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RECOVERY OF ALIPHATIC ACIDS FROM BLACK LIQUOR

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This invention relates to a process of extracting certain aliphatic acids from the black liquor which results from neutral or alkaline pulping of wood.

Black liquor obtained from the pulping of wood by alkaline or neutral liquors contains large quantities of low molecular weight aliphatic acid salts. The type of salt is dependent on the type of liquor used in the pulping of wood. Kraft black liquor, for example, contains the aliphatic acid salts as the sodium salts. Other types of black liquors may contain ammonium, potassium, calcium, or magnesium salts of aliphatic acids.

The aliphatic acid salts are primarily composed of a salt of acetic acid with a smaller amount of a salt of formic acid, and it is with the extraction of acetic and formic acids that the invention is chiefly concerned. Also present are salts of propionic acid. Throughout the present specification and claims the term "aliphatic acids" will be used to designate a mixture of two or more of the above acids. The quantities of the various aliphatic acid salts in a black liquor are largely dependent on the type of wood pulped. Propionic acid salts will be present in substantial quantities in black liquors resulting from the pulping of some types of wood, but in small quantities or not at all in black liquors from the pulping of other types of wood. Acetic acid and formic acid salts, however, have been found to be present in substantial quantities in black liquors from the pulping of all types of woods.

Although the aliphatic acids have great utility, e.g. formic acid as an assistant in the dyeing and finishing of textiles, acetic acid in the manufacture of rayons and plastics, and propionic acid in the manufacture of plastics, at the present time these aliphatic acids are generally being burned or wasted to the sewer for want of an economical method of recovering them from black liquor.

Difficulties are encountered in the recovery of the aliphatic acids from black liquor because of the presence therein of large quantities of inorganic and organic materials.

In liquid extraction processes the generally used solvents for the separating of aliphatic acids from aqueous solutions are unsuitable because of the formation of emulsions, the carry over of inorganic materials in the extract, the difficulty of removing these inorganic materials, the difficulty of recovering the solvent used for extraction, and the high heat costs.

We have now found that the use of cyclohexanone as the extracting solvent eliminates or greatly decreases the problems of separating aliphatic acids from black liquor.

In accordance with this invention it is first necessary to obtain a black liquor which has the aliphatic acids in the free acid form and which contains the free aliphatic acids in sufficient concentration for practical extraction. Unless the aliphatic acids are of sufficient concentration unduly large amounts of cyclohexanone will be required for extraction and the size of the plant required to recover the aliphatic acids will be excessive. The concentration of aliphatic acids can be brought to a practical level most easily by the evaporation of water from the black liquor.

It is necessary that the concentration of the black liquor precede the acidification of the black liquor, for unless the aliphatic acids are in the form of salts much of the aliphatic acid content will be lost with the evaporation of

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the water. It has been found that when black liquor has been evaporated to a solids concentration of approximately 25 to 60%, and the aliphatic acids then liberated to the free acid form, the acids will be in sufficient concentration for practical extraction. Above approximately 60% solids, although the aliphatic acids are of sufficient concentration for practical extraction, the black liquor becomes too viscous for practical handling.

After the black liquor has been concentrated, the black liquor is acidified with any strong mineral acid, usually sulfuric, to convert the aliphatic acid salts to aliphatic acids. It has been found that sufficient acid should be added to reduce the black liquor pH to approximately 2.0 to 4.0. Above a pH of 4.0 emulsion problems are encountered during the extraction. At a pH of 2.0 all the aliphatic acids have been liberated from their salts, and further lowering of the pH increases the mineral acid consumption and aggravates the corrosion problem.

Where black liquor from alkaline pulping is used, the acidification also serves to precipitate the lignin from the black liquor. The precipitated lignin may be removed from the black liquor by coagulation and filtering in known manner.

After concentration and acidification, the black liquor is ready for extraction of aliphatic acids contained in it by the use of cyclohexanone. The extraction of the black liquor with cyclohexanone may conveniently be carried out in a counter-current extraction column of known type. Any method of contacting the black liquor with cyclohexanone may be used, however, such as mixer-settlers, centrifugal extractors or pulse columns. Where a counter-current extraction process is utilized a ratio of one-quarter to two volumes of cyclohexanone to one volume of concentrated and acidified black liquor has been found to provide excellent separation of the aliphatic acids from the black liquor. Where the black liquor has been concentrated to a solids concentration of approximately 25 to 60% and acidified to a pH of 4.0 or below, no emulsion problems are encountered within the above range of ratios of cyclohexanone to black liquor.

During the extraction of the black liquor with cyclohexanone a small amount of water and solids from the black liquor will be dissolved in the cyclohexanone along with the aliphatic acids and carried with the extract. A small amount of cyclohexanone will also be dissolved in the black liquor and will remain with the black liquor. It has been found that the problems of carry-over of water and solids in the extract, and of cyclohexanone in the black liquor residue, do not detract from the process because of the characteristics of cyclohexanone.

The small amount of water in the extract may substantially be removed by distillation without loss of any aliphatic acids. Water and cyclohexanone have been found to form an azeotrope which boils at 97° C. As this azeotrope boils at a lower temperature than any of the aliphatic acids, it may be distilled without loss of the aliphatic acids. The water and cyclohexanone distilled in the azeotrope may be directly recycled for further extraction of black liquor or the azeotrope allowed to cool and form phases from which the cyclohexanone may be decanted and recycled. If desired the small amount of cyclohexanone remaining in the water phase may be distilled as a water-cyclohexanone azeotrope and this also recycled.

After removal of water from the extract the aliphatic acids may easily be separated from the cyclohexanone by distillation. The aliphatic acids thus obtained are a clear colorless mixture and contain very little if any impurities.

If desired, this mixture of aliphatic acids may be separated by known methods into fractions containing the individual aliphatic acids.

The aliphatic acids of chief interest have boiling points considerably below that of cyclohexanone, and may be distilled without evaporating any substantial amount of the cyclohexanone. In other processes employing solvents which boil at lower temperatures than the aliphatic acids, any solids in the extracts remain in the acids, and this necessitates, as a separate step, the distillation of the acids. A considerable saving in heat costs is therefore obtained. Also, since the solids picked up in the extract during the extraction of black liquor with cyclohexanone always remain in solution, no difficulties are encountered when the cyclohexanone is reused without removing the solids.

After the aliphatic acids have been separated from the extract, the remaining cyclohexanone containing the small quantities of solids may therefore be recycled to the extraction column for further extraction of black liquor.

The small quantity of cyclohexanone dissolved in the residue black liquor may be removed from the black liquor by steam distillation of a water cyclohexanone azeotrope, and the cyclohexanone recovered by the methods described for the recovery of cyclohexanone from the water-cyclohexanone azeotrope distilled from the extract.

The following is a preferred illustrative example of the process of this invention.

Black liquor from a neutral sulfite pulping process was concentrated by evaporation of water to a 40% solids content. This concentrated black liquor was acidified to a pH of 2.5 by the addition of sulfuric acid in appropriate quantity. The concentrated and acidified black liquor was contacted with cyclohexanone in a counter-current extraction column. The ratio of black liquor to cyclohexanone fed to this column was two volumes of black liquor to three volumes of cyclohexanone. The water was removed from the extract by distillation of a water-cyclohexanone azeotrope, and the cyclohexanone recovered from the distilled azeotrope was reused. The aliphatic acids were then distilled from this extract. Ninety-three percent of the aliphatic acids contained in the black liquor were recovered in the distillate. The remaining extract containing cyclohexanone and a small amount of solids was returned to the extraction column for further use. The cyclohexanone in the black liquor residue was stripped by steam distillation of a water-cyclohexanone azeotrope and the cyclohexanone recovered for reuse in the extraction column. The total recovery of cyclohexanone was above 99%.

It is to be understood that references to "cyclohexanone" as an extracting solvent in the specification and claims of this invention are intended to mean either pure cyclohexanone or cyclohexanone which contains small quantities of water or impurities, or both, as the cyclohexanone recovered from the process of this invention will contain small quantities of impurities, water, or both. It is one of the advantages of this invention that the cyclohexanone containing small quantities of impurities or water can be reused without any detrimental effect on the separation of the aliphatic acids from the black liquor.

Various changes may be made in the steps specifically set forth without departing from the spirit of our invention or the scope of the appended claims.

We claim:

1. The process of obtaining an aliphatic acid component selected from the group consisting of formic, acetic, and propionic acids and mixtures thereof from black liquor resulting from the neutral or alkaline pulping of wood and containing salts of a plurality of said acids which comprises concentrating said black liquor to a solids content of between 25 and 60%, acidifying the black liquor to a pH between 2 and 4 thereby converting the acid salts to the free acids, dissolving the aliphatic acid component from the concentrated acidified black liquor with cyclohexanone, removing the cyclohexanone-aliphatic acid component solution obtained thereby from the black liquor, and recovering the aliphatic acid component by distillation.

2. The process of claim 1 wherein from one-quarter to two parts by volume of cyclohexanone are employed in dissolving the aliphatic acid component from one part of black liquor.

3. The process of claim 1 wherein water dissolved in the cyclohexanone during the dissolving of the aliphatic acid component from the black liquor is removed from the cyclohexanone-aliphatic acid component solution prior to distillation of the aliphatic acid component by distilling off an azeotrope of water and cyclohexanone.

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