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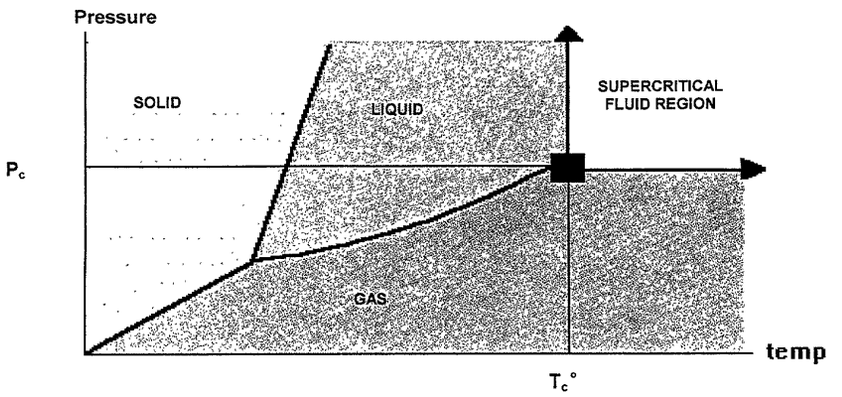
(54) Methods of treating cellulose fibres and products obtained thereby

(57) A method for reducing the level of or removing wood extractives from cellulose fibres and products comprising cellulose fibres, by the use of a supercritical or near supercritical fluid in order to increase the absorption rate of such cellulose fibres and products comprising cellulose fibres. Also disclosed are cellulose fibres and products comprising cellulose fibres, such as cellulose tissue paper, sanitary napkin or towel, nonwoven industrial wipes, baby diaper, incontinence garments, or pulp having improved qualities, such as improved absorption rate.



$T_c = 31.1°$ C
$T_p = 73.8$ bar

Figure 2

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Description

TECHNICAL FIELD

[0001] The present invention relates to a method using a supercritical or near supercritical fluid for removal of wood extractives from cellulose fibres and products comprising cellulose fibres to improve the qualities thereof and to cellulose fibres and products comprising cellulose fibres having improved qualities.

BACKGROUND OF THE INVENTION

[0002] Kitchen towels and household towels are products, which should have good wetting and absorption properties such as absorption rate and absorption capacity, especially with respect to absorption of a liquid such as an aqueous medium. Also very important is the rate for the uptake of a liquid. This means that when wiping liquid from a surface it is necessary for the towel to absorb the liquid as quickly as possible or in other words to remove the liquid from the surface by in some way binding it to the towel by e.g. an absorption process.

[0003] There are several possibilities of obtaining a towel with good absorption properties such as the absorption rate, for example by adding an absorption booster as an additive during the production of towels. Examples of such absorption boosters may be surfactants. The addition of a surfactant to the pulp, i.e. chemically or mechanically fiberised wood, results in a pulp having improved absorption properties such as a faster absorption rate for liquid uptake.

[0004] The disadvantage of using an absorption booster is that in general it is regarded as leading to a decrease in the strength properties of the towel and the capillary pressure of the fibrous web. Another disadvantage with absorption boosters like, e.g. surfactants, is that they tend to loose their wettability property with time. It is also important to mention that chemicals should be avoided, as much as possible, in hygiene paper due to problems with toxicity and allergic reactions.

[0005] It is known that cellulose fibres and products comprising cellulose fibres normally are subject to ageing phenomena, *i.e.* their behaviour with respect to e.g. wettability and absorption rate change during storage. After a certain period of time it is generally found that the wetting and absorption properties of the products have significantly decreased as compared to the wetting and absorption properties directly after production. Other properties like colour and strength of the cellulose fibres and products comprising cellulose fibres may also be affected. One reason for this phenomenon is the outflow of so called "wood extractives", *i.e*. some wood extractives will migrate from the inner side of the cellulose fibres or the inner side of the cellulose fibre product to the outer or outermost surface of the cellulose fibres or cellulose fibre product and more or less homogeneously coat or cover the outer surface with such wood extractives. As such wood extractives generally are of a hydrophobic nature this means that the outer surface of the cellulose fibres or the outer surface of the cellulose fibre product, *i.e.* that surface which is to be exposed to the liquid to be absorbed, becomes more hydrophobic and, accordingly, it will tend to repel an aqueous based liquid. The result is that the wettability properties decrease.

[0006] The "wood extractives" are contemplated to be fibre compounds, such as, e.g. low molecular fatty acids. Suggested, as a theory, is that after migration from the interior of the fibres, these compounds covers the fibres and make them more hydrophobic. As a result the surface tension is reduced which in turn leads to a decrease in the absorption properties and the tissue product becomes less wettable.

[0007] One possibility to remove these hydrophobic compounds is to extract them from the pulp used. Extraction procedures are well known and organic solvents are often used. One of the preferred best non-flammable solvent to be used for removal of unpolar substances is dichloromethane (DCM). However, the use of DCM is not altogether harmless since it contains chlorine and should for this reason be avoided. Furthermore, dichloromethane is an organic solvent that should be avoided for environmental reasons.

[0008] From US 5,009,746 it is known how to remove sticky contaminants from secondary cellulose fibres by the use of supercritical carbon dioxide. The sticky contaminants are all additives added to the paper to make it suitable for its purpose, such as adhesives and the like.

[0009] From the fragrance industry it is known to use supercritical carbon dioxide in an extraction procedure to remove non-polar chemicals (Caragay, A.B. *Perfume and Flavorist* 1981, 6:43-55; Schultz, E.G. and Randall, J. N. *Food Tech*. 1970, 24:94-98).

SUMMARY OF THE INVENTION

[0010] The need for a method for treating cellulose pulp and cellulose fibres in order to prevent/slow down ageing processes of the cellulose fibres is evident from reasons described above. Furthermore, there is a need for a method and products to meet increasing economical and environmental demands as well as a method for the production of such a product in a large scale.

[0011] It is an object of the invention to provide a method for reducing the level of or substantially removing wood extractives imparting - due to ageing - decreased absorption rate from cellulose fibres comprising contacting the fibres with a supercritical or near supercritical fluid to extract the wood extractives and removing the extract from the fibres so as to obtain improved cellulose fibres with a reduced content of extractives which impart decreased absorption rate. The use of such a method during manufacturing of cellulose fibres or an absorbent product containing cellulose fibres will prevent or slow down ageing processes and lead to an increased quality of the cellulose fibres or the product thereof, especially with respect to increased absorption properties such as, e.g. an increased absorption rate of a liquid to the cellulose fibres or to a product comprising cellulose fibres due to the removal of the ageing substances in an early phase.

[0012] It is also an object of the invention to provide a method for reducing the level of or removing wood extractives from cellulose fibres, such method being adapted for large scale production, cost-efficient, simple and which does not negatively affect the fibres treated.

[0013] Furthermore, it is an object of the invention to provide cellulose fibres and/or products comprising cellulose fibres having improved qualities, e.g. absorption properties such as the absorption rate.

[0014] Specifically, it is an object of the invention to provide a stratified absorbent product comprising the above mentioned improved cellulose fibres which results in a relatively cheap product having improved absorption properties such as the absorption rate due to the previous removal of wood extractives.

[0015] To achieve these and other objects, the present invention relates to a method for reducing the level of or removing wood extractives from cellulose fibres, wherein the fibres are brought into contact with a supercritical or near supercritical fluid for a period of time sufficient to reduce the level of or to substantially remove the wood extractives.

[0016] The invention also refers to the use of a supercritical fluid or near supercritical fluid for reducing the level of or substantially removing wood extractives from cellulose fibres.

[0017] In a further aspect the invention refers to extracted cellulose fibres or products produced thereof, such as a fibrous web, tissue paper, sanitary napkin, baby diaper, incontinence garment, non-woven industrial wipes, comprising reduced levels of or being substantially free from wood extractives.

[0018] In a specific aspect the invention provides a method for reducing the level of or substantially removing a more specific group of wood extractives compared to the relatively unspecific extraction of wood extractives which is obtained by using well-known methods employing organic solvent extraction. Thus, by use of the method according to the present invention the composition of wood extractives removed from the cellulose fibres is different compared with the composition of wood extractives obtained after extracting cellulose fibres with dimethylchloromethane (DCM). By use of the method according to the invention, the most hydrophobic compounds such as triglycerides and sterylestes are extracted in a more efficient way while the less hydrophobic compounds, such as lignin, are extracted to a decreased degree and retained in the fibres. However, if desired, by adjusting the extraction parameters (increased pressure, addition of co-solvent e.g. methanol) lignin can be extracted to various extents.

[0019] In still a further aspect the invention refers to a stratified product comprising cellulose fibres comprising at least one outer layer and possibly at least one middle layer, wherein at least one of the outer layers have a high amount of extracted virgin cellulose fibres or pulp.

[0020] Use of the method according to the invention will increase the qualities of the resulting absorbent product, such as the absorption rate of the final product comprising cellulose fibres by preventing the disadvantages generally observed by ageing of such product. Further, the method considers environmental aspects since a supercritical fluid like, e.g., carbon dioxide, CO_2, is less toxic and not flammable compared to known alternatives like, e.g., DCM. As a further advantage, the method according to the invention is much cheaper compared to conventional extraction methods due to the use of less expensive fluids e.g. the use of CO_2.

SHORT DESCRIPTION OF DRAWING

[0021]

Fig. 1 is a schematic view of an extractor that can be used in accordance with the present invention,
fig. 2 is a phase diagram of carbon dioxide showing the critical point and the supercritical region of the fluid,
fig. 3a is a table (table 2) showing the amount of extractives obtained by the present method compared to the amount obtained by means of a known solvent extraction method,
fig. 3b is a diagram showing the composition of wood extractives in the extracts from Example 2, and
fig. 4 is a table (table 3) showing the results from measurement of absorption in Example 3.

DETAILED DESCRIPTION OF THE INVENTION

[0022] As revealed above the present invention relates to the use of a supercritical or near supercritical fluid (SF)

for removing wood extractives from cellulose fibres and absorbent products comprising improved cellulose fibres. In the present context, the term "improved cellulose fibres" is used to denote any kind of cellulose fibres that have been subjected to the method according to the present invention, *i.e.* improved cellulose fibres are cellulose fibres which have been subject to a purification procedure in which an amount of impurities like wood extractives have been removed from the fibres.

[0023] The term "cellulose fibre" is intended to mean any natural cellulose containing fibres, e.g. wood fibre, cotton fibre or hemp fibre, preferably virgin cellulose fibres or substantially virgin fibres. The major component in pulp is the natural cellulose fibre.

[0024] The term "virgin" with cellulose fibre is intended to mean not reclaimed. Virgin pulp according to this definition is made from such cellulose fibres and may be the result of mechanical, chemical (e.g. sulphate or sulphite), or chemimechanical pulping.

[0025] The term "wood extractives" is intended to mean compounds, such as aliphatic compounds (mainly fats and waxes), terpenes, terpenoids and phenolic compounds, such compounds being inherent in and extractable from the cellulose. Wood extractives mainly include hydrophobic compounds e.g. fatty acids, resin acids, fats (glycerol esters e.g triglycerides) and waxes (esters of other alcohols, e.g. sterylesters) defined according to an analytical procedure for quantitative determination of wood extractives and lignins (Örså, F and Holmbom, B. *J. Pulp and Paper Sci*. 1994, 20:J361-J365).

[0026] The term "supercritical or near supercritical fluid" is intended to mean any fluid presented under supercritical or near supercritical pressure and temperature conditions, within narrow ranges for the specific fluid wherein still most of the fluid behaves supercritical. Herein, the critical temperature and the critical pressure is abbreviated T_c and P_c, respectively.

[0027] In the supercritical state, substances behave partly as a gas and partly as a liquid. Their densities are liquid-like but in respect of diffusivity or penetration capabilities they resemble gases. The density of a supercritical fluid may be continuously changed without phase separation by changes in pressure and/or temperature. Density dependent properties such as solvent power also undergo corresponding changes.

[0028] As discussed above, the present invention uses a supercritical or a near supercritical fluid, such as, e.g., carbon dioxide to remove an amount of wood extractives from cellulose fibres. The critical temperature and pressure for pure carbon dioxide are 31.1°C and 73.8 bar, respectively. Of course as used in the present invention, carbon dioxide (or any other solvent employed) is not operating in a simple, pure state, but as a part of a multi-component system. It is possible, therefore, that depending upon the particular system, the advantages of the invention can be achieved even though the pressure and/or temperature used are not above the critical values for pure carbon dioxide (or any other solvent employed). It is in this sense that the term "near supercritical" is used herein.

[0029] Wood extractives can be divided into three subgroups: aliphatic compounds (mainly fats and waxes), terpenes and terpenoids, and phenolic compounds. A large variety of aliphatic compounds exist in the resin. The fatty acids occur mostly as esters (glycerol esters) present as di- or triglycerides. Compounds which are, according to the invention, of specific interest to remove are hydrophobic compounds, such as fats *i.e.* esters of glycerol, e.g. tri- and diglycerides; waxes *i.e.* esters of alcohols, e.g. sterylesters, fatty acids and resin acids. These compounds give rise to problems in pulping and paper making, and one effect is a decrease in absorption properties. The content of wood extractives and their composition vary greatly among different wood species and also within the different parts of the same tree. The concentration of extractives in pulp is, however, mainly dependent on which process that have been used for producing the pulp where mechanical and chemimechanical contain the highest amounts and sulphite pulp contain high amounts of extractives after pulping.

[0030] In other words, the term "wood extractives" denotes a relatively large and unspecific group of compounds, namely such compounds contained in the wood or cellulose fibres that are extractable by means of an organic solvent. The amount and composition of the wood extractives extracted from specific cellulose fibres depend on i) the specific organic solvent used, ii) the conditions employed during extraction such as, e.g., the temperature, the flow conditions and the number of extractions, and iii) the specific type of cellulose fibres or wood fibres employed. In the present context, the wood extractives which are of main interest to remove from the cellulose fibres are those which give rise to an unwanted ageing phenomenon, namely a decrease in the wetting and absorption properties, strength and/or colour of the fibres. The improved cellulose fibres obtained according to the invention may of course still contain wood extractives of any of the above-mentioned types; the main point is that some of the unwanted wood extractives have been removed to a degree that is sufficient to obtain improved properties of the cellulose fibres, cf. above.

[0031] The cellulose fibres used according to the invention may be any cellulose fibre or product comprising cellulose fibres. However, preferably virgin cellulose fibres are used, since such fibre includes a high content of wood extractives. During storage, cellulose fibre is aged due to outflow of so called "wood extractives". Virgin fibres and pulps contain wood extractives although the contents varies greatly among different wood species and also due to the pulping and bleaching conditions used in the production of different pulps. Even low levels of wood extractives such as the level found in bleached chemical pulps can affect the absorption properties of the fibres in a negative way.

[0032] In reclaimed pulps the extractives consists mainly of additives originating from the paper making process, printing and other converting processes to make the paper suitable for its purpose, so called extractable stickies. The wood extractives are only a minor part of the extractable stickies in such pulps.

[0033] The cellulose fibres to be used according to the invention may be selected from the group consisting of Kraft (sulphate) pulp, sulphite pulp, mechanical pulp and HTCTMP pulp (High Temperature Chemi Thermo Mechanical Pulp).

[0034] According to the invention the level of these wood extractives is reduced or substantially removed compared to conventional extraction methods using DCM according to standard SCAN C 7:62. In one embodiment herein, the ratio is calculated between the total extract content - measured according to Example 1 - and the extract content obtained by a standard method SCAN C 7:62 is at least about 0.5 such as at least about 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.85, 0.90 or about 0.95.

[0035] Particularly the removal of triglycerides and/or sterylesters is beneficial and their removal increases the absorption rate in the final cellulose fibres and products comprising cellulose fibres. The relative amount of sterylesters and/or triglycerides in the extract is higher, ~ 2 times for sterylesters and ~ 3 times for triglycerides, using supercritical fluid CO_2 as the extraction method compared to solvent extraction using DCM (Fig. 3). Furthermore, by means of the present method the amount of lignin is retained in the cellulose fibres to a high degree. The amount of lignin extracted can be varied to some extent by adding a solvent modifier such as methanol to the CO_2 and by adjusting pressure and temperature. According to a specific embodiment of the present invention, the lignin content of the extract is ≤ 5%,

[0036] The method according to the invention for reducing the level of or substantially removing wood extractives from cellulose fibres implies the use of a supercritical or near supercritical fluid. Examples of such fluids are CO_2, ethane and ethylene. Further examples of fluids to be used according to the present invention are given in table 1 below. Preferably CO_2 is used, due to the fact that it is readily available and rather inexpensive as well as not toxic or not flammable.

Table 1

Solvent	*Critical temperature, T_c(°C)*	*Critical pressure P_c(bar)*
Carbon dioxide	31.1	73.8
Ethane	32.2	48.8
Ethylene	9.3	50.4
Propane	96.7	42.5
Propylene	91.9	46.2
Cyclohexane	280.3	40.7
Isopropanol	235.2	47.6
Chlorotrifluoromethane	28.9	39.2

[0037] In principle, the cellulose fibres could be treated at any stage such as before or after bleaching. Experience shows that the extraction result is better if fresh fibres are used, but also older fibres can be extracted.

[0038] The supercritical or near supercritical fluid is used at a temperature and pressure optimal for the fluid, with pressures above from about 70 bar, preferably from 140 and most preferably from 200 bar to about 500 bar and temperatures above about 25° C, preferably in the range from about 31° C to 150° C and most preferably in the range from 31° C to 90° C. An example of a phase diagram for CO_2, with the supercritical fluid region marked, is shown in figure 2.

[0039] In one embodiment, the cellulose fibres are contacted with the supercritical or near supercritical fluid under conditions where the temperature is at least the critical temperature (T_C) for the intended supercritical fluid, or at least about 1.5, such as at least about 2 times higher than T_C and/or the pressure is at least the critical pressure (P_C) for the intended supercritical fluid, or at least about 2, at least about 3, at least about 4, at least about 5 such as at least about 6 times higher than P_C.

[0040] The extraction apparatus used may be the one shown in figure 1. With reference to figure 1 there is shown an extractor (1) in the form of a heated oven (2) with a sample cell (3) included, having a supercritical fluid supply tank (4), a supercritical fluid pump (5), a modifier pump (6), extract collection tube/s (7) all connected in a tubing system (8).

[0041] The process according to the invention may be as follows. A pulp sample is prepared. Then the pulp sample is homogenised and packed into a sample cartridge, further placed into the sample cell (3). CO_2 is supplied from the supply tank (4) pumped and controlled via (5) and (6) into the heated oven (2) and over the sample cell (3). The sample is extracted by carbondioxide at a specified temperature and pressure. The resulting extract is then collected (7) by trapping the extract into a vial filled with an organic solvent e.g. DCM.

[0042] The present invention also refers to extracted cellulose fibres, preferably based on or substantially based on virgin cellulose fibre, which fibres have reduced levels of or are substantially free of wood extractives. An improved

fibrous web made of cellulose fibres has, at least after an initial period of time of at least about two days, such as at least about 10, 90 or about 180 days, a higher liquid absorption rate, such as at least about 5, 12, 20, 30 or about 50% higher, than a fibrous web made of parent cellulose fibres as evidenced by the method described in Example 3.

[0043] Present invention also refers to a fibrous web comprising the improved cellulose fibres described above. In one embodiment, the fibrous web comprises cellulose fibres which have a reduced level of or is substantially free from wood extractives which impart - due to ageing - decreased absorption rate of the cellulose fibres. In still another embodiment the fibrous web described above has a liquid absorption rate at almost the same order of magnitude during storage for such as at least about 2, 10, 30, 90 or about 180 days. Further, such fibrous web is used for the production of an absorbent product.

[0044] The cellulose fibres according to the present invention is useful for preparing absorbent products such as tissue paper, non-woven and absorbent articles such as baby diapers, incontinence garments and sanitary napkins. The tissue paper comprises e.g. kitchen towel, household towel, toilet paper, handkerchief and facials. Apart from cellulose fibres, the non-woven comprises polymeric fibres, such as regenerated cellulose (viscose, rayon), polypropylene, polyester, polylactide, or polyamide. The non-woven can be bonded by any of the regular types of bonding mechanism, e.g. by thermo-bonding, by entangling or by hydro entangling. This type of non-woven are mostly used for industrial and offset wipes. Regarding the absorbent articles the fibres according to the invention is used mainly in the surface and acquisition material and in the absorption core. The tissue paper, nonwoven and surface, acquisition and core materials of the absorbent articles should comprise at least 10% preferably at least 30% and most preferably at least 50 % by weight of the extracted cellulose fibres.

[0045] In a further aspect the present invention refers to a stratified absorbent product such as tissue or nonwoven based on the above extracted cellulose fibres. The stratified absorbent product of the invention comprises at least one outer layer and at least possibly one middle layer, at least one of the outer layers having at least about 10%, such as at least about 30% or at least about 50% by weight of the dried sheet of the extracted cellulose fibres. By such an absorbent product it is possible to reduce costs and at the same time provide a product having good absorption properties such as the high absorption rate.

[0046] It is also advantageous to make a multi-ply tissue paper or nonwoven absorbent product. At least one outer surface having at least about 10%, such as at least about 30% or at least about 50% by weight of the dried sheet of the extracted cellulose fibres. This absorbent product could be built up of two plies being stratified as above or not being stratified. The absorbent product could further have three or more plies whereby at least one of the outer plies should contain extracted pulp. The outer plies may be multi- or single-layered.

[0047] The tissue product may also comprise man-made polymeric fibres, such as regenerated cellulose (viscose, rayon), polypropylene, polyester, polylactide, or polyamide. The tissue may contain up to 50% by weight of polymeric fibres. Different amounts of polymeric fibres can be used in different layers and/or plies.

[0048] As used herein a stratified or multi-layered product means an absorbent product where the layers have been brought together when they are still wet either through the use of a multi-layered headbox or by couching together several wet webs. This gives a stratified or multi-layered web (ply) where the layers are very hard to separate.

[0049] As used herein a multi-ply product means an absorbent product where two or more plies are laid together when dry to work as one unit. The layers can be plybonded although it is not necessary. The plybonding can be achieved through mechanical plybonding, e.g. through embossing or knurling. It can also be achieved through adhesive bonding of the plies, e.g. in a dot pattern, as continuos network or with adhesive applied all over the plies.

EXAMPLES

Example 1 Supercritical fluid (SF) extraction of pulp

[0050] This example describes, without limiting the invention, the extraction of pulp with CO_2 as the supercritical fluid.

Definition

[0051] Wood extractives are defined as the amount of material, which can be extracted from a virgin fibre pulp sample with neutral organic solvents (e.g. hexane, dichloromethane). The method described within this example illustrates a procedure to extract such components by means of supercritical carbondioxide being as efficient as conventional solvent extraction methods.

Principle

[0052] The pulp sample is homogenised and packed into a sample cartridge. The cartridge is placed in the extractor (1) in the sample cell (2) where it is extracted by carbondioxide at a specific temperature and pressure. The resulting

extract is trapped and collected in a vial (6) filled with dichloromethane (DCM) (figure 1).

Reagents

[0053] Carbondioxide, CO_2 (Air Liquide, SFC quality) pressurised with 110 bar helium and DCM (Riedel deHaën, p. a. quality). The pulp used in this particular example is bleached sulphite pulp "Excellent" from SCA Hygiene Products GmbH in Mannheim.

Apparatus

[0054] A principal drawing of an extractor to use in this invention is illustrated in figure 1. This figure is not intended to limit the invention.

[0055] ISCO SF 3560 with two pumps and automated extractor (figure 1)
Sample cartridge for use at high temperature (crystalline polymer)
Collection vials 20 ml
Balance with an accuracy of 0.0001 g
Vials 4 ml

Sample preparation

[0056] Dry the collection vials at 100°C. The vials are cooled in a vacuum dessicator after drying and weighed to the nearest 0.0001 g. The dry matter of the pulp is determined according to ISO 638:1979. An exact amount of the sample is weighed to the nearest 0.0001 g into the sample cartridge (a rod can be used for this purpose).

Extraction

[0057] The sample cartridges are placed in the extractor. The weighed collection vials are also placed in the extractor. A computer file describing the method for extraction of fibre pulp is loaded from the control unit of the extractor.

[0058] This method file uses the following extraction parameters:

Extraction chamber temperature	80°C
Extraction chamber pressure	448 bar
Restrictor temperature	80°C
Collection temperature	30°C
Restriction flow (CO_2)	1.5 ml/min
Extraction time	40 min
Collector solvent	Dichloromethane

[0059] After completed extraction the collection vials are evaporated under nitrogen gas flow to dryness. The vials are subsequently dried in a vacuum drying oven at 40°C for three hours. The vials with the dried extract are then weighed to the nearest 0.0001 g.

Extract content

[0060] The extract content is calculated according to formula A below A.

$$\text{Extract content \%} = \frac{(We-Wc) \times 100}{Ws \times DM}$$

We = Weight of collection vial + dried extract
Wc = Weight of collection vial
100 = Conversion factor for %
Ws = Weighed amount of sample for extraction
DM = Dry matter of pulp sample

[0061] Results are shown in figure 3a. The results show that the method according to the invention is at least as sufficient as the DCM method.

Example 2

Comparison of supercritical CO_2 extraction and solvent extraction with dichloromethane.

[0062] This example is a comparison between super critical CO_2 extraction and solvent extraction with dichloromethane (DCM) of different pulp materials. For the DCM extraction a standard method (SCAN C 7:62) was used where the pulp is refluxed with DCM in a soxhlet apparatus for six hours followed by a graviometric determination of the extract content.

[0063] The pulp samples are prepared according to the invention with the method described in Example 1. The total extract content and the composition of the extractives in the extracts are shown in figure 3.

[0064] From the results shown in figure 3a, it appears that the SF-CO_2 extraction is as effective as the solvent extraction with respect to the total extract content. From figure 3b it appears that certain compositions are preferably extracted with SF-CO_2 compared to the conventional method using DCM. In particular, the low level of extracted lignin after using the SF-CO_2 method shows that the method is very selective in removing wood extractives.

[0065] Also seen in figure 3 is the increase in percentage extracted sterylesters and triglycerides out of the total percentage extractives, viz. ~55% triglycerides when using SF-CO_2 compared to ~15% when using DCM, *i.e.* > three times more when using SF-CO_2. Also, conventional methods extract large amounts of less defined compounds, about 40% in this particular example with DCM as extraction fluid. Since highly hydrophobic compounds like sterylesters and triglycerides effect the absorption rate in a negative way, an increased removal of such compounds is of high value for the present invention. Results are shown in figure 3b.

Example 3

Measurement of absorption rate before and after extraction with CO_2

[0066] This example describes the absorption rate in sheets prepared from extracted or unextracted sulphite pulp.

Definition

[0067] Absorption rate is the mean velocity with which a liquid drop of a defined volume is fully absorbed into a paper sheet. The mean velocity is calculated in that the defined volume is divided by the time needed for the liquid drop of the defined volume to be fully absorbed into the paper. The absorption time needed is dependent on both the wettability *i.e.* surface chemistry and the basis weight, *i.e.* network structure of the cellulose fibres used.

Principle

[0068] A tissue sheet made from a dynamic sheet former called Formette was used in a lab scale equipment for the manufacturing of Formette sheets. The absorption was measured using a high-speed video system.

Material

[0069] Extraction of sulphite pulp as in Example 1. Fibres were extracted twice, but no significant amount of extractives was removed in the second extraction. Formette sheets of unextracted or extracted sulphite pulp with a basis weight of 36.7 and 40.8 g/m^2 respectively. No additives such as wet strength agents were added and the materials are uncrept. Liquid to be absorbed in this example is water.

Apparatus

[0070] High speed video (MotionScope, Redlake Imageing, model PCI 500 S). A Plexiglass plate is used as a sample support.

Procedure

[0071] The drop volume is 5µl and the number of drops measured is 10. The distance between drop and sample surface before application of drop is 5 mm and each drop is applied and measured on an individual and well separated spot.

Analysis

[0072] The absorption rate is measured using the high-speed video system. The measurements are not made under climatised conditions. The temperature is normally varying between 20-25° C while the relative humidity normally varies between 30-75%. Therefore one should pay most attention to the difference between materials measured at the same occasions, *i.e*. under the same conditions rather than comparing absolute numbers of absorption time and rate from different occasions. Due to the variation in basis weight, normalised absorption times have also been calculated, assuming a linear relationship with decreasing values between the basis weight and the absorption time *i.e*. the higher the basis weight, the lower the absorption time.

Normalisation of absorption times	$T_{measured} * (W_{measured}/W_{aimed})$ where W=basis weight (g/m^2) (W_{aimed} is in this case 40 g/m^2)
Calculation of relative change in absorption time	$((T_{extracted} - T_{unextracted})/T_{unextracted})* 100$ where T = absorption time (ms)
Calculation of absorption rate	r = V/T where V = volume of a drop (in this case 5 µl)
Calculation of relative change in absorption rate	$((r_{extracted} - r_{unextracted})/ r_{unextracted}) * 100 = T_{unextracted}$ $(1/T_{extracted} - 1/ T_{unextracted}) * 100$

[0073] Results (average value of 10 drops) are shown in figure 4. The difference between the unextracted and extracted samples obtained the same day are all significant (95% confidence interval), where the extracted samples show a faster absorption time. As seen in figure 3, the relative decrease in absorption time as well as the relative change in absorption rate is improved already after two days. Also, the results show an improvement over time. Due to variations in temperature and relative humidity, one should pay most attention to the difference between materials measured at the same occasions, *i.e.* under the same conditions rather than comparing absolute numbers of absorption time and rate from different occasions.

Example 4

Method for the determination of wood extractives in papermaking

[0074] This procedure refers to a published method (Örså, F and Holmbom, B. *J. Pulp and Paper Sci*. 1994, 20: J361-J365). This analytical procedure has been developed to enable a quantitative determination of wood extractives and lignins in papermaking processes. As used in present invention, extraction with supercritical carbon dioxide replaces published extraction step with methyl tert.butyl ether (MTBE). Sililation and gas chromatography (GC) for the determination of extractives follow the extraction procedure. A short thin-film capillary column enables direct determination of free fatty and resin acids, sterols, steryl estes, triglycerides and lignanes. All samples are determined quantitatively relative a standard.

Claims

1. A method for reducing the level of or substantially removing wood extractives comprising contacting the fibres with a supercritical or near supercritical fluid to extract the wood extractives and removing the extract from the fibres so as to obtain improved cellulose fibres with a reduced content of extractives.

2. The method according to claim 1, wherein the supercritical or near supercritical fluid is selected from the group consisting of carbon dioxide, ethane, ethylene, propane, propylene, cyclohexane, isopropanol and chlorotrifluoromethane.

3. The method according to claim 2, wherein the supercritical or near supercritical fluid is carbon dioxide.

4. The method of any of the preceding claims, wherein the contacting of the cellulose fibres with the supercritical or near supercritical fluid is made under conditions where the temperature is at least T_C for said supercritical or near supercritical fluid, or at least about 1.5, such as at least about 2 times higher than T_C and/or the pressure is at least P_C for said supercritical or near supercritical fluid, or at least about 2, at least about 3, at least about 4, at

least about 5 such as at least about 6 times higher than P_C.

5. The method according to any of the preceding claims, wherein the wood extractives in the extract are substantially hydrophobic substances.

6. The method according to claim 5, wherein the wood extractives in the extract comprise hydrophobic substances selected from the group consisting of fatty acids, resin acids, sterylesters and triglycerides defined according to an analytical procedure for quantitative determination of wood extractives and lignins as defined according to the method in Example 5.

7. The method according to any of the preceding claims, wherein the wood extractives in the extract comprise substances selected from the group consisting of lignin or sterols defined according to an analytical procedure for quantitative determination of wood extractives and lignins as defined according to the method in Example 5.

8. The method according to any of the preceding claims, wherein the wood extractives are substances which are defined according to the method in Example 2.

9. The method according to any of the preceding claims, wherein the extracted wood extractives are collected in an organic solvent.

10. The method according to claim any of the preceding claims, wherein the ratio calculated between the total extract content - measured according to Example 1 - and the extract content obtained by a standard method SCAN C 7: 62 is at least about 0.5 such as at least about 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.85, 0.90 or about 0.95.

11. Cellulose fibres obtainable by the method claimed in any of claims 1-10.

12. Cellulose fibres having a reduced level of or being substantially free from wood extractives, which impart - due to ageing - decreased absorption rate to the cellulose fibres.

13. Use of cellulose fibres according to any of claims 11 or 12 for the production of a fibrous web.

14. Use of cellulose fibres according to any of claims 11 or 12 for the production of an absorbent product.

15. An improved fibrous web comprising cellulose fibres according to any of claims 11 or 12.

16. The fibrous web according to claim 15, wherein the improved fibrous web at least after an initial period of time of at least about two days, has a higher liquid absorption rate, such as least about 5, 12, 20, 30 or about 50% higher rate, than the parent cellulose fibres as evidenced by the method described in Example 3.

17. A fibrous web comprising cellulose fibres, which have a reduced level of or is substantially free from wood extractives, which impart - due to ageing - decreased absorption rate to the cellulose fibres.

18. Use of a fibrous web according to any of claims 15-17, for the production of an absorbent product.

19. A method for reducing the level of or substantially removing wood extractives comprising contacting the fibres with a supercritical or near supercritical fluid to extract the wood extractives and removing the extract from the fibres so as to obtain improved cellulose fibres with a reduced content of extractives, wherein an improved fibrous web of said cellulose fibres is prepared and wherein the improved fibrous web at least after an initial period of time of at least about two days, has a higher liquid absorption rate, such as least about 5, 12, 20, 30 or about 50% higher rate, than the parent cellulose fibres as evidenced by the method described in Example 3.

20. An absorbent product comprising cellulose fibres according to any of claims 11 or 12.

21. An absorbent product comprising cellulose fibres, which have a reduced level of or is substantially free from wood extractives, which impart - due to ageing - decreased absorption rate of the absorbent product.

22. Absorbent product according to any of claims 20 or 21, wherein the product is a cellulose tissue paper, sanitary napkin or towel, nonwoven industrial wipes, baby diaper, incontinence garments.

23. Stratified absorbent product comprising cellulose fibres according to any of claims 11 or 12 or a fibrous web according to any of claims 15-17, comprising at least one outer layer and possibly at least one middle layer, the outer layers having a high amount of improved cellulose fibres.

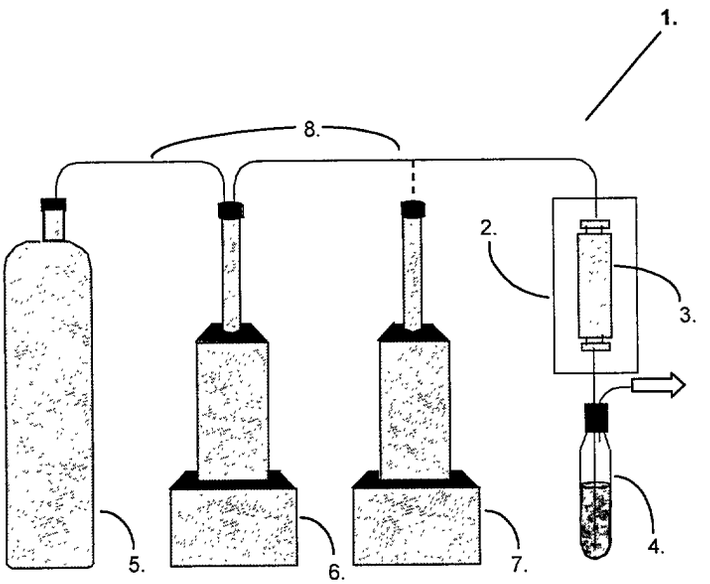
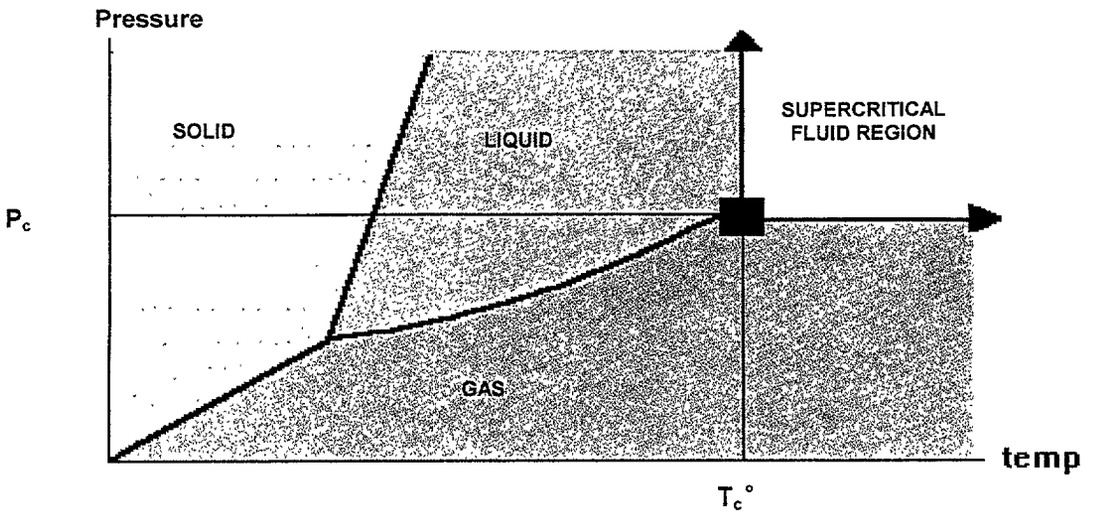


Figure 1



$T_c = 31.1°$ C

$T_p = 73.8$ bar

Figure 2

Table 2

Sample	Solvent extraction – Dichloromethane	SF-CO_2 extraction 6500 psi, 80°C
Mechanical pulp – TMP	0.80 %	0.70 %
Kraft pulp	0.12 %	0.09 %
HTCTMP	0.11 %	0.10 %
TCF Kraft pulp	0.05 %	0.03 %

Figure 3a

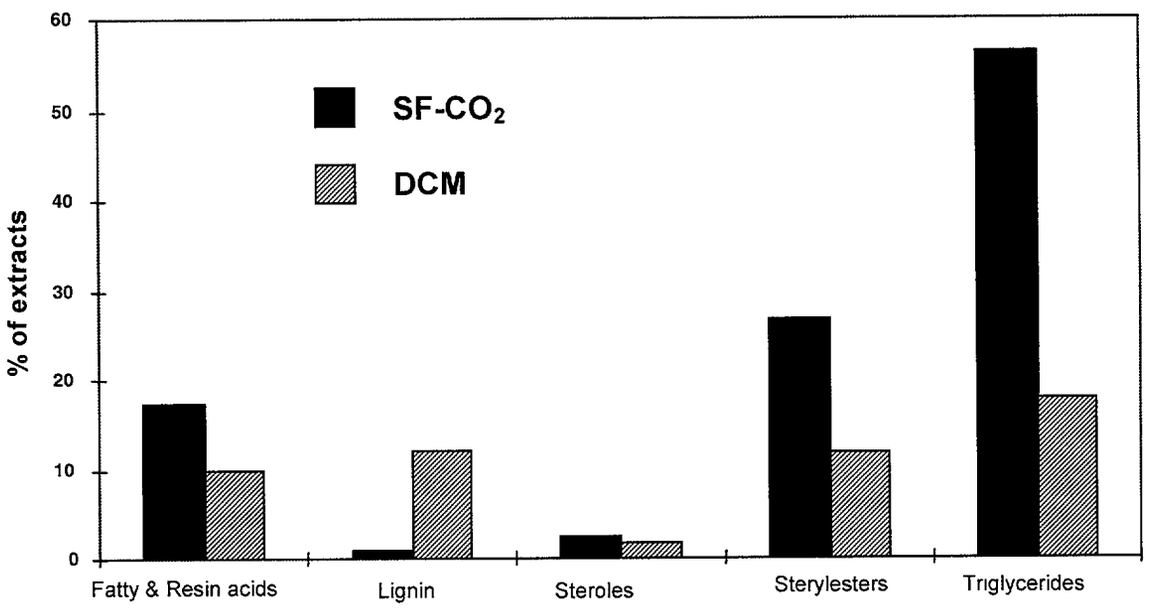


Figure 3b

Table 3[a]

	Absorption time (ms)				
Ageing time:	Fresh	2 days	19 days	98 days	185 days
Unextracted (Unex.)	296	431	535	452	474
Extracted (Ex.)	251	318	393	276	311
Unextracted normalised (UnExnorm)	272	395	491	415	435
Extracted normalised (Exnorm)	256	324	401	282	317
Difference = Exnorm. – UnExnorm.	-16	-71	-90	-133	-118
Relative change in absorption time (based on normalised values)	-5.9	-18	-18	-32	-27
Relative change in absorption rate (based on normalised values)	6%	22%	22%	47%	37%

[a] All values are calculated as a mean value of 10 drops, each 5µl.

Figure 4

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 85 0190

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D21C
B01D
A61L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13 March 2001	Bernardo Noriega, F

CATEGORY OF CITED DOCUMENTS

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