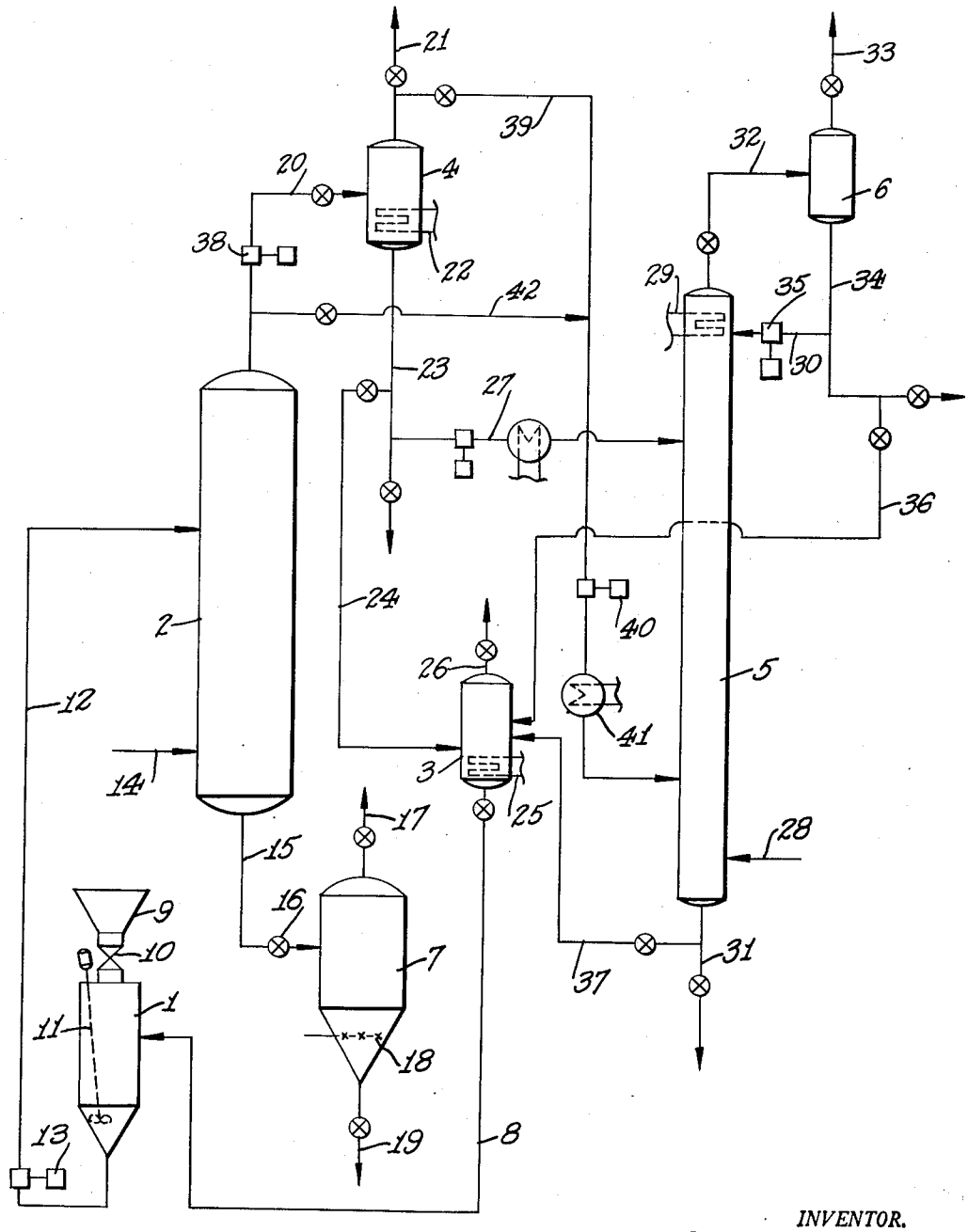
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EXTRACTION OF OLEIFEROUS MATERIALS

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EXTRACTION OF OLEIFEROUS MATERIALS

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This invention relates to an improved method for recovering fatty materials, and similar high molecular weight materials, from the solid materials with which they are normally associated in nature. Such solid materials are referred to hereinafter as "oleiferous solid materials." Such oleiferous materials include various oil-bearing beans, seeds and nuts designated generally as oil seeds, and including soybeans, cottonseed, linseed, peanuts, palm nuts and cocoanuts. Other oil-bearing solid materials of animal, vegetable and marine origin also are included within the term oleiferous solid materials, such as animal tissue, including fish livers, vegetable fibers, nut shells, etc.

The invention relates particularly to extraction processes employing solvents whose boiling points are lower than the preferred temperature of extraction. In particular the invention relates to an improvement in the process of extracting oleiferous materials with relatively low-boiling solvents. Such solvents may be defined as those whose critical temperature is not substantially higher than 450° F. and preferably are lower than 325° F. Of these, the solvents which are normally gaseous are preferred because of the relative ease with which they may be separated from the oil and the residual solid material.

The low-boiling hydrocarbons represent a desirable class of solvents because of their relative inertness and low cost. While the low-boiling olefin hydrocarbons may be employed they are less desirable than the low-boiling paraffins such as ethane, propane, the butanes, the pentanes and the hexanes, from the point of view of inertness. Of the paraffins, propane is preferred ordinarily because of the high degree of solubility of the oils in that solvent and its relatively low critical temperature which permits operating in a temperature range not injurious to the oils. However, ethane or the butanes can be employed to almost as great advantage. While relatively pure hydrocarbons are preferred mixtures of them may be employed. For example, mixtures of ethane and propane or mixtures of butane and methane may be employed in the proportions suitable to form solvents having the desired properties. While the normally gaseous hydrocarbons are particularly advantageous for use as solvents in the improved method other solvents having relatively low critical temperatures may be employed, such as ammonia, dichlordifluor methane, dimethyl ether, methyl fluoride and halogenated hydrocarbons in general.

The use of such relatively low-boiling solvents requires maintaining the extraction zone under

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a substantial superatmospheric pressure to prevent vaporization of the solvent, and when relatively high temperatures are employed this may involve an operating pressure in the extraction zone of 500 to 1000 pounds per square inch. In accordance with the improved method of this invention oleiferous solid materials, to be subjected to the extraction treatment in an extraction zone which is maintained under substantial superatmospheric pressure, are first mixed, in a finely divided condition, with oil previously extracted from similar solid oleiferous material, to form a slurry of the oil and the solid. The slurry is then pumped into the extraction zone against the pressure thereof and into contact with the solvent. The oil employed for forming the slurry may constitute a portion of the whole oil previously extracted from similar solid material or the slurry oil may consist of a fraction of such previously extracted oil. The slurry is formed by mixing the oil and solids at relatively low pressure, for example atmospheric pressure, and the resulting slurry is then easily transferred by means of a pump to the zone of higher pressure without danger of escape of solvent from the extraction zone or the introduction of gaseous oxygen from the atmosphere into the extraction zone.

The invention will be described further, and in more detail, by reference to various specific modifications which are illustrated in the accompanying drawing, which is a schematic representation of apparatus suitable for carrying out such modifications. In the further description of the invention propane will be referred to as the solvent, but it is to be understood that the principles of operation are the same in the use of any of the preferred solvents mentioned above, the operating conditions being changed only in accordance with the character of the oil to be extracted and the physical properties of the solvent.

Referring to the drawing, the principal pieces of equipment represented are a slurry tank 1, an extractor 2, a propane stripper 3, a separator 4, a fractionating tower 5, and a separator 6. The slurry of oil and oleiferous solid material is formed in tank 1 and subjected to extraction treatment in extractor 2. The extracted solids are treated for the recovery of propane in separator 7, and slurry oil is recovered as a lower phase in separator 4, tower 5 or separator 6, and prepared for use by the evaporation of residual propane in stripper 3.

The slurry oil is transferred from stripper 3 through line 8 to slurry tank 1. Finely divided

oleiferous material, such as ground oil seeds, is introduced into slurry tank 1 from hopper 9 through valve 10. Valve 10 may be of any suitable construction but conveniently is a star feeder arranged for continuously introducing measured quantities of oleiferous solids into tank 1. The slurry is formed and maintained by suitable stirring means 11.

The slurry is continuously pumped through line 12 into an intermediate point of extractor 2. Pump 13 is provided in line 12 for transferring the slurry from the substantially atmospheric pressure of slurry tank 1 to the superatmospheric pressure of extractor 2.

Liquefied propane is introduced continuously into the lower part of extractor 2 through line 14. Extractor 2 preferably is somewhat elongated vertically whereby the solid material introduced through line 12 is permitted to settle through an upflowing stream of propane over a substantially long path of contact in order to effect the maximum desired extraction of oil from the oleiferous solids. A substantial space is provided in extractor 2 above line 12 to permit maximum settling of solids out of the stream of propane.

Extractor 2 ordinarily is maintained at the temperature of maximum solubility of the oil in the propane in order to provide efficient extraction. This may vary from about room temperature to 160° F. Consequently the pressure imposed on extractor 2 may vary from about 50 pounds per square inch to about 700 pounds per square inch. The propane may be charged to extractor 2 at a rate equivalent to a ratio of 3 to 10 or more volumes of liquid propane per volume of the oil to be extracted and the slurry oil introduced through line 12 into extractor 2.

The unextracted solid material is withdrawn from the bottom of extractor 2 through line 15 which connects with separator 7, as a slurry of propane and solids. Pressure is reduced substantially at 16 whereby the propane is substantially completely evaporated and withdrawn from separator 7 through line 17. To assist evaporation heat may be introduced into separator 7 at 18. To further assist vaporization steam may be injected at 18. The relatively dry solid material, such as seed meal, is withdrawn from the bottom of separator 7 through line 19 by any suitable means, such as a star feeder.

The extract solution is withdrawn from the top of extractor 2 through line 20 which connects with separator 4. In accordance with one modification of the invention the extract solution is subjected to reduced pressure in separator 4 to effect evaporation of propane, which is withdrawn for reuse through line 21. To assist evaporation heat may be applied to the solution in separator 4, as by heating means 22. The extract oil is withdrawn from the bottom of separator 4 through line 23. A portion of the extract oil flowing through line 23 is diverted through line 24 which connects with stripper 3. In stripper 3 the extract oil is subjected to suitable treatment, as by heat applied through means 25, to vaporize residual propane, which is removed through line 26. The slurry oil thus formed is transferred from stripper 3 through line 8 to slurry tank 1, as described.

Any suitable ratio of slurry oil to solids may be employed in forming the slurry, it being understood that it is preferred to employ the smallest ratio necessary to form a pumpable slurry. The minimum ratio necessary will be affected by the character of the oil and solid and the quantity of oil in the solid, but a weight ratio of oil to solid of at least 1:1 ordinarily is necessary. This refers to solids prepared in the usual manner for extraction by adjusting the moisture content to the optimum level for solvent extraction.

Extract oil withdrawn from separator 4 through line 23 may be transferred, through line 27, to an intermediate point in a fractionating tower 5 in which the oil is subjected to suitable fractionation treatment by countercurrent contact of the oil with an upflowing stream of additional liquid propane, which is introduced into the lower part of tower 5 through line 28. Tower 5 is operated at a temperature, set by the temperature of the propane introduced through line 28, in the temperature range in which solubility of the oil in the propane decreases with rising temperature. This range extends from a few degrees above the critical temperature to approximately 100° F. below the critical temperature. For propane the usual operating temperature range for tower 5 is from about 150° F. to 210° F. although slightly higher or lower temperatures may be employed under certain circumstances. In tower 5 the extract oil from line 27 is subjected to countercurrent extraction as the oil flows downwardly as a heavy liquid phase in contact with the upflowing propane or extract phase. The extract is subjected to rectification treatment in tower 5 above line 27 by heating the extract to a higher temperature, by heating means 29, or by refluxing the tower with extract from line 30, or by both means.

By suitable control of temperature conditions in tower 5 the extract oil may be closely fractionated ,and distributed between the extract and the raffinate in any desired manner. The fraction recovered in the extract phase is composed of constituents having a relatively low molecular weight, whereas the raffinate is composed of constituents having a relatively high molecular weight. The raffinate is withdrawn from the bottom of tower 5 through line 31 and the extract phase is withdrawn overhead through line 32. Line 32 connects with separator 6 in which the pressure on the extract phase is substantially reduced to permit evaporation of propane which is withdrawn overhead for reuse through line 33. Heat may be applied in separator 6 to assist vaporization. The extract oil fraction thus recovered in separator 6 is withdrawn therefrom through line 34. A portion of this extract oil may be employed to reflux tower 5 and for this purpose line 30, provided with a pump 35, connects line 34 with the upper part of tower 5. Tower 5 is substantially elongated vertically and is suitably provided with contact means to assist in effecting intimate contact of the counter-flowing liquid phases.

In accordance with another modification of the invention the slurry oil is provided by diverting a portion of the relatively low molecular weight extract oil fraction from line 34. For this purpose line 36 is provided to connect line 34 with stripper 3. In this modification line 24 is not employed, and the oil introduced into stripper 3 through line 36 is treated in the manner previously described to provide the slurry oil for passage through line 8. This modification is advantageous in that the quantity of oil necessary to form a slurry is reduced and the burden placed on the extractor 2 by the slurry oil is minimized since the relatively low molecular weight extract

oil fraction is relatively more soluble in the propane solvent.

In accordance with another modification of the invention raffinate from line 31 may be employed as a source of the slurry oil. For this purpose line 37 is provided to connect line 31 with stripper 3.

In accordance with another modification of the invention the extract solution emerging from extractor 2 through line 20 may be treated without vaporization of propane to separate a fraction of the oil content thereof for use as slurry oil. In this modification the extract solution is heated in line 20, or in separator 4, to a temperature above the temperature of maximum solubility of the oil in the propane to precipitate a separate oil phase, while maintaining the extract solution under a pressure effective to prevent substantial vaporization of the propane. The extract solution is heated to a temperature, ordinarily within the range of 140° to 180° F., to precipitate a portion of the oil sufficient in volume to provide the required amount of slurry oil. A pump 38 is provided in line 20 to introduce the extract solution in separator 4 against the high pressure necessary in this modification. The heating of the extract solution according to this modification lowers the solubility of the oil in the propane and causes a portion of the oil to precipitate and form a separate, lower, liquid phase. The lower phase includes some propane but in a propane: oil ratio much lower than the corresponding ratio in the extract solution.

The lower phase material is transferred from separator 4 through lines 23 and 24 to propane stripper 3, while the upper liquid phase is withdrawn from separator 4 for futher treatment in any suitable manner. For example, the oil content of the upper phase from separator 4 may be separated from the propane in separate separation means similar to separator 4 and the oil thus obtained passed to fractionating tower 5 for further treatment in a manner similar to the first-described modification of the process of the invention.

Alternatively, the extract solution may be heated in separator 4 to a temperature sufficiently high to precipitate all, or substantially all, of the oil contained in the extract solution. In this operation the resulting upper phase contains nearly all of the propane and at most a relatively small amount of the oil, while the lower phase contains most of the oil and a small amount of the propane. In accordance with this modification a portion of the lower phase may be passed to stripper 3 to produce slurry oil, in the manner described, while the remainder is passed through line 27 to an intermediate point of tower 5. The upper phase liquid, consisting of propane, is passed from separator 4 through lines 21 and 39 to a relatively low point of tower 5. If necessary, a pump 40 is provided in line 39. Cooling or heating means are provided in line 39 at 41 to adjust the temperature of the propane phase to the operating level desired in tower 5. By this method the lower phase material from separator 4 is subjected to stripping in tower 5 by the propane phase from line 39. Additional propane is introduced as necessary through line 28 to assist in the stripping action.

In accordance with a further modification of the invention the extract solution emerging from extractor 2 through line 20, or the upper phase material emerging from separator 4 after the precipitation of a part of the oil to obtain a slurry oil, is transferred directly to tower 5 for rectification and fractionation. This operation is carried out in the absence of any material introduced into tower 5 through line 27. If the extract solution is first heated in separator 4 to obtain a slurry oil precipitate, the remaining extract solution is passed through lines 21 and 39 to tower 5 in the manner described. For transferring the extract solution directly from line 20 to tower 5, line 42 is provided to connect line 20 with line 39. The extract solution is thus passed from a low point in tower 5 upwardly through the tower in countercurrent contact with a downwardly flowing oil phase produced in the tower by imposing a higher temperature on the top of the tower, as by heating means 29, and by refluxing the tower with extract from line 36. The extract solution is thus subjected to rectification and fractionation with the formation of separate fractions which are recovered at 34 and 31. The lower liquid phase flows downwardly through tower 5 and may be subjected to final stripping by means of propane from line 28.

Slurry oil from separator 4, tower 5 or separator 6 may be obtained in connection with any of the foregoing modifications of the invention. When the slurry oil is obtained by heating the extract solution to a high temperature under pressure in separator 4 the finely divided solid material which is inevitably suspended in the liquid stream flowing out of the extractor 2 through line 20 is occluded in the droplets of lower phase liquid precipitated in separator 4. By this means the fines from the extractor are separated from the extract oil without filtration. This likewise applies to the operation of tower 5 to obtain a raffinate which is to be used as the slurry oil.

I claim:

1. A method for treating oleiferous solid materials with solvent in an extraction zone to obtain an oil extract from said solid material which comprises introducing into the extraction zone a solvent whose boiling point is lower than the temperature of extraction, maintaining said extraction zone at the extraction temperature and under a superatmospheric pressure effective to maintain the solvent in liquid condition, mixing said solid material in a finely divided condition at a point external of said extraction zone with a slurry oil comprised of components of said oil extract to form a slurry, pumping said slurry into said extraction zone against the pressure thereof and into contact with said solvent, withdrawing an extract solution containing said oil extract from said extraction zone, separating from said extract solution at least a fraction of said extract oil, and recycling said extract oil to said slurry-forming step to serve therein as said slurry oil.

2. The method of claim 1 in which a normally gaseous solvent is employed.

3. The method of claim 1 in which a normally gaseous hydrocarbon solvent is employed.

4. A method for treating a charge material comprised of naturally occurring non-fatty solvents containing intimately associated fatty material with solvent in an extraction zone to obtain an oil extract from said solid material which comprises introducing a normally gaseous solvent into said extraction zone, maintaining said extraction zone under superatmospheric pressure effective to maintain the solvent in liquid condition, mixing said solid material in a finely divided condition at a point external to said extraction zone with a slurrry oil comprised of components

of said oil extract to form a slurry, pumping said slurry into said extraction zone against the pressure thereof and into contact with said solvent, separating an extract solution containing said oil extract from said solid material, fractionating said oil in the presence of said normally gaseous solvent to separate the oil into a plurality of fractions, and recycling at least a portion of a fraction thus obtained to said slurry-forming step for admixture with more of said charge material to form a slurry, in the manner described.

5. In the extraction of an oil extract from a charge material comprised of naturally occurring non-fatty solids containing intimately associated fatty material by treatment with a normally gaseous solvent, the improved method which includes the steps of: reducing said charge material to a finely divided condition and forming a pumpable slurry by mixing said finely divided charge material with at least an equal amount of slurry oil comprised of components of said oil extract; pumping said slurry into an extraction zone under a pressure sufficiently high to maintain said solvent in a liquid condition; contacting said slurry with said solvent in said extraction zone to dissolve said oil extract in an extract solution including some suspended fines; withdrawing said extract solution from said extraction zone and increasing the temperature of said solution to a temperature in the range of temperatures near the critical temperature of the solvent in which solubility decreases as temperature increases, said temperature being sufficiently high in said range to precipitate a relatively heavy lower phase fraction occluding suspended fines; withdrawing said lower phase fraction together with suspended fines and stripping solvent therefrom; and recycling said stripped fraction to said slurry-forming step to be used therein as said slurry oil and to return fines which had been suspended in the extract solution to said extraction zone.

6. In the paracritical fractionation of an oil extract from a charge material comprised of naturally occurring non-fatty solids containing intimately associated fatty material by treatment with a normally gaseous solvent, the improved method which includes the steps of: reducing said charge material to a finely divided condition and forming a pumpable slurry by mixing said finely divided charge material with at least an equal amount of slurry oil comprised of components of said oil extract; pumping said slurry into an extraction zone under a pressure sufficiently high to maintain said solvent in a liquid condition; contacting said slurry with said solvent in said extraction zone to dissolve said oil extract in an extract solution; withdrawing said extraction solution from said extraction zone and paracritically fractionating said extract solution with said solvent at temperatures in the range of temperatures near the critical temperature of the solvent in which solubility decreases as temperature increases; withdrawing one of said fractions and stripping solvent therefrom; and recycling said stripped fraction to said slurry-forming step to be used therein as said slurry oil.

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