SONOCHEMICALLY MODIFIED WHEAT STRAW FOR PULP AND PAPERMAKING TO INCREASE ITS ECONOMICAL PERFORMANCE AND REDUCE ENVIRONMENTAL ISSUES

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Wheat straw (an agricultural by-product) was pulped by an alkaline anthraquinone (AQ) process. Then the straw pulp was treated by high-power ultrasound under different noble-gas (argon, krypton, xenon) combinations. The pulps' degree of beating and acid-insoluble lignin content were measured. Handsheets were made from sonicated and control pulps and tested for paper tensile strength. In this study we explore which noble-gas combination with ultrasound may be more useable to reduce the lignin content and enhance fibrillation. We also describe the most effective ultrasound-assisted, modified alkaline pulping process. Overall, we found that in two steps ultrasonification decreased the residual lignin contents more then 75 %, the pulp fibrillation increased from 12 to 70 °SR within 20 min. of ultrasound irradiation, and the tensile index of the handsheets increased by 65%. For sustainable paper production, it is required to develop alternative paper resources. Paper made from alternate fiber resources with efficient technology will improve our living standards without sacrificing the environment, our habitat. High frequency ultrasound-based pulp processing offers significant improvements, and it reduces energy and chemical consumptions for pulp and paper production.

Keywords: *Sonochemistry, Ultrasound, Wheat straw, Alkaline pulping*

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INTRODUCTION

The chemical industry and large scale industrial technology for the manufacture of cellulosic pulp traditionally have relied to a large extent on the utilization of softwoods. Because paper production is increasing, pine forests have been more and more insufficient for this rapid growth, so that utilization of hardwoods has increased in the last decades. Most of these technologies developed for mass production of paper are based on the utilization of trees. Their theory and implementation have made it possible to increase the profitability of wood processing technologies. However harvesting and cutting of forest trees to obtain cellulose have reached the level of irreversible damage, and there can be serious environmental issues.

Agricultural residues such as wheat straw, which is the most frequently used annual plant in the pulp and paper industry, have been considered as fibrous raw materials for almost one hundred years. Wheat straw can yield about 4.0 t/a.ha amount of biomass annually from one hectare, compared to 1.0 t/a.ha for pine, because softwoods need to grow for many years before cutting [Annus 1991]. Nearly 300 million tons of wheat straw are produced yearly in North America and Europe and only 8% of the world paper industry's total fibre consumption comes from wheat straw [Paper Technology 2006]. In the first half of the twentieth century, straw was still a significant raw material for the paper industry, yet its consumption in the industrial states has rapidly decreased since the 1940s [Rab 1993]. Wheat straw can be represented again as a significant fiber substitution opportunity for the next centuries. To date, straw pulps have been manufactured mainly by soda-anthraquinone and neutral or alkaline sulfite processes.

In cases of trees, only a curtain part of it is utilizable or worth obtaining as papermaking fibrous material, while in the case of annual plants the whole plant – including leaves, nodes –, can be utilized for that purpose. Comparing the annual yields, we can assume that the biomass volume obtainable annually by photosynthesis in an arable unit is much higher in cases of annual plants than woods. The cellulose content of wheat straw stem is almost same as woods (35-40%), the hemi-celluloses content is higher (45-55%), while their lignin content is lower (15-20%).

Application of ultrasound techniques in the food industry result in more attention to the depolymerization of macromolecules, the preparation of emulsions, the disruption of biological cells, and the deflocculation of other solid materials that exist as flocs. It has been found that the extraction of organic compounds contained within the body of plants and seeds by a solvent are significantly improved by use of powerful ultrasound. The first direct extraction of lignin polymer by use of ultrasound has been reported in 2002 [Sun et. Al. 2002].

The aim of this study was to show how combinations of ultrasound in the presence of noble gas could be used for direct extraction of lignin molecules from alkali-anthraquinone pretreated wheat straw for papermaking. Ultrasound is a useful tool in nearly every case where a liquid and a solid must react. Furthermore, since ultrasound can radiate through large volumes of liquid, it is well suited for industrial applications. Liquid processing rates of 200 L/min are routinely accessible with acoustic power of 20 kW per unit [Suslick 2001].

EXPERIMENTAL

Materials

In manufacturing pulp from wheat straw (triticum aestivum), the whole wheat stem including leaves and knots were used. Wheat stems of suitable chopped size (20-40 mm) were pulped with alkaline anthraquinone (AQ) treatments.

Methods

Pulping procedures were carried out in a batch digester, rotating autoclave. The reaction temperature was 150°C, reaction time 20 min, and the reagents NaOH 15% and AQ 0.1% on o.d raw material. After washing the pulp, different ratios of pulp to water (2g in 140 ml, 2g in 210 ml and 2g in 280 ml distillated-water) and 2g in 210 ml distillated water under argon, krypton and xenon noble-gas compilations were irradiated by high-power ultrasound. The irradiation was carried using a TESLA sonication system

(20 kHz) provided with a transducer at sonic power of 150W/h and sonication time of 20 min in distilled water solution at room temperature, without cooling the reactor vessel. After the measurement of beating degree, the pulp was filtrated on a filter-paper and stored at 5°C until further chemical and mechanical testing, without blending or screening. Mineral acids were used to solubilize and hydrolyze carbohydrates in cell wall samples, leaving the lignin residue to be determined by gravimetric methods according to MSZ-EN 8234-87. The straw was burned at 575±25°C for 2 hours, and the residual minerals, i.e. the inorganic materials, were determined as ash content according to MSZ-ISO 1762.

RESULTS AND DISCUSSION

In this study six alkaline wheat straw pulp preparations were treated with application of ultrasound with and without noble-gas combinations. The anthraquinone-alkaline pulping procedure resulted in 55-65% yields of fibrous raw material at 17°SR degree of beating. The drainability of the pulps is summarized in Fig. 1.

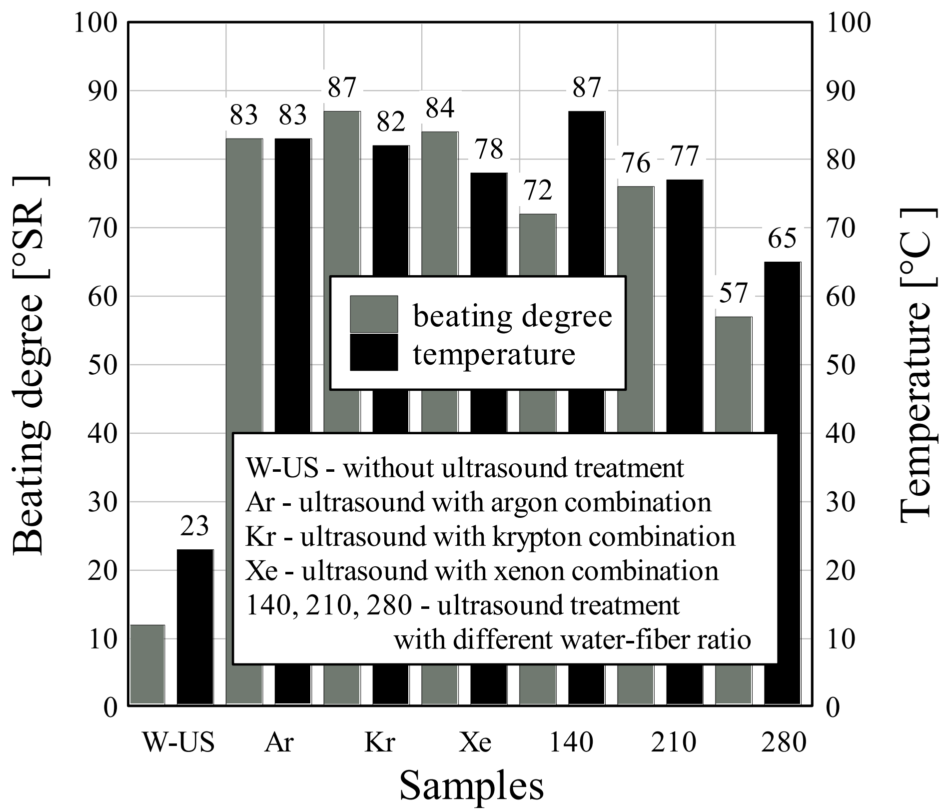


Fig. 1. Variation of beating degree under different ultrasound treatments

The ultrasonic treatment of the pulps resulted in increasing refining of the 140 and 210 samples, whereas there was a decrease in the case of the 280 sample. If the fiber-to-water ratio is lower, the mechanical effect of ultrasound on the cell walls is stronger, resulting in an increased fibrillation. This helps also to dissolve the lignin components, and makes the cell wall structure accessible for further chemical reactions. All of the noble-gas and ultrasound combinations had the same result in terms of beating degree. In the present stage of the investigation it is not possible to ascertain which noble-gas has stronger influence on wheat straw pulp. Please note that the temperature changed during the sonication treatments. All of the results follow logically from the beating results; however the temperature rise did not have any physical consequences.

The acid-insoluble lignin fractions – reduced by ash – of the samples are shown in Fig. 2.

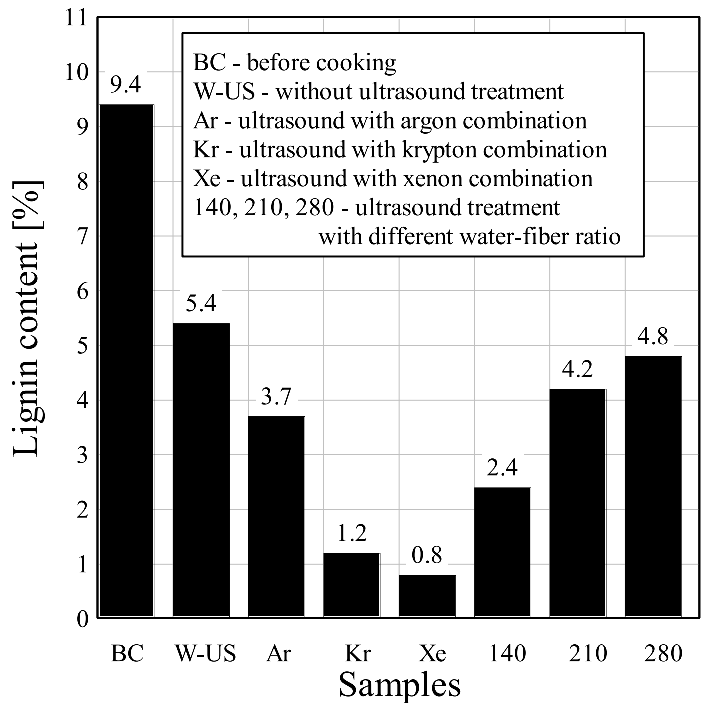


Fig. 2. Variation of lignin content of wheat straw and wheat straw pulp under different ultrasound treatments

The lignin content of the non-processed straw was 9.4%. After alkaline-athraquinone cooking treatment, the lignin content decreased to 5.4%. The ultrasonic irradiation resulted 2.4, 4.2 and 4.8% residual lignin in the experiments, in which 2g wheat straw pulp were suspended in 140, 210 and 280 ml distilled-water, respectively. The irradiation conditions were maintained constant; however the dissolution of lignin components from cell walls increased. During the irradiation of the densest water-fiber sample, more than half of the total lignin in the cooked pulp was released. The noble-gas combination resulted in raising lignin extractions from the fiber walls. The highest efficiency of the ultrasound-assisted lignin solubility was found when xenon gas was present during the treatment. It has been reported [Suslick 1989] that if xenon fills a cavity, the peak temperature reached during cavity implosion will be high, because xenon conducts heat poorly and retains the heat of the collapsing cavity – compared to argon, This is because xenon gas has the highest molecular weight among the noble gases considered. Consequently, the chemical effects of ultrasound do not arise from a direct interaction with molecular species: No direct coupling of the acoustic field on a molecular level is responsible for sonochemistry or sonoluminescence. These derive from acoustic cavitation, which serves as an effective means of concentrating the diffuse energy of sound. However, as one would expect, the sonolysis of water produces both strong reductants and oxidants, which leads primary products H_2 and H_2O_2 of dissociation of water [Riesz 1985]. The latter may help the degradation and dissolution of lignin macromolecule through the well known bleaching reactions.

Using the obtained pulps we have produced standard laboratory hand sheets and measured their tensile strength. Results of the measurement are shown in Fig. 3.

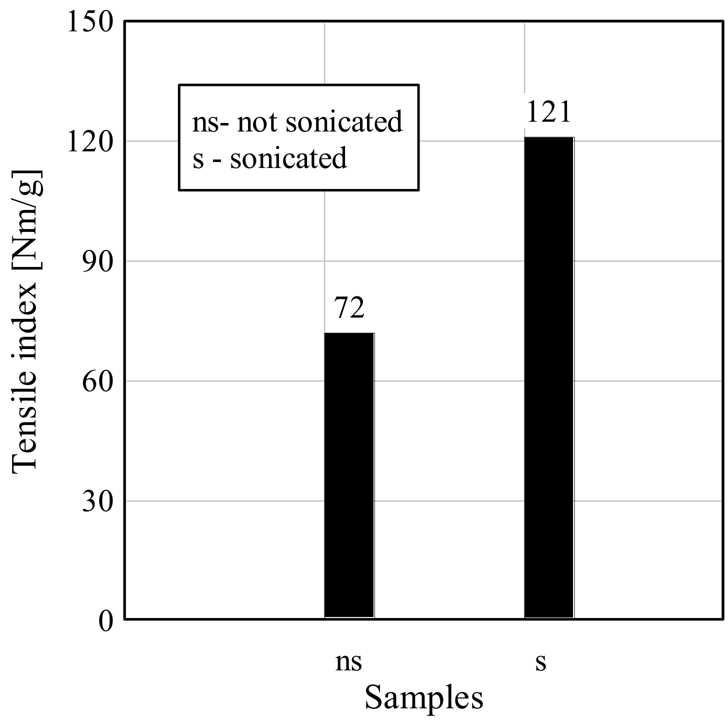
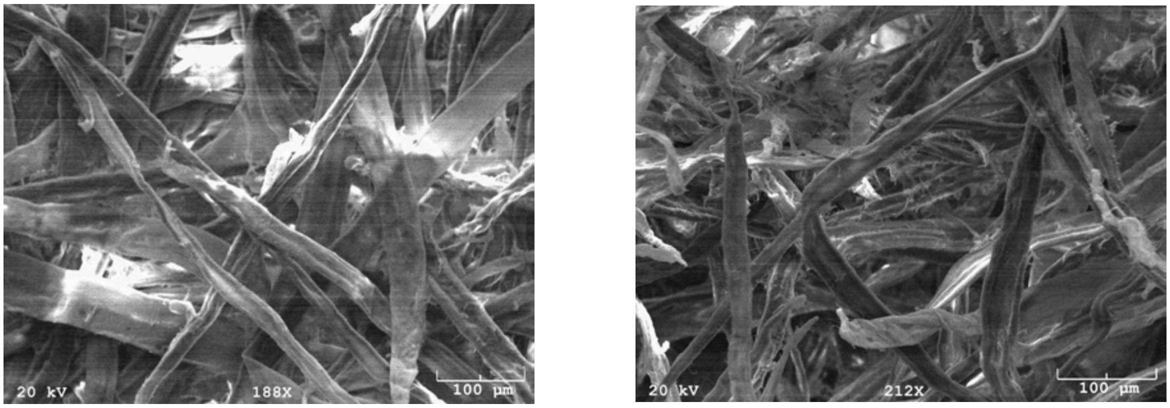


Fig. 3. Effect of sonication on the tensile index of paper test sheets from straw pulp

When analyzing the data it should be taken into account that freeness of the unbleached pulp made of wheat straw is only 17°SR, while that of sonically bleached and milled straw pulp is 45°SR. It has been previously reported (Hernadi 2006) that unbleached wheat straw kraft pulps have 74-76 Nm/g tensile strength at 35°SR and bleached pulps have 65 Nm/g at 42°SR. Based on physical properties, it can be stated that the tensile strength of unbleached, alkaline cooked wheat straw pulp was 72 Nm/g, while that of sonically bleached and sonically milled straw pulp was 121 Nm/g. Without mechanical milling of straw pulps, almost a doubling of tensile strength could be achieved by using ultrasound.

Further on we compared the pulp samples by electron-microscopy. Figure 4 shows electron-microscopy photos of the pulps. Based on the photos it can be stated that sonication resulted in a strongly fibrillated structure, and there was no diameter difference between the two pulps.



a) *b)*

Fig. 4. Scanning electron microscopy images of *a)* non-sonicated and *b)* sonicated straw pulps

CONCLUSIONS

1. Ultrasound-irradiation of wheat straw pulp in the presence of inert gases, after alkaline AQ pre-treatment made possible the further dissolution of 31.5-85.2% of the lignin content.
2. SEM images showed that the increased fibrillation of fibers resulted in higher tensile strength of the sonicated straw paper.
3. Based on the results we would like to build a larger, pilot-scale high-power ultrasonic reactor to evaluate the industrial possibilities of sound-induced straw pulping.

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