

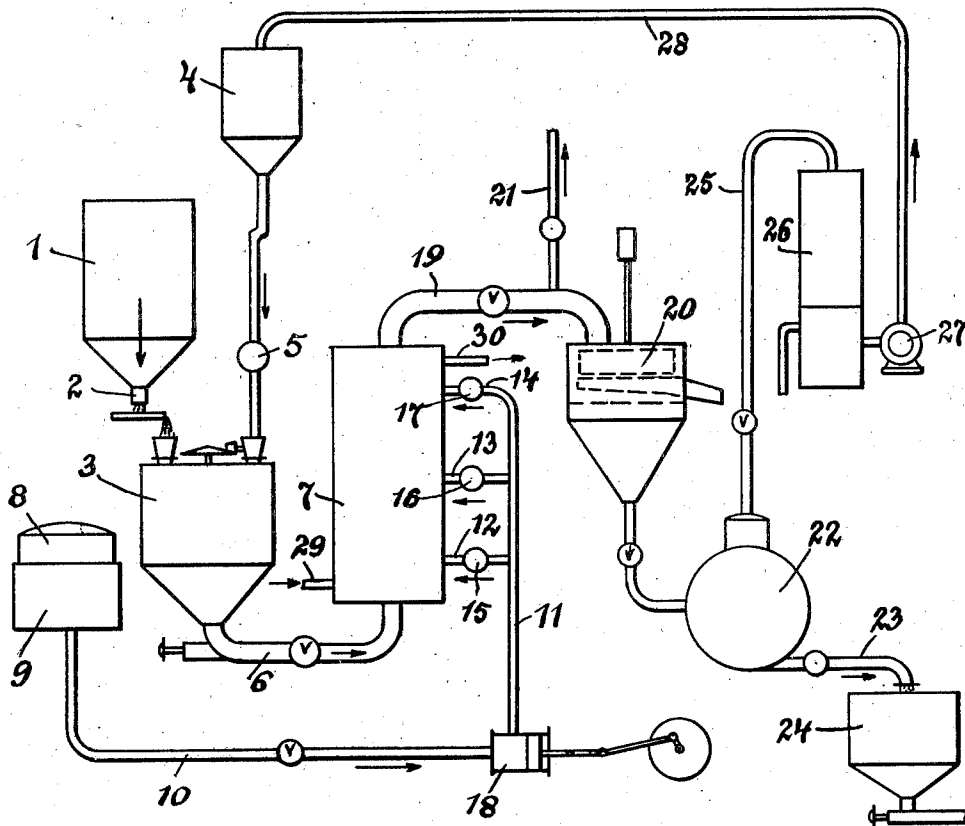
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PRODUCTION OF EXTRACTS FROM SOLID CARBONACEOUS MATERIAL

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PRODUCTION OF EXTRACTS FROM SOLID
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This invention relates to a method of producing extracts from solid carbonaceous fuel material such as coal, lignite, peat.

In particular, the invention relates to a method of producing such extracts in the presence of solvents consisting of, or containing, hydrogenated oils, such as tetraline, under elevated pressure and at raised temperature.

We described in our U. S. Patent 1,881,927 a method of producing such extracts by treating solid carbonaceous material with organic solvents at raised temperatures and elevated pressures. The temperatures are raised in such a way that they are close to the decomposition temperatures of the original solid carbonaceous material and of its solid residues resulting when the extraction process continues. The decomposition temperature of the original material and of the residues is easily ascertained by experimentation as the temperature at which the material starts to develop gases, i. e. decomposes. The extraction process is preferably performed in closed vessels, so that the pressure rises with rising temperature.

However the extraction may be performed, in general solvents are used containing hydrogenated oils, and the material is extracted at elevated temperatures and raised pressures. The elevated temperatures in general do not exceed about 390° to about 415° C., depending on the character of the carbonaceous material under extraction, while the pressures generally start at about 10 atmospheres per sq. cm., do not exceed about 60 to 70 atmospheres per sq. cm., and may not reach about 100 atmospheres.

By the term "hydrogenated oils" liquid hydrocarbons are meant, having a boiling point above room temperature up to about 250° C., and being obtained by hydrogenating carbonaceous material as such or hydrocarbons of a lower hydrogen content. For instance coal tar oils or lignite tar oils may be hydrogenated to give proper solvents for extraction purposes. Naphthalene may be hydrogenated to give tetraline which is one of the best solvents for extraction purposes. These and other hydrogenated oils may be used alone or in admixture to other organic solvents such as phenols which represent acidic oils, phenol containing oils, certain fractions of tar, etc.

These solvents are used for the extraction in any suitable proportion. The weight of the solvent present may be about equal to that of the solid carbonaceous material under treatment, or it may exceed it, for instance in a ratio of 1.5:1.

If such solvents are used in an extraction proc-

ess raised temperature and elevated pressure, it has been found that the hydrogenated oils present in the solvent are somewhat dehydrogenated. In other words, taking for instance tetraline, it decomposes in part into naphthalene and hydrogen. The absolute amount of hydrogen split off from the tetraline is not very high, and it remains for instance in a process carried out according to our Patent 1,881,927, below about 1% calculated upon the carbonaceous material under treatment, or it amounts to a few per cent calculated upon the hydrogenated oil applied. The hydrogen split off appears in part as a gas forming elementary hydrogen, or methane, while another part of this hydrogen in its atomic and therefore very active state combines with the extracts, increasing their combined hydrogen content by a few tenths of one percent. Therefore one cannot ascertain any substantial hydrogenation of the coal under treatment which would afford an addition of an amount of hydrogen to the carbonaceous material between about 10% to 15% calculated upon the carbonaceous material to be hydrogenated. Furthermore, such hydrogenation would require very active catalysts. Whereas a hydrogenation of carbonaceous material, or extracts, results in the formation of benzine, liquid oils, etc., only some pitch-like products are obtained under the conditions referred to, by combining hydrogen in the small amounts mentioned above with the extracts.

In order to render such extractions more economical, the solvents used are to be recovered. The recovered solvents consisting of hydrogenated oils and substantial amounts of their dehydrogenation products, are first to be treated in order to transform said dehydrogenation products again into the desired hydrogenated oils. Taking, for instance, tetraline which has been decomposed in part into naphthalene and hydrogen, the latter having been combined in part with the extracts and escaped in part as a gas, the naphthalene is to be converted into tetraline by addition of hydrogen in well known processes. For this rehydrogenation, however, a separate apparatus was necessary heretofore, and its operation involved substantial costs.

According to this invention, these disadvantages are removed by performing the extraction of coal at elevated pressure by means of hydrogenated oils in the presence of hydrogen under pressure. Thereby it may either occur that hydrogen is prevented from being split off from the hydrogenated oils due to the presence of an adequate amount of uncombined hydrogen in the

same vessel, or, if hydrogen is split off from the solvent and combined in its atomic and therefore very active state with the extracts, such hydrogen is replaced by the free molecular hydrogen introduced to this effect into the vessel and caused to combine with the remains of the dehydrogenated oil. In order to secure such combination of hydrogen with the dehydrogenated solvent media, suitable catalysts may be introduced into the vessel which are capable of assisting this combination while they do not promote a combination between hydrogen and the extracts themselves. A catalyst of such such character is for instance molybdenum dioxide.

Let us take as an example a process of extraction according to our patent mentioned above, treating thereby a gas coal having about 28% of volatile constituents, utilizing a solvent consisting of about 20% phenols and about 80% tetraline. 1 ton of this gas coal mixed with 1.5 tons of these solvent media. The mixture is brought into a vessel which is closed afterwards, whereupon the temperature is raised so as to be close to the decomposition temperatures of the carbonaceous material and its residues which result while the extraction process continues. Thus the temperature may be raised to 330°, 350°, 380°, 400° C. The last temperature mentioned must not be exceeded, and it forms the decomposition temperature of the last solid residues of the original material. If this temperature were surpassed, the residues would decompose, furthermore, the extracts would be coked and would deteriorate. While the yield may amount up to 85%, provided the process described is observed and about 400° C. is not exceeded, it would be materially reduced if such temperature were exceeded.

During this treatment the pressure in the enclosed vessel increases according to the rising temperatures up to about 70 to 80 atmospheres per sq. cm.

In other cases in which another coal is treated up to temperatures of 410 and 415° C. depending upon the decomposition temperature of the last residue, the pressure may rise up to near 100 atmospheres.

The pressures vary, obviously due to decomposition of the solvent media used which depends upon their nature whereby the varying amounts of hydrogen split off assist in raising the pressure which, however, even in extreme cases, does not exceed about 100 atmospheres.

Reverting to the example of treating gas coal with 28% volatile constituents and a solvent media containing about 80% tetraline, we ascertained that at the end of the process approximately 19% of the tetraline present had been dehydrogenated to naphthalene. Heretofore, this naphthalene would have to be rehydrogenated after the solvent medium has been separated from the extracts, and the solid residues. If, however, according to this invention hydrogen were introduced into the vessel in proper amounts sufficing to rehydrogenate the naphthalene when formed during the preceding extraction, dehydrogenation of the solvent media can successfully be prevented. In practice, preferably an excess of hydrogen will be introduced.

Taking the example mentioned above, it has been found that by introducing hydrogen into the vessel not 19% of the tetraline present is decomposed, but only 5% or less. In general, commercially obtainable tetraline already contains naphthalene, up to about 5%. If such tetraline is

used for the purpose of the invention, the content of naphthalene remains constant at about 5%, and is not increased during the continuing extraction process.

This result was particularly achieved if a catalyst of the character mentioned above was used, such as molybdenum dioxide.

The amount of hydrogen consumed in the example given above is relatively low and remains within the limits of about 0.6 to 1% calculated on tetraline. It results therefrom that the hydrogen under pressure introduced in the vessel and present during the extraction, is consumed solely for rehydrogenating naphthalene resulting from decomposition of tetraline during the extraction process, while substantially no hydrogen is combined with the extract produced. As a matter of fact, in the example we have in mind practically no liquid hydrocarbon or oil could be finally ascertained resulting from hydrogenation of any extract. The extract obtained in this case is still solid and of pitch-like character.

However, one may introduce only part of the hydrogen together with the starting mixture while the balance is introduced later on during the process, or one may introduce the hydrogen only later on. For this purpose hydrogen may be compressed and released into the vessel.

If vertically standing high pressure autoclaves are used, part of the hydrogen may be introduced together with the initial mixture of coal and solvent, another part or parts later on at a lower, or middle, or upper point at this autoclave.

Although the pressure in the autoclave is materially increased by the presence of additional hydrogen not derived from decomposition of materials under treatment, the temperatures of treating the original solid material and its residues are not influenced in practice and not substantially changed, particularly not raised.

Although the extract obtained according to our previous invention is ready to react with other ingredients to a very high degree, it does not combine with the hydrogen at the temperatures used for extraction, due to the fact that no suitable catalysts are present. If a catalyst like molybdenum dioxide is used it may be added to the original mixture of coal and solvent media. Its amount is very small and it may pass off with the residues and not be recovered.

One exemplification of the invention may be described with reference to the drawing which shows in a diagrammatical way an apparatus suitable for performing the invention. The solid carbonaceous material, as broken in the mine, or being comminuted to any desired degree, is introduced into the hopper 1, and delivered through a port 2 into a mixer 3. The liquid solvent medium consisting of hydrogenated oils, or hydrogenated oils in mixture with acidic oils such as phenols, or other preferably organic solvents, is introduced into the container 4 and released through valve 5 into the mixer 3.

The relative amounts of carbonaceous material and solvent thus delivered into the mixer 3 may be suitably adjusted so that e. g. the same weight of carbonaceous material and solvent media, or the latter ones in excess, are brought into the mixer 3. The mixture so obtained is then released through a pipe 6 into the autoclave 7 which is a preferably vertical cylindrical vessel of iron or other suitable metal adapted for high pressure operation. The autoclave is heated in any convenient way such as by heated gases introduced into a jacket of the vessel by pipes

29, 30. Hydrogen in a steel bottle 8 is put into a receiver 9 from which the hydrogen is released into the autoclave 7 through pipes 10, 11 and branches 12, 13, 14. It may enter through the valves 15, 16, 17 into any desired part of the autoclave. If the hydrogen in the bottle 8 is not under sufficient pressure, this may be increased by means of a pump 18.

The extracts dissolved in the solvent media are led through pipe 19 into a vessel 20 in which the solution is filtered. Hydrogen and other gases, if developed during extraction, may be released through pipe 21. In the vessel 20 the material is filtered for instance in the manner described in our copending application Ser. No. 14,794, filed April 5, 1935, and the solution so separated from any solid residues of the starting material is delivered into the still 22 in which the solvent media are driven off by suitable heating, while the still liquid or viscous extracts now separated from the solvent media are delivered through pipe 23 into a container 24. Vapors and gases evolved in the still 22 pass through pipe 25 into a condenser 26 which is cooled by any suitable cooling medium in a way not shown in detail, and the so condensed and recovered solvent media are driven off the condenser and forced into pipe 28 by pump 27. The solvent media are returned thereby into container 4.

In this example no hydrogen is added to the mixture of solid material and solvents before entering the vessel 7. In this vessel, however, hydrogen may be added to the mixture at any stage of the procedure and at any point in the vessel. For this purpose, the branches 12, 13, 14 with valves 15, 16, 17 are provided. Furthermore, the pump 18 may furnish any pressure necessary to force hydrogen into the autoclave, even if the pressure in the autoclave is considerably raised during the procedure.

The temperature in the autoclave may be raised stepwise or continuously, preferably so as to keep it close to the decomposition temperatures of the solid material just under treatment. Thereby the pressure is increased either step by step or continuously above about 10 atmospheres per sq. cm., and accordingly the pressure of the hydrogen has to be adjusted when forced into the autoclave during operation. By adding hydrogen to the mixture, the pressure developed with rising temperature is increased above a point resulting in absence of hydrogen. At the end of the treatment when the decomposition temperature of the last solid residues is reached, the pressure will exceed about 80 to 100 atmospheres per sq. cm.

If desired, a catalyst of the character mentioned above, in small amounts, fractions of 1% by weight of the carbonaceous material up to a few percent of it, may be added e. g. in the mixer 3. Generally, it does not pay to recover this catalyst after having been used in the autoclave 7.

The solvent media containing hydrogenated oils recovered in the condenser 26 are suitable to be used again in a subsequent extraction process, and do not need any costly rehydrogenation in a separate apparatus and process.

What we claim is:

1. A method of producing extracts from solid carbonaceous material by means of solvents consisting in the main of tetraline and phenols, at raised temperatures and elevated pressures, whereby part of said solvents is de-hydrogenated, comprising heat treating said material with said solvents in a closed vessel at temperatures kept

close to the decomposition temperature of said material and the solid residues resulting therefrom during extraction, introducing hydrogen delivering gases in a minimum amount of about 1% of said tetraline, introducing molybdenum-dioxide as catalyst, raising the temperature up to the highest decomposition temperature of said residues between about 380 to about 415° C., thereby raising the pressure above about 70 up to below 100 atmospheres per sq. cm. and whereby substantial re-hydrogenation of said dehydrogenated solvents is caused, separating the extracts so obtained from said solid residues and said solvents, and introducing said recovered solvents into a subsequent similar extraction process.

2. In a method of producing extracts from solid carbonaceous fuel material by means of solvent media comprising hydrogenated oils, at raised temperatures and elevated pressures, whereby dehydrogenation of part of said oils occurs, the step of treating said material with said solvent media in the presence of added hydrogen containing gases within a temperature range of about 300° C. to about 415° C. and within a pressure range of about 10 atmospheres to below 100 atmospheres per sq. cm., said hydrogen amounting to about 1 to 5% of said solvent media, thereby dehydrogenating part of said oils and producing extracts slightly hydrogenated by the hydrogen given up by said part but substantially rehydrogenating said part by said added hydrogen.

3. In a method of producing extracts from solid carbonaceous fuel material by means of solvents comprising hydrogenated oils and acid oils, at raised temperatures between about 300° and 415° C. and elevated pressures between 10 to below 100 atmospheres whereby part of said oil is dehydrogenated, the novel step of heat treating said material in the presence of said solvents and added hydrogen containing gases, said hydrogen amounting to about 1% to 5% of said solvents, thereby producing extracts and dehydrogenating part of said oils and producing extracts slightly hydrogenated by the hydrogen given up by said part but substantially rehydrogenating said part by said hydrogen.

4. A method of producing extracts from solid carbonaceous fuel material by means of solvents comprising hydrogenated oils, at raised temperatures and elevated pressures, comprising the steps of heat treating said material in the presence of said solvents in a closed vessel, raising the temperature step by step or continuously so that it remains close to the decomposition temperatures of the original material and solid residues resulting during treatment whereby dehydrogenation of part of said oils and slight hydrogenation of the extract thus obtained by the hydrogen given up by said part occurs, adding hydrogen in an amount sufficient to rehydrogenate oils which have been dehydrogenated in this process, thereby rehydrogenating substantially said dehydrogenated oils, then stopping said heat treatment after the decomposition temperature of the last solid residue is approximately attained, separating said extracts from said residues and solvents, thereby recovering said solvents including said rehydrogenated oils, and introducing said recovered solvents into a subsequent similar process of extraction.

5. A method of producing extracts from solid carbonaceous fuel material by means of solvents comprising hydrogenated oils and acid oils, at

raised temperatures and elevated pressures, comprising the steps of heat treating said material in the presence of said solvents in a closed vessel, raising the temperature step by step or continuously, so that it remains close to the decomposition temperature of the original material and of the solid residues resulting during treatment, whereby dehydrogenation of part of said oils and slight hydrogenation of the extract thus obtained by the hydrogen given up by said part occurs, adding hydrogen in an amount sufficient to rehydrogenate oils which have been dehydrogenated in this process, thereby rehydrogenating substantially said dehydrogenated oils, then stopping said heat treatment after the decomposition temperature of the last solid residue is approximately attained, separating said extracts from said residues and solvents, thereby recovering said solvents including said rehydrogenated oils, and introducing said recovered solvents into a subsequent similar process of extraction.

6. In a method of producing extracts from solid carbonaceous fuel material by means of solvents comprising hydrogenated oils, at raised temperatures up to about 300° to 420° C. and elevated pressures up to about 10 to below 100 atmospheres per sq. cm., whereby dehydrogenation of part of said oils occurs, the step of introducing hydrogen containing gases in amounts sufficient to rehydrogenate substantially any product resulting from dehydrogenation of said solvents during extraction but insufficient for hydrogenating any substantial amount of extracts produced, employing catalysts in an amount suitable to promote said rehydrogenation but insufficient for substantially promoting hydrogenation of said extracts by said introduced hydrogen, thereby slightly hydrogenating the extract thus obtained by the hydrogen given up by said solvents rehydrogenating said products substantially during the same extraction process in which they have been dehydrogenated.

7. In a method of producing extracts from solid carbonaceous fuel material by means of solvents comprising hydrogenated oils and acid oils, at raised temperatures up to about 300° to 420° C. and elevated pressures up to about 10 to 200 atmospheres per sq. cm., whereby dehydrogenation of part of said oils occurs, the step of introducing hydrogen containing gases in amounts sufficient to rehydrogenate substantially any product resulting from dehydrogenation of said solvents during extraction but insufficient for hydrogenating any substantial amount of extracts produced, employing catalysts in an amount suitable to promote said rehydrogenation but insufficient for substantially promoting hydrogenation of said extracts by said introduced hydrogen,

thereby slightly hydrogenating the extract thus obtained by the hydrogen given up by said solvents rehydrogenating substantially said products during the same extraction process in which they have been dehydrogenated.

8. A method of producing extracts from solid carbonaceous fuel material by means of solvents consisting in the main of tetraline and phenols at raised temperatures up to about 300° to 420° C. and elevated pressures of about 10 to below 100 atmospheres per sq. cm. whereby part of said solvents is dehydrogenated, comprising heat treating said material in the presence of said solvents in a closed vessel at rising temperatures kept close to the decomposition temperatures of said material under treatment and the solid residues resulting therefrom during proceeding extraction until the highest decomposition temperature of said residues is reached, whereby dehydrogenation of part of said tetraline occurs, introducing during said extraction hydrogen delivering gases in an amount of about 1% to 5% of said tetraline and employing a catalyst of the class including molybdenum-dioxide, thereby slightly hydrogenating the extract thus obtained by the hydrogen given up by said solvents substantially recovering by rehydrogenation said previously dehydrogenated part of tetraline, and separating the extracts so obtained from said solid residues and said solvents.

9. A method of producing extracts from solid carbonaceous fuel material by means of solvents consisting in the main of tetraline and phenols at raised temperatures up to about 300° to 420° C. and elevated pressures of about 10 to below 100 atmospheres per sq. cm. whereby part of said solvents is dehydrogenated, comprising heat treating said material in the presence of said solvents in a closed vessel at rising temperatures kept close to the decomposition temperatures of said material under treatment and the solid residues resulting therefrom during proceeding extraction until the highest decomposition temperature of said residues is reached, whereby dehydrogenation of part of said tetraline occurs, introducing during said extraction hydrogen delivering gases in an amount of about 1% to 5% of said tetraline and employing a catalyst of the class including molybdenum-dioxide, thereby slightly hydrogenating the extract thus obtained by the hydrogen given up by said solvents substantially recovering by rehydrogenation said previously dehydrogenated part of tetraline, separating the extracts so obtained from said solid residues and said solvents, and introducing said solvents including said recovered tetraline into a subsequent similar extraction process.

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