-

Environmental Engineering and Management Journal

March 2021, Vol. 20, No. 3, 389-396
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

FRACTIONATION OF AGRICULTURAL WASTE BIOMASS BY MEANS OF INTEGRATED BIOREFINERY CONCEPT

Adrian Cătălin Puiţel[1*], Gabriel Dan Suditu[2], Mircea Teodor Nechita[2], Dan Gavrilescu[1]

[1]*"Gheorghe Asachi" Technical University of Iaşi, Faculty of Chemical Engineering and Environmental Protection "Cristofor Simionescu", Department of Natural and Synthetic Polymers,*
[2]*"Gheorghe Asachi" Technical University of Iaşi, Faculty of Chemical Engineering and Environmental Protection "Cristofor Simionescu", Department of Chemical Engineering*
73 Prof. D. Mangeron Blvd., 700050, Iasi, Romania

Abstract

Separation of lignocellulosic biomass components aims to produce materials and chemicals by processing a widely available and renewable category of raw materials. Corn stalks represent an important category of agricultural waste which can be processed into papermaking pulp. An often mentioned disadvantage of corn stalk usage as raw material in pulping process is the high amount of hemicelluloses, considered responsible for the alkali consumption during pulping and poor results in sorted pulp yields. Hemicelluloses contained by corn stalks can be extracted in a fiber based biorefinery processing approach in which extractive preliminary treatments forego pulping. We have investigated the effect of autohydrolysis process parameters (temperature and process time) on: yield of obtained pulp, the mechanical strength of laboratory paper sheets and sugar and lignin content of autohydrolysis liquors. It was found that in autohydrolysis, moderate conditions - 120°C and up to 90 minutes of treatment- leads to improvements in sorted pulp yields with minor drops in total yield values. The decreases of mechanical strength may be considered acceptable within a limit of 25% loss compared with control sample. In comparison with control pulping, the total solid yield decreased for all preatreated samples. The autohydrolysis loss of material ranged from 12% to 25%, while the concentration of sugars reached 6.25g/L for glucose and 4.22 g/L for xylose oligomers.

Key words: corn stalks, lignin, mechanical strength, monosaccharaides, pulp

Received: June, 2020; Revised final: August, 2020; Accepted: January, 2021; Published in final edited form: March, 2021

1. Introduction

The pulp and paper industry properly illustrate the biorefinery concept, which incorporates the production of materials, chemicals and energy, through established technological processes that maximizes the value of wood chain. In pulp and paper industry, wood is traditionally the most used virgin fiber source causing forest overexploitation in many parts of the world. The industry is facing a continuous need for virgin fiber resources to overcome different market demands. Moreover, packaging is lately turning towards green alternatives by replacing plastics with fiber-based materials such as paper and cardboard. In such context, a shift of the industry to processing nonwood fiber sources is acknowledged. Attractiveness of non-wood fiber sources resides in their lower lignin content, availability and shorter growing cycle.

Most of the disadvantages of nonwoods are linked to their higher than wood content of hemicelluloses, ash and extractives, may be solved in an integrated lignocellulosic biorefinery concept approach, which must be able to efficiently use local-regional available feedstocks as raw material. After wheat, corn is the most cultivated crop in the world.

* Author to whom all correspondence should be addressed: e-mail: puitelac@ch.tuiasi.ro; Phone: +40 232 278683 / 2135; Fax: +40 232 271311

According to literature data, corn farming reached 18.6% of total cultivated cereals in the European Union (Eurostat, 2019). Corn stover yields are in the range of 1.7 - 4.5 t/ha. The medium harvest rate of 2.49 t/ha in which mass of stalks represent at least 70%. Habitually corn stover end uses: animal feed and bedding, combustion in power plants. Corn stover presents a particular interest for fermentative sugars and further ethanol production (Zhao et al., 2018). In such contexts, lignin and hemicelluloses are extracted from raw materials by various physico-chemical treatments and the remaining solid residue, often impure cellulose is considered a raw material for sugar production by hydrolysis and further fermentation to ethanol (Ying et al., 2018). Corn stalks are least frequently studied as raw material for papermaking fiber production than straws and other agri-wastes.

Conversion of agri-wastes by integrated fiber based biorefinery concept is an approach through which renewable alternatives are to be converted into valuable commodities such as: fibers, lignin, chemicals, bio-fuels and energy. In this case, pulping process aims at lignin removal and liberation of cellulose fibers. Cellulose fibers obtained from non-woods are of use for paper and packaging products - reestablish the papermaking properties of recycled paper; paper for food contact packaging. Pulping is also a critical step for processing involving enzymatic conversion to sugars (Patil et al., 2019).

Hemicelluloses content of some of these types of resources are responsible for low pulp yield due to degradation in the initial phases of pulping and alkali consumption. In this case, the removal of biomass' hemicelluloses is used as an initial extraction step to convert them to sugars which could be subsequently fermented by microorganisms to the much-valued ethanol and other chemicals. Lignin and extractives may be separated and converted to various chemicals or energy (Lauwaert et al., 2019). Literature studies regarding extraction of the hemicelluloses from both woods and nonwoods indicate that the most common types of pre-treatments are: alkaline extraction (Egüés et al., 2012); acid hydrolysis (Zimbardi et al., 2007; Zhao et al., 2018) and finaly autohydrolysis (Buruiana et al., 2014). The autohydrolysis, also referred as hot water pretreatment, leads to the lowest drops in yields, intrinsic viscosity of pulps and better preservation of mechanical strength (Jahan and Rahman, 2012).

The choice between different types of treatments is in strong dependence with the final purpose of the extraction. In this respect, some authors showed that alkaline pretreatment is preferable for higher efficiency hemicellulose extraction from corn stalks (Egüés et al., 2012). The same study of Egüés et al., 2012 indicated that hot water treatment leads to hemicelluloses dissolution with minor quantities of undesirable compounds. Liquid hot water pre-treatement is also targeted towards removal of hemicelluloses and also to the increase of enzymatic digestibility of the remaining cellulose fraction (Buruiana et al., 2014; Lü et al., 2017). Such severe treatment conditions involve high temperature (over 160°C), which cause cellulose degradation and loss of mechanical strength over acceptable limits for papermaking. In order to preserve the papermaking properties autohydrolysis condition should be milder. In the light of these, the data published by Jahan and Rahman (2012) have shown that a single stage hot water treatment of 60 minutes at 150°C leads to minor pulp yield loss and lower but acceptable paper strength. However, their study was not extended to further investigations regarding the effect of autohydrolysis parameters on pulp properties or liquour sugar content.

A primary objective of the current work was to determine the effect of autohydrolysis pretreatment stage of corn stalks on soda pulping process results in terms of total solid yield, sorted pulp yield, pulp viscosity and mechanical strength properties. A secondary objective of our work was the investigation of obtained autohydrolysis liquors in terms of sugars (soluble xylose and glucose oligomers) and lignin content.

2. Materials and methods

2.1. Raw materials

Corn stalks were kindly donated by local farmers in Iasi county from Romania. Before analysis and laboratory pulping trials, a preliminary processing stage which included removal of leaves and dirt, conditioning to about 10% moisture, chopping to 10 cm pieces for pulping and grinding for chemical analysis was performed.

2.2. Analytical methods

The chemical composition of corn stalks were established by the following analytical methods: cellulose (Kurschner and Hoffer ethanol-nitric acid method); holocellulose (Wise sodium chlorite method); lignin (TAPPI T 222 om-02, 2002); ash (TAPPI T 211 om-02, 2002) and 1% sodium hydroxide solubility (TAPPI T 212 om-02, 2002). Determination of glucan and xylan content of corn stalks was performed after a two stage complete hydrolysis of corn stalks (72% and 4% sulfuric acid) as described in NREL standard method Determination of Structural Carbohydrates and Lignin in Biomass (TP-510-42618). The hydrolysis resulted sugars were separated and determined using a HPLC chromatography system equipped with Phenomenex Rezex RPM-Monosaccharide Pb^{+2} (8%) 300 x 7.8 mm heated at 75°C and a Shimadzu RID 10A refractive index detector. The mobile phase consisted of ultrapure water with a flow of 0.6 mL/minute.

Determination of the total sugars (oligosaccharides forms of glucose, xylose) content of autohydrolysis resulted liquors was performed following the NREL method Determination of Sugars, Byproducts, and Degradation Products in Liquid Fraction Process Samples Laboratory Analytical Procedure (LAP) TP-510-42623. The acid soluble lignin content in autohydrolysis liquors was determined by measuring the absorbance of diluted filtrates at 320 nm and using an absorptivity coefficient of 30 L/g cm as recommended by NREL.

2.3. Autohydrolysis treatment and pulping of corn stalks

In this study, the autohydrolysis time and temperature impact on the soda pulping of corn stalks were investigated. In this way, the temperature and autohydrolysis time were varied: 120 °C, 140 °C and 160 °C and 60 to 180 minutes. Typical experiments involved using 300 g of oven dried corn stalks which were treated in a rotary pressurized stainless steel reaction vessel equipped with electric heating and temperature controller at a and solid to liquid ratio of 1:5. Samples of autohydrolysis liquor were withdrawn from the reactor each 30 minutes after reaching the set temperature of autohydrolysis process in order to determine the content of oligomers of glucose, xylose, arabinose and lignin. The pre-treated corn stalks were washed, dried to convenient moisture (8-10%) and further used for soda pulping. The loss of material during autohydrolysis was determined gravimetrically.

The control soda pulping (in which untreated corn stalks were used) process conditions were as follows: solid to liquid ratio of 1:5; heating time - 30 minutes; cooking time - 40 minutes at a temperature of 120ºC. The active alkali charge - 12 % expressed as NaOH units. The pressure during pulping was kept constant at 0.2MPa. The autohydrolysis treated corn stalks pulping trials were performed in the same conditions as control pulping. The obtained pulps were screened on a 2 mm screen to determine the sorting yield and used for further analysis and sheet formation.

2.4. Pulp and laboratory sheets characterization

The overall process - autohydrolysis pretreatment and soda pulping total yield and sorted pulp pulping yields (gravimetric method); The obtained pulp was subjected to determination of intrinsic viscosity (ISO 5351:2010) and mechanical strength properties in unbeaten state (17-18°SR) and five minutes beaten (850 rotations) pulps beaten. A Jokro mill was used for beating (ISO 5264-3:1979). The obtained laboratory sheets were subjected for analysis of tensile strength (ISO 1924:2008) and burst strength (ISO 2758:2001).

3. Results and discussion

3.1. Chemical composition of raw materials

The chemical composition of corn stalks as of other types of lignocellulosic biomass, includes: cellulose, hemicelluloses and lignin. The results regarding the corn stalks used in the current study are displayed in Table 1. The values were comparable to other data presented in other similar existing studies (Cheşcă et al., 2018; Hu et al., 2018; Zhang et al., 2015).

It should be noted that the values reported in the literature vary greatly as function of many factors including the variety of corn and cultivation area. Threre are also some minor differences regarding the values of cellulose and lignin content caused by the method diffferences. In case of cellulose, its determination by NREL method involves the hydrolysis to glucose via two steps of sample treatment (hydrolysis with sulphuric acid 72% and posthydrolysis with sulphuric acid 4%). These results in higher values due to its cuantification as glucose oligomers which could result from hydrolysis of cellulose but also from hemicellulosic branches such as glucomanan (Bajpai, 2018).

The data displayed in Table 1 shows that corn stalks may be considered an adequate material for pulping, but as in case of other nonwoods raw materials some considerations regarding the pulping process should be discussed. In this particular case, the lower lignin content and high content of 1% sodium hydroxide solubility value may indicate that the pulping should be performed in milder conditions with lower alkali charges. The high value of hemicelluloses, mainly represented by pentosans indicates the opportunity of their extraction prior to pulping process (Egüés et al, 2012).

Table 1. Chemical composition of corn stalks

Chemical composition (%)						
Cellulose	*Acid insoluble lignin*	*Acid soluble lignin*	*Xylan*	*Holocellulose*	*NaOH (1%) solubility*	*Ash*
42.2[a] (±1.05)	22.1[b] (±0.88)	0.92[b] (±0.18)	-	70.89[c] (±1.02)	44.5[e] (±0.68)	4.34[d] (±0.28)
43.05[f] (±0.35)	19.56[f] (±0.48)	1.07[f] (±0.38)	18.7 (±0.58)	-	-	-
40.9[g]	16.6[g]	-	23.07	-	-	-
30.89[h]	23.49[h]	-	15.77[h]	-	-	-
38.0[i]	18.5[i]	-	26.1[i]	-	-	5.1[i]

[a]- Determined according to method Kurschner and Hoffer method; [b]- determined according to TAPPI T 222 om-02, 2002; [c]- determined according to sodium chlorite Wise method; [d]- determined by TAPPI T 211 om-02, 2002; [e]- determined according to T 212 om-02, 2002; [f]- determined according to NREL TP-510-42618; [g]- reported by Zhang et al. (2015), [h]- Hu et al.(2018); [i]-Cheşcă et al. (2018).

3.2 Impact of autohydrolysis pretreatment on process yield, pulp and laboratory sheets quality

The autohydrolysis pretreatment significantly affects both the values of overall process solid yield and sorted pulp yield. In case of the reference sample (without pretreatment) the determined total yield was 48.3% while the sorted yield value was 29.5%. These aspects can be observed in Figs. 1-2 which indicate that the increase of either the autohydrolysis time or temperature leads to significant drops in both total yield and sorted pulp yield. At constant temperature, both solid yield and sorted pulp yield are significantly affected by the increase of treatment time. The reference (unhydrolised) sample showed higher values of total yield compared to all of the autohydrolysed samples. In case of sorted pulp yield, the autohydrolysis treatment had a positive effect by increasing its values for the samples with 60 minutes of autohydrolisis treatment at temperatures of 120 and 140°C. The values obtained for overall process solid yield were comparable with the results mentioned in other studies (Sarwar Jahan and Mostafizur Rahman, 2012). When compared to control pulping, in our study the total solid yield decreased for all the preatreated corn stalk experimental trials with values ranging from about 3% to 56%. In case of sorted pulp yield, a parameter which reflects the potential usage of resulted pulping material for papermaking, the only experiments which were recorded with increased values (range between 14% to 23%) were those performed at 120°C and autohydrolysis time below 90 minutes.

Fig. 3 displays the variation of pH of the autohydrolysis liquor, while Fig. 4 shows the intrinsic viscosity of pulp samples obtained after autohydrolysis treatment at different temperatures and process time. From Fig. 3 the continuous drop of pH as autohydrolisys time and temperature increase may be visualized. The pH decrease is a result of acetic acid formation during decomposition of hemicelluloses at high temperatures as mentioned by different authors (Buruiana et al., 2014; Lü et al., 2017; Pola et al., 2019).

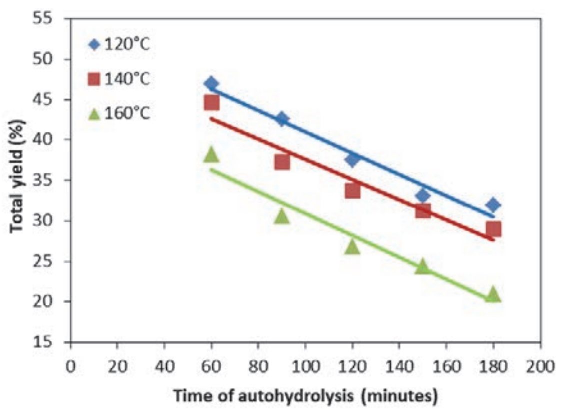

Fig. 1. Effect of autohydrolysis pretreatment on overall process yield

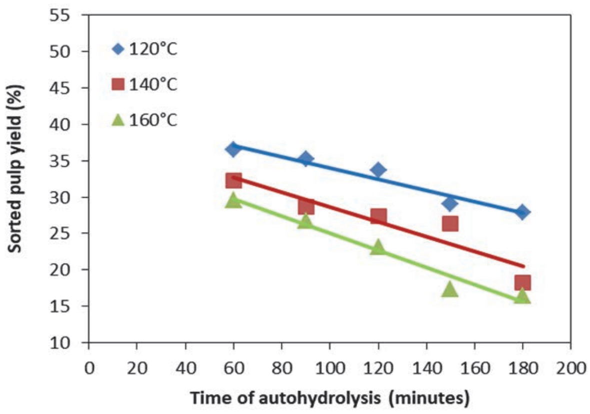

Fig. 2. Effect of autohydrolysis pretreatment on sorted pulp yield

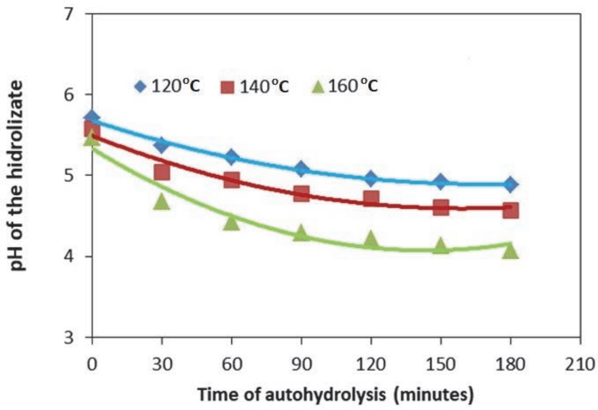

Fig. 3. The variation of autohydrolysis liquor pH during autohydrolysis

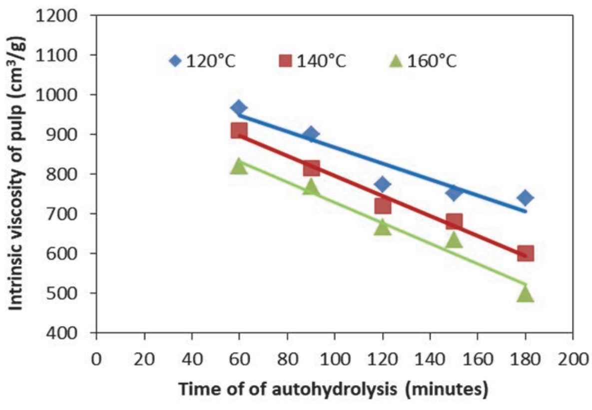

Fig. 4. The effect of autohydrolysis pretreatment parameters on pulp intrinsic viscosity

The autohydrolysis pretreatment has a significant impact on pulp viscosity which is directly correlated with cellulose degree of polymerization. While the intrinsic viscosity value of the reference sample was 1089 cm^3/g, the viscosity of pulps obtained from autohydrolysed corn stalks decrease linearly both with temperature and at constant temperature with autohydrolysis time as observable in Fig. 4. The recorded viscosity loss ranged from 11% to 38% as compared to the reference pulp sample.

Figs. 5-8 show the variation of tensile strength and of the burst strength of the obtained paper sheets in both unbeaten and beaten state. As compared with reference sample (tensile index for unbeaten and beaten pulp sheets - 39.5 N.m/g and 62.4 N.m/g; burst index 2.3 kPa·m^2/g for unbeaten and 3.27 kPa·m^2/g beaten pulp sheets- it may be observed that mechanical properties are significantly affected by the autohydrolysis treatment.

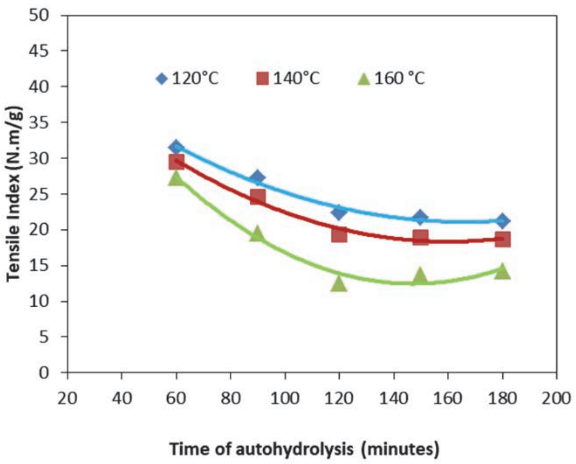

Fig. 5. The variation of tensile index of laboratory paper sheets in case of unbeaten pulps as function of time of autohydrolysis process performed at different temperatures

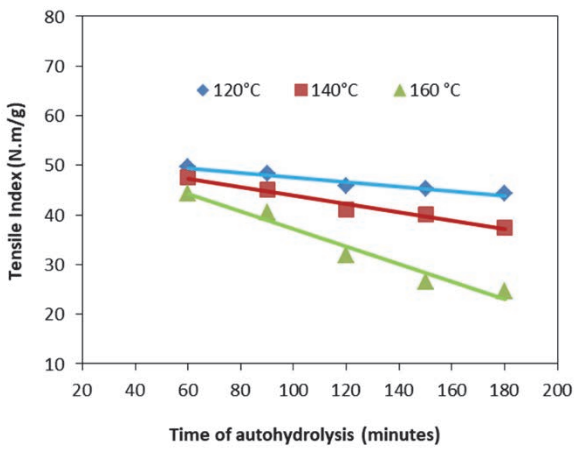

Fig. 6. The variation of tensile index of laboratory paper sheets in case of beaten pulps as function of time of autohydrolysis process performed at different temperatures

The observed mechanical strength loss of the laboratory obtained paper sheets can be easily associated with the same phenomena observed for the viscosity decrease - cellulose degradation during the hemicellulose extraction process associated with the pH drop caused by the release of acetic acid (Liu et al., 2015). The mechanical strength loss compared to reference sample for the unbeaten and beaten pulps was found to be up to 64% fort the tensile strength and 66% for burst strength. As regarding to the suitability of the fibers for producing packaging papers, the determined tensile and burst index values indicate that most favorable conditions for corn stalk treatment with acceptable strength loss is that performed at lower temperature (120°C and 140°C for at most 60 minutes). The observed increase of strength of obtained paper sheets occurring after beating is a result of the increase apparent density and fiber bonding (Motamedian et al., 2019).

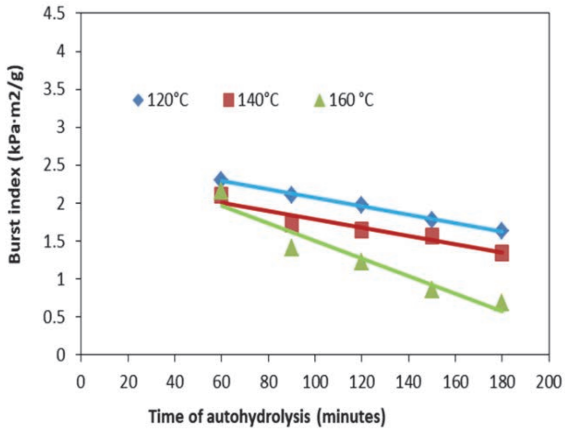

Fig. 7. The variation of burst index of laboratory paper sheets in case of unbeaten pulps as function of time of autohydrolysis process performed at different temperatures

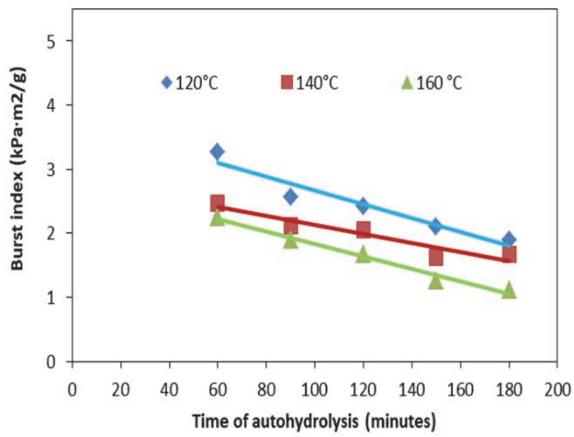

Fig. 8. The variation of burst index of laboratory paper sheets in case of beaten pulps as function of time of autohydrolysis process performed at different temperatures

3.3. Characterization of autohydrolysis resulted liquid stream

The chemical composition profile of autohydrolysis resulted liquid stream fraction is rather complex and includes: sugars (both as monomers and oligomers either extracted or resulted as products of polysaccharide hydrolysis; organic acids - mainly acetic acid originating from hemicelluloses acetyl groups cleavage; furfural and the hydroxymethylfurfural formed by dehydration of pentoses and hexoses; lignin and lignin degradation products and other water soluble extractives as well as mineral salts previously determined as ash (Rivas et al., 2012; Santos et al., 2018). These chemicals make up the amount of corn stalks autohydrolysis loss of mass which is also as function of the treatment time and temperature as it may be observed in Fig. 9., and could end up to about 25% at highest temperature and residence time of 160°C and 180 minutes of treatment. The increase of either process time or temperature leads to the increase of the corn stalks mass loss. At 160 °C the mass los percentage seems to be much more important than the values at 120 °C and 140 °C, being almost double. The overall range of autohydrolysis loss of material ranged from 12% to 25%. The obtained data regarding autohydrolysis mass loss are in accordance with reported literature data. By example, Buruiana et al. (2014) reported a weight loss of 24% by treating corn stover at 180°C for 30 minutes, while Egues et al. (2012) reported a higher loss of about 39% for corn stalks treated at 160°C for 60 minutes.

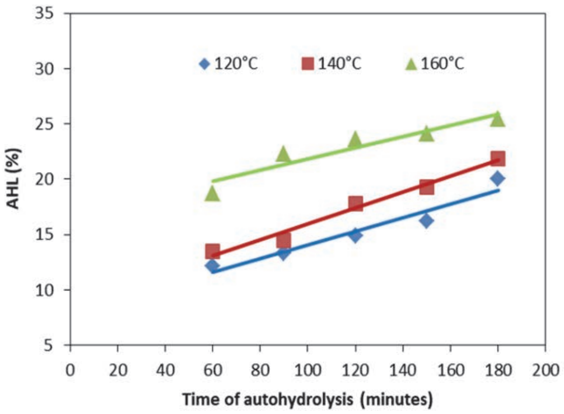

Fig. 9. The effect of autohydrolysis parameters on the corn stalk loss of mass - AHL (%) in autohydrolysis liquor samples

A increasing trend is also observed in case of lignin concentration variation displayed in Fig. 10. also increased in respect with temperature and time. The concentration of lignin in autohydrolysis liquour samples varied from 6 g/L to about 14g/L. In case of lignin, the literature mentions it as unwanted in case of use hydrolysis liquors as raw material for fermentative processes, therefore its elimination is necessary (Chen et al., 2016).

The evolution of the concentrations of sugars (determined as sum of monomers and oligomers of glucose and xylose respectivelly after posthydrolysis at 121°C) with time and temperature of the autohydrolysis process can be visualized in Fig. 11 and Fig. 12. The glucooligomers concentration in corn stalks autohydrolys liquour decreses almost linearly at all temperatures. This aspect was found as contradictory to literature reports which mostly report the increase of glucose and its oligomers in autohydrolysis liquours of agri-waste biomass with time and treatment temperature (Aboagye et al., 2017; Moniz et al., 2013). The glucose concentrations which were higher in lower temperature and residence time hydrolysates are sugesting that it originates in the pith as free gluose or oligomers (Dong et al., 2011; Jones et al., 1979; Yan et al., 2006).

We hypothesized that these glucose and glucooligomers were extracted during heating to autohydrolysis set temperature period and further degraded due to effect of pH decrease and pretreatment conditions. In case of glucose the maximum concentration of 6.25g/L was observed for the sample of autohydrolysis liquour extracted at the reach of 120°C (initial moment of treatment).

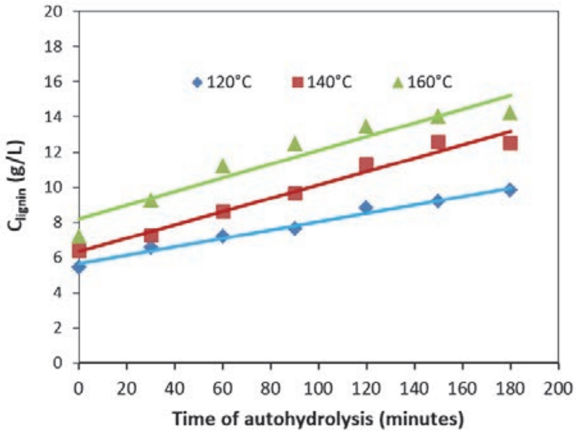

Fig. 10. The effect of autohydrolysis temperature and time on the lignin concentration in autohydrolysis liquor

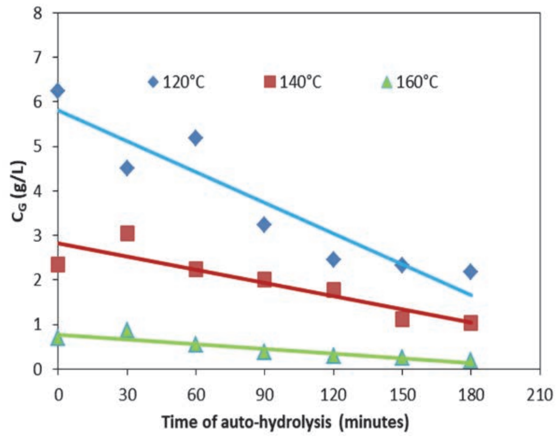

Fig. 11. The decrease of glucose and glucose oligomers concentration in the autohydrolysis liquours

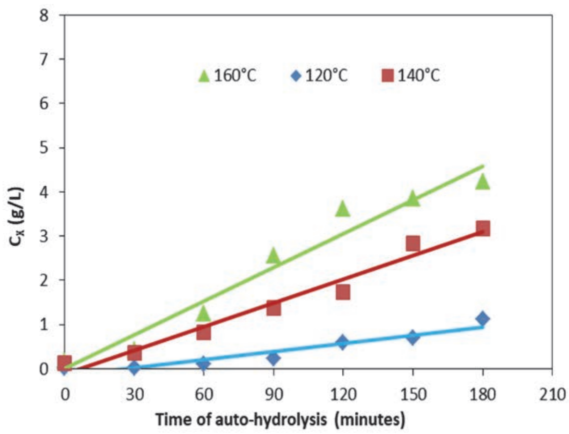

Fig. 12. The increse of xylose oligomers concentration in the autohydrolysis liquid streams

During the autohydrolysis process the xylose oligomers concentration in the produced autohydrolysis liquours increase with both time and temperature. The concentration of xylooligomers have indicated a much lower yield of extraction than those reported in the literature. Chen et al. (2016) reported an efficiency of about 13.5% (on o.d. corn stalks) or water extraction of xylose oligomers at 160°C for 180 min at a solid to liquid ratio of 1/10 for fine grounded stalks.

The same authors concluded that extending the pretreatment time for more than 180 minutes leaded to the decrease in the extracted xylan and oligomers due to degradation reasons. The concentration drops of xylose and coresponding oligomers are a result of their conversion to furfural at high temperatures (Buruiana et al., 2014; Khalili and Amiri, 2020; Koo et al., 2019; Zhang et al., 2011). However most of the cited studied report the use of corn stalks in finely ground state for exeperimental purposes, while in our case the fragmentation of stalks was limited to chopping to sizes of 5-6 cm. This shows a considerable difference in active surface which could end up in higher values of extraction yield (Liu et al., 2013). In case of xylose oligomers the highest concentration was achieved by extracting corn stalks for 180 minutes at 160°C.

4. Conclusions

The autohydrolysis treatments affect both pulping yields and pulp properties and the extent of induced variations have been found to be in good correlation with temperature and process time. In order to obtain pulps with acceptable yield and mechanical strengths suitable for packaging paper moderated temperatures and autohydrolysis time are recommended. The selection of preliminary treatment temperature and time should take into considerations the minimum acceptable fiber yield and maximum acceptable loss of mechanical strength according to final destination of obtained fibers. The mechanical strength loss compared to reference sample for the unbeaten and beaten pulps was found to be up to 64% fort the tensile strength and 66% for burst strength.

When compared to control pulping, in our study the total solid yield decreased for all the preatreated corn stalk experimental trials with values ranging from about 3% to 56%. In case of sorted pulp yield, a parameter which reflects the potential usage of resulted pulping material for papermaking, the only experiments which were recorded with increased values (range between 14% to 23%) were those performed at 120°C and autohydrolysis time below 90 minutes. The recorded intrinsic viscosity loss ranged from 11% to 38% as compared to the reference pulp sample.

The analysis of resulted autohydrolysis liquid streams confirmed the presence of lignin and sugars in amounts which also depended on the process parameters. While the overall range of autohydrolysis loss of material ranged from 12% to 25%. The concentration of lignin in autohydrolysis liquour samples varied from 6 g/L to about 14g/L. In case of glucose the maximum concentration of 6.25g/L eas observed for the sample of autohydrolysis liquour extracted at the reach of 120°C (initial moment of treatment), while in case of xylose oligomers, the highest concentration was achieved by extracting corn stalks for 180 minutes at 160°C.

Acknowledgements
This work was supported by a research grant of the TUIASI, project number GnaC2018_15 / 2019.

References

Aboagye D., Banadda N., Kambugu R., Seay J., Kiggundu N., Zziwa A., Kabenge I., (2017), Glucose recovery from different corn stover fractions using dilute acid and alkaline pretreatment techniques, *Journal of Ecology and Environment*, **41**, 26-34.

Bajpai P., (2018), *Wood and Fiber Fundamentals*, In: *Biermann's Handbook of Pulp and Paper,* Bajpai P. (Ed.), 3rd Edition, Elsevier, 19-74.

Buruiana C.T., Vizireanu C., Garrote G., Parajó J.C., (2014), Optimization of corn stover biorefinery for coproduction of oligomers and second generation bioethanol using non-isothermal autohydrolysis, *Industrial Crops and Products*, **54**, 32-39.

Chen H., Liu Y., Kong, F., Lucia L.A., Lou R., (2016), Dissolution of pentosan in corn stalk by hot water and purification using ion exchange resin, *Cellulose Chemistry and Technology*, **50**, 669-674.

Cheșcă A.M., Tofănică B.M., Puițel A.C., Nicu R., Gavrilescu D., (2018), Environmentally friendly cellulosic fibers from corn stalks, *Environmental Engineering and Management Journal*, **17**, 1765-1771.

Dong Y.F., Jie L., Hui J., Rui F. Y., Teng F.Y., (2011), Comparison of enzymatic hydrolysis of leaves, husks and pith of corn stalk, *Advanced Materials Research,* **365**, 240-244.

Eurostat, (2019), Eurostat statistics explained -Agricultural production – crops, On line at: https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Agricultural_production_-_crops#Cereals.

Egüés I., Sanchez C., Mondragon I., Labidi J., (2012), Effect of alkaline and autohydrolysis processes on the purity of obtained hemicelluloses from corn stalks, *Bioresource Technology*, **103**, 239-248.

Han Q., Gao X., Zhang H., Chen K., Peng L., Jia Q., (2019), Preparation and comparative assessment of regenerated cellulose films from corn (*Zea mays*) stalk pulp fines in DMAc/LiCl solution, *Carbohydrate Polymers*, **218**, 315-323.

Hu X., Cheng L., Gu Z., Hong Y., Li Z., Li C., (2018), Effects of ionic liquid/water mixture pretreatment on the composition, the structure and the enzymatic hydrolysis of corn stalk, *Industrial Crops and Products*, **122**, 142-147.

Jones R., Krull L., Blessin C., Inglett G., (1979), Neutral sugars of hemicellulose fractions of pith from stalks of selected plants, *Cereal Chemistry*, **56**, 441-442

Jahan S.M., Rahman M.M., (2012), Effect of pre-hydrolysis on the soda-anthraquinone pulping of corn stalks and *Saccharum spontaneum* (kash), *Carbohydrate Polymers*, **88**, 583-588.

Khalili F., Amiri H., (2020), Integrated processes for production of cellulosic and hemicellulosic biobutanol from sweet sorghum bagasse using autohydrolysis, *Industrial Crops and Products*, **145**, 111-118 .

Koo B., Park J., Gonzalez R., Jameel H., Park S., (2019), Two-stage autohydrolysis and mechanical treatment to maximize sugar recovery from sweet sorghum bagasse, *Bioresource Technology*, **276**, 140-145.

Lauwaert J., Stals I., Lancefield C.S., Deschaumes W., Depuydt D., Vanlerberghe B., Devlamynck T., Bruijnincx P.C.A., Verberckmoes A., (2019), Pilot scale recovery of lignin from black liquor and advanced characterization of the final product, *Separation and Purification Technology*, **221**, 226-235.

Liu Z.H, Lei L., Pang F., Jin M.J., Li B.Z., Kang Y., Dale B. E., Yuan Y.J., (2013), Effects of biomass particle size on steam explosion pretreatment performance for improving the enzyme digestibility of corn stover, *Industrial Crops and Products*, **44**, 176-184.

Liu L., Liu W., Hou Q., Chen J., Xu N., (2015), Understanding of pH value and its effect on autohydrolysis pretreatment prior to poplar chemi-thermomechanical pulping, *Bioresource Technology*, **196**, 662-667.

Lü H., Shi X., Li Y., Meng F., Liu S., Yan L., (2017), Multi-objective regulation in autohydrolysis process of corn stover by liquid hot water pretreatment, *Chinese Journal of Chemical Engineering*, **25**, 499-506.

Moniz P., Pereira H., Quilhó T., Carvalheiro F., (2013), Characterisation and hydrothermal processing of corn straw towards the selective fractionation of hemicelluloses, *Industrial Crops and Products*, **50**, 145-153,

Motamedian H.R., Halilovic A.E., Kulachenko A., (2019), Mechanisms of strength and stiffness improvement of paper after PFI refining with a focus on the effect of fines, *Cellulose*, **26**, 4099-4124.

Patil R.S., Joshi S.M, Gogate P.R., (2019), Intensification of delignification of sawdust and subsequent enzymatic hydrolysis using ultrasound, *Ultrasonics Sonochemistry*, **58**, 104656, doi: 10.1016/j.ultsonch.2019.104656.

Pola L., Collado S., Paula Oulego P., Mario Díaz M., (2019), Production of carboxylic acids from the non-lignin residue of black liquor by hydrothermal treatments, *Bioresource Technology*, **284**, 105-114.

Rivas S., Gullón B., Gullón P.,Alonso L., Parajó A., (2012), Manufacture and properties of bifidogenic saccharides derived from wood mannan, *Journal of Agricultural and Food Chemistry*, **60**, 4296-4305.

Santos T.M., Alonso M.V., Oliet M., Domínguez J.C., Rigual V., Rodriguez F., (2018), Effect of autohydrolysis on Pinus radiata wood for hemicellulose extraction, *Carbohydrate Polymers*, **194**, 285-293.

Yan G.L., Cao C.M., Lu L., Meng Q.X., (2006), Comparison of main chemical composition and in vitro digestibility in various sections of corn stalks, *Journal of China Agricultural University*, **11**, 70-74.

Ying W., Shi Z., Yang H., Xu G., Zheng Z., Yang J., (2018), Effect of alkaline lignin modification on cellulase–lignin interactions and enzymatic saccharification yield, *Biotechnology for Biofuels*, **11**, 214-232.

Zhang Q., Zhang P., Pei Z.J., Xu F., Wang D., Vadlani P., (2015), Effects of ultrasonic vibration-assisted pelleting on chemical composition and sugar yield of corn stover and sorghum stalk, *Renewable Energy*, **76**, 160-166.

Zhang H., Jin Q., Xu R., Yan L., Lin Z., (2011), Kinetic studies of xylan hydrolysis of corn stover in a dilute acid cycle spray flow-through reactor, *Frontiers of Chemical Science and Engineering*, **5**, 252-257.

Zhao Y., Damgaard A., Christensen T.H., (2018), Bioethanol from corn stover - a review and technical assessment of alternative biotechnologies, *Progress in Energy and Combustion Science*, **67**, 275-291.

Zimbardi F., Viola E., F Nanna., Larocca E., Cardinale M., Barisano D., (2007) Acid impregnation and steam explosion of corn stover in batch processes, *Industrial Crops and Products*, **26**, 195-206.