

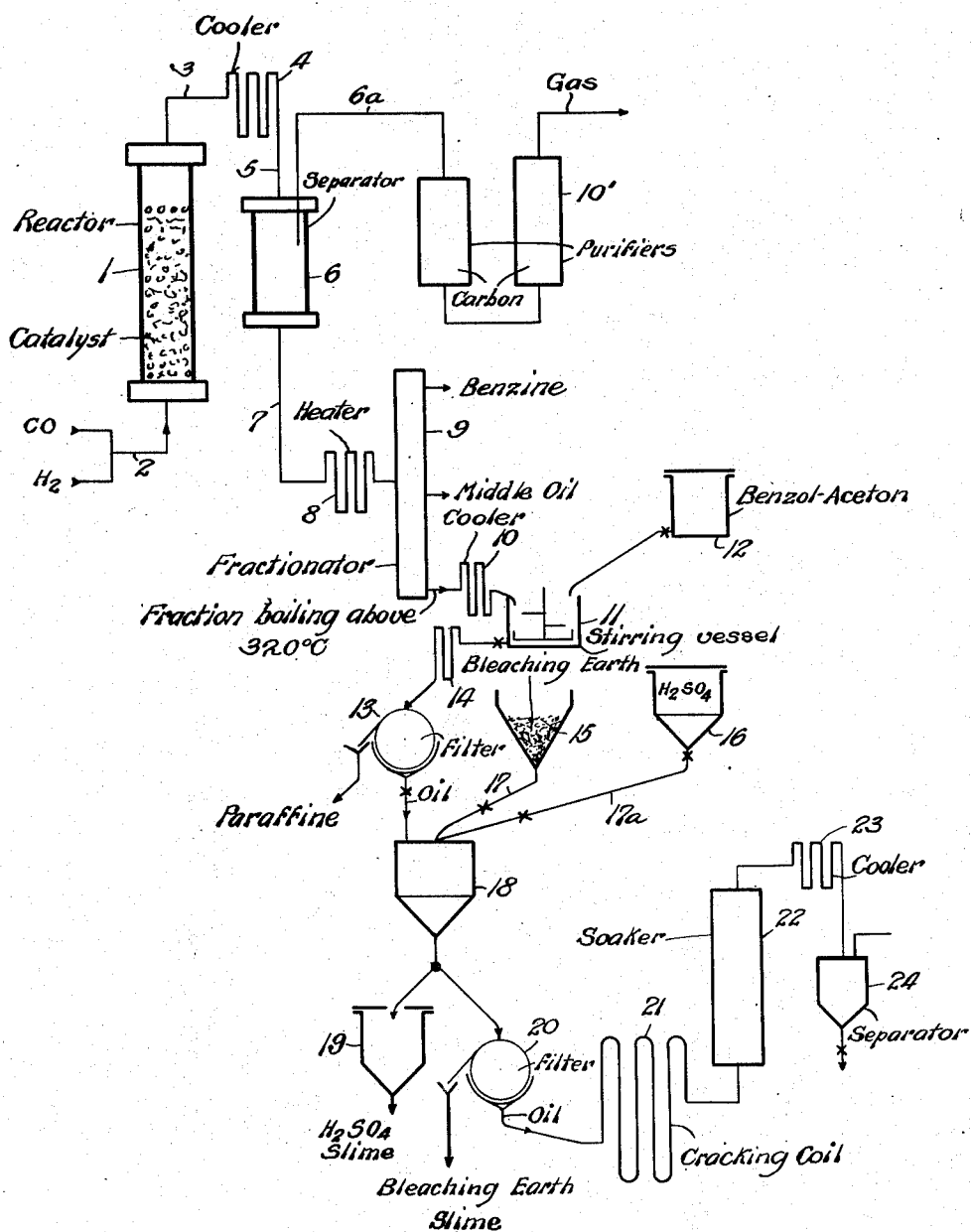
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CRACKING HYDROCARBON MIXTURES

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## CRACKING HYDROCARBON MIXTURES

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The present invention relates to improvements in the cracking of hydrocarbon mixtures obtained by the reduction of carbon monoxide.

In the cracking of oils loss by the formation of coke is frequently encountered which is partly attributable to the impurities contained in the oils and partly to the small hydrogen content of the initial materials. In order to avoid this drawback it has been proposed to free the initial materials from asphalt and impurities containing sulphur or nitrogen and the like and to provide that they contain sufficient hydrogen.

We have now found that even oils having the said nature, from the composition of which a marked formation of coke during cracking would not be expected, frequently form large amounts of coke, contrary to expectation. In particular it is impossible to crack without a strong formation of coke the higher fractions of the mixtures of hydrocarbons prepared from carbon monoxide and hydrogen. Although these products have been prepared from carefully purified gases and are therefore free from the substances known to lead to the formation of coke, such as asphalt or impurities containing sulphur or nitrogen and are moreover very rich in hydrogen (they contain about 18 parts of hydrogen for each 100 parts of carbon), unusually high waste by the formation of coke takes place in the cracking of the said oils. Thus for example an oil boiling above 325° C. which has been prepared by reduction of carbon monoxide and which has been freed from paraffin wax gives a coke residue of about 14 per cent when cracked at from 550° to 600° C. This is the more surprising because other substances of quite similar composition, even when they are not so pure and are poorer in hydrogen, as for example petrolatum which contains only 15 parts of hydrogen for each 100 parts of carbon, give only quite a small formation of coke when cracked.

We have now found that the said difficulties attributable to a hitherto unexplained cause can be avoided by subjecting the hydrocarbon mixtures of high boiling point formed by the hydrogenation of carbon monoxide to a pretreatment with an agent known to be suitable for the refining of oils (hereinafter referred to as refining agent), in spite of the high hydrogen content and a degree of purity which would apparently render a refining unnecessary.

As refining agents there may be mentioned in particular concentrated sulphuric acid, metal halides, as for example aluminum chloride, ferric chloride, boron fluoride, zinc chloride and titanium chloride. When using the said substances

it is preferable subsequently to carry out an aftertreatment with bleaching earths or alkali.

Substances having a refining effect by physical action may also be used for the pretreatment of the oils, as for example selective solvents, such as phenols, keto acids, glycol acetate, liquid sulphur dioxide and liquid ammonia.

In spite of their very high hydrogen content, the initial oils are also changed by a pretreatment with hydrogen in such manner that a considerably smaller formation of coke takes place in the subsequent cracking. This treatment with hydrogen may be carried out by leading the oils of high boiling point prepared from carbon monoxide and hydrogen, preferably directly after the separation of the constituents of lower boiling point, together with the residual gas formed in the reduction of the carbon monoxide or with fresh hydrogen, over known hydrogenation catalysts, such as metal compounds of the 5th to the 8th groups of the periodic system, in particular the sulphides or oxides, and especially those of the 6th group, at atmospheric or, preferably, at increased pressure, as for example from 20 to 200 atmospheres or more, and at temperatures of from 250° to 475° C.

The refining with agents, such as sulphuric acid, metal halides or hydrogen, having a chemical action as well as with agents having a physical action is effected under conditions of temperature and duration of time as may be used for the refining of other hydrocarbon mixtures, such as mineral oils or tars or their distillation products and the like.

As initial materials there may be mentioned the higher fractions, in particular those boiling above 250° C., and preferably above 325° C., of products which have been prepared from carbon monoxide and hydrogen at temperatures of from 150° to 250° C., at atmospheric or increased pressure, as for example 1 to 20 atmospheres or higher, in the presence of catalysts, as for example a substance containing cobalt or iron or nickel. It is preferable to free the said oils from paraffin wax before the treatment with the said substances. The cracking of the pretreated oils is carried out at atmospheric or increased pressure at temperatures of from about 500° to 700° C., or more, preferably in the presence of catalysts, as for example metals, oxides, halides, phosphates, sulphides of metals, metalloid halides, halogens or hydrogen halides or mixtures of the said substances. The cracking products thus obtained, in particular the benzene and middle oil fractions, constitute especially good initial materials for

the production of high quality lubricating oils by polymerization or condensation.

The invention will be better understood by reference to the accompanying drawing which depicts schematically the operations involved. A mixture of carbon monoxide and hydrogen is fed into reactor 1 containing a catalyst, such as is subsequently referred to, through line 2. The products leave the reactor through line 3 and pass to separator 6 via cooler 4 and line 5. The gases escape from the separator through line 6 and purifiers 10 which contain carbon. The liquid product passes from separator 6 by way of line 7, thence through heater 8 to the fractionator 9. In said fractionator the liquid product is split into fractions comprising benzene, middle oil and the fraction boiling over 350° C. The latter fraction, after traversing cooler 10, is introduced in stirring vessel 11 with a mixture of benzol and acetone stored in vessel 12, for the purpose of removing paraffin. The product from the stirring vessel passes by way of cooler 14 to filter 13 where the paraffin is removed. The oil is conveyed to vessel 18 and is therein treated with bleaching earth and sulfuric acid conducted to vessel 18 from vessels 15 and 16 by way of lines 17 and 17a respectively. The sulfuric acid component of the mixture passes to vessel 19. The oil is filtered in filter 20 to remove the bleaching earth slime and is then subjected to cracking into coil 21 and its associated soaking drum 22. The products are cooled in cooler 23 and separated in separator 24.

The following example will further illustrate the nature of this invention but the invention is not restricted to this example.

### Example

A mixture of carbon monoxide and hydrogen in the ratio of 1:2 is led at 200° C. over a catalyst containing cobalt, thorium and bleaching earths. The fraction boiling above 320° C. of the oil thus obtained is free from paraffin wax and then treated with about 2 per cent sulphuric acid and subsequently with bleaching earth. The oil thus prepared is cracked at from 550° to 600° C. while returning the products of high boiling point; in this way 72 per cent of oil, consisting to the extent of 58 percent of benzine and middle oil, 27 per cent of gaseous hydrocarbons and 0.5 per cent of coke are obtained. If the pretreatment of the oil be carried out with phenol, the formation of coke amounts to 0.9 per cent. If the same initial oil be cracked under the same conditions but without the pretreatment, 52 per cent of oil, 33 per cent of gaseous hydrocarbons and 14 per cent of coke are obtained.

What we claim is:

1. A process for the cracking of hydrocarbon mixtures, boiling above 250° C., which are substantially free from asphalts, sulphur and nitrogen compounds, and which result from the reduction of carbon monoxide which comprises pretreating such hydrocarbon mixture with a refining agent having an acid reaction and then subjecting the mixture to cracking.

2. In the process as claimed in claim 1 treating a hydrocarbon mixture resulting from the reduction of carbon monoxide which boils at a temperature above 325° C.

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