Evaluation of the technical and environmental performances of extraction and purification processes of arabinoxylans from wheat straw and bran

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A B S T R A C T

A process for hemicelluloses fractionation and purification from wheat straw and bran has been investigated and technical considerations (yields, purity) have been coupled to environmental characterizations (water consumption, carbon dioxide emissions) in order to develop an environment-friendly process. Extraction by twin-screw extrusion gave a yield in arabinoxylans equal to 8.5% (weight of (arabinose + xylose) in the extract after fractionation/dry weight of the destarched bran). The extraction of 86 kg of straw and bran (with a ratio 6.2:1) with 5.8 kg of NaOH in pellet form resulted in the production of a complex extract containing 1.0 kg of arabinoxylan polymer, which required concentration and purification steps. Evaporation (EV) followed by ethanol precipitation (P) and freeze-drying (FD), gave a yield in hemicellulosic powder of 36.5% (dry weight of powder/dry weight of extract after liquid/solid separation) with a total sugar content equal to 48.4% but also used a large amount of ethanol. The other studied purification process was based on a combination of ultrafiltration (UF), anion exchange chromatography (CHR) and spray-drying (SD). It gave a yield in hemicellulosic powders of 24.6% and a total sugar content equal to 28.7%. The technical performances of the second process appear to be less attractive but with a lower energetic and ethanol consumption. Thus secondly the environmental impacts (water consumption and CO_2 emission) of the ultrafiltration step were quantified. Life Cycle Assessment data (Ecoinvent) were used to convert materials used for the infrastructure and energy consumed during functioning into carbon dioxide emissions and water consumptions. Results have shown that environmental impacts due to the operating conditions are higher than those relative to raw material involved in the installation. The study showed that this kind of approach allows the determination of optimum conditions for the ultrafiltration step.

1. Introduction

Wheat straw and bran, as well as other cereal by-products are a large source of cell-wall polysaccharides such as hemicelluloses, cellulose and lignin. A proportion of this is used in animal feed and paper production, but the main part is discarded as a waste product [1]. Hemicelluloses are made of a β-(1–4)-xylan backbone with branching α-L-arabino-furanosyl groups [2]. This polysaccharide has the potential to be integrated into a wide variety of applications, such as film-former substances, thickeners, adhesives, emulsifiers, stabilizers and binders in the food, pharmaceutical and cosmetics industries [2–4]. Therefore, recovery processes has been studied for a long time and the literature propose diverse multistep extraction and purification procedures to isolate xylans from annual plant fibres and seeds coats [5]. Different solvents could be used as barium hydroxide [6], dimethyl sulfoxide [7], alkali hydroxide solutions [8–10]. Alkaline treatment is one of the more widespread processes. It disrupts the cell walls by hydrolyzing ester linkages between the hemicelluloses and the other parietal components and dissolving the hemicelluloses, lignin and silica. The liberated hemicelluloses can then be recovered in aqueous media [3] with a hemicelluloses extraction yield of 50% after 2 h in 1% NaOH solution [11]. Higher recovery yields can be obtained but with longer residence time [12]. Thus, other extraction technologies have been studied to improve the recovery efficiency like steam explosion [13,14] or chemical extraction assisted by ultrasonication [15]. Steam explosion can achieve high extraction yields, but results in

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hydrolytic depolymerisation of hemicelluloses, which is attractive for alcoholic fermentation or xylose transformation [16], but not for hetero-polysaccharides isolation [17]. Many different purification treatments have been studied such as microfiltration [10] and ultrafiltration [18] but it appears that the isolation and purification of water and alkali soluble biomass solids requires pre-treatment with hydrogen peroxide prior to precipitation or ultrafiltration. Furthermore, xylans in powder form may be recovered by freeze drying or spray drying from an aqueous solution or suspension [17]. However, even if the extraction of hemicelluloses at pilot scale has been studied by few authors [10,19,20], it needs to be developed at industrial scale [16]. Because it is a continuous process, which could be scaled up at industrial scale, twin-screw extrusion was investigated for straw/bran co-extraction using sodium hydroxide. This technique combines chemical, thermal and mechanical actions to remove the dissolved molecules from the plant tissue by continuous squeezing in the screw press [20] and it has proved to be a very good method of alkaline extraction of hemicelluloses from wheat bran [21]. This technique presents lower extraction yields and selectivity than batch extraction but it has the advantage to be continuous and to require lower amounts of reagents and water [13,21]. The twin-screw fractionation leads to the production of complex solutions containing the biopolymers but also their breakdown products and the co-extracted molecules (proteins, lignin, and inorganic salts). This makes important the development of purification steps but could be difficult because it can involve a combination of many steps, which could be expensive and un-environmentally friendly [18]. Until now, processes for the fractionation and purification of interesting compounds from plant matter were mainly designed with the aim of increasing yields and purity and reducing production costs [22–24]. Even if some efforts have been made to reduce the amount of chemicals and energy consumption involved in the process, no methodology has been developed to analyse the environmental impacts of yield-improvement decisions and changes. Thus, more developmental efforts are needed on effective separation methods to improve the environmental impact of new processes. Today, more and more authors are interested in process environmental design [25,26] and legislation is increasingly in favour of "clean-processes", which makes the idea of taking into account yields, costs and environmental concerns when designing plant matter fractionation processes, very attractive.

The objective of this work was to evaluate processes for the fractionation and purification of wheat straw and bran hemicelluloses. Firstly, data was collected on extraction and purification methods such as twin-screw extrusion, membrane and chromatographic separation techniques. Results allowed comparison of different ways of obtaining hemicellulosic powders. Secondly, this data was used to assess the environmental impacts of the process, with the specific case of ultrafiltration being taken as an example, in order to design an environment-friendly process.

2. Materials and methods

2.1. Raw material and pre-treatments

The extrusion was carried out using same origin wheat bran and straw (Arteris, France). The dry matter content of the straw was 91.5%. Before extrusion, the bran was destarched by blending 25 kg for 15 min in ten volumes of water at 40 °C in a 300 L capacity, stirred reactor. Starch milk and starch-free bran were then separated three time by filtration to obtain starch-free bran with a starch content lower than 1% of dry matter weight. This bran was then dried at 45 °C for 24 h. Before extrusion, the starch-free bran was 93.4% dry matter content. Wheat straw was first crushed using a hammer crusher (Electra BC-P) fitted with a 6 mm sieve. Raw material compositions are given in Table 1.

Table 1
Composition of the initial plant matter.

	Wheat straw %[a]	Starch-free wheat bran %[a]
Dry matter content	91.5	93.4
Ash content	7.5	3.1
Organic content	92.5	96.9
Proteins (N*5.7)	2.1	14.1
Cellulose	29.2	14.8
Hemicelluloses	34.9	49.7
Lignin	17.8	5.3

[a] Expressed on the recovered dry matter.

2.2. Twin screw extrusion

Experiments were conducted using a co-penetrating and co-rotating twin-screw extruder (Clextral BC45). The 1.4 m-long barrel of the extruder was composed of seven modules with a dedicated profile for alkaline treatment of plant matter. Four of them (C, D, E and G) were heated by induction belts (5 kW) and water-cooled (500–1000 L/h). There were two reverse-pitch screw elements with grooved peripheral slots in the screw for leakage flow, and a series of 1 cm-long bilobal elements with neutral pitch splayed at 90° to each other, were used to knead the plant matter. The 10 cm-long filter element mounted on the last section was perforated with conical holes (1 mm inlet, 2 mm outlet). This filter element was used to optimise solid/liquid separation [20].

Wheat bran and sodium hydroxide were blended at room temperature for 1 h before extrusion. The initial liquid/solid ratio was 7 and was increased to 10 just before the extrusion. The mixture was injected into the extruder (B) by using an exocentric-screw pump (Nemo, 2NE40A). Straw was also added at this level using a screw feeder, and mixed with the alkaline dough in the first zone of the barrel through the neutral pitch element and the reverse-pitch screw element successively. Wash water was injected downstream from this zone (E) by a piston pump (Clextral, DKM K20-2-P32), and the mixture was carried through the second reverse pitch located just downstream of the filtration module.

This exact screw profile has been previously described [21] and the conditions of extrusion for optimal hemicellulose yields were as follows:

- Bran/NaOH = 2 (the weight of NaOH pellets is equal to 51.3% of the bran organic content, and 7.2% of the total organic content (straw + bran));
- Straw/Bran = 6.2;
- Screw rotation speed = 150 rpm;
- Wash water flow = 92 kg/h;
- Induction belt temperature = 50 °C.

Screw rotation speed and barrel temperature were monitored from a control panel.

2.3. Liquid/solid separation

Two techniques were compared for the liquid–solid separation of the extract produced during extrusion. Centrifuge filtration (Rousselet, RC50PXR) relies on the particle size difference. Batches of 20 kg of extract were introduced into a 34 L capacity tank equipped with a 10 μm porosity, 0.50 m^2 surface area polypropylene membrane. Particles were separated at 2000 rpm for 10 min.

A centrifuge separator (Alpha-Laval, CLARA20 LAPX 404) equipped with 400 μm spaced discs was used for clarifying the extract. The latter was introduced continuously at a flow rate of 100 L/h via an impeller pump (Schneider, Reform B-FU). Clarification was at 11,130 g, and separated sludge was drawn off every 8 min.

2.4. Concentration and purification process

2.4.1. Evaporation

The extract was concentrated by evaporation in a 300 L reactor with heater jacket (Tournaire). A vacuum pump lowered the pressure to −100 mbar and steam injected into the reactor's jacket (Aura, MAXI120) heated the extract to 40 °C.

2.4.2. Ultrafiltration apparatus

Filtration apparatus comprised a 36 L capacity feed reservoir, a rheostat controlled bilobal-pump, a filtration cartridge and a pressure gauge to allow manual membrane pressure adjustment. Manometers measured inlet and outlet membrane module pressure, and transmembrane pressure (TMP) is the average of these two values. The ultrafiltration (UF) membrane used for the alkaline extraction was a hollow fibre polyethersulfone type (GE Healthcare, UFP-30-C9A) with a molecular weight cut-off (MWCO) of 30 kDa and a surface area of 1.15 m^2. The module was 5.4 cm external diameter and 52 cm long. The extract was concentrated by percolation through the membrane at room temperature. The permeate flow rate was measured gravimetrically with an electronic balance.

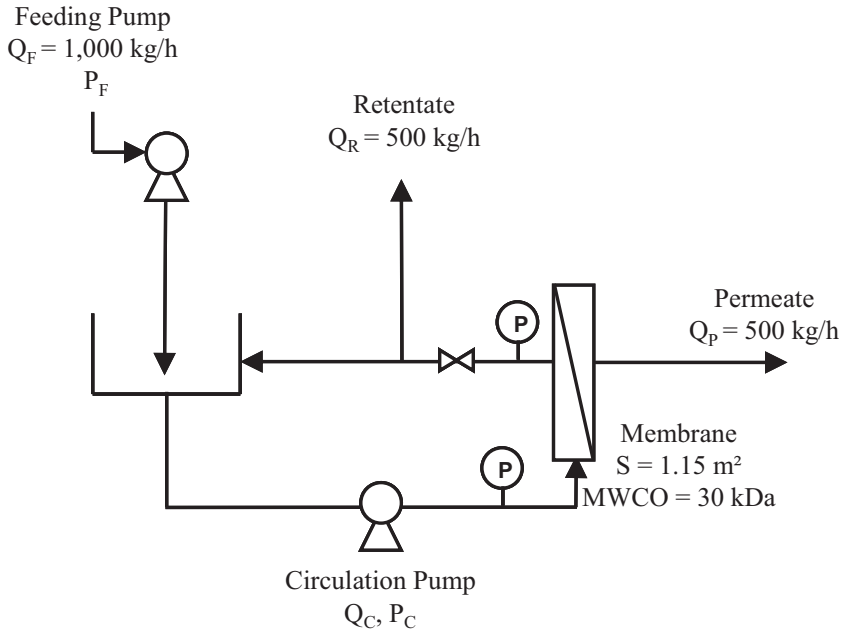

Fig. 1. Ultrafiltration apparatus.

2.4.3. Anion-exchange chromatography

Chromatography was performed with a strong anion-exchange resin (Rohm and Haas, Amberlite FPA 96A98Cl). Before use, 1 L of resin was degassed for 12 h in 2 L of stirred, demineralised water. Chromatography was on 10 L batches, the resin stirred with the extract for 30 min and separation between extract and resin performed by Büchner-filtration. Resin was then reconditioned using deionised water and regenerated with 2 L of 1 M sodium hydroxide solution.

2.4.4. Alcoholic precipitation

In order to recover hemicelluloses at different levels of treatment, the alkaline extracts were precipitated with acid and alcohol at different steps of the process. Acetic acid was added to the extract up to pH 5.5, followed by 3 volumes of ethanol for 1 volume of solution. The solution was then stored at 4 °C overnight to improve precipitation. Aggregated hemicelluloses were then recovered by wringing out the simple filtration cloth and then drying to obtain powders.

2.5. Obtaining powders

Hemicellulosic powders were obtained using two different methods: spray-drying or freeze-drying.

The extract was spray-dried in a Mini Spray-Dryer (Büchi, B-290) under constant operating conditions: inlet and outlet air temperatures 135 °C and 85 °C respectively, air pressure 470 L/h (6.35 bar) and feed rate 0.25 L/h.

For freeze drying (Cryo Rivoire, PILOT27), extract and precipitated hemicelluloses were placed in aluminium trays. The samples were cooled to −40 °C and the pressure was decreased to −300 mbar allowing sublimation of moisture content, which then froze in a cold-trap. The temperature was then gradually increased to 20 °C and dried samples recovered.

2.6. Analytical

Dry matter was gravimetrically determined at 103 °C for 24 h. The ash content was measured by thermogravimetric analysis after calcination at 550 °C for 5 h. Proteins (%N*5.7) were determined using a Kjeldahl automated device (Foss, Kjeltec 2200). Individual neutral sugars were analysed by gas-liquid chromatography (GLC) after hydrolysis (2 h in 4 N H_2SO_4 at 100 °C), and conversion of individual sugar into alditol acetates (rhamnose, fucose, arabinose, xylose, mannose, galactose, glucose). An estimation of the three parietal constituents contained in the solids (cellulose, hemicelluloses, and lignins), was made using the ADF-NDF method of Van Soest and Wine [27,28].

Powder colours were determined (International Commission of Illumination) using a Spectro-colorimeter (Konica Minolta, CM-508I). The powder colour was expressed three dimensionally using the $L^*a^*b^*$ system. The L value gives the relative powder luminance from total black ($L^* = 0$) to total white ($L^* = 100$). The a^* value represents the colour spectrum between red (positive values) and green (negative values) and the b^* value, that between yellow (positive values) and blue (negative values) [29].

All determinations were carried out in duplicate.

2.7. Environment-friendly design of the ultrafiltration step

Ultrafiltration was used as an example to illustrate an environment-optimised designed step, and the theoretical UF apparatus is shown in Fig. 1. A feed pump continuously supplied the extract and a circulation pump forced it to percolate through the ultrafiltration membrane. Due to data availability, the following membrane compositions were considered: polypropylene (PP) for the UF fibre (1 kg/module), acrylonitrile–butadiene–styrene (ABS) for the membrane extremities (0.16 kg/module), and polyurethane (PU) for the external part of the module (0.22 kg/module). Membranes are considered to have an average life in use of 10,000 h. The volume concentration factor achieved is 2.

The methodology used compared scenarios under different conditions, implying definition of a functional unit (FU) as a reference, and this was defined as: "Concentrating 1000 kg of extract/h with a volume concentration factor of 2". The influence of circulation flow rate and TMP on carbon dioxide emissions and water consumption during concentration were studied using Ecoinvent v2.1 [30], a database used in Life Cycle Assessment (LCA) methodology to quantify water consumption and carbon dioxide emissions implied by the use of energy and materials. The data collected was separated into two different categories. The first, "operating", is the energy consumption of the UF apparatus during functioning, and the second, "installation", is due to the material used for the treatment of one FU by ultrafiltration.

3. Results and discussion

3.1. Extraction and purification process

3.1.1. Process presentation

Depending on the variety, wheat bran contains about 20% starch [9]. In aqueous solution, hydrolysis of polysaccharide intramolecular bonds can lead to an increase in viscosity and formation of a gel. This phenomenon appears at temperatures between 50 and 100 °C in aqueous media but decreases to 20 °C in alkaline media. For this reason, the presence of starch can make some processes like centrifugation or ultrafiltration impossible and a pre-treatment of bran is then essential [31]. During twin-screw extrusion, thermal, mechanical and chemical actions are applied to the plant matter to extract molecules from the tissues by continuous squeezing in the screw press. The use of reverse pitch-screw elements induces a compression of the plant matter due to the decrease of the cross flow section. This phenomenon implies the formation of a dynamic plug at the end of the extruder, inducing a compression, which improves chemical action on the plant matter and leads to liquid/solid separation even with a low liquid/solid ratio.

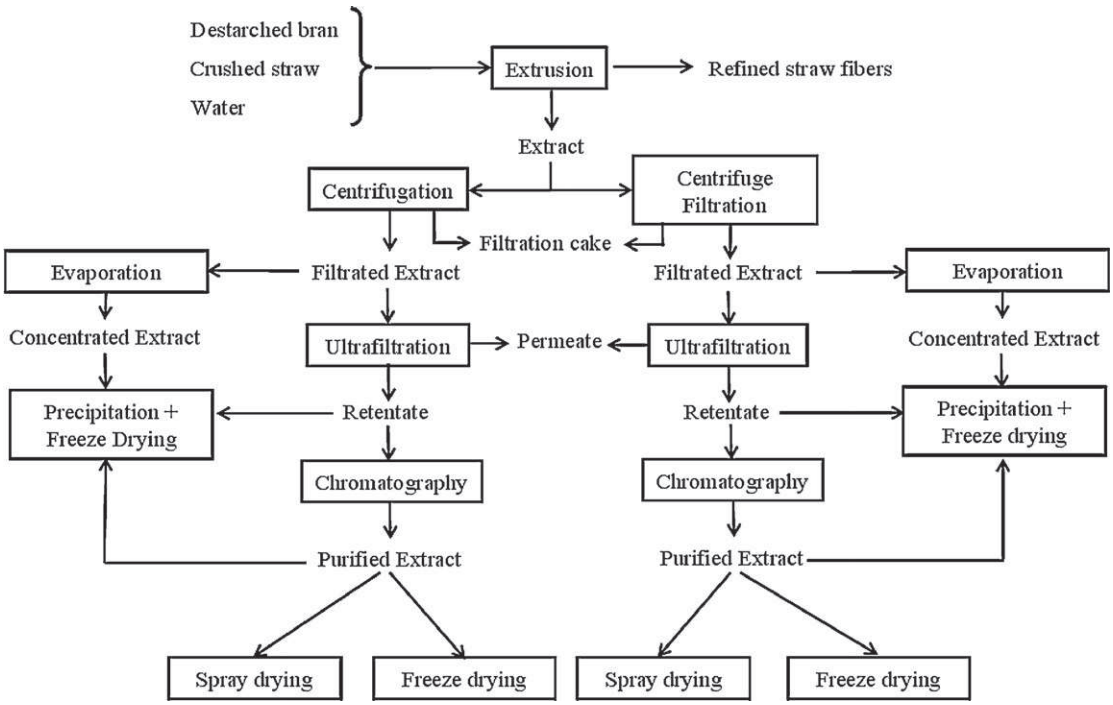

Fig. 2. Fractionation and purification process of hemicelluloses from wheat straw and bran.

A previous study [32] has shown that this plug is closely connected to a minimum size of fibres in the plant matter and 6 mm was determined as the optimum size for the straw material. During extrusion, alkali/plant matter and straw/bran ratios, pH of the media, temperature, and screw rotation speed are crucial parameters. Optimal parameters given in part 2.2 have been determined in a previous work [21]. This extraction leads to the production of two fractions; one solid, composed of refined straw fibres, and the other liquid (extract), mainly containing hydrosoluble compounds. An extra solid–liquid separation step is required for an industrial scale process. Two systems were compared: centrifuge filtration and centrifugation, and the extract then requires further refining and concentration treatments, managed by different operation units. On the one hand, extract concentration is managed by water evaporation (EV) followed by ethanol precipitation (P). On the second hand, a combination of UF and discolouration by ion exchange chromatography (CHR) is studied. Finally, several process units were tested to obtain hemicellulosic powders without the precipitation step: spray-drying (SD) and freeze-drying (FD). The overall process is shown in Fig. 2.

3.1.2. Fractionation process: extrusion and filtration

The twin-screw extruder provided a continuous fractionation process and results obtained are given in Table 2. At the output, two fractions were obtained: refined straw fibres, which have relatively high dry matter content (34.5%); and an extract, containing mainly the hydro-soluble compounds (3.1% of dry matter content). Because of the large quantities of wash water introduced into the extruder, large amounts of extract are produced with low dry matter content. Under the experimental conditions, 151 kg of refined straw fibres and 400 kg of extract were obtained which represent 15.0 kg/h and 3.6 kg/h of dry matter flow rate respectively. Furthermore, twin-screw fractionation is not a selective process and other compounds are co-extracted with xylans, like proteins and lignins, justifying the further purification steps. Moreover, Table 2 point out that the extract contains large quantities of ash (34.6%) which come from the considerable quantities of NaOH used during extrusion step (low Bran/NaOH ratio).

Extrusion gave 12.8% yield of organic matter in the extract and 87.2% in the refined straw fibres (recovered organic matter weight/organic matter weight of the vegetable material introduced in the extruder (straw + bran)). However, Zeitoun et al., 2010 [20],

Table 2
Extract composition after extrusion and liquid–solid separation processes.

	Extrusion		Centrifugation		Centrifuge filtration	
	Refined straw fibres	Extract[a]	Cake[c]	Filtered extract[b]	Cake[c]	Filtered extract[b]
Dry matter flow rate (kg/h)	15.0	3.6	1.7	4.5	0.2	0.5
Dry matter content (%)	34.5	3.1	9.8	2.5	12.8	2.6
Ash content (wt% dry matter)	3.3	34.6	16.4	39.3	15.1	41.6
Organic content (wt% dry matter)	96.7	65.4	83.6	60.7	84.9	58.4
Proteins (wt% dry matter)	2.2	8.5	3.9	10.4	2.6	10.9
Arabinose + Xylose (wt% dry matter)	n.d.	n.d.	n.d.	9.9	n.d.	10.9
Yields (%)[d]	87.2	12.8	33.1	66.9	30.8	69.2

[a] Liquid extract obtained after extrusion.
[b] Liquid extract obtained after liquid–solid separation step (centrifugation or centrifuge filtration).
[c] Matter in suspension retained by the liquid–solid separation step (centrifugation or centrifuge filtration).
[d] % of organic matter (ash-free) recovered during the unit process step. Expressed as the dry weight of recovered organic matter/dry weight of introduced organic matter ((bran + straw) for extrusion yield and (extract) for centrifugation and centrifuge filtration yields).

Table 3
Extract composition before and after concentration steps.

	Filtered extract (centrifuged)[a]	Ultrafiltrated extract[b]	Evaporated extract[c]
Dry matter content (%)	2.5	3.6	5.7
Ash content (wt% dry matter)	39.3	29.4	43.2
Organic content (wt% dry matter)	60.7	70.6	56.8
Proteins (wt% dry matter)	10.4	13.9	10.5
Arabinose + Xylose (wt% dry matter)	9.9	14.1	10.6
Yields (%)[d]	66.9	83.3	100.0

[a] Extract obtained after centrifugation.
[b] Extract obtained after ultrafiltration.
[c] Extract obtained after evaporation.
[d] % of organic matter (ash-free) recovered during the unit process step. Expressed as the dry weight of recovered organic matter/dry weight of introduced organic matter ((extract) for centrifugation yield and (centrifuged extract) for ultrafiltration and evaporation yields).

showed that during twin screw extrusion, straw was mainly needed to support bran material in the extruder to improve the liquid/solid separation. As bran is pre-soaked in alkali 1 h before the extrusion, hemicelluloses are mainly extracted from bran. This hypothesis was confirmed by previous study which pointed out the fact that the refined straw fibres composition is close to the initial straw composition [20]. Moreover, the xylose/arabinose ratio is 2.3, which is close to those of hemicelluloses from wheat bran ($x/a = 2$) [10,33] but far from those of straw ($x/a \approx 6$) [34]. Obviously, lignins and small amounts of xylans are co-extracted from straw, but the above reasons explain why, even if the straw is not totally inert, it could be interesting to calculate the yield of arabinoxylans by considering only the dry weight of bran.

The liquid/solid separation step decreases the quantity of dry matter in the extract from 3.1% to about 2.5%. This reduction is mainly due to removal of suspended material, essential to the further ultrafiltration step. The arabinoxylans composition of the extract after centrifugation reached 9.9% of the recovered dry matter. The yield in arabinoxylans of the extraction step is then of 8.5% (weight of (arabinose + xylose) in the extract after centrifugation/dry weight of the destarched bran). This result appeared to be less efficient than those of literature, where yields after extraction were find equal to 34.1% for alkaline extraction after sodium chloride delignification [10], and between 21.9% and 36.8% for alkaline extraction assisted by ultrasound treatment [15].

But this process was managed at a pilot scale and presents other advantages, like to be continuous process, with short retention time, and give the opportunity to find issues for refined straw fibres (vegetable-based materials).

The analysis of the extract and cake composition of the liquid/solid separation process does not reveal any real differences between centrifugation and centrifuge filtration, but the dry matter flow rate is significant (respectively 4.5 kg/h and 0.5 kg/h): centrifugation is nine times more efficient at treating the extract, showing that it is a better option in the process conception. Therefore, the following results will just describe the centrifugation option.

3.1.3. Concentration: evaporation vs ultrafiltration

Traditionally, concentration was performed by evaporation [32], but ultrafiltration was also a well-established separation process in industry. Low molecular weight cut-off UF membranes can purify and concentrate complex polysaccharide mixtures. Therefore this technique has been investigated for purification, especially for demineralisation because of the large ash content. Moreover, UF could also separate arabinoxylans from co-extracted molecules. Hemicelluloses are thus purified because low molecular mass solutes pass through the membrane while large molecules are retained. At least the ability of UF to concentrate the solution [4,35] is an interesting advantage that allows the reduction of treated volumes and therefore implies a cost reduction.

The extract from centrifugation is concentrated with a volume concentration rate of 2. Figures given in Table 3 show that for ultrafiltration and evaporation, concentration is effective with dry matter increases of +44% and +128% respectively compared to the filtered extract. UF seems to be less efficient at concentrating whole dry matter because it is also purifying the extract. In fact, this process unit allows the separation of small components like ions and free sugars, from large molecules like arabinoxylans and proteins. Therefore, ultrafiltration treatment leads to a demineralisation of 46% (weight of mineral content take off from the introduced extract/weight of mineral content of the extract before UF). The opportunity to improve the demineralisation rate could be study in the future by performing a diafiltration of the extract which consist to inject demineralised water to substitute the permeate in order to evacuate the entire mineral content from the extract.

An increase in the amount of organic matter in the ultrafiltrated extract is also observed. This is explained by the fact that only small organic molecules are removed but proteins are concentrated as well as xylans. The arabinoxylans composition of the extract after evaporation is equal to 10.6% whereas the one of ultrafiltration reached 14.1% of the recovered dry matter.

3.1.4. Yields in xylans and powder colouration

The extract was dark brown, due to the presence colouring compounds. These molecules appear to be large molecules because they are also retained by UF. Thus, an extra-step is required to de-colour the extract, and anion exchange chromatography (CHR) could be combined with UF to achieve this [4].

The influence of all the purification steps on dry matter yields and total sugar content of final powders is presented in Table 4.

Table 4
Yields and sugar composition of powders at each step of the process.

Extract treatment after centrifugation[a]	Yields[b] (%)	Total sugar (%)[c]	Protein (%)[c]	Ash (%)[c]
EV + P + FD	36.5	48.4	12.9	9.4
UF + P + FD	38.2	46.7	15.6	5.5
UF + CHR + P + FD	33.7	50.6	13.5	5.2
UF + CHR + FD	55.8	27.9	8.3	15.7
UF + CHR + SD	24.6	28.7	11.6	3.1

[a] EV = Evaporation; P = Precipitation; FD = Freeze Drying; UF = Ultrafiltration; CHR = Ion exchange Chromatography; SD = Spray Drying.
[b] Expressed as the dry weight of powder (with ash content)/dry weight of the extract after centrifugation.
[c] Expressed on the recovered dry matter.

Table 5
Powder colouration at each step of the process.

Extract treatment after centrifugation[a]	L^*	a^*	b^*
EV + P + FD	56.8	4.2	18.1
UF + P + FD	58.9	4.5	18.0
UF + CHR + P + FD	61.9	3.8	15.5
UF + CHR + FD	47.2	7.4	27.9
UF + CHR + SD	66.2	5.9	31.3

[a] EV = Evaporation; P = Precipitation; FD = Freeze Drying; UF = Ultrafiltration; CHR = Ion exchange Chromatography; SD = Spray Drying.

Yields are expressed as the dry weight of powder/dry weight of the extract after centrifugation. The two first lines of the table allow comparing the ultrafiltration and evaporation effects. It confirms that UF removes about 50% of ash, and small organic molecules like free sugars. This explains the decrease of the sugar content but also the increase of the protein content because large molecules are retained.

The addition of the ion exchange chromatographic step decreases the recovery yields from 38.2% to 33.7%. However, this is linked to an increase of the total sugar proportion (46.7–50.6%) and a decrease of the protein concentration (15.6–13.5%).

A test for recovering hemicellulosic powders by spray-drying has been attempted to check the feasibility of this technology. The yield of this step is low (24.6%) because many conditions still have to be optimised to limit the loss of stuck matter on the cyclone wall.

Colour measurement was made on all the solid samples (Cf. Table 5). When precipitation is used, it appears that both UF and chromatography improve the lightness of the powder. However, without precipitation, the powder was darker when obtained by freeze-drying (L^* = 47.2) while it was lighter after spray-drying (L^* = 66.2). These results showed that the drying technique strongly influenced the final powder colouration. This result also indicates that the precipitation is also an efficient process for the decolouration. All these trials indicate that the process combining UF + CHR + SD could be used for the production of xylans enriched powder, but should be improved to eliminate large molecules such as some coloured compounds and proteins.

3.2. Environmental design: focus on the ultrafiltration step

All these process units were compared in terms of yields and total sugar content. When developing a green process, there is a need for a tool that would include environmental impacts. Such a tool is presented in this part, illustrated by the calculation made on ultrafiltration results which allow comparing many conditions. In ultrafiltration process designs, one of the factors most studied is the influence of transmembrane pressure on membrane performance [24]. The higher the permeate flux the better process cost efficiency. But an increase in the permeate flow rate needs an increase in the circulation flow rate or the transmembrane pressure, and this can influence the environmental impact of the process. Therefore the influence of ultrafiltration parameters on carbon dioxide emissions and water consumptions was also studied.

3.2.1. The influence of ultrafiltration parameters on ultrafiltration performance

Firstly, membrane surface phenomena during ultrafiltration were investigated by studying the influence of the TMP on the permeate flux at different steady circulation flow rates (756, 882 and 1063 kg/h). This approach allows investigation of the capability of ultrafiltration to achieve purification, and evaluation of possible membrane fouling. The results (Fig. 3) showed an increase in permeate flux with TMP increase, but at the highest TPM a limit permeate flux seems to be reached. A rising circulation flow rate also

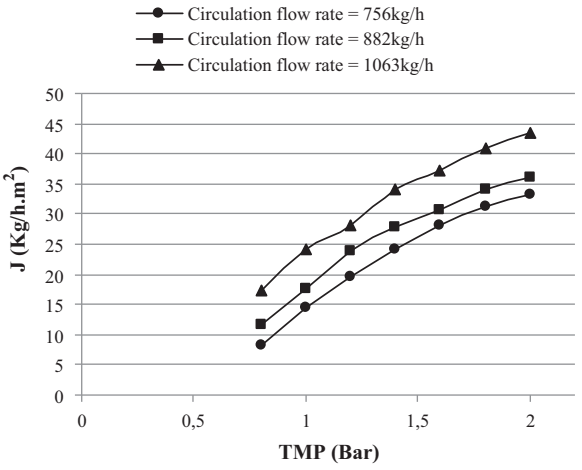

Fig. 3. Permeate flux versus pressure under various circulation flow rates.

increases permeate flux. These results indicate that a polarisation layer arises during filtration, and this is created by the accumulation of retained molecules at the membrane surface, and acts as an extra-resistance to permeate flow. This resistance increases when TMP rises but decreases when flow rates rise, thus optimal conditions need to be defined, and usually this is achieved using technical criteria, e.g. working below the limit permeate flux. However, these results were also used to calculate the carbon dioxide emissions and water consumption linked to the "operating" and "installation" conditions, in order to optimise the process regarding environmental criteria.

3.2.2. Quantification of carbon dioxide emissions and water consumption for "operating" and "installation"

In order to quantify the carbon dioxide emissions and water consumption relative to the ultrafiltration unit process, the previously mentioned functional unit (FU) is used. For each circulation flow rate value, permeate flow rate (Q_p) is measured in kg/h and the permeate flux (J_p) is calculated. This value, obtained for a single module is then used to calculate the number of modules (N) required to achieve one FU by:

$$N = \frac{Q_p^{FU}}{J_p \times S} = \frac{Q_p^{FU}}{Q_p}$$

where, Q_p^{FU} is the permeate flow rate relative to the FU (500 kg/h, in order to treat 1000 kg/h with a volume concentration factor of 2) and S is the membrane surface area.

"Operating" data are the sum of the energy consumed by the feed pump (P_F) and the circulation pump (P_C). The feed flow rate (Q_F) is always 1000 kg/h and the consumption relative to the feed pump does not vary. However, the energy consumed by the circulation pump should be multiplied by the number of modules (N) in order to obtain energy consumption relative to circulation. These calculations are made according to the following formulae:

$$P_F = \mathrm{TMP} \times Q_F$$

$$P_C = (\mathrm{TMP} \times Q_C) \times N$$

"Installation" data were then evaluated thanks to an inventory of the raw material used in the manufacture of UF modules (Cf. paragraph 2.7), but the impact of the membrane fabrication has not yet been taken into account in this calculation.

At this point, the energy due to the operating conditions and the raw materials involved in the infrastructure of the UF process constitute an inventory. The Ecoinvent database is built to give data

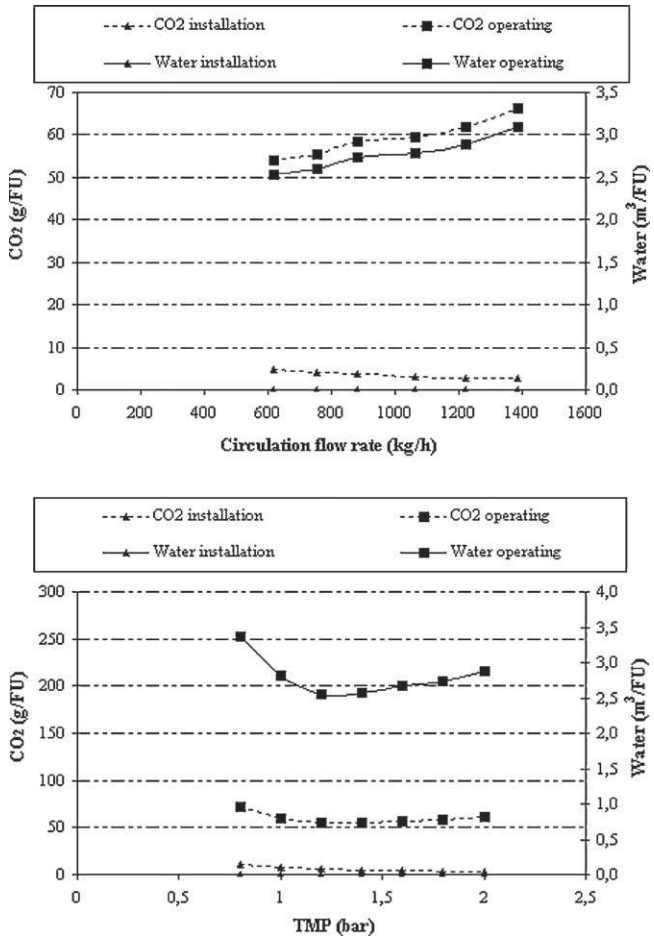

Fig. 4. Carbon dioxide emissions and water consumption curves: comparison between "installation" and "operating" impacts.

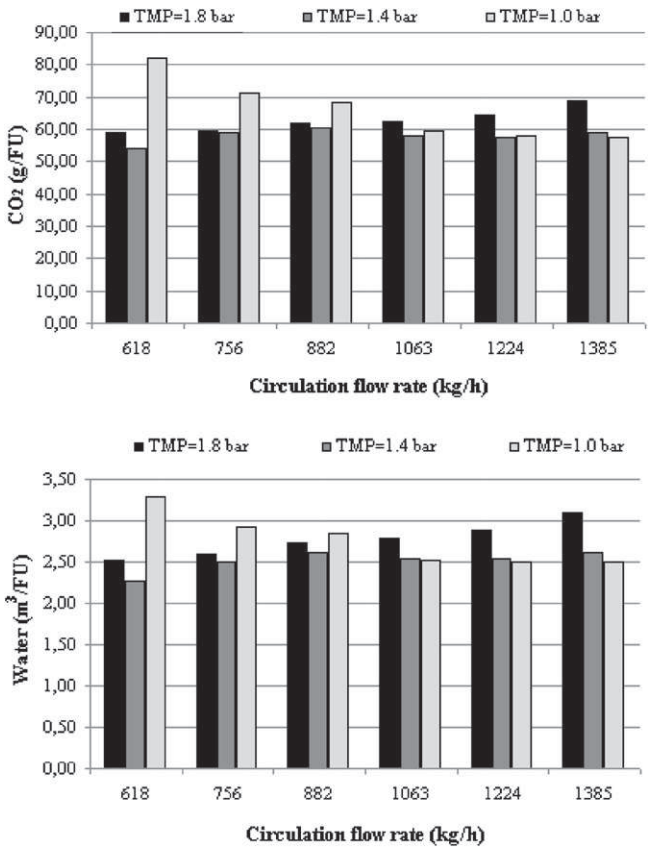

Fig. 5. Carbon dioxide emissions and water consumptions for different TMP-circulation flow rate pairings.

such as the kg of carbon dioxide emitted or the m^3 of water used per kWh of energy consumed or per kg of a produced material. This allows converting the energy and raw material previously listed into carbon dioxide emissions and water consumption, and then comparing two aspects of a process (operating vs installation). In this paper, it was used on operating and installation data to calculate the carbon dioxide emissions and water consumption for the process.

3.2.3. Comparison between "installation" and "operating"

Firstly, the relative importance of the impacts from "operating" and "installation" emissions was compared (Fig. 4). Results indicate that, within the limits of the system considered, the carbon dioxide emissions and water consumptions relative to "operating" are much higher than those for "installation", and this difference depends on membrane average life (10,000 h) that could be reduced by considering membrane fabrication or membrane composition. Furthermore, this conclusion depends on experimental conditions, for example the membrane configuration, the solution type, etc.

The shape of the graphs confirms that at constant TMP, the increase of circulation flow rate induced an increase in environmental impacts, especially for "operating" lines. However, at constant circulation flow rate, the lowest TMP is not the optimal one: the minimum carbon dioxide emissions appear to be at 1.3 bar, and this result could be explained by the influence of the permeate flux value on the module number and therefore on the number of recirculation pumps required.

3.2.4. Influence of TMP and circulation flow rate on carbon dioxide emissions and water consumption

The model here can also be used for optimisation of the process. In this case, the sum of the operating and installation data is taken and the bar charts obtained (Fig. 5) represent the carbon dioxide emissions and water consumptions due to each TMP-Circulation flow rate pairing. From an environmental point of view, the optimal circulation flow rate depends on the TMP: at 1 bar pressure, working at 1385 kg/h is better, but at 1.8 bar, 618 kg/h appears to be best. For water consumption as well as carbon dioxide emission, the bar chart shows that under the specific conditions of this study, the optimal point is defined at 1.4 bar and 618 kg/h.

4. Conclusion

An extrusion process of arabinoxylans from wheat has been tested at a large scale in the laboratory and different kinds of purification techniques have been studied. After twin-screw co-extraction of wheat bran and straw, it appears that the centrifuge separator is the most efficient tool for the removal of particles. At this level, it takes 86 kg of straw and bran (with a ratio 6.2:1), plus 5.8 kg of NaOH (in pellet form), to produce an extract containing 1.0 kg of arabinoxylan polymer. Then the extract could be concentrated by ultrafiltration and decoloured by anionic exchange chromatography. The final powders are recovered by spray drying or freeze-drying. Obtained yields are low than those founded in literature, however twin screw extrusion presents other advantages (continuous process, short retention times, opportunity to find issues for refined straw fibres, etc.) and appeared to be an alternative extraction method at industrial scale if technical and economic efficiency are optimised.

This study demonstrates that optimisations are possible based on both production yields and environmental impact of each process. An approach has been developed which takes into account carbon dioxide emissions and water consumption. Results show that for the ultrafiltration apparatus used, environmental impacts due to the operating conditions are higher than those for the installation. The study shows that this kind of approach allows optimum conditions to be obtained in the light of environmental criteria. Nevertheless, the model requires many improvements such as better definition of the environmental impact key parameters or optimisation of the system under consideration (membrane manufacture, ultrafiltration apparatus design).

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References

[1] Sun R, Lawther JM, Banks WB. Influence of alkaline pre-treatments on the cell wall components of wheat straw. Industrial Crops and Products 1995;4(2):127–45.
[2] Swennen K, Courtin CM, Lindemans GCJE, Delcour JA. Large-scale production and characterisation of wheat bran arabinoxylooligosaccharides. Journal of the Science of Food and Agriculture 2006;86(11):1722–31.
[3] Fang JM, Sun RC, Salisbury D, Fowler P, Tomkinson J. Comparative study of hemicelluloses from wheat straw by alkali and hydrogen peroxide extractions. Polymer Degradation and Stability 1999;66(3):423–32.
[4] Andersson A, Persson T, Zacchi G, Stålbrand H, Jönsson A-S. Comparison of diafiltration and size-exclusion chromatography to recover hemicelluloses from process water from thermomechanical pulping of spruce. Applied Biochemistry and Biotechnology 2007;137–140(1):971–83.
[5] Ebringerová A, Heinze T. Xylan and xylan derivatives – biopolymers with valuable properties, 1. Naturally occurring xylans structures, isolation procedures and properties. Macromolecular Rapid Communications 2000;21(9):542–56.
[6] Bergmans MEF, Beldman G, Gruppen H, Voragen AGJ. Optimisation of the selective extraction of (glucurono)arabinoxylans from wheat bran: use of barium and calcium hydroxide solution at elevated temperatures. Journal of Cereal Science 1996;23(3):235–45.
[7] Lawther JM, Sun R, Banks WB. Extraction, fractionation, and characterization of structural polysaccharides from wheat straw. Journal of Agricultural and Food Chemistry 1995;43(3):667–75.
[8] Maes C, Delcour JA. Alkaline hydrogen peroxide extraction of wheat bran nonstarch polysaccharides. Journal of Cereal Science 2001;34(1):29–35.
[9] Brillouet JM, Joseleau JP, Utille JP, Lelievre D. Isolation, purification and characterization of a complex heteroxylan from industrial wheat bran. Journal of Agricultural and Food Chemistry 1982;30(3):488–95.
[10] Bataillon M, Mathaly P, Nunes Cardinali AP, Duchiron F. Extraction and purification of arabinoxylan from destarched wheat bran in a pilot scale. Industrial Crops and Products 1998;8(1):37–43.
[11] Sun, Fang JM, Tomkinson J. Characterization and esterification of hemicelluloses from rye straw. Journal of Agricultural and Food Chemistry 2000;48(4):1247–52.
[12] Chanliaud E, Saulnier L, Thibault JF. Alkaline extraction and characterisation of heteroxylans from maize bran. Journal of Cereal Science 1995;21(2):195–203.
[13] Montané D, Farriol X, Salvado J, Jollez P, Chornet E. Fractionation of wheat straw by steam-explosion pretreatment and alkali delignification. Cellulose pulp and byproducts from hemicellulose and lignin. Journal of Wood Chemistry and Technology 1998;18(2):171–91.
[14] Glasser WG, Wright RS. Steam-assisted biomass fractionation. II. Fractionation behavior of various biomass resources. Biomass and Bioenergy 1998;14(3):219–35.
[15] Hromádková Z, Kováciková J, Ebringerová A. Study of the classical and ultrasound-assisted extraction of the corn cob xylan. Industrial Crops and Products 1999;9(2):101–9.
[16] Puls J, Saake B. Industrially isolated hemicelluloses. In: Tenkanen PGaM, editor. Hemicelluloses: science and technology. American Chemical Society; 2004. p. 387.
[17] Glasser WG, Kaar WE, Jain RK, Sealey JE. Isolation options for non-cellulosic heteropolysaccharides (HetPS). Cellulose 2000;7(3):299–317.
[18] Jorda J, Marechal P, Rigal L, Pontalier PY. Biopolymer purification by ultrafiltration. Desalination 2002;148(1–3):187–91.
[19] Annison G, Choct M, Cheetham NW. Analysis of wheat arabinoxylans from a large-scale isolation. Carbohydrate Polymers 1992;19(3):151–9.
[20] Zeitoun R, Pontalier PY, Marechal P, Rigal L. Twin-screw extrusion for hemicellulose recovery: influence on extract purity and purification performance. Bioresource Technology 2010;101(23):9348–54.
[21] Maréchal P, Jorda J, Pontalier PY, Rigal L. Twin screw extrusion and ultrafiltration for xylan production from wheat straw and bran. In: Gatenholm P, Tenkanen M, editors. Hemicelluloses: science and technology. American Chemical Society; 2003. p. 38–51.
[22] Sun RC, Tomkinson J, Wang YX, Xiao B. Physico-chemical and structural characterization of hemicelluloses from wheat straw by alkaline peroxide extraction. Polymer 2000;41(7):2647–56.
[23] Swennen K, Courtin CM, Van der Bruggen B, Vandecasteele C, Delcour JA. Ultrafiltration and ethanol precipitation for isolation of arabinoxylooligosaccharides with different structures. Carbohydrate Polymers 2005;62(3):283–92.
[24] Persson T, Jönsson AS. Isolation of hemicelluloses by ultrafiltration of thermomechanical pulp mill process water – influence of operating conditions. Chemical Engineering Research and Design 2010;88(12):1548–54.
[25] Alexander B, Barton G, Petrie J, Romagnoli J. Process synthesis and optimisation tools for environmental design: methodology and structure. Computers & Chemical Engineering 2000;24(2–7):1195–200.
[26] Burgess AA, Brennan DJ. Application of life cycle assessment to chemical processes. Chemical Engineering Science 2001;56(8):2589–604.
[27] Van Soest PJ, Wine RH. Use of detergents in the analysis of fibrous feeds. Journal of the Association of Official Analytical Chemists 1967;50:50–6.
[28] Van Soest PJ, Wine RH. The determination of lignin and cellulose in acid detergent fiber with permanganate. Journal of the Association of Official Analytical Chemists 1968;51:780–7.
[29] Li Y, Makio A, Michio M. Development of an Imaging Colorimeter for skin Color Measurement and its clinical application. In: Color communication and management. 2003.
[30] Ecoinvent. Ecoinvent data v 2.2. Swiss Centre for Life Cycle Inventories; 2010.
[31] Raynal-Ioualalen R. Procédé de fractionnement des sons de blé. Extraction et étude des propriétés fonctionnelles des arabinoxylanes. France, Toulouse: Institut National Polytechnique, Ph.D. thesis; 1996, p. 324.
[32] Maréchal P. Analyse des principaux facteurs impliqués dans le fractionnement combiné de pailles et de sons de blé en extrudeur bivis: obtention d'agromatériaux. France, Toulouse: Institut National Polytechnique, Ph.D. thesis; 2001, p. 350.
[33] Shiiba K, Yamada H, Hara H, Okada K, Nagao S. Purification and characterization of two arabinoxylans from wheat bran. Cereal Chemistry 1993;70(2):209–14.
[34] Sun R, Lawther JM, Banks WB. Fractional and structural characterization of wheat straw hemicelluloses. Carbohydrate Polymers 1996;29(4):325–31.
[35] Nabarlatz D, Torras C, Garcia-Valls R, Montané D. Purification of xylo-oligosaccharides from almond shells by ultrafiltration. Separation and Purification Technology 2007;53(3):235–43.