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Hydrothermal Treatment of Grape Skins for Sugars, Antioxidants and Soluble Fibers Production

Andrea Bassani*, Noemi Alberici, Cecilia Fiorentini, Gianluca Giuberti, Roberta Dordoni, Giorgia Spigno

Università Cattolica del Sacro Cuore, Department for Sustainbale Food Process (DiSTAS), Via Emilia Parmense 84, 29122 Piacenza, Italy
andrea.bassani@unicatt.it

The valorisation and the reuse of agricultural residue and food waste are gaining more attention in the last years as are directly related to environmental sustainability. For this reason, the aim of this study is to evaluate the influence of autohydrolysis operating conditions for a high yield recovery of sugars, soluble fiber and antioxidants from grape skins. In this work, an experimental campaign using a lab-scale batch autohydrolysis reactor is scheduled based on statistical methods to assess the influence of some process variables (like water to skins solids ratio or working temperaure) on some selected key performance indicators (KPIs), like sugars, sugar degradation products, phenolic compounds, antioxidant compounds and fiber recovery. As a comparison, different agricultural residue, like wheat straw, are considered. Entering in the details, the volume of the recovered autohydrolysis liquid fraction is measured and analyzed to calculate the release yield of both total solids and specific components, including antioxidant activity according different in vitro assays tests such as and ABTS assay. Therefore, this work presents an innovate autohydrolysis process for the valorization of waste grape skins for the production of added-value compounds through a potentially green technology.

1. Introduction

In recent years, environmental sustainability is a big issues for different goods or services at various stages of their life. The food sector is directly related to this problem because environmental damage is mainly due to food waste, which has negative effects on economy, environment and society (Papargyropoulou et al., 2014). Nowadays, there are two different ways to contrast the negative effects of food waste. The first is to directly reduce food waste by raising consumer awareness, the other way is the recycle and the reuse of food waste to produce new products, either destined to food industry or exported to other sectors such as cosmetics (Santana-Méridas et al., 2012). For this second case, there are several studies concerning treatments carried out on food waste matrices, aimed at extracting nutrients or improving physical or chemical-physical properties (Vadivel et al., 2017). Two main treatment methods can be identified: those that use enzymatic preparations (Gruppi et al., 2017) and those that use hydrothermal treatments (Spigno and De Faveri, 2007a). In this study, high pressure hydrothermal treatment was investigated and in particular for its application on grape pomace. The latter was chosen because Italy is one of the first grape producer in the world (about 8.2 Mtons/year in 2016) due to the high demand coming from the wine industry. However, the wine making process generates a considerable amount of residues, like grape skins. The latter have gained increasing attention as a potential cost-effective source of sugars, antioxidant and both soluble and insoluble fibers (e.g. cellulose and hemicellulose). Conventional solvent extraction technologies have been widely investigated for the recovery of these components, while water autohydrolysis, generally studied for lignocellulosic materials (Ruiz et al., 2011), has never been applied on grape pomace. Autohydrolysis is a potentially environmental-friendly process because no chemicals have to be added avoiding the consequent waste generation and environmental impact (Garrote et al., 2007). Therefore, the aim of this work is to investigate different operating conditions of the selected hydrothermal treatment in order to provide a wide range of data for a possible future processing of this by-product. In particular, the recovery of cellulose, hemicellulose and lignin in the solid

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residue and the recovery of antioxidant compounds in the liquid residue were analysed. Moreover, these treated products could be used as food additives or as additives in bio-film production (Bassani et al., 2019). Furthermore, assuming a possible use of the treated products as such, water holding capacity and oil retention capacity were evaluated, because are essential properties in order to classify the residue as functional fibres (Garau et al., 2007). Finally, the results obtained were compared with the one of European project Newpack, in which wheat straw was used as a raw material instead of grape pomace. Indeed, one of the goal of Newpack project is to maximize the recovery of cellulose from wheat straw through autohydrolysis process. Then recovered cellulose will be converted into nanocellulose in order to be include into bio-film, improving its barrier and mechanical properties.

2. Material and Methods

An initial experimental plan was set up to try to see the effects of high pressure hydrothermal treatment on fermented grape pomace (GP) of Barbera red grape variety from winemaking process and on wheat straw from Piemonte (Northern Italy). For the collected grape pomaces, the skins were manually separated from seeds and other impurities and then sent to the hydrolysis treatment. The sample was taken with distilled water, with different liquid to solid (L/S) ratio, into a high pressure reactor, with a volume capacity of 960 mL. The reactor was operated manually with the desired temperature for 15 minutes. The rotation was controlled manually at 200 rpm. The different velocities of rotation seem not effecting the outlet composition, but a slow agitation is usually suggested in order to have a proper mixing. After the reaction, the reactor was slowly cooled down exchanging heat with a room at ambient temperature. Then, the hydrolyzed sample was taken out and was filtered through Whatman filter paper (No. 595). The solid was dried at 60°C for 24 h and weighed. The solid were then analysed for the soluble and insoluble dietary fibre content, oil retention capacity (ORC), water holding capacity (WHC), structural carbohydrates (SC) in order to evaluate cellulose, hemicellulose and lignin recovery. On the other hand, the liquid, coming from autohydrolysis reaction, was used for the analysis of total phenol content and antioxidant capacity (FRAP and ABTS assays). The experimental plan consists of several duplicate tests which are different for the inlet L/S ratio and for the maximum final temperature reached. In particular, 4 tests were carried out with L/S equal to 1.5, 5.0, 10.0, 20.0 at a maximum constant temperature equal to 175°C and 3 other tests with L/S constant equal to 20.0 varying the maximum temperature equal to 175°C, 195°C and 210°C. The analytic methods used are reported in the next paragraphs.

2.1 Dietary Fibre

Dietary fibre is defined as a mixture of complex organic substances, including hydrophilic compounds, such as soluble and insoluble polysaccharides and non-digestible oligosaccharides, as well as a range of non-swellable, more or less hydrophobic, compounds such as cutin, suberin and lignin. The analysis of soluble and insoluble dietary fibre was assessed through an enzymatic assay (Megazyme, K-TFDR-200 A), according to AOAC Method 991.43.

2.2 Structural Carbohydrates

Cellulose, hemicellulose and lignin contents were assessed as reported by according to the method proposed by Sluiter et al. (2010) based on a quantitative saccharification of polysaccharides through a strong acid hydrolysis followed by a dilute acid hydrolysis. Acid soluble lignin (ASL) is determined from absorbance reading at 320 nm of the hydrolysate (applying the absorbance coefficient of 30 L g-1 cm-1). Acid insoluble lignin (AIL) is calculated from the solid residue after moisture and ash content determination. Total lignin comes from the sum of these two fractions. Hemicellulose is estimated from the concentration of xylose (evaluated with Megazyme kit, K-Xylose-02/11) in the liquors multiplied by the correction factor of 0.90, while cellulose (glucan) is estimated from the concentration of glucose (evaluated with (Megazyme kit, GOPOD-format, K-Gluc-07/11) in the liquors multiplied by 0.88 for hexoses (Spigno et al., 2008).

2.3 Water holding capacity (WHC), oil retention capacity (ORC)

WHC and ORC were evaluated as reported by (Mateos-Aparicio et al., 2010). Briefly for WHC 500 mg of sample were hydrated with 30 ml distilled water for 18 h at room temperature. The sample was then centrifuged at 3000 g for 20 min and the residue fresh weight recorded. WRC was calculated as the amount of water retained by the pellet (g water/g sample dw). For the ORC the same protocol was followed, but with extra virgin olive oil (acidity 0.7°) for distilled water. ORC was expressed as g oil/g sample dw.

2.4 Tappi Method

The TAPPI methods have been mainly developed to evaluate the lignin, cellulose and hemicellulose content in wood and residues of unbleached pulps (Rowell, 2012). The procedure consists in the following main steps:

- Extraction of the sample with ethanol–toluene to evaluate the ethanol-toluene extractives (T204 cm-97).
- Evaluation of lignin content in the free-extractive sample (T222 om-98).
- Evaluation of holocellulose (cellulose + hemicellulose) content in the free-extractive sample (holocellulose) (Wise et al., 1946).
- Evaluation of cellulose content in the holocellulose residue (Rowell, 1983)
- Estimation of the hemicellulose content as the difference from holocellulose and cellulose.

TAPPI methods was used for whet straw characterization due to its high content of cellulose, hemicellulose and lignin like in wood residue.

2.5 Total Phenol Content and antioxidant capacity

The content in free extractable phenolic compounds and antioxidant compounds was assessed through extraction of the dried powders of the solid with ethanol 60% (1/8 w/v) at 40 °C for 1h 30 min under stirring (SKI 4 ARGOLAB) and analysis of the extracts separated by centrifugation for the following parameters:

- Total phenols, based on the Folin-Ciocalteu's assay (García et al., 2011), expressing the results as mg of gallic acid equivalents (GAE, based on a calibration curve with standard of gallic acid) on dry weight of the samples (mgGAE/gdw).
- Antioxidant activity was evaluated according to FRAP and ABTS radical assay (Vellingiri et al., 2014) and the results were expressed as mmolFe(II)/gdw and on mmolTrolox/gdw respectively.

It is important to underline the fact that, the Folin-Ciocalteau assay may be affected by other compounds with a reducing power like sugars or product of Maillard reactions. So for this reason, direct readings at 280 nm and 320 nm were done, because are not influenced by the oxidative state of phenolic compounds (Spigno et al., 2007b). In the first case the results are expressed with the same unit of measurement as in the Folin-Ciocalteau assay (mgGAE/gdw), in the second case they are expressed in milligrams of equivalent chlorogenic acid (mgCAE/gdw).

3. Results and Discussion

3.1 Raw material characterization

The characterisation of grape marc and wheat straw is provided in Table 1. It is important to underline that wheat straw was characterized only in terms of moisture content and structural carbohydrates (i.e. cellulose, hemicellulose and lignin) because, as already mentioned, the European project, Newpack, have the aim of optimize the cellulose recovery. On the contrary, grape pomace was characterized also in terms of dietary fiber, water holding capacity and oil absorption capacity because the aim of this study is to investigate the variability of these properties at different operating conditions.

Table 1 Grape pomace and wheat straw characterization

	Grape Pomace	Wheat Straw
Moisture Content (%)	4.17 ± 0.60	7.85 ± 0.73
Cellulose (% on dw)	10.00 ± 1.00	32.89 ± 0.67
Hemicellulose (% on dw)	1.02 ± 0.01	25.29 ± 0.67
Insoluble Lignin (% on dw)	26.29 ± 2.15	17.32 ± 0.27
Soluble Lignin (% on dw)	0.52 ± 0.04	-
Ash (% on dw)	10.41 ± 0.08	5.64 ± 0.26
Dietary Soluble Fiber (% on dw)	10.27 ± 0.45	-
Dietary Insoluble Fiber (% on dw)	32.71 ± 0.67	-
Water Holding Capacity (% on dw)	3.65 ± 0.28	-
Oil Retention Capacity (% on dw)	3.28 ± 0.89	-

3.2 Solid phase characterization

The solid recovered after the different hydrothermal treatments was analysed for several aspects. As first, the aim was to evaluate the solid yield of these treatments and the potential recovery of cellulose, hemicellulose and lignin. The results of the analyses, obtained through the structural carbohydrate analytical method, are shown in Table 2 and Table 3. As expected, the solid yield shows a decreasing trend with respect of the

increase of temperature and of the increase of L/S ratio. Indeed, higher temperature leads to higher degradation of the solid, while a higher amount of water is an advantage for hydrolysis reactions that are thermodynamically disadvantaged. It is useful to point out that the recovery of solids seems to stabilize around 50% if L/S ratio increases. Therefore a further increase in this ratio will not significantly change the recovery of the solid. Cellulose recovery does not seem to be affected by L/S ratio, while a significant cellulose degradation was observed for temperature above 200°C. These same values can be found using wheat straw and in particular there is a recovery of cellulose equal to 83.2 ± 2.2 % at 195 °C. This is significant because, presenting a higher cellulose content than grape pomace, wheat straw can be a valid solution for the recovery of cellulose. Regarding the hemicellulose fraction, L/S ratio does not significantly influence hydrolysis, even if, compared to cellulose, hemicellulose are hydrolyzed about 15% more. On the other hand, the increase of temperature leads to an increase of hemicellulose hydrolysis, up to the complete hydrolysis at 210 ° C. Finally, acid insoluble lignin was partially solubilized and no significant difference can be highlighted between treatments at different temperatures and treatments at different solid ratio.

Table 2 Solid Yield, Cellulose, Hemicellulose and Lignin recovery at constant temperature (175°C)

L/S ratio	Solid Yield (%)	Cellulose Recovery (%)	Hemicellulose Recovery (%)	Insoluble Lignin Recovery (%)
1.5	73.79 ± 5.79	97.18 ± 17.90	79.72 ± 2.75	10.05 ± 0.67
5.0	57.11 ± 9.42	98.96 ± 16.64	85.67 ± 3.56	8.98 ± 0.66
10.0	59.57 ± 3.42	83.88 ± 7.92	73.31 ± 3.45	6.89 ± 0.79
20.0	52.06 ± 0.46	94.00 ± 7.69	82.71 ± 11.48	8.93 ± 0.47

Table 3 Solid Yield, Cellulose, Hemicellulose and Lignin recovery at constant L/S ratio (20:1)

Temperature [°C]	Solid Yield (%)	Cellulose Recovery (%)	Hemicellulose Recovery (%)	Insoluble Lignin Recovery (%)
175	52.06 ± 0.46	94.00 ± 7.69	82.71 ± 11.48	8.93 ± 0.47
195	54.19 ± 6.95	93.61 ± 15.29	37.12 ± 4.65	10.78 ± 1.19
210	46.98 ± 2.04	79.58 ± 3.85	6.69 ± 0.82	9.21 ± 0.72

As already mentioned, the treated grape pomace has also been characterized in terms of dietary fiber, WHC and ORC in order to evaluate their variability with respect to the change of operating conditions (Table 4 and Table 5). The soluble fibre content is very low in all cases, while the concentration of insoluble fibre is higher if compared to the insoluble fiber of grape pomace before treatment. However, it is important to point out that has not been possible to give a definitive explanation for some results. For example, the value of insoluble fiber at 195 °C is lower than the others with the same L/S ratio. For this reason, some additional tests will be planned as future work in order to better clarify this behavior. Concerning the water holding capacity, the results show an increase in the capacity to absorb with the increase of L/S ratio and show a decrease with respect to an increase of temperature. However, the samples have a global low water holding capacity (Yamazaki et al., 2005). Therefore, if the treatment is aimed to maximise WHC, the operating conditions need to have high L/S ratio and low temperature. In addition, it is interesting to notice that WHC is always higher id compared to the untreated sample and so these treatments have a positive effect on this property. Finally, oil retention capacity show, after all the treatments, a higher value than the untreated sample, but there are no significant differences with the variation of temperature or of L/S ratio.

Table 4 Dietary Fiber, WHC and ORC at constant temperature (175°C)

L/S ratio	Soluble Dietary Fiber (% on dw)	Insoluble Dietary Fiber (% on dw)	WHC (% on dw)	ORC (% on dw)
1.5	1.18 ± 0.57	62.93 ± 5.29	4.17± 0.04	4.20 ± 0.03
5.0	0.21 ± 0.31	73.14 ± 1.00	3.75 ± 0.16	4.32 ± 0.10
10.0	0.19 ± 0.27	59.69 ± 0.58	5.87 ± 0.70	4.17 ± 0.13
20.0	0.41 ± 0.58	80.69 ± 0.61	6.75 ± 0.70	4.71 ± 0.33

Table 5 Dietary Fiber, WHC and ORC at constant L/S ratio (20:1)

Temperature [°C]	Soluble Dietary Fiber (% on dw)	Insoluble Dietary Fiber (% on dw)	WHC (% on dw)	ORC (% on dw)
175	0.41 ± 0.58	80.69 ± 0.61	6.75 ± 0.70	4.71 ± 0.33
195	n.a.	67.82 ± 1.04	5.91 ± 0.11	5.82 ± 0.08
210	0.60 ± 0.36	79.14 ± 1.81	4.51 ± 0.69	5.22 ± 0.34

3.3 Liquid phase characterization

The liquid recovered after the different hydrothermal treatments was analysed for the total amount of phenol and its antioxidant capacity. It is important to underline that for liquid to solid ratio equal to 1.5 and 5 no liquid were recovered. The results, reported in Table 6 and Table 7, show strong increasing of the total phenol content with respect of S/L ratio increase, while no significant effect was highlighted with the variation of hydrolysis temperature. The values obtained from the Folin-Ciocalteau assay are confirmed also by direct reading at 280 nm for the case of constant temperature, while in case of constant L/S ratio, the three different treatments show an increase of phenol recovery with the increase of temperature. This could be explained by the solubilisation of lignin that, at high temperature with the successive formation of sugar degradation compounds. On the other hand, in case of direct readings at 320 nm the value shows a clear degradation of these compounds at 210°C and a low phenol extraction with an S/L ratio equal to 10.0. For this reason, the extraction of phenolic compounds is favoured by the use of greater amount of water. As expected, the results were also confirmed by FRAP and ABTS assay which show no influence of the hydrolysis temperature, while the antioxidant power increases with respect of the increase of L/S ratio, especially for FRAP assay.
Therefore, the results point out that, in the case of a treatment aimed to recover antioxidant hydrolysates, it would be advisable to choose a treatment with high L/S ratio, while it is not possible, at the moment, to select the optimal temperature. For this reason, further test will be done in order to asses this aspect. Finally, Table Table 8 shows the results obtained in Newpack project for liquid phase characterization. It is important to underline that only one condition was evaluated just for as brief comparison with this work because was antioxidant recovery is not the main aim the project. However, the Folin, Frap and ABTS assays confirm that a raw material with high content of cellulose and lignin release less antioxidant compounds and so are more suitable for cellulose recovery. On the contrary, grape pomace could be used for antioxidant recovery that could be apply into pharmaceutical or cosmetics products.

Table 6 Total phenol content, antioxidant capacity and reducing power at constant temperature (175°C)

L/S ratio	Liquid Yield	Total Phenol (mgGAE/gdw)	280 nm (mgGAE/gdw).	320 nm (mgCAE/gdw)	FRAP (mmolFe(II)/gdw)	ABTS (mmolTrolox/gdw).
10.0	73.75 ± 3.54	2186.68 ± 75.19	2456.35 ± 2.31	263.81 ± 2.08	21.14 ± 0.96	6.66 ± 0.55
20.0	84.75 ± 3.18	4425.86 ± 92.15	4105.80 ± 19.91	3882.61 ± 8.19	43.90 ± 2.84	13.35 ± 0.56

Table 7 Total phenol content, antioxidant capacity and reducing power at constant L/S ratio (20:1)

Temperature [°C]	Liquid Yield	Total Phenol (mgGAE/gdw)	280 nm (mgGAE/gdw).	320 nm (mgCAE/gdw)	FRAP (mmolFe(II)/gdw)	ABTS (mmolTrolox/gdw).
175	84.75 ± 3.18	4425.86 ± 92.15	4105.80 ± 19.91	3882.61 ± 8.19	43.90 ± 2.84	13.35 ± 0.56
195	81.13 ± 0.18	4027.80 ± 59.03	4681.26 ± 35.02	3972.32 ± 9.27	43.53 ± 1.50	13.20 ± 0.52
210	87.88 ± 2.30	4237.32 ± 150.5	6368.68 ± 4.06	610.24 ± 0.69	55.18 ± 3.24	14.57 ± 0.62

Table 8 Total phenol content, antioxidant capacity and reducing power using wheat straw

L/S ratio	Temperature [°C]	Total Phenol (mgGAE/gdw)	FRAP (µmolFe(II)/gdw)	ABTS (µmolTrolox/gdw).
20.0	195	27.44 ± 15.18	373.91 ± 45.08	123.85 ± 7.00

4. Conclusions

The aim of this work was to test hydrothermal treatment at high pressure (i.e. autohydrolysis) on grape pomace to study and evaluate the effects of the treatment on the solid and on the liquid obtained. The treatment was evaluated at different operating conditions, changing the final temperature reached and the inlet ratio between solid and liquid. The autohydrolysis was proved to be very effective for the extraction of antioxidant compounds from grape pomace and could represent a suitable and sustainable alternative, from an environmental point of view, for the recovery of these compounds that will be used in cosmetics or pharmaceutical sectors. At the same time, autohydrolysis was also proved to be effective in terms of cellulose recovery from the solid residue. However, grape pomace is probably not very suitable for this goal due to its low cellulose content. For this reason, wheat straw can be a good alternative if the final goal is cellulose recovery. Indeed, with the same percentage of cellulose recovered, the initial amount of cellulose is higher in wheat straw. On the contrary, wheat straw releases few antioxidant compounds whose recovery will not be economically sustainable. As already mentioned, this work is the base for possible future developments, studies and applications of the treated compounds. For sure, further analysis will be carried out to better understand the behaviour of the treated grape pomace such as the evaluation of free sugars and the

evaluation of the degradation products of sugars through HPLC analysis. This will allow to evaluate different optimal conditions depending on the aim selected, like cellulose, antioxidant, or specific compound recovery.

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References

Bassani A., Montes S., Jubete E., Palenzuela J., Sanjuan A. P., Spigno, G., 2019, Incorporation of Waste Orange Peels Extracts Into Pla Films, Chemical Engineering Transactions, 74, 1063-1068.

Garau, M. C., Simal, S., Rossello, C., & Femenia, A. (2007). Effect of air-drying temperature on physico-chemical properties of dietary fibre and antioxidant capacity of orange (Citrus aurantium v. Canoneta) by-products. Food chemistry, 104(3), 1014-1024.

García A., Amendola D., González M., Spigno G., Labidi J., 2011. Lignin as natural radical scavenger. Study of the antioxidant capacity of apple tree pruning lignin obtained by different methods. Chemical Engineering Transactions, 24, 925-930, DOI: 10.3303/CET1124155.

Garrote G., Falqué E., Domínguez H., Parajó, J. C., 2007, Autohydrolysis of agricultural residues: Study of reaction byproducts, Bioresource Technology, 98(10), 1951-1957.

Gruppi A., Garrido G.D., Dordoni R., De Faveri D.M., Spigno G., 2017. Enzymatic wheat conditioning. Chemical Engineering Transactions 57, 1777-1782, DOI: 10.3303/CET1757297.

Mateos-Aparicio I., Redondo-Cuenca A., Villanueva-Suárez M.J., 2010. Isolation and characterisation of cell wall polysaccharides from legume by-products: Okara (soymilk residue), pea pod and broad bean pod. Food Chemistry, 122, 339-345.

Papargyropoulou E., Lozano R., Steinberger J. K., Wright N., bin Ujang Z., 2014, The food waste hierarchy as a framework for the management of food surplus and food waste, Journal of Cleaner Production, 76, 106-115.

Rowell R., 1983, The chemistry of solid wood: based on short course and symposium sponsored by the division of cellulose, paper, and textile chemistry at the 185th meeting of the American Chemical Society, Seattle, Washington, March 20–25, pp. 70–72.

Rowell R. M. (2012), Handbook of wood chemistry and wood composites, CRC press.

Ruiz H. A., Ruzene D. S., Silva D. P., da Silva F. F. M., Vicente A. A., Teixeira J. A., 2011, Development and characterization of an environmentally friendly process sequence (autohydrolysis and organosolv) for wheat straw delignification, Applied biochemistry and biotechnology, 164(5), 629-641.

Sluiter A., Hames B., Ruiz R., Scarlata C., Sluiter J., Templeton D., Crocker D., 2010, Determination of structural carbohydrates and lignin in biomass, Laboratory analytical procedure, (TP-510-42618).

Santana-Méridas O., González-Coloma A., Sánchez-Vioque R., 2012, Agricultural residues as a source of bioactive natural products. Phytochemistry reviews, 11(4), 447-466.

Spigno G., De Faveri D. M., 2007a, Antioxidants from grape stalks and marc: Influence of extraction procedure on yield, purity and antioxidant power of the extracts, Journal of Food Engineering, 78(3), 793-801.

Spigno G., Tramelli L., De Faveri, D. M., 2007b, Effects of extraction time, temperature and solvent on concentration and antioxidant activity of grape marc phenolics. Journal of food engineering, 81(1), 200-208.

Spigno G., Pizzorno T., De Faveri, D. M., 2008, Cellulose and hemicelluloses recovery from grape stalks, Bioresource Technology, 99(10), 4329-4337.

Vadivel V., Moncalvo A., Dordoni R., Spigno G.. 2017, Effects of an acid/alkaline treatment on the release of antioxidants and cellulose from different agro-food wastes, Waste Management, 64, 305-314.

Wise L.E., Murphy M., D'Adieco A., 1946, Chlorite holocellulose, its fractionation and bearing on summative wood analysis and on studies on the hemicelluloses, Paper Trade J., 122 (2), 35–43.

Yamazaki E., Murakami K., Kurita O., 2005, Easy preparation of dietary fiber with the high water-holding capacity from food sources. Plant foods for human nutrition, 60(1), 17-23.