activated as mentioned above. Similarly, the metals may be precipitated as insoluble compounds in the presence of, or the compounds may be added to, a slurry of an undried support, after which the composite catalyst mass is filtered, dried and activated by the foregoing procedure.

These catalysts may be used to promote the hydrogenation of heavy petroleum fractions to produce jet fuels boiling in the range of about 250 to 500° F., in accordance with this invention, by carrying out the reactions in fixed beds or fluidized beds suspended in a vapor stream of the reactants. The various techniques applicable to fixed bed operation, moving bed operation, or fluid cracking manipulations, which are known in the art, may be used to carry out the invention whether applied by using a single reaction zone or a two-stage operation.

In the treatment of stocks containing considerable amounts of sulfur over the catalysts of this invention, some loss in activity occurs with time on stream with the result that the rate of conversion gradually decreases. The extent of loss in activity will be dependent upon the amount of sulfur in the charge and the degree of severity employed in the hydrogenation treatment. The use of hydrogen/feed mole ratios of 4 or above are usually employed to maintain high catalyst activity for longer periods of time when such high-sulfur stocks are used.

In order to restore the catalyst to its maximum activity, the various known regenerative techniques may be employed wherein the catalyst is subjected to oxidation or burning to remove the accumulated deposits, followed by reduction with hydrogen, after which charging

the hydrocarbon feed stock can be continued. In another method of regeneration the activity may be fully restored in numerous cycles by employing intermittent charging of the heavy petroleum fraction oil, maintaining a continuous flow of hydrogen. In this manner the catalyst activity is restored by intermittent treatment with hydrogen alone.

What is claimed is:

1. The method of producing jet fuel hydrocarbons boiling in the range of about 250° to 550° F. which comprises, subjecting a catalytic cycle stock boiling from about 439° to 629° F. to a first-stage catalytic reaction in the presence of hydrogen at temperatures between about 800° and 875° F., controlling the space velocity in said first-stage reaction to within values of between about 3.0 and 10.0 to promote selective cracking, immediately transferring the products from said first-stage to a second-stage catalytic reaction in the presence of hydrogen at temperatures between about 675° and 725° F. and liquid volume hourly space velocities of from about 0.5 to 3.0 to promote hydrogenation, controlling the hydrogen/hydrocarbon mol ratios in both reaction stages to within about 2.0 to 10.0, the catalyst present in both stages being a composite catalyst consisting of about 2.5 weight percent of nickel and about 3.5 weight percent of cobalt deposited on a silica-alumina support containing about 87 weight percent silica and about 13 weight percent alumina, and separating from the products of said second stage a fraction boiling from about 250° to 550° F. which qualifies as a jet fuel.

2. The method of producing jet fuel hydrocarbons boiling in the range of about 250° to 550° F. which comprises, subjecting a catalytic cycle stock boiling from about 439 to 629° F. to a first-stage catalytic reaction in the presence of hydrogen at temperatures between about 800° and 875° F., controlling the space velocity in said first-stage reaction to within values of between about 3.0 and 10.0 to promote selective cracking, immediately transferring the products from said first-stage to a second-stage catalytic reaction in the presence of hydrogen at temperatures between about 675° and 725° F. and liquid volume hourly space velocities of from about

0.5 to 3.0 to promote hydrogenation, controlling the hydrogen/hydrocarbon mol ratio in both reaction stages to within about 2.0 to 10.0, the catalyst present in both stages being a composite catalyst consisting of about 1.9 weight percent of nickel and about 6.0 weight percent of tungsten deposited on a silica-alumina support containing about 87 weight percent silica and about 13 weight percent alumina, and separating from the products of said second stage a fraction boiling from about 250° to 550° F. which qualifies as a jet fuel.

3. The method of producing jet fuel hydrocarbons boiling in the range of about 250° to 550° F. which comprises, subjecting a catalytic cycle stock boiling from about 439 to 629° F. to a first-stage catalytic reaction in the presence of hydrogen at temperatures between about 800° and 875° F., controlling the space velocity in said first-stage reaction to within values of between about 3.0 and 10.0 to promote selective cracking, immediately transferring the products from said first-stage to a second-stage catalytic reaction in the presence of hydrogen at temperatures between about 675° and 725° F. and liquid volume hourly space velocities of from about 0.5 to 3.0 to promote hydrogenation, controlling the hydrogen/hydrocarbon mol ratios in both reaction stages to within about 2.0 to 10.0, the catalyst present in both stages being a composite catalyst consisting of an acidic-type silica-alumina cracking catalyst promoted with nickel and a metal selected from the group consisting of cobalt and tungsten, the total amount of metal promoter being 4 to 15% by weight of the catalyst and the amount of nickel present in the catalyst being from 0.5 to 5% by weight, and separating from the products of said second stage a fraction boiling from about 250° to 550° F. which qualifies as a jet fuel.

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