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SYNTHETIC PROCESS FOR PREPARING HYDROCARBONS, PARTICULARLY GASOLINE

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It is known that the mixture of carbon monoxide and hydrogen usually called water gas and passed under ordinary or high pressure and at a high temperature over a catalyst is converted into hydrocarbons. By this method the complete series—of hydrocarbons from methane up to the solid paraffins—has been obtained including gasoline, gas oil and like. By a suitable choice of the catalyst, of the temperature and of the pressure, a predetermined fraction of the hydrocarbons, as for example the gasoline fraction may be selectively obtained, with a corresponding reduction in hydrocarbons belonging to the other fractions.

The catalysts used in such a synthetic process are formed of metals such as iron, nickel and cobalt (called base metals hereafter), which are able to form carbides.

Experiment shows that the yield of the synthetic process is increased when these base metals are mixed with small quantities of metals of higher atomic weight, such as copper and oxides of alkali metals, such as aluminum oxide and thorium oxide.

It is also known that in order to secure a good yield of the synthetic process the base metals of the catalyst must be pure and to this end they are preferably obtained from their oxides or their carbonates or extracted from other compounds; they may be obtained by electrolysis or by passing through the carbonyl stage.

As indicated by Fischer & Tropsch on the one hand, and on the other hand by Shatwell & Craxfort, as well as others, carbides of the base metals of the catalysts used, i. e. Fe, Ni, Co, form during the synthetic process, said carbides acting efficiently in the process reactions.

However, while the theoretical yield of the synthetic process is as high as about 190 grs. of hydrocarbons for each cubic meter of water gas used, the yield commercially obtained in the past is about 110 grs. and only exceptionally 130–140 grs. of hydrocarbons for each cubic meter of water gas used.

Following extensive research and experiments I have discovered that this somewhat low yield is due to the fact that in most cases the catalysts used are formed with the basic metals themselves, leaving their carbide formation as a "chance" formation during the process or in other words no sufficient attention has been given to the part played by these carbides in the process reactions.

Specifically, I have found that the yield of the synthetic process may be materially increased when instead of the "chance" formation of the carbides of the base metals in the catalytic action, use is made of catalysts comprising essentially preformed carbides, preferably the higher grade carbides of said metals.

Accordingly, the invention mainly consists, in the synthetic manufacture of hydrocarbons, particularly those corresponding to the gasoline fraction, by means of water gas and hydrogen, in using, from the beginning of the process, catalysts substantially composed of carbides and particularly the higher grade carbides of the so called base metals such as iron, nickel and cobalt.

To prepare the carbides, particularly the higher grade carbides of the base metals of the catalytic action, any known method may be used, but such carbides are preferably prepared as follows or in a similar manner.

Starting from a pure metal, in a finely divided state, and for example extracted by chemical action from a suitable compound thereof, preferably through the carbonyl stage, said metal is caused to absorb carbon by subjecting it, in heated conditions, to the action of a body or substances capable of giving off carbon, the operation being conducted so as to avoid fritting the grains or decomposing the formed carbides.

To this end a moderated heating temperature is used while a continuous motion is imparted to the material under treatment. When the operation is completed, the carbide powder is cooled, preferably in the presence of inert gas or alternatively of carbonaceous substances.

The operation may be conducted as follows.

The powder of the selected bass metal is introduced in a tube made of steel, ceramic, quartz or the like, preferably electrically heated as by placing the tube in an electric oven. The tube is heated to a temperature of 250–450° C. according to the base metal used, while passing through the tube any suitable gas capable of giving off the necessary carbon, for example carbon monoxide, methane, lighting gas, petroleum vapors, ether in vapor state, alone or in various admixtures, the absorbing operation being controlled either by the contraction of the gas volume passed through the tube or by the chemical analysis thereof. On the other hand continuous motion is imparted to the tube, as by rotating said tube slowly about its axis, by shaking it, or by other means.

Instead of using a carburetting medium in gaseous form, the metallic powder may also be mixed with solid cements, such as bone charcoal or the like, the tube or crucible containing the

mixture being hermetically closed and heated for the necessary time which may be easily determined by some prior tests.

When the carburetting operation is completed, the tube contents are quickly cooled below the temperature at which the carbides are liable to decompose, and such cooling is preferably obtained by means of a gaseous medium, formed of one or more inert gases, such as nitrogen, or neutral gases, such as helium, or also of one or more carburetting gases, such as those used in the carburetting operation, or yet also by means of liquid hydrocarbons, such as gasoline or benzol, the temperature of the cooling medium being adapted to cool the contents of the tube or crucible rapidly to a very low temperature.

Good results have been obtained by the use of temperatures lower than 0° C. and preferably lower than —190° C.

In this way the decomposition of the formed carbides as well as the formation of pyrophoric carbides are avoided.

The carbide powder of the base metals thus obtained is then crushed by known means, as in a ball mill, a mortar or the like and sifted. The grains of the same size are then mixed in known manner with suitable quantities of powder of copper or alkali metal oxides and agglomerated under pressure while heating moderately as an excess heat is able to cause decomposition of the formed carbides.

Bodies in the shapes of lozenges, rings or other shape are then prepared, and subsequently introduced in known manner within catalysis apparatus such as water cooled tubes or the like.

Instead of lozenges, rings and the like, plates or plate elements similar to filtering plates may be formed, through which is then passed the gaseous current to be subjected to the synthetic process.

Instead of carburetting the powder of the base metals separately, said powder may first be mixed with the powder of copper and of alkali metal oxides, the mixture being then subjected to the carburetting operation.

The lozenges, rings, plates or the like are subsequently formed with this carburetted mixture, but it has been found that the efficiency of the contact bodies produced by this method is less than when the base metal is carburetted separately and afterwards mixed with the additions.

As known in the art, after a certain period of use the contact bodies become charged with solid paraffins, which are removed by means of superheated vapor, after which they are again subjected to a carburetting operation in order to regenerate the carbides of the base-metals in the aforesaid described manner.

Owing to the use of preformed carbides, particularly higher carbides from the beginning of the synthetic operation, the yield thereof is materially increased. For example, with a catalyst containing iron carbides, a yield as high as 155 grams, of hydrocarbons has been obtained for each cubic meter of water gas used.

The catalysts copper, nickel and cobalt may be subjected to a carburetting operation effected between 250° C. and 450° C. to form a catalyst mainly formed of carbides of said metals.

I claim:

1. The process of synthesizing hydrocarbons corresponding to gasoline which consists in subjecting heated powdered nickel while under constant agitation to carburetion to convert the major part of the nickel to carbide, rapidly cooling the product, agglomerating the carbide with copper oxide, passing carbon monoxide and hydrogen over the mixture to effect the synthesis and restoring the efficiency of the mixture by periodic carburetting treatments.

2. The process of manufacturing hydrocarbons similar to gasoline which consists in passing carbon monoxide and hydrogen over an agglomerated catalyst consisting of powdered nickel carbide intimately mixed with copper oxide.

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