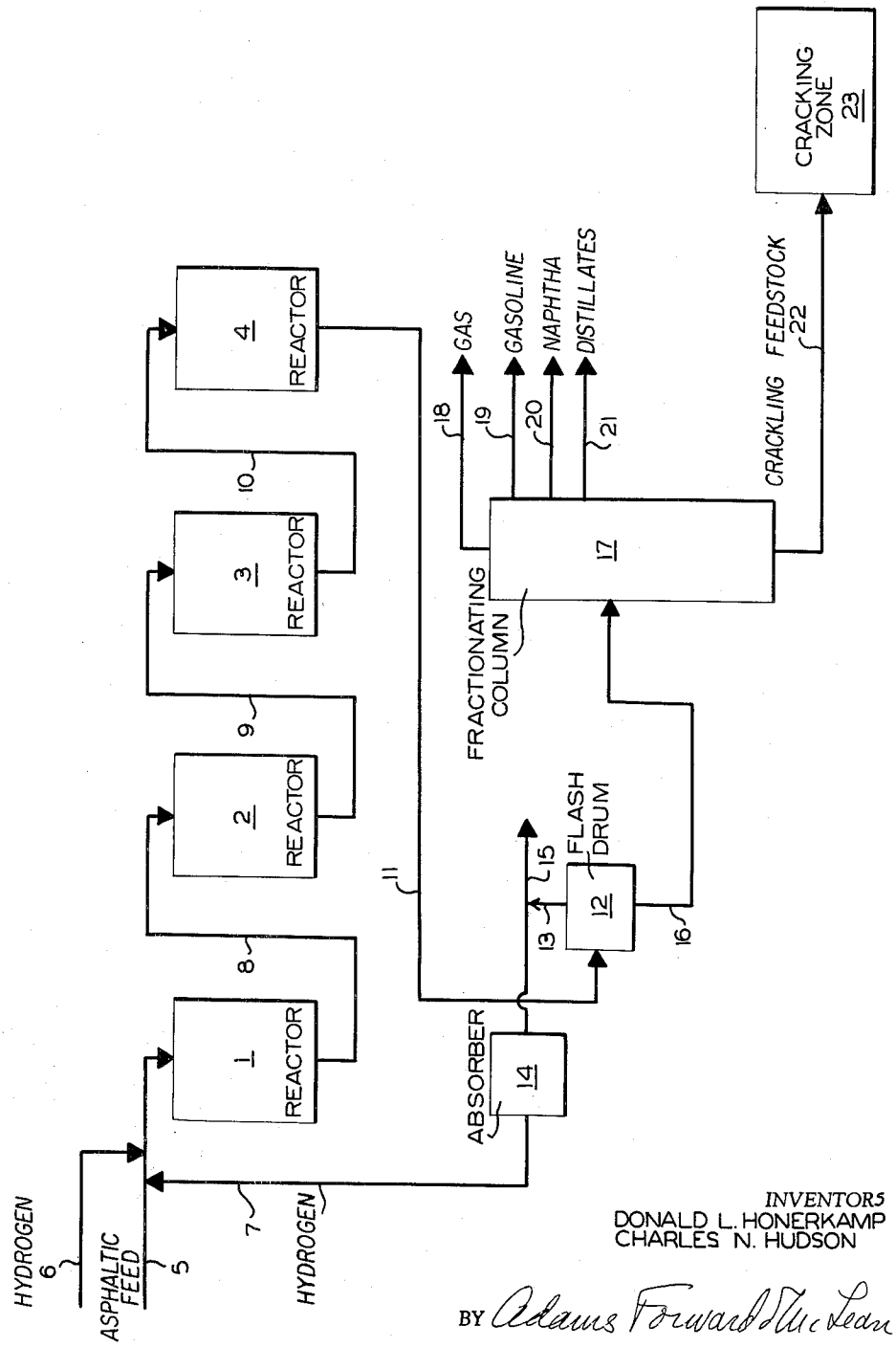
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PROCESS FOR HYDROCRACKING AN ASPHALT RESIDUAL FEED STOCK

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PROCESS FOR HYDROCRACKING AN ASPHALT RESIDUAL FEED STOCK

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Our invention relates to an improvement in the hydrocracking of asphalt-containing petroleum residual fractions to produce lower boiling materials and more particularly to a method of producing high yields of feedstock for catalytic cracking.

It has heretofore been proposed to hydrocrack petroleum residual fractions by passing such fractions together with hydrogen into contact with a hydrogenation catalyst under elevated conditions of temperature and pressure to produce gasoline and the like. In hydrocracking, it is frequently desirable to operate at relatively mild conditions of pressure, e.g. about 1000 p.s.i.g. in order to reduce capital and operating costs, and it is also desirable in this case to recycle the residual portion of the hydrocracked product, in order to produce as much gasoline and the like as possible from a given quantity of fresh feed. In hydrocracking petroleum residual fractions under relatively mild conditions of pressure and with recycling, it is found, however, that undue fouling and plugging of the reaction system takes place.

In accordance with our invention we have discovered a new and improved process for producing high yields of catalytic cracking feedstock under the select operating conditions of relatively high pressure, low temperature and low space velocity. This improved process facilitates the feeding of material boiling above the gas oil range, for instance the approximate 650° F. plus product, to a catalytic cracking unit while allowing only a minimum of cracking due to low temperatures in the hydrocracking operations. By feeding all of the 650+ product to catalytic cracking, the problems such as fouling and plugging associated with recycling and separation of the residual fraction are overcome in the high pressure operation. Further, this process by utilizing susbtantially all of the heavier boiling products, provides more catalytic cracking feedstock and thus eventually more of the desired products boiling in the gasoline boiling range, etc. Normally, in the catalytic cracking step, there is a conversion of about 50 to 80% of the feedstock to products boiling in the gasoline boiling range and below. In the hydrocracking stage the conditions of high pressure, etc. allow for long operating cycles which are economically desirable in light of the large volumes of catalysts required. Also, as there is low space velocity, long catalyst life and only infrequent regeneration of the catalyst is generally required.

Hence, our invention is an improved process for hydrocracking of asphalt-containing petroleum residuals in which the feed is passed under hydrocracking conditions in admixture with hydrogen into contact with a hydrocracking catalyst. The feed for our process is generally heavy residual crude, for example, penetration range asphalts having a penetration of about 250 or less at 77° F. The catalysts utilized in our process are those normally employed in the hydrocracking of heavy petroleum oils. Examples of suitable catalyst ingredients are molybdenum, tungsten, vanadium, chromium, cobalt, nickel, iron and tin and their oxides and sulfides. Mixtures of these materials or compounds or two or more of the oxides can be employed. For example, mixtures or compounds of the iron group metal oxides or sulfides with the oxides or sulfides of group VI left column of the periodic table constitute very satisfactory catalysts. Examples of such mixtures or compounds are nickel molybdate, tungstate or chromate (or thiomolybdate, thiotungstate or thiochromate) or mixtures of nickel oxide with molybdenum, tungsten or chromium oxides. Minor amounts of these catalytic ingredients can be dispersed on or carried by other materials, such as oxides, silicates, or mixtures of oxides and silicates. Synthetic cracking catalysts of this type are generally the activated oxides of aluminum and the like, mixtures of oxides of silica with oxides of magnesium, boron, aluminum, titanium, zirconium. Specific examples of suitable cracking catalysts are cobalt-molybdena on alumina, nickel-tungsten oxide on alumina, nickel-tungsten sulfide on alumina, and cobalt-molybdenum on silica-alumina. In view of the large amounts of catalysts utilized in this invention the catalyst particle size should be as large as practical while remaining consistent with the strength and effectiveness requirements of the process in order to minimize costs, pressure drops and the like.

The hydrocracking zone of our process has relatively high pressure conditions generally from about 2000 to 3000 p.s.i.g. with a preferred pressure range of from about 2200 to 2700 p.s.i.g. The temperature used in the hydrocracking zone is generally from about 760 to 810° F. with a preferred temperature range of from about 780° F. to 800° F. The residual feed is contacted with hydrogen in the hydrocracking zone. The free hydrogen in the hydrocracking zone is generally from about 2000 to 7000 standard cubic feet per barrel of fresh residual feed and it is convenient to provide most of the hydrogen by recycle of gas. Make-up hydrogen can be added as desired. The resulting hydrogen consumption is from about 500 to 1500 standard cubic feet per barrel of fresh feed. The weight hourly space velocity (WHSV), weight units of feed introduced into the reaction zone per weight unit catalyst per hour, will be within the range of about .1 to 1 WHSV based on the amount of total fresh hydrocarbon feed. The preferred space velocity is from about .3 to 0.7 WHSV. The amount of catalyst required for very low space velocities increases inversely with decreasing WHSV, e.g. a 10,000 barrel a day unit requires 280,000 pounds of catalyst at .7 WHSV while an increase to 487,000 pounds would be required at .3 WHSV. The conditions chosen may also vary with the asphalt feed and with the quality and volume of fluid catalytic cracking feedstock desired.

Our new process provides for the normal amounts of light hydrocracked products of high quality boiling in the gasoline and distillate fuel range and shows further a marked increase of from about 20 to 40 percent or more of a fluid or gas oil boiling range material suitable for use as a catalytic cracking feedstock when compared with the amounts presently available from residual fuel reduction processes. The type, capacity and sequence of the reactor or reactors used in the hydrocracking zone of our invention is dependent upon plant requirements, catalysts employed, process variables and the like.

An example of a suitable embodiment of this invention is shown diagrammatically in the drawing where hydrogen is admixed with an asphalt feed and the mixture then passes in contact with a catalyst in a series of reactors and the product along with hydrogen is then passed to a flash drum where hydrogen and certain light volatile constituents are removed overhead and recycled to the hydrocracking zone substantially as shown. The liquid product is then removed to an atmospheric fractionating column where gas, gasoline, naphtha and distillate fuel separate overhead and the material boiling above the gas

oil range then passes from the bottom of the column to a catalytic cracking unit.

Our process facilitates obtaining an exceptionally high yield of catalytic cracking feedstock of good quality and at the same time minimizing cracking and hydrogen consumption while maintaining catalyst activity for long periods of time. Further, our invention minimizes the capital investment required as the process eliminates the need for expensive vacuum units or their equivalents normally employed in the separation of the feedstock as required in commercial catalytic hydrocracking processes. The catalytic cracking zone may be any desired type of catalytic cracking operation. Thus, the catalytic cracking may constitute the moving bed type of cracking or fluidized catalytic cracking. In each of these types of operation, any of the various well known cracking catalysts may be employed. Generally, such catalysts are the metal oxide types and preferably include silica based catalysts such as silica-alumina, silica-magnesia, or silica gel promoted with metal oxides which are adsorbed thereon. Typical cracking conditions are temperatures in the range of about 750° to 1050° F. and pressures ranging from atmospheric to 3000 p.s.i.g. pressure in the absence of hydrogen. The catalytic agent employed is regenerated intermittently or continuously in order to restore or maintain the activity of the catalyst. For typical operation, catalytic cracking of this feedstock would result in conversion of about 50 to 80% boiling in the gasoline boiling range and below.

The data from Table I which follows illustrate some of the advantages of our process. The operating conditions of our invention are shown in column 1 of Table I.

As shown above, each set of conditions of columns 2–8 meets only with limited success or fails to meet some of the requirements of product quality and quantity. This is shown by column 2 where substantially the same conversion level is obtained but the product quality is inferior in that unsatisfactory amounts of metal contaminants such as vanadium and nickel are present, and thus it would not be possible to feed all of the 650° F. plus product to a fluid catalytic cracking unit. Column 3 has a higher conversion, consequently less cracking feed and also the product quality is inferior. In column 4, the product quality is high but the yield of catalytic cracking feed is low due to the high conversion rate. This high conversion rate would, of course, not result in the desired amounts of 650° F. plus product normally used as feed for cracking processes. In the runs of columns 5 and 6 and little cracking took place, and the product quality was unacceptable and a large part of the total liquid product is of the type normally used as a residual fuel. If bottoms or residual fuel is present in too large amounts it would not be practical to use the entire 650° F. plus material in a subsequent cracking process as there would be catalyst fouling and inordinate coke make. In column 7, the low pressure and high temperature result in short operating cycle due to catalyst deactivation causing shut down for catalyst replacement or regeneration; also the product quality is not sufficiently high even though the yield is good. In column 8, the product quality is not quite as acceptable, the 650° F. plus yield is low and the operating cycles would normally be short due to the high temperature and low pressure conditions resulting in catalyst deterioration which, of course, would

TABLE I

	Asphalt feedstock	Column No.							
		1	2	3	4	5	6	7	8
Operating conditions:									
Pressure, p.s.i.g.		2,500	2,500	2,500	2,500	2,500	2,500	1,500	1,500
Temperature, °F.		790	820	849	820	790	750	840	820
WHSV		0.3	1.0	1.0	0.3	3.0	0.3	1.0	0.3
Stream time, lb. oil/lb. cat.		18	4	4	13	12	13	4	13
Once-thru H_2, SCF/B		6,000	6,000	6,000	6,000	6,000	6,000	6,000	6,000
Conv. to 950° F., weight percent		56.5	55.9	61.0	84.6	26.3	20.9	48.6	74.5
H_2 cons., SCF/B		1,500	1,200	1,590	2,110	670	1,000	960	1,395
Yields, weight percent:									
C_1–C_3		2.3	2.4	5.3	4.9	1.2	0.8	3.5	4.5
Butanes		1.1	1.2	2.9	2.2	1.1	0.3	1.4	1.6
C_5–180° F.		2.8	3.7	4.4	5.0	1.7	1.1	2.9	3.6
180–370° F.		8.7	6.5	9.0	14.7	2.2	3.0	5.9	11.4
370–650° F.		23.8	19.2	21.3	36.2	5.0	8.3	19.7	26.9
650–950° F.		16.5	21.1	17.1	21.4	15.3	6.8	13.7	25.0
950° F. plus btms.		43.2	43.8	38.6	15.0	72.7	78.9	50.9	25.0
H_2S		2.5	2.0	2.2	2.5	1.5	1.7	2.1	2.7
NH_3		0.3	0.7	0.2	0.9	0.1	0.1	0.2	0.3
H_2O		0.6	0.6	0.6	0.6	0.2	0.2	0.6	0.6
Catalyst deposits		0.3	0.3	0.4	0.4		0.2	0.5	0.5
H_2 cons.		−2.1	−1.8	−2.3	−3.2	−1.0	−1.4	−1.4	−2.1
Total		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total liquid product inspections:									
° API	9.2	28.0	22.9	26.4	35.2	14.3	15.0	21.8	25.3
SUS/100° F.			338	108	46	19,600	18,500	274	60
Carbon res. (D189)	18.3		7.54	6.65	0.49	14.71	13.06	8.48	3.84
C_5 insolubles	13.2	1.16	5.28	4.50	0.36	8.95	8.34	6.53	2.62
Percent C	85.34	85.22	85.86	85.82	84.93			87.04	85.82
Percent H	10.57	12.32	11.87	12.07	12.94			11.51	12.04
Percent N	0.40	0.05	0.22	0.21	0.07	0.35	0.34	0.27	0.15
Percent S	2.83	0.12	0.70	0.69	0.20	1.62	1.49	0.89	0.36
NiO (p.p.m.)	30	<0.3	16	9	0.7	17	15	9	3
V_2O_5 (p.p.m.)	50	<0.4	8	10	<0.2	23	17	11	4
Inspections of cuts:									
650–950° F.:									
° API		27.4	24.5	27.0	27.7	20.0		23.1	24.1
Percent S		0.04	0.09	0.12	0.03	0.52	0.44	0.19	0.06
C residue		0.03	0.07	0.06	0.003	0.02	0.21	0.08	0.05
950° F. plus btms.:									
° API		21.0	14.2	12.5	25.0	10.9	11.5	11.3	13.9
Percent S		0.42	1.19	1.46	0.13	2.1	1.72	1.56	1.08
C residue		5.24	14.33	15.94	4.39	17.6	17.27	19.14	15.42
NiO (p.p.m.)		1	25	16	1		22	19	12
V_2O_5 (p.p.m.)		2	23	22	<0.4		29	24	15

result in time-consuming, expensive plant shut downs so that the catalyst could be regenerated or replaced. Pressures materially above 3000 p.s.i.g. are uneconomic due to equipment costs and unnecessary hydrogen consumption.

The following example illustrates the invention and is considered together with the accompanying drawing which shows an arrangement of apparatus in which one adaptation of our invention is carried out.

Example

To an asphalt feed entering the process at the rate of 10,000 barrels per day, hydrogen gas is added at the rate of 2,000 standard cubic feet per barrel of asphalt feed with a hydrogen-rich gas recycle rate of about 4000 s.c.f./b. The mixture is then introduced into a hydrocracking reactor **1** by means of lines **5**, **6** and **7**, respectively. Reactors **1**, **2**, **3** and **4** are provided with a catalyst bed of cobalt-molybdena-alumina catalyst. The catalyst analyzes approximately 2.5% Co and 8.5% MoO_3. The amount of catalyst present in the reactors is such that the weight hourly space velocity is .3 based on the total fresh feed. The temperature in the hydrocracking zone is about 790° F. and the pressure is about 2500 p.s.i.g. Intercoolers can be placed between reactors to maintain the reaction temperature. By operating in this manner, the hydrogen consumption is approximately 1500 standard cubic feet per barrel of fresh asphalt feed. The product, together with the unconsumed hydrogen after completing their run through the reactors **1**, **2**, **3** and **4** is transported by lines **8**, **9** and **10**, is then removed from the bottom of the last reactor by means of line **11** and is then introduced into flash drum **12** where it is maintained at a temperature of approximately 200° F. by a cooling means (not shown). The flash drum is operated at substantially the same pressure as the reactor, namely at a pressure of 2500 p.s.i.g. Unconsumed hydrogen as well as certain volatile constituents of the product such as C_1 to C_3 hydrocarbons, hydrogen sulfide, ammonia and water are recovered overhead from the flash drum **12** by means of lines **13** and passed to absorber **14** to purify the hydrogen by hydrogen sulfide, some hydrocarbons and ammonia removal. Hydrogen from the absorber is recycled to reactor **1** by means of line **7**. In order to prevent excessive build-up of volatile constituents in the recycle gas a gas release line **15** is provided. Substantially all of the liquid product is removed from flash drum **12** by means of line **16** and thus introduced into an atmospheric fractionating column 17. From the atmospheric fractionating column 17 overhead products are recovered. Light gases are removed by line **18**. Line **19** removes gasoline at a rate of approximately 300 barrels a day. Naphtha is removed by line **20** at a rate of about 900 barrels per day. Distillate fuel is removed by line **21** at a rate of about 2400 barrels per day. From the bottom of the atmospheric fractionating column 17 the 650° F. plus product is removed by line **22** at a rate of approximately 6000 barrels per day. The aniline point, percent hydrogen and K factor indicate that the 650° F. plus hydrocracked product should be an excellent catalytical cracking feedstock. The 650° F. plus product is then transported by line **22** to a fluid catalytic cracking unit **23**. The yield of 650° F. plus product entering into the catalytic cracking zone is about 60 percent by weight of the total feed. The catalytic cracking zone is of the fluid bed type and the catalytic cracking feed from **22** is contacted with silica-alumina catalyst at a temperature of from about 750° F. to 1050° F. and about atmospheric pressure until a conversion of about 50 to 80 percent of the feedstock into a product boiling in the gasoline boiling range and below is obtained. Inspection of the fluid

catalytic cracking feed yielded from this process was compared with that of a conventional virgin gas oil as shown in Table II which follows:

TABLE II

Inspections	650° F. plus product from hydrocracking	Sour West Texas virgin gas oil	Mid-Continent virgin gas oil
° API	22.8	21.6	27.3
Pour	40	100	90
KV/122° F		54.3	18.6
KV/210° F	18.5		
Refractive index	1.5130	1.5161	1.4960
Aniline point, ° F	223	186.4	189.5
Carbon residue	1.50 con.	0.44 rams.	0.25 con.
nC_5 insolubles	2.03		
Percent C	87.10	86.35	86.36
Percent H	12.67	12.30	12.76
Percent S	0.03	1.63	0.52
Percent N		0.14	0.09
NiO, p.p.m	<0.16	<0.16	0.3
V_2O_5, p.p.m	<0.20	<0.20	1.9
K (vis-grav.)	12.05	11.68	11.93
K (grav.-50% pt.)	12.18	11.88	12.00
ASTM vac. dist.:			
IBP	412	475	450
5	675	662	601
10	718	721	644
20	761	776	684
30	819	812	711
40	881	834	738
50	941	863	763
60	985	892	800
70	1,043	924	848
80		961	903
90		1,000	962
95		1,032	
Yields, from fluid catalytic cracking:			
Dry gas, weight percent	11.5		9.2
Butanes, vol. percent	13.0		16.8
Gasoline, vol. percent	45.1		46.5
Coke, weight percent	7.2		4.5

The hydrocracked stock gives slightly more coke and gas, but less butanes and gasoline after fluid catalyst cracking than that of virgin stock, but the yields of this invention are superior to those stocks of the same boiling range produced in most other conventional residual fuel reduction processes.

We claim:

1. A method of producing gasoline boiling range products from an asphalt residual feedstock having a penetration of up to about 250 at 77° F. which consists essentially of contacting said asphalt residual feedstock in the presence of hydrogen with a hydrocracking catalyst at a temperature of about 760° F. to 810° F. under a pressure of about 2000 to 3000 p.s.i.g., a weight hourly space velocity of about .1 to 1, a hydrogen rate of from about 2000 to 7000 standard cubic feet per barrel of fresh feed to obtain a hydrogen consumption rate based on fresh feed of from about 500 to 1500 standard cubic feet per barrel of fresh feed, separating residual hydrocarbons boiling essentially above about 650° F. and cracking said residual hydrocarbons in the presence of a silica-based cracking catalyst to obtain gasoline boiling range products.

2. The process of claim 1 wherein the hydrocracking catalyst is cobalt-molybdena-alumina.

3. The process of claim 2 wherein the hydrocracking temperature is about 780° F. to 800° F., the pressure is about 2200 p.s.i.g. to 2700 p.s.i.g. and the weight hourly space velocity is about .3 to 0.7.

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