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Xylans are a valuable alternative resource: Production of D-xylose, D-lyxose and furfural under microwave irradiation

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ABSTRACT

The influence of microwave irradiation on hydrolysis of xylan and simultaneous epimerization of the D-xylose to D-lyxose has been studied. An acidic solution of xylan was treated with catalytic amount of sodium molybdate and the composition of the reaction mixture was analyzed. Short reaction times of hydrolysis and subsequent epimerization reaction provided an equilibrium reaction mixture of D-xylose and D-lyxose (1.6:1) without significant formation of undesirable side products. Obtained pentoses can be reduced to the corresponding alditols (D-xylitol and D-lyxitol) in very good yields (88% and 85%) or can be further dehydrated to furfural (53%). Combined use of Mo(VI) catalyst and microwave irradiation allows better conversions and substantial reduction of reaction times (400-fold) compared to that obtained by conventional heating. Studied stereospecific transformation of xylan proceeds with high selectivity, short reaction times and very good yields that makes this approach attractive also for preparative purposes.

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1. Introduction

During the last decades there has been increased interest in the development of environmentally friendly processes for preparation of valuable chemicals from agricultural waste. As the availability of the fossil fuel reserves will become limited, renewable naturally abundant resources are becoming a viable and important alternative resource. Carbohydrates are the most abundant and inexpensive naturally occurring compounds. They are mostly present as biopolymers (cellulose, hemicellulose, starch) and belong to the most intensively studied precursors with a wide range of properties and applications (Belgacem & Gandini, 2008). Lignocellulosic biomass, as an abundant renewable resource, has the potential to become a sustainable supply for the production of chemical intermediates and biofuels. One important and valuable chemicals, furfural, obtained by dehydration of pentoses can be used to replace petrochemicals or can be further converted to a range of products including plastics, pharmaceuticals and agrochemicals (Xia, Lin, Tonga, & Beltramini, 2011). Utilization of this potential requires effective conversion of lignocellulose into useful intermediates, such as monosaccharides, that are ideal alternatives for the construction of enantiopure target molecules.

Hemicellulose is, after cellulose and starch, the third most abundant biopolymer in Nature (20–35 wt.%). This plant cell wall polysaccharide is mainly found in woods, grasses, algae and cereals. The major constituents of hemicelluloses are xylans, polysaccharides consisting of D-xylose units linked with $(1 \rightarrow 4)$-β-glycosidic linkages. They are essentially linear polymers with short branched-chains. Xylose is always the sugar monomer present in the largest amount, but some monosaccharides (arabinose, mannose, rhamnose, glucose) or uronic acids (glucuronic, mannuronic, galacturonic) are also present (Ebringerová & Heinze, 2000; Belgacem & Gandini, 2008). These polymers can be easily hydrolyzed to monomeric sugars, by the use of mineral acids as well as hemicellulase enzymes (Mansilla et al., 1998; Chen & Gong, 1985). The challenge for the effective utilization of lignocellulosic waste material is to use this bio-based resource for production of high-value products such as xylose, xylitol, and furfural (Prakasham, Sreenivas, & Hobbs, 2009; Zhang, Yu, Wang, Dong, & Peng, 2013). Extensive efforts have been expended to achieve efficient polysaccharide depolymerisation. Conversion should be economical, environmentally friendly and technologically practical at the same time. In recent years microwave irradiation has received increasing interest in many chemical reaction studies, including organic and inorganic syntheses, due to remarkable enhancement of the reaction rates, higher yields and improved selectivity (Loupy, 2006). The basic mechanisms observed in microwave-assisted processes are dipolar polarization and conduction. It is known that the presence of salts can frequently enhance effects of dielectric loss and microwave coupling could produce superheating (Gabriel, Gabriel, Grant, Halstead, & Mingos, 1998; Kunlan et al., 2001). Many thermochemical conversion technologies are known and several studies

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have appeared that describe the transformation of hemicellulose in a microwave field (Binder & Raines, 2009; De, Dutta & Saha, 2011).

We have recently reported that the formation of rare aldoses can be facilitated by combined action of transition-metal catalyst and microwave irradiation. Molybdate ions were investigated as a catalyst for the isomerization of various reducing sugars. It was shown that transformation proceeds very efficiently in microwave field (Hricovíniová, 2006, 2008, 2009). The rapid and convenient production of D-mannose from starch (Hricovíniová, 2011) prompted us to investigate this approach on other types of polysaccharides and to study this catalyzed transformation in detail. Herein we described a novel approach applied to hydrolysis of xylans to produce rare pentoses employing the catalytic effect of Mo(VI) ions and microwave irradiation as the thermal energy source. This method is directed to rapid release of D-xylose from xylans and its immediate transformation to rare aldose, D-lyxose. The combination of two steps makes the method possible to achieve reaction mixture of two valuable pentoses, D-xylose and D-lyxose, which could be easily transformed to the corresponding alditols (D-xylitol and D-lyxitol) or furfural.

2. Experimental

2.1. Materials and methods

Beechwood xylan, birchwood xylan and 4-*O*-methyl-D-glucurono-xylan isolated from beechwood. Standards: D-xylose, D-lyxose, furfural (2-furalaldehyde, 99%). All chemicals and materials used were purchased from commercial suppliers. Microwave reactions were performed in a multimode microwave reactor CEM Discover consisting of a continuous focused microwave power delivery system with operator-selectable power; microwave frequency source of 2.45 GHz. The reactions were performed in sealed glass tubes and were stirred magnetically to prevent hot spots. Conversions and the purities of the products were determined by NMR spectroscopy. High-resolution NMR spectra were recorded in a 5 mm cryoprobe on Varian 600 VNMRS spectrometer. The experiments were carried out at 25 °C or 30 °C in D_2O. One-dimensional ^1H and ^{13}C NMR spectra as well as two-dimensional COSY and HSQC were used to determine ^1H and ^{13}C chemical shifts. FT-IR spectra were measured on a Nicolet 6700 spectrometer with DTGS detector and OMNIC 8.0 software using 128 scans at the resolution of 4 cm^{-1} with diamond ATR technique. UV absorption spectra were recorded on Beckman DU-7 UV–Visible spectrophotometer. Optical rotations were determined at 20 °C with an automatic polarimeter Perkin–Elmer Model 141 using 1-cm cell. Melting points were measured on a Kofler hotstage microscope. Separations of the free sugars were accomplished by column chromatography on Dowex 50W X8 resin in the Ba^{2+} form (200–400 mesh). Paper chromatography was performed by the descending method on Whatman No. 1 paper using ethyl acetate–pyridine–water (8:2:1) as the mobile phase. The chromatograms were made visible by means of alkaline silver nitrate. All chemicals were reagent grade and used without further purification.

2.2. Hydrolysis of xylan in the presence of sodium molybdate under microwave irradiation

Xylan (500 mg) was dissolved in 0.25 M HCl (10 ml) and $Na_2MoO_4{\cdot}2H_2O$ (50 mg) was added to obtain a stock solution. Sealed tubes (1 ml) were exposed to microwave irradiation 200 W for different lengths of time (10 s–5 min). The vessels were removed from the microwave reactor, the reaction mixtures were treated with Amberlite IRA-400 HCO_3^- and H^+ form to remove the catalyst. The reaction mixtures were analyzed by NMR spectroscopy measurements and the ratio of xylan/xylose/lyxose was determined by integration of selected resonances in ^1H NMR spectra.

2.3. Hydrolysis of xylan in the presence of sodium molybdate with conventional heating

Xylan (500 mg) was dissolved in 0.25 M HCl (10 ml) and $Na_2MoO_4{\cdot}2H_2O$ (50 mg) was added. The tube was sealed and heated in an oil-bath at 90 °C for 0–25 h. Samples (0.5 ml) were taken at selected intervals, treated with Amberlite IRA-400 in the HCO_3^- and H^+ form to remove the catalyst. The composition of the reaction mixture was analyzed by ^1H NMR spectroscopy.

2.4. Xylan hydrolysis and epimerization reaction in semi-preparative scale

For a typical procedure beechwood xylan (1 g) was dissolved in 0.25 M HCl (20 ml) and $Na_2MoO_4{\cdot}2H_2O$ (100 mg) was added. The weight ratio of reactants is the same as applied in previous model experiments. The sealed tube was exposed to microwave irradiation (200 W) for 3 min. The reaction mixture was treated batch-wise with an excess of the cation/anion ion-exchange resin, filtered off, washed with water and combined filtrates were evaporated. The composition of the reaction mixture was analyzed by ^1H NMR spectroscopy. The syrupy residue was fractionated by column chromatography on Dowex 50W X8 (200–400mesh) in Ba^{2+} form with water as eluent. Fractionation of the syrupy residue afforded D-xylose (0. 604 g, 60%) and D-lyxose (0.314 g, 31%). Analytical data were in accordance with literature cited (Collins, 1998).

2.5. Reduction of D-xylose to D-xylitol

To a solution of D-xylose (1 g) in water (10 ml) was added an aqueous solution of sodium borohydride (0.2 g/5 ml H_2O). The reaction mixture was kept at room temperature for 3 h. When the reduction was complete the reaction mixture was acidified with a few drops of acetic acid, deionized with cation/anion ion-exchange resin and evaporated to dryness. Crystallization from ethanol afforded optically inactive D-xylitol (880 mg; 88%). Analytical data and NMR spectra were in accordance with literature (Collins, 1998; Angyal & Le Fur, 1980).

2.6. Reduction of D-lyxose to D-lyxitol

To a solution of D-lyxose (1 g) in water (10 ml) was added an aqueous solution of sodium borohydride (0.2 g/5 ml H_2O). Reaction was worked up in exactly the same way as mentioned in previous procedure. Crystallization from methanol afforded D-lyxitol. Yield 85%; analytical data and NMR spectra were in accordance with literature (Collins, 1998; Angyal & Le Fur, 1980).

2.7. Microwave-assisted dehydration of xylan to furfural

Xylan (2 g) was dissolved in 0.1 M HCl (10 ml) and $Na_2MoO_4{\cdot}2H_2O$ (50 mg) was added to obtain a stock solution. The sealed tube (1 ml) was inserted into the microwave reactor and exposed to microwave irradiation (300 W) for different lengths of time (1–10 min). Upon completion of the reaction the sample was cooled down to room temperature and reaction mixture was extracted with diethylether and evaporated. Furfural, isolated as yellow oil was analyzed by UV, IR and NMR techniques. Yield 53%; UV 278 nm (Martinez, Rodriguez, York, Preston, & Ingram, 2000); ν_{max} (ATR, diamond), 1462 cm^{-1}, 1473 cm^{-1} (C=C of aromatic ring), 1666 cm^{-1} (Ar C=O), (Sashikala & Ong, 2007); δ_H (D_2O, 599.84 MHz): ring protons were shown in aromatic region

6.6–9.6 ppm (Shin & Cho, 2008). Analytical data and NMR spectra were in accordance with literature cited.

2.8. Dehydration of xylan with conventional heating

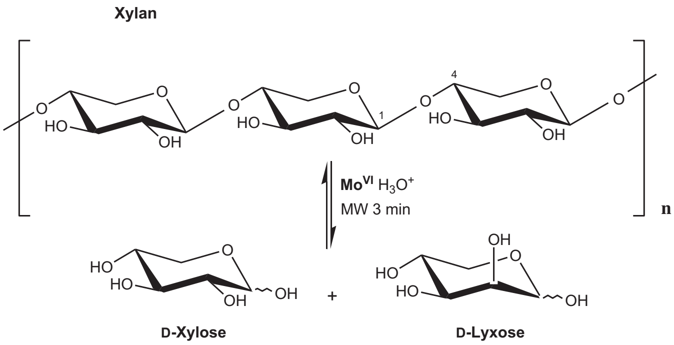
Xylan (2 g) was dissolved in 0.1 M HCl (10 ml) and $Na_2MoO_4 \cdot 2H_2O$ (50 mg) was added. The round bottom flask was placed in an oil-bath and refluxed at 150 °C (10–120 min). The reaction was worked up in exactly the same way as mentioned in previous experiment. Furfural yield 36%.

3. Results and discussion

In connection with adding value to lignocellulose biomass, the application of appropriate catalytic system in combination with microwave field represents an innovative approach with processing advantages. Here we show the application of microwaves in combination with hexavalent molybdenum catalyst as an efficient method for the production of commercially interesting chemicals. D-Xylose, D-xylitol, D-lyxose, D-lyxitol or furfural can be prepared from xylan-based polysaccharides from various sources. Molybdate ions act as a powerful catalyst for the epimerization of reducing sugars (Bílik, 1972, 1983) and have a number of unique features (Porai-Koshits & Atovmyan, 1974; Petruš, Petrušová, & Hricovíniová, 2001). Reaction conditions are the prime factors that affect the yield and composition of the reaction mixture. The influence of different variables, such as acid concentration, amount of catalyst, microwave power and reaction time, were evaluated for identification of xylan conversion and product distribution.

3.1. Microwave-assisted conversion of xylan

Many polysaccharides require harsh conditions to degrade. While cellulose is crystalline and strongly resistant to hydrolysis, hemicellulose containing predominantly D-xylose units (linked as in cellulose by (1 → 4)-β-glycosidic linkages), has an amorphous structure with little strength (Nishiyama, Sugiyama, Chanzy, & Langan, 2003). Microwave irradiation results in polarization of polar bonds (such as C—O—C in glycosidic linkages) and increases their reactivity. Therefore, a microwave field is able to enhance the hydrolytic cleavage of macromolecular chains. Experimental trials of the acid hydrolysis of xylan to sugar monomers in a microwave field were carried out by means of a multimode microwave reactor consisting of a continuous focused microwave power delivery system with operator-selectable power. Various concentrations of hydrochloric acid (0.1 M, 0.25 M, 0.5 M, 0.75 M and 1.0 M) were tested for the hydrolysis of xylan samples. The depolymerization of (1 → 4)-β-xylopyranosyl linkages to D-xylose units worked already in 0.1 M hydrochloric acid. We observed that hydrolysis of xylan is predominantly determined by acid concentration independently of xylan source used. As expected, faster conversion of xylan to D-xylose can be reached in the reaction performed using higher concentrations of acid.



Scheme 1. Reaction scheme of xylan hydrolysis and simultaneous epimerization reaction of obtained D-xylose to D-lyxose in microwave field.

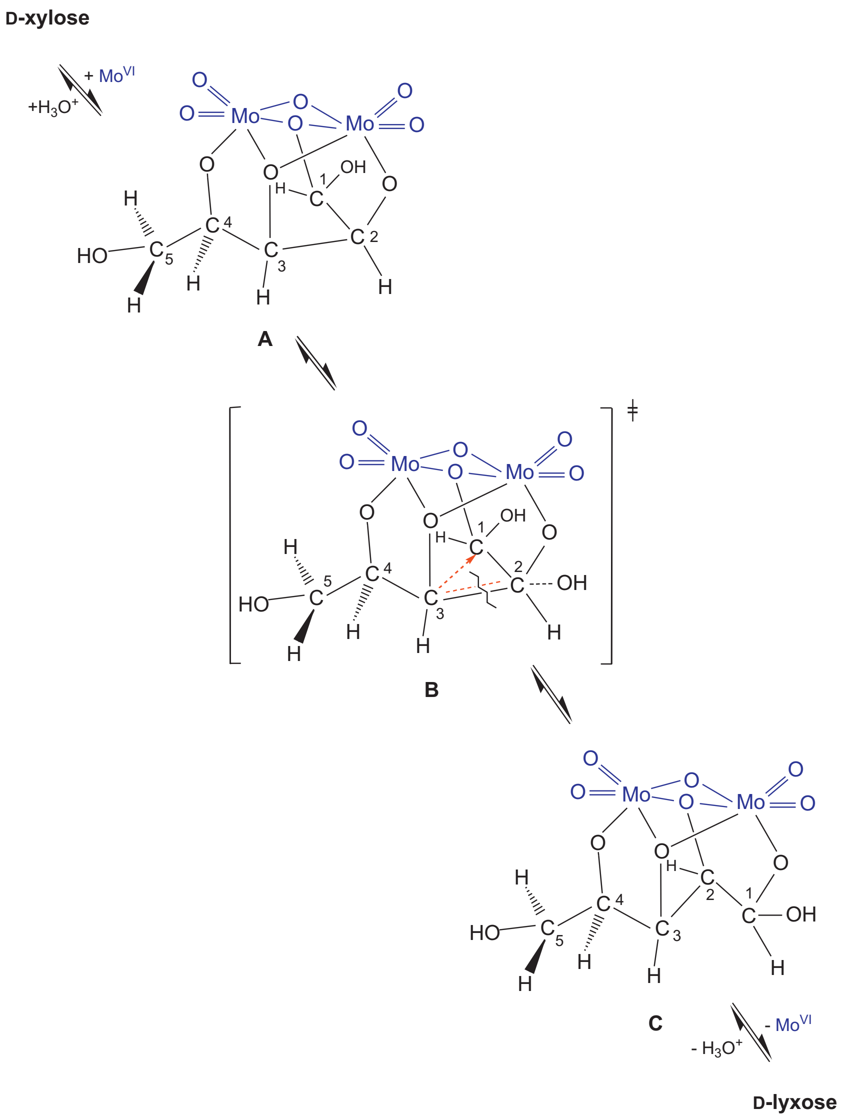
Several experiments were designed on exploitation of the catalytic system that would improve xylan hydrolysis with subsequent epimerization of D-xylose monomer. Beechwood xylan was selected as the model compound for determination of the influence of microwave-induced Mo(VI)-catalyzed conversion of hemicelluloses to epimeric pentoses, D-xylose and D-lyxose. Experiments on the combined hydrolysis and isomerization reaction in one step have been carried out using a catalytic amount of sodium molybdate and dilute hydrochloric acid. It was found that a 0.5% solution of sodium molybdate was a sufficiently high concentration of this catalyst and led to very good conversion to desired products.

The efficiency of thermochemical conversion, selectivity and product distribution was examined and the best results were obtained by performing the reaction at 200 W of microwave power. In the optimized reaction conditions, a 5% solution of xylan in 0.25 M hydrochloric acid with a catalytic amount of sodium molybdate was exposed to microwave irradiation for different time periods. Selected reaction conditions led to complete depolymerization of xylan and high conversion by means of D-xylose and D-lyxose content. The analysis of ^1H NMR spectra indicated that xylan was completely hydrolyzed and converted to the equilibrium mixture of D-xylose and D-lyxose (1.6:1) within 3 min. The reaction scheme of the combined xylan hydrolysis and simultaneous epimerization reaction of obtained D-xylose to D-lyxose is illustrated in Scheme 1.

In the present work, the yields of D-xylose/D-lyxose were compared using three different xylan substrates. Xylans from beech wood, birch wood and 4-*O*-methyl glucuronoxylan from beechwood were tested. The solution of each xylan sample was exposed to microwave irradiation under previously optimized conditions. The ratio of sugars present in the equilibrium reaction mixture with respect to the production of D-xylose and D-lyxose was determined by ^1H NMR spectroscopy. The transformation occurs in 3 min reaching comparable final concentrations. Table 1 summarizes all the data obtained for various xylan samples heated in microwave field or by conventional heating. Mo(VI) catalyst in combination with microwave power, caused only minor differences of higher overall conversion to D-xylose/D-lyxose among three different xylans tested. It should be also noted that the increasing amount of catalyst did not influence the product composition.

Table 1
Comparison of microwave and conduction-heated samples of the combined xylan hydrolysis and simultaneous epimerization reaction of obtained D-xylose to D-lyxose. Both partial and full conversions are shown for conventional oil-bath heating to demonstrate considerable differences between microwave and conventional approaches in reaction kinetics and amounts of xylose/lyxose formations.

Xylan source	MW field		Conventional		Heating	
	Time (min)	xylan/Xyl/Lyx (%)	Time (h)	xylan/Xyl/Lyx (%)	Time (h)	Xylan/Xyl/Lyx (%)
Beechwood xylan	3	0/62/38	10	6/68/25	20	0/70/30
Birchwood xylan	3	0/63/37	10	7/68/24	20	0/69/31
4-*O*-Methyl-glucuronoxylan	3	0/61/39	10	7/67/25	20	0/68/32



Scheme 2. Mechanism of the Mo(VI)-catalyzed epimerization reaction of D-xylose to D-lyxose. The equilibrium reaction mixture of two epimeric aldoses is reached in microwave field after 3 min.

In order to compare these data with semi-preparative experiment we performed the reaction in microwave field using 1 g of beechwood xylan. Fractionation of the reaction mixture by column chromatography afforded pure epimers D-xylose (60%) and D-lyxose (31%). Xylan hydrolysis is predominantly determined by acid concentration but the simultaneous mutual interconversion of D-xylose and D-lyxose is governed by highly stereospecific isomerization reaction that is catalyzed by molybdate ions (Bílik, 1983).

The mechanism of this stereospecific transformation is based on the fact that D-xylose units create catalytically active complexes in the presence of molybdate ions. Catalytically active complexes lead to isomerization of D-xylose to D-lyxose through the rearrangement of carbohydrate carbon skeleton. The accepted mechanism is depicted in Scheme 2. The first step is the complex formation of binuclear molybdate species with four adjacent hydroxyl groups (on C-1, C-2, C-3 and C-4) of the acyclic hydrated form of D-xylose (Scheme 2A). This rigid framework holds the acyclic carbohydrate skeleton in required conformation for stereospecific carbon backbone rearrangement. Rearrangement occurs through a transition state (Scheme 2B) in which C-1 and C-2 are enantiomeric. Bond formation between C-2 and C-3 regenerates the starting D-xylose, while bond formation between C-1 and C-3 produces the 2-epimer, D-lyxose (Scheme 2C). These results matched well with our previous observations and are also in agreement with NMR experiments analyzing the mechanism of this transformation with ^{13}C-enriched saccharides (Petruš et al., 2001).

Microwave irradiation, as a non-conventional energy source, has a strong influence upon the kinetics and thermodynamics of this reaction. The obtained data suggest that the coordination ability of the Mo(VI)-catalyst under the given reaction conditions enables simultaneous efficient depolymerisation of xylan and formation of epimeric D-lyxose in one step. It should be also noted that the presence of molybdate salts improves efficiency of energy absorption from microwave source and thus, the reaction proceeds faster compared to the reaction without the catalyst (Hricovíniová, 2006). Under identical reaction conditions (0.5% Na_2MoO_4 in 0.25 M HCl) the microwave irradiated samples of xylan were compared with samples prepared by conduction heating (90 °C, oil-bath). Under conventional conditions the equilibrium reaction mixtures were obtained after long heating. Xylan was completely hydrolyzed to D-xylose after 3–4 h. Formation of D-lyxose started after 2 h and the maximum was reached in about 20 h. The final equilibrium mixture is comparable to that found in previous studies of D-xylose/D-lyxose epimerization (Hricovíniová, 2006).

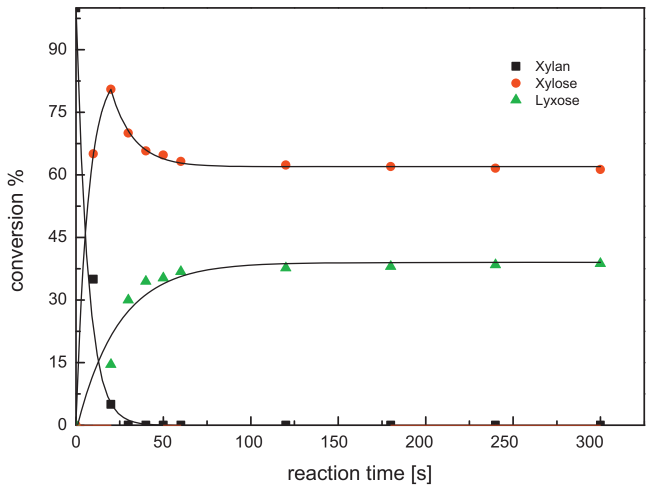


Fig. 1. Conversion of beechwood xylan (■) to D-xylose (●) and D-lyxose (▲) as a function of time in microwave field.

Different reaction kinetics and thermodynamics under conventional conditions, compared to microwave conditions, are seen in large differences in both time course and the composition of reaction mixture during reaction. After 10 h of heating the ratio of xylose/lyxose was 2.7:1 and the equilibrium mixture of xylose/lyxose 2.2:1 was reached after 20 h of heating. The composition of the reaction mixture in terms of xylan, D-xylose and D-lyxose content as a function of time is depicted in Figs. 1 and 2. As shown in Fig. 1, after 25 s more than 80% of xylan is hydrolyzed to D-xylose monomers in microwave field. Epimerization of D-xylose to D-lyxose starts in 30 s, simultaneously with the hydrolysis of xylan. Results indicate that sufficient reaction time (3 min) facilitated the epimerization of D-xylose to D-lyxose, whereas prolonged duration might lead to the occurrence of side reactions and traces of furfural were also observed. Fig. 2 shows the kinetics for the reaction under conventional, oil-bath heating. After 2 h, about 45% of xylan is hydrolyzed to D-xylose monomers and formation of D-lyxose starts. The maximum value of D-lyxose is reached after 20 h.

The results obtained by application of two heating techniques clearly show that microwave irradiation caused the differences in the equilibration of the reaction mixtures and thus led to faster conversions and higher yields. Owing to differences in the mode of energy transfer different ratios of stereoisomers as a function of time were observed. The reaction equilibrium was shifted in both cases to the aldose with the lower value of conformational instability, thus a larger amount of D-xylose was present. A high input of energy allows the reaction to overcome the energy barrier for products formation very fast (2–3 min) compared to conventional conditions (20–25 h).

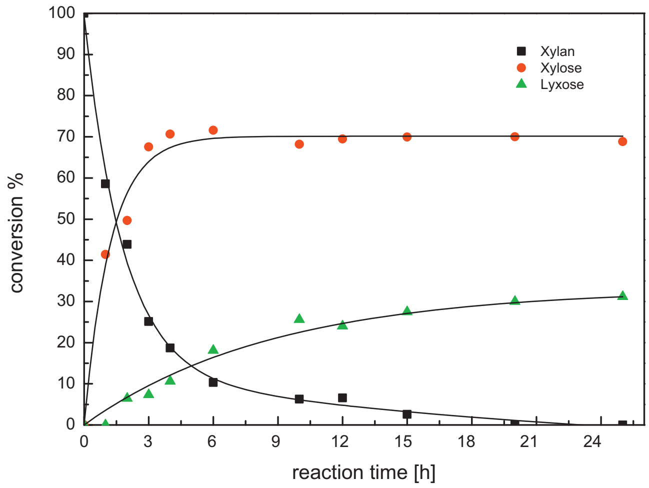


Fig. 2. Conversion of beechwood xylan (■) to D-xylose (●) and D-lyxose (▲) as a function of time under conventional, oil-bath heating.

Scheme 3. The microwave-assisted transformation of xylan to furfural.

Xylose and lyxose were obtained from various xylan samples in a one-pot transformation. D-Lyxose occurs rarely in Nature and it can be obtained only by chemical synthesis (Bílik & Caplovic, 1973; Giudici & Griffin, 1974). D-Xylose is an important compound mainly for its conversion to D-xylitol with its wide variety of applications. It metabolizes easily and independently of insulin in the human body and produces the same amount of energy which highlights its application in all diabetic foods. Xylitol, with sweetening power matching that of sucrose, is applicable as a sugar substitute in the food processing industry. It can be used as an additive in foods, beverages, pharmaceuticals and nutraceuticals (Granström, Izumori, & Leisola, 2007). Industrially, xylitol is produced by catalytic hydrogenation or by enzymatic reduction of D-xylose. However, industrial bioconversion of detoxified hemicellulosic hydrolysate by yeast strains to xylitol is complicated by inhibitory effects of the often detected phenolic by-products (Wisniak, Hershkowitz, Leibowitz, & Stein, 1974; Zhang, Geng, Yao, Lu, & Li, 2012). Compared to enzymatic production, chemical catalysis employing Mo(VI) salts could offer attractive advantages. Utilizing an efficient catalytic system and water as the solvent has many advantages. Moreover, this approach is environmentally friendly and inexpensive. Xylitol and lyxitol can be prepared by the reduction of D-xylose or D-lyxose with sodium borohydride which leads to these alditols in very good yields (88% and 85%).

3.2. Microwave-assisted dehydration of monosaccharides from xylan to furfural

The production of furfural from xylan in microwave field was also analyzed. Pentoses, as precursors for furfural, are formed during the hydrolysis of hemicellulose. The hydrolysis reaction proceeds about 50 times faster than the dehydratation reaction, thus the latter becomes the limiting step. The use of microwaves in the dehydration of pentoses revealed a notable effect on the reaction rate. It is important to conclude that the yield of furfural also depends on the substrate concentration therefore maximum generation of pentoses during hydrolysis is necessary. The optimal reaction conditions were found a 20% solution of xylan in 0.1 M hydrochloric acid. Microwave-assisted acid-catalyzed thermochemical conversion was carried out by irradiation of xylan samples for a different time periods at 300 W. The obtained reaction mixture was extracted with diethyl ether and furfural was determined by UV spectrophotometry (Martinez et al., 2000). Composition of the reaction mixture was analyzed also by ^{1}H NMR spectroscopy. The direct production of furfural from xylan *via* hydrolysis followed by dehydration reaction was about 42% after 5 min. The reaction scheme of the combined xylan hydrolysis, epimerization reaction and dehydration to furfural is illustrated in Scheme 3. The synthesis of furfural from xylan was also carried out using oil-bath heating (150 °C, 30 min). Under these conditions we obtained maximum 28% yield of furfural. Longer reaction times and nonselective heat transfer at the surface of reaction vessels resulted in the loss of furfural due to the formation of secondary reactions and undesired by-products that decreased its final yield.

However, the furfural formation in the molybdate-catalyzed transformation of xylan sample using microwave field was higher. The process involves combined hydrolysis, epimerization and dehydration reactions in a single step and thus provided higher amounts of furfural (53%) compared to reaction without Mo(VI) ions (42%). Xylan dehydration with conventional heating in the presence of molybdate yielded 36% of furfural that is also higher compared to 28% without Mo(VI) ions. The presence of molybdate ions in acidic solution may lead to the complexation with D-xylose released during hydrolysis. It is very likely that this interaction promotes the stabilization of the acyclic form of D-xylose that is quickly equilibrated with its furanose and pyranose forms. The less stable pyranose ring leads *via* 2,5-anhydride in dehydratation pathway to 2-furaldehyde (Antal, Leesomboon, & Mok, 1991). Microwave irradiation as a non-conventional energy source in combination with catalyst has a strong influence on the course of reaction. Conversion to furfural is in accordance with literature data where furfural yields rarely exceeded 50–60% when produced from hemicellulose biomass *via* one step procedure. Furfural yields are limited by side reactions such as homopolymerizarion, degradation or condensation (Yemis & Mazza, 2011). The molybdate salts thus play a double role in the presented reaction: Mo(VI) acts as a catalyst that enables stereospecific conversion of D-xylose to D-lyxose and at the same time molybdate salts cause improvement of the dielectric properties of the solution, that lead to higher energy transfer to solution from a microwave source. The present approach should provide access to useful alternatives for the preparation of many interesting chemical intermediates and biofuels based on sugar derivatives.

4. Conclusions

In summary, microwave irradiation in combination with Mo(VI) catalyst has been shown to be a very effective route of transformation of cheap natural lignocellulosic biopolymers. The influence of microwave-induced Mo(VI)-catalyzed conversion of xylans to epimeric pentoses was studied. D-Xylose and D-lyxose were obtained in one step procedure by the combined hydrolysis and epimerization reaction in very good yields. Moreover, this catalyst was also efficient in the transformation of mixed source of pentoses to furfural, where three simultaneous steps (hydrolysis, epimerization and dehydration reaction) are combined in a one-pot reaction. Dramatically shorter reaction times (about two orders) and higher yields of products compared to conventional methods make the method attractive and applicable also on a semi-preparative scale. Experimental results reveal that Mo(VI)-catalyzed isomerization reactions may provide an interesting alternative toward achieving platform chemicals from abundant renewable resources.

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