

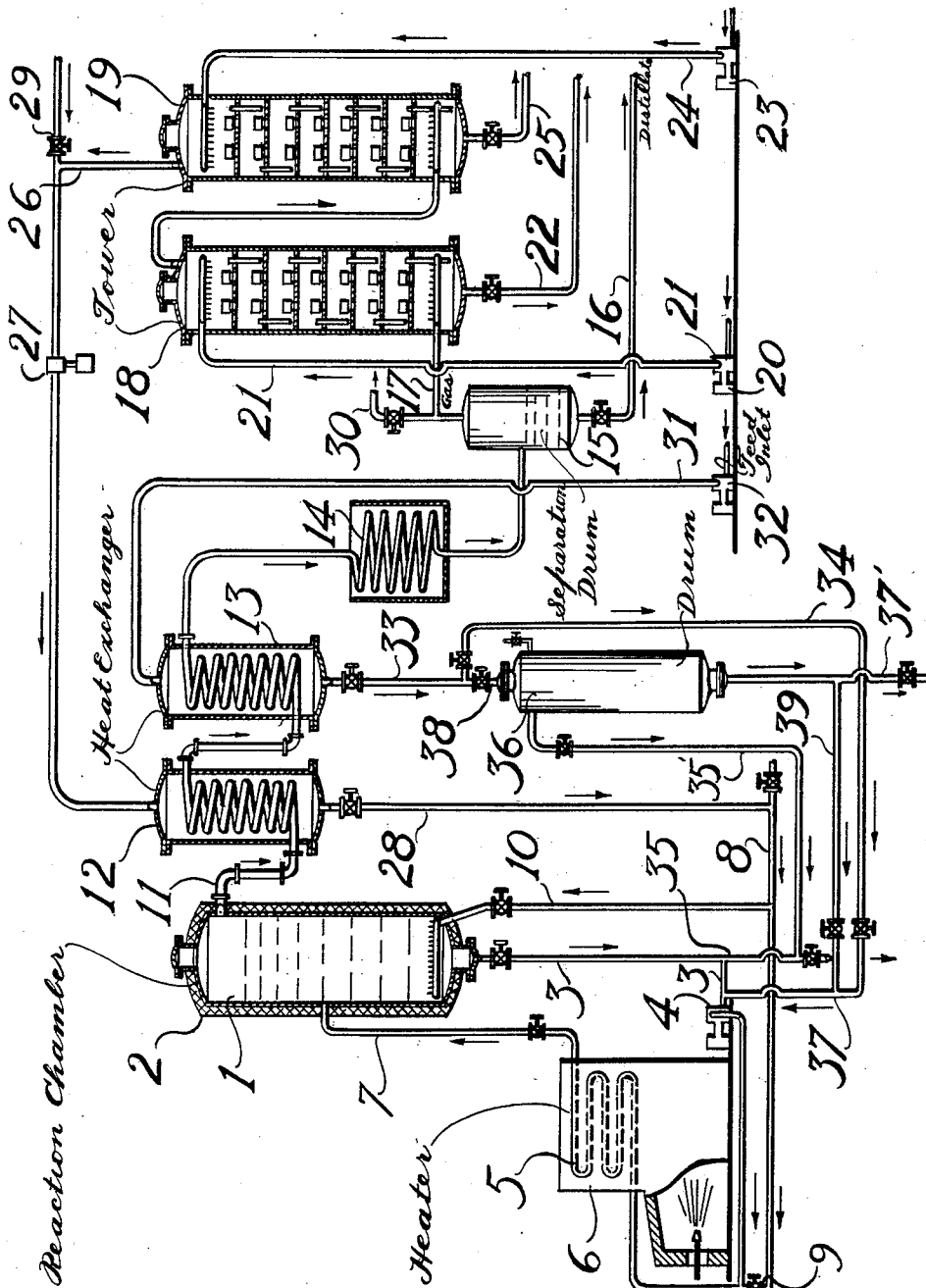
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IMPROVED METHOD FOR DESTRUCTIVE HYDROGENATION OF CARBONACEOUS MATERIALS

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## UNITED STATES PATENT OFFICE

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## IMPROVED METHOD FOR DESTRUCTIVE HYDROGENATION OF CARBONACEOUS MATERIALS

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The present invention relates to improvements in the art of destructive hydrogenation of carbonaceous materials and more specifically comprises an improved method for carrying out the destructive hydrogenation process for relatively long, practically indefinite, periods. My invention will be fully understood from the following description and the drawing which illustrates an apparatus constructed for that purpose.

The drawing is a semi-diagrammatic view in sectional elevation of an apparatus for destructive hydrogenation of carbonaceous materials according to my invention.

Referring to the drawing, reference character 1 designates a reaction chamber or drum adapted to withstand pressures of 200 atmospheres or higher at a temperature of about 1000° F., as well as the corrosive action of the reactants. The drum is suitably protected against loss of heat by insulation 2 and may be heated in any suitable manner, such as electrically, but I prefer to maintain the temperature of the drum by withdrawing a part of its contents by pipe 3 and forcing it by the action of a suitable pump 4 through a coil 5 arranged in a furnace setting 6. Heated material is discharged from coil 5 through line 7 back into drum 1.

Hydrogen or a gas rich in free hydrogen is fed from a supply pipe 8 into branch pipe 9 which communicates with the inlet of coil 5. Hydrogen may also be fed from pipe 8 into drum 1 by pipe 10.

Vapor and gas leave drum 1 by a vapor pipe 11 and flow through heat exchangers 12 and 13 before discharge to condenser 14 and separation drum 15. Distillate is removed from drum 15 by line 16 to storage (not shown) or to stills for removing low boiling components from heavier oils which may be returned as feed to drum 1, as will be understood.

Fixed gas from drum 15 is passed by line 17 through two towers 18 and 19 in series for purification. Tower 18 is fed with oil by pump 20 and line 21 and oil saturated with gaseous or low boiling hydrocarbons is removed by line 22. Tower 19 is fed with an aqueous soda solution or the like for removal

of hydrogen sulphide. The solution is forced through pipe 24 by pump 23 and is discharged by line 25. Purified gas then flows by line 26 to booster pump 27 and is returned to feed line 8 by line 28, being preheated by passage through exchanger 12.

Fresh hydrogen or a gas rich in the same enters the system by pipe 29 and gas may be bled from the system by pipe 30.

Feed oil enters by pipe 31 and is forced by pump 32 through exchanger 13 and flows by lines 33 and 34 to line 3. Line 3 is fitted with a valved sampling line 35 and a drum 36 is connected to lines 33 and 3 by valved lines 37 and 38 for introduction of fresh catalyst, as will be described. A valved line 35' is provided connecting the upper part of drum 36 with circulation line 3.

In the operation of my process crude oils, reduced crudes, and other petroleum cuts may serve as the feed stock and other carbonaceous material such as tars, cracked residues, or a suspension of pulverized coal in oil, may be used. Such carbonaceous material is converted to low boiling oil under pressure of hydrogen in excess of about 25 atmospheres, although I prefer to use about 200 atmospheres and temperatures from 800 to 970° F. Hydrogen is continuously fed to the drum 1 and vapors are continuously removed. Catalysts such as chromium and molybdenum oxides or the like which are not susceptible to sulfur poisoning may be suspended in the oil to increase the rate of hydrogenation. Such catalysts as these which retain their hydrogenating activity in the presence of sulfur or sulfur-containing compounds are aptly termed "sulfactive". I have found in the operation of the above systems, particularly on heavy asphaltic materials, that there is a steady increase of asphalt which necessitates short runs due to coke formation. I have also discovered that in order to insure steady continuous operation without danger of plugging by excessive coke formation, the ratio of "asphalt" to "catalyst" in the body of material being treated should be maintained below about .5 as determined below. The ratio should never be allowed to rise above about 1.0 or 1.5

since it is then impossible to prevent coke formation in a few hours even by addition of fresh catalyst. The suspension, of course, must always be free-flowing.

5 When operating on oil or other ash-free hydrocarbon material, samples of the suspension in the drum are withdrawn at intervals of an hour or more. The sample may be taken from the drum or from the  
10 circulation line by pipe 35. A 10 cc. sample is first filtered and the residue is washed with naphtha to a constant weight which represents "total solids" in the sample. This residue is then washed with benzol or other solvent capable of dissolving asphalt to a  
15 constant weight which represents the "catalyst" in the sample. The difference between "total solids" and "catalyst" is taken as "asphalt". If the ratio of "asphalt" to "catalyst" is above  
20 about .5, a suitable quantity of powdered catalyst calculated to restore the proper ratio is introduced into drum 36. The normal flow of oil from line 33 through line 34 and into line 3 is then diverted by manipulation  
25 of proper valves so that part of the oil passes through drum 36 carrying the catalyst into the circulation system.

If an ashy material such as coal is being treated as a suspension in oil, the procedure  
30 must be changed to allow for the ash and coal in the sample which will remain undissolved by benzol and appear as "catalyst" in the above described test but which should not be included in determining the ratio above described. Correction for the ash and coal in  
35 the sample may be made by chemical analysis of the asphalt free residue or by calculation of the amount of ash in the system, as will be understood.

40 To prevent accumulation of ash in the system, the recirculated material may be withdrawn at intervals by use of lines 35' and 37' and drum 36 or continuously by suitable lines (not shown).

45 As an example of the operation of my process, the following runs are given on topped Crane-Upton crude oil of 23.5 A. P. I. The temperature of the oil is 850° F., the pressure 3000 pounds per square inch in both  
50 runs, and a gas rich in free H<sub>2</sub> is circulated at the same rate and largely in excess of that quantity required for reaction with the oil. The distillation rate in each case is approximately the same and both distillates contains  
55 about 22% of material boiling below 374° F. In one run, the ratio of "asphalt" to "catalyst" is maintained below about .5. This is accomplished, as above described, by the addition of catalyst from time to time. The  
60 run proceeds for about 300 hours without any indication of coke formation. In a second run, no attempt is made to maintain the proper ratio of "asphalt" to "catalyst" and after the fifth hour, the ratio is about 1.0.  
65 The run is discontinued after the thirteenth

hour when it is evident that the apparatus is rapidly becoming plugged. The percent of catalyst in the recirculating line in the first run is approximately 20%, and in the second run about 10%. The catalyst in each case has the same composition.

My process is not to be limited by any theory of the mechanism of the process nor by any illustrative example given merely by way of illustration but only by the attached  
7 claims in which I wish to claim all novelty inherent in my process.

I claim:

1. An improved process for the destructive hydrogenation of heavy asphalt-containing materials, comprising maintaining a body of such material at decomposition temperature in the presence of hydrogen under high pressure and in contact with a solid catalyst resistant to sulfur poisoning suspended in the material and holding the ratio of "asphalt" to "catalyst" below about 1.5.

2. An improved process for the destructive hydrogenation of heavy asphalt-containing materials, comprising maintaining a body of such material under temperature between the approximate limits of 800 and 970° F. and under a hydrogen pressure in excess of 25 atmospheres in the presence of a sulfactive catalyst suspended in the material and holding the ratio of "asphalt" to "catalyst" below about .5.

3. Process according to claim 2, in which vapors are continuously removed from the body of material undergoing decomposition.

4. Process according to claim 2, in which fresh catalyst is added to the body of material at intervals whereby the limiting ratio of "asphalt" to "catalyst" is maintained.

5. Process according to claim 2, in which heavy asphalt-containing material is continuously withdrawn from the body of material undergoing decomposition, heated, and returned to the body.

6. Process according to claim 2, in which fresh heavy asphalt-containing material is continuously forced into the body of material undergoing decomposition through a fresh feed line and in which fresh catalyst is added from time to time by placing it in a closed vessel, connecting said vessel into the fresh feed line and passing the fresh feed through said vessel and into the body of material undergoing decomposition.

7. An improved process for the destructive hydrogenation of asphalt-containing hydrocarbon oil which comprises suspending in the oil a sulfactive catalytic material, forcing the suspension into a reaction zone maintained at a decomposition temperature and under pressure of hydrogen in excess of 25 atmospheres sufficient to keep higher boiling constituents in liquid phase, maintaining the ratio of asphaltic constituents to catalyst in the reaction zone below about .5, and con-

tinuously removing lower boiling constituents formed in the reaction.

8. Process according to claim 7, in which the reaction zone is maintained at a temperature within the approximate range of 800 to 970° F. and the lower boiling constituents are continuously removed in vapor form.

9. Improved process for the destructive hydrogenation of heavy asphalt-containing hydrocarbon oil which comprises suspending in the oil a sulfactive catalyst comprising metal oxides, forcing the suspension into a reaction zone maintained at a temperature between 800 and 970° F. and under pressure of hydrogen in excess of 25 atmospheres sufficient to hold the heavier constituents in liquid phase, continuously removing a stream of suspension from the reaction zone, heating the same in admixture with hydrogen, returning the heated mixture to the reaction zone, and continuously maintaining the ratio of asphaltic materials to suspended catalyst in the reaction zone below about .5.

10. In the hydrogenation of fluent carbonaceous material under pressure of hydrogen between 25 and 200 atmospheres at temperatures between 800 and 970° F. and in the presence of finely divided sulfactive metal oxides suspended in the carbonaceous material, the improvement which comprises maintaining the ratio of heavy asphaltic materials formed in the hydrogenation to metal oxides below about 1.5, while the materials are under reaction conditions.

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