

[54] **UPGRADING OF CRUDE OIL BY COMBINATION PROCESSING**

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[22] Filed: **Feb. 27, 1970**

[21] Appl. No.: **14,908**

[52] U.S. Cl. ....208/57, 208/92, 208/93

[51] Int. Cl. ....C10g 37/00

[58] Field of Search .....208/57, 92, 93, 80

[56] **References Cited**

**UNITED STATES PATENTS**

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3,172,842	3/1965	Paterson.....	208/80

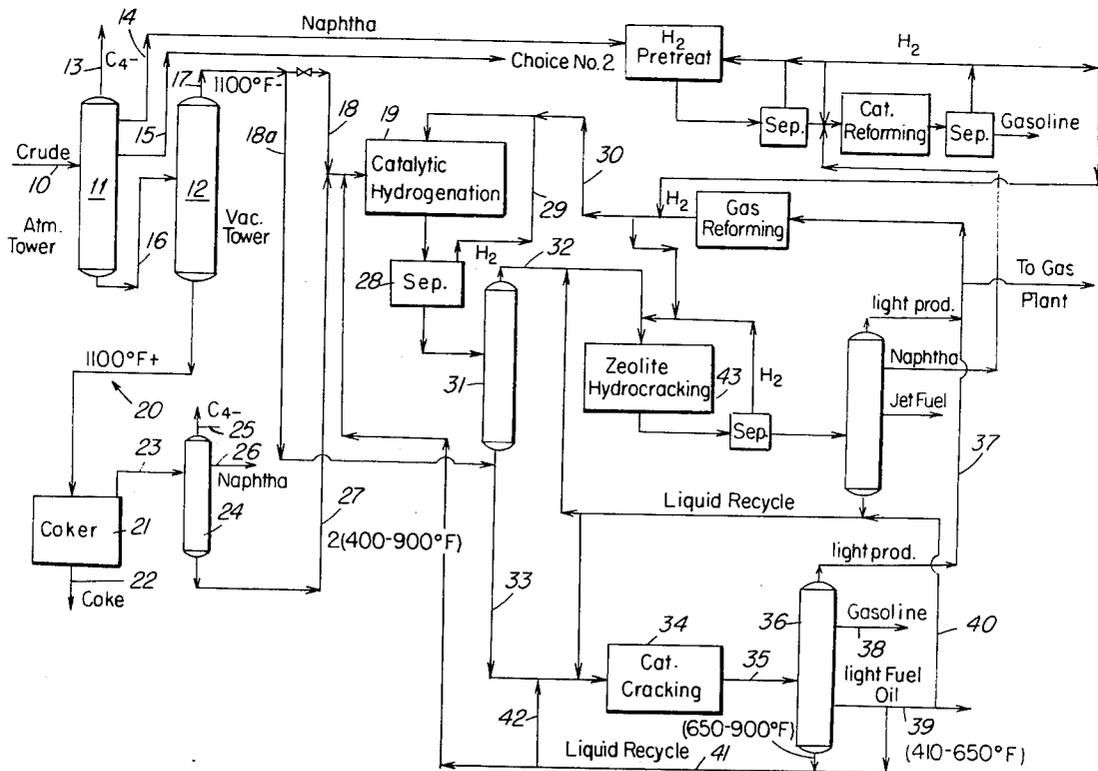
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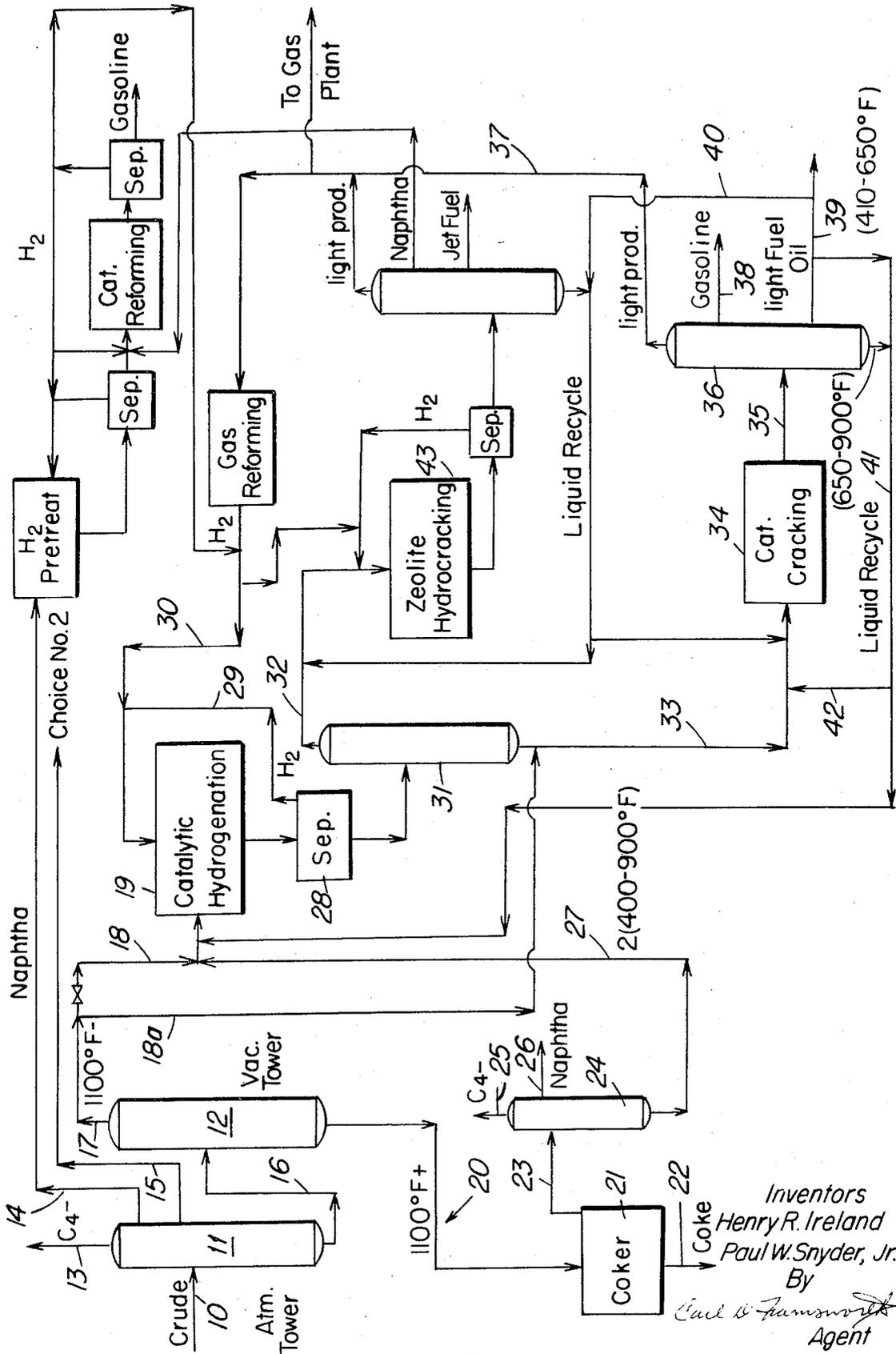
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[57] **ABSTRACT**

Efficient utilization of hydrogen and catalyst compositions is achieved in a petroleum refinery operation by a specific combination of unit operations which tend to optimization of premium products. A significant feature of this combination is catalytic hydrogenation of a fraction boiling above the gasoline range up to 1,100° F. followed by cutting or separating the hydrogenated product to form a high boiling fraction boiling above about 700° F. as charge to a crystalline aluminosilicate catalytic cracking operation with the low boiling fraction thereof boiling below about 700° F. being charge to catalytic hydrocracking.

**7 Claims, 1 Drawing Figure**





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## UPGRADING OF CRUDE OIL BY COMBINATION PROCESSING

### BACKGROUND OF THE INVENTION

The invention is concerned with the catalytic refining of crude petroleum and fractions thereof for the production of liquid fuels. It is adaptable to refining for both fuels and lubricants, in which case portions of certain fractions may be diverted to lubricant processing in the manner well known in the art; the principles of this invention being applied to that portion of the refinery input intended for fuels production.

The input to a petroleum refinery is crude petroleum constituted by a complex mixture of literally thousands of diverse compounds of carbon and hydrogen with minor amounts of sulfur, nitrogen and metals. These compounds vary from very simple aliphatic compounds such as short chain paraffins through naphthenes, aromatics, heterocyclic and open chain compounds of sulfur and nitrogen to fused ring compounds such as pyrene and the metal bearing porphyrins. Each individual compound or group of like compounds could be treated alone with considerable ease to produce the products demanded by modern industrial and consumer equipment. The processing of complex mixtures, however, is made necessary by the economics of an industry in which current prices cannot be met by expensive separation and individual processing of chemical types.

The problems of refining are intensified to a considerable degree by (1) the necessity for input of several different crude types to each refinery in order to meet the output demands; and (2) the unfortunate disparity between the hydrogen/carbon ratio of the total liquid output (the "premium product slate") and that of the composite of crude inputs. A typical fuels refinery will face a slate of premium products (gasoline, kerosene, jet fuel, diesel fuel and No. 2 burning oil) in which the hydrogen content is 11.0 - 15.0 wt. %. Typical crudes available in large supply have the following hydrogen content. For example:

Crude	Hydrogen (wt. %)
Alaskan Crude (Cook Inlet)	12.89
California	
San Ardo	11.11
San Joaquin Valley	11.75
Wilmington	11.64
Libyan	13.41
Mid-Continent	13.44
Kuwait	12.87
Oficina	12.67
West Texas	12.55

The petroleum refiner faces a clear-cut alternative: reject carbon, add and reject hydrogen in the refining system. Typically he does some of each and this invention is concerned with a combination operation in which some carbon is rejected as by formation of petroleum coke, asphalt or heavy fuel very poor in hydrogen and commanding a low price. Despite flexibility to accommodate some carbon rejection, the invention also concerns itself with that portion of a fuels refinery characterized by hydrogen addition. Advantages are provided in management of the hydrogen in such manner that this element essential to premium liquid fuels shall be husbanded for the desired purpose. This conservation of assets applies to both sources of hydrogen, viz., that present in the refinery input and that manufactured from any suitable source, including refinery by-products.

Efforts have been made to apportion the tasks of petroleum refining among different types of equipment according to their respective capabilities. Of interest in this respect are U.S. Pat. Nos. 3,172,842 and 3,245,900 to Paterson.

Many unit operations are known for input of hydrogen to the total refinery system. Catalytic hydrodesulfurization, denitrogenation, conversion of aromatics to saturated compounds and demetallization all result in some input of

hydrogen. Some is also rejected from the system in removing impurities, e.g. sulfur and nitrogen are withdrawn as hydrogen sulfide and ammonia, respectively. Hydrocracking also introduces hydrogen to the system. A recently introduced technique involves hydrogenation of charge to catalytic cracking for purposes described in U.S. Pat. No. 3,413,212, P.B. Weisz.

### SUMMARY OF THE INVENTION

This invention relates to the cracking of hydrocarbons to produce conversion products such as gasoline, jet fuels, light fuel oils and hydrogen. More particularly the present invention is concerned with the method for optimizing upon the combination of gasoline producing or refining steps comprising particularly catalytic cracking and hydrocracking operations. In accordance with the method of this invention heavy hydrocarbon charge stock boiling above about 700° F. of acceptable nitrogen and polycyclic aromatic levels are cracked with a crystalline aluminosilicate cracking catalyst under catalyst cracking conditions with that portion of the hydrocarbon charge stocks boiling below about 700° F. being preferably subjected to elevated pressure hydrocracking conditions in the presence of a catalyst composition comprising a crystalline aluminosilicate cracking component. The separation steps and cracking combination above identified is enhanced to a considerable degree by hydrogenating the charge so as to improve upon the hydrogen concentration of the heavy charge and reduce the level of polycyclic aromatics therein as well as reduce its nitrogen content below about 500 ppm of nitrogen. Thus we have found that the hydrogen available from the crude input and from generated hydrogen may be more selectively directed to premium products by the specific combination of processing steps herein described.

Despite the name "coke" applied to carbonaceous solids produced in a refinery, these materials contain a small amount of hydrogen. The solid product of delayed coking typically contains 4 wt. % hydrogen, unimportant to its use as solid fuel. The "Coke" deposited on catalysts in the refinery may contain 6-8 wt. % hydrogen, a typical value for catalytic cracking operation. The coke on catalyst is burned for regeneration of the catalyst, converting its hydrogen to water which is discharged from the process.

Light gaseous hydrocarbons are useful fuel but command a low price in the United States. They require an inordinate share of the available hydrogen. Methane is 25 wt. % hydrogen. Ethane contains 20 percent hydrogen by weight.

The invention is concerned with processing a 650° to 1,100° F. hydrocarbon fraction which has been separated from lower and higher boiling portions of a crude charge and a 400° to 900° F. petroleum fraction obtained from thermal and catalytic cracking. Processing of the 400° to 1,100° F. fraction is achieved by a combination of steps which includes the catalytic hydrogenation thereof to remove nitrogen constituents to an acceptable level below 500 ppm and more usually to below 200 ppm. In addition the polycyclic aromatic found in the charge are hydrogenated thereby reducing their deactivating effect upon the catalyst subsequently contacted as by cracking; and permit conversion of an otherwise very refractory stock. Following hydrogenation, the hydrogenated hydrocarbon fraction is separated, into at least two fractions, one boiling above and one below a characteristic temperature selected from within the range of 650° to about 700° F. This separation will depend upon specific factors peculiar to the nature of the crude, the product slate and idiosyncracies of catalyst and equipment employed. The heavier fraction that has its crackability improved and nitrogen level reduced to a tolerable level by hydrogenation is transferred to catalytic cracking which consumes no additional hydrogen. The lighter fraction goes to catalytic hydrocracking, requiring hydrogen, wherein the catalyst aging rate is improved by processing the light fraction in the absence of the heavier fraction. There are further benefits realized when the crystalline aluminosilicate

zeolite cracking catalysts are used by more selectively converting the hydrogenated heavy fraction. This result is attributed to their hydrogen transfer capability.

#### DESCRIPTION OF DRAWING

The concepts of the present invention are more conveniently considered with reference to a particular embodiment in which those concepts are utilized in a complete fuels refinery. The drawing attached hereto is a diagrammatic representation (simplified flow diagram) of the fuels refinery of this invention. It will be understood by those skilled in the art that portions of certain streams may be diverted for special purposes such as lube refining without material effect on the fuels manufacture specifically shown. For example, a portion of the vacuum tower bottoms may be processed for bright stock. Suitable portions of other fractions may be processed to manufacture neutral oils.

The processing flow arrangement represented by the drawing illustrates one scheme for practicing the method and concepts of this invention. Some alternative flow arrangements are provided for depending on the crude source, market demand, variations in crude, specific characteristics of catalyst at the time in question and other like factors.

Referring more particularly to the exemplary showing in the drawing: a crude petroleum is supplied to fractionating equipment 11 by a line 10, as from crude storage adjacent the refinery. Crude fractionation may be of any style suited to the purposes discussed and is here shown as a two-stage operation including an atmospheric tower 11 operating at enough pressure above atmospheric to overcome downstream pressure drop prior to pumps on subsequent units, and a vacuum tower 12 operating at a top pressure of about 2 pounds per square inch absolute.

Overhead product from atmospheric tower 11 is constituted by light products of the crude, if any be present, withdrawn by line 13 and transferred to a gas plant, not shown, for recovery of components desired for pressuring gasoline (butanes), liquified petroleum gas, feed to gas reforming, or furnace fuel.

A naphtha stream is taken from tower 11 by line 14 to be processed for motor gasoline in a catalytic reformer described hereinafter or for other purposes such as manufacture of solvents or basic chemicals, e.g. ethylene, aromatics. The end point of the naphtha may vary between about 350° F. and 400° F. depending on specific demands of the refinery. That naphtha end point effectively determines the initial boiling point of the next higher fraction such as a choice No. 2 fuel oil boiling up to about 650° F. and removed from tower 11 by line 15. Generally this fraction in line 15 will boil in the range of 400° F. up to 650° F.

Bottoms from atmospheric tower 11 is passed by line 16 to vacuum tower 12 for distillation under reduced pressure imposed, for example, by a barometric condenser, not shown, on the overhead product withdrawn by line 17. The overhead product in line 17 generally will boil in the range of from about 650° F. up to about 1,100° F. The overhead fraction in line 17 is normally passed by line 18 to hydrogenation in zone 19. However, if the hydrocarbon fraction in line 17 is sufficiently saturated or low in metal it may be passed directly to catalytic cracking in zone 34 thus by-passing hydrogenation zone 19 and subsequent separation in zones 28 and 31.

Bottoms from vacuum tower 12 and boiling above about 1,100° F. are transferred by line 20 to suitable processing equipment. In a refinery processing for lubricants as well as fuels, a portion of this stream may be diverted to deasphalting, solvent extraction and dewaxing stages as known for such products. The stream in line 20 may also be used, in whole or part, for heavy fuel or charge to asphalt manufacture. In the preferred embodiment shown here, the heavy fraction from the vacuum tower 12 is passed to a coking unit 21 which is conveniently of the type known as delayed coking of fluid coking. Products from the coker are solid fuel, withdrawn at 22 for use in furnaces, as electrode coke, etc., and a vaporized

fraction passing by line 23 to a fractionator 24 where light products for the gas plant and naphtha for further processing are withdrawn by lines 25 and 26, respectively. This coker naphtha may be passed to preheat step 57. Bottoms from fractionator 24 pass by line 27 to be blended with the stream in line 18 as feed to catalytic hydrogenation, it being understood that portions thereof may be diverted to other purposes, as is true of other streams heretofore mentioned.

As the art well knows, severity of hydrotreating varies with boiling point to achieve a desired degree of desulfurization, denitrogenation and conversion of fused ring aromatics to partially or fully hydrogenated compounds more amenable to cracking and capable of acting as hydrogen donors. The higher the boiling point of the charge, the greater the severity required for any desired degree of effect by catalytic hydrogenation. This is explicable from knowledge that the higher boiling fractions of petroleum contain greater amounts of polycyclics and contain polycyclics of greater complexity. Sulfur, nitrogen, metals and unsaturated carbon atoms secreted within the web of fused rings are understandably more resistant to effective attack by hydrogen, activation by catalysts or both. The range of effective severity can be a full order of magnitude. Naphthas and light gas oils can be effectively hydrotreated at space velocities of 4-5 liquid volumes per volume of catalyst per hour (LHSV) over a catalyst and at conditions of temperature, pressure and hydrogen concentration such that a residuum will require a space velocity of 0.5 LHSV. It has therefore been customary to hydrotreat relatively narrow fractions in order that conditions may be adjusted to the needs of a relatively small variety of chemical groups.

We have now found that, for the purposes of our combined process, that advantages may be achieved by hydrotreating the total hydrocarbon charge (boiling 400° F. to 1,100° F.) and particularly that portion to be supplied to catalytic cracking (either or of Fluid) and hydrocracking. Hydrogenation and nitrogen removal to specific levels (about 200 ppm) improve the catalytic crackability of heavy gas oils and the lighter fraction is made more suitable for charging to hydrocracking to reduce the catalyst aging rate. The severity of treatment is dictated by the most refractory, (most difficult to crack) portion of the charge as might be expected. This effect may be due in part to hydrogen donors and to the diluent effect of the lighter components in the composite. Effective hydrotreating for purposes of catalytic cracking and catalytic hydrocracking (not wholly coincident) are served and improvement in economical overall use of hydrogen is attained by practicing the present combination of processing steps.

The hydrocarbon charge passed to catalytic hydrogenation, boiling as herein defined and vaporizable at about 2 psia is contacted in a hydrogenation zone 19 with a suitable hydrogenation catalyst known in the art in the presence of hydrogen under sufficient pressure to achieve a limited desired degree of conversion. Conversion is controlled during hydrogenation so that less than about 500 but preferably less than 200 ppm of nitrogen remains in the hydrogenated effluent. Molecular weight reduction up to about 40 percent of material boiling below 400° F. can be sustained with visible and with ultraviolet light absorbance of the 700° F. fraction to maintain indication of less than 5 ppm polycyclic aromatics therein.

In general, we may use any of the hydrotreating catalyst known to the art for this purpose. These usually have moderately strong hydrogenation/dehydrogenation activity functions in the form of metals, oxides and sulfides of metals in Groups VI and VIII of the Periodic Table. Cobalt molybdate on alumina and cobalt molybdate silica zirconia are typical. The hydrotreating will be conducted at a pressure in the range of 1,500 to 2,000 psig hydrogen partial pressure at 700° F. to 770° F. and LHSV suitable for reducing nitrogen in the hydrogenated effluent to less than 500 ppm and preferably to at least 200 ppm.

We find that conjoint hydrogenation of the process fractions boiling above naphtha, that is boiling between about

400° F. and preferably above 650° F. and capable of vaporization without severe cracking produced significant advantages for the overall operation. The hydrogenation severity is substantially less than that normally required for optimum hydrotreating of the heavier portion, boiling upwards of 650° F. The severity will vary with differing crude sources and is best defined with respect to the product flowing from catalytic hydrogenation. In general, cracking is held to a low level — less than about 20 percent conversion to materials boiling in the naphtha range or lower; that is, below about 400° F. Condensed ring aromatics are desirably hydrogenated to such an extent that no more than one aromatic ring remains, the final ring being the most difficult to saturate and being desirably retained, if possible. The content of multiple ring aromatics, as determined by absorption of ultra-violet light and defined by Theory and Application of Ultra-Violet Spectroscopy of H. H. Jaffe and Milton Orchin, John Wiley & Sons, Published 1962, should not exceed about 5 ppm by weight.

The effluent of catalytic hydrogenation unit 19 passes to a relatively high pressure separator 28 from which hydrogen is taken off for recycle through line 29 to mix with fresh make-up hydrogen from line 30 as hydrogen feed to unit 19. The liquid hydrocarbons from separator 28 are transferred to a fractionator 31 wherein they are split into a lower boiling overhead fraction withdrawn as vapor by line 32 and a higher boiling liquid bottoms fraction withdrawn by line 33.

The "cut point" or temperature representing division between the fractions taken from fractionator 31 vary within a relatively narrow range and will generally be in the neighborhood of about 700° F. Depending on such circumstances as the desired product slate, character of the crude utilized, and aging rate of the hydrocracking catalyst, the cut point may be as low as 600° F. for example to maximize catalytic gasoline and save reformer capacity or it may be raised to about 750° F. so that among other results, an increase in the jet fuel production will be realized.

The higher boiling bottoms from fractionator 31 is transferred by line 33 to catalytic cracking unit 34 which may be any of several types known to the art. Good results are obtained using a rare earth exchanged crystalline aluminosilicate in combination with a silica-alumina matrix as the catalyst such as that described in U.S. Pat. Nos. 3,140,249 and 3,140,253 for catalytic operation in either a Thermoform Catalytic Cracking Unit (TCC) or a Fluid Catalytic Cracking Unit (FCC). The FCC style cracking unit is particularly advantageous and preferred for processing the very heavy high end point fractions herein discussed.

Conditions of cracking will generally be set for obtaining relatively high levels of conversion consistent with that which can be readily achieved at relatively high gasoline make and quality when the charge stock to the cracker is the high boiling hydrocarbon fraction obtained from hydrogenation as defined in accordance with this invention. In localities and at times of high distillate fuel demand, the conversion level may be adjusted to meet a different desired product slate and one which will provide a high quality fuel in the combination to which the invention is directed.

Hydrocarbon effluent obtained from the catalytic cracking step 34 passes by line 35 to a fractionator 36, from which several streams are withdrawn. A light overhead portion, C<sub>3</sub> and lighter together with some butanes and butenes, is taken by line 37 to blend with a similar product from the hydrocracker for utilization in a manner presently to be described. Gasoline is withdrawn as an intermediate product

by line 38 for processing in the manner known to the art by reforming, treating, stabilization and blending with other components to manufacture finished motor fuel. A second intermediate fraction or distillate fuel oil is removed from the fractionator 36 by line 39. This fraction normally has a boiling range in the interval 400° F. to about 650° F. and up to about 700° F., and provides domestic heating oils, diesel fuels and the like after further contact in finishing steps well known in the art. Depending on the relative demand for different products, i.e. domestic heating oil versus jet fuel, a portion or all of the light fuel at line 39 may be transferred to the hydrocracking step 43 as indicated by broken line 40. Under some circumstances a portion of the light oil fraction in line 39 may be recycled with the 650° to 900° F. bottom fraction by line 41 to the hydrogenation step 19.

The bottoms fraction from fractionator 36, which may include a part or all of the fraction designated "light fuel oil" (as by suitable adjustment of fractionator operation) may be returned or recycled by line 41 and 42 as charge for the catalytic cracker 39. For some types of operation, the overall efficiency of the system is considerably improved by hydrogenation of this cycle stock before charging to catalytic cracking. It is particularly amenable to effect joint hydrogenation of this recycle charge with fresh feed in reactor 19 as shown in the drawing as an alternative to direct recycle to the catalytic cracker by line 42. The preferred catalytic cracking operation of this invention processes recycle hydrocarbon material which has passed through hydrogenation reactor 19. This provides a further opportunity for interchange between components for cracking with and without hydrogenation, relatively lighter compounds being thereafter diverted to hydrocracking relatively free of fused ring aromatics and multiple ring compounds which generally have a high boiling point.

Turning now to the hydrocracking unit indicated generally at 43, the light fraction removed from splitter 31 by line 32 and boiling below about 700° F. is converted in the presence of hydrogen under elevated pressure hydrocracking conditions in the presence of a catalyst characterized by an active crystalline aluminosilicate cracking component and by a hydrogenation component which will include a Group VIII metal as metal, oxide or sulfide. Preferably, the crystalline cracking component is embedded in a matrix such as silica-alumina which also has cracking activity. The hydrogenation component may be incorporated in either the crystalline or the amorphous cracking component, but preferably it is in both.

Typical operating conditions for the hydrocracking step discussed herein include a temperature selected from within the range of 500° F. up to about 800° F., a pressure selected from within the range of 1,000 to 2,000 and preferably from 1,200 psig up to about 1,600 psig hydrogen pressure, a LHSV in the range of from about 0.5 up to about 1.0 (volumes of fresh feed per volume of catalyst per hour). Unconverted liquid product and boiling generally in the range of from about 550° F. up to about 700° F. is recycled to the hydrocracking step. The recycle to fresh feed ratio is generally maintained at about 0.60. Hydrogen recycle ratio may be in the range of from about 1,000 to about 10,000 SCF/B, it being preferred to maintain hydrogen recycle rates in the range of 3,000 to 7,000 SCF/B.

In order that one may more fully appreciate the improved method and combination of processing steps herein defined, the following table of data is presented.

Example	Hydro-treating	Hydro-cracking	Low pressure catalytic cracking	
H <sub>2</sub> pressure, p.s.i.g.-----	2,000	1,600	*15-20	
LHSV, v./hr./v-----	0.8	.54	17	
Temperature, ° F.-----	750	580	925	
			700° F. +	
	Raw	700° F., pretreated	Raw	Pretreated

Table—Continued

Example	Hydro-treating	Hydro-cracking	Low pressure catalytic cracking					
			D-7		D-9Z		Si/Al	
			Raw	Pret.	Raw	Pret.	Raw	Pret.
Charge Stock:								
API.....	18.6	30.8	10.3				30.7	
Aniline point, ° F.....	131.4	131.8	153.5				207.8	
Nitrogen, p.p.m.....	710	0.7	1300				1.7	
Hydrogen, wt. percent.....	10.69	12.55	9.68				12.65	
Product Yields:								
Coke, wt. percent.....			13.1	5.6	7.9	3.7	12.5	5.1
Dry gas, wt. percent.....			3.1	6.9	8.7	5.0	7.6	6.1
C <sub>1</sub> s, vol. percent.....	0.5	21.1	9.3	21.0	4.7	17.6	6.1	17.0
C <sub>2</sub> plus gasoline or naphtha, vol. percent.....	14.2	95.3	30.6	57.5	28.8	58.7	23.4	33.8
400° F. plus Btms. vol. percent.....	95.9							
C <sub>4</sub> plus product, vol. percent.....	100.6	116.4	39.9	78.5	33.5	76.3	39.5	50.8
Conversion, vol. percent.....	4.1	100	51.3	78.6	39.9	74.6	41.5	54.0

1 C/O.

\*Total pressure.

It will be observed that high yields of C<sub>5</sub><sup>+</sup> gasoline are produced by the combination to which the present invention is particularly directed and significant improvements in product yields are realized from the hydrogenated charge passed to catalytic cracking over that obtained with raw charge not previously hydrogenated. It is to be further observed that the D9Z catalyst provided a better product distribution than either D7 type catalyst or an amorphous silica-alumina cracking catalyst.

The D9Z type of catalyst referred to in the above table of data was a cracking catalyst having a composition comprising 5 percent REY dispersed in a cracking base comprising 58 percent silica, 2 percent zirconia and 40 percent clay. The D7 type of catalyst, on the other hand, comprised 5 percent REY dispersed in a silica-alumina matrix comprising 13% Al<sub>2</sub>O<sub>3</sub> and 87% SiO<sub>2</sub>.

Hydrocracking step 43 may employ one or more reactor vessels known in the prior art and comprising a plurality of catalyst beds which will be suitable for handling the exothermic reactions to be encountered therein. The reaction products are removed and passed by line 44 to separator 45 wherein a hydrogen rich recycle gas is separated from hydrocarbon product material. The separated hydrogen rich gas is recycled to the hydrocracking step by line 46. Hydrogen rich make up gas obtained from reforming may be added to the gas in line 46 by line 47. The hydrocarbon product separated in separator 45 is then passed by line 48 to a fractionator 49. In fractionator 49, the product of hydrocracking is separated to permit recovery of an overhead light product fraction withdrawn by line 50, a naphtha fraction withdrawn by line 51 and a jet fuel fraction boiling in the range of from about 400° F. to about 550° F. withdrawn by line 52. Insufficiently converted hydrocarbon material boiling above about 550° F. is withdrawn from the lower portion of fractionator 49 by line 53 for recycle to the hydrocracking step. Under some circumstances depending on the source of the hydrocarbon materials being processed, the liquid recycle fraction in line 53 may be passed to the hydrogenation step 19 by a line not shown.

In the processing combination shown, light product gases in line 37 obtained from catalytic cracking and light product gases in line 50 obtained from hydrocracking are combined and passed to a gas reforming step 55 by line 54. In gas reforming step 55, conditions are selected to convert the light gases passed thereto into hydrogen or at least a hydrogen rich gaseous stream. Such an operation is known in the prior art. Hydrogen thus produced is recovered and passed by line 30 and line 47 to catalytic hydrogenation and hydrocracking discussed before.

The naphtha product of hydrocracking removed from fractionator 49 by line 51 is thereafter passed to a catalytic reforming step 56 wherein it is subjected to reforming conditions to improve upon its octane rating in a manner well known in the prior art. In addition to the above, straight run

nitrogen therefrom. The thus treated naphtha is then passed naphtha separated from fractionator 11 is passed by line 14 to hydrogen pretreating unit 57 for removal of sulfur and by line 58 to separator 59 wherein a recycle gas stream is separated from the naphtha pretreated with hydrogen in step 57. The recycle gas is passed by lines 60 and 61 as recycle to step 57. Pretreated naphtha is passed by line 62 to catalytic reforming step 56. The reformed naphtha is passed by line 64 to separator 65 wherein a reformate or gasoline product is separated from gaseous components comprising hydrogen. Separated hydrogen is recovered and passed by lines 66, 63 and 67 to pretreat step 57 or by line 66 and 68 to be mixed with hydrogen rich gas in line 30 or by line 66, 63 and 69 as gas recycle to catalytic reforming step 56.

Under some circumstances when processing a paraffin rich charge low in polycyclic aromatics and containing less than about 500 ppm N<sub>2</sub>, the material separated in tower 12 and boiling in the range of 650° F. up to 1,100° F. may be passed by lines 17 and 18a directly to catalytic cracking. However, if the charge is low in nitrogen but high in polycyclic aromatics, then it needs to pass through the hydrogenation step 19. Also a charge containing nitrogen in an amount which is usually more than about 200 ppm of nitrogen will be passed through the catalytic hydrogenation step 19 described above before further processing.

The combination of processing steps thus described and the example of data presented in table provide support for the concept of this invention and attest to the unexpected results obtained by such a processing arrangement.

Having thus provided a general discussion of the concept of this invention and presented specific examples in support thereof, it is to be understood that no undue restrictions are to be imposed by reasons thereof except as defined by the appended claims.

We claim:

1. A method for optimizing a processing combination for upgrading a hydrocarbon charge material which comprises selecting from a crude oil source by distillation a hydrocarbon fraction boiling throughout the range of from about 650° F. to about 1,100° F.,

hydrogenating said hydrocarbon fraction under conditions to reduce nitrogen therein below about 500 ppm and hydrogenate polycyclic condensed ring compounds, separating the hydrogenated product of said hydrocarbon fraction to obtain a fraction boiling up to about 700° F. from a hydrogenated fraction boiling above 700° F., catalytically cracking said hydrogenated fraction boiling above 700° F. by contact with a crystalline aluminosilicate cracking catalyst under conditions to produce gasoline, a light fuel oil product and an incompletely converted higher boiling fraction, recycling the high boiling fraction to the process, catalytically hydrocracking said hydrogenated fraction boil-

ing below about 700° F. under conditions to obtain a naphtha fraction, a jet fuel boiling range fraction and a higher boiling insufficiently converted hydrocarbon fraction, and

recycling the insufficiently converted hydrocarbon fraction to the process.

2. A method for refining a crude oil to useful products which comprises

- a. separating and recovering from said crude oil, a straight run naphtha fraction, a light fuel oil fraction, a gas oil fraction boiling throughout the range 650° F. to about 1,100° F. and a heavy fraction boiling above 1,100° F.,
- b. coking said heavy fraction and recovering a naphtha fraction separately from a heavier fraction boiling in the range of 400° F. to about 900° F.,
- c. passing said gas oil fraction boiling throughout the range 650° F. to 1,100° F. in combination with said product of coking boiling in the range of 400° F. to about 900° F. in combination with a liquid recycle fraction from catalytic cracking to a catalytic hydrogenation step,
- d. reducing nitrogen contaminates in the hydrocarbon charge in said catalytic hydrogenation step to less than 500 ppm concurrently with hydrogenating polycyclic condensed ring compounds existing in the charge,
- e. separating the effluent of said catalytic hydrogenation step into a hydrogen rich fraction for recycle thereto, a hydrocarbon fraction boiling up to about 700° F. and a hydrocarbon fraction boiling above about 700° F.,
- f. catalytically cracking said fraction of catalytic hydrogenation boiling above about 700° F. and separating the cracked product effluent into a light products fraction, a gasoline fraction, a light fuel oil and a heavier fraction boiling above about 650° F.,
- g. catalytically hydrocracking said fraction of catalytic hydrogenation boiling up to about 700° F. and separating the product effluent thereof into a light products fraction, a naphtha fraction, a jet fuel fraction and a heavier recycle fraction boiling above about 550° F.,
- h. reforming the light products fraction of catalytic cracking and hydrocracking to form hydrogen for use in said catalytic hydrogenation step and said hydrocracking step,
- i. removing by hydrogenation sulfur and nitrogen contaminates from said straight run naphtha fraction before passage to a catalytic reforming step in admixture with naphtha obtained from the effluent of said catalytic hydrocracking,

- j. separating hydrogen rich gases from reformed naphtha obtained from said catalytic reforming and employing hydrogen rich gases thus obtained in said reforming step, in said straight run naphtha hydrogenation step and as make up hydrogen passed to said catalytic hydrogenation and hydrocracking steps.

3. A method for upgrading fractions of a crude oil boiling above about 650° F. which comprises

- a. recovering from crude oil a hydrocarbon fraction boiling throughout the range of 650° F. to about 1,100° F. from a higher boiling fraction boiling above 1,100° F.,
- b. thermally converting said higher boiling fraction under conditions to produce naphtha and a fuel oil fraction boiling from about 400° F. up to about 900° F.,
- c. combining said thermally produced fuel oil fraction with said hydrocarbon fraction boiling throughout the range of 650° F. to about 1,100° F.,
- d. catalytically hydrogenating said combined fractions under conditions to hydrogenate polycyclic aromatic compounds therein and reduce nitrogen therein to less than 500 ppm,
- e. separating the product effluent of said catalytic hydrogenation into hydrocarbon fractions boiling up to about 700° F. and a fraction boiling above 700° F.,
- f. passing the hydrocarbon fraction boiling above about 700° F. to catalytic cracking and passing the fraction boiling up to about 700° F. to hydrocracking and
- g. recovering from said cracking steps, light product material, hydrocracked naphtha, catalytic gasoline, jet fuels, light fuel oil and insufficiently converted recycle hydrocarbon materials.

4. The method of claim 3 wherein insufficiently converted recycle hydrocarbons recovered from said catalytic cracking are combined with the hydrocarbon charge to the catalytic hydrogenation step.

5. The method of claim 3 wherein crystalline zeolites are a part of the catalysts employed in each of the hydrocracking and catalytic cracking steps.

6. The method of claim 3 wherein hydrogen required for said catalytic hydrogenation and hydrocracking steps is obtained from reforming straight run naphtha in combination with the naphtha product of hydrocracking and conversion of light products recovered from the cracking steps with hydrogen rich gases.

7. The method of claim 3 wherein light fuel oil product of the catalytic cracking step is passed as a part of the charge to the hydrocracking step.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,671,419 Dated June 20, 1972

Inventor(s) H. R. IRELAND  
P. W. SNYDER, JR.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

- Column 4, line 36 : After "either" insert --TCC--
- Column 6, line 58 : After "700" insert --°--
- Column 7, line 75 : After "run" insert --naphtha separated from fractionator 11 is passed by line 14 to hydrogen pretreating unit 57 for removal of sulfur and--
- Column 8, line 22 : Delete entire line 21 : "nitrogen therefrom. The thus treated naphtha is then passed"
- Column 8, line 23 : After "and" insert --nitrogen therefrom. The thus treated naphtha is then passed--

Signed and sealed this 12th day of December 1972.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents