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CRACKING OF LIQUID HYDROCARBON PRODUCTS

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Mathias Pier
Ernst Donath

Inventors

By: Irish John

Their Attorneys
The present invention relates to the cracking of liquid hydrocarbon products in the presence of catalysts.

In the cracking of liquid hydrocarbon products (which expression also includes mixtures of liquid hydrocarbons with solid substances, as for example distillation residues), in particular of those hydrocarbon products which are rich in asphalts and unsaturated compounds, such as olefinic hydrocarbons, in the presence of catalysts, the activity of the latter is often impaired by the constituents having a high molecular weight of the nature of asphalgetic and resinous bodies which are present in the initial material and/or are formed during the reaction. We have now found that in the working up of the said hydrocarbon products rich in asphalts and unsaturated hydrocarbons, i.e., products containing more than 4 per cent and usually more than 5 per cent of asphalts, this drawback can be overcome by carrying out the reaction in the presence of from 20 to 40 per cent of carbonaceous materials which under the reaction conditions are liquid and remain substantially undecomposed. Suitable carbonaceous materials are for example anthracene oil or aromatic heavy oils (usually boiling above 350° C.) which are free from asphalts and are derived, for example, from cracking or destructive hydrogenation processes carried through at high temperatures, as for example of 500° C. or more. As a rule use is made of those cyclic compounds which are practically free from asphalgetic and resinous substances as well as from unsaturated aliphatic hydrocarbons. The said carbonaceous materials may be added to the material to be treated either prior to or during the cracking process. The amount of the carbonaceous material to be added depends on the nature of the initial material.

As initial materials for the cracking come into question, for example mineral oils or tars and the high boiling products obtained therefrom by distillation, cracking or destructive hydrogenation or the residues resulting from these processes. Middle oils of any origin are also suitable. These initial materials are subjected to cracking by heating to from 400° to 700° C. in the presence of a catalyst having a splitting action. Especially when employing high-boiling initial materials it has proved useful to add these catalysts while in a finely dispersed form, in which the single particles have a size of about from 0.01 to 0.06 millimetre or less. As catalysts come into question metals, in particular those of the 1st to the 4th and the 8th groups, as for example copper, zinc, aluminium, silicon, titanium, thorium, iron, as well as vanadium or chromium, or the compounds of these metals, as for example the oxides and halides, such as bauxite or other known catalysts having a splitting action on hydrocarbons. The catalytically active metals or metal compounds may also be applied to carriers, such as active carbon, coke, lignite coke and the like. When the catalyst is employed in a finely divided form, it is of advantage to add it in small amounts, as for example of from 0.5 to 5 per cent. The catalyst is then led, in conjunction with the initial material, through the cracking apparatus and afterwards removed from the reaction product.

Besides, there may also be added halogen or metal halides, or with particular success organic halogen compounds, such as carbon tetrachloride, ethylene dichloride, chloroform, benzoyl chloride and the like.

The process may be effected by means of an apparatus such as is depicted diagrammatically in the accompanying drawing.

On the drawing:
Reference numeral 1 indicates a hopper from which catalyst is fed to vessel 2 by means of a worm conveyor 3. In vessel 3 the catalyst is contacted with fresh oil introduced through pipe 4. The mixture of catalyst and fresh oil is then fed to mixing vessel 5 equipped with a stirrer 6 in which the heavy aromatic oil employed is introduced through 6a. The mixture of catalyst, fresh oil and heavy aromatic oil is fed by means of pump 7 to coil 8 wherein it is heated by means of hot combustion gases, coil 9 discharging into the reaction vessel 10. The products of the reaction escape from the reaction vessel through line 10 and, after passing through condenser 11, are discharged into the heavy oil separator 12. The uncondensed gases and vapors escape from separator 12 through line 12a and pass via condenser 13 to the collecting vessel 14. The gases leave the collecting vessel 14 by means of pipe 15. The heavy oil which collects in vessel 12 may be supplied by means of pump 16 and line 17 to the mixing vessel 5.

The following example serves to illustrate how the present invention may be carried out in practice, but the invention is not restricted to this example.

**Example**

A mineral oil distillation residue which boils above 325° C., is mixed with 20 per cent of its weight of anthracene oil and 1 per cent of a
finely divided activated lignite coke impregnated with a solution containing iron chloride and nickel chloride. The mixture is then heated up to 470° C. in a tubular system heated with combustion gases, the pressure maintained in the tubes being 70 atmospheres, whereupon the heated mixture is led into an enlarged reaction vessel. The reaction product issuing from this vessel contains 32 per cent of benzine besides the anthracene oil which is practically unchanged. The anthracene oil is recovered by distillation in vacuo and then employed again as additional substance.

If the reaction is carried out without an addition of anthracene oil the yield of benzine is considerably smaller and the operation must be interrupted after a short period due to the separation of coke in the apparatus.

What we claim is:

In a process for cracking liquid hydrocarbon products boiling above 325° C., rich in polymerizable unsaturated hydrocarbons and containing more than 4% of asphalt in the presence of solid catalysts having a splitting action, the particles of said catalyst having a size less than .06 mm., and in the absence of any substance tending to depress the formation of resinous products, the improvement which comprises avoiding a poisoning of the catalyst by any asphalt and resinous constituents present in the parent materials and formed during the reaction, by heating such products to a cracking temperature within the range of 400 to 700° C. while in admixture with from about 20 to 40% of a substantially aromatic heavy oil boiling above 350° C., which effects dissolution of said asphalt and resinous constituents, said oil remaining undecomposed at the cracking temperature selected.

MATHIAS PIER.
ERNST DONATH.