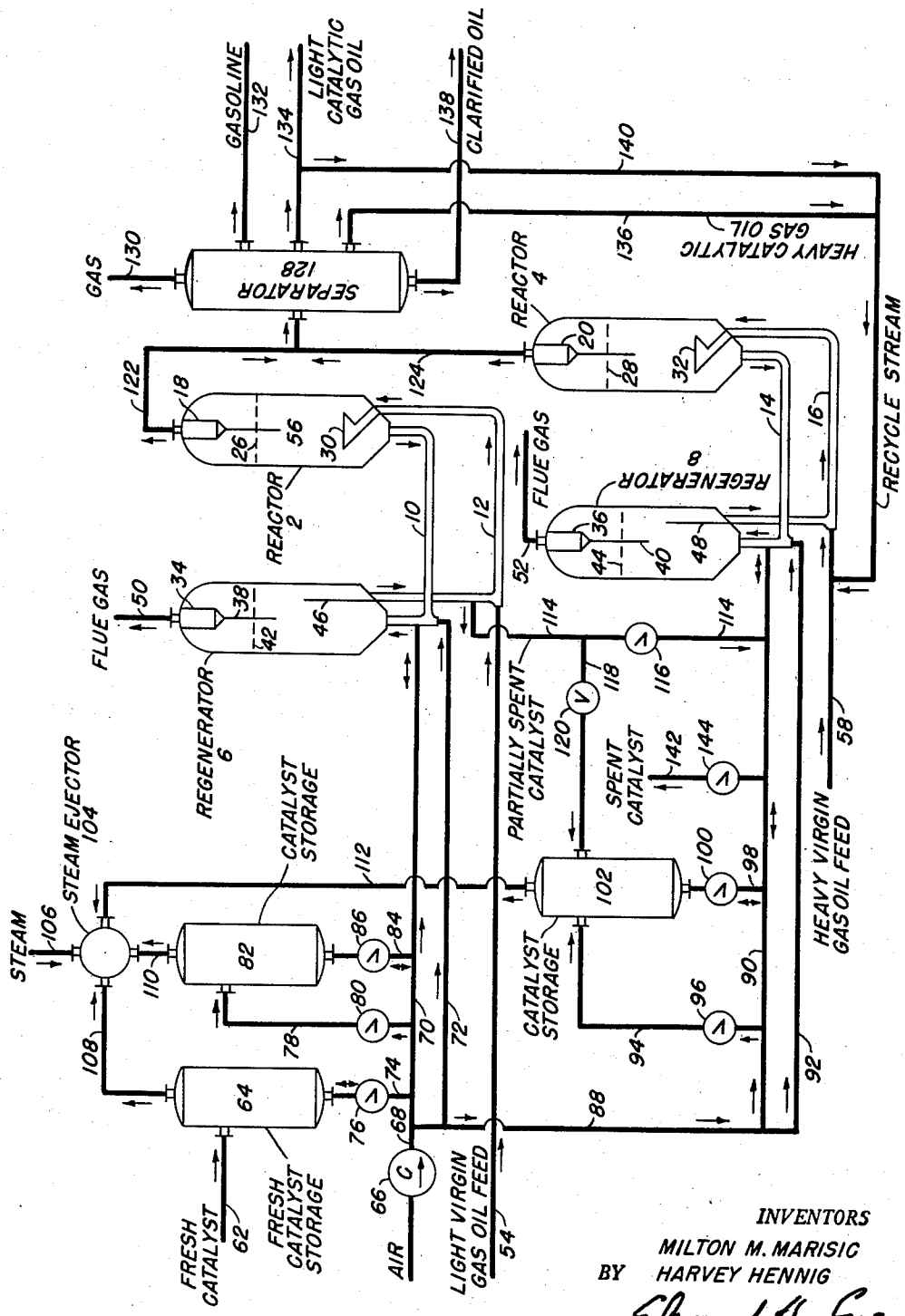
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CATALYTIC CRACKING PROCESS

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CATALYTIC CRACKING PROCESS

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1 Claim. (Cl. 208—80)

The present invention relates to a process for the production of high octane motor fuels having superior performance and engine cleanliness characteristics wherein two gas-oil feeds are subjected to separate catalytic cracking reactions under particular conditions and the products are subjected to fractionation in a common fractionating system.

It is recognized in the art that the presence of olefins in the higher boiling fractions of motor gasoline has a detrimental effect on the high-speed engine performance and on the road-test lead susceptibility of the gasoline. Also, it is recognized that recycle stocks and lighter gas-oils are more refractory to cracking than virgin stocks and heavy gas-oils. The prior art teaches the cracking of light recycle hydrocarbons, produced by cracking at 800° to 1200° F., and the cracking of heavy recycle stocks from the same source at lower temperatures. In accordance with the present invention, light, more refractory, virgin gas oils boiling in the range of about 500° to 790° F. are subjected to cracking at low temperatures of about 800° to 850° F. in a fluid or moving bed catalyst zone containing a catalyst of high activity. Heavy, less refractory, virgin gas oil boiling in the range of about 775° to 1000° F. plus recycle stocks produced by the separate treatments of the light and heavy virgin gas oils are cracked at higher temperatures of about 900° to 980° F. over a catalyst which is less active than that used in the cracking of the light gas oil. A common, synthetic-crude, fractionating system is used for the products from both stages of the process. The high catalyst activity in the first zone, wherein the light gas oil is being treated, is maintained by periodically or continuously withdrawing used catalyst from the zone and adding fresh catalyst as make-up. The catalyst withdrawn from the first zone is added as needed to the second zone where heavy virgin oil plus the more refractory recycle hydrocarbons are being cracked. It has been found that maximum conversion to desirable highly branched paraffinic hydrocarbons and minimum conversion to undesirable olefinic hydrocarbons can be accomplished in the first reaction zone by excluding catalytic recycle gas oils and virgin gas oil boiling above about 790° F. from this zone, by maintaining high catalyst activity, and by maintaining low reaction temperatures.

Accordingly, it is a primary object of this invention to provide a process for the production of high quality motor fuels.

A second object of the invention is to provide a process for the simultaneous conversion of two different gas-oil feeds in separate conversion zones under particular conditions and employing a common product recovery system whereby the maximum yield of high quality gasoline is obtained.

A further object of the invention is to provide a process for the production of gasoline wherein the proportion of fixed gases is reduced, an increase in 400° F. end point gasoline is experienced, there is a reduction in the amount of coke, and the products are higher in branched-chain paraffin and naphthene hydrocarbon contents and lower in olefin content.

These objects and other advantages of the invention will become apparent from the description. By a light virgin gas oil, as the term is used in the description, is meant a distillation fraction obtained from natural crude oil, said fraction boiling at about 500°–790° F., and, the use of the term heavy virgin gas oil is intended to mean that portion of natural crude oil which boils above 790° F. Recycle stocks and recycle oils are defined as catalytically cracked petroleum fractions boiling above gasoline.

The invention is best explained by reference to the attached flow diagram which shows the general scheme of passage of feed, catalyst and products through a two-reactor system. Although the invention is applicable to moving bed or fluidized type of operations, it will be described in a fluidized system for purposes of illustration.

Referring to the drawing, reactors 2 and 4 are shown connected to separate regenerators 6 and 8, respectively, by means of lines 10, 12, 14 and 16. Each reactor has a cyclone separator, 18 and 20, respectively, and a catalyst return pipe extending below fluidized catalyst levels 26 and 28. Incoming lines 12 and 16 terminate in the lower portion of each reactor in dispersing means 30 and 32.

Regenerators 6 and 8 are equipped with cyclone separators 34 and 36, and return pipes 38 and 40, extending below fluid catalyst levels 42 and 44, respectively. Baffles 46 and 48 serve to catch portions of the regenerated catalyst for return to the reactors via lines 12 and 16. Flue gas outlets 50 and 52 are provided for the regenerators. Line 54 conveys feed hydrocarbons to line 12 and through disperser 30 into fluidized zone 56 of reactor 2.

Fresh catalyst is introduced by line 62 into fresh catalyst storage tank 64. A compressed air system supplied by compressor 66 furnishes air through line 68 and branch lines 70 and 72, the latter connecting directly into line 10 near the bottom of regenerator 6, and the former connecting into line 10 at a point closer to the bottom of the regenerator. Line 70 has branch line 74, controlled by valve 76 leading to fresh catalyst storage 64, branch line 78 leading into catalyst storage 82, and branch line 84 controlled by valve 86 leading to the bottom of catalyst storage 82. Line 70 and its branch lines are used to transfer catalyst to and from catalyst storage means 64 and 82.

Air compressor 66 also supplies air through line 88 and branch lines 90 and 92 which are in turn connected to corresponding points in line 14 leading to regenerator 8. Secondary branch line 94, controlled by valve 96, and line 98, controlled by valve 100, lead to the top and bottom of catalyst storage 102.

A common steam ejector 104 is provided for the two separate reactor-regenerator systems, operating from steam supplied by line 106 and connected to storage 64 by line 108, to storage 82 by line 110, and to storage 102 by line 112. Partially spent catalyst from regenerator 6 passes through line 114, controlled by valve 116, into line 90. Branch line 118, controlled by valve 120, leads from line 114 to catalyst storage 102.

Products from reactor 2 pass through line 122 to combine with products from reactor 4 in line 124, and the combined streams pass through line 126 into common product separation system 128. Fixed gases are removed at line 130, gasoline products at line 132, light catalytic gas oil at line 134, heavy catalytic gas at line 136 and clarified oil at line 138. A portion of the light catalytic gas oil passed through branch line 140 may be combined with the heavy catalytic gas oil in line 136 to form recycle which is mixed with incoming feed in line 58 going

to reactor 4. Spent catalyst is removed from line 90 by line 142 controlled by valve 144.

An illustrative example shows the benefits that may be gained by the practice of this invention. A Mid-Continent crude is fractionated to give:

Fraction	Boiling Range, ° F.		° API	Vol. percent of Crude	Percent
	IBP	EP			
Light Gas-Oil	500	780	32.4	31.6	63.3
Heavy Gas-Oil	780	1,100	19.7	18.3—	36.7
				49.9	100.0

The following table shows the results when (I) processing the feeds conventionally in a fluid catalytic cracking unit, and (II) when processing the feeds according to this invention. Under case II the process conditions and feeds are given under "reactor 2" and "reactor 4," as described in the drawings.

Operating Conditions	I	II	
		Reactor 2	Reactor 4
Reactor Temp., ° F	950	825	950
Space Velocity, Wt./Hr./Wt.[1]	1.6	0.7	2
Catalyst-Oil Ratio [2]	8	12	10
Catalyst Activity [3]	30	35	29
Feeds:			
Fresh Feed, Vol. Percent	100	63.3	36.7
Cycle Oils, Percent Fresh Feed	50	0	136
Cycle Oils, Percent Total Available Fresh Feed	50	0	50
Conversion, Vol. Percent Fresh Feed [4]	70	55.2	70
Yields, Percent of Fresh Feed:			
C_3 and lighter, wt. Percent	9.1	7.9	
C_4's, Vol. Percent	15.3	13.6	
C_5—400 Gasoline, Vol. Percent	50.6	53.3	
Light Cycle Oil, Vol. Percent	25.0	25.0	
Decant Oil, Vol. Percent	5.0	5.0	
Coke, Wt. Percent	7.4	7.3	
PRODUCTS			
C_5—400 Gasoline Quality:			
Octane Rating—			
F-1 (Research) clear	93.2	91.2	
+ 3 cc. TEL	97.5	96.3	
F-2 (Motor) Clear	80.2	78.9	
+ 3 cc. TEL	84.7	85.0	
Composition, Wt. Percent—			
Olefins	38	26	
Aromatics	32	27	
Paraffins and Naphthenes	30	47	
Total	100	100	

[1] Oil feed, lb./hr., per pound of catalyst in reactor.
[2] Pounds of catalyst circulated per unit time divided by pounds of oil feed per unit time.
[3] Catalyst activity as measured by Houdry Cat-A-test.
[4] Conversion equals fresh feed less liquid products boiling above gasoline divided by the fresh feed, expressed as a percentage.

It is seen from the above examples that the practice of the present invention produces a gasoline of improved performance and engine cleanliness characteristics containing more branched-chain paraffins and fewer low-boiling olefins than do those gasolines produced by conventional cracking processes. Further advantages of the invention are that the yield of gasoline is increased, and less fixed gases and butanes are produced at equal conversion levels.

The requite conditions for this invention are that the light virgin gas oil be catalytically cracked in a reactor containing high activity catalyst at relatively low temperatures, in the order of about 800° to 850° F., and the heavy virgin gas oil, plus any recycle gas oils from both reactors, be processed at higher temperatures in the order of about 900–950° F. over a less active catalyst in the second reactor system. By relatively high catalyst activity is meant that the catalyst has an activity of about 33 to 36 as measured by the Houdry Cat-A-test, the distillation-plus-loss test, or any related method of determining catalyst activity, as widely known and used in the prior art. The Houdry Cat-A-test is in wide-spread use for evaluating catalysts and is described in detail in the article entitled "Standard Laboratory Method for the Determination of Cracking Catalyst Activity," by J. Alexander, Jr., API Processings, 27th Annual Meeting, vol. 27 (III), 1947, page 51. The Jersey D+L test is described by Conn and Connolly in their article entitled "Testing of Cracking Catalysts," Industrial and Engineering Chemistry, vol. 39, No. 9, page 1138. The catalyst activity in the second reactor system is maintained at about 25 to 30 as measured by the Houdry Cat-A-test, or the so-called D+L test. These values for catalyst activity are only illustrative and are not necessarily limitations on the invention, as long as the difference between the catalyst activity levels is no less than about 2 and no greater than about 15, as measured by those test methods using actual, small-scale catalytic cracking units to give an arbitrary value of the catalyst activity.

Accordingly, the catalyst activity in reactor 2 may be between 32 and 34 as measured by the Houdry Cat-A-test, and the activity in reactor 4 may be from 28 to 30. Alternatively, the activity in reactor 2 may be from 36 to 40 and the activity in reactor 4 may be from 30 to 32. It is to be understood that these activity values will vary somewhat with different light and heavy feed stocks, and with the temperatures, pressures and space velocities used. It is preferred that the differential in catalyst activity range from about 5 to 8 for most consistent results.

The high activity in reactor 2 is maintained by appropriate withdrawal of equilibrium catalyst from regenerator 6 through line 114, and addition of fresh catalyst from catalyst storage 82. The lower activity in reactor 4 is maintained by appropriate withdrawals from the regenerator 8 and by adding partially spent, regenerated catalyst either through line 116 or from catalyst storage 102.

The activity of the catalyst in each system will depend somewhat on the rate of fresh catalyst addition and the type of feeds employed. Relatively clean feeds that cause little loss in catalyst activity permit greater activity levels in both reactor systems. Thus, if the heavier feeds processed in reactor 4 tend to poison the catalyst, then the resulting greater catalyst additions required will cause the reactor system 2 to operate at a higher catalyst activity level while maintaining the desired activity level in the reactor 4.

In connection with a fluid type system with which this invention is illustrated, transfer and withdrawal of catalyst to and from the two reactor systems is very readily accomplished. Assuming that both reactors are in operation and the withdrawal of 200 lbs. of catalyst per hour from regenerator 6 will maintain the desired catalyst activity level of 35 in reactor 2, this withdrawal is accomplished by adjustment of valves 116 and 120 allowing used-regenerated catalyst to flow through line 114. Fluid levels 26 and 42 are maintained by the simultaneous addition of fresh catalyst to the reactor system 2 from catalyst storage 64. This is accomplished by opening valve 76, allowing catalyst to flow into line 70 where it is picked up by air from line 68 and carried to line 10 of regenerator 6. Catalyst storage means 82 is provided for catalyst storage during shutdown of the unit. Steam ejector 104 serves to create a vacuum within vessels 64, 82 and 102, thereby facilitating transfer of catalyst into these vessels. Air is supplied to catalyst storage vessel 102 of reactor-regenerator system 4—8 by means of lines 88, 90 and 94, to effect transfer of regenerated catalyst. Air is also passed through line 72 into regenerator 6, and through line 92 into regenerator 8, to accomplish the necessary rejuvenation of the catalyst.

One of the principal advantages of the invention is that the gasoline boiling range fractions produced contain a much lower percentage of olefins (26 wt. percent) as opposed to conventional methods (38 wt. percent). Ole-

fins in higher boiling gasoline fractions have a detrimental effect on high-speed engine performance as reflected by road test lead susceptibility. This reduction in olefin content along with the increases in octane rating, amount of branched-chain paraffins and naphthenes and general increase in the quality of products produced by the present method, plus increased yield, is accomplished by excluding from the first reactor the catalytic recycle gas oils and virgin gas oil boiling above about 790° F., and processing these feeds separately. The lower temperatures thereby made possible in the first reactor are conductive to chain-branching reactions with relatively little olefin production.

Any catalytic cracking catalyst or catalyst composition may be used in the practice of this invention. The conventional catalysts used in fluidized catalyst cracking operations or suspensoid cracking procedures may be used. These catalysts are oxides of metals of groups II, III, IV, and V of the periodic chart of the atoms, Welch Mfg. Co., 1941. A preferred catalyst comprises silica-alumina having from about 5 to 20 weight percent of alumina, containing such other constituents as ThO_2, WO_3, MoO, BeO, CdO, Bi_2O_3, UO_3, B_2O_3, U_2O_5, Fe_2O_3, SnO_2, MnO, Cr_2O_3, CaO Tl_2O_3, MgO and Ce_2O_3 present in concentrations varying from 0.05 to 0.5%. Magnesium-calcium oxide-silica composites may be used. A typical catalyst may contain particles smaller than 40 mesh, about 30% being smaller than 325 mesh.

The invention has been described in relation to certain methods of determining catalytic activity. Other methods of evaluating catalyst activity may be used. One skilled in the art realizes that the catalyst activity ratings for a given catalyst will vary somewhat, depending on the test method and conditions used, and that certain physical properties of the catalysts, such as density (aerated, freely settled, compacted and under pressure), particle size, sieve analysis, gas-producing factor, carbon-producing factor, aromatic adsorption index, and estimated surface area have an influence on or reflect the catalyst activity. Likewise, chemical properties, such as the content of iron and sodium, and catalyst age and carbon content, in addition to the chemical composition, influence the activity and must be taken into account. Catalyst activity measurements based on the determination of surface area may be used. However, in general, the best procedure is to determine the catalyst activity by employing small-scale laboratory cracking units in which the catalyst may be subjected to conditions which approximate the

condition met in the larger commercial unit, as described by Rescorla, Ottenweller and Freeman in their article "Evaluation of Catalysts for Catalytic Cracking," Anal. Chem., vol. 20, No. 3, March 1948, page 196. The Universal Oil Products Fluid test and the Kellogg Fluidized Fixed-Bed test may be used. These tests are described by Rescorla et al.

Having described and illustrated the invention, the only limitations attaching thereto appear in the appended claim.

What is claimed is:

The process for producing high quality motor fuels of reduced olefin content which consists of subjecting virgin gas oils boiling in the range of about 500° to 790° F. to catalytic cracking in a first reaction zone at temperatures of about 800° to 850° F. in the presence of a catalyst having an activity level of about 33 to 36 as determined by the Houdry Cat-A-test, separating the products from said first reaction zone, withdrawing used catalyst from said first reaction zone to a regeneration zone, subjecting heavy virgin gas oils boiling in the range of about 775° to 1000° F. to catalytic cracking in a second reaction zone at temperatures of about 900° to 980° F. in the presence of a catalyst having substantially the same composition as the catalyst in said first reaction zone and having an activity level of about 25 to 30 as determined by the Houdry Cat-A-test, separating the products and used catalyst from said second reaction zone, supplying fresh catalyst to said first reaction zone at a rate sufficient to maintain said activity level therein, withdrawing regenerated catalyst from said regeneration zone, supplying said regeneration catalyst to said second reaction zone at a rate sufficient to maintain said activity level therein, combining the products from said first and second reaction zone, and separating therefrom a gasoline boiling range product of enhanced quality.

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