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METHOD OF PRODUCING EXTRACTS FROM SOLID CARBONACEOUS MATERIALS

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Fig. 1

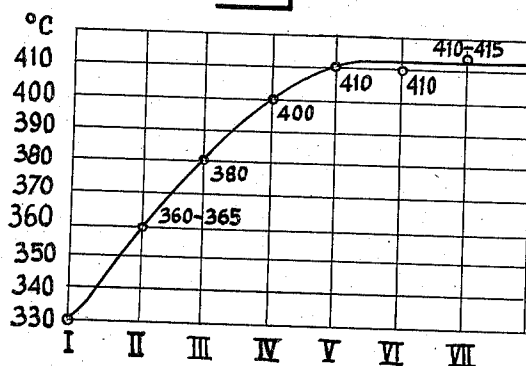


Fig. 2

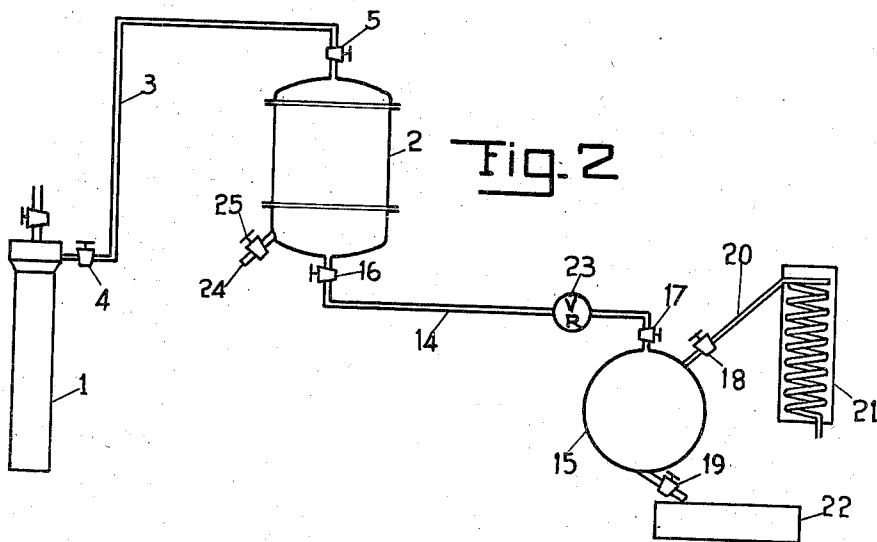


Fig. 3

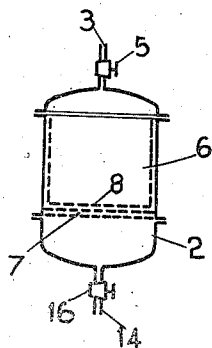
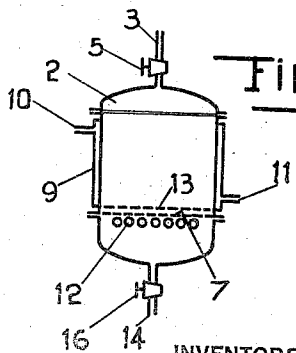


Fig. 4



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METHOD OF PRODUCING EXTRACTS FROM
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2 Claims. (Cl. 196—14)

This invention refers to a method of producing extracts from solid carbonizable fuel material such as coal, lignite, or peat. Such extracts are usually made by treating the material with suitable solvent media at elevated temperature and, advantageously, raised pressure.

Various methods have been suggested to this effect. Among others, the inventors themselves suggested a method of producing extracts which resulted in surprisingly high yields of extracts. This method has been based on the following observation. If e. g. coal is treated in an autoclave with suitable solvent media such as a mixture of lower and higher boiling organic oils, thereby gradually raising the temperature and observing the simultaneously rising pressure by means of an indicator then at a certain temperature a sudden increase of the pressure is observed. This sudden increase is due to the fact that a decomposition of the material under treatment takes place whereby gases are evolved. If therefore during a subsequent treatment of material of the same kind with the same solvent media the temperature is kept a few degrees centigrade below decomposition temperature established by that previous experiment, a certain yield of extracts can be obtained. However, no matter how long such treatment at this temperature might be extended or how often it might be repeated, the yield of extracts does not materially increase. Thus the inventors established by their previous investigations that after having obtained a first yield of extracts in the way described, the temperature of treatment might be elevated without causing decomposition, i. e. evolving material amounts of gases indicated by suddenly increasing pressure. According to the observation of the inventors, this phenomenon is due to the fact that by the first treatment all the constituents capable of decomposition at the first established temperature are extracted from the carbonizable material and dissolved by the solvent media which protect the extracts against further decomposition, and a balance of solid carbonizable material remains the constituents of which cannot decompose at this temperature. If, however, the temperature is gradually being raised more and more above the first temperature at which decomposition occurred, a certain higher temperature will be reached at which a new decomposition occurs indicated by a sudden rise of pressure. Therefore, the second extraction of the solid carbonizable material which remained after the first treatment has to be made at a temperature higher than previously used but

by a few degrees centigrade lower than the second and higher temperature of decomposition established in the way described. Surprisingly, in this second stage a further substantial yield of extracts can be obtained in addition to that which resulted in the first treatment at a temperature below the first decomposition temperature of the material. In continuing this procedure, one may cautiously raise the temperature more and more, thereby obtaining additional yields of extracts until a temperature is reached at which the last yields of extracts are achieved and no additional amounts of extracts are obtainable, neither by repeating nor by extending the heat treatment at the last and highest temperature, nor by further raising this temperature. In the last case neither decomposition can be observed (no sudden increase of pressure occurring any more) nor do additional extracts result. This last temperature depends on the constitution of the carbonizable material under treatment, and this and all the foregoing temperatures of treatment being close to, but below decomposition temperatures of the carbonizable material under treatment are to be established in the simple way described hereinbefore for every individual material.

The inventors further established that the treatment may also be performed at about the individual decomposition temperatures themselves if only a small amount of gases is evolved thereby, i. e. the decomposition of a small part of the constituents does not matter.

This proves that according to this previous suggestion of the inventors the extraction may be effected at elevated temperatures which are stepwise or gradually raised in such a way that they are close to the decomposition temperatures of the solid carbonizable material under treatment and increased with increasing amounts of extracts extracted from the material and dissolved by the solvent media used. The pressure under which the treatment is to be performed is usually the natural pressure at the temperature applied because the treatment is performed in a closed vessel (autoclave). Additional pressure may be used without deviating from the spirit of this suggestion.

As solvent media the inventors used among others a mixture of 40 parts naphthalene, 40 parts tetraline and 20 parts of a tar phenol, boiling at about 230° C. under normal pressure. They furthermore used a mixture of tetraline and phenol in a ratio of for instance 1:1. But any other solvent media, especially oils, and mixtures

of them, may be used such as hydrogenated and/or acidic oils, for instance anthracene oil alone or in admixture with phenol, i. e. an acidic oil or other oils, such as tetraline, i. e. hydrogenated oil, or benzole.

In the drawing, Fig. 1, a diagram is shown for the treatment of a long flaming coal with a solvent medium consisting of 40 parts naphthalene, 40 parts tetraline and 20 parts tar phenol obtained by distillation of coal between 180° to 230° C. The long flaming coal has been powdered or suitably broken up and then mixed with the solvent medium. The amount of solvent medium applied depends upon its nature and that of the carbonizable material to be extracted. Thus, for instance, the weight of the solvent medium applied may be equal to that of the carbonizable material, or it may be lower or it may exceed it.

The coal and the solvent are deposited in an autoclave provided with a stirring device and treated therein for about three to four hours. It has been established by special experiments made with this coal that a first decomposition occurs at 330° C. The constituents decomposing at about this temperature having been extracted, the remaining solid carbonizable material decomposes a second time at 360° C. whereupon, after additional extracts have been obtained at this second temperature range, a third, fourth and fifth decomposition temperature occur at about 380°, 400° and 410° C. Therefore, as the diagram shows, the coal has been heated up to about 330° C., and the first extracts obtained which may remain in the solvent medium or may be removed from it. Thereupon the temperature has been gradually increased up to 410° to 415° C., and a second, third, fourth and fifth extract have been obtained at about 360°, 380°, 400° and 410° to 415° C., respectively. There is no use to further raise the temperature or to repeat the treatment at about 410° C. because, as shown in the diagram, no additional extracts could be obtained at a sixth and seventh extraction.

The pressure in the autoclave has been ultimately raised up to about 70 to 90 atmospheres. Because of this rising temperature no disintegration of the solvent medium took place in spite of the fact that the temperature has been actually raised substantially above the boiling temperature under normal atmospheric pressure of some parts of the solvent medium. By the first extraction about 37% extract, calculated upon the weight of the original, not disintegrated coal material, has been obtained. By the second extraction additional 8% have been obtained, and by the further extractions additional yields resulted so that the entire yield of extracts amounted to about 74%. The remaining solid material consisted of coal and ash not capable of disintegration. As a matter of fact, depending upon the nature of the coal under treatment, yields up to 94% may be obtained in this way.

The extracts obtained are highly active and easily to be converted into any other desired useful product. So, for instance, they can be easily and fully hydrogenated and transformed thereby into benzine and other valuable and particularly lower boiling liquid fuel, or into higher boiling, particularly lubricating oils etc.

Now, the inventors faced a difficulty in separating the extracts dissolved in the solvent media from the not disintegrated remainders. The extracts being solid at normal temperature up to over about 200° C., coal extracts up to about 230°

to 250° C., it is to be expected that a separation can conveniently be effected by gradually cooling the solvent media containing the extracts. But the inventors established that inevitably some ash and other not disintegrated parts of the original carbonizable material remain in the extracts in a small amount and, usually, in a very high degree of fine dispersion. It is desirable, however, for many uses to obtain absolutely pure carbon material as extract which is free from ash and any other not extracted particles of the original carbonizable material. The separation of these undesired substances from the extracts is difficult, however, because of their extremely fine dispersion and small size. It has been tried to separate these undesired materials by centrifugation or filtration. By centrifugation, however, no separation of such extremely fine particles from an oily solution can be effected. If normal filtration is applied, the paper, fabric or cake used for filtration at normal or moderately elevated temperature will be obstructed very quickly whereby the filtration is stopped and new filters have to be inserted. No better results have been obtained by diluting the solution with additional solvent media so that the amount of the latter ones materially exceeds that of the extracts dissolved therein. If, however, the solution is simply allowed to stand so that the heavier solid particles dispersed in the solvent may settle, no complete separation could be obtained because of the extremely fine dispersion of the particles.

According to the invention, the extracts still dissolved in the solvent medium as previously used for extraction, or concentrated or diluted, are filtered under raised pressure and at highly elevated temperature. Surprisingly, practically pure extracts are thereby obtained, the content of undesirable solid particles being substantially below 1% and amounting, as a great number of experiments have proven, only to a few tenths of one per cent, to as low as one tenth of one per cent.

For this filtration any suitable filter, and filter material, may be used. It has been proven advantageous to use as such filter material the solid remainders of the carbonizable material after completion of the extraction. In other words, the part of the original material which is not capable of disintegration by extraction and which remains therefore not disintegrated after completion of the process, is most suitable as filter material for the extracts.

In the drawings, an apparatus adapted to perform the method according to the invention is shown in a merely diagrammatic way. Fig. 2 shows the entire apparatus, Figs. 3 and 4 different structures of the part of the apparatus adapted to perform the filtration forming the subject matter of this invention.

In Fig. 2, 1 is the closed vessel (autoclave) in which the mixture of carbonizable material and the selected solvent media are introduced. The material is being heated in the autoclave 1, and after completion of the extraction in the way explained hereinbefore particularly with reference to Fig. 1, the solution comprising the solvent media and extracts is transferred in any suitable way to the filter device 2. The tube connection 3 in Fig. 2 may, or may not exist. In the first case, suitable valves are to be inserted at the points 4 and 5, respectively. In the second case, the solution may be transferred in any other suitable way from the autoclave 1 into the filter vessel 2.

The filter vessel is resistant against high pressure and contains, as shown in Fig. 3, an exchangeable wire basket 6. Another net of wire 7 is inserted in the vessel 2, spaced from and below the bottom 8 of the basket 6. Between the nets 7 and 8 filter material is inserted such as a cake consisting of the not disintegrated remainder of the carbonizable material from a previous extraction, as described above. In such case, the width of the meshes of the nets may amount to between about 0.1 to 2 millimeters. If using other filter material, the width of the meshes may be chosen smaller or larger as the case may be. The meshes may be slightly larger than the particles of which the filter cake consists.

Reverting to Fig. 2, if the solution comprising the solvent medium and extracts is transferred into the vessel 2, suitable pressure and heat are to be applied. If the solution is still hot from the treatment in the vessel 1 usually no additional heating is necessary. If, however, the solution has cooled off, additional heat may be applied. In the same way, if the solution is transferred from the autoclave 1 through the pipe 3 into the vessel 2, the pressure which existed at the last stage of the extraction in the vessel 1 at the highest temperature produced, may be sufficient to perform the filtration in the vessel 2. If in such a way the solution is transferred from the vessel 1 into the vessel 2, the pressure will decrease corresponding to the increased space now being offered to the vapors developing from the solution. This space consisted at first only of the vapor room of the vessel 1 while it consists during the transfer of the solution into vessel 2 of the vapor room of the latter and of the vessel 1. But such reduced pressure will usually be sufficient. If, however, the solution is transferred in another way from vessel 1 into vessel 2, and if the solution is cooled by this transfer, the application of additional pressure in the vessel 2 might sometimes be advisable. That can easily be done by establishing a connection between the top of the vessel 2, for instance at 5, with a boiler in which a certain amount of the solvent medium is heated up to such a degree that the vapors evolved have the desired pressure which is then exerted upon the level of the solution contained in vessel 2.

The vessel 2 may be made of any suitable material and coated inside or outside with a heat insulating material. Such material may be arranged between the walls of the basket 6 and the side walls of the vessel 2. Or, as shown in Fig. 4, the walls of the vessel 2 may be covered on the outside with a jacket 9, and any suitable heating means such as steam or heated water, may be led through the jacket. Connecting pipes are shown at 10 and 11, respectively. The jacket may serve either as a heat insulating means or to positively convey additional heat into the solution within the vessel 2. If internal heating is desired, heating pipes 12 may be inserted into the vessel 2. In Fig. 4, two net works 13 and 14 are shown between which the filter material may be inserted.

Average temperatures suitable for the process according to the invention are 150° to 170° C. But it is to be understood that the temperatures are to be chosen higher or lower according to the constitution and physical properties, particularly viscosity, of the solvent medium and the extracts. As the lowest limit, a temperature range of about 75° to 100° C. may be given. The pressure may as a rule be chosen above about five

atmospheres per square centimeter, and very good results have been obtained within the range of 10 to 20 atmospheres.

If the filter cake contains the not disintegrated remainders of the carbonizable material previously disintegrated in vessel 1, it may be mixed with other filter materials producing the desired more or less porous structure of the cake, such as suitably powdered coke, pumice-stone, or coal.

After the filtration, the filtered solution may be led through a pipe 14 into a still 15 which may be heated in any suitable way not shown in Fig. 2, in order to separate the extracts from the solvent media. The latter are distilled off at suitable and carefully chosen and adjusted temperatures, while the extracts remain in the still. To this effect, at 16, 17, 18, 19 suitable valves are to be provided. The valves 16, 17 may be open during filtration of the material in the vessel 2, while the valves 18, 19 are closed, so that the filtered solution may continuously flow through the pipe 14 into the still 15. If distillation has to be done, the valves 16, 17, or at least 17 are to be closed while valve 18 has to be opened so that the solvent medium distilled off by heating the still 15 and applying vacuum may pass the pipe 20 and the cooler 21 in which it is condensed and may then flow into any desired container (not shown). Then, the valve 19 may be opened, and the extracts now entirely separated from the solvent media and freed to the highest desirable extent from solid particles are delivered into the container 22. During filtration it might be advisable to close the valve at 16 to avoid the expansion of vapors into the pipe 14 and, if valve 17 would be open, into the still 15, whereby under certain circumstances the pressure may be undesirably lowered. If a very large vessel 1 in comparison with the vessel 2 has been used, however, such addition of space by that of still 15 may be desirable in order to obtain a pressure in the vessel 2 in the range of, for instance, 10 to 20 atmospheres, while the pressure in the vessel 1 during extraction may have been about 70 to 90 atmospheres. In such a case, the pipe 14 and still 15 are to be made to resist such high pressure. Otherwise, a pressure reduction valve may be inserted into pipe 14 at any desired place, such as 23.

The filter material is disposed between two nets 7, 8, and 7, 13, respectively, to secure a certain thickness of the material which has to be suitably established for different solutions. As a result of filtration, the particles dispersed in the solution are withheld by the filter material and accumulate during operation above the filter cake. It is desirable to remove from time to time such excess material accumulating above the filter cake. To this effect, the vessel 2, Fig. 3, may either be opened at the top, and the basket 6 with the material accumulated therein be removed and a new and empty one inserted. Or, by disposing the filter as low as possible within the vessel 2, an outlet 24 may be arranged through which, after opening a suitable valve arranged at 25, any excess particles accumulated above the net 13 may be drained off. Both, the material drained off and the filter material may then be washed with a suitable solvent medium, such as the one used for extraction, in order to recover any amount of soluble pure coal material retained by the filter material or contained in the mass drained off. Thus extremely high efficiency of the process can be secured. The solvent medium used for these washing purposes may

then be recovered by distillation or coking of the filter material, and of the remainders drained off, and lastly of the remainders of the original carbonizable material treated within, and after completed disintegration taken off the vessel 1. Instead of, or in addition to, distillation and coking, a washing with low boiling materials like benzole may be applied, and the benzole then driven off and recovered.

10 The extracts so obtained are of pure carbon material of high activity, ready for immediate use or to be subjected to further treatment, such as hydrogenation. They are much more valuable since they have a degree of purity unknown up to 15 now, due to the special method of filtration proposed by the inventors. The surprising results obtainable with materials of highest purity are well known.

It is to be understood that the new method of 20 filtration according to this invention may be used for purifying any extracts of carbon material and extracts obtained with any suitable process, and the invention therefore is not limited to the application upon extracts obtained with surprisingly large yields according to the previous suggestions of the same inventors.

In the appended claims, the term "extract" comprises both the extract separated more or less from the solvent medium and the extract still 30 dissolved in the solvent which, in some cases, may be concentrated or diluted before filtering. Furthermore, the term "solvent" comprises both a single solvent medium or any suitable mixture of solvent media.

35 What we claim is:

1. In a method of producing extracts from solid carbonizable fuel material by treating it with solvent media comprising organic solvents boiling under normal pressure above about 100° C., said

treatment performed at elevated temperatures between about 330° C. and 415° C.—the step of separating the extracts still dissolved in solvent media of said type from undissolved solid residues of said material, such as ashes, by filtering under 5 excess pressure on one side of the filter within the pressure range of about 5 to 20 atmospheres per square centimetre and within the temperature range of about 75° C. to 170° C., until the content of said undissolved solid residues has de- 10 creased substantially below 1%.

2. A method of producing extracts containing substantially less than 1% solid residues, such as ashes, from coal material by extracting said material with organic solvents boiling above about 15 100° C., at normal pressure and subsequently separating the dissolved extracts from insoluble solid residues of said coal material, said extraction and separation being performed at raised temperatures and pressures, comprising the following 20 steps: (a) treating solid coal material with said organic solvents at temperatures raised up to about 400° C. to 415° C. and under pressures rising with said temperatures up to about 70 to 90 atmospheres per square centimetre, said tempera- 25 tures held close to the decomposition temperatures of said material and its residues under treatment, thereby obtaining substantial yields of extracts; (b) separating said extracts by filtering from said solid undissolved residues within a tem- 30 perature range of about 75° C. to 170° C. and a pressure range of about 5 to 20 atmospheres per square centimetre; (c) and performing the steps (a) and (b) in closed space by lowering the temperatures and pressures finally reached in 35 step (a) to those of step (b).

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