

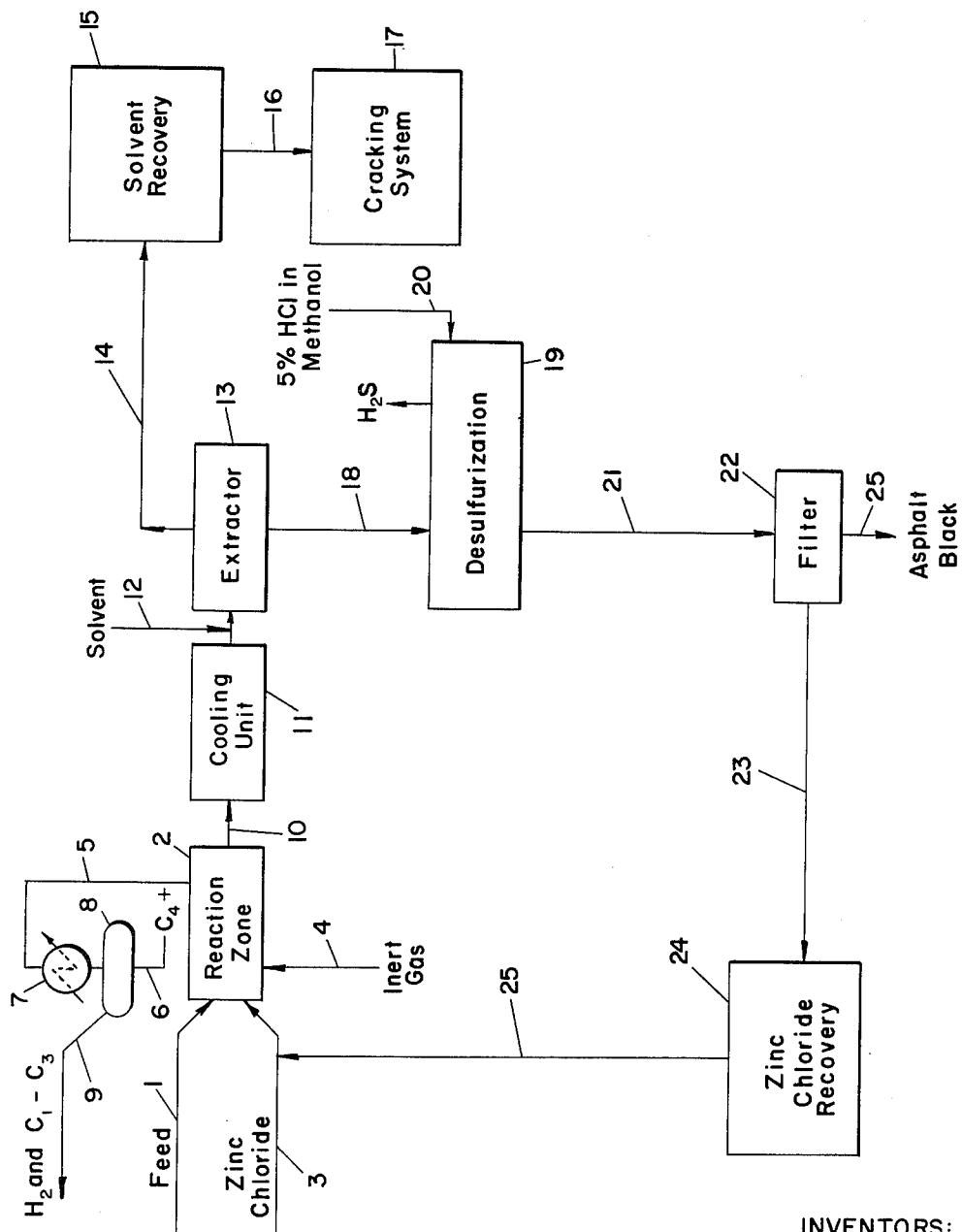
Dec. 14, 1965

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3,223,618

PRODUCTION OF CRACKING FEED STOCKS

Filed Sept. 28, 1962



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3,223,618

PRODUCTION OF CRACKING FEED STOCKS
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Filed Sept. 28, 1962, Ser. No. 226,998

1 Claim. (Cl. 208—247)

This application is a continuation-in-part of applica- 10
tion Serial Number 214,128 filed August 1, 1962.

This invention relates to the production of cracking feed stocks. More specifically the invention is directed to a process for treating whole or reduced asphalt base crude petroleum oils to obtain high grade feed stocks for cracking, particularly catalytic cracking.

Numerous processes have been suggested for the upgrading of asphaltic crude oils to condition them for cracking. These oils contain relatively large amounts of sulfur, nitrogen and metals including vanadium, nickel and iron. In addition, asphaltic oils form coke under cracking conditions which reduces the activity of cracking catalysts. Coke is also a detriment in thermal cracking because it plugs process units and transfer lines. Such processes as solvent extraction, hydrogenation and treatment with acids and solid adsorbents have been used in the past to prepare heavy oils for cracking. All of these processes have disadvantages and limitations, one of these being high cost.

The present invention is based on the discovery that asphaltic oils can be prepared for cracking by treatment with zinc chloride in a process which yields valuable by-products thus lowering treating costs. In copending application Serial Number 214,128, filed August 1, 1962, there is described a process for converting heavy petroleum fractions into a unique spectrum of products by treatment with zinc chloride. We have found that coke formers, sulfur, nitrogen and metals can be removed from whole or reduced asphaltic crude oils employing zinc chloride to provide a high quality thermal or catalytic cracking stock. The process is particularly applicable to the preparation of stocks for catalytic cracking because of the sensitivity of the catalysts to coke, sulfur, nitrogen and metals.

Suitable feeds for the process are asphaltic petroleum fractions having initial boiling points ranging from 200–700° F. These oils contain from 10–50 vol. percent asphaltic components and have an A.P.I. gravity ranging from 0.0 to 30 and a viscosity of from 10 to 2200 seconds (SUS) at 210° F. The feeds can be whole crude or crudes reduced by topping, vacuum distillation, vis-breaking or solvent deasphalting. High sulfur and metals content are common in West Texas, Mexican and Venezuelan crudes. The feed can be blended with cutter stock, cycle oil from cracking, recycle from the zinc chloride treating step, or other refinery streams.

The feeds can contain from 0 to 10 wt. percent sulfur, from 0 to 5 wt. percent nitrogen and from 0 to 2 wt. percent (0–2000 p.p.m.) metals. The chief metal contaminant is vanadium and it is usually present in amounts ranging from 0.0 to 1.0 wt. percent. Metals are usually present in the form of organometallic compounds.

The zinc chloride treating step is described in the above mentioned copending application. The oil and zinc chloride are treated in any suitable reactor with heating to maintain a temperature in the range of from about 220 to about 500° C. and with agitation. No special type of contacting equipment is required. Batch or continuous operation can be used.

Zinc chloride can be added as a powder, a semi-solid

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mass or a solution in water, alcohols, ethers, aldehydes or other suitable solvents since it is not easily obtained in anhydrous form it will usually contain at least 5% water. Technical or crude grades of zinc chloride give satisfactory results. Amounts ranging from .1 to 200 wt. percent or more (based on the oil feed) can be used, with amounts ranging from 1 wt. percent to 50 wt. percent being preferred. In one embodiment the zinc chloride is activated with pyridine or other organic nitrogen base. The action of zinc chloride is at least partly catalytic.

Temperature control is critical. The treating is carried out at temperatures between about 220° C. and 500° C. with a temperature range of 250° C. to 450° C. being preferred. The optimum temperature range is 300–400° C. It is important to note that materials such as aluminum chloride and ferric chloride cannot be used at temperatures within this range because they sublime and distill under practical operating temperatures.

Temperatures above 450° C. cause considerable cracking of the oil which is not the desired reaction and for this reason it is preferable to operate below 450° C. Very little reaction occurs below 220° C.

Pressure is not critical and for reasons of convenience atmospheric or ambient pressure is preferred. Pressures ranging from 5 p.s.i.a. to 500 p.s.i.a. are suitable. Reaction times can vary from 10 minutes to 50 hours depending in part on the temperature and on the type and amount of feed. One skilled in the art can coordinate the conditions to arrive at optimum yields.

The zinc chloride treating step produces a gas-vapor fraction, a liquid fraction and a solid fraction. The gas-vapor fraction contains from about 1.0 to about 3.0 wt. percent hydrogen and a C₁–C₁₂ fraction. The liquid fraction comprises from 40–70 wt. percent of an oil having a low sulfur, nitrogen and metals content which is an excellent stock for catalytic cracking. The solid product of the zinc chloride treating step represents from about 15–40 wt. percent of the original feed. It contains a major proportion of a material which we call asphalt black and may or may not contain small amounts of asphaltenes. Coke formers, sulfur, nitrogen and metals are concentrated in the solid product.

The asphalt black product produced by the zinc chloride treating step is unique. Most solid products resulting from treatments of heavy asphaltic materials are soluble in the common hydrocarbon solvents. Asphalt black is not soluble in hexane, benzene or CCl₄. The X-ray diffraction pattern has a between plane spacing of 3.38–3.43 Angstroms. Asphalt black has a surface area ranging from about 65 to about 125 square meters per gram. It is infusible below 500° C. The hydrogen to carbon molecular ratio ranges between .35 and 0.80. One sample had the following partial analysis: 75.15% carbon; 3.37% hydrogen; 12.03% oxygen; 0.47% nitrogen; 2.41% sulfur.

It can be used as a coloring agent, adsorbent, polymer filler and as a component of agricultural mulches, coatings and carbon electrodes.

The process of the invention is illustrated by the drawing which shows a preferred embodiment not intended to limit the disclosure.

An asphaltic oil contaminated with coke formers, sulfur, nitrogen and metals containing compounds is fed through line 1 to a reaction zone 2. As previously stated the feed can be augmented or modified with recycle or additional feed components to adjust feed composition and properties. The latter materials are blended with the feed by means of appropriately placed input lines, not shown. ZnCl₂ is fed to the reactor through line 3. The reactor is preferably maintained at a temperature of 300–

400° C. Inert gas such as nitrogen, helium, argon, etc. can be swept through the reactor through line 4 to maintain the reactants in a relatively oxygen free atmosphere. This can be done by sweeping the inert gas through the reactor before the reactants are introduced if desired. As the reaction progresses a gas-vapor stream containing hydrogen and C₁-C₁₂ hydrocarbons is flashed off through line 5. This gas-vapor fraction usually comprises about 5-10 wt. percent of the reaction products. It contains from about 1 to about 3 wt. percent high purity hydrogen. A C₄+ fraction is recovered through line 6 after cooling the gas-vapor fraction in heat exchanger 7 and phase separation in separator 8. Hydrogen and C₁-C₃ hydrocarbons are recovered as overhead through line 9. These gases are subsequently separated into hydrogen and hydrocarbon components in any desired manner with conventional gas separating techniques and equipment, not shown. The liquid and solid reaction products, still mixed with zinc chloride, are removed from reaction zone 2 by line 10 and passed through cooling unit 11 wherein the product stream is cooled to a temperature of about 50° C. The liquid and solid reaction products are then contacted with a solvent from line 12 in extractor 13. Extraction temperatures ranging from 0° to 400° C. can be used. Suitable solvents include non-polar solvents such as low molecular weight hydrocarbons containing 3-10 carbon atoms, i.e., propane, pentane, hexane, naphtha, benzene, toluene, xylene or other solvents like acetone, CCl₄, etc. The extract is passed by line 14 to solvent recovery zone 15. Solvent is recovered in zone 15 and preferably recycled by means not shown. The improved cracking feed substantially decreased in coke formers, sulfur, nitrogen and metals is then passed by line 16 to a conventional cracking system 17. As previously stated the cracking can be thermal or catalytic or a combination process.

The solid product from extractor 13 which we term asphalt black is insoluble in propane, pentane, naphtha, benzene and carbon tetrachloride. It is to be understood that the use of solvent extraction for separation of the asphalt black from the liquid product is non-limiting and other separation techniques such as filtration, centrifuging, adsorption, etc., can be employed in conjunction with or instead of solvent extraction.

The asphalt black is fed by line 18 to desulfurization zone 19. A solution of 5% HCl in methanol is fed by line 20 into the desulfurization zone. The HCl converts ZnS (made in the reaction zone 2) to ZnCl₂ with the subsequent release of H₂S. The sulfur recovered from the H₂S amounts to about 0.5 wt. percent of the feed. The desulfurization treatment can be omitted if desired. The solids are then passed by line 21 to a filter 22. The material is heated to about 65° C. to solubilize the ZnCl₂ prior to or during filtration. The ZnCl₂ is discharged by line 23 to a recovery zone 24 and the asphalt black is recovered through line 25. The zinc chloride can be recovered from the methanol by crystallization, spray drying or by distillation. The ZnCl₂ is recycled through line 25. The asphalt black can be treated to recover metals if desired.

The liquid product is passed to a thermal, catalytic or combination cracking operation. Any conventional type of cracking can be employed.

Suitable types of catalytic cracking are the fluidized bed, fixed bed and moving bed types. Catalysts can be oxides of metals of groups II, III, IV and V of the Periodic Table.

Major process variables such as temperatures, pressure, catalyst to oil ratio and space velocity for the various types of cracking are well known to those skilled in the art.

The features of the various types of cracking which may be used in the cracking step of this invention are discussed in Petroleum Processing, May 1957, pages 98-102 and 119-121.

The following example shows the effect of the process on Boscan crude having the following properties:

Initial boiling point ° F. 456

A.P.I. gravity at 60° F. 11.4

5 Pour test ° F. +65

Viscosity-Saybolt seconds-furol:¹

At 180° F. 222

At 210° F. 90

10 ¹ see. Saybolt furol-seconds is approximately equal to 10 sec. SUS.

Elemental composition: Percent

C 84.43

H 9.67

H/C 1.36

O 1.26

N 0.90

S 4.77

Metals: Percent

20 Vanadium 0.67

Nickel 0.53

Iron 0.53

25 406.5 grams of the feed was placed in a reactor at 100° C. and atmospheric pressure and the reactor was swept with nitrogen, 102.0 grams of commercial reagent grade ZnCl₂ was added in powder form. The mixture was heated with stirring and the initial reaction temperature was about 250-275° C. as evidenced by the evolution of hydrogen. The reactants were maintained at a temperature of 320-360° C. for 23 hours. The gas and vapor products were continuously flashed off at about 320° C. and the hydrocarbons separated from hydrogen by collection in an air cooled trap followed by a Dry Ice cooled trap. In addition to hydrogen, the products included ethane, propane, isobutane, n-butane, iso-pentane, n-pentane, hexanes, propylene, butylenes, pentenes, hexenes and aromatic ends. The quantitative analysis was—H₂—1.3 wt. percent; C₁-C₆—5.5 wt. percent; C₆C₁₂—7.4 wt. percent.

30 40 The liquids and solids from the reactor were cooled to about 50° C. and washed with 3-500 cc. volumes of n-hexane. 51.5 wt. percent hexane solubles (based on the feed) were recovered. The fraction had an A.P.I. 45 gravity at 60° F. of 21.6 and a viscosity at 210° F. of 4 Saybolt-seconds furol. The sulfur content was 2.4 wt. percent as compared with 4.77 wt. percent in the crude feed. Metals content was drastically reduced, the amounts being vanadium —.0006 wt. percent; nickel —.0001 wt. percent and iron —.0003 wt. percent. This material is well suited for thermal or catalytic cracking as the specifications indicate. By the way of comparison the hexane solubles of Boscan crude which has not been treated with zinc chloride have the following properties: 55 4.67 wt. percent sulfur, viscosity at 210-9 Saybolt furol seconds and A.P.I. gravity at 60° F.—17.4. This indicates that mere solvent extraction of the crude does not provide a satisfactory cracking stock.

An atmospheric bottoms sample of a Venezuelan crude 60 oil having an initial boiling point of 650° F. contained 2.69 wt. percent sulfur. After treatment with zinc chloride the hexane solubles contained only 1.06 wt. percent sulfur and the oil was satisfactory for cracking in the presence of a sulfur sensitive catalyst.

65 Equivalent reductions in metals, coke formers, sulfur and nitrogen are obtained by treating other crude oils and reduced crudes in the zinc chloride treating step of the invention.

The process of the present invention can be used in 70 conjunction with other petroleum processing steps such as coking, propane deasphalting, furfural extraction, vacuum distillation, visbreaking, hydrodesulfurization, reforming the like.

We claim:

75 A process for producing a high quality catalytic crack-

ing feed stock comprising the steps of contacting an asphalt base crude petroleum fraction contaminated with coke formers, sulfur, nitrogen and metals with zinc chloride at a temperature in the range of from 220 to 500° C., said petroleum fraction having an initial boiling point ranging from 200-700° F., containing 10-50 vol. percent asphaltic components and having an A.P.I. gravity ranging from 0.0 to 30 and a viscosity of from 10 to 2200 seconds (SUS) at 210° F., and separating a gas-vapor fraction, an asphalt black fraction insoluble in benzene, and 10 a liquid fraction, said liquid fraction being substantially decreased in coke formers, sulfur, nitrogen and metals and suitable for catalytic cracking.

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