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# APPLICATION OF DISTILLERY REFUSE IN PAPERMAKING: NOVEL METHODS OF TREATED DISTILLERY REFUSE SPECTRAL ANALYSIS

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## ABSTRACT

The aim of this work is to show utilization of waste fibres from a distillery refuse as a by-product of bioethanol production of the first generation. Today, many companies utilize the fibrous waste for Dried Distillers Grains with Solubles (DDGS) production or for combustion. The first alternative utilization purpose of the distillery refuse is papermaking and/or making products with high content of fibres. Those DDGS contain proteins and fibres but their combination in the forage mixture makes some problems in weight loss of animals – the fibres prevent the absorption of proteins and other nutritional compounds. This work presents some spectral properties of treated distillery refuse and some physical-mechanical properties of beaten distillery refuse. In addition, optical properties of produced paper sheets are monitored if these are made of beaten and bleached distillery refuse.

KEYWORDS: DDGS, distillery refuse, NIR spectroscopy, bioethanol, waste fibre, holocellulose.

## INTRODUCTION

During the last decade, distillery refuse from bioethanol production has been utilized for feed material production and was used as a fuel as well. The distillery refuse is a mixture consisting of holocellulose (cellulose and hemicellulose), proteins, lignin and ash-forming elements. If suitable separation methods are used, the ratio of fibrous material to other mixture components increases. Efficiency of some separation methods is studied: filtration, sedimentation and centrifugation. Filtration and sedimentation are not effective because the separation processes take a long time (days) and they are space-consuming. The most effective separation method is centrifugation because the centrifugation process takes a few minutes and it is space-saving. Many works about the centrifugation process engineering are described (Towler and Sinnott 2008). When centrifugation process parameters are modified, the separated fractions contain

different concentration of compounds compared to original mixture which depends on molecular weight and the particle size or the density, respectively. The result is that heavy particles such as holocellulose are separated in the bottom fraction and soft particles such as proteins are separated in the top fractions.

For the distillery refuse treated by centrifugation, it is possible to utilize Fourier transform near-infrared spectroscopy (FT-NIR), described for application in papermaking using the distillery refuse in our early work (Pažitný et al. 2010a). The utilization of Fourier transform near-infrared spectroscopy in spectral analysis of biological materials is well described in other studies (Huang et al. 2008, Russ et al. 2009, Russ and Fišerová 2011). Some book publications deal with identification of compounds in mixtures and with identification of major compound in mixtures of biological origin (Workman and Weyer 2008) because of high selectivity of this method (Burns and Ciurczak 2008).

As distillery refuse is a mixture of organic compounds with holocellulose content near 50 % with a possibility of holocellulose/residual compounds ratio enhancement (proteins, lipids and lignin), the FT-NIR reflectance spectroscopy can be used to determine the holocellulose content with utilization of the Partial least squares method. In addition, the ratio of holocellulose in distillery refuse to proteins and lignin can be changed by centrifugation and varied by modification of process parameters. The holocellulose and total fibre content as a by-product of bioethanol production such as mentioned DDGS is very high which causes the progressive weight loss of commercially kept animals and their products such as eggs and meat. That is why it is more advantageous to separate the fibrous material such as holocellulose from proteins and lipids and to use the fibrous residue in papermaking.

The main objective of this work is to show how fibrous compounds may be utilized such as holocellulose from the distillery refuse treated by centrifugation in papermaking and to verify applicability of spectral methods for mixtures obtained from the distillery refuse treated by centrifugation and drying.

## MATERIAL AND METHODS

### Material

Distillery refuse was obtained from a company concentrated on producing bioethanol and DDGS. The distillery refuse was produced from corn as a by-product during bioethanol production and it contains 34 % oven-dry material on average. The raw distillery refuse was treated by centrifugation with variation of process parameters (retention time, rotation frequency etc.) to obtain the material with different holocellulose content.

100 % centrifuged and decanted distillery refuse and the distillery refuse combined with pulp of coniferous wood were beaten in a laboratory plant Valley holander for 10, 20, 30, 40, 50, 60, 70 and 80 minutes, according to the ISO 5264-1. Similarly, 100 % pulp of coniferous wood was beaten in that plant according to the ISO 5264-1.

The centrifuged, decanted and beaten material was bleached with 4.0 N sulphuric acid (first series) or with 5.2 N sodium hydroxide (second series) in the first step. The bleached material was treated in the P-D-P sequence (first series). Distilled water was used for decrease of concentration of the suspension.

In papermaking, the distillery refuse treated by centrifugation, decanting, beating and combined with bleached hardwood pulp was used. The paper sheets for testing with areal weight 100 $g.m^{-2}$ were prepared according to the ISO 5269-2.

## Methods

The centrifugation was carried out by the laboratory centrifuge type K26D by VEB MLW Zentrifugenbau Engelsdorf (Germany). Five centrifugation parameters were modified to obtain the different holocellulose content: retention time, rotation frequency, temperature and number of centrifugation cycles.

14 samples obtained from distillery refuse by the modification of the centrifugation parameters were investigated and compared with the original sample of distillery refuse. The samples were analyzed by accredited methods and quantitative analyses of some compounds were carried out. The extractive compounds were analyzed according to the ISO 624. The acid-insoluble residue (*Klason lignin*) was determined by the official method Tappi T 222 om-98. The acid-soluble lignin was determined spectrophotometrically by the useful method Tappi UM 250 and holocellulose was analyzed by the quantitative method of Wise. Each sample was air-dried before analyzing but the values of concentration of the compounds mentioned are valid for 100 % oven-dry treated distillery refuse.

The spectral properties of air-dried samples of distillery refuse treated by centrifugation and the original sample of distillery refuse were monitored with an Infrared spectrometer iS 10 by Nicolet. For NIR measurements, Integrat IRTM extension by PIKE Technologies was used. NIR data from the spectrometer were collected using the software Omnic version 8.0 by Thermo Scientific. The experiment setup was following:

| | |
|---|---|
| Number of scans | 128 |
| Resolution | 4 |
| Data spacing | 0.4821.cm$^{-1}$ |
| Format of conversion performance | absorbance (Log (1/R)) |

The collected spectra were analyzed and evaluated by the software TQ Analyst version 8.0 by Thermo Scientific. The Partial Least Squares (PLS) method used for analyses was incorporated in the software TQ Analyst version 8.0.

The Water Retention Values (WRVs) of the centrifuged and decanted distillery refuse combined with pulp of coniferous wood, 100 % pulp of coniferous wood and 100 % centrifuged and decanted distillery refuse they were beaten in the laboratory plant Valley holander for 0, 10, 20, 30, 40, 50, 60, 70 and 80 minutes were analyzed according to the ISO 23714: 2007.

The bleached paper sheets were prepared by the following experiment: In the first series, the centrifuged and decanted distillery refuse treated by beating for 30 minutes was treated with 4.0 N sulphuric acid for 1.5 h or 3.5 h, at 22 °C or 80°C while stirring. The concentration of oven-dry distillery refuse was 5.0 % or 10.0 %. In the second series, the beaten distillery refuse was treated with 5.2 N sodium hydroxide for 3.0 h at 95°C while stirring. The concentration of the suspension was 3.0 %. Air-dried distillery refuse was mixed with bleached hardwood pulp in a ratio of 70:30 which was utilized for oven-dry materials. Due to better brightness values in the first series, this work was limited to bleaching of the distillery refuse which was treated with 4.0 N sulphuric acid for 3.5 hours at 22°C. In the P-D-P sequence of bleaching, the distillery refuse from previous acidic treatment (first series) were chemically bleached. In all stages of the P-D-P bleaching sequence, the concentration of the oven-dry material was 3.0 %. In the first P-stage, 0.2 % ethylenediaminetetraacetic acid (EDTA), 5.0 % hydrogen peroxide and 3.5 % sodium hydroxide were used for bleaching (retention time: 1 hour, temperature: 80°C, pH = 11.0). In the D-stage, 1.5 % chlorine dioxide was used (retention time: 2 hours, temperature: 65°C, pH = 2.9) and in the second P-stage, the mixture of 0.1 % EDTA, 1.0 % hydrogen peroxide and 0.5 % sodium hydroxide was used (retention time: 1 hour, temperature: 95°C, pH = 12.0).

Brightness of prepared sheets was measured by an apparatus ELREPHO (Lorentzen & Wettre, Elrepho 950 ERIC ®), according to the ISO 2469 and ISO 2470.

## RESULTS AND DISCUSSION

### Major compounds of corn distillery refuse

The first application of distillery refuse made of corn in papermaking was described. Content of the major compounds such as holocellulose and lignin were monitored during separation process parameter modification. Spectral data of the samples containing those compounds were analyzed because of two reasons: they are major compounds of the mixture and they are being the main parts of the fibrous network of distillery refuse. Some works about papermaking published holocellulose and lignin content (Sánchez et al. 2010). Tab. 1 shows the differences of holocellulose and total lignin content in original distillery refuse, centrifuged distillery refuse and some raw materials they are utilized in papermaking.

*Tab. 1: Differences in holocellulose and total lignin content in selected raw materials and materials obtained from some crops in technological processes.*

| Raw/treated material | Holocellulose | Lignin | Fibrous network (holocellulose + total lignin) |
|---|---|---|---|
| | (% o.d.) | | |
| Hesperaloe funifera | 76.5 | 7.3 | 83.8 |
| Kenaf | 78.9 | 15.6 | 94.5 |
| Bagasse | 73.9 | 21.7 | 95.6 |
| Cotton stalks | 72.9 | 21.5 | 94.4 |
| Wheat straw | 72.2 | 18.3 | 90.5 |
| Rice straw | 60.7 | 21.9 | 82.6 |
| Original distillery refuse | 42.3 | 20.6 | 62.9 |
| Centrifuged distillery refuse | 66.8 | 19.4 | 86.2 |

Tab. 1 shows that the most materials routinely utilized for papermaking contain comparable amount of oven-dry holocellulose and total lignin. Due to the high concentration of components they are characteristic for fibrous network of raw materials and materials obtained from the crops in technological processes. The mentioned materials are suitable for papermaking.

According to our findings, it is possible to modify concentration of compounds in the fibrous network by selective change of centrifugation parameters also because of high molecular weight. 14 samples of centrifuged distillery refuse and one original sample of distillery refuse were analyzed by methods for lignin content determination and by the Wise's method for holocellulose content determination. The results of analysis of these samples are shown in Tab. 2.

The highest values for concentration were obtained when number of centrifugation cycles was modified; also the differences of holocellulose content between the first and the last cycle were high. However, the average total lignin content was 19.99 %, the difference between this value and the maximum value was 1.81 %, the minimum value 2.79 %, respectively.

*Tab. 2: Content of oven-dry (105°C) extractives, Klason lignin, acid-soluble lignin and holocellulose in distillery refuse treated by centrifugation and in original sample of distillery refuse (entry 1); modified process parameters: retention time (entries 2-5), rotation frequency (entries 6-9), temperature (entries 10-12) and number of centrifugation cycles (entries 13-15).*

| Sample number | Extractives | Klason lignin | Acid-soluble lignin | Total lignin | Holocellulose |
|---|---|---|---|---|---|
| | (% o.d.) | | | | |
| 1 | 9.38 | 9.38 | 11.2 | 20.6 | 42.3 |
| 2 | 7.90 | 9.05 | 10.9 | 20.0 | 51.9 |
| 3 | 8.30 | 7.90 | 10.8 | 18.7 | 54.4 |
| 4 | 8.78 | 7.72 | 11.8 | 19.5 | 53.2 |
| 5 | 8.85 | 9.53 | 11.3 | 20.8 | 52.1 |
| 6 | 11.4 | 10.0 | 11.8 | 21.8 | 47.4 |
| 7 | 8.10 | 8.52 | 11.5 | 20.0 | 54.4 |
| 8 | 8.74 | 9.76 | 10.1 | 19.9 | 53.1 |
| 9 | 8.28 | 8.73 | 11.6 | 20.3 | 53.0 |
| 10 | 8.51 | 10.2 | 11.3 | 21.5 | 50.5 |
| 11 | 8.18 | 10.1 | 10.7 | 20.8 | 54.4 |
| 12 | 8.49 | 5.91 | 11.3 | 17.2 | 52.9 |
| 13 | 7.86 | 8.57 | 10.8 | 19.4 | 53.5 |
| 14 | 6.46 | 8.87 | 11.0 | 19.9 | 60.4 |
| 15 | 5.51 | 9.09 | 10.3 | 19.4 | 66.8 |

The mentioned differences were relatively negligible. Therefore the total lignin content was constant even when any process parameter was modified. As mentioned, the best separation of holocellulose was achieved when the number of centrifugation cycles increased. The difference between holocellulose content in the last cycle and in the original distillery refuse was 24.50 %. In this case, the total increment of fibrous network was 23.30 % because of low change in total lignin content. During the modification of number of centrifugation cycles and the modification of some other process parameter, the holocellulose content was not constant. However, the holocellulose content was almost constant during the temperature modification.

## Spectral properties of corn distillery refuse

14 samples of distillery refuse obtained by modification of centrifugation parameters were analyzed by NIR spectroscopy and the results of spectral analysis were compared with spectrum of the original sample of distillery refuse. Fig. 1 shows the NIR spectrum of those samples and the sample of original distillery refuse which contrast with spectrum of holocellulose and total lignin they were separated from distillery refuse mixture by analytical methods mentioned in chapter Methods.

Fig. 1 depicts typical overtone and combination bands of holocellulose and lignin. "Packaging" curve is built by those bands and it is characteristic for bonds C-C, C=O in lignin (range of wavenumbers 4430–4130.cm$^{-1}$) and H-C-H in holocellulose (intensive band with wavenumber 4261.cm$^{-1}$).

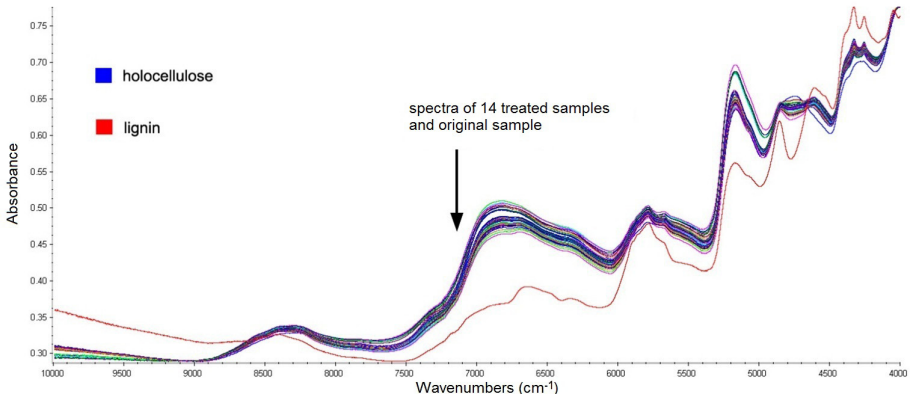


*Fig. 1: NIR spectra of 14 samples modified by centrifugation and original sample of distillery refuse.*

NIR spectral methods are very selective and sensitive when there are high concentrations of compounds. For this reason, the mentioned compounds and included bonds can be detected with high accuracy. However, the final "packaging" curve is a mixture of each band and that is why some bands can be hidden within a band of higher absorbance, e.g. the bands of lignin with range of wavenumbers 7500–4800.cm$^{-1}$. This situation can occur if the distillery refuse is combined with wood pulp. One of the reasons of that is the presence of cations of various metals. This fact was supported by spectra of paper sheets in our previous study (Pažitný et al. 2010b) where the majority of spectral bands originating sheets made of corn distillery refuse had higher value of absorbance than paper sheet made of corn distillery refuse combined with non-bleached pulp. Some authors published extensive information about the content of metallic cations in other types of distillery refuse too (Bustamante et al. 2009).

NIR methods include determination of major compounds content because these methods are highly selective and it is possible to use them in supporting of quantitative analysis. In addition, the NIR methods are non-destructive. That is the reason why the content of mentioned compounds was not modified during the experiment. To obtain information about the holocellulose or lignin content, software TQ Analyst version 8.0 by Thermo Scientific was used. Fig. 2 presents calibration of spectral data in terms of holocellulose content by PLS method. Homogenized and air-dried distillery refuse was analyzed three times and each sample in form of powder was shuffled manually. In all cases, there are relatively small differences between calculated values of holocellulose content. Therefore this method can be utilized for determination of holocellulose content in unknown sample of distillery refuse. The utilization of calibration curves in NIR methods with application of PLS method was published in a study where authors analyzed the lignin fraction and the cellulose fraction in archaeological wood by NIR spectroscopy (Sandak et al. 2010).

In case of holocellulose content analysis the NIR cross validation was precise because the correlation coefficient $R^2$ was high (0.9721). The average prediction error of the holocellulose content, calculated as root-mean square error of cross validation (RMSEC) was 1.42 %. The lowest errors of holocellulose content calculation were obtained by pre-processing of spectra and the best model of prediction which was reached after spectral parameters optimization done by software TQ Analyst version 8.0. The most suitable spectral range was 6831-4683.cm$^{-1}$.

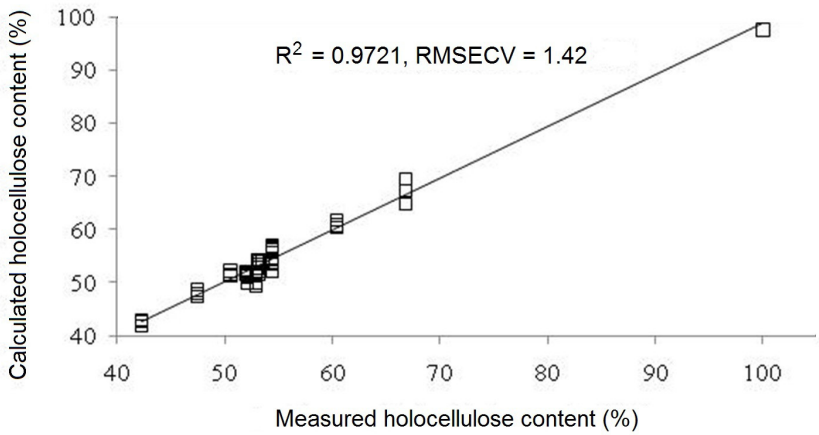


*Fig. 2: Calculation of the holocellulose content in treated distillery refuse with including of spectra of holocellulose and original sample by PLS method.*

The spectra of similar compounds in the mentioned literature were used for calibration with eventual good correlation coefficients and RMSEC values, $R^2$ = 0.9420 and RMSEC = 1.440, for calibration of lignin spectra and $R^2$ = 0.9890 and RMSEC = 0.603, for calibration of cellulose spectra. However, the spectral ranges were different due to different software used and different calculation parameters of spectral data pre-processing (Sandak et al. 2010).

Still, it must be mentioned that the results of NIR spectroscopy combined with PLS method presented in this work are preliminary study for biological compounds content determination by FT-NIR method, such as holocellulose and lignin. Many more samples of distillery refuse treated by centrifugation parameters modification will have to be analyzed and the samples should have different chemical and biological composition due to the creation of reliable prediction models for holocellulose content and other biological components content determination.

## Treatment of distillery refuse by beating in Valley holander

Physical structure of the centrifuged and decanted distillery refuse was being modified during beating it in the laboratory plant Valley holander. Obtained Water Retention Value (WRV) values for each time of beating are depicted in Fig. 3. However, the degree of SR (Schopper-Riegler) value for time of beating is more common in beating description. The reason for utilization of WRV values time-dependence was non-effective application and difficult applicability of experimental process at a measurement. The beating in Valley holander was non-shorting but fibrillation beating, according to the ISO 5264-1.

Fig. 3 depicts beating lines for the laboratory plant Valley holander for 0, 10, 20, 30, 40, 50, 60, 70 and 80 minutes. In case of distillery refuse, there were significantly lower values of WRV than in both cases of distillery refuse combined with pulp of coniferous wood and 100 % pulp of coniferous wood, for each time of beating. The critical moment in beating of 100 % distillery refuse occurred after 10 minutes of beating (WRV = 140.9 %), so at the beginning of the experiment. The WRV values increased negligibly after that point which means that the point with the constant value of WRV was considered in 30th minute (WRV = 142.6 %).

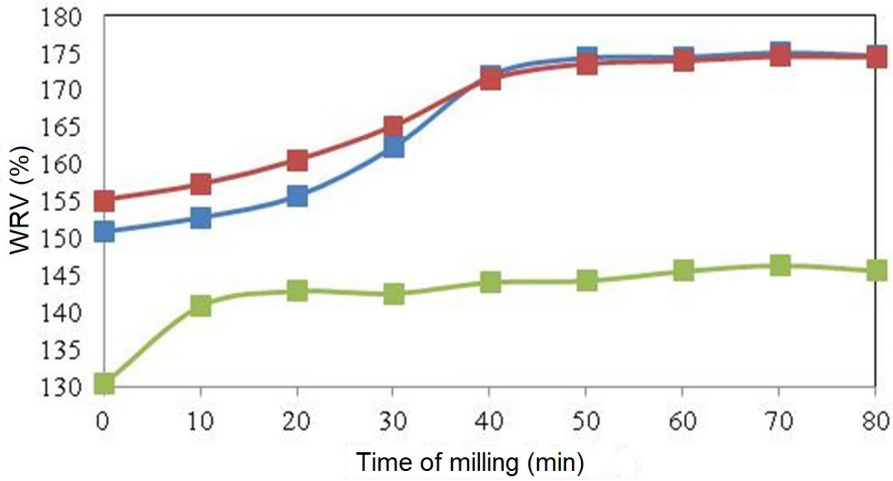


*Fig. 3: Time-dependence of WRV values of centrifuged and decanted distillery refuse, pulp made of coniferous wood and their mixture after beating in a laboratory plant Valley holander (■ 100 % pulp, ■ 80:20 pulp: Distillery refuse, ■ 100 % distillery refuse).*

The difference between WRVs in 10th and 30th minute was 1.7 % which was a low value against the value of WRV of original sample (WRV = 130.4 %, time of beating: 0 minutes). However, the difference between WRVs in 10th and 20th minute of beating was higher (ΔWRV = 2.0 %) therefore the beating of centrifuged and decanted distillery refuse in Valley holander for 30 minutes was considered optimal.

Small differences were determined between WRVs of initial samples when the 100 % coniferous wood pulp and mixture of pulp and the distillery refuse in a ratio of 80:20 (ΔWRV = 4.2 %, time of beating: 0 minutes). However, the differences between WRVs of 100 % centrifuged and decanted distillery refuse and 100 % coniferous wood pulp were high (ΔWRV = 24.7 %, time of beating: 0 minutes). Also the differences between WRVs of mixture of that pulp with centrifuged and decanted distillery refuse in a ratio of 80:20 (ΔWRV = 20.5 %, time of beating: 0 minutes) were relatively high. This trend was observed for each time. However, the breakpoint occurred after 40 minutes of beating when the difference between WRVs of beaten distillery refuse combined with the pulp and 100 % pulp was negligible (ΔWRV = 0.5 %). This trend was stable during additional minutes of beating. Therefore the materials mentioned in this study can be beaten for 40 or more minutes, except of 100 % centrifuged and decanted distillery refuse with optimal beating for 30 minutes.

## Bleaching of distillery refuse

The centrifuged, decanted and beaten distillery refuse were pre-treated and bleached according to the procedures described in chapter Methods. Tab. 3 presents the results for pre-treatment of two series of centrifuged, decanted and beaten distillery refuse and changes in brightness of prepared paper sheets after changing of bleaching parameters (e.g., time, type of pre-treatment).

The value of brightness of paper sheets made of the mixtures of original distillery refuse treated by centrifugation, decanting and beating and bleached hardwood pulp in a ratio of 70:30 was 38.1 %.

*Tab. 3: Brightness of paper sheets prepared by pre-treated distillery refuse combined with bleached hardwood pulp in a ratio of 70:30.*

| Concentration of oven-dry distillery refuse (%) | Retention time (h) | Brightness after ISO 2469 and 2470 (%) | |
|---|---|---|---|
| | | Acidification, 22°C/80°C | Alkaline treatment, 95°C |
| 3.0 | 3.0 | - | 35.7 |
| 5.0 | 1.5 | 40.8/40.3 | - |
| 10.0 | 1.5 | 37.4/38.6 | - |
| 5.0 | 3.5 | 41.2/40.8 | - |
| 10.0 | 3.5 | 37.0/40.6 | - |

In the case of alkaline treatment, the value of brightness was low relative to higher values of brightness in case of the acidic treatment. Tab. 3 shows that the values of brightness were higher in case of 5.0 % concentration than in case of 10.0 % concentration. However, temperature was found to have low influence on the values of brightness, except of the last entry (concentration: 10.0 %, retention time: 3.5 hours). The reason of such running of bleaching could be the decreased rigidity of suspension in case of 5.0 % concentration. Thus the improvement of acid admittance into the pores of the distillery refuse could be achieved.

4.0 N sulphuric acid was used because more concentrated acid would have eventually caused damage of fibres and fibrous network. The distillery refuse contains bivalent metal cations (e.g., $Cu^{2+}$, $Fe^{2+}$, $Mn^{2+}$) that cause coloration of the prepared paper sheets. Those cations can be removed by utilization of acids of low concentration because of forming easily soluble salts (e.g., $CuSO_4$, $FeSO_4$, $MnSO_4$). It was not necessary to use sulphuric acid of high concentration because the bivalent metal cations content was low, in range of 4.0-57.0 mg of bivalent metal cations per kg of oven-dry distillery refuse. That was the second reason why to use sulphuric acid of lower concentration. Similarly, the utilization of alkaline treatment was not advantageous because using of low concentration of sodium hydroxide caused damage of fibrous network although it reacted with lignin. Lignin remained in the suspension because it was not soluble in water. Therefore it could not be removed with water from that suspension. Combination of that fact and difficult removal of bivalent metal cations from suspension caused the decrease of brightness value of the distillery refuse by 2.4 % after alkaline treatment.

The pre-treated distillery refuse was bleached in three bleaching stages. Tab. 4 shows the results of bleaching by two alkaline bleaching stages and one acidic bleaching stage, in term of brightness of bleached paper sheets.

*Tab. 4: Brightness of paper sheets prepared by bleached distillery refuse combined with bleached hardwood pulp in a ratio of 70:30.*

| Bleaching procedure | Initial sample | 1st peroxide stage | Chlorine dioxide stage | 2nd peroxide stage |
|---|---|---|---|---|
| Brightness after ISO 2469 and 2470 (%) | 41.2 | 73.9 | 80.9 | 83.7 |

In both the first and the second stage of peroxide bleaching procedures, EDTA was used due to inhibition of catalytic decomposition of hydrogen peroxide by influence of bivalent metal cations. In the first peroxide bleaching stage, concentration of used EDTA was higher than concentration in the second one because it was supposed that bivalent metal cations were chelated by EDTA which may have resulted in the decrease of EDTA concentration. However, the main and direct bleaching agent was hydrogen peroxide as published in a former study (Topalovic et al. 2007).

The brightness value of paper sheets made of distillery refuse which was pre-treated by centrifugation, decanting, beating and acidic pre-treatment and bleached hardwood pulp in a ratio of 70:30 was 41.2 %. The initial material from pre-treatment was used in the first bleaching procedure as an input material. Similarly, the final material from each procedure was used as an input material for the next procedure. For each bleaching stage, the trend of brightness values increased rapidly. That is why those bleaching methods can be utilized in chemical and bleaching treatment of corn distillery refuse and other similar materials.

## CONCLUSIONS

Today, the distillery refuse obtained as a by-product in bioethanol production from corn and also from other agricultural crops are utilized in DDGS production. This study suggests the possibility of production conversion which is related to conversion of technology and production procedures. In this study, the production of paper sheets is represented. The paper sheets were prepared from distillery refuse by previous treatment: centrifugation, decanting, beating in Valley holander, acidic pre-treatment and bleaching.

NIR reflectance spectra of 14 samples of centrifuged and decanted distillery refuse with different holocellulose content were obtained. The spectrum of original sample of distillery refuse was also measured. All NIR spectra were used for calibration in which high correlation coefficient ($R^2$ = 0.9721) and good RMSEC value (RMSEC = 1.42 %) were obtained. These data are comparable with literature.

The best results in centrifugation of distillery refuse were obtained when the number of centrifugation cycles was modified because of high differences in holocellulose content between each centrifugation cycle. The holocellulose content increased at least 6.4 %. It was found that acidic pre-treatment of distillery refuse which was treated by centrifugation, decanting and beating in Valley holander was better to use because of an increase in brightness values of paper sheets made of pre-treated distillery refuse combined with bleached hardwood pulp in a ratio of 70:30. In fact, the brightness values were affected by properties of input materials such as concentration of bivalent metal cations.

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