United States Patent Office 3,697,413 Patented Oct. 10, 1972

3,697,413

SIMULTANEOUS PRODUCTION OF GASOLINE AND LPG

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Filed Feb. 5, 1971, Ser. No. 113,002
Int. Cl. C10g 13/00, 23/00, 37/00
U.S. Cl. 208—59 6 Claims

ABSTRACT OF THE DISCLOSURE

A multiple-stage hydrocracking process for the simultaneous production of gasoline and LPG (liquefied petroleum gas). A first stage functions to produce from about 40.0% to about 90.0% of the desired quantity of gasoline. Heavier material is processed in the second stage at LPG-producing conditions. The hydrocracked effluent from both stages is introduced into a common separation zone from which the gasoline and LPG are recovered, and from which the heavier material is withdrawn and introduced into the second stage.

APPLICABILITY OF INVENTION

The present invention relates to the conversion of heavy hydrocarbonaceous charge stocks into lower-boiling hydrocarbon products. More specifically, the inventive concept herein described is directed toward a hydrocracking process for the simultaneous production of gasoline boiling range hydrocarbons and LPG (liquefied petroleum gas). Hydrocarbonaceous charge stocks, contemplated for conversion in accordance with the present invention, constitute heavier-than-gasoline hydrocarbon fractions and/or distillates. Since "gasoline boiling range hydrocarbons" is intended to connote hydrocarbon fractions having an initial boiling point of about 100° F. to about 125° F. and an end boiling point which may range from 350° F. to about 450° F., the contemplated charge stock will have an initial boiling point above the end boiling point of the desired gasoline fraction. It is understood that the precise boiling range of any gasoline fraction varies from locale to locale and with ever-changing marketing demands. In general, the end boiling point of the charge stocks will be about 1050° F. or less, generally considered to be that temperature at which distillation can be effected without encountering thermal cracking. Hydrocarbonaceous materials, containing hydrocarbons which would normally boil above a temperature of 1050° F. (considered in the art as "black oils") are suitable, but will generally require a pretreatment for the purpose of converting the 1050° F.-plus material into lower-boiling hydrocarbons. Thus, suitable charge stocks include kerosene fractions, light gas oils boiling up to a temperature of about 600° F., heavy vacuum or atmospheric gas oils boiling up to a temperature of about 1050° F. and either intermediate, or overlapping fractions and mixtures thereof.

The utilization of the present invention is most applicable in those areas where there exists a continuing but varying demand for gasoline boiling range hydrocarbons and, simultaneously, a continuing demand for liquefied petroleum gas by virtue of the fact that such areas are not in close proximity to sources of natural gas. In these areas, marketing demands for LPG and gasoline continually fluctuate in any given period of time. For example, in relatively cold seasons, the demand for LPG increases while the demand for gasoline boiling range hydrocarbons decreases; obviously, during relatively warm periods the reverse is true. Present-day hydrocracking units are generally designed for a specific function; that is, either for maximum gasoline production, or for maximum production of LPG. In either situation, it is extremely difficult to approach closely the desired quantities of both gasoline and LPG, especially during a period of continuing fluctuations. With a single-stage hydrocracking system, operating to produce a given quantity of gasoline, one must be content to accept whatever volumetric yield of LPG results. Again the reverse is true with respect to those single-stage units which are producing maximum quantities of LPG.

The present novel multiple-stage hydrocracking process offers a measure of control, while simultaneously producing gasoline and LPG, in response to the fluctuating market demands. In general, the first zone will function to produce from about 40.0% to about 90.0% of the desired quantity of gasoline while the second zone serves to maximize LPG, accompanied by the production of the remainder of the gasoline boiling range hydrocarbons. During those periods when LPG is in greater demand, the first zone will function to produce less gasoline while the second zone is conducted at an operating severity which increases the production of LPG.

OBJECTS AND EMBODIMENTS

An object of the present invention is to convert heavy hydrocarbonaceous charge stocks into lower-boiling hydrocarbon products. A corollary objective is to produce LPG and gasoline boiling range hydrocarbons simultaneously from charge stocks boiling above the gasoline point boiling range.

Another object of my invention is to afford a measure of control with respect to the quantities of LPG and gasoline produced in a hydrocracking process.

Therefore, in one embodiment, my invention is directed toward a process for the simultaneous production of LPG and gasoline boiling range hydrocarbons, from a heavier-than-gasoline charge stock, which process comprises the steps of: (a) hydrocracking said charge stock, in a first catalytic hydrocracking reaction zone, at conditions of temperature and pressure selected to produce gasoline range hydrocarbons; (b) separating the resulting hydrocracked effluent, in a first separation zone, at substantially the same pressure and a temperature selected to provide a first vaporous phase containing gasoline boiling range hydrocarbons, and a normally liquid phase; (c) hydrocracking said normally liquid phase in a second hydrocracking catalytic reaction zone, at conditions of temperature and pressure selected to produce LPG; (d) introducing the resulting second zone hydrocracked effluent into said first separation zone; and, (e) separating said vaporous phase, in a second separation zone, at substantially the same pressure and a temperature in the range of about 60° F. to about 140° F. to recover gasoline boiling range hydrocarbons and LPG, and to provide a second vaporous phase.

Other embodiments of my invention involve preferred processing conditions and techniques, and catalytic composites for utilization in the hydrocracking reaction zones. In one such other embodiment, the first separation zone

Oct. 10, 1972 R. J. J. HAMBLIN 3,697,413

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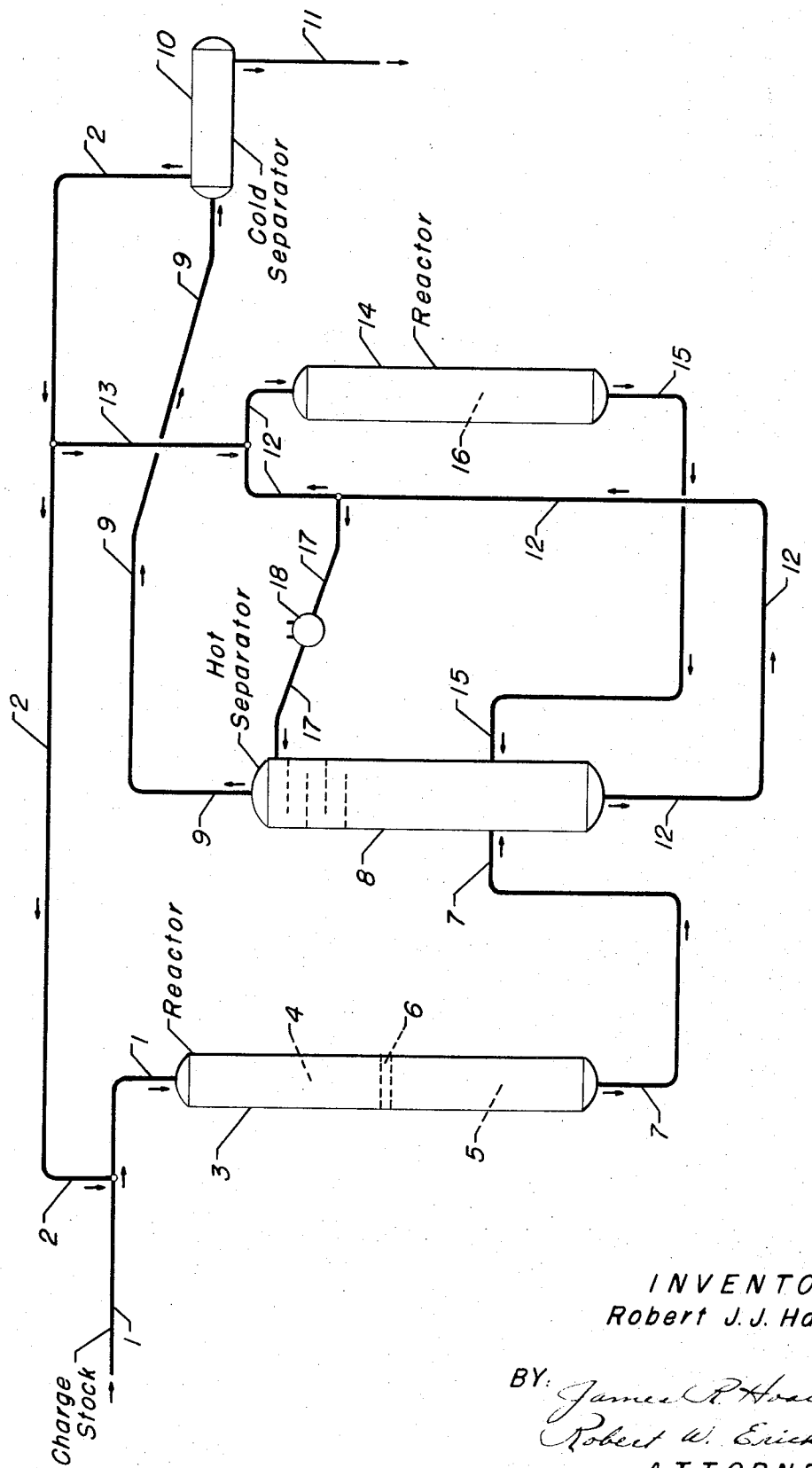

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evident to those possessing skill in the art of petroleum refining technology. The drawing will be described in connection with a commercially-scaled unit designed to process about 74,000 barrels per day of a blend of gas oils having a gravity of about 23.6° API, and containing 0.94% by weight of sulfur and 1,380 p.p.m. of nitrogenous compounds. The initial boiling point of the gas oil blend is about 538° F., the 50.0% volumetric distillation temperature is about 749° F. and the end boiling point is about 1,021° F., with the intended objects being the maximum production of a heptane-380° F. end point gasoline fraction and about 30.0% by volume, based upon fresh feed, or liquefied petroleum gas. The gas oil charge stock in line **1** is admixed with a hydrogen-rich recycle gaseous phase in line **2** and, after heating to a temperature of about 650° F., is introduced into reactor **3**. The upper portion of reactor **3** contains a desulfurization catalyst bed **4** comprising 1.8% by weight of nickel and 16.0% by weight of molybdenum, combined with a carrier material of 63.0% by weight of alumina and 37.0% by weight of silica. The pressure imposed on the reactor **3** is about 1850 p.s.i.g., and the charge stock contacts the desulfurization catalyst at a liquid hourly space velocity of about 0.85 with the hydrogen concentration being about 10,000 s.c.f./bbl.

In the lower portion of reactor **3**, immediately below desulfurization catalyst bed **4**, is hydrocracking catalyst bed **5**. The two catalyst beds are separated by a suitable grid, or plate **6** which serves to prevent commingling of the two catalytic composites. The hydrocracking catalyst bed **5** is a composite of about 5.30% by weight of nickel and a carrier material comprising about 40.0% by weight of faujasite dispersed within an alumina-silica matrix. A hydrogen quench stream is introduced just prior to hydrocracking catalyst bed **5** in order to decrease a temperature of the desulfurized effluent from about 750° F. to about 725° F. The hydrocracked product effluent, at a temperature of about 750° F. is introduced via line **7** into hot separator **8** at a pressure of about 1800 p.s.i.g. Hot separator **8** contains a rectifying section which is refluxed in a manner hereinafter set forth in order to control the end boiling point of the vaporous phase withdrawn as an overhead through line **9** at a temperature of about 380° F. Higher boiling material is removed as a normally liquid bottom stream through line **12**, and introduced therethrough, in admixture with recycle hydrogen from line **13**, into second hydrocracking reaction zone **14**, at a pressure of about 1825 p.s.i.g. and a catalyst bed inlet temperature of about 725° F.

Hydrocracking reactor **14** contains a bed of catalyst **16** comprising about 5.2% by weight of nickel combined with a faujasitic carrier materal of which about 92.3% by weight is zeolitic. The liquid hourly space velocity is about 0.47 and the hydrogen concentration is about 13,000 s.c.f./bbl. The effluent from reactor **14** is withdrawn by way of line **15** and introduced into hot separator **8**. In order to control the separation effected in hot separator **8**, the rectifying section is refluxed with a portion of the hot separator bottom stream being diverted from line **12** through line **17** containing heat-exchanger **18**. The principally vaporous phase in line **9** is cooled and condensed to a temperature of about 100° F., and introduced into a cold separator **10** at a pressure about 1750 p.s.i.g.

A hydrogen-rich gaseous phase is withdrawn from cold separator **10** by way of line **2**, and, preferentially, is treated for the purpose of removing hydrogen sulfide and/or light paraffinic hydrocarbons prior to being recycled therethrough to combine with the charge stock in line **1**. A portion of the recycle gas is diverted by way of line **13** to combine with the separator bottoms in line **12**, prior to introducing the same into reactor **14**. A principally liquid phase is withdrawn from cold separator **10** through line **11** and subjected to separation facilities to provide the desired products slate.

The following table indicates the component yields and product distribution of the process as illustrated, and are inclusive of an overall hydrogen consumption in an amount of about 2,140 s.c.f./bbl., or 3.54% by weight of the total fresh feed charge stock.

TABLE II.—PRODUCT YIELD AND DISTRIBUTION

Component	Weight percent	Volume percent
Ammonia	0.17	
Hydrogen sulfide	1.00	
Methane	0.34	
Ethane	0.48	
Propane	3.44	6.20
Butanes	14.05	22.52
Pentanes	10.07	14.70
Hexanes	14.36	18.98
Heptane (389° F.)	59.63	71.17

The desired gasoline fraction is produced in a yield of 71.17% by volume of fresh feed. When taken in conjunction with the hexanes and pentanes, the latter being 93.0% isopentane, the volumetric yield of normally liquid hydrocarbons becomes 104.85% by volume of fresh feed. It should be noted that the 28.72% by volume PLG(C_3/C_4 concentrate) is just slightly less than the target quantity.

The inherent flexibility of the present process will be evident to those having the requisite expertise in petroleum refining arts. By varying the operating severity in catalyst bed **5**, the quantity and quality of the feed to reactor **14** can be varied. Varying the operating severity in catalyst bed **16** offers a measure of control over the product slate.

The foregoing specification clearly illustrates the method of effecting the present invention and the benefits to be afforded through the utilization thereof.

I claim as my invention:

1. A process for the simultaneous production of LPG and gasoline boiling range hydrocarbons, from a heavier-than-gasoline charge stock, which comprises the steps of:

(a) hydrocracking said charge stock, in a first catalytic hydrocarcking reaction zone, at conditions of temperature and pressure selected to produce gasoline boiling range hydrocarbons;

(b) separating the resulting hydrocracked effluent, in a first separation zone, at substantially the same pressure and a temperature selected to provide a first vaporous phase containing gasoline boiling range hydrocarbons, and a normally liquid phase;

(c) hydrocracking said liquid phase in a second catalytic hydrocracking reaction zone, at conditions of temperature and pressure selected to produce LPG;

(d) introducing the resulting second zone hydrocracked effluent into said first separation zone; and,

(e) separating said vaporous phase, in a second separation zone, at substantially the same pressure and a temperature in the range of 60° F. to about 140° F. to recover gasoline boiling range hydrocarbons and PLG, and to provide a second vaporous phase.

2. The process of claim **1** further characterized in that at least a portion of said second vaporous phase is recycled to both of said first and second hydrocracking reaction zones.

3. The process of claim **1** further characterized in that the maximum catalyst temperature in said second hydrocracking zone is greater than that in said first hydrocracking zone.

4. The process of claim **1** further characterized in that said charge stock is sulfurous and is desulfurizsed prior to hydrocracking in said first hydrocracking reaction zone.

5. The process of claim **4** further characterized in that said first hydrocracking reaction zone contains a bed of desulfurization catalyst disposed above a bed of hydrocracking catalyst.

6. The process of claim 1 further characterized in that said first separation zone contains a rectifying section and a portion of said normally liquid phase is introduced therein as reflux thereto.

References Cited

UNITED STATES PATENTS

3,047,490	7/1962	Myers	208—59
3,180,819	4/1965	Claussen et al.	208—59
3,215,617	11/1965	Burch et al.	208—59
3,256,178	6/1966	Hass et al.	208—89
3,516,925	6/1970	Lawrance et al.	208—111

3,583,902	6/1971	Masologites et al	208—59
3,617,483	11/1971	Child et al.	208—59

FOREIGN PATENTS

1,472,728	1/1967	France	208—59

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U.S. Cl. X.R.

208—89, 103