

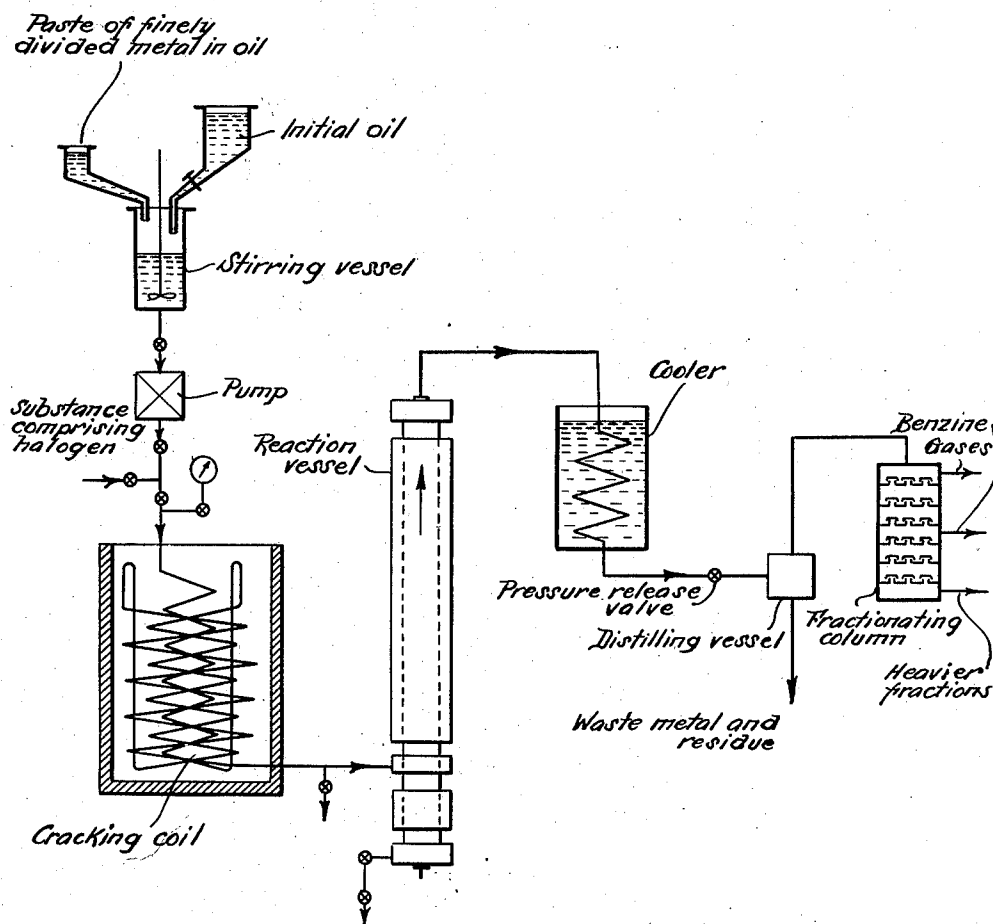
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PRODUCTION OF VALUABLE HYDROCARBONS

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PRODUCTION OF VALUABLE HYDROCARBONS

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1 Claim. (Cl. 196—52)

The present invention relates to improvements in the production of valuable hydrocarbons in particular by cracking hydrocarbon oils.

It is already known that certain metal halides, especially aluminium chloride, iron chloride, tin chloride and zinc chloride, exert a very favorable action in the thermal treatment of hydrocarbons, such as mineral oils and tars, both as regards splitting and as regards refining. It has already been proposed to use the corresponding metals and halogens instead of the already prepared metal halides. In most of the processes hitherto known, however, it is necessary to add large amounts of the said additional substances to the oils or the like to be treated in order to obtain a satisfactory effect. Apart from the consequent high cost of the additions, there is also a very high waste of initial materials because the reaction takes place with the simultaneous formation of considerable amounts of polymerization products. Furthermore the large amounts of halogen hydracids set free during the reaction lead to strong corrosion of the apparatus which can only be overcome with difficulty and with considerable expense. Usually amounts for example of from 8 to 10 per cent of aluminium chloride (calculated with reference to the initial material) must be employed in order to obtain a yield of about 50 per cent of hydrocarbons of low boiling point. Furthermore it is usually only possible to work in discontinuous operation and the throughputs per unit of time are very small so that large reaction vessels must be employed; this is attended by great difficulty. The regeneration of the aluminium chloride and the like, which are used in large amounts, cannot be effected economically in practice. Moreover no economical use has hitherto been found for the large amounts of polymerization products simultaneously formed. In spite of the work and proposals made in the field concerned, the said processes have therefore not been used generally.

I have now found that in the preparation of valuable hydrocarbons from hydrocarbon oils of higher boiling point, such as mineral oils, tars, their distillation, cracking, hydrogenation and destructive hydrogenation products, as well as destructive hydrogenation products of solid carbonaceous materials, such as coals, by thermal splitting in the presence of metals or alloys and of halogens or agents supplying halogens under the working conditions which halogens or agents supplying halogens may also be collectively designated as agents comprising halogens, the said drawbacks can be avoided by leading the oil to

be treated at temperatures of at least 400° C. and under such high pressures that the oil remains wholly or partly in the liquid phase through the reaction vessel at such a speed that it is kept at the reaction temperature only for a few minutes, the metals or alloys being suspended in small amounts in the oil. When working in this manner the pressure is from 50 to 200 atmospheres or more depending on the oil used as initial material. The temperature in the reaction vessel is preferably from about 420° to 500° C. in contrast to the temperature of from 160° to 200° C. employed when working by the processes hitherto known. According to the present invention, the oil remains in the reaction chamber only for a few minutes, as for example from 1 to 5 minutes, whereas in the prior processes this period amounted to from 36 to 48 hours. Thus by the process according to this invention extremely high throughputs are possible and this is of great importance from the point of view of economy. Another important advantage of the process according to this invention is that only very small amounts of additions are necessary in order to obtain a marked effect. The amounts of added metal and halogen are generally speaking less than 1 per cent with reference to the initial oil, as for example between 0.02 and 0.2 per cent of aluminium and between 0.07 and 0.7 per cent of chlorine. Since the amounts added are so small, the cost is negligible and the regeneration of the said substances is unnecessary. At the same time, the danger of corrosion is entirely avoided or can be prevented by much simpler means and at much less cost.

The properties of the benzine obtained according to this invention when used in automobile or like engines are excellent, the anti-knock properties being especially good. After a light refining with sulphuric acid, an octane value of from 70 to 72 is obtained in a Cooperative Fuel Research motor. Still higher octane values can be obtained by varying the reaction conditions, as for example by employing higher temperatures or allowing the oil to remain in the reaction chamber for longer periods.

Furthermore the waste by gasification and formation of tar is very small by reason of the fact that the oil is heated to the high temperature only for a very short period of time. With the same initial materials and the same final products, the total waste according to this invention is only from one half to one third of the waste according to the usual non-catalytic cracking processes.

The process according to this invention may be carried out in different ways. For example it is possible to work with a straight passage of the oil through the reaction chamber, thereby obtaining mainly benzine, fuel oil and heating oil. The oil which is not converted by the first passage may also be wholly or partly returned to the process, only a very small amount of heating oil thus being obtained. The process may thus be adapted in each case to the market requirements.

The metals or alloys to be added may be employed as such or in the form of compounds which are decomposed to form metals under the reaction conditions. The said substances may be mixed with the initial oil or may be introduced during operation at a point before or in the reaction chamber either as such or dissolved in special substances, as for example carbon tetrachloride, which serve at the same time as substances supplying chlorine or other halogen. Suitable metals are, for example, aluminium, magnesium, zinc, iron, nickel, molybdenum or their alloys. They are preferably employed in a very finely divided form, as for example in the form of metal powders as are used for the production of bronze colors. If the metals are to be employed in the form of decomposable compounds, the metal carbonyls, such as the carbonyls of iron, nickel or molybdenum, or organic metal compounds, such as zinc ethyl may for example be employed.

The halogens may be introduced as such or in the form of a compound which readily splits off halogen, as for example hydrogen halides or organic halogen compounds, such as carbon tetrachloride, ethylene dichloride, chloroform, benzoylchloride, benzylchloride, ethylene dibromide or the corresponding iodine compounds or many other organic halogen compounds, either alone or in solution or in admixture with other substances promoting the reaction.

Two or more metals or alloys may also be simultaneously employed; similarly different halogens may be employed at the same time. The metal powders may also be previously activated with very small amounts of iodine, and in the process itself chlorine may then act as the second halogen.

The amount of addition to be employed depends on the initial oil and the desired final product; the optimum amount can be ascertained by a preliminary experiment in each case.

The following example and the accompanying self-explanatory drawing describing the working up of middle oil obtained by the destructive hydrogenation of Mid-German brown coal and mineral coal tar will further illustrate the nature of this invention, but the invention is not restricted to this. Example.

Example

The initial oil has the following boiling range:—

up to 180° C.	6.0 per cent
up to 200° C.	40.5 per cent
up to 275° C.	98.0 per cent.

Its specific gravity at 20° is 0.836.

0.05 per cent of aluminium bronze is suspended in the oil and then 0.20 per cent of carbon tetra-

chloride is added. The oil with the said additions is then forced under a pressure of from 90 to 100 atmospheres by means of a high-pressure pump through a preheating coil into a reaction vessel. The temperature of the reaction vessel is kept at 460° C. The oil remains in the reaction vessel for about three minutes. The product which passes over is cooled and has the following boiling range:—

up to 180° C.	49.6 per cent
up to 200° C.	67.4 per cent
up to 275° C.	95.5 per cent.

Its specific gravity at 20° C. is 0.815.

The octane value (anti-knock value) of the benzine boiling up to 180° C. is 71.5.

The gasification, calculated with reference to the initial oil is 4.5 per cent and the formation of tar, i. e. constituents boiling above 235° C. is 4 per cent.

When working under otherwise identical conditions but without the addition of aluminium and chlorine, the final product has the following boiling range:—

up to 180° C.	21.0 per cent
up to 200° C.	47.0 per cent
up to 275° C.	96.3 per cent.

Its specific gravity at 20° C. is 0.830.

Thus by one passage through the reaction chamber more than twice the amount of benzine is obtained according to this invention than according to the usual cracking process without any additions.

It therefore follows that in practice more than twice the yield of benzine can be obtained with any given cracking plant and this is of very great importance from the point of view of expense. There are also further savings by reason of the smaller gasification, of the lower temperatures, of the smaller refining waste and of the better exploitation of the resulting benzine by reason of its better anti-knock properties and better boiling curve.

What I claim is:—

A process for treating liquid hydrocarbon mixtures to produce a splitting of the hydrocarbons of said mixtures into lower boiling hydrocarbons which comprises adding to said mixtures from .02 to 1 percent with reference to said mixtures of a catalyst comprising a single finely grained solid metal selected from the class consisting of nickel and molybdenum and from .07 to .7 percent with reference to said mixtures of an organic halogen compound, which under the conditions of working is capable of splitting off halogen or halogen hydrides, preheating said mixtures in the presence of the added catalyst, passing said mixtures into a reaction, maintaining said mixtures therein in the absence of added hydrogen for a period of only 1 to 5 minutes at a temperature of 420 to 550° C. and a pressure of at least 50 atmospheres, the conditions being so correlated with the hydrocarbon mixtures that said mixtures remain for the most part in the liquid phase.

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