



(86) Date de dépôt PCT/PCT Filing Date: 2013/07/01
(87) Date publication PCT/PCT Publication Date: 2014/01/16
(45) Date de délivrance/Issue Date: 2020/04/28
(85) Entrée phase nationale/National Entry: 2015/01/07
(86) N° demande PCT/PCT Application No.: FI 2013/050723
(87) N° publication PCT/PCT Publication No.: 2014/009604
(30) Priorité/Priority: 2012/07/11 (FI20120229)

(51) Cl.Int./Int.Cl. *C08B 37/14* (2006.01),
B01J 3/00 (2006.01), *D21C 1/02* (2006.01),
D21C 1/10 (2006.01)
(72) Inventeur/Inventor:
VON SCHOULTZ, SEBASTIAN, FI
(73) Propriétaire/Owner:
CH-BIOFORCE OY, FI
(74) Agent: ROBIC

(54) Titre : PROCEDE POUR L'EXTRACTION DE BIOMASSE
(54) Title: METHOD FOR EXTRACTING BIOMASS

(57) **Abrégé/Abstract:**

Method for extraction of biomass with water in order to separate hemicelluloses from a fibrous structure. According to the invention the biomass is impregnated under reduced pressure with the extraction fluid in order to prevent the degradation of the components to be extracted. During extraction the extract is circulated through the fiber matrix in order to remove unwanted components from the extract. According to the invention the extract is reused for extracting untreated biomass in order to increase the consistency of the extract.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



WIPO | PCT



(10) International Publication Number
WO 2014/009604 A1

(43) International Publication Date
16 January 2014 (16.01.2014)

(51) International Patent Classification:

C08B 37/14 (2006.01) *D21C 1/02* (2006.01)
B01J 3/00 (2006.01) *D21C 1/10* (2006.01)

(21) International Application Number:

PCT/FI2013/050723

(22) International Filing Date:

1 July 2013 (01.07.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

20120229 11 July 2012 (11.07.2012) FI

(72) Inventor; and

(71) Applicant : VON SCHOULTZ, Sebastian [FI/FI];
Levontie 197, FI-21600 Parainen (FI).

(74) Agent: ÖHMAN, Ann-Marie; Kaivokatu 15 B 23, FI-20520 Turku (FI).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,

DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: METHOD FOR EXTRACTING BIOMASS

(57) Abstract: Method for extraction of biomass with water in order to separate hemicelluloses from a fibrous structure. According to the invention the biomass is impregnated under reduced pressure with the extraction fluid in order to prevent the degradation of the components to be extracted. During extraction the extract is circulated through the fiber matrix in order to remove unwanted components from the extract. According to the invention the extract is reused for extracting untreated biomass in order to increase the consistency of the extract.



WO 2014/009604 A1

Method for extracting biomass

Field of the invention

5 The present invention relates to a method for extracting sugars and derivatives thereof and the corresponding polysaccharides especially hemicelluloses from lignocellulosic biomass with hot water. In particular the present innovation concerns a method to produce high concentration of high purity hemicellulose extract with minimal use of water. The extract is circulated through the biomass several times
10 and as a result the concentration of the hemicelluloses in the water phase is increased. The circulating loop is vital in order for the non-hemicellulose material, such as lignin, to be adsorbed back to the biomass. The circulation also enables gentle extraction conditions regarding temperature, pressure and pH as the method does not require maximum extraction during the first extraction loop. Minimal
15 oxidation and degradation of the hemicelluloses is achieved by removing virtually all of the air and especially oxygen gas from inside of the pores of the biomass during a impregnation step assisted by reduced pressure. The concentration of the extract is increased by using the same extract in several extractions of new and previously un-extracted biomass.

20

Description of Related Art

Wood based biomass contains about 25% of hemicelluloses. Extraction of biomass is a very well known process and has traditionally been extracted with alkali.
25 During this kind of treatment hemicelluloses are degraded and the fibrous material is decomposed.

Traditional extraction with only hot water degrades the sugars into toxic compounds such as furfural.

30

Steam explosion is another well known method for extracting carbohydrates from biomass. However, even this method involves the formation of toxic compounds.

A recent method for extracting hemicelluloses from biomass involves continuous flow of hot water extraction. The problem with this method is, that it produces a very diluted extract containing up to 30% lignin impurities (WO 2009/122018 and
5 Leppänen et al.: Pressurized hot water extraction of Norway spruce hemicelluloses using a flow-through system, Wood Sci Technol (2011) 45:223–236)

All the known extraction methods of hemicelluloses results in extremely low solids content of the extract, and require expensive concentration of the extract. This
10 results in an economically unsound product for transport and further treatment. (WO0034568, US2008029233, US8136747, DE3225074).

A recent patent publication WO2007090926 describes a method for recovering hemicelluloses with higher concentration through steam hydrolysis. The drawback
15 with this approach is that hydrolysis always involves deacetylation of the hemicelluloses which effectively lowers their water solubility and also degrades the polymers by lowering the molar mass. Chemical and food industry are interested in polysaccharides with high molar mass which the aforementioned method is unable to provide.

20 Publication WO0061276 discloses a method for hydrolysis of hemicelluloses primarily into monomeric sugars which is a drawback especially if polymers are desired.

25 The main problem with known methods is the fact that they do not efficiently prevent oxidation, hydrolysis, degradation and deacetylation of the biomass. Especially the presence of air and oxygen gas inside of the pores of the biomass has prevented an efficient and gentle extraction procedure. Traditionally biomass impregnation and air removal from inside of biomass capillaries has been for
30 example achieved through presteaming of biomass with high temperature steam and high pressure. However, this procedure causes oxidation and hydrolysis of

hemicelluloses and is therefore unsuited for extracting hemicelluloses without degradation.

Summary of the Invention

It is an aim of this invention it to overcome the problems related to known art and to provide an improved method for extracting biomass with water.

- 5 In particular, it is an aim of the invention to provide a method which effectively minimizes oxidation and degradation of the biomass extract.

It is further an aim to provide a method to concentrate and purify the extract with minimal water consumption, without the need for expensive evaporation and purification steps.

- 10 More specifically, the invention provides a method for treating a biomass containing a fibrous structure and polysaccharides, comprising:

- subjecting the biomass to extractive treatment in which the biomass is heated in aqueous phase at a pressure below 8 bar and at a temperature under 160°C, for separating the polysaccharides from the biomass;

wherein:

- 15 - the biomass is impregnated with the extraction water under reduced pressure of at least 0.3 bar under pressure, prior to extraction;

- oxygen gas level is kept at a minimum throughout the extraction by continuous recirculation of the extract through the biomass;

- 20 - the polysaccharide rich extract is separated from the biomass into a oxygen gas reduced environment as a first fraction;

- the fibrous structure of the biomass is recovered as a second fraction;

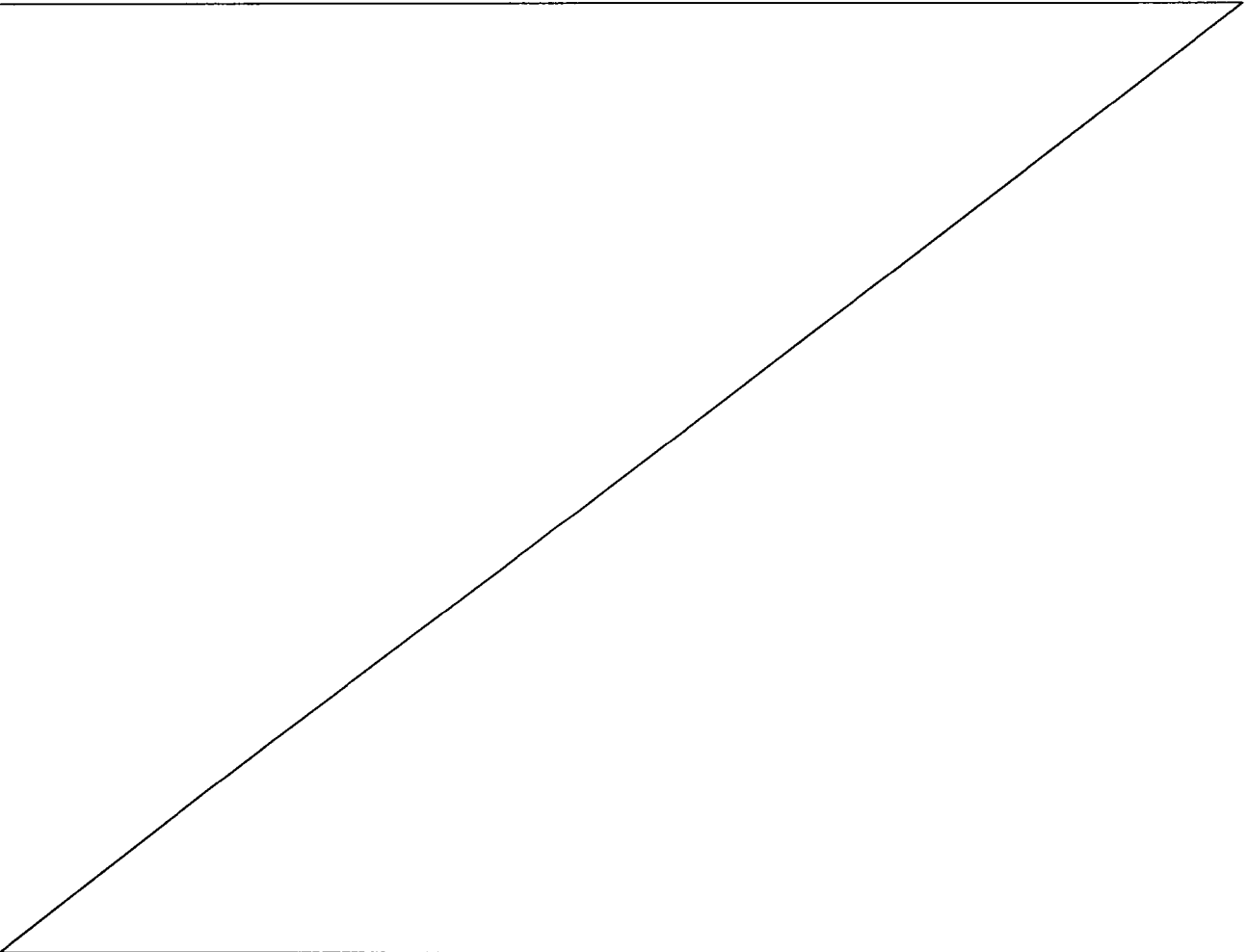
- the extract is reused for the extraction of un-extracted biomass; and

- at least one of the fractions is subjected to further treatment.

Detailed Description of the Invention

The present invention is based on the finding that air and more specifically oxygen gas causes severe oxidation and degradation of sugars and polysaccharides at high temperatures. Reducing the air pressure inside of a reactor containing biomass, following the filling of the reactor with water
5 effectively fills the capillaries of the biomass resulting in an almost completely oxygen free environment inside of the biomass.

The present invention is further based on the finding that recirculation of the extract through the biomass purifies the extract from unwanted compounds such as lignin and other polyphenols. The presence of phenolic substances such as lignin in the extract lowers the capacity of microbes to
10 digest polysaccharides and therefore the production of biofuels becomes less economical.



The method according to the invention allows a long time for the extract to be kept at high temperatures without significant oxidation and degradation of the molecules and polymers in the extract. This further allows the extract to be reused for
5 extraction of un-extracted biomass which enables the consistency of the extract to be increased significantly without evaporation of the solvent.

By removing hemicelluloses from the fiber fraction the energy value and the lignin content of the biomass increases. At the same time the fiber fraction properties
10 become more suitable for the making of pellets and chipboards.

Therefore, present invention comprises of the steps:

- Feed the biomass into an reactor
- Remove most of the air and oxygen gas from the biomass by reducing the
15 pressure inside of the reactor
- Impregnate the biomass with the extraction water. During the first extraction this is plain water and in later extractions this is the extract from the previous extraction
- Start circulating the extraction water through the biomass
- 20 - Increase the temperature to extraction temperature
- Circulate the extraction fluid until desired consistency and purity is reached
- Remove the extraction water from the reactor
- Remove the biomass from the reactor
- Start over from the first step

25

Examples

The effect of extract circulation and impregnation under reduced pressure (0.8 Bar under pressure) was investigated. The biomass was 200 grams (O.D.) of Scott spine
30 chips (Pinus Sylvestris). The water to wood ration was 5:1. The extraction water was kept at 150°C for two hours. In experiments with circulation, the extract had circulated 10 times through the biomass. The pH of the extract was measured every

half hour. In experiments where the biomass was impregnated, hence most of the air and oxygen gas was removed from the reactor, no changes in pH could be noted. In experiments without impregnation under reduced pressure a significant pH drop, typically over one pH unit was recorded. This indicated that the formation of acids, especially through deacetylation of the biomass did not occur in the experiments with impregnation. The yield of the extractions is shown in Figure 1. The extracts were analyzed by gas chromatography for carbohydrates (SundbergA, SundbergK, Lillandt C, HolmbomB (1996) Determination of hemicelluloses and pectins in wood and pulp fibers by acid methanolysis and gas chromatography. Nord Pulp Pap Res J11(4):216-219) and lipophilic extractives (F. Örså, B. Holmbom and J. Thornton, Wood Sci. Technol. 31 (1997) 279). Lignin was determined according to the method by Iiyama et al. (Iiyama, K.; Wallis, A. F A. An improved acetyl bromide procedure for determining lignin in wood and wood pulps. Wood Sci. Technol. 1988, 22, 271-280). The samples without impregnation and circulation contained 55% hemicelluloses, 35% lignin and 5% lipophilic extractives and 5% unidentified. Samples without impregnation and with circulation contained 90% hemicelluloses, 1.5% lipophilic extractives and 8.5% unidentified. Samples with impregnation and circulation contained 96% carbohydrates and 0.5% lipophilic compounds. The remaining 3.5% was unidentified. The results clearly show that the circulation removes most of the initially released lignin and extractives. The impregnation and air and oxygen removal procedures clearly increases the extraction yield and reduces the amount of unidentified components which are most likely oxidized lignin fragments. By comparing the extract composition when using both impregnation and circulation with an extract produced according to the method described in WO2009122018, we can clearly see the benefits of using the method described in this document (Figure 2). This method produces an extract without unwanted impurities, especially lignin.

Figure 1 shows the extraction yield of six different extractions:

- two without impregnation under reduced pressure and without circulation of extract

- two without impregnation under reduced pressure but with circulation of the extract
 - two with impregnation under reduced pressure and circulation of the extract.
- 5 Oxidation of the extracted components was prevented by keeping the extract in oxygen gas reduced environment. Extracting under minimized presence of oxygen gas produces a clear yellow and transparent extract. However, if the extract comes in contact with oxygen gas, it turns dark brown within minutes and the oxidization will continue even at room temperature. Extracts which were removed from the
- 10 reactor into nitrogen saturated environment did not show signs of oxidization nor did the color of the extract change.

By reusing the extract from previous extraction the consistency of the extract could be increased significantly by each batch without any significant changes in the pH

15 of the extract or the molar mass and composition of the carbohydrates. Figure 3 shows the consistency increase of the extract by reusing the extract.

Claims

1. A method of treating a biomass containing a fibrous structure and polysaccharides, comprising:

- subjecting the biomass to extractive treatment in which the biomass is heated in aqueous phase at a pressure below 8 bar and at a temperature under 160°C, for separating the polysaccharides from the biomass;

wherein:

- the biomass is impregnated with the extraction water under reduced pressure of at least 0.3 bar under pressure, prior to extraction;

- oxygen gas level is kept at a minimum throughout the extraction by continuous recirculation of the extract through the biomass;

- the polysaccharide rich extract is separated from the biomass into a oxygen gas reduced environment as a first fraction;

- the fibrous structure of the biomass is recovered as a second fraction;

- the extract is reused for the extraction of un-extracted biomass; and

- at least one of the fractions is subjected to further treatment.

2. The method according to claim 1, wherein said temperature is about 150°C.

3. The method according to claim 1 or 2, wherein the polysaccharide rich extract comprises oligomers and polymers.

4. The method according to claim 3, where the polysaccharide rich extract is hydrolyzed or used as food for microbes in the production of fuel or as raw material for chemical products.

5. The method according to claim 1, where the second fraction is further treated to separate lignin from the fibrous structure.
6. The method according to claim 1, where the second fraction is used for the production of paper and cardboard.
7. The method according to claim 1, where the second fraction is used for the production of pellets or as raw material for fuel.
8. The method according to claim 1, where the second fraction is used for the production of particle board.
9. The method according to any one of claims 1 to 8, wherein the biomass is wood-based.
10. The method according to claim 9, wherein said wood-based biomass comprises chips or sawdust.
11. The method according to claim 9 or 10, wherein said wood-based biomass comprises, crushed chips.
12. The method according to any one of claims 1 to 8, wherein the biomass is non-wood.
13. The method according to claim 12, wherein said non-wood biomass is bagasse or straw.

1/2

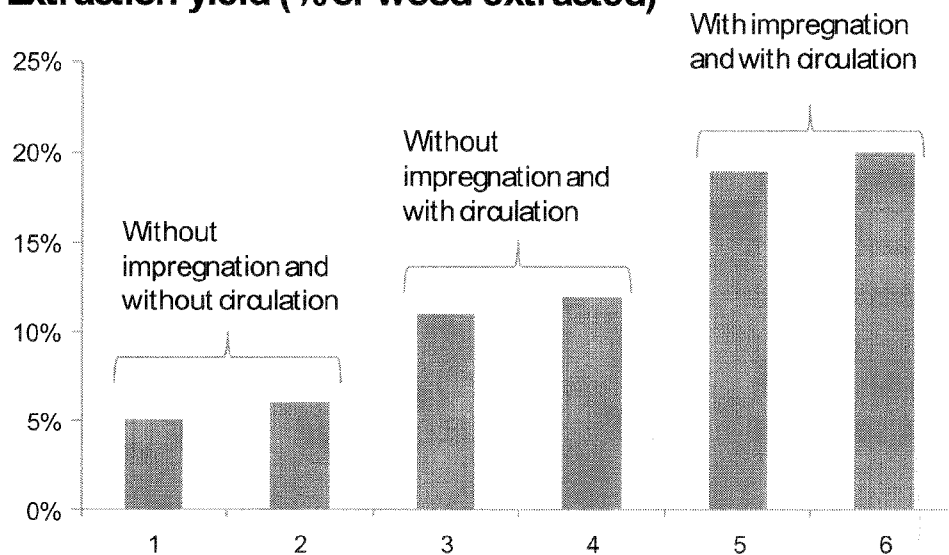
Extraction yield (% of wood extracted)

Figure 1. The effect of vacuum impregnation of biomass and circulation of the extraction water.

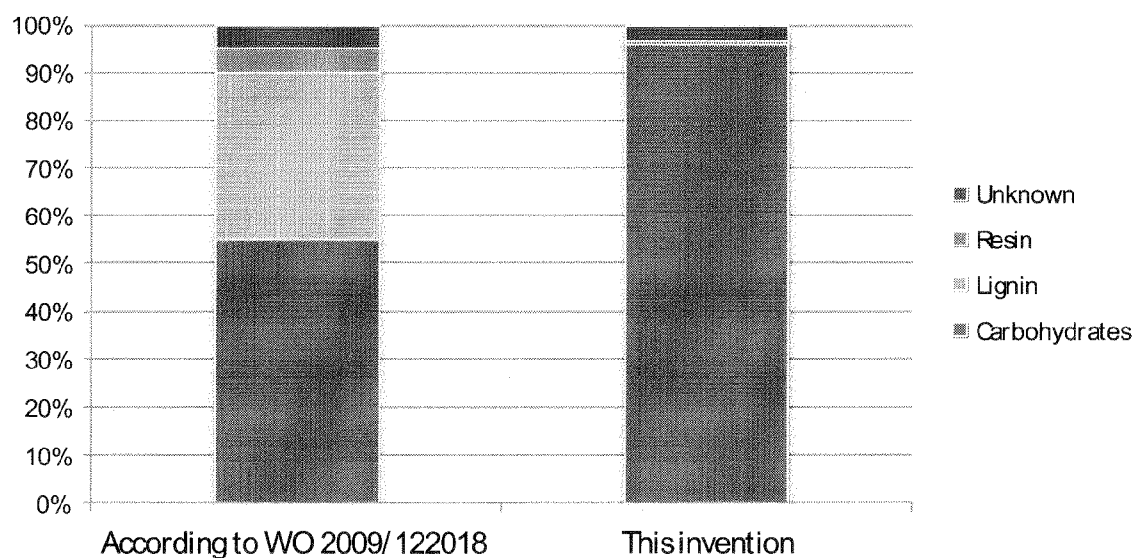
Percent of extract dry solids

Figure 2. Extract composition according to method described in WO2009122018 and in this invention.

2/2

Solids content of extract

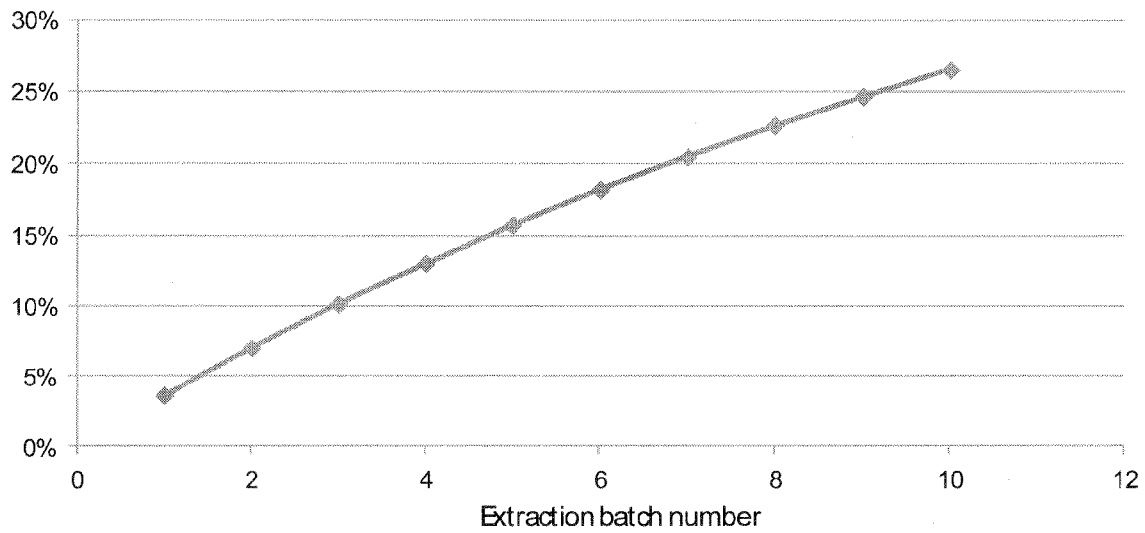


Figure 3. Solids content increase as a result of the reuse of extraction water in multiple extractions.