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METHOD OF OBTAINING LOW BOILING OILS FROM HIGHER BOILING OILS

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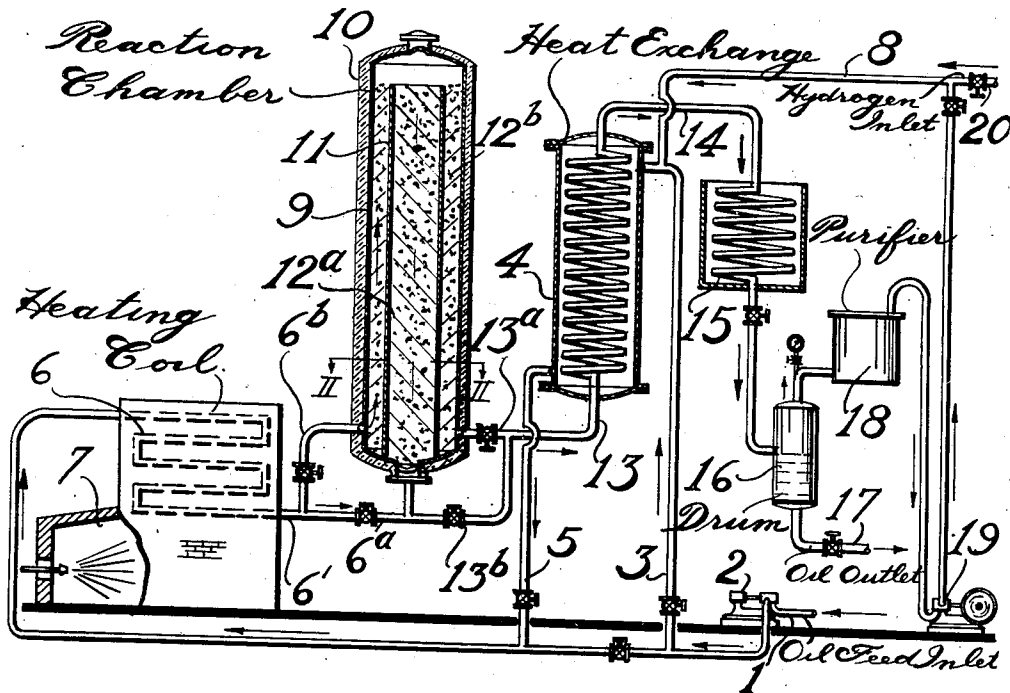


Fig. -1

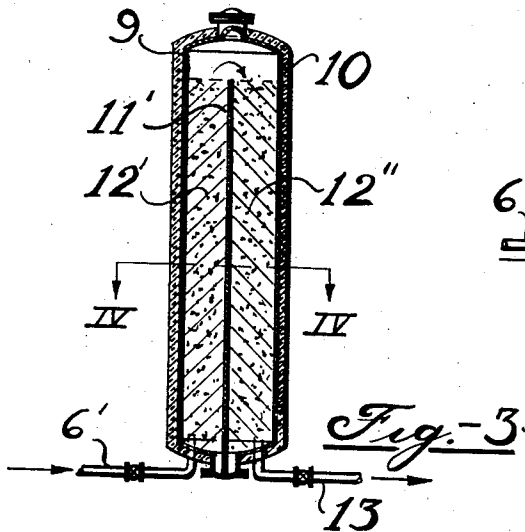


Fig. -3

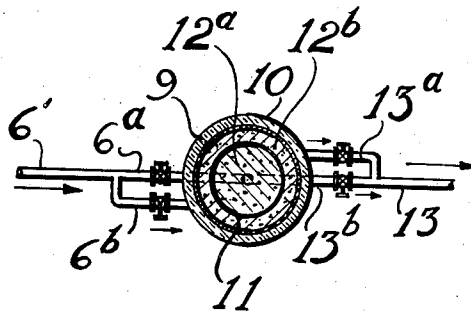


Fig. -2

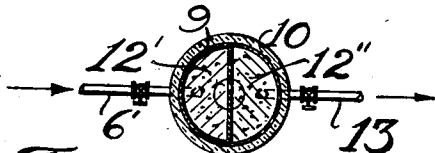


Fig. 4

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METHOD OF OBTAINING LOW BOILING
OILS FROM HIGHER BOILING OILSMarion W. Boyer, Baton Rouge, La., assignor to
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4 Claims. (Cl. 196—53)

The present invention comprises an improved method for obtaining valuable low boiling hydrocarbons from higher boiling products by the action of hydrogen and also an improved apparatus for carrying out the process. The invention will be fully understood from the following description and the drawing which illustrates the construction of the apparatus.

Fig. 1 is a diagrammatic view in elevation of an apparatus constructed to carry out the improved process and indicates one structure of the reaction chamber.

Fig. 2 shows a horizontal section of the reaction chamber taken along the line II—II of Fig. 1.

Fig. 3 is a vertical elevation of a reaction chamber constructed according to a modified form of my invention and

Fig. 4 is a section taken along the line IV—IV of Fig. 3.

Referring to the drawing particularly Figs. 1 and 2 oil such as gas oil, kerosene or the like is withdrawn from any suitable storage, not shown, through a line 1 to a feed pump 2 which forces the oil by pipe 3 through a heat exchanger 4 and by line 5 to a fired coil 6 which is arranged in a suitable setting 7. Hydrogen under high pressure is supplied by a pipe 8 and mixes with the oil in pipe 3 prior to passage through the exchanger 4. The heated mixture of oil and hydrogen is discharged from the coil 6 through a discharge line 6' into the base of a suitable reaction chamber 9. The reaction chamber is lagged with an insulating layer 10 to prevent excessive loss of heat and is adapted to withstand high temperature and pressure, for example; temperatures above about 900° F. and pressure of 3000 pounds per square inch or more, as well as the corrosive effects of the reactants. The drum may be constructed or lined with a suitable metal such as a low carbon steel containing above 10% of nickel and chromium and a tube 11 of the same material is disposed within the reactor, so that the incoming oil and gas may be introduced to the interior of the tube through line 6a and after flowing upward through the tube passes over the edge at the top of the drum and then downwardly flow through the annular space between the tube 11 and the wall of the reactor 9 and leave the drum through line 13a. Alternately, the oil and gas may enter the drum through line 6b by closing the valves in lines 6a and 13a, in which case the mixture passes first through the annular space, then through the tube and out

through line 13b. The reactor is packed with a suitable catalytic material, both within the tube at 12a and in the annular space indicated at 12b. The position of the tube is indicated more clearly in Fig. 2. It is preferred that the tube be of such size as to provide substantially the same cross sectional area within the tube as in the annular space, although the proportion may vary considerably, as will be understood. The mixture of oil vapor and gas from 13a or 13b passes into line 13 and thence through exchanger 4 and line 14 to a condenser 15. Condensate and gas are separated in a drum 16 preferably under full pressure and the oil is withdrawn by line 17 to any suitable storage, not shown. The gas is taken to a suitable purifying system 18 which may comprise an oil scrubbing system operated at high pressure capable of removing hydrogen sulfide and other constituents. Purified gas is then recompressed by a booster pump 19 and recirculated to the hydrogen feed pipe 8. Fresh hydrogen may be added by line 20.

Referring to Fig. 3 a modification of the drum construction is shown in which a metal partition 11' is placed vertically in the drum so as to divide it into two sections 12' and 12''. The wall is substantially tight at the base of the drum, but a passage way is left connecting the two divisions over the top of the wall, as shown. As before, the drum is packed with a suitable catalytic material and the reaction mixture is added by line 6' to one side of the partition 11' and is withdrawn from the other side by the line 13. The sectional view of this modification is shown in Fig. 4.

In the operation of this process oils capable of complete vaporization, such as gas oils, kerosene, naphthas and the like are forced through a heating coil with hydrogen and the hot mixture is then discharged into a reaction chamber packed with a suitable catalyst. The oil may be more or less completely vaporized in the coil 6 or such vaporization may be brought about by contact with the catalytic mass which causes a substantial evolution of heat. The reaction drum is preferably held at a temperature in excess of about 900° F. and may be in excess of 950 or 1000° F. The pressure should be in excess of about 20 atmospheres, but it is preferred to operate at 200 atmospheres or more. As catalytic agents oxides of chromium, molybdenum and tungsten, either in admixtures with each other or with other oxides such as magnesia and lime, alumina and zinc oxides, may be used.

Since there is a marked evolution of heat within the drum due to the reaction which takes place it is sometimes extremely difficult to control the temperature and it has been found that the temperature may vary from time to time by more than 50° or even 100° F. in the various parts of the drum. This condition is highly undesirable since it produces un-uniform products and the extremes of temperature often have a deleterious effect on the activity of the catalytic mass. It has been found that satisfactory results can be obtained by causing the oil and vapor to pass and repass through the reactor in such a manner that there is an exchange of heat between the incoming and the outgoing materials. This can readily be effected by placing a tube within the reactor as shown in Figs. 1 and 3, or by the use of a partition wall shown in Figs. 3 and 4.

As an example of the operation of this process two experiments are carried out under substantially the same conditions as follows:—A gas oil having a gravity of 38.7° A. P. I. and boiling below about 620° F. with a sulphur content of .146% is fed at a rate of two volumes of oil per volume of reactor space per hour. The volume of hydrogen is about 2300 cubic feet per barrel of oil. The temperature is about 950° F. and a catalyst of tungsten and magnesium oxides is used. In the first case the flow through the oven is by a single passage upward and it is found that from time to time there are variations in temperature of as much as 60° F. in different parts of the reactor. In the second experiment the oven is constructed with a central tube according to the preferred modification of the present invention. In this case it is found that the maximum variation of temperature from point to point in the reactor is about 2° F. over a period of 130 hours. In each case about 75% of the fresh feed is converted into a product boiling below about 400° F. which is admirably adapted for use as a motor fuel, and the fractions boiling above 400° were continuously recycled through the reactor with the fresh feed. There was little or no deposit of carbonaceous material on the catalyst, and it is clearly shown that operation with the two pass type of reactor is decidedly more uniform and gives substantially better results than with the single pass reactor.

The invention is not to be limited by any theory of the mechanism of the reactor nor to any examples which may have been given for purely illustrative purposes, but only by the following claims in which I wish to claim all novelty inherent in the invention.

I claim:

1. In the exothermic hydrogenation of hydrocarbon oils in the presence of catalytic materials which promote the hydrogenation, the improvement which comprises preheating a stream of oil and hydrogen causing said stream to flow continuously longitudinally through one portion of the catalytic mass in one direction and then causing the stream to flow continuously longitudinally through an adjacent portion of the catalytic mass in the opposite direction, the entire mass of catalyst being maintained at a reaction temperature solely by the exothermic heat of the reaction and provision being made for rapid interchange of heat between the adjacent portions of the stream flowing in opposite directions.

2. In the destructive hydrogenation of hydrocarbon oils under pressures between 20 and 200 atmospheres and at temperatures above 900° F. in which a stream of oil and hydrogen is preheated and then passed continuously through a reaction vessel packed with lumps of a catalytic material which promotes the hydrogenation, the method of maintaining a uniform temperature throughout the catalytic mass which comprises dividing an elongated mass of catalytic material into a plurality of smaller masses by means of longitudinal baffles, connection between one mass and another being by flow around the top of the baffles, and causing the stream of oil and hydrogen to flow continuously longitudinally in opposite direction through adjacent portions of the catalytic mass, whereby the stream of oil and hydrogen flows in heat interchange relationship with the stream in the adjacent portion of the catalytic mass.

3. In a process for destructively hydrogenating hydrocarbon oil under pressure in excess of 20 atmospheres at temperatures above 900° F. and in the presence of a catalytic material, the improvement which comprises preheating a stream of oil and hydrogen causing the stream of hydrogen and oil to flow continuously in one direction through the central portion of the catalytic mass and in the opposite direction through the outer surrounding portion of the catalytic mass, in such manner that there is a rapid interchange of heat between adjacent portions of the stream flowing in opposite directions.

4. Process according to claim 3 in which the cross sectional area of the central portion of the catalyst mass is approximately equal to the cross sectional area of the outer surrounding portion of the catalyst mass.

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