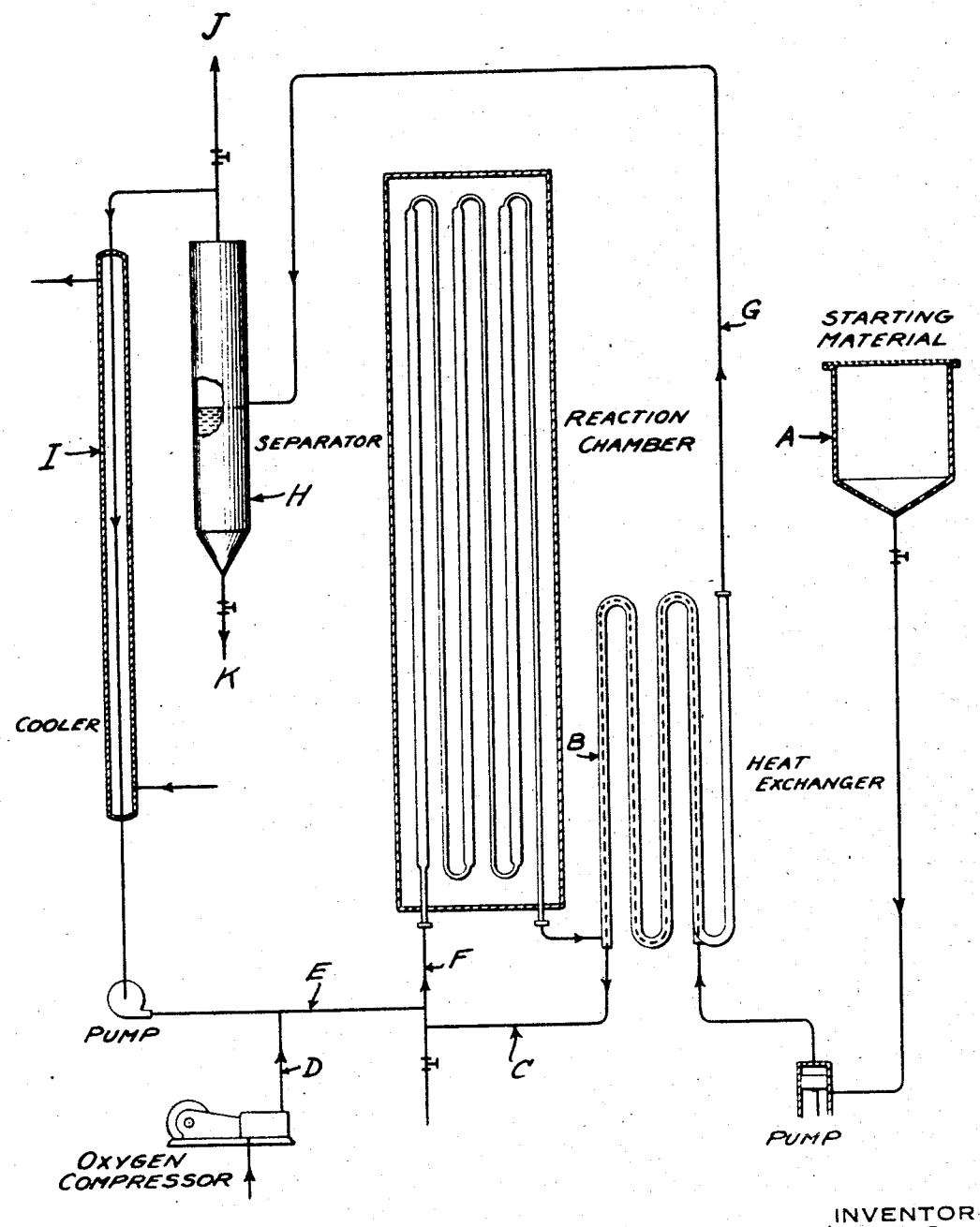
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PRODUCTION OF LIQUID FUEL

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PRODUCTION OF LIQUID FUEL

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My invention relates to the production of fuel for internal combustion engines and more especially Diesel engines. It is more particularly concerned with a process for converting products resulting in the hydrogenation of carbon or other carbonaceous matter into readily ignitable products.

Hitherto the value of a fuel for Diesel engines was determined in the first line by the percentage of hydrogen in the fuel. Generally speaking high-grade Diesel oils are required to contain not less than 12% hydrogen. Recent investigations have now shown that the hydrogen content is not the only factor determining the suitability of a liquid fuel for the operation of Diesel engines. Natural petroleum products are known which contain more than 12% hydrogen, but which are not readily ignitable and therefore unfit for use in Diesel engines. On the other hand solid fuel such as mineral coal, brown coal etc. can be converted by a slight hydrogenation into products poor in hydrogen, which are highly reactive and well suited for use in Diesel engines. These hydrogenation products poor in hydrogen contain only about half the hydrogen present in normal Diesel oils, but their reactivity is such that in spite of the low hydrogen content they can be burnt without difficulty in the Diesel engine. At ordinary temperature the primary products poor in hydrogen are as a rule solid. By cautiously carrying on the hydrogenation and adding some more hydrogen the primary products can be converted into thinly fluid oils which, while containing a somewhat higher percentage of hydrogen, lack the favorable burning properties of the primary products. The excellent reactivity of the primary products has been lost, at least partly, by the continued hydrogenation. Ready ignition is obtained only when still more hydrogen is added, which can be done only by an expensive process.

According to the present invention I succeed in rendering the oils poor in hydrogen, which have been produced from coal either directly or by way of the solid, slightly hydrogenated products, readily ignitable. I obtain this by subjecting the oils to a thermic treatment in the presence of oxygen or gases or compounds containing or splitting off oxygen.

I am aware that it has already been suggested to improve the ignition capacity of aromatic oils by converting part of these oils into aromatic oxygen compounds. In view of the conversion of tar oils into readily ignitable Diesel oils it has been suggested to act with oxygen on the anthracene fraction in the gas phase at temperatures ranging from 400 to 600° C. in order to form quinones. Owing to the autoxidizable properties of the quinones one thus obtains, together with the other fractions of the tar oil forming the starting material, a fuel, the properties of which are greatly superior to those of the starting material.

My invention differs fundamentally from the mode of proceeding mentioned here above. My invention does not consider the treatment of some of the fractions of the starting product with oxygen, but requires the whole or at least the greater part of the oil to be acted upon with oxygen, this treatment being further distinguished from the process previously suggested by being carried through not in the gas phase, but in the liquid phase. It must be carried through at temperatures ranging from 150 to 350° C.

However under these conditions of reaction the hydrocarbons are not converted into oxygen compounds, but I merely cause a slight oxidation of the starting material to take place, which is accompanied by a certain dehydrogenation and which unexpectedly suffices to convert the oils into readily ignitable Diesel oils.

Owing to these considerably simpler conditions of operation the process according to the present invention is greatly superior, from an economical point of view, to the process previously suggested. It also renders the products capable of wider use, since according to the new process not only aromatic oils, but also oils of an altogether different chemical constitution and even oils which are altogether free from aromatic constituents, can be converted into readily ignitable oils.

In practicing my invention I may for instance proceed as follows:

Example 1

A product obtained by a slight hydrogenation of mineral coal was converted by continued hydrogenation into liquid oils. The fraction of this oil, which boiled within the range of 200 and 380° C., contained 8.35 per cent hydrogen. This fraction was treated in a reaction system at 230° C. under a pressure of 20 atm. with air until about 40 liters oxygen from the air were consumed per kilogram oil. The oxygen was avidly absorbed by the oil under development of heat, so that in the air escaping from the reaction vessel were present at first only 1.5% oxygen. By the oxygen treatment the oil was changed only immaterially, its colour being a little darker,

its viscosity only slightly higher, while the boiling-point curve is drawn further apart and the end boiling-point has become somewhat higher. The smell of the oil is changed, the percentage of hydrogen has dropped from 8.35 to 8.12%. The percentage of phenols has also dropped somewhat. In the treatment small quantities of water have formed and apparently also some oxygen has been taken up directly by the oil. Apart therefrom the formation of slight quantities of polymerization products has been ascertained. After clarification in a filter the oil was tested in a Diesel engine at a compression of 42 atm. above normal for ignition capacity as compared with the untreated oil. It was found that while the untreated oil showed retarded ignition already when under half load and spark failure under quarter load, the oil treated according to this invention could still be used under no load without any difficulty, and under all loads the engine ran smoothly.

The process according to the present invention can be adapted to the character of the individual oil to be treated. The gases containing oxygen may be passed through the oil or the oil may be made to trickle, together with the gases containing oxygen over a filling material in a tower-shaped reaction vessel. The quantity of oxygen used may also vary within certain limits. As a rule the temperatures employed in this process range between 150 and 350° C. The process may be carried out at a pressure above normal or under atmospheric pressure. I have found it advantageous to operate with high velocities of flow in order to avoid exposing the oil for an unduly long time to the action of oxygen and of an elevated temperature.

I may either operate with air or with air enriched with oxygen or with pure oxygen. When treating the oils at higher temperatures the oxygen of the air may be diluted in a simple manner by the exhaust gases poor in oxygen which result in the process. I have found it advantageous to operate in the presence of catalysts adapted to transfer oxygen and I have found that I can use all kinds of well-known catalysts of this description, either simple or composite, including compounds of manganese, copper, vanadium, chromium, molybdenum etc., either singly or mixed with each other. The catalysts may either be arranged as solid substances in the reaction chamber or they may be suspended in the oil. They may also be used in oil-soluble form, for instance under the form of oxalates, borates, oleates or resinates. I may use for this purpose the usual contacts such as for instance manganese borate, lead oleate, cobalt resinate, or the corresponding carbonyls, such as for instance nickel carbonyl. This part of the invention is illustrated in the following example.

Example 2

A hydrogenation oil poor in hydrogen which was recovered by hydrogenating mineral coal extract was forced by pumping together with air, in the proportion of 120 liters air per 1 liter oil, at a temperature of 280° C. and under a pressure of 10 atm. in the reaction vessel over contact bodies impregnated with vanadic acid. The gas escaping from the vessel still contained 3.5% oxygen. The oil thus treated, after separation of the water and after filtration, was tested in the Diesel engine. The ignition capacity, the pure exhaust, the soft working and the consumption figures showed that the oil was equal to a gas oil rich in hydrogen. It was further found that the treatment, described above, of the hydrogenation oils poor in hydrogen not only improved the ignition capacity of the oils, but also the dissolving capacity for the bituminous substances resulting after a slight hydrogenation of coal and still solid, but highly reactive. By dissolving these products in a hydrogenation oil poor in hydrogen which was treated in accordance with this invention, one thus obtains a very readily ignitable fuel which burns smoothly and is therefore distinguished by its high economy when used for low speed large size Diesel engines since they can be produced from solid fuel as a mixture at considerably lower expense as the merely liquid oil.

This part of the invention will be explained more in detail in the following example.

Example 3

In 75 parts by weight of the hydrogenation oil poor in hydrogen, which was treated as described in Example 1, 25 parts of the slightly hydrogenated coal product mentioned above, from which the oil itself was produced, were dissolved. One thus obtains a viscous fuel of about 15° Engler at 20° C., which can be burnt softly and without leaving any residue in Diesel engines with a preliminary chamber and also in engines with direct injection, after the first ignition has been induced by a fuse.

The invention is not limited to the hydrocarbon oils which can be produced from solid fuel by hydrogenation, but it may be applied also to other oils of low igniting capacity, for instance the oils obtained by distillation of solid bituminous fuel such as mineral coal, browncoal, oil slate and the like. I may also improve, according to this invention, oils rich in hydrogen which in consequence of their inner structure are very stable and can be ignited only at higher temperatures. In this group of oils belong for instance certain Asiatic kinds of petroleum, which contain terpene constituents, and oils which have been subjected to a cracking treatment at high temperature, such as for instance slate oils, which were subjected during its production to distilling temperatures of 600° C. and above. Similarly gas oils which have passed repeatedly through a cracking apparatus and have thereby been rendered so stable that they could only be split up into benzine at higher temperatures and under great losses of gas, can also be converted according to this invention into readily ignitable Diesel oils. Preferably such middle oils, when treated according to the present invention, will be subjected to higher temperatures.

The treatment of hydrocarbon oils, which were not recovered by the hydrogenation of coal or a still solid, slightly hydrogenated coal product, in connection with the addition of such slightly hydrogenated coal products shall be described more in detail in the following example.

Example 4

In 62 parts by weight of a distillate from mineral coal distillation tar are dissolved 35 parts of a solid bitumen obtained by slight hydrogenation of mineral coal. The solution is treated at 220° C. with air. After removal of the water formed in the reaction and after filtration a viscous Diesel fuel is obtained which is excellently suited for use in stationary engines and works free from objections under any load. Instead of treating a solution of distillation tar and solid bituminous

material, as described above, one might also treat the distillate from distillation tar by itself and dissolve in it the bituminous solid material only after the treatment.

The invention is further illustrated in accordance with the attached drawing in which container A illustrates a vessel in which may be placed the hydrocarbon product which is to be treated with oxygen. The initial hydrocarbon product is then forced by means of a pump through the heat exchanger B into the line C, where it is brought in contact with an oxygen-containing gas, such as air, which is introduced by means of an oxygen compressor through the lines D and E. The admixed hydrocarbon material and oxygen-containing gas are led through line F into the reaction chamber as shown and after the desired degree of oxidation has been reached, the modified hydrocarbon product is returned through heat exchanger B, then through line G to the separator H. Incondensible gases may be drawn off at J, while condensible hydrocarbon products may be condensed in the cooler I. The modified hydrocarbon may be separated from any immiscible reaction products, such as water, by separately valving off the modified product and immiscible reaction products from the separator H. Products condensed in the cooler I may if desired be pumped into the reaction chamber by way of line E.

The treatment of middle oils of low igniting capacity with oxygen of the air in accordance with the present invention is, in the majority of cases, the most economical way for improving the igniting capacity of the oils. I may however also operate my invention in a similar manner with combined oxygen, and if in such case active oxygen is used, operation at lower temperatures and even at normal temperature is frequently possible. This applies for instance to the treatment with activated oxygen (ozone) and with peroxides, for instance with H_2O_2 and its salts, and to the treatment with chromic acid, nitric acid and the like.

It has thus been found that contrary to universal belief the igniting capacity of oils poor in hydrogen can be considerably improved by an oxidizing or dehydrogenating treatment, so that these oils, as far as their igniting capacity is concerned, resemble the gas oils rich in hydrogen. This result is the more surprising as it is for instance well-known that the thermic cracking treatment of petroleum products with simultaneous splitting off of hydrogen always leads to a diminution of the igniting capacity of the products treated.

Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

I claim:

1. A process for making difficultly ignitable Diesel power fuels more readily ignitable which comprises treating such a fuel in the liquid phase with a gas comprising oxygen in such proportions and for such a reaction period that no substantial proportions of oxygen-containing hydrocarbon compounds are formed and the boiling curve of the distillable portion of the starting material is not substantially altered, the treatment taking place between 150° C. and 350° C.

2. The process as claimed in claim 1 which comprises using as initial material a difficultly igniting Diesel power fuel poor in hydrogen.

3. The process as claimed in claim 1 which comprises using as the initial material a difficultly igniting Diesel power fuel poor in hydrogen obtained by a mild hydrogenation of coal.

4. The process as claimed in claim 1 which comprises using an initial material composed of a difficultly igniting hydrocarbon oil and a product obtained by a mild hydrogenation of coal dissolved therein.

5. The process as claimed in claim 1 which comprises a treatment of the initial material with the said gas at increased pressure.

6. The process as claimed in claim 1 which comprises treating the initial material with the said gas in the presence of a catalyst capable of transferring oxygen.

7. In the process for the production of readily ignitable fuels for Diesel engines as claimed in claim 1 the further step of adding to the hydrocarbon oils treated in the said manner with said gas a product obtained by a mild hydrogenation of coal.

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