

UNITED STATES PATENT OFFICE

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POLYMERIZATION OF CYCLE OIL FROM
HIGH-TEMPERATURE STEAM CRACKING
PROCESSMinor C. K. Jones, Mountainside, N. J., assignor
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6 Claims. (Cl. 260—82)

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This invention relates to a process for refining a highly cracked gas oil to obtain a satisfactory heating oil and valuable resin by-products.

Especially since there has been a great demand for normally gaseous unsaturated hydrocarbons, such as ethylene and butadienes, intensive cracking processes have been developed for converting large proportions of petroleum feed stocks to these gases. These cracking processes yield naphtha distillates that contain considerable amounts of aromatics mixed with unstable unsaturated hydrocarbons. They also yield a heavy tar and a "cycle gas oil" or intermediate distillate fraction which contains considerable amounts of aromatic compounds and unstable hydrocarbons.

The complexity and instability of the cycle gas oils formed by intense cracking make them difficult to use in the same manner as ordinary cycle stocks. Only a small portion of highly unstable cycle gas oils can be recycled satisfactorily for intense re cracking; frequently none is recycled. Therefore, large quantities of the highly cracked gas oils have to be withdrawn from the cracking system. They are unsatisfactory for use as a domestic heating oil even after being given a customary acid treatment and after blending with a large proportion of a regular refined domestic heating oil. They also are highly odoriferous. Therefore, there has been an urgent requirement for a method of treating such highly cracked gas oils to recover commercially-useful products therefrom.

An object of this invention is to provide a method of treating economically the described gas oils of high instability to produce more valuable commercial products therefrom.

Another object is to provide a method of treating the highly cracked intermediate fraction to yield satisfactory heating oils and commercially useful thermoplastic resins so that the fraction is made entirely utilizable in commercial products.

High temperature cracking yields aromatic gasoline distillates which have been found difficult to treat with active clays, but the controlled catalytic process of the present invention is surprisingly effective for treatment of higher boiling cycle oil distillates formed by cracking at high temperatures in the range 1050° F. to 1500° F. in the presence of steam at low pressures of about 1 to 2 or several atmospheres. These cycle distillates boiling in the range of about 350° F. to 700° F., relatively high in unstable, unsaturated compounds and high boiling phenols, are exceptionally adapted for a catalytic clay treatment to form the desired by-products.

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A procedure for attaining the stated objects consists in treating a cycle gas oil from a high-temperature steam-cracking of gas oil feed with a catalytically active clay at a temperature in the range 350° F. to 450° F., under a pressure of about 15 to 400 pounds per square inch absolute, and at contact rate from ½ to 2 vol. oil/vol. clay/hr.

The oil is preferably percolated through a fixed bed of catalytically active clay with adjusted temperature, pressure, and contact time, and the liquid product separated from the clay is rerun to recover a distillate and polymer as bottoms, preferably after washing with caustic. The oil filters down through the clay, which is in granular or lump form, and washes away polymer from the clay. The clay is of an adsorptive type which is catalytically active for promoting polymerization of unsaturated hydrocarbons. For example, floridin earth, fuller's earth, acid-treated clays, heat-activated clays, or similarly active siliceous adsorbents, such as zeolites, may be used.

For the purpose of illustration, a preferred mode of operation will be described with reference to a typical cycle gas oil from a high-temperature steam-cracking process in the following example.

TABLE I

Cracking operation data

Fresh feed to cracking furnace,	
lbs./hr. -----	40,322
Total feed to cracking furnace,	
lbs./hr. -----	41,517
Steam feed to cracking furnace,	
lbs./hr. -----	8,025
Cracking temperature, coil outlet,	
°F. -----	1212-1246
Cracking pressure, pounds/square	
inch -----	25
Products:	
Tar, lbs./hr. -----	7,110
Tar gravity, °A. P. I. -----	8.2
Cycle gas oil, lbs./hr. -----	5,870
Cycle gas oil gravity, °A. P. I. -----	24.2
Aromatic naphtha distillate	
lbs./hr. -----	9,980
Distillate gravity, °A. P. I. -----	49.4

The clay-treating run was made at 392° F. average clay temperature, 100 pounds per square inch gauge pressure, and 1 volume of oil per volume of active clay per hour feed rate.

The clay-treated oil product was caustic

washed and rerun to separate 84% heating oil distillate as overhead from 16% polymer bottoms. Inspections of the heating oil cut in comparison with inspections of the cycle gas oil stock subjected to the clay treating are given in the following Table II.

TABLE II
Clay treatment

	Feed	Product
Heating Oil Inspections:		
Gravity, °A. P. I.-----	23.4	27.5
Aniline Point, °F.-----	56	88
Diesel Index-----	13.1	24.2
Acid Heat--ASTM, °F-----	104	48
Phenol Number, mg./100 ml. equiv. t-amyl phenol-----	7,500	250
Bromine Number, cg./g-----	29.2	21.2
Diene Number, cg./g-----	5.1	1.2
Storage Test, g. sediment/25 gal. (six months)-----	36	11
Distillation:		
I. B. P., °F.-----	352	250
10%-----	417	426
50%-----	473	489
90%-----	580	566
F. B. P.-----	636	606
Recovery, %-----	97.5	98.5
Burning Quality-----	(1)	(2)

¹ Unsatisfactory.
² Satisfactory.

The resulting heating oil product of the catalytic clay treatment was suitable in all characteristics for domestic heating oil requirements except in forming slightly more sediment on storage than is formed by the best regular heating oils. Such a product can be blended in large proportions with lower sediment forming oils to give a highly satisfactory heating oil, or can be made entirely satisfactory by making the clay treatment conditions a little more effective in removing sediment-forming components, as by prolonging the contact time or slightly increasing the temperature in the optimum range to about 400° F. or slightly above, yet below 450° F. When the storage test shows a slightly lower sediment content in a six-month storage test, the oil is completely satisfactory even without blending.

The polymer resin recovered as bottoms from the rerunning of the clay-treated oil had the following characteristics:

Gravity-----	4.9
Flash, °F-----	390
Vis./210° F., S. S. U-----	293
Diene number, cg./g-----	4.6

The resin is solid at room temperature and is tacky when heated. It has satisfactory appearance and odor and has been demonstrated to be completely satisfactory for use as a core oil. It may also be utilized for other purposes, such as an adhesive for wood veneer, adhesive for sawdust in compounding wallboard, extender and plasticizer for coating compositions, plastics, natural and synthetic rubber compositions, and the like. It can be sulfurized or be co-vulcanized with rubber or unsaturated copolymers.

The steam-cracked cycle oils are indicated, by the phenol number, to have a rather high phenolic content, of the order of 5% to 10%, and are indicated, by the diene number, to have a rather high content of conjugated double bond compounds. Evidently, from the results obtained, the phenolic and conjugated double bond compounds enter, to a large degree, into the formation of the resin with unstable sediment-forming components when the oils are given the described treatment and these components are re-

moved from the desired heating oil components. The chemical composition of the recovered resins is, therefore, complex and unique.

The conditions of the treatment for obtaining satisfactory heating oil and resin products from the cycle stocks boiling in the range 350° F. to 700° F. have to be carefully controlled, because with excessive heating, the active adsorbent is capable of accelerating decomposition reactions which result in degradations of the products. The optimum temperature is, therefore, established to be of the order of 350° F. to 450° F. The treating pressure is variable but should be sufficient to maintain the oil in liquid phase, and accordingly is generally increased with increase in the treating temperature. However, the space velocity should be kept within prescribed limits like the temperature in order to obtain adequate treatment without undesired decomposition.

The invention is not intended to be limited by the specific example, which has been given to illustrate how a preferred embodiment is accomplished. Various changes may be made and are intended to come within the scope of the invention defined in the appended claims.

I claim:

1. The method of obtaining more valuable products from a high-temperature steam cracked cycle oil boiling in the range of about 350° F. to 700° F., which comprises contacting said oil in liquid phase with an active polymerizing adsorbent at a space velocity between ½ to 2 volumes of the oil per volume of the adsorbent per hour while the adsorbent is at a temperature in the range 350° F. to 450° F.

2. The method of producing stable heating oil and useful polymer by-products from a high-temperature cracking process, which comprises in combination the steps of cracking a gas oil feed at 1050° F. to 1500° F. in the presence of steam at about 1 to several atmospheres of pressure, separating from resulting cracked products an intermediate fraction boiling in the range 350° F. to 700° F., percolating said fraction in liquid phase through a catalytic adsorptive clay at a space velocity of ½ to 2 volumes of the fraction per volume of the clay per hour while the clay is at temperatures in the range 350° F. to 450° F., caustic washing the thus clay-treated fraction, distilling from the washed clay-treated fraction a heating oil and recovering a polymer bottoms therefrom.

3. The method of producing stable heating oil and useful polymer by-products, which comprises the steps of cracking a gas oil feed at about 1200° F. in the presence of steam, separating from resulting cracked products a cycle oil boiling in the range 350° F. to 700° F., contacting said cycle oil with adsorptive clay for a reaction period of about one hour while the clay is at an average temperature of about 400° F. and between the limits of 350° F. and 450° F., caustic washing the thus clay-treated oil, distilling about 84% of the washed, clay-treated oil overhead to recover a stable heating oil distillate, and recovering about 16% of the washed clay-treated oil as polymer bottoms.

4. The method of obtaining more valuable products from a high-temperature steam-cracked petroleum oil fraction containing substantial amounts of phenolic and conjugated double bond components boiling in the range of 350° F. to 700° F., which comprises contacting said oil fraction in liquid phase with a catalytically active siliceous adsorbent at a space velocity of ½ to 2

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volumes of the oil per volume of the adsorbent per hour while the adsorbent is at a temperature in the range 350° F. to 450° F., and separating from the thus-treated oil fraction a heating oil product of relatively low phenolic, conjugated double bond and sediment-forming compound content.

5. A process of preparing a stabilized heating oil and a useful resin from a cycle gas oil of high-temperature steam cracking boiling in the range of about 350° F. to 700° F., which comprises polymerizing sediment-forming components, phenolic components, and diene components of said cycle gas oil to a polymer resin as said oil is contacted in liquid phase with a polymerizing adsorbent at a temperature in the range of 350° F. to 450° F. with a space velocity of $\frac{1}{2}$ to 2 volumes of said oil per volume of the adsorbent per hour, washing away said resin from the adsorbent by unreacted components of the thus treated oil, and separating said unreacted components from the resin by distillation to ob-

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tain a heating oil distillate having lowered contents of phenolic, diene, and sediment-forming components.

6. The process as defined in claim 5, wherein said resin mixed with the adsorbent-treated oil is caustic washed before the distillation.

MINOR C. K. JONES.

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