Sept. 24, 1940. H. BUETEFISCH ET AL 2,215,869

PRODUCTION OF VALUABLE LIQUID PRODUCTS FROM PRESSURE EXTRACTS OF SOLID CARBONACEOUS MATERIAL

Filed Nov. 19, 1937 2 Sheets-Sheet 1

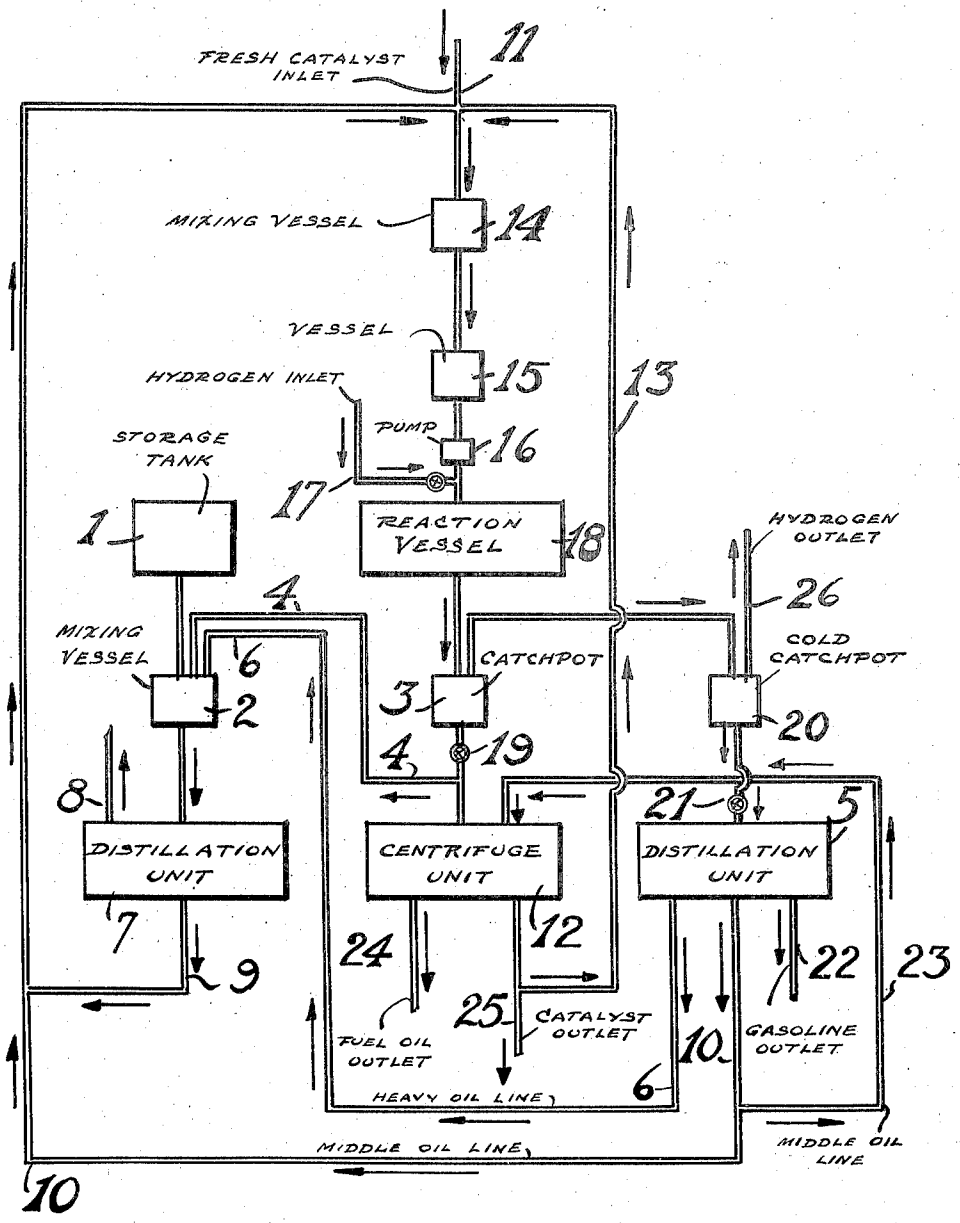


Fig. 1.

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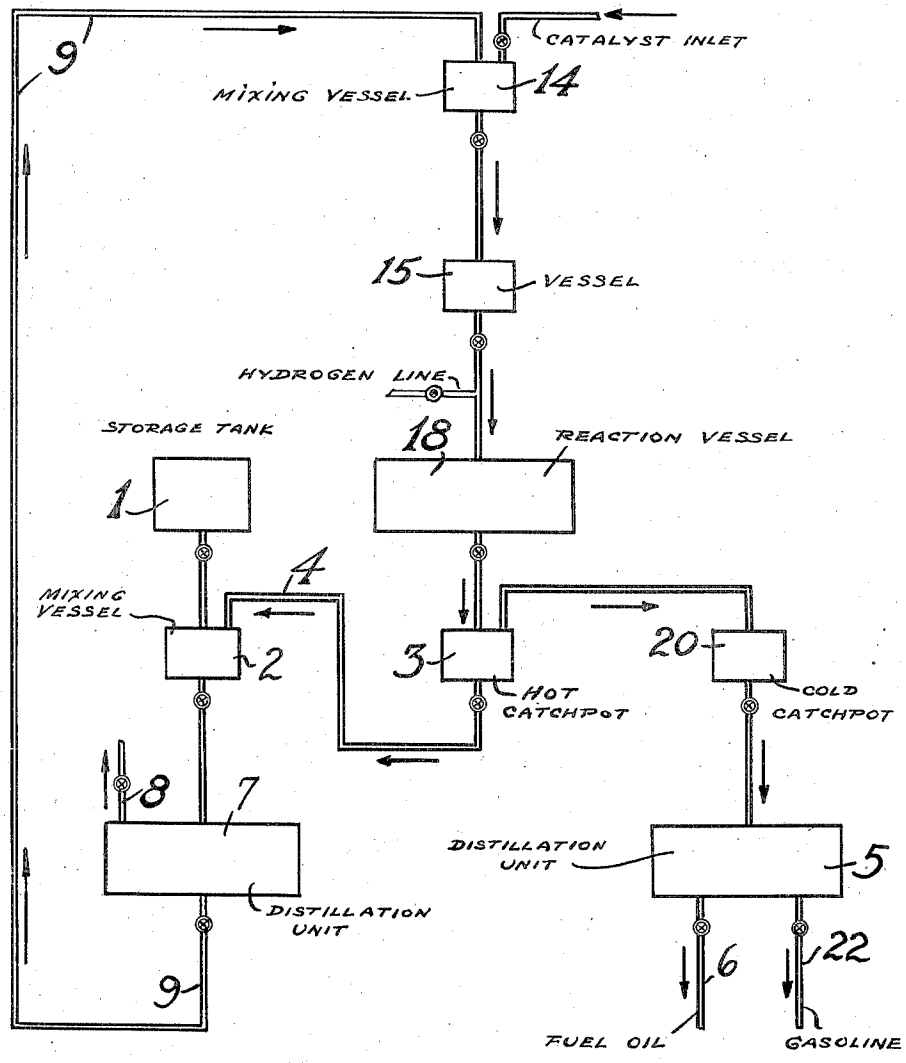


Fig. 2.

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Patented Sept. 24, 1940 2,215,869

UNITED STATES PATENT OFFICE

2,215,869

PRODUCTION OF VALUABLE LIQUID PRODUCTS FROM PRESSURE EXTRACTS OF SOLID CARBONACEOUS MATERIAL

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Application November 19, 1937, Serial No. 175,396
In Germany November 21, 1936

1 Claim. (Cl. 196—53)

The present invention relates to improvements in the destructive hydrogenation of products obtained by extraction under pressure of solid carbonaceous materials.

In the production of gasoline or other hydrocarbon oils by destructive hydrogenation of products obtained by extraction under pressure from solid carbonaceous materials, such as various sorts of coal, including brown coal and bituminous coal, shale or peat, difficulties often occur which are due to the fact that substances of high molecular weight separate in the reaction vessel. The yield of the desired product may thus be considerably lowered.

For the sake of brevity the products obtained by extraction under pressure from solid carbonaceous materials will hereinafter be called "pressure extracts."

We have now found that pressure extracts are converted into valuable liquid products in an uninterrupted smooth operation free from trouble and with a minimum of losses by subjecting to destructive hydrogenation a mixture of said pressure extracts and products of high molecular weight resulting from a previous destructive hydrogenation of another portion of the same or another pressure extract, and which have been collected as liquids without substantial cooling from the hot reaction products issuing from the reaction vessel in which said previous destructive hydrogenation has been carried out. The whole of the said products of high molecular weight, or only a portion thereof may be added to the pressure extracts to be destructively hydrogenated. If desired, the mixture to be destructively hydrogenated may in addition contain hydrocarbon oils obtained by a process different from the destructive hydrogenation of pressure extracts, for example middle or heavy oils resulting from the direct destructive hydrogenation of solid carbonaceous materials or of distillation or carbonization products thereof such as low or high temperature tars, fractions of mineral oils, or heavy hydrocarbon solvents such as tetrahydronaphthalene or mixtures thereof. But usually the addition of such hydrocarbon oils of other origin is dispensed with and it is, accordingly, a great advantage of the present process that the whole operation can be rendered "self-supported" as regards added oil.

It was not to be expected that the admixture of said products of high molecular weight obtained in the destructive hydrogenation of pressure extracts would avoid the aforesaid difficulties.

It is preferable to admix the products of high molecular weight resulting from a previous destructive hydrogenation with the fresh extract, before the extraction agents are removed from the latter.

The said products of high molecular weight are, as a rule, obtained by passing the products issuing from the reaction vessel or vessels in which the destructive hydrogenation of the extract is carried out into a hot catchpot adjacent to the reaction vessel and which is maintained at about the reaction temperature or at a temperature only slightly lower than that prevailing in said vessel and in which a part of the hydrogenation products collects in the liquid state. As already indicated these products collected in the liquid state, or only a portion thereof, are recycled in accordance with the present invention to the destructive hydrogenation of pressure extract. The portion not recycled is preferably divided by mechanical means into a liquid portion and a sludgy or solid residue. Vaporous and gaseous products and surplus hydrogenating gas escape from said hot catchpot, and if desired after heat exchange, liquid products are collected therefrom in a cold catchpot after condensation by cooling. The liquid from the cold catchpot is then usually fractionated by distillation onto heavy oil, middle oil (boiling range between 180° to 200° C. and 325° to 350° C.) and gasoline (end boiling point 180° to 200° C.).

The heavy oil which forms the residue of this distillation is, when desired, also admixed with the pressure extract to be destructively hydrogenated.

A part of the middle oil fraction may be used as a diluent for the mixture to be destructively hydrogenated, and another part as a diluent in order to facilitate the mechanical separation for example by filtering or centrifuging, into oil and sludgy residue or solids of that portion of the products collected in the hot catchpot which is not recycled to the destructive hydrogenation (mechanical oil recovery). By said mechanical separation solid catalyst material may also be recovered. The centrifuged or filtered oil is, inter alia, a valuable fuel oil. The rest of the middle oil may serve as an ingredient of Diesel oil or of fuel oil, or it may be converted into gasoline by catalytic destructive hydrogenation in the vapour phase, or it may be used for any desired other purpose.

The process in accordance with the present invention is carried out in a particularly advantageous manner, which allows of continuously

converting without trouble pressure extracts into gasoline with a high octane number on the one hand and into valuable Diesel and fuel oils with a low pour point on the other hand by employing part of the middle oil as diluent in the mechanical oil recovery and mechanically separating solid catalyst and solid residue from the oil, thus recovering a valuable fuel oil, as already stated, and recycling to the destructive hydrogenation carried out in accordance with the present invention the rest of the liquids collected in the cold catchpot by cooling and condensing which have a boiling range above that of gasoline. In this way all fuel oil may be recovered as such at one point in the plant.

The destructive hydrogenation is usually carried out at temperatures between 250° and 600° C., preferably at temperatures between 450° and 500° C. and at pressures above 50 atmospheres, usually at pressure of at least 200 atmospheres, for example 300, 400, 500, 600, 700, 1000 atmospheres or more.

The destructive hydrogenation is carried out with the aid of hydrogenating gas, that is to say hydrogen or gases comprising sufficient free hydrogen. Catalysts useful in the destructive hydrogenation of carbonaceous materials may be employed, for example, these comprising heavy metals of groups V, VI, VII or VIII of the periodic table or compounds thereof, more particularly oxides, hydroxides, or sulphides, for instance, molybdic acid, tungstic acid or sulphides of molybdenum or tungsten, or also organic compounds of tin or zinc, for example tin salts of low molecular weight organic acids. Metallic iron, iron oxide or iron hydroxide, or natural or artificial masses which contain iron oxide or hydroxide in substantial amounts, such as for example bog iron ore or lux-mass (residue of the chemical disintegration of bauxite) may be employed with advantage. The catalysts may be supported by a carrier substance such as active carbon, brown coal small coke, fuller's earth, bleaching earths, for example bentonite or Terrana, silica gel, alumina or magnesia. If desired, halogen, hydrogen halides or compounds furnishing these under the reaction conditions may be added, for example, chlorine, iodine, bromine, iodoform, carbon tetra-chloride, ammonium chloride or the like. The catalysts are either finely dispersed in the initial material or stationary catalysts are employed.

The solid carbonaceous initial materials from which the extracts are obtained comprise various sorts of coal, more particularly brown coal or bituminous coal, peat, oil shales and the like. The pressure extracts are obtained with advantage by treating finely ground solid carbonaceous materials with a solvent such as hydrocarbon oils having a high boiling range, more particularly, hydrocarbon oils of cyclic nature, such as anthracene oil, tetrahydro-naphthalene, hydro-indene and the like or middle oils resulting from the destructive hydrogenation of solid carbonaceous materials or of pressure extracts or with phenolic materials, for example cresols, or with mixtures of these materials. The extraction is usually carried out at elevated temperatures between 250° and 470° C., preferably at from 400° to 460° C. and preferably under pressures of, say, 20, 50, 100, 150, 200 or 300 atmospheres or more, if desired, in stages of increasing temperatures or pressures or in the presence of catalysts, such as halides of heavy metals, or limited amounts of hydrogen or gases containing hydrogen or using several of these conditions simultaneously.

The extraction under pressure may be carried out as a batch process or as a continuous process.

The following examples will further illustrate how the present invention may be carried out in practice, but the invention is not restricted to these examples.

Example 1

Referring to Fig. 1, in the accompanying diagrammatical drawings, which illustrate plants suitable for carrying out the process of the present invention, 1 is a storage tank in which a pressure extract to be hydrogenated is stored in admixture with the solvent which has served for the extraction. The mixture passes from this tank into mixing vessel 2. Part of the products of high molecular weight collected in the liquid state in hot catchpot 3, enters mixing vessel 2 through line 4, and heavy oil from distillation unit 5 is simultaneously supplied thereto through pipe 6. The mixture then passes into distillation unit 7, in which the solvent which had served for the extraction is removed through pipe 8. The mixture freed from solvent issues from the distillation unit through pipe 9. Middle oil from distillation unit 5 is supplied through pipe 10 to the mixture, on its way to the reaction vessel. Fresh catalysts may be supplied through pipe 11 and recycled catalyst from centrifuge-unit 12 added through pipe 13. The finely divided catalyst is admixed to the materials to be hydrogenated in mixing vessel 14. The mixture then passes through vessel 15, in which the feed is measured. The mixture is then forced into the system by means of pump 16; hydrogen is added through pipe 17, and the whole enters reaction vessel or vessels 18. If desired, a preheater or a heat-exchanger or both in which the hot gaseous and vaporous products issuing from hot catchpot 3 serve to preheat the mixture of hydrogen and oils may be arranged before vessel 18. The products issuing from the reaction vessel or vessels pass into hot catchpot 3. The pressure on the products which are collected in the liquid state in hot catchpot 3 is released by means of valve 19. Part of these liquid products then passes through pipe 4 into mixing vessel 2, as already stated, and the other part into the centrifuge-unit 12. The products which escape in the gaseous or vaporous state from hot catchpot 3 pass through a cooler (not shown) into cold catchpot 20. The pressure over the liquid collected in cold catchpot 20 is released by means of valve 21, through which the liquid passes on its way to distillation unit 5. In this distillation unit the liquid from cold catchpot 20 is fractionated into heavy oil, which is recycled to the hydrogenation chamber through pipe 6, into gasoline, which is removed through pipe 22, and into middle oil. Part of this middle oil is recycled to the hydrogenation chamber through pipe 10, as already stated, and the other part is passed through pipe 23 into the centrifuge-unit 12, where it is admixed to the liquid products from hot catchpot 3, thus facilitating the centrifuging treatment (mechanical oil recovery). Fuel oil free from solids is removed from centrifuge-unit 12 through pipe 24. As already stated, the catalyst recovered from centrifuge-unit 12 is recycled to the hydrogenation chamber through pipe 13; if desired or necessary, the catalyst may also be removed from the unit through pipe 25. The hydrogen which escapes from cold catchpot 20 through pipe 26 may be

freed from gaseous hydrocarbons and the like before it is supplied to hydrogen pipe 17.

An extract obtained by extracting bituminous coal from the Ruhr with a mixture consisting of 60 per cent of tetrahydronaphthalene, 20 per cent of naphthalene and 20 per cent of cresols at 410° C. under a pressure of 100 atmospheres is hydrogenated in the plant described at 480° C. under a pressure of 300 atmospheres, finely divided bog iron ore being employed as catalyst. From the products of high molecular weight collected in the hot catch pot in a previous destructive hydrogenation of another portion of the same pressure extract 75 tons are added to every 100 tons of fresh pressure extract, together with 5 tons of finely divided bog iron ore. 25 tons of middle oil are recycled to the hydrogenation chamber whereas 5 tons are passed to the mechanical oil recovery. The throughput of fresh pressure extract is 0.45 kilogram per litre of reaction space and per hour. The following products are obtained for every 100 tons of pressure extract:

(1) 30 tons of gasoline having an end boiling point of 200° C., a specific gravity of 0.832 at 15° C., which is readily refined by means of sulphuric acid and which, due to its very high octane number (85) is more particularly suited for improving gasolines with poor octane number by blending.

(2) 55 tons of fuel oil having a pour point between −10° and −20° C.

(3) From 3 to 4 tons of water.

(4) A gaseous mixture, from which light hydrocarbons may easily be recovered.

Example 2

Referring to Fig. 2 of the accompanying diagrammatical drawings 1 is a tank in which the pressure extract to be hydrogenated is stored in admixture with the solvent which has served for the extraction. The mixture passes from this tank into mixing vessel 2. The products collected in the liquid state in hot catchpot 3 enter mixing vessel 2 through pipe 4. The mixture then passes into distillation unit 7 in which the solvent which has served for the extraction, is removed through pipe 8. The mixture freed from solvent is then passed through pipe 9 to vessel 14, in which finely divided bog iron ore may be added as catalyst. The mixture then passes through vessel 15 in which the feed is measured and from there into the converter unit 18, where the destructive hydrogenation takes place. The products withdrawn in the vaporous state from hot catchpot 3 are passed through a cooler (not shown) into cold catchpot 20.

After separation in said cold catchpot from the uncondensed products the liquid enters distillation unit 5 from which gasoline is withdrawn through pipe 22 and fuel oil through 6. The pipes supplying hydrogen (fresh and recirculated), coolers, preheaters, and other accessory parts of the plant are not shown in order to simplify the diagrammatical drawings.

5.6 kilograms of a mixture consisting of 33.3% by weight of an extract from bituminous coal and 66.7% by weight of liquid products containing catalyst (bog iron ore) collected in the hot catchpot in a previous destructive hydrogenation of another portion of the same extract, are subjected to destructive hydrogenation together with hydrogen at a temperature of 485° C. under a pressure of 650 amospheres in a converter having a content of 3.1 litres. The throughput of extract is 0.6 kilogram per hour and per litre of the content of the converter, the amount of hydrogen being 10 cubic metres per hour (measured at atmospheric temperature and pressure). The temperature in the hot catchpot is kept at 450° C. 158 kilograms of vaporous products (85% by weight of the extract) are withdrawn per hour from the hot catchpot.

29.3% by weight of gasoline having a very high anti-knock value are obtained from the products withdrawn from the distillation unit. The rest is a mixture of middle oil and heavy oil, which is free from asphalt and has a viscosity of 1.5° Engler at 20° C. and a pour point of −60° C. The losses due to the formation of gases and water amount to 15% by weight with respect to the initial extract.

The amount of liquid product withdrawn from the hot catchpot is 3.73 kilograms per hour. It has a pour point of 0° C. and shows a viscosity of 20° Engler at 50° C. Without removal of the catalyst, it is mixed to fresh extract, thus yielding a mixture which is readily pumpable.

What we claim is:

An improved process for obtaining valuable liquid products from pressure extracts of solid carbonaceous materials, which comprises subjecting an extract of a solid carbonaceous material to destructive hydrogenation, separating hydrogenation products which are liquid from those which are vaporized under the full pressure of reaction and without substantially cooling, admixing a portion of the unvaporized liquid constituents of high molecular weight with fresh pressure extract of solid carbonaceous materials before the extraction agent is removed from said fresh extract, removing extraction agent from the resulting mixture and subjecting said mixture to said destructive hydrogenation treatment.

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