April 18, 1967 R. H. KOZLOWSKI 3,314,878

HYDROCARBON CONVERSION FOR LIGHT GAS PRODUCTION

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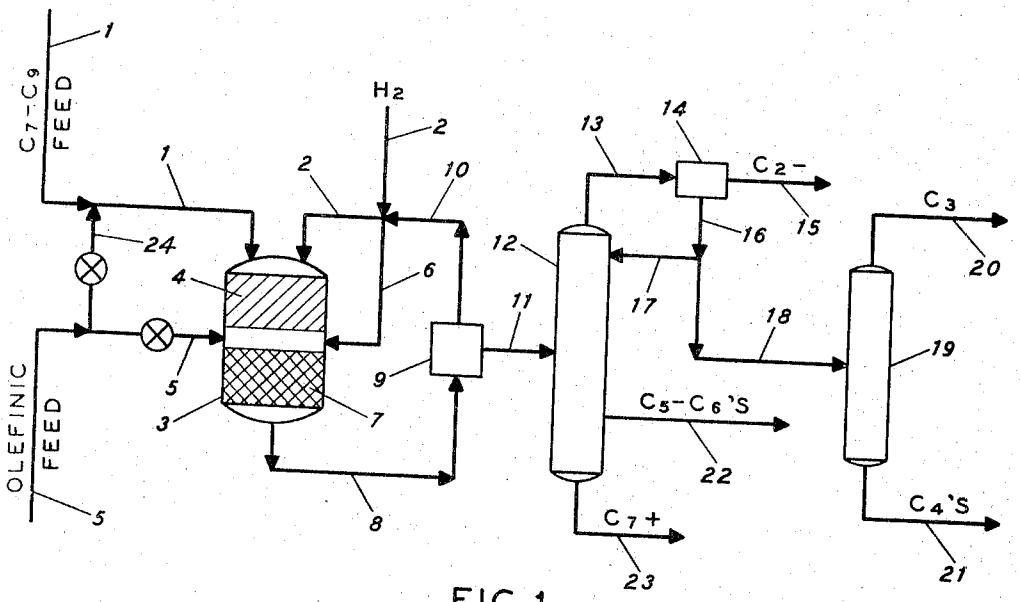


FIG. 1

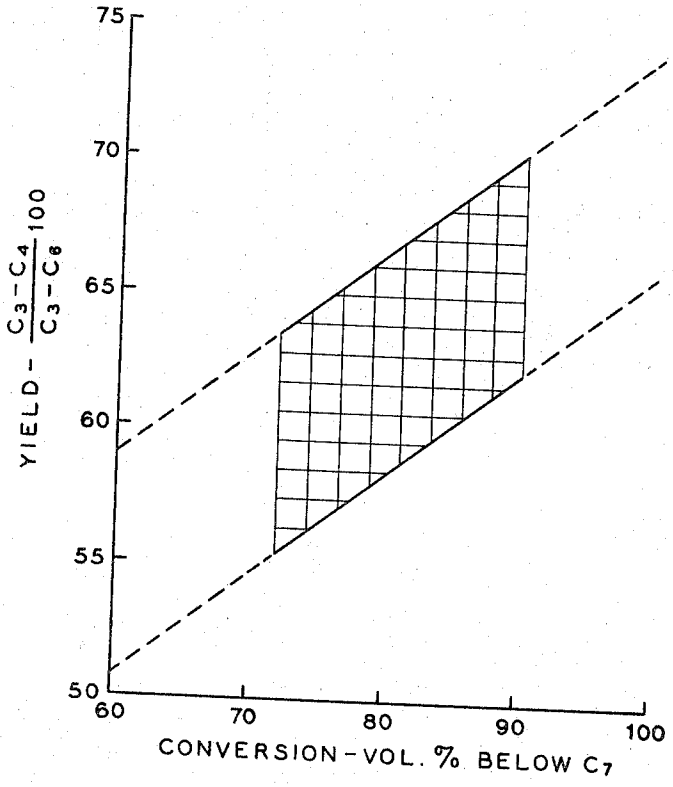


FIG. 2

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HYDROCARBON CONVERSION FOR LIGHT GAS PRODUCTION

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10 Claims. (Cl. 208—58)

This invention relates to a process for the catalytic conversion of hydrocarbon distillates to light gases. More particularly, the invention relates to a catalytic conversion process for hydrocracking hydrocarbon distillates to light gases. Still more particularly, the invention relates to a combination catalytic conversion process for hydrocracking hydrocarbon distillates to light gases and for hydrogenating olefins to paraffins.

The refiner is currently faced with the problem of how to dispose of low boiling distillates, i.e., C_7–C_9 light straight run gasoline fractions boiling between about 170°–320° F. which have no gasoline potential because of their low octane number. In many areas the refiner is also faced with a problem of disposing of large amounts of low boiling olefinic feeds. This is especially true where there is an imbalance between i-butane and butenes which are used in preparing "alkylate." In contrast, the refiner has the problem of meeting the demand for propane and n-butane used in LPG and i-butane used in preparing "alkylate."

Heretofore, the refiner has found it difficult to achieve high yields of propane and butanes from low boiling distillates in a hydrocracking process operating at low pressures while maintaining high conversions to products boiling below the initial boiling point of the feed. In Patent 2,428,692, high yields of butanes and pentanes were obtained from a cycle stock boiling between about 290° and 470° F. only by destructively hydrogenating at high pressures and high hydrocarbon recycle rates. In addition, very low yields of propane were obtained in this destructive hydrogenation process. It would be desirable if a low-pressure process were available for hydrocracking low value distillates into higher yields of high value propane and butane gases than previously obtainable without the necessity of hydrocarbon recycle.

Heretofore, the refiner has carried out reactions for hydrocracking distillate feeds and hydrogenating olefinic feeds in separate reactors and has recovered the products from separate distillation systems. This has resulted in an uneconomical and inefficient process. It would be desirable if an economical process were available for hydrocracking a distillate feed and hydrogenating an olefinic feed in the same reactor and recovering the combined products from a common distillation system.

It is an object of the present invention to provide a process for hydrocracking a low boiling hydrocarbon distillate feed and hydrogenating a low boiling olefinic feed on a once-through basis at low pressures in the same reactor and recovering the products from a common distillation system.

This invention will be more clearly understood and further objects and advantages thereof will be apparent from the foregoing description when read in connection with the accompanying drawings, in which:

FIGURE 1 is a diagrammatic illustration of a simplified embodiment of process units and flow paths suitable for carrying out one embodiment of the present invention;

FIGURE 2 is a graphical illustration of the conversion to products boiling below the C_7 boiling range plotted against the product yield expressed at

$$\frac{C_3-C_4}{C_3-C_6}\times 100$$

A preferred method of operating the process of the present invention is to contact the hydrocarbon distillate feed and hydrogen in a hydrocracking zone with a hydrocracking catalyst comprising a hydrogenating-dehydrogenating component and an active cracking component at operating conditions of about 550°–750° F., about 800–1000 p.s.i.g. and about 0.3–1.0 LHSV on a once-through basis to convert above about 60% of said distillate feed to products boiling below the C_7 boiling range and to contact the effluent from said hydrocracking zone and an olefinic feed selected from the group consisting of C_3–C_6 olefins in a hydrogenation zone with a hydrogenation catalyst consisting essentially of a hydrogenating-dehydrogenating component and a non-active, non-acidic cracking component selected from the group consisting of silica, titania, zirconia, bauxite, charcoal and alumina, at operating conditions of about 500°–775° F., about 800–1000 p.s.i.g. and about 0.1–10 LHSV on a once-through basis to convert above about 90% of said olefinic feed to paraffins. If desired the olefinic feed first may be contacted in a hydrogenation zone with the hydrogenating catalyst, and the effluent from the hydrogenation zone and the distillate feed then may be contacted in a hydrocracking zone with the hydrocracking catalyst. However, this method of operation is not preferred because the effluent from the hydrogenation zone causes lower hydrogen partial pressure and dilution of the reaction mix in the hydrocracking zone.

Suitable hydrocarbon feeds to the hydrocracking zone include distillates boiling between 170°–320° F. such as C_7–C_9 naphthas. Suitable hydrocarbon feeds to the hydrogenation zone include C_3, C_4, C_5 and C_6 olefins or any combination of such olefins. Such naphthas and olefins may be obtained from the thermal cracking or catalytic cracking of various stocks including those obtained from petroleum, gilsonite, shale and coal oil. The naphtha feeds are generally of low octane number, and hence, a low value to the refiner.

The process of the present invention becomes much more economical with feed containing less than 50 p.p.m. of total nitrogen and preferably less than 10 p.p.m. and still more preferably less than 1 p.p.m. The naphthas suitable as feeds to the hydrocracking zone are generally quite low in nitrogen content and do not require pretreatment. In the case the naphtha feeds are not available which are inherently low in nitrogen, acceptable nitrogen levels can be reached by other conventional methods such as acid treatment or hydrofining. On the other hand, the olefins suitable as feeds to the hydrogenation zone often contain more than preferred levels of nitrogen. The nitrogen content of the olefinic feeds may be decreased to preferred levels by any suitable method. One method particularly adapted to these types of low boiling olefinic feeds is washing the olefins countercurrently with water in a packed column. By water washing in this manner, total nitrogen levels of 5 p.p.m. have been decreased to about 0.3 p.p.m. with water to hydrocarbon ratios of 8.

The operating conditions in the hydrocracking zone include perssures in the range of about 800–1000 p.s.i.g. It has been found that this range is critical in order to obtain the desired yields and conversions in the hydrocracking zone. It has been found that as the pressure is reduced below 800 p.s.i.g. down to about 500 p.s.i.g. there occurs a drastic reduction in conversion below C_7 and yield as described above. As the pressure is increased from 1000 p.s.i.g. up to about 1700 p.s.i.g., there is a noticeable decrease in the conversion below C_7 and yield as described above. At pressures outside the range of about 800–1000 p.si..g. there is also an increase in the fouling rate of the hydrocracking catalyst. The operating conditions for the hydrocracking zone also include temperatures in the range of about 550°–750° F., preferably 600°–750° F., and space velocities in the range of about

0.3–1.0 LHSV. Below 550° F. the temperature is insufficient to convert the feed to the desired products and above 750° F. the fouling rate of the hydrocracking catalyst becomes too great to warrant further operation. By operating at such conditions, the once-through conversion in the hydrocracking zone is above about 60% to products predominantly comprising C_3, iC_4 and nC_4. That is,

$$\frac{C_3-C_4}{C_3-C_6}\times 100$$

is above about 50% and the remainder of the product is a C_5–C_6 high octane gasoline blending stock. The remaining C_7+ material has a higher octane number and is a better reforming feed than the original distillate.

The hydrocracking catalyst comprises a hydrogenating-dehydrogenating component such as any Group VIII metal, preferably platinum or sulfides of nickel and/or cobalt intimately associated with a solid, active, acidic cracking component. The active, acidic component may comprise any of the conventional cracking catalysts such as silica-alumina, silica-alumina-zirconia, acid-treated clays and the like. A preferred active, acidic component for use in the hydrocracking catalyst of the present invention is comprised of synthetically prepared silica-aluminas having silica contents in the range of from about 70 to 99%. The total amount of hydrogenating-dehydrogenating component can vary from about 0.1–10 weight percent (calculated as metal) of the catalyst composition. It has been found that hydrocracking catalysts having metal levels above this range foul at an excessive rate when used in the process of the present invention. The hydrocracking catalyst of the present invention may be prepared in a manner as set forth in Patent No. 2,944,006.

The hydrogenation zone operating conditions include at least about 1000 s.c.f. hydrogen/bbl. of olefinic feed, an LHSV from about 0.1–10, pressures in the range of about 800 to 1000 p.s.i.g., and temperatures in the range of about 500–775° F.

The hydrogenation catalyst comprises a hydrogenating-dehydrogenating component and a, i.e. non-acidic, cracking component. The hydrogenating component comprises at least one of the Group VI and at least one of the Group VIII metals, preferably cobalt-molybdate. The non-active cracking component comprises silica, titania, zirconia, bauxite, charcoal or alumina. The preferred hydrogenation catalyst comprises cobalt-molybdate on alumina as prepared in a manner set forth in Patent No. 2,878,193.

Referring now to FIGURE 1 there is shown a simplified schematic illustration of a preferred embodiment of process units and flow paths suitable for carrying out the process of the present invention. A distillate feed is passed through line **1** to reactor **3** where it is hydrocracked by contact with hydrocracking catalyst in zone **4** in the presence of make-up hydrogen, supplied through line **2**, under suitable conditions as discussed above. A water-washed olefinic feed is passed through line **5** to reactor **3** where it is hydrogenated by contact with hydrogenation catalyst in zone **7** in the presence of make-up hydrogen, supplied through lines **2** and **6**. The effluent from hydrocracking zone **4** is passed to hydrogenation catalyst zone **7**. The effluent from zone **7** is passed through line **8** to high pressure separator **9**. From high pressure separator **9**, hydrogen is recycled to line **10** to reactor **3** and a hydrocarbon stream is passed through line **11** to distillation column **12**. Column **12** overhead is passed through line **13** to reflux drum **14**. From reflux drum **14**, a C_2- fraction is removed through line **15** and a C_3–C_4 fraction is removed through line **16**. A portion of the C_3–C_4 fraction is refluxed to distillation column **12** through line **17** and the remaining portion is passed as feed to column **19** through line **18** where the C_3 product is recovered through line **20** and C_4's are recovered through line **21**. The C_4's may be separated further into an nC_4 product and an iC_4 product in another column not shown. A high octane C_5–C_6 blending stock is recovered from column **12** through line **22** and a C_7+ bottoms fraction is passed through line **23** to be blended with the C_5–C_6 stock or passed to further processing such as catalytic reforming.

If desired, a portion of the olefinic feed may be passed through lines **24** and **1** to hydrocracking zone **4**.

Referring next to FIGURE 2 there is shown a graphical illustration of the hydrocracking conversion to products boiling below the C_7 boiling range as a function of the product yield expressed as

$$\frac{C_3-C_4}{C_3-C_6}\times 100$$

The broad band between the two parallel lines represents a region in which most of the results would fall if one were to operate within the range of hydrocracking conditions of the process of the present invention. The cross-hatched section between the two solid parallel lines represents a region in which the laboratory data fell. This figure indicates that by means of one embodiment of the process of the present invention, products predominantly comprising C_3, iC_4 and nC_4 hydrocarbons can be obtained at overall conversions below C_7 above about 60%.

Examples

Table I below indicates the inspections of the various naphtha feed stocks used as feed to the hydrocracking zone in the examples below.

TABLE I.—NAPHTHA FEED INSPECTIONS

	Feed		
	North African	Arabian	Sumatra
Gravity, ° API	60.4	61	60.5
ASTM D-86, ° F., LV Percent:			
St	211	215	210
5	221	227	225
10	222	228	228
30	232	240	238
50	241	252	251
70	253	266	268
90	274	284	292
95	281	291	302
EP	313	322	355
Octane No., F–1 Clear		36.0	36.0
F–1+3 ml. TEL/gal		58.5	62.6
Total Nitrogen, p.p.m	0.1	0.1	0.27
Sulfur, p.p.m	12	146	36

Example 1

Table II below indicates the operating conditions and product yields obtained by hydrocracking the North African and the Arabian naphtha feed of Table I on a once-through basis by contact with a NiS_x (6 wt. percent Ni) and silica-alumina catalyst.

TABLE II.—OPERATING CONDITIONS AND PRODUCTS YIELDS

	Feed	
	North African	Arabian
Run No.	1	2
Operating Conditions:		
Pressure, p.s.i.g	800	780
Temperature, ° F	680	664
LHSV	0.3	0.3
Total Gas Rate, s.f.c./b	5,960	5,580
Conversion below C_7, LV percent	83.8	82.3
Product Yields, Wt. percent:		
C_1	0.06	0.03
C_2	0.32	0.13
C_3	16.6	13.4
iC_4	28.4	28.1
nC_4	10.8	8.7
C_5's	21.0	20.4
C_6's	9.2	14.1
C_7+	16.2	17.5
Total C_3–C_4	55.8	50.2
Total C_3–C_6	86.0	84.7
$\frac{C_3-C_4}{C_3-C_6}\times 100$	64.9	59.3

Example 2

Table II below indicates the critical effect pressure has on hydrocracking the North African naphtha feed of Table I in the presence of a NiS_x (6 wt. percent Ni) and silica-alumina catalyst. Table III shows that with all other conditions remaining essentially constant, there is a decrease in the conversion below C_7 and

$$\frac{C_3-C_4}{C_3-C_6}\times 100$$

when the hydrocracking reaction is operated in a pressure range other than about 800–1000 p.s.i.g.

TABLE III

Run No.	3	4	5
Operating Conditions:			
Pressure, p.s.i.g.	800	500	1,100
Temperature, ° F.	712	719	719
LHSV	0.3	0.3	0.3
Total Gas Rate, s.c.f./b.	6,070	5,490	6,150
Conversion below C_7, LV percent	87.4	76.6	86.1
Product Yields, Wt. Percent:			
C_1	0.08	0.07	0.08
C_2	0.33	0.55	0.46
C_3	17.4	13.2	16.2
iC_4	31.1	23.2	26.8
nC_4	13.7	9.7	11.6
C_5's	15.6	18.1	22.8
C_6's	7.7	9.0	9.3
Total C_3–C_4	62.2	46.1	54.6
Total C_3–C_6	85.5	73.2	86.7
$\frac{C_3-C_4}{C_3-C_6}\times 100$	72.7	63.0	63.0

Example 3

Table IV below indicates the operating conditions and product yields obtained on hydrocracking the North African naphtha feed of Table I in the presence of a 0.5 wt. percent Pt and silica-alumina catalyst.

TABLE IV

Run No.	6
Operating conditions:	
Pressure, p.s.i.g.	900
Temperature, F.	753
LHSV	0.95
Conversion below C_7, LV percent	81.0
Product yields, wt. percent:	
C_1	0
C_2	0
C_3	15.0
iC_4	20.6
nC_4	16.5
iC_5	12.2
nC_5	7.2
C_6's	9.5
Total C_3–C_4	52.1
Total C_3–C_6	81.0
$\frac{C_3-C_4}{C_3-C_6}\times 100$	64.3

Example 4

Table V below indicates the inspections of a pentene fraction obtained from the fluid catalytic cracking of a Sumatra heavy gas oil, used as the feed to the hydrogenation zone.

TABLE V.—PENTENES FEED INSPECTIONS

89.1° API
85 bromine No.
~70 calculated percent olefins
Ave. N_2 content:
4.7 p.p.m. before H_2O wash
0.35 p.p.m. after H_2O wash

Table VI below indicates the operating conditions, product yields and product properties obtained on hydrocracking the Sumatra naphtha feed of Table I on a once-through basis in the presence of a NiS_x (6 wt. percent Ni) disposed on silica-alumina. Table VI also indicates the operating conditions, product yields and product properties obtained on hydrocracking this same feed at the same conditions and hydrogenating downstream in the same reactor the effluent from the hydrocarcking zone and the water-washed pentene feed of Table V on a once-through basis in the presence of a Co (3.5 wt. percent)–Mo (12 wt. percent) disposed on alumina catalyst. Table VI shows that the leaded octane number of the C_7+ bottoms is 77.0 on hydrocracking and 75.0 on hydrocracking with olefin hydrogenation compared to a leaded octane number of 62.6 for the fresh Sumatra feed of Table I. Thus, the C_7+ bottoms can be blended with the C_5–C_6 products to give a gasoline product having an overall leaded octane number of 93 on hydrocracking and 95 on hydrocracking with olefin hydrogenation. Table VI also shows that by hydrocracking with olefin hydrogenation the bromine number of the C_5–C_6 products is 0.03 which indicates that greater than 99% of the olefins in the feed to the hydrogenation zone were hydrogenated to paraffins.

TABLE VI

	Run No. 7	Run No. 8
	Zone Hydrocracking	Zone Hydrogenation
Operating Conditions:		
Pressure, p.s.i.g.	750	750
Temperature, ° F.	1 630	2 700
LHSV	0.3	1.0
Total Gas Rate, s.c.f./b.	5,700	16,800
Conversion Below C_7, LV percent	86.3	
	Hydrocracking Alone	Hydrocracking with Olefin hydrogenation
Product Yields, Wt. percent (Based on Naphtha feed):		
C_1	0.03	0.04
C_2	0.13	.14
C_3	14.2	13.8
iC_4	28.7	30.3
nC_4	10.1	10.4
C_5's	20.5	58.3
C_6's	14.7	15.9
C_7	13.6	17.7
Total C_3–C_4	53.0	
Total C_3–C_6	88.2	
$\frac{C_3-C_4}{C_3-C_6}\times 100$	60.1	
C_5–C_6 Product Properties:		
Bromine No.		0.03
Octane No. F-1+3 ml. TEL/gal.	98.5	99.3
C_7+Bottoms Properties:		
Bromine No.		0.07
Octane No. F-1+3 ml. TEL/gal.	77.0	75

[1] Average.
[2] Maximum.

Although only specific embodiments of operation of the present invention have been described, numerous variations could be made in those embodiments without departing from the spirit of the invention and all such variations that fall within the scope of the appended claims are intended to be embraced thereby.

I claim:

1. A hydrocracking-hydrogenation process which comprises contacting a hydrocarbon distillate feed boiling between about 170° and 320° F. and hydrogen in a hydrocracking zone with a hydrocracking catalyst comprising a hydrogenating-dehydrogenating component and an active acidic cracking component comprising a conventional cracking catalyst at operating conditions of about 550°–750° F., about 800–1000 p.s.i.g. and about 0.3–1.0 LHSV on a once-through basis thereby converting above about 60 percent of said distillate feed to products boiling below the C_7 boiling range and predominantly comprising C_3,

iC_4 and nC_4 hydrocarbons, and contacting the effluent from said hydrocracking zone and an olefinic feed selected from the group consisting of C_3–C_6 olefins in a hydrogenation zone with a hydrogenation catalyst consisting essentially of a hydrogenating-dehydrogenating component and a nonactive non-acidic cracking component seletced from the group consisting of silica, titania, zirconia, bauxite, charcoal and alumina, at operating conditions of about 500°–775° F., about 800–1000 p.s.i.g. and about 0.1–10 LHSV on a once-through basis to convert above about 90 percent of said olefinic feed to paraffins.

2. A process as in claim 1, wherein said hydrocracking catalyst comprises nickel sulfide and silica-alumina.

3. A process as in claim 1, wherein said hydrocracking catalyst comprises platinum and silica-alumina.

4. A process as in claim 1, wherein said hydrogenation catalyst comprises cobalt-molybdenum and alumina.

5. A process as in claim 1, wherein said olefinic feed is water-washed prior to contact with said hydrogenation catalyst.

6. A hydrocracking-hydrogenation process which comprises contacting an olefinic feed selected from the group consisting of C_3–C_6 olefins and hydrogen in a hydrogenation zone with a hydrogenation catalyst consisting essentially of a hydrogenating-dehydrogenating component and a nonactive non-acidic cracking component selected from the group consisting of silica, titania, zirconia, bauxite, charcoal and alumina, at operating conditions of about 500°–775° F., about 800–1000 p.s.i.g. and about 0.1–10 LHSV on a once-through basis to convert above about 90 percent of said olefinic feed to paraffins and contacting

the effluent from said hydrogenation zone and a hydrocarbon distillate feed boiling between about 170° and 320° F. in a hydrocracking zone with a hydrocracking catalyst comprising a hydrogenating-dehydrogenating component and an active acidic cracking component comprising a conventional cracking catalyst at operating conditions of about 550°–750° F., about 800–1000 p.s.i.g. and about 0.3–1.0 LHSV on a once-through basis, thereby converting above about 60 percent of said distillate feed to products boiling below the C_7 boiling range and predominantly comprising C_3, iC_4 and nC_4 hydrocarbons.

7. A process as in claim 6, wherein said hydrogenation catalyst comprises cobalt-molybdenum and alumina.

8. A process as in claim 6, wherein said olefinic feed is water-washed prior to contact with said hydrogenation catalyst.

9. A process as in claim 6, wherein said hydrocracking catalyst comprises nickel sulfide and silica-alumina.

10. A process as in claim 6, wherein said hydrocracking catalyst comprises platinum and silica-alumina.

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