METHOD OF RECOVERING AQUEOUS N-METHYLIDENEMORPHOLINE-N-OXIDE SOLUTION USED IN PRODUCTION OF LYOCCELL FIBER

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Abstract

A method of recovering an aqueous N-methylmorpholine-N-oxide (NMMO) solution used in production of Lyocell fiber includes: decoloring the aqueous NMMO solution by mixing the same with activated carbon using an agitation blower and by alternately energizing and de-energizing the agitation blower to contact the activated carbon with the aqueous NMMO solution thoroughly in an energy-efficient manner; filtering the aqueous NMMO solution which has been decolored through coarse filtration followed by ultrafiltration to remove the activated carbon and impurities from the aqueous NMMO solution; and concentrating the aqueous NMMO solution which has been filtered using one of a mechanical vapor recompression evaporator and a triple effect evaporator to remove water from the aqueous NMMO solution.
FIG. 1
PRIOR ART

wood pulp

mixing

dissolving

spinning

washing

Lyocell fiber

NMMO recovery

NMMO
FIG. 2

101 decoloring
102 filtering
103 concentrating
104 refinement

wood pulp

NMMO

recovered aqueous NMMO solution

water solution

aqueous NMMO solution

Lyocell fiber

washing

spinning

dissolving

mixing
METHOD OF RECOVERING AQUEOUS N-METHYLMORPHOLINE-N-OXIDE SOLUTION USED IN PRODUCTION OF LYOCELL FIBER

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority of Taiwanese application no. 099107591, filed on Mar. 16, 2010.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention
[0003] This invention relates to a method of recovering a solvent used in production of fiber, more particularly to a method of recovering an aqueous N-methylmorpholine-N-oxide solution used in production of Lyocell fiber.

[0004] 2. Description of the Related Art
[0005] Lyocell fiber is made from natural cellulose. Consequently, waste products of Lyocell fiber are naturally decomposable and are environmentally friendly. Lyocell fiber has mechanical strength similar to that of synthetic fiber, a good draping property, a sufficient thickness, and nice hygroscopicity. Furthermore, Lyocell fiber is comfortable to touch, is easy to be dyed, can be easily blended with natural or synthetic fiber different from Lyocell fiber, and can be easily processed.

[0006] Referring to FIG. 1, a conventional method of producing Lyocell fiber includes the following four steps: mixing, dissolving, spinning, and washing. Wood pulp is mixed with an N-methylmorpholine-N-oxide (NMMO) solvent so as to dissolve cellulose. After the cellulose is dissolved, Lyocell filaments are formed by virtue of spinning. Subsequently, the Lyocell filaments are washed to remove NMMO remaining in the same, thereby forming Lyocell fiber.

[0007] Since NMMO is nontoxic, is not stinking and has a high boiling point, the method of making Lyocell fiber via the NMMO solvent is more environmentally friendly compared to a conventional method of making synthetic fiber. However, the NMMO solvent is costly. In order to reduce the cost of mass production of Lyocell fiber, NMMO is usually recovered and reused. An NMMO recovery rate may be over 95.5%.

[0008] Nevertheless, a conventional method of recovering NMMO used in production of Lyocell fiber must be improved to facilitate NMMO recovery and to enhance NMMO recovery efficiency so that the cost of mass production of Lyocell fiber can be further reduced.

SUMMARY OF THE INVENTION

[0009] Therefore, the object of the present invention is to provide a method of recovering an aqueous N-methylmorpholine-N-oxide (NMMO) solution used in production of Lyocell fiber to facilitate NMMO recovery and to enhance NMMO recovery efficiency.

[0010] According to this invention, a method of recovering an aqueous NMMO solution used in production of Lyocell fiber comprises: decoloring the aqueous NMMO solution by mixing the same with activated carbon using an agitation blower and by alternately energizing and de-energizing the agitation blower to contact the activated carbon with the aqueous NMMO solution thoroughly in an energy-efficient manner; filtering the aqueous NMMO solution which has been decolored through coarse filtration followed by ultrafiltration to remove the activated carbon and impurities from the aqueous NMMO solution; and concentrating the aqueous NMMO solution which has been filtered using one of a mechanical vapor recompression evaporator and a triple effect evaporator to remove water from the aqueous NMMO solution.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Other features and advantages of the present invention will become apparent in the following detailed description of the preferred embodiment of this invention, with reference to the accompanying drawings, in which:

[0012] FIG. 1 is a flow chart to illustrate a conventional method of producing Lyocell fiber;

[0013] FIG. 2 is a flow chart to illustrate the preferred embodiment of a method of recovering an aqueous N-methylmorpholine-N-oxide solution used in production of Lyocell fiber according to this invention and the method of producing Lyocell fiber shown in FIG. 1; and

[0014] FIG. 3 is a schematic diagram to illustrate a decoloring step of the preferred embodiment.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0015] Referring to FIG. 2, according to the present invention, the preferred embodiment of a method of recovering an aqueous N-methylmorpholine-N-oxide (NMMO) solution used in production of Lyocell fiber includes steps 101-104. The conventional method of producing Lyocell fiber shown in FIG. 1 is also illustrated in FIG. 2. After the washing step for production of Lyocell fiber, an aqueous NMMO solution having a low concentration of NMMO is formed. In addition to NMMO, the aqueous NMMO solution also contains a trace of N-methylmorpholine (NMM) that arises from cleavage of NMMO, which is caused by heating during the dissolving step.

[0016] Step 101 is decoloring of the aqueous NMMO solution. Even though heat energy provided during the dissolving step of the conventional method of producing Lyocell fiber is able to increase dissolving efficiency, the heat energy gives rise to coloration. Therefore, the aqueous NMMO solution contains pigments and is required to be decolored. Referring to FIG. 3, the aqueous NMMO solution 3 to be recovered is disposed in a tank 21, and activated carbon powder 4 having adsorbability and suspendability is added into the aqueous NMMO solution 3. The activated carbon powder 4 and the aqueous NMMO solution 3 are mixed together using an agitation blower 22. The agitation blower 22 is alternately energized and de-energized so as to contact the activated carbon powder 4 with the aqueous NMMO solution thoroughly in an energy-efficient manner and so as to increase adsorption efficiency of the activated carbon powder 4.

[0017] When the agitation blower 22 is energized to rotate a blade thereof, pressurized air is supplied to the tank 21 so as to agitate the aqueous NMMO solution 3 such that the activated carbon powder 4 is effectively mixed with the aqueous NMMO solution 3 and such that adsorption on the activated carbon powder 4 occurs. When the agitation blower 22 is de-energized, suspension of the activated carbon powder 4 and adsorption on the activated carbon powder 4 occur. A timed switch 23 is used to repeatedly energize and de-energize the agitation blower 22. A ratio of a duration to energize the agitation blower 22 to a duration to de-energize the agitation blower 22 ranges from 1:3 to 1:6. A total time of the
decoloring of the aqueous NMMO solution 3 is not longer than 8 hours. In this embodiment, the total time of the decoloring of the aqueous NMMO solution 3 is 8 hours. Preferably, the amount of the activated carbon powder 4 is 0.05 wt % - 0.10 wt % based on the total weight of the aqueous NMMO solution 3.

[0018] In step 102, the aqueous NMMO solution which has been decolorized is filtered through coarse filtration followed by ultrafiltration (UF) so as to remove the activated carbon powder 4 and impurities from the aqueous NMMO solution. The coarse filtration is conducted using a filter material that has a pore size ranging from 1 μm to 100 μm so that the activated carbon powder 4 and the impurities of large particle size can be removed. The ultrafiltration is conducted using a filter material that has a pore size ranging from 0.01 μm to 1 μm so that the impurities of small particle size can be removed. The aqueous NMMO solution which has been filtered by the coarse filtration and the ultrafiltration has cleanliness similar to that of a fresh NMMO solvent.

[0019] The coarse filtration is conducted using a cartridge filter. Preferably, in order to increase the speed of the coarse filtration, a filter aid is coated on a surface of a cartridge of the cartridge filter, and the filter aid is added into the decolored aqueous NMMO solution. The amount of the filter aid is 0.03 wt % - 0.05 wt % based on the total weight of the decolored aqueous NMMO solution. The filter aid is made from diatomaceous earth and cellulose. Preferably, the weight ratio of the diatomaceous earth to the cellulose is 4:1. The filter aid is able to increase a filtration area, and is capable of effectively preventing the activated carbon powder 4 from accumulating on an outer layer of the filter cartridge and from plugging the filter cartridge. Consequently, the speed of the coarse filtration is not reduced.

[0020] It should be noted that a sludge resulting from the coarse filtration could be centrifugally dried after the coarse filtration is completed. The dried sludge contains the activated carbon powder 4 and the filter aid. After an outer portion of the dried sludge, which contains a larger amount of the activated carbon powder 4, is scraped off, the dried sludge containing the filter aid can be reused in the coarse filtration step.

[0021] In step 103, the aqueous NMMO solution which has been filtered is concentrated. In this embodiment, the filtered aqueous NMMO solution initially has an amount of NMMO, which ranges from 6.5 wt % to 8.0 wt % based on the total weight of the filtered aqueous NMMO solution, and is concentrated so that the amount of NMMO in the concentrated aqueous NMMO solution ranges from 50 wt % to 55 wt % based on the total weight of the concentrated aqueous NMMO solution. When one ton of Lyocell fiber is produced, 90 tons of water have to be removed from the filtered aqueous NMMO solution in order to form the concentrated aqueous NMMO solution that has a qualified NMMO concentration. Accordingly, compared to steps 101, 102, and 104, step 103 requires large workload. The filtered aqueous NMMO solution can be concentrated using one of a mechanical vapor recompression (MVR) evaporator and a triple effect evaporator so as to remove water from the aqueous NMMO solution according to an output of Lyocell fiber. Thus, a water solution without NMMO and the concentrated aqueous NMMO solution are formed. The resultant concentrated aqueous NMMO solution has an NMMO concentration the same as that of an NMMO solvent commercially available in the market. The resultant water solution can be used in the washing step of the method of producing Lyocell fiber to wash the Lyocell filaments. Since almost all portions of the aqueous NMMO solution resulting from the method of producing Lyocell fiber are reusable, the method of this invention is very environmentally friendly and cost effective.

[0022] The triple effect evaporator is composed of three evaporator vessels connected in series and is able to use vapor many times, thereby being capable of efficiently using heat energy. The triple effect evaporator is usually utilized for an aqueous solution. Pressure in the first evaporator vessel (i.e., the first effect) is higher than pressure in the second evaporator vessel (i.e., the second effect), and the pressure in the second evaporator vessel is higher than pressure in the third evaporator vessel (i.e., the third effect). Live steam is used to heat the first evaporator vessel. Since a boiling point of water decreases as pressure decreases, vapor boiled off in the first evaporator vessel can be used to heat the second evaporator vessel, and vapor boiled off in the second evaporator vessel can be used to heat the third evaporator vessel. Consequently, the live steam is only necessary for the first evaporator vessel. The vapor boiled off in the first and second evaporator vessels has a temperature lower than that of the live steam. Based on a result of actual operation of the triple effect evaporator, one ton of water can be removed from the filtered aqueous NMMO solution by virtue of 0.5 ton of the live steam. The triple effect evaporator consumes a lot of the live steam, but only a relatively small amount of electricity. Preferably, the triple effect evaporator is suitable for the aqueous NMMO solution resulting from production of a small amount of Lyocell fiber.

[0023] Mechanical vapor recompression (MVR) is the evaporation method by which a mechanically driven compressor is used to compress, and thus, increase the pressure of the vapor produced. In the MVR system, an external heating source, e.g., electricity is provided in the beginning of the compression step for heating the to-be-recovered aqueous NMMO solution in a closed container so as to increase the temperature of the NMMO solution over a vapor temperature, thereby producing vapor (i.e., live steam). The vapor thus produced is recompressed via the mechanically driven compressor such that high-pressure vapor of 107°C is formed. Heat energy for the subsequent part of the compressing step can be provided by the high-pressure vapor, i.e., the high-pressure vapor is able to serve as a heating medium that can be repeatedly used for continuously evaporating the aqueous NMMO solution. When the high-pressure vapor is repeatedly used to transfer heat, the high-pressure vapor can be rapidly cooled and condensed to form a clean water solution. Furthermore, when the clean water solution is drained out, a heat exchange can be induced between the outflow clean water solution and the inflow aqueous NMMO solution. By virtue of the MVR evaporator, one ton of water can be removed from the aqueous NMMO solution using 0.003-0.03 ton of live steam. The MVR evaporator consumes a small amount of the live steam, but a lot of electricity. Preferably, the MVR evaporator is suitable for the aqueous NMMO solution resulting from production of a large amount of Lyocell fiber.

[0024] The aqueous NMMO solution can be concentrated to have 70 wt % - 80 wt % of NMMO by virtue of the triple effect evaporator or the MVR evaporator. Nevertheless, the aqueous NMMO solution is only required to have 50 wt % - 55 wt % of NMMO for being reused in production of Lyocell
fiber. Thus, in order to save energy, the aqueous NMMO solution having 50 wt %–55 wt % of NMMO is not further concentrated.

[0025] Step 104 is refinement of the concentrated aqueous NMMO solution to oxidize a trace of NMM contained in the concentrated aqueous NMMO solution to NMMO. Besides a small amount of NMM (less than 0.06 wt %) already contained in a fresh NMMO solvent, some NMM may be produced due to cleavage of a small portion of NMMO during production of Lyocell fiber. In this embodiment, the amount of NMM in the concentrated aqueous NMMO solution ranges from 0.1 wt %–0.3 wt %. When the concentrated aqueous NMMO solution is not subjected to the refinement step and hence has more NMM, the concentrated aqueous NMMO solution has a worsened ability to dissolve cellulose such that events (e.g., obstruction of spinneret holes and breaks of filaments) adversely affecting spinning efficiency may easily occur during the spinning step of production of Lyocell fiber. Furthermore, Lyocell fiber thus formed may have undesired physical properties such as poor strength. In order to ensure that the aqueous NMMO solution recovered by the method of this invention can be used to produce Lyocell fiber having a satisfactory quality, the refinement step is preferably conducted.

[0026] To perform the refinement step, an oxidizing agent and a neutralizing agent are used. To be specific, an oxidizing agent is added to the concentrated aqueous NMMO solution so as to oxidize a trace of NMM contained in the same to NMMO. After completion of the oxidation, a neutralizing agent is added to the concentrated aqueous NMMO solution to neutralize the oxidizing agent remaining in the same. The amount of NMMO in the aqueous NMMO solution is hence increased (i.e., purity of NMMO is increased). Potentiometric titration is applied to detect the result of the redox reaction in the aqueous NMMO solution so that required amounts of the oxidizing agent and the neutralizing agent can be decided.

[0027] In this embodiment, the oxidizing agent is H₂O₂, and the neutralizing agent is N₂H₄·H₂O (hydrazine hydrate). NMM in the concentrated aqueous NMMO solution is oxidized by the oxidizing agent at a temperature of 80±2°C. When the reaction temperature is excessively high, NMM and H₂O₂ in the concentrated aqueous NMMO solution may be easily cleaved and volatilized, the redox reaction may be too intense, and energy may be wasted. On the contrary, when the reaction temperature is excessively low, the redox reaction may not effectively proceed, thereby decreasing refining efficiency. The reaction temperature is hence set as 80±2°C.

[0028] A chemical equation of the oxidation of NMM in the concentrated aqueous NMMO solution is as follows:

\[
\text{C}_6\text{H}_7\text{NO} + \text{H}_2\text{O}_2 \xrightarrow{80^\circ \text{C}, 2 \text{ hr}} \text{C}_6\text{H}_7\text{NO}_2 + \text{H}_2\text{O}
\]

A chemical equation of the neutralization of the remaining oxidizing agent in the concentrated aqueous NMMO solution is as follows:

\[
\text{N}_2\text{H}_4\cdot\text{H}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{N}_2
\]

According to detection of the amount of NMM in the concentrated aqueous NMMO solution and the molar ratio of NMM to H₂O₂ in the first chemical equation, a rough required amount of H₂O₂ is calculated. However, in order to make sure that almost all of NMM can be oxidized, an actual amount of H₂O₂ added to the concentrated aqueous NMMO solution is more than the calculated rough required amount of H₂O₂. After the oxidation of NMM, the neutralizing agent is added to neutralize the excessive H₂O₂. Referring to the first and second chemical equations, even though the oxidizing agent and the neutralizing agent are added to the concentrated aqueous NMMO solution, products only include H₂O, N₂, and NMMO. N₂ can be directly spread into air, and H₂O becomes a part of the refined aqueous NMMO solution. Thus, no impurities and side products are formed during the refining step such that the recovered aqueous NMMO solution has high purity of NMMO and does not adversely affect the quality of Lyocell fiber.

[0029] Based on the experimental results, the NMMO recovery rate is over 99.5% when the aqueous NMMO solution is recovered using the method of this invention. By virtue of the recovered aqueous NMMO solution obtained using the method of this invention, a cost of mass production of Lyocell fiber can be reduced. The method of this invention only requires equipments that are easily accessible and that can be simply installed. Due to the method of this invention, an efficiency of recovering the NMMO aqueous solution is satisfactory.

[0030] While the present invention has been described in connection with what is considered the most practical and preferred embodiment, it is understood that this invention is not limited to the disclosed embodiment but is intended to cover various arrangements included within the spirit and scope of the broadest interpretation and equivalent arrangements.

What is claimed is:

1. A method of recovering an aqueous N-methylmorpholine-N-oxide (NMMO) solution used in production of Lyocell fiber, comprising:
   - decoloring the aqueous NMMO solution by mixing with the same with activated carbon using an agitation blower and by alternately energizing and de-energizing the agitation blower;
   - filtering the aqueous NMMO solution which has been decolored through coarse filtration followed by ultrafiltration to remove the activated carbon and impurities from the aqueous NMMO solution; and
   - concentrating the aqueous NMMO solution which has been filtered using one of a mechanical vapor recompression evaporator and a triple effect evaporator to remove water from the aqueous NMMO solution.

2. The method of claim 1, further comprising adding an oxidizing agent to the aqueous NMMO solution which has been concentrated to oxidize N-methylmorpholine contained in the aqueous NMMO solution to N-methylmorpholine N-oxide; and adding a neutralizing agent to the concentrated aqueous NMMO solution to neutralize the oxidizing agent remaining in the concentrated aqueous NMMO solution.

3. The method of claim 1, wherein a ratio of a duration to energize the agitation blower to a duration to de-energize the agitation blower ranges from 1:3 to 1:6, and a total time of the decoloring of the aqueous NMMO solution is not longer than 8 hours.

4. The method of claim 1, wherein the amount of the activated carbon is 0.05 wt %–0.10 wt % based on the total weight of the aqueous NMMO solution.

5. The method of claim 1, wherein the coarse filtration is conducted by using a cartridge filter that includes a cartridge
having a surface coated with a filter aid, and by adding the filter aid to the decolored aqueous NMMO solution, the filter aid being made from diatomaceous earth and cellulose.

6. The method of claim 5, wherein the amount of the filter aid is 0.03 wt % - 0.05 wt % based on the total weight of the decolored aqueous NMMO solution, and a weight ratio of the diatomaceous earth to the cellulose is 4:1.

7. The method of claim 5, further comprising centrifugally drying a sludge resulting from the coarse filtration.

8. The method of claim 1, wherein the coarse filtration is conducted using a filter material that has a pore size ranging from 1 μm to 100 μm, and the ultrafiltration is conducted using a filter material that has a pore size ranging from 0.01 μm to 1 μm.

9. The method of claim 1, wherein, after the concentrating step, the amount of N-methylmorpholine N-oxide in the aqueous NMMO solution ranges from 50 wt % to 55 wt % based on the total weight of the aqueous NMMO solution.

10. The method of claim 2, wherein the oxidizing agent is H₂O₂, and the neutralizing agent is N₂H₄·H₂O.

11. The method of claim 10, wherein N-methylmorpholine in the concentrated aqueous NMMO solution is oxidized by the oxidizing agent at a temperature of 80±2°C.