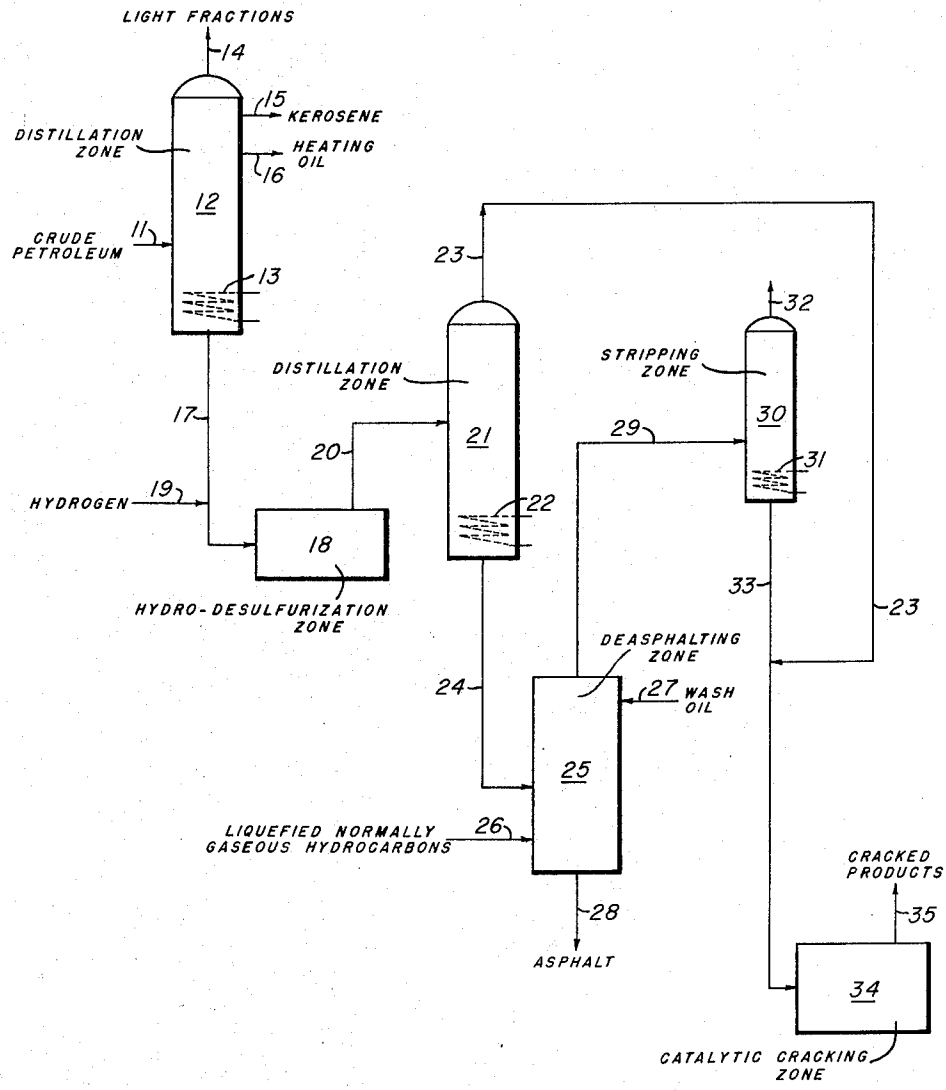
Dec. 25, 1956 H. G. CORNEIL ET AL 2,775,544

PRODUCTION OF CATALYTIC CRACKING FEED STOCKS

Filed Feb. 28, 1955



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United States Patent Office 2,775,544
Patented Dec. 25, 1956

2,775,544

PRODUCTION OF CATALYTIC CRACKING FEED STOCKS

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Application February 28, 1955, Serial No. 490,744

6 Claims. (Cl. 196—24)

The present invention is directed to a method for increasing yields of catalytic cracking feed stock. More particularly, the invention is directed to a method for treating reduced or total crude petroleum to obtain increased yields of cracking stock therefrom. In its more specific aspects, the invention is directed to catalytic cracking of treated reduced or total crude whereby improved yields of catalytic cracking stocks are charged to catalytic cracking operations.

The present invention may be briefly described as a method for increasing the yields of catalytic cracking stock obtainable from crude petroleum. These improved yields are obtainable by subjecting the total crude or reduced crude to hydrodesulfurization conditions in the presence of a catalyst to form a hydrodesulfurized product. A first gas oil fraction is removed, preferably by distillation, from the product and the hydrodesulfurized product after removal of gas oil is then subjected to deasphalting conditions tin the presence of liquefied, normally gaseous hydrocarbon to obtain a second gas oil fraction. The first and second gas oil fractions are then combined and may be charged to a catalytic cracking operation, such as one of the the fluidized solids or powder type.

The reduced crude employed in the practice of the present invention may suitably be a crude petroleum which has had the light ends removed therefrom, such as gasoline, kerosene, and heating oil fractions but contains the gas oil fractions originally present in the crude petroleum. Such reduced crudes may boil substantially above 600° F. As exemplary of reduced crude petroleums may be mentioned reduced crudes from West Texas and those from the Hawkins field in Northeast Texas. As exemplary of such framtions a reduced crude from West Texas may comprise about 48 volume percent of the crude, whereas one from the Hawkins field may comprise about 66 volume percent of crude. Alternately the total crude may be employed.

The temperatures employed in the hydrodesulfurization zone in the practice of the present invention may

suitably range from about 700° to about 850° F. but preferably in the range from about 750° to about 800° F.

Pressures employed in the hydrodesulfurization step may range from about 100 to about 1500 pounds per square inch gauge with pressures in the range from 400 to 800 pounds per square inch gauge preferred.

The space velocities in hydrodesulfurization may range from about 0.25 to about 5 volumes of feed per volume of catalyst per hour but preferably from 0.25 to 2 volumes of feed per volume of catalyst per hour.

Hydrogen is beneficial in the present invention and may be employed in the hydrodesulfurization step in an amount in the range from 500 to 6000 cubic feet of hydrogen per barrel of feed mixture. A preferred amount of hydrogen is in the range from 1000 to 3000 cubic feet of hydrogen per barrel of feed mixture. Any hydrogen-containing gas may be employed which suitably may be make gas from a hydroforming or other reforming operation.

The catalyst employed in the practice of the present invention may be any desulfurization catalyst or any desulfurization-cracking catalyst of which there are many on the market. Examples of these types of catalysts will include cobalt molybdate, preferably on a support such as alumina, nickel tungsten sulfide, molybdenum sulfide and many other catalysts of this nature which are not deactiviated by contact with sulfur containing materials. The cobalt molybdate catalyst is to be preferred. It is to be noted, however, that while we term the catalyst "cobalt molybdate" this catalyst actually may be mixtures of oxides of cobalt and molybdenum preferably on a support such as alumina.

In the practice of the deasphalting step of the present invention a liquefied, normally gaseous hydrocarabon such as those well known in the deasphalting art is employed. Specific examples of liquefied, normally gaseous hydrocarbons which may be used may be mentioned ethane, propane, propylene, butylene, butane, including iso and normal butane and mixtures thereof. The ethane under some conditions may contain ethylene and be used suitably in the present invention. Because of pressure limitations in operating equipment, it is preferred to use butane, propane, propylene, butylenes or mixtures thereof with a desirable commercial mixture consisting of about 30% butanes and about 70% propane.

The amount of liquefied, normally gaseous hydrocarbon employed as a solvent in the deasphalting operation of the present invention is within the range of about 2 to about 10 volumes of the solvent per volume of residual petroleum fraction employed as a feed stock to the deasphalting zone. As a specific example, it has been found that about 3.2 volumes of liquefied, normally gaseous hydrocarbon solvent by volume of residual oil charged is a desirable commercial ratio.

The temperature at which the deasphalting step is conducted may be within the range of 100° to 300°. There may be a temperature gradient in the deasphalting step with the highest temperature at the deasphalted oil outlet. The temperature gradient may be within the range of 0° to 60°. As a specific example a 20° gradient may be used with the top of the tower at the point where the deasphalted oil is withdrawn being maintained at 180° F. and the bottom of the tower where the asphalt is introduced with the residual oil being 160° F.

The present invention is particularly useful in preparing a feed stock for catalytic cracking operations and particularly catalytic cracking operations of the fluidized solids or powder type. The catalytic cracking operation may be either of the upflow or downflow type. In the upflow operation the vaporized hydrocarbon is contacted with the fluidized solids in a suspension and the suspension flowed upwardly through a reaction zone. Likewise in the so-called upflow operation the catalyst is regenerated by suspending the catalyst in a combustion inducing gas, such as air, and flowing the suspension through a regeneration zone where a combustion operation takes place.

In the so-called downflow operation, the catalyst is suspended in vaporized hydrocarbons and flowed into a reaction zone in which a disperse phase and a dense phase is maintained with the catalyst being removed from the disperse phase and returned to the dense phase and with the reaction products flowing out of the reactor and the catalyst flowing downwardly therefrom. In the so-called downflow cracking operation, the catalyst fouled with carbonaceous material and/or coke is regenerated by suspending it in a combustion supporting gas, such as air, and flowing same into a regeneration zone wherein a disperse phase and a dense phase are maintained, the combustion products being led off from the disperse phase after separation of a major amount of catalyst therefrom and the catalyst dropped back into the dense phase and then removed therefrom for reuse in the reaction zone.

The catalytic cracking of fractions of petroleum oil is well known to the art. A description of such a catalytic cracking operation may be found in U. S. Patent 2,587,554, issued February 26, 1954, in the name of John Weikart.

In such catalytic cracking operations it has been found that if the charging stock contains as much as three pounds of nickel per thousand barrels of charge stock, the catalytic cracking process is adversely affected. In general, other metal components such as vanadium and iron are undesirable in the same manner as is nickel but are less troublesome; on a weight basis it may be considered that vanadium is perhaps ⅕ as troublesome as nickel and iron is perhaps ½ as troublesome as nickel. Hereafter in the specification and claims where the expression "equivalent to three pounds of nickel per thousand barrels of oil" appears, it is to be understood that this is intended to encompass the metal components nickel, vanadium and iron with nickel used at its full value, vanadium considered at ⅕ its actual weight value and iron considered at ½ its actual weight value.

In the deasphalting step of the present invention, a wash oil may be employed if desired to remove metallic contaminants from the second gas oil fraction. This wash oil may suitably be a residual fraction from Hawkins crude mentioned supra or may suitably be a tar obtained by thermally cracking catalytic cycle stock resulting from the catalytic cracking operation mentioned supra. Likewise, the wash oil may suitably be a fraction of catalytic cycle stock boiling above 900° F. and obtained by distillation of the catalytic cracked product or by deasphalting combined with distillation of the fraction of the catalytically cracked product. This wash oil boils substantially above 900° F. and may have a specific gravity of about 1 to about 1.2 and serves to remove about 75% of metal contaminants in the material charged to the deasphalting zone.

The present invention will be further illustrated by reference to the drawing in which the single figure is a flow diagram of a preferred mode.

Referring now to the drawing, a crude petroleum, such as one from the Hawkins field or from West Texas, is introduced into the system from a source, not shown, by way of line **11** and is charged thereby into a distillation zone **12** which may suitably be a plurality of fractional distillation towers provided with all auxiliary equipment necessary for fractional distillation. For illustrative purposes only, distillation zone **12** is shown as a single distillation tower which suitably may be provided with suitable vapor liquid contacting means, such as bell cap trays and the like, for sharp and precise separation. Zone **12** is provided with a heating means illustrated by steam coil **13** and line **14** for withdrawal of light fractions including gasoline and the like, line **15** for removal of kerosene and line **16** for withdrawal of a heating oil fraction. The reduced crude is withdrawn from zone **12** by way of line **17** and charged thereby into a catalytic hydrodesulfurization zone **18**. Alternatively the crude charged by line **11** may be charged directly into zone **18** by-passing zone **12**. Hydrogen is admixed with the reduced crude flowing in line **17**, the hydrogen being introduced by line **19**. In hydrodesulfurization zone **18** the reduced crude is desulfurized under the conditions mentioned supra. The hydrodesulfurized products issue from zone **18** by line **20** and are introduced into a second distillation zone **21** which may be similar to distillation zone **12**. Distillation zone **21** is provided with a heating means illustrated by steam coil **22** and is provided with lines **23** and **24**.

A first gas oil fraction is removed from the desulfurized product by way of line **23** and the residual desulfurized product is then charged by way of line **24** into a deasphalting zone **25**. In deasphalting zone **25** liquefied, normally gaseous hydrocarbon, such as propane, or a mixture of propane and butane and the like is introduced by line **26** and flows upwardly countercurrent to the desulfurized product introduced by line **24**. A wash oil of the type mentioned supra is also introduced into zone **25** by line **27** in contact countercurrently with the ascending deasphalted oil removing metal contaminants therefrom. The asphalt containing metal contaminants is discharged from zone **25** by line **28** while the deasphalted oil which is a second gas oil fraction is removed from zone **25** by line **29** and charged thereby into a stripping zone **30** equipped with a heating means, such as steam coil **31**, for removal of normally gaseous hydrocarbon from the second gas oil fraction by way of line **32**. The second gas oil fraction is then withdrawn from zone **30** by line **33** and has admixed with it a first gas oil fraction obtained by line **23** from zone **21**.

The combined gas oil fractions are then charged to a catalytic cracking zone **34** which is one of the type mentioned before and the combined gas oils are then subjected to catalytic cracking operations to obtain a cracked product by way of line **35** which suitably may form a source of the wash oil introduced into line **27**.

It will be seen from the foregoing description taken with the drawing that a simple process is provided for obtaining increased yields of cracking stock from crude petroleum.

In order to illustrate the invention further, runs were made in which the residuum from a crude from the Hawkins field was deasphalted in one instance and a crude from the Hawkins field was hydrodesulfurized and the residuum from the hydrodesulfurized crude was then deasphalted. The desulfurization operations were conducted at a temperature of 750° F., and at a pressure of 800 pounds per square inch gauge employing a cobalt molybdate catalyst.

The deasphalting was carried out with a solvent mixture of 70% propane and 30% butane at a solvent mixture to oil ratio of 4 to 1 and a temperature of 170° F. followed by a treat with a wash oil with the same solvent in the same ratio at a temperature of 150° F. The results of these operations are presented in the following table:

TABLE

Deasphalting of residua from virgin and hydrodesulfurized Hawkins crudes

	Virgin Crude	Hydrodesulfurized Crude
Yield of Residuum from Crude Distillation, Vol. Percent of Crude	30.2	22.4
Yield of Deasphalted Oil, Vol. Percent of Residuum	29.9	39.5
Yield of Deasphalted Oil, Vol. Percent of Crude	9.0	8.8
Yield of Gas Oil Distilled from Crude (First Gas Oil) Vol. Percent	33.5	38.6
Total Catalytic Cracking Feed, Vol. Percent of Crude	42.5	47.4
Yield of Asphalt, Vol. Percent of Crude	21.2	13.6
Inspections on 600–1040° F. Gas Oil Distilled from Crude (First Gas Oil Fraction):		
Gravity, ° API	22.6	25.4
Sulfur, Wt. Percent	2.3	0.31
Analine Point, ° F	170	179
Pour Point, ° F	85	85
Vis./130° F., SSU	110	95.4
Vis./210° F., SSU	46.3	44.5
Refractive Index, 106° F	1.5052	1.4967
Conradson Carbon	0.72	0.30
Molecular Weight	371	351
Med. Boiling Point, ° F	812	794
Inspections on Deasphalted Oil (Second Gas Oil Fraction):		
Gravity, ° API	19.1	20.8
Sulfur, Wt. Percent	2.3	1.1
Analine Point, ° F	224	229
Pour Point, ° F	70	110
Vis./130° F., SSU	5684	3,175
Vis./210° F., SSU	305	278
Molecular Wt	842	747
Conradson Cargon, Wt. Percent	3.4	3.2
Nitrogen, Wt. Percent	0.12	0.12
Refractive Index, 40° C., N_D^{40}	1.5147	1.5098

It will be seen from these data that the yields of deasphalted oil, which is gas oil from the virgin residuum, is 29.9%, whereas the yield from the hydrodesulfurized residuum is 39.5%. This improvement in yield is a result due to treatment of the crude under hydrodesulfurization conditions. It is to be noted that the yield of residuum is reduced by hydrodesulfurization but this reduction coupled with the increased yield of the second gas oil fraction reduces the yield of the low value asphalt more than the proportional reduction resulting from conversion of the reduced crude obtained during the hydrodesulfurization step. This reduction in residuum provides another advantage per se in that the size of the deasphalting plant may be reduced proportionately. The yield of total catalytic cracking feed stock is much greater in the case of the hydrodesulfurized crude than in the case of the virgin crude. The data further indicate and reflect that the quality of the gas oil produced from the hydrodesulfurized crude is significantly better than that obtained from the virgin crude; special attention is directed to the sulfur content.

It is contemplated that the first gas oil fraction may be obtained by a first deasphalting operation under adjusted conditions by a second deasphalting operation under more severe conditions and the two gas oil fractions then combined. It will be preferred, however, to recover the first gas oil fraction by distillation of the hydrodesulfurized reduced crude.

The present invention is quite useful and has numerous advantages in that it allows the production of increased

amounts of feed stocks for catalytic cracking operations and improves the catalytic cracking operations by not only removing the sulfur compounds but also by removing the metal contaminants.

The nature and object of the present invention having been completely described and illustrated, what we wish to claim as new and useful and to secure by Letters Patent is:

1. A method for increasing the yields of catalytic cracking stock obtainable from a reduced crude petroleum feed stock boiling above about 600° F. which comprises subjecting said crude to conditions of hydrodesulfurization to form a hydrodesulfurized product, removing a first gas oil fraction and lighter fractions from said products, subjecting said hydrodesulfurized product after removal of gas oil to deasphalting conditions to obtain a second gas oil fraction and combining said gas oil fractions to obtain augmented yields of catalytic cracking stock.

2. A method for increasing the yield of catalytic cracking stock obtainable from a reduced crude petroleum feed stock boiling above about 600° F. which comprises subjecting said crude to conditions of hydrodesulfurization to form a hydrodesulfurized product, distilling said hydrodesulfurized product to obtain a first gas oil fraction, together with lighter fractions, subjecting the bottoms fraction from said hydrodesulfurized product to deasphalting conditions to obtain a second gas oil fraction, and then combining said gas oil fractions to obtain augmented yields of catalytic cracking stock.

3. A method for increasing the yield of catalytic cracking stock obtainable from a reduced crude petroleum feed stock boiling above about 600° F. which comprises subjecting said crude to conditions of hydrodesulfurization to form a hydrodesulfurized product, distilling said hydrodesulfurized product to obtain a first gas oil fraction, together with lighter fractions, subjecting the bottoms fraction from said hydrodesulfurized product to deasphalting conditions to obtain a second gas oil fraction and then subjecting said combined gas oil fractions to catalytic cracking conditions.

4. A method for increasing the yield of catalytic cracking stock obtainable from a reduced crude petroleum feed stock boiling above about 600° F. which comprises subjecting said crude to hydrodesulfurization conditions at a temperature in the range between about 700° and 850° F. in the presence of hydrogen in an amount in the range between 500 and 6000 cubic feet per barrel of reduced crude at a pressure in the range from 100 to 1500 pounds per square inch gauge in contact with a hydrodesulfurization catalyst to form a hydrodesulfurized product, distilling said hydrodesulfurized product to obtain a first gas oil fraction, together with lighter fractions, subjecting the bottoms fraction from said product to deasphalting conditions in the presence of a liquefied, normally gaseous hydrocarbon to obtain a second gas oil fraction, and then combining said gas oil fractions to obtain augmented yields of catalytic cracking stock.

5. A method in accordance with claim 4 in which the hydrodesulfurization catalyst is cobalt molybdate on alumina.

6. A method in accordance with claim 4 in which the liquefied, normally gaseous hydrocarbon comprises a mixture of propane and butane.

References Cited in the file of this patent

UNITED STATES PATENTS

2,188,012	Pilat et al.	Jan. 23, 1940
2,393,288	Byrns	Jan. 22, 1946
2,500,757	Kiersted	Mar. 14, 1950
2,528,586	Ford	Nov. 7, 1950
2,686,150	Porter et al.	Aug. 10, 1954
2,691,623	Hartley	Oct. 12, 1954