

## Conference Paper

# Natural Xylan Production From Corncobs (*Zea Mays L.*) With Extraction Method

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**Abstract**

Corn (*Zea mays L.*) not only used as food by humans, however also used for animal feed and industrial materials but in part of corncobs still untapped, corncobs is a lignocellulosic material with 38,99% fiber which contain the highest xylan (12,4%) compared with other agricultural waste. The objective of this research was to get xylan from corncobs with extraction method. Xylan extraction from corncobs were done in two steps, firstly delignification process in NaOCl with concentration 0,5 on temperature 28°C, solids which resulting from immersion in NaOH solution with concentration 5%, 10%, 15%, and 20% for 24 hours with temperature 20, 40, and 70°C. the resulting of filtrate were neutralized with HCL 6N, futhermore centrifuge during 30 minute with 4000 rpm. Water soluble xylan can separated with ethanol 95% with ratio supernatan and ethanol 1:3, yielding 12.9% of xylan. The solubility of xylan produced with alkali (NaOH 1%), HCl 1N, ethanol, in cold and hot water was observed. Quantitative and qualitative analysis of xylan were done using HPLC by measuring retention time. The instrumen used with HPLC Shimadzu C-R3A, C18 column type, water mobile phase, Refractive index detector with flow rate 0,8 ml/minute result showed with purity 96%.

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**Keywords:** xylan, corncobs, extraction

## 1. Introduction

In Indonesia, corn not only used for food, also animal feed and industrial material. Until the day needs and demands are more increasing. The total waste of corn, like straw and corncobs also increasing such as the increasing of needs and demands of corn. Today, increased production of corn still increase even it fluctuated. In 2003, corn production in Indonesia reach 9,66 million tons/year are increase 1,42% compared with in 2002 is only 9,53 million tons/year. Corn production on 2014 with 19,01 million tons shilled corn dried or increase 0,50 million tons (2,68 %) compared with 2013 (Kementrian Pertanian, 2017). Corn production on 2015 estimated 20,67 million tons or increasing 1,66 million tons (8,72%) compared with 2014. Increasing production estimated happen because increasing harvest area 160,48 thousand hectares (4,18 %) and increasing productivity 2,16 quintal/hectares (4,36 %) (Anggraini, 2016)

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Corn cobs also used as raw material of xylitol because content xylan compound reach 12,4 – 12,9% (Alam, 2017) and selulose 32,3 – 45,6% (lou et al., 2015). Corn cobs is the biggest part of corn waste. Estimated 40-50% of corn is corn cobs, also affected from variety of corn. Therefore it can be estimated from 13 million tons corn production will produce waste corn 10,6 million tons/year. Based on this, there needs to be attention and handling for its utilization so that it is more valuable. Corn cobs are lignocellulosic (38.99% fiber content) containing the highest xylan (12.4%) compared to other agricultural wastes (Richana et al., 2004). According to (Irawadi, 2016) corn fruit consists of 30% waste in the form of corn cobs. When converted to the amount of corn production in 2008, Indonesian state has the potential to produce 4,456,215 tons of corn cobs. The amount of waste can be very big and will be potential if it can be used properly.

Xylan is hemicellulose which is a polymer of pentose or xylose with a bond of  $\beta$ -1,4 whose number of monomers ranges from 150-200 units (Sunna and Antranikian, 2016). Hemicellulose is a polymer of sugar monomers (anhydro sugars) which according to its constituents, hexose (glucose, mannose and galactose), pentose (xylose, arabinopranose, arabinofuranose), hexuronic acid (glucuronate, methylglucuronate and galacturonate) and deoxihexose (rhamnose). The main chain of hemicellulose can consist of only one type of monomer (homopolymer), for example xylan, or can consist of two or more monomers (heteropolymers), for example glucomannan (Kulkarni et al., 1999). Xylan extraction can be produced by various methods. As Yoshida et al. (1994), Sofyanto. (2017), or Rowley et al. (2013). and fructose (Abou et al. 2008). Xylan can be extracted from biomass using alkali (KOH or NaOH) or dimethyl sulfoxide (DMSO) which has been carried out (Suryanto & Irma. 2017); but the extraction of DMSO is only for the extraction of xylan which is soluble in water. Xylan has substituents which are around the ring of the core structure of xylan. Xylan from angiosperm is O-acetyl-4-O-methylglucuronoxilan. This polysaccharide consists of  $> 70$ -il-xylopiranose which forms bonds with  $\beta$  -1,4-glycosides. Every 10 xylose carries a 4-O-methylglucuronic acid which is in two xylose positions. The xylan composition of gymnosperms has more 4-O-methylglucuronoxilan, 4-O-methylglucuronic acid is placed in two carbon chains (Sunna and Antranikian, 1997). Examples of gymnosperms that contain xylan are pine, the examples of angiosperms are rice, corn, and other cereals. As an industrial raw material, xylan can be used as a mixture of nylon and resin manufacturing materials. Xylan hydrolysis produces furfural which can be used as an industrial solvent for petroleum, reactive solvents for phenol resins, disinfectants and as starting material for producing various chemicals and other polymers (Mansilla et al., 1998). In addition xylan can be processed into sugar xylitol, through the process of hydrolysis of xylan to xylose, then hydrogenated to xylitol. Xylitol

has advantages over sugar (sucrose), as a low-calorie sweetener, has a low glycemic index, and in metabolism does not require insulin so it does not increase blood sugar. Therefore xylitol is good for diabetics (Anonymous, 2004). Currently xylitol is widely used for toothpaste because it can strengthen teeth and is anti caries. In the development of bioprocess xylan, it is used for the carbon source substrate in the growth media of xylanase-producing microbes. Xylanase is an enzyme that can hydrolyze xylan to xylose. Xylanase can be used for animal feed mixtures, syrup purifiers, xylose sugar making and paper whitening process materials. Based on the promising prospect of xylan as an industrial raw material in the future, it is necessary to assess the potential of corn cobs as a source of xylan. Thus this study aims to obtain the extraction method and characteristics of xylan from corn cobs waste.

## 2. Material and Method

### 2.1. Materials

The study was conducted at the Chemical Engineering Vocational School D3 Diponegoro University. The scope of the research includes extracts of xylan from corn cobs, and characterization of xylan. Corn varieties of corn cobs are taken from Kendal Kaliwungu. After harvesting the corn is dried with the cob, then piping is done. Before milling, corn cobs are dried to a little moisture content by drying with an oven for 48 hours.

### 2.2. Extraction of xylan from corn cobs

This research was carried out in several stages, at the initial stage is a proximate analysis of raw materials including water, ash and fiber content (AOAC, 1984) to determine the condition of corn cobs to be used. Stage one is xylan extraction by modifying the method of Yoshida et al. (1994) by determining the concentration of NaOCl in the delignification process and the subsequent stages of xylan deposition by appropriate comparison of supernatants and ethanol (v / v), then solubility tests, qualitative and quantitative tests of xylan obtained from the extraction.

The flow chart of the xylan extraction process is presented in Figure 1. The dried corn cobs are milled until they reach a size of 40 mesh through a sieve. A sample of 50 g was put into a plastic container and then soaked in NaOCl solution with a concentration of 0.5 for 5 hours at 28°C (delignification process). After 5 hours the sample is rinsed

with water and filtered. Furthermore, the resulting solid was soaked in NaOH solution at a concentration of 5%; 10%; 15% and 20 for 24 hours at 20°C; 40°C; 70°C.

This immersion aims to extract xylan. After 24 hours, filtering is carried out. The resulting filtrate was collected to measure the pH, then neutralized using HCl 6N, and centrifuged for 30 minutes with a rotational speed of 4000 rpm. The supernatant produced by centrifugation contains xylan.

Xylan which is soluble in water can be separated by adding 95% ethanol. Ethanol is added to a liquid containing xylan (supernatant) with a comparison of supernatant-ethanol is 1: 1, 1: 2, 1: 3 and 1: 4. This comparison is intended to determine the ratio of how much xylan can be produced optimally. The experimental design used in this study was Factorial Complete Random Design

### 3. Results and Discussion

Before extracting xylan, the characterization of its raw material is first analyzed including water, ash and fiber content (Table 1). High fiber content is expected can increase the yield of xylan produced. The observation results of the ash content is greater than the data presented by Koswara (1991), which is 1.33%. But for fiber the results of this study are smaller than the previous study, which is 39.0% (Richana et al., 2004). The difference is due to differences in varieties and age of corn harvest.

#### 3.1. Yield and mass balance

Xylan extraction is affected by delignification treatment. The delignification process uses sodium hypochlorite (NaOCl) with concentration of 0.5%. The lowest yield was produced in the delignification process using 5%, 10%, 15% and 20% NaOH concentrations. The lowest yield was 5%, while the highest yield was obtained in the delignification process using 20% NaOH concentration. This is due to the high concentration of NaOH which can make hemicellulose in the material lost or dissolved in the delignification process while at a low concentration of 5% only a small portion of hemicellulose dissolves. The treatment of ethanol solvents also affects the xylan yield. The highest yield was obtained from extraction using ethanol at a ratio of 1: 3 (v / v). The interaction between NaOH concentration treatment and the comparison of supernatant with ethanol did not significantly affect the xylan yield produced.

Duncan's test results showed that the ethanol ratio with high supernatant also produced high xylan yield. The greater the volume of solvent used, the greater the yield

of xylan produced so that the result will increase to the saturation point of the solvent (Table 2). Increasing the amount of solvent means increasing the solvent's ability to completely extract xylan. If the amount of solvent is added continuously, an optimal point can be obtained which can extract all the existing xylan so that the addition of the next solvent does not need to be done again. From the results of this study the highest yield was obtained in the delignification process with 0.5% sodium hypochlorite concentration and xylan deposition process with ethanol ratio: 3: 1 supernatant (v / v).

TABLE 1: Moisture, ash and fibre contents of corn cob.

Composition	means	Deviation Standard
moisture	6,43	0,61
Ash	1,86	0,26
fibre	25,43	0,59

TABLE 2: Xylan- extract yield of corn corb using solvents treatment.

Supernatant Ethanol	NaOH			
	5%	10%	15%	20%
1:0	9,38 <sup>c</sup>	9,15 <sup>c</sup>	8,75 <sup>d</sup>	8,53 <sup>d</sup>
1:1	11,11 <sup>a</sup>	10,98 <sup>a</sup>	10,67 <sup>b</sup>	10,54 <sup>b</sup>
1:2	11,89 <sup>a</sup>	11,47 <sup>a</sup>	11,32 <sup>a</sup>	11,03 <sup>a</sup>
1:3	12,56 <sup>a</sup>	12,21 <sup>a</sup>	11,97 <sup>a</sup>	11,64 <sup>a</sup>
1:4	12,56 <sup>a</sup>	12,22 <sup>a</sup>	11,97 <sup>a</sup>	11,66 <sup>a</sup>

Remarks: Value followed by the same letter are not significantly different at the 0.05 level by DMRT

The results of observations of rendemen from several treatments ranged from 7.64% to 12.56% (g xilan / g corncob). With a fiber content of 25.43% (Table 1), the ratio of xylan in fiber ranges from 30.04% - 50.88%. This result is consistent with Jaeggles (1975) study of xylan levels in corn cobs fibers ranging from 30-40%. According to Thu and Preston (1999) the ratio of xylan in corn cobs fibers was 28%, lower than the results of this study, while previous studies (Richana et al. 2004) resulted in a ratio of xylan in fiber of 31.8%. This difference is due to different varieties and ages of corn. The stages of the xylan extraction process from material preparation to the resulting xylan and mass balance are presented in Table 3. The cobs needed in this study were 50 g after being filtered with 40 mesh in each treatment. At first the corn flour is soaked in 500 ml of 0.5% NaOCl solution for 5 hours. After filtering the pulp and supernatant were obtained, the pulp was obtained 178.54 g. The pulp has cellulose and xylan content, while the

supernatant is a soluble lignin. The pulp is then dried at 28oC for 24 hours, the water content of the pulp becomes 37.1%.

TABLE 3: Balance of mass extraction of xylan from corn cobs.

Input Material		Process	Output Material		Residue Material	
(TJ) Corn cob	Weight (g) 72	Milling	Corn cob flour	Weight (g) 50	Corn cob Residue	Weight (g) 22
Corn cob flour NaOCl 0,5%	50 575	Delignification	Precipitate	178,54	Solvent+lignin	446,46
Precipitate NaOH	178,54 400	Extraction I	Supernatant	306,52	Precipitate	272,02
Supernatant HCl 6N	306,52 63,07	Neutralization	Supernatant	280,72	Precipitate	88,87
Supernatant	280,72	Extraction II	Xylan	6,69	Supernatant	935,23
Ethanol 95%	661,2	Drying	Dry-Xylan	5,98	Evaporated water	0,71

TABLE 4: Solubility of xylan in some solvents.

Solvent	Solubility
NaOH 1%	+++ (very soluble)
Hot water	++ (soluble)
Cold water	+ (few soluble)
HCl 1N	- (insoluble)

The next process is soaking to separate the pulp with the supernatant. Cellulose settles under alkaline conditions, so that the addition of cellulose NaOH will precipitate. Supernatant is neutralized by adding HCl, then the sediment is filtered. The resulting supernatant contained xylan, then 95% ethanol was added with a ratio of 1: 3 (v / v). Addition of ethanol will cause xylan to settle or clot so that it is easily separated. Wet xylan obtained 6.69 g, then dried to a moisture content of 10.67% which is 5.98 g of xylan.

From the results of mass balance analysis, to get 12% xylan yield, 5.98 g, 50 g of corn cobs flour, 575 ml of 0.5% NaOCl, 63.07 ml of 6N HCl and 661.2 ml of 95% ethanol were needed.

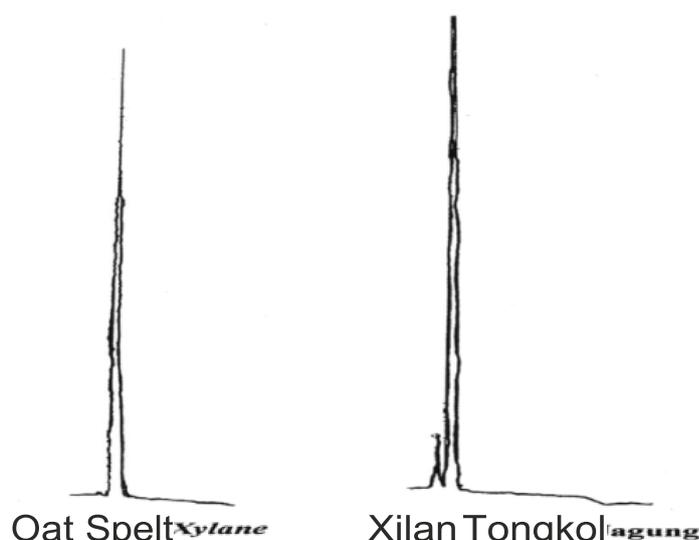
### 3.2. Xilan solubility

The solubility of xylan (Table 4) shows that the xylan dissolves completely in alkali (1% NaOH), dissolves in hot water and is slightly soluble in cold water, and insoluble in acid (1N HCl). Solubility of a polymer, including carbohydrates, will decrease with the higher molecular weight. Xylan is difficult to dissolve in cold water but soluble in water heated

at 100°C (Vandamme and Derycke, 1983). This also happened in the results of this study, namely xylan is only slightly soluble in cold water. Based on these results, corncob xylan can be used for liquid and alkaline media (for alkalophilic bacteria) because it is alkaline soluble, and in hot or cold water.

### 3.3. Qualitative and quantitative analysis of xylan

After xylan extract was obtained, xylan analysis was performed using High Performance Liquid Chromatography (HPLC). This analysis is used to determine the quality and purity of xylan. The results of the analysis show that the extracted product is xylan by the retention time.



**Figure 1:** Chromatogram from xylan extraction from corn cobs and xylane oat spelt as standard.

Standard retention time of oat spelt xylane is 2.59 minutes and 2.57 minutes for corn cobs (Figure 1). Xylan purity is 97.47% by adding xylan standard (oat spelt xylan from Sigma) to chromatogram xylan corncob. Corn cobs have a very high peak diagram and a small peak. This shows that the xylan extract of corn cobs can be assumed to be almost pure.

The results of this xylan extract research, it turns out that corncob is a potential source of xylan. The average xylan yield was 10.95%, soluble in 1% NaOH and hot water and had a high xylan purity. Based on these results corn cobs have prospects for xylan industrial raw materials and xylan-based processing, furfural and xylitol. Basically, all ingredients containing xylan can be used for the above products. However, it is necessary to consider the efficiency and potential of the raw material. As for furfural

products according to the rules of UNCTAD / GATT (1979) it is recommended that raw materials are ingredients that contain a minimum of 12-20% xylan. Thus, corn cobs are suitable for furfural and xylitol products. According to Saha (2002) and Richana et al. (2007) xylan is very prospective for bioprocess. Xylan can be used for microbial growth media in liquid media because it has soluble properties in hot water, then it can be used for alkaline microbial isolation because it dissolves in 1% NaOH, and can produce pure xylanase-producing microbes (free cellulase).

#### 4. Conclusion

Addition of NaOCl concentration in the delignification process and the ratio of supernatant and ethanol to xylan extraction have an effect on increasing xylan yield. Combination of 0.5% NaOCl concentration treatment and supernatant ratio: ethanol 1: 3 (v / v), resulting in the highest xylan yield (12.56%). HPLC analysis proves that the xylan produced has high purity. Xylan is very soluble in alkali (1% NaOH) and dissolves in hot water. Based on these results, corncob xylan can be used for liquid and alkaline media (for alkalophilic bacteria) because it is soluble in alkali, and dissolved in hot or cold water. Corn cobs have prospects for the xylan, furfural and xylitol sugar industry raw materials because they can produce high xylan yields.

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