July 25, 1939. T. W. PFIRRMANN 2,167,250

PROCESS OF MAKING A SOLID BITUMINOUS HYDROCARBON PRODUCT

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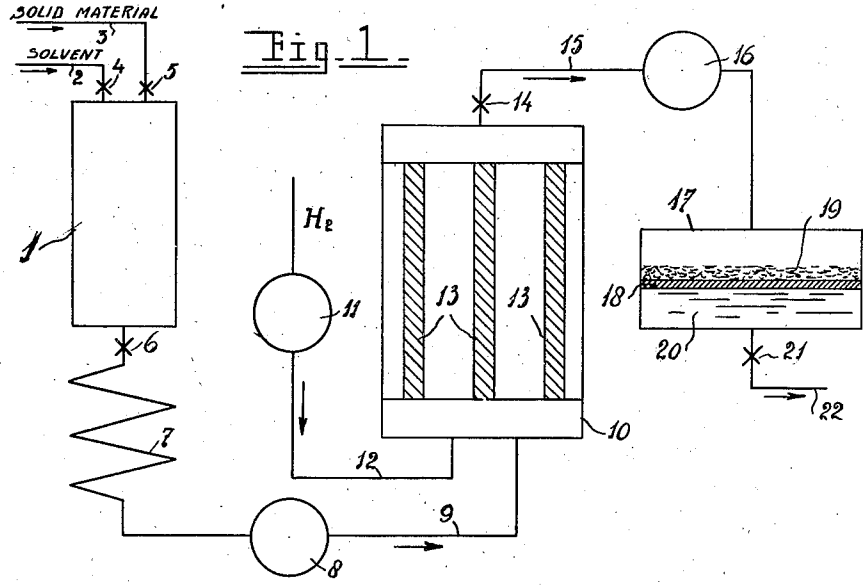


Fig. 1.

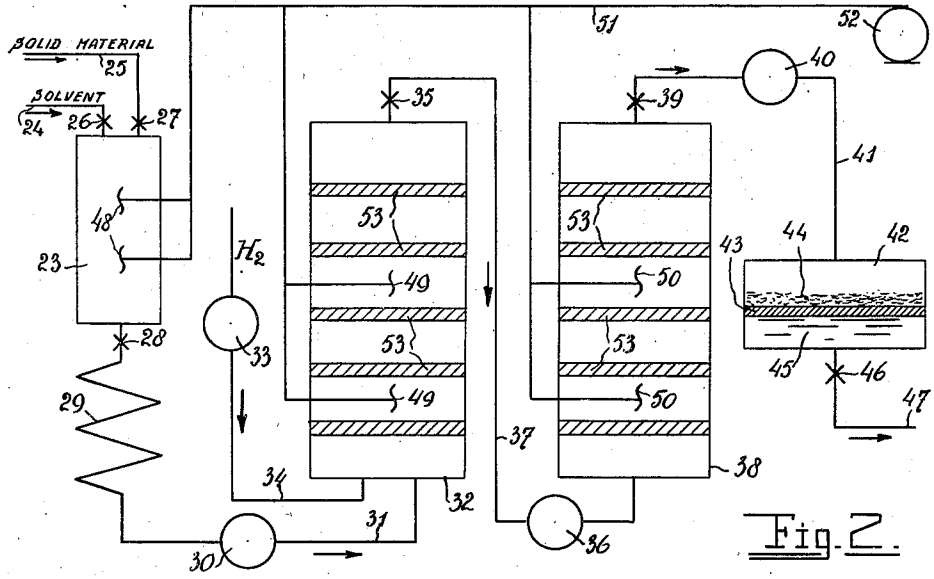


Fig. 2.

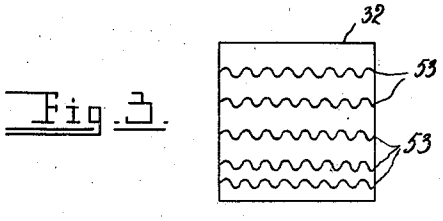


Fig. 3.

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PROCESS OF MAKING A SOLID BITUMINOUS HYDROCARBON PRODUCT

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5 Claims. (Cl. 196—53)

My invention relates to the treatment of non-asphaltic pyrobituminous materials including for instance pit coal, brown coal, wood, peat and other solid carbonaceous materials for the production of solid, soluble and fusible bituminous hydrocarbons. It relates more particularly to means for carrying this process through in a manner whereby valuable products are obtained with a particularly high yield.

Bituminous coal has been converted into liquid hydrocarbons by treating the coal at an elevated temperature with hydrogen in great excess to the calculated quantity and under elevated pressure. In this process the recovery of liquid hydrocarbons capable of being distilled is aimed at, and the maximum yield is obtainable only if the coal and the molecular fragments, respectively, which may have been formed in the process, are altogether saturated with hydrogen. Even if treating coal and operating in the presence of highly active catalysts, this process will lead to a yield substantially not exceeding 90%.

I have now found that valuable products, suitable for many purposes, can be obtained at a high yield, if the solid carbonaceous materials are acted upon at a pressure above normal, for instance at 100, but preferably at 250 to 450 and more atmospheres, and at comparatively low temperatures, ranging between 350 and 450° C., in the presence of distributing agents of an aromatic or naphthenic character, which can be distilled, with a quantity of hydrogen, which is not sufficient to completely saturate the carbonaceous materials and to convert them into normally liquid products. The high yield obtainable according to this new process leads to an almost complete conversion of the carbonaceous material into valuable products, which are solid at room temperature, are fusible and are soluble in a great number of solvents.

The products obtainable in this manner are particularly valuable and can be used with great advantage for a great many purposes, since they are extremely labile and readily reactive and have a low ignition temperature. In this specification the products obtained by the incomplete saturation with hydrogen will be termed "primary products". I have found that these products dissolve only in aromatic and in naphthenic hydrocarbons, while paraffinic and most of the olefinic hydrocarbons act towards precipitating them.

Obviously, in the processes hitherto suggested, progressive hydrogenation of the carbonaceous substances with hydrogen in excess of the calculated quantities leads to a progressive splitting of fractions of the primary product and to their conversion into paraffinic and olefinic hydrocarbons. In proportion as the percentage of paraffinic substances increases, the primary product dissolved in the reaction mixture is bound to be precipitated and to be ultimately rendered insoluble by polymerization. Therefore, since under these conditions of incomplete conversion the reaction product is treated at normal temperature for the separation of the insoluble parts from the soluble matter, the precipitation of the primary product will cause the precipitated constituents to remain in the ashes. The admixing, to the carbon, of middle or heavy oils to form a paste must also lead to a precipitation of the primary products, since most of these oils also belong to the paraffinic or olefinic kind. Therefore present-day hydrogenation processes are governed by the rule that the higher the percentage of hydrogen going into reaction, the higher the yield of hydrogenation products, while the presence of insufficient quantities of hydrogen leads to an unsatisfactory yield.

In contradistinction thereto the increased yield obtainable according to the present invention is based on the conception that the coal or other non-asphaltic pyrobituminous material is converted into a paste by admixing with it solvents which contain no material percentages of paraffinic or olefinic hydrocarbons and that the starting material thus prepared is acted upon with less than the equivalent quantity of hydrogen.

The process according to this invention therefore consists in treating coal or other non-asphaltic pyrobituminous material in the presence of solvents of an aromatic and/or naphthenic character with hydrogen under a pressure above normal and at a temperature approaching or slightly exceeding 400° C., the reaction being interrupted before substantial quantities of paraffinic and/or olefinic hydrocarbons have formed.

In view of the further treatment of the products to be obtained I prefer using solvents capable of being distilled, the boiling point of which lies below the temperature of reaction or may be lowered correspondingly by distillation at reduced pressure, in order not to be compelled to expose the reaction product, during such further treatment, to a temperature above the reaction temperature. I may also use solvents, such as for instance tetra-hydronaphthalene, which are particularly capable of taking up and giving off hydrogen.

I may also carry out the present process in

such a manner that the reaction mixture, which may for instance consist of finely ground coal reduced to a paste by adding about 70–80% by weight of a middle tar oil fraction, is forced, by pumping, together with 2–5% by weight hydrogen, calculated for carbon, through two or three autoclaves connected in series and provided with stirring mechanism, the reaction mixture being preferably preheated to about 410° C. From the last autoclave of the series the mixture is withdrawn with the aid of a pressure reduction device and is discharged into the filters. Since at the beginning the consumption of hydrogen is very great, the partial hydrogen pressure in the second autoclave will drop considerably and in the last autoclave has dropped so far that the absorption of hydrogen ceases almost completely, whereby the formation of paraffinic hydrocarbons is prevented automatically from taking place. In the residual matter remaining on the filters, after washing and freeing it from solvents, not more than about 1–5% of the pure coal (carbon) in the starting material is enclosed, the residual matter mainly consisting of ashes.

I may also connect the autoclaves in such a manner that the mixture of coal and solvent is forced in from one, the preheated hydrogen from the other end. The reaction mixture is withdrawn from the last autoclave before any substantial quantities of paraffinic and olefinic hydrocarbons have been formed.

According to the nature of the coal to be treated and to the percentage of hydrogen brought to reaction, the temperature of reaction will as a rule be within the range of about 380 to 425° C. In the individual reaction vessels different temperatures may be maintained. As a rule the reaction comes to an end within 60 to 90 minutes and by adding catalysts the reaction period may be reduced to 40 to 60 minutes. By using temperatures above those indicated above the period of reaction may be still further shortened. Any known hydrogenation catalyst may be added with advantage, and I prefer admixing such catalyst with the coal during the grinding.

In carrying out my invention I may for instance proceed as follows:

Example 1.—Conversion of mineral coal

The mineral coal, after being ground and dried at a high temperature to free it altogether from moisture, is mixed with a mineral coal distillate boiling within the range of 250 to 320° C. to form a paste which is treated with hydrogen at 410° C. under a pressure of 250 atmospheres above normal. The reaction mixture is withdrawn from the autoclaves in proportion as 4% hydrogen is consumed. The highly viscous reaction mixture is first filtered, preferably under pressure and at a temperature of about 150 to 300° C. The filter cake is once more reduced to a paste by admixing some solvent and is once more filtered. The temperature in the filter may be raised beyond that prevailing during the first filtration step. The solvent which still adheres to the solids is evaporated with the aid of hot gas and recovered by condensation, but may also be recovered by dry distillation. From the filtered solution the solvent is removed by distillation and returned for further use. No losses of solvent will thus occur, but if some solvent should be lost, such loss will be compensated for by the formation of minute quantities of hydrocarbons boiling substantially within the same limits of temperature.

A bituminous mineral coal from the Ruhr-District with 6.5% ashes and 35% volatile constituents, when treated according to this process, yielded the following products, calculated on pure coal:

	Percent by weight
Filtered coal bitumen solidifying at about 85° C	89.5
Gas mixture consisting of carbon dioxide, methane and higher hydrocarbons	4.3
Water	2.9
Losses	0.8

In the filtered residual ash is still found 2.5% by weight of unconverted coal substance, so that the total yield amounts to 97.5%. In the filtered coal bitumen, which may be styled the primary product, there is still found 0.10% ashes.

Example 2.—Brown coal

Brown coal or lignite, after having been carefully dried and finely ground, is reduced to a paste by mixing it in the proportion of 10:7.5 with a mineral coal tar fraction boiling within the range of 180 to 300° C., which can always be reused, and is treated at 400° C. and under a pressure of 250 atmospheres above normal with hydrogen, until about 3.5% by weight hydrogen has been consumed. Calculated on 100 parts coal there were thus obtained:

	Parts
Coal bitumen, free from ashes and solidifying at about 30° C	81.4
Water	7.2
Gaseous products, mainly CO_2 and some methane	8.7

1.8 parts of the pure coal in the starting material were still present in the filtered residual matter, not having been converted, so that the total yield obtained with this brown coal amounted to 98.2%. The coal bitumen separated from the ashes by filtration still contained 0.12% ash constituents.

Instead of mineral coal tar fractions I may use as solvents also benzene derivatives and tar fractions, boiling within similar ranges of temperature, produced by the distillation of brown coal and containing phenols. In such a case I prefer proceeding in such a manner as to prevent hydrogenation of the phenols present, for instance by dispensing with the use of catalysts or operating in the absence of such catalysts which might induce hydrogenation of the phenols. Thus for instance no catalysts containing tungsten or molybdenum should be used in combination with substances having an alkaline reaction, when using solvents containing phenols.

Similarly as mineral and brown coal also peat, wood and similar non-asphaltic pyrobituminous materials can be converted into the primary product with a substantially equal yield. In contradistinction to the known process of coal extraction also such kinds of coal may successfully be treated according to this invention which are poorer in bitumen or which contain a low percentage of volatile substances.

The new process also allows adjusting within wide limits the liquefaction and solidification points of the primary product by regulating (varying) the percentage of hydrogen present in the reaction vessel and partly also by varying the temperature. When operating in the presence of a higher percentage of hydrogen and at a higher temperature, primary products melting at lower temperatures are obtained; in contradistinction thereto the presence of a lower per-

centage of hydrogen or operation at a lower temperature results in the formation of primary products melting at higher temperature. It is also possible to obtain a fair yield of primary products with the percentage of hydrogen reduced to 1% and less, and in this case the quantity of solvent is preferably raised. The primary products obtained in such a case melt at a higher temperature. For instance, when combining only 0.8% hydrogen with the carbon and operating with a proportion of 120 parts by weight solvent to 100 parts coal, even when starting from brown coal up to 92% of the primary product can be obtained at 385° C., however, the solidification point of the primary brown coal product thus obtained will be close to 100° C.

I can also produce products solidifying at any temperature between 150° and 20° C. and even below this temperature. In all these cases the proportion of coal converted remains approximately constant, but if primary products melting at lower temperature are produced, the yield will drop gradually, since an increased formation of gas and water will take place. Under equal conditions of operation brown coal always yields a product of lower melting point than mineral coal, and I am thus enabled to greatly vary the character of the primary product to be obtained by starting from a mixture of brown coal and mineral coal.

In the operation of the process according to this invention it may prove advantageous to subject the coal to a special preliminary treatment, for instance by heating it to a higher temperature. When operating according to the new process, gases are formed by decomposition, which tend to reduce the partial pressure of the hydrogen. By drying the raw material at a higher temperature I am enabled to remove part of these gases of decomposition before starting the operation. I may for instance heat the coal for a short period of time to 400° C. A brown coal having undergone such treatment will yield during the hydrogenation reaction only about half the amount of water and carbon dioxide as a coal not so pretreated.

I may also influence the properties of the primary bitumen by subjecting the coal to be hydrogenated to a chlorination treatment, whereby the combination with hydrogen is favorably influenced, the primary oil produced from chlorinated coal also showing different melting points.

I can greatly reduce the reaction period by operating in the presence of catalysts. I may use any of the well known hydrogenation catalysts and I prefer adding them to the coal during the grinding. I have found that the process can be carried through with particular advantage in the presence of catalysts which do not mix with the reaction mixture, but are fixedly arranged in the reaction vessel. I may use for instance metal alloys in the form of bands or ribbons which are arranged within the reaction vessel in such manner as to allow the solid and liquid reacting substances to pass through freely. I have found an alloy prepared from 15 parts by weight tin, 10 parts iron, 5 parts nickel and 2 parts molybdenum to be suitable. I may replace these metal ribbons for instance by pulverulent contact agents formed into a paste by the addition of water and deposited in the meshes of fine-meshed wire-cloth or on other supports or carriers such as corrugated ribbons or the like. A mixture of 75 parts by weight powdered ferric oxide, 25 parts stannic hydroxide, 10 parts chromium or aluminium fluoride and 5 parts zinc chloride formed into a thick paste by the admixture of water or a dilute tragacanth solution has been found suitable. The carriers, such as wire netting, filled or coated with the contact mass are wound up, while the mass is still moist, and are then dried and, if necessary converted into the catalytically active state, by reduction. In this manner mixed contacts are formed which are fixed in place and which allow the reacting substances to pass freely through the reaction vessel.

In the drawing affixed to this specification and forming part thereof, apparatus adapted for use in practising my invention are shown diagrammatically by way of example.

In the drawing

Fig. 1 is a flow sheet illustrating the process when carried through in one reaction vessel;

Fig. 2 is a flow sheet illustrating the process when carried through with the aid of two autoclaves.

Fig. 3 is a cross sectional view of the autoclave 32 of Fig. 2.

Referring to the drawing and first to Fig. 1, 1 is a mixing vessel into which solvent and solid material are introduced through pipes 2 and 3, fitted with valves 4 and 5, respectively. The mixture is drawn off through the valve 6 and is heated in the coil 7; with the aid of the pump 8 the mixture is conveyed through the pipe 9 and forced into the pressure vessel 10, into which hydrogen is also forced through the pipe 12 with the aid of the pump 11. Bands or ribbons 13 of a catalytically active metal alloy are arranged in the pressure vessel in such manner as not to prevent the mixture from passing through the valve 14 and the pipe 15, through which the converted mass is conveyed by means of the pump 16 to the filtering device 17 in which filtration can be carried through at an elevated temperature. 18 is the filter on which the filter cake 19 collects, whereas the filtrate 20 is delivered through the valve 21 and piping 22.

In Fig. 2, 23 is the mixing vessel for the solvent and the solid material which are introduced by the pipes 24 and 25 fitted with valves 26 and 27, respectively. The mixture is drawn off through valve 28 and heated in the coil 29. With the aid of the pump 30 the mixture is conveyed through the pipe 31 into the first autoclave 32, into which hydrogen is forced through the pipe 34 by means of the pump 33. The partly converted mass is drawn off from the autoclave 32 through the valve 35 and conveyed by means of the pump 36 through pipe 37 into the autoclave 38, from which the converted mass is drawn off through the valve 39 and led with the aid of pump 40 through pipe 41 into the filtering device 42, in which filtration can be carried through at an elevated temperature. 43 is the filter on which the filter cake 44 collects, while the filtrate 45 is delivered through valve 46 and pipe 47. Mixing and/or stirring devices 48, 49 and 50 are driven by means of the shaft 51 and the motor 52. In the autoclaves 32 and 38 corrugated ribbons 53 are arranged consisting of fine-meshed wire cloth filled or coated with a suitable contact mass. The shape of these catalysts, which are fixed in position, provides a large contact surface without preventing the material from passing through the vessels.

Owing to the far reaching possibilities of adjustment and variation of the process steps and

of the character and composition of the reactants, the primary product has been found to be suitable for a great number of different uses.

The product, free from ashes, may be used as starting material for further hydrogenation, whereby the advantage is obtained that the auxiliary substances, such as catalysts or metals, serving to react with the water for the generation of atomic hydrogen, can always be regenerated for further use at low costs. The primary product is soluble in most of the aromatic and naphthenic hydrocarbons, in hydrocarbons poor in hydrogen and in mixtures such as are obtained for instance when refining oils with liquid sulphur dioxide. They are thus distinguished from the products of the coal extraction process hitherto suggested, which dissolve only in a comparatively small number of solvents. Consequently the primary product of the present process can be used as starting material for the production of blacking (black lacquer) and as black printing ink. It may further be used in the manufacture of roofing paper and as an impregnation material.

It is particularly useful for road construction, and it is possible to directly produce such road construction materials from coal and to adapt them to the requirements of the road covering, which may arise in each individual case. In such a case the removal of the ashes by filtration may mostly be dispensed with.

As compared with the coal, the primary product contains a higher precentage of hydrogen and also in this point distinguishes favorably from the product resulting in the coal extraction process hitherto suggested. Its ignition and flash points are very favorable ones, and the primary product may therefore be used with great advantage as fuel in internal combustion engines. Into such engines it may be introduced either in the form of a powder or in molten or dissolved state. I have found that contrary to all expectations, although the percentage of hydrogen in the primary products is considerably lower than in gas oil, these products are readily ignitible and their combustion in Diesel engines will proceed substantially like that of gas oil. Since the primary products are solid substances at ordinary temperature, they are preferably introduced into existing Diesel engines in molten or dissolved state. In order to reduce the disadvantages resulting from high viscosity and in order to save solvent, I prefer preheating them, for instance by the heat of the exhaust gases.

In utilizing the primary products obtained according to the present invention as fuel in internal combustion engines I have for instance obtained the following results:

A primary bitumen produced from brown coal and containing 7.8% hydrogen and melting at about 70° C. was dissolved in a tar oil fraction in the proportion of 2:1. This solution was injected at a temperature of about 60° C. into a three-cylinder Diesel engine of 30 H. P. provided with an entering chamber and running with 600 revolutions per minute. This engine operated faultlessly under all loads and in hot condition it could be started without using any light oil. When the tar oil constituent was raised to 50%, the engine ran under ⅕ load without any misfire. Only when operating under no load misfire occurred, which may be attributed to the considerable retardation of the ignition caused by the tar oil. With tar oil alone the engine ran faultlessly only under full load. No disturbing depositions or residues from the combustion could be ascertained. Contrary to all expectations it was found that from a primary product which can be produced from coal at low costs and which according to all conceptions hitherto prevailing was believed to be unsuitable for use in the Diesel engine in view of its physical and chemical properties, a fuel for Diesel engines can be produced which, when admixed with less suitable Diesel fuels including tar oil, will greatly improve them.

In further experiments I have tried to produce a solvent free, as far as possible, from tar oil, and I have for instance succeeded in obtaining an advantageous solvent by the distillation of primary bitumen. When subjected to distillation, primary products produced from brown coal yield up to 60% by weight of a suitable solvent. By sparingly hydrogenating primary bitumen one can for instance produce from 100 kgs. primary bitumen up to 90% of a suitable solvent which is better adapted for use in the Diesel engine than for instance tar oil. No gas oil and no liquid fuel rich in paraffine should be used as solvents for the primary bitumen. Solvents containing a considerable percentage of aromatic or naphthenic hydrocarbons are best suited for this purpose. Suitable solvents can also be obtained for instance by diluting tar oil with gas oil. One may also increase the percentage of hydrogen in tar oil by hydrogenation, and the product resulting from such treatment will form a superior solvent for primary bitumen. After the addition of 3–5% hydrogen tar oil has lost all such properties which render its use in Diesel engines objectionable. Brown coal tar and tar obtained in the distillation of mineral coal can be used as such, but they also may be improved and diluted by hydrogenation. The possibilities recited above of using solvents are not exhaustive, and the solvents applicable in each individual case will have to be chosen and produced according to the raw materials available.

The primary product may also be used as fuel for furnaces, since it melts readily and can be supplied to oil burners like a liquid.

These ranges of application of the primary product can still be amplified, since the costs of production of the primary product are comparatively low, this being due, apart from the ease of reaction, to the high yield of primary products.

Processes have become known, whereby coal is converted into liquid or soluble organic compounds by treating the coal at a pressure above normal and in the presence of heavy petrol or the like with hydrogen. This mode of proceeding does not lead to products of the kind here claimed, since these products are not soluble in paraffinic hydrocarbons such as petrol.

It has further been suggested, when hydrogenating coal under pressure, to add high boiling fractions of petroleum or tar as distributing agents, the hydrogen being, however, present in excess of the calculated quantity. Obviously a process of this kind does not lead to products of the kind here claimed.

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. The process of producing normally solid extracts from solid carbonaceous fuel material which comprises admixing said fuel material with a solvent for the bituminous material to be produced in the process, which solvent is one belonging to one of the aromatic and naphthenic series,

is stable under the conditions of the subsequent treatment with hydrogen and is substantially free from paraffinic and olefinic hydrocarbons, subjecting the admixed fuel material and solvent in an extraction vessel under high superatmospheric pressure of at least 100 atmospheres to a temperature ranging from about 350 to about 450° C. while in the presence of added hydrogen-containing gases, and limiting the volume of hydrogen-containing gases consumed during extraction to an amount which will not produce substantial hydrogenation and liquefaction of the normally solid extracts.

2. The process of treating non-asphaltic pyrobituminous materials for the production of solid, soluble and fusible bituminous hydrocarbons which comprises forming a paste by mixing one part by weight of the comminuted starting material and at least about 0.7 part of a solvent for the bituminous material to be produced in the process, which solvent is one belonging to one of the aromatic and naphthenic series, is stable under the conditions of the subsequent treatment with hydrogen and is substantially free from paraffinic and olefinic hydrocarbons, forcing such paste and hydrogen into the reaction zone and causing reaction to take place at a temperature ranging between 350 and 450° C. under a high superatmospheric pressure of at least 100 atmospheres, the quantity of hydrogen introduced and made to react being less than that required to produce, by complete saturation of the starting material, a substantial amount of normally liquid products, which might exert a precipitating action on the soluble and fusible bituminous hydrocarbons resulting in the process.

3. The process of treating non-asphaltic pyrobituminous materials for the production of solid, soluble and fusible bituminous hydrocarbons which comprises forming a paste by mixing one part by weight of the comminuted starting material and at least about 0.7 part of a solvent for the bituminous material to be produced in the process, which solvent is one belonging to one of the aromatic and naphthenic series, is stable under the conditions of the subsequent treatment with hydrogen and is substantially free from paraffinic and olefinic hydrocarbons, forcing such paste and hydrogen into the reaction zone and causing reaction to take place at a temperature ranging between 350 and 450° C. under a pressure of 250 to 450 atmospheres, the quantity of hydrogen introduced and made to react being less than that required to produce, by complete saturation of the starting material, a substantial amount of normally liquid products, which might exert a precipitating action on the soluble and fusible bituminous hydrocarbons resulting in the process.

4. The process of treating non-asphaltic pyrobituminous materials for the production of solid, soluble and fusible bituminous hydrocarbons which comprises forming a paste by mixing one part by weight of the comminuted starting material, with at least about 0.7 part of a solvent for the bituminous material to be produced in the process, which solvent is stable under the conditions of the subsequent treatment with hydrogen and is one belonging to one of the aromatic and naphthenic series, forcing such paste and hydrogen, the latter in a quantity less than that required to produce under the conditions of the reaction a substantial amount of a saturated hydrogenation product which might exert a precipitating action on the soluble and fusible bituminous hydrocarbons resulting in the process, into the first of a plurality of autoclaves connected in series causing reaction to take place between the starting material and the hydrogen at a temperature within the range of 350 and 450° C. and under a pressure ranging between 350 and 450 atmospheres, withdrawing the product of reaction from the last autoclave and separating the liquid from the solid matter.

5. The process of producing normally solid extracts from solid carbonaceous fuel material, which comprises admixing said fuel material with a solvent comprising tetrahydronaphthalene, subjecting the admixed fuel material and solvent in an extraction vessel under high superatmospheric pressure, to a temperature of the order of 400° C., while in the presence of added hydrogen-containing gases, and limiting the volume of hydrogen-containing gases consumed during extraction to an amount which will not produce substantial hydrogenation and liquefaction of the normally solid extracts.

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