

Formic acid aided hot water extraction of hemicellulose from European silver birch (*Betula pendula*) sawdust

Werner Marcelo Goldmann ^{a,*}, Juha Ahola ^a, Marja Mikola ^a, Juha Tanskanen ^a

^a *Chemical Process Engineering, Faculty of Technology, University of Oulu, P.O. Box 4300, Oulu 90014, Finland*

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Highlights

- Hydrolysis of hemicellulose with low cellulose degradation was achieved
- Obtained a residual solid product low on hemicellulose and high on cellulose
- The lignin concentration in the extract fell below the detection limit of 3 g/L

Abstract

Hemicellulose has been extracted from birch (*Betula pendula*) sawdust by formic acid aided hot water extraction. The maximum amount of hemicellulose extracted was about 70 mol% at 170 °C of the total hemicellulose content, measured as the combined yield of xylose and furfural. Lower temperatures (130 and 140 °C) favored hemicellulose hydrolysis rather than cellulose hydrolysis, even though the total hemicellulose yield was less than at 170 °C. It was found that formic acid greatly increased the hydrolysis of hemicellulose to xylose and furfural at the experimental temperatures. The amount of lignin in the extract remained below the detection limit of the analysis (3 g/L) in all cases. Formic acid aided hot water extraction is a promising technique for extracting hemicellulose from woody biomass, while leaving a solid residue with low hemicellulose content, which can be delignified to culminate in the three main isolated lignocellulosic fractions: cellulose, hemicellulose, and lignin.

1. Introduction

Lignocellulosic feedstocks (LCFs) have gained research interest and industrial relevance due to their potential for production of fine chemicals (and their precursors) within the biorefinery concept (Budzinski & Nitzsche. 2016).

LCFs are mainly composed of cellulose, hemicellulose and lignin. Although cellulose is usually the main target for refining and has a currently high value in the pulp and paper industry, hemicellulose and lignin are also key components of LCFs. Simple polysaccharides (e.g. xylan) can be obtained from hemicellulose. These polysaccharides can be depolymerized into their simple sugar monomers, such as xylose (Dutta & Chakraborty, 2015). The sugar monomers can then be further reacted into specialty chemicals like furfural (Wang *et al.* 2015) and xylitol (Yadav *et al.* 2012). Organosolv pulping has been used to remove hemicellulose and lignin from LCF's, using solvents such as ethanol (Xu *et al.* 2007), formic acid (Li *et al.* 2012), and acetic acid (Sahin & Young, 2008). One alternative is to first reduce the hemicellulose content in the LCF before delignification.

A feasible pathway to isolate hemicellulose and consequently reduce the hemicellulose content in the initial LCF is by hot water extraction (Krogell *et al.* 2014). Typically, hot water extraction is done at temperatures above the normal boiling point of water, which allows for a better solubilization of the hemicellulose and depolymerization of polysaccharides (e.g. xylan to xylose) (Maurya *et al.* 2015). Factors such as temperature (Rissanen *et al.* 2016), time (Tunc & van Heiningen, 2008), and chip size (Song *et al.* 2012) have been explored in hot water extraction. Krogell *et al.* (2013) have reported mass yields of 95% of total hemicellulose (75% of total dissolved solids) with 170 °C hot water extraction for 2 hours of spruce with particle size 0.5-0.7 mm, and 73% of total hemicellulose (63% of total dissolved solids) for particle size 8-12.5 mm. These results were obtained with a liquid to wood ratio of about 11. Li *et al.* (2013) reported yields of 61.5 wt% of xylose and furfural in the hot-water-extracted liquor at 170 °C (particle size 27*1.8*1.2 mm) for 1 hour. They reported that the amount of xylose and xylose-oligomers and xylose-polysaccharides in the liquor was 65 wt% of the total sugars, while the xylose monosaccharides were much less than 65 wt% of the total sugars, indicating a less effective hydrolysis of xylan to xylose than other carbohydrates.

Diluted sulfuric acid has been utilized for acid hydrolysis of hemicelluloses (Liu *et al.* 2012). Additionally, hydrolysis of wheat pulp in formic acid medium with the purpose of extracting glucose has been reported (Kupiainen *et al.* 2012). During formic-acid-aided hot water extraction, hemicellulose (namely xylan) is depolymerized into xylose, which is in turn dehydrated into furfural. Side-reactions occur within the

xylose-furfural pathway, as well as degradation of furfural, where polymerization occurs and undesired water-insoluble humins are formed from xylose and furfural (Hu *et al.* 2012, Wang *et al.* 2015). There has been reports of pretreatment of corn stover with 4 g/L of formic acid (Xu *et al.* 2009), and hemicellulose extraction from hardwood at 1 and 10 g/L of formic acid (Tunc *et al.* 2014). Nevertheless, there is not extensive knowledge on the effect of higher concentration of formic acid on hot water extraction with the express purpose of extracting hemicellulose.

The objective of hot water extraction of hemicellulose is to remove as much hemicellulose from wood as possible. This is achieved by the hydrolysis of polysaccharides (hemicellulose) to smaller oligomers and the monosaccharide xylose (and its dehydration product, furfural). When the targets of the extraction are xylose and furfural, acid-catalyzed hydrolysis can benefit the extraction by allowing a more effective hydrolysis from polysaccharides to monosaccharides. Formic acid plays a role in decreasing the transition state energies of the hydrolysis reaction (Zhang *et al.* 2014). Additionally, formic acid has been reported to catalyze the dehydration reaction of xylose to furfural (Lamminpää *et al.* 2012). Moreover, dissolution of the lignin matrix by formic and acetic acids during pulping (Watkins *et al.* 2015) suggests that formic acid has a solvent effect, additional to its catalytic effect. Formic acid has also been shown to catalyze the hydrolysis of cellulose to glucose and HMF (Kupiainen *et al.* 2014).

The purpose of this work was to assess the effect of formic acid in hot water hemicellulose extraction with respect to the yield of the xylose and its dehydration product, furfural.

2. Materials and methods

2.1. Sawdust and solvents

Birch (*Betula pendula*) sawdust was obtained from a Finnish sawmill. The birch utilized for this study contained 33 wt% of hemicellulose, 38 wt% of cellulose, and 24 wt% of lignin, with about 4 wt% of extractives and about 1 wt% of ash. Given that hemicellulose is mainly composed of pentose polysaccharides (Scheller & Ulvskov. 2010),

the hexose determination was deemed not crucial. Analytical grade (98-100 vol%) formic acid and ultrapure water were utilized as solvents in the extractions.

2.2. Sawdust analysis

The sawdust analysis was carried out in duplicate. The moisture content of the samples was obtained by drying the samples in an oven at 105 °C to constant weight. The ash content was determined using the procedure described by Sluiter et al. (2008a). Wood samples (3 g) were extracted with 150 mL of acetone for 4 hours by Soxhlet extraction to remove organic extractives (TAPPI T 280 pm-99. 1999). Extractive-free samples were utilized to determine lignin and holocellulose content. Klason lignin was determined after a two-step acid hydrolysis of the wood sample according to Sluiter et al. (2008b). Acid-soluble lignin was determined by UV-Vis spectroscopy from the hydrolysate obtained from the hydrolysis according to the procedure described by Erhman (1996). The amount of lignin is presented as a sum of acid-insoluble and acid-soluble lignin. Holocellulose was prepared from extractive-free samples, applying the procedure described by Rowell et al. (2005). The extractive-free sample (1.5 g), 48 mL distilled water, 0.3 mL acetic acid, and 0.75 g sodium chlorite were allowed to react in a 100 mL Erlenmeyer flask in a water bath (70-75 °C). After 60 minutes, 0.3 mL acetic acid and 0.75 g NaClO₂ were added. After each succeeding hour, 0.3 ml acetic acid and 0.75 g NaClO₂ were added. After 5 hours, the flask was allowed to cool and the solid holocellulose was filtered. The solid residue was washed with distilled water until the yellowish color was removed. Finally, the solid was washed with acetone. The holocellulose was dried overnight in an oven at 105 °C, cooled in desiccator for an hour and weighed. The residual lignin content in holocellulose was determined by the above-mentioned methods. The α -cellulose content was determined from the holocellulose, applying previously published procedures (Styarini *et al.* 2012, Tappi T203 cm-99. 2009, Yokoyama *et al.* 2002). Half a gram (0.5 g) of holocellulose and 25 ml of 17.5 % NaOH were placed in a 250 mL beaker and stirred until the holocellulose was completely dispersed. The stirrer was then removed and washed with 5 mL of 17.5 % NaOH to make total reagent content in the beaker 30 mL. The beaker was stirred thoroughly with a glass rod and placed in a water bath at 25°C. After 30 min from the first addition of NaOH, 30 mL of distilled water was added to the suspension and stirred thoroughly with the glass rod. The flask was left in the bath for another 30 min (for a total

of 60 min), after which the suspension was stirred and filtered. The solid α -cellulose was washed first with distilled water, then with 15 ml of 10 % Acetic acid, and finally with 400 ml distilled water. The hemicellulose content was obtained by subtracting the α -cellulose content from the holocellulose content.

2.3. Extraction procedure

The extractions were carried out in 40-mL zirconium reactors fitted with zirconium screw caps and fluoroelastomer O-rings. The preheating was done via a heating block with wall temperature between 300 – 400 °C, where the bodies of the reactors were inside the heater while the top structures (the caps and the O-rings) remained above the heater walls (allowing the O-rings to remain within temperature specifications). Additionally, the contact with the heating block was only kept until the target temperature (in the range of 1 – 4 minutes depending on the final temperature).

After preheating to the target temperature, the reactors were moved to a fluidized sand-bath at constant temperature. After the reaction time, the reactors were quenched in a water vessel to at least 35°C before being opened. A sample from the extract was taken with a conventional 3-mL syringe with a steel needle and subsequently filtered through a 0.45- μ m PTFE syringe filter. The filtrate was then diluted 1:7 (200 μ L : 1.4 mL) in ultrapure water and analyzed by HPLC.

The indicators of the extraction were the yield of xylose, furfural, glucose, HMF, and lignin in the liquid product, as well as the extraction yield ratio of the hemicellulose products to cellulose products. One of the objectives of the extraction was to keep the glucose, HMF, and lignin yields as low as possible in the liquid product, as only hemicellulose products (xylose, furfural) were desired in the liquid. The maximum amount of hemicellulose available was 33 wt% of the dry wood mass. In order to estimate the yield of hemicellulose, the molar mass of the xylan monomer unit was approximated by subtracting the molar mass of water from xylose to obtain the molar mass of a single xylan unit (i.e. 132.11 g/mol). This was under the assumption that the hemicellulose was composed of mostly large chains of xylan. Similarly, for cellulose, the molar mass of a single glucan unit was approximated

(162.14 g/mol) from the molar masses of glucose and water. The calculation of the molar yield percentage (Y_i) was done according to the following equations (Eq. 1-4):

$$Y_{xylose}(\text{mol}\%) = \frac{m_{xylose}(\text{g})}{x_{hemicellulose} \cdot m_{sawdust}(\text{g})} * 87.97 \quad (1)$$

$$Y_{furfural}(\text{mol}\%) = \frac{m_{furfural}}{x_{hemicellulose} \cdot m_{sawdust}} * 137.49 \quad (2)$$

$$Y_{glucose}(\text{mol}\%) = \frac{m_{glucose}}{x_{cellulose} \cdot m_{sawdust}} * 90.00 \quad (3)$$

$$Y_{HMF}(\text{mol}\%) = \frac{m_{HMF}}{x_{cellulose} \cdot m_{sawdust}} * 128.57 \quad (4)$$

$$\text{Extraction Yield Ratio (EYR)} = \frac{Y_{xylose} + Y_{furfural}}{Y_{glucose} + Y_{HMF}} \quad (5)$$

Where m_i is the mass of compound i obtained from the HPLC analysis, $m_{sawdust}$ is the mass of dry sawdust, and x_i is the mass fraction of hemicellulose (0.33) or cellulose (0.38) in the birch dry sawdust. The constants were calculated based on the molar masses of the compounds and sugar units. Additionally, the extraction yield ratio was calculated as the ratio between of the combined yield of xylose and furfural to the combined yield of glucose and HMF (Eq. 5).

2.4. HPLC analysis

HPLC analysis was performed with an Agilent 1200 HPLC equipped with a Coregel 87 H3 column. The method used a 10 μL injection volume, a flowrate of 0.8 mL/min for 40 minutes at a column temperature of 60 $^{\circ}\text{C}$. The mobile phase was composed of 0.005 M H_2SO_4 . The detectors utilized were Refractive Index Detector (RID) and Diode Array Detector (DAD). The DAD was set to 210 nm and 280 nm with 4nm bandwidths; the reference wavelengths were 250 nm and 320nm respectively with 100 nm bandwidths.

2.5. Lignin analysis

The lignin content in the liquid was estimated by UV-spectrophotometry. There are procedures described to analyze lignin content by UV spectrophotometry, such as measuring the absorbance at about 205 nm maximum (Ehrman. 1996) or at the 280 nm maximum (Hatfield & Fukushima. 2005). However, it was found experimentally that both furfural and HMF have characteristic absorption spectra in the same range as lignin, thus making the determination challenging. The lignin content in the liquid was estimated using a Shimadzu 1800-series double beam UV-spectrophotometer between the wavelengths of 300 and 250 nm, with a 1 cm path-length quartz cuvette. Using the information obtained from the HPLC, the spectra from furfural and HMF were subtracted from the sample spectrum by use of calibration curves of furfural and HMF at their characteristic maxima around 280 nm. The lignin content was estimated using a calibration curve (slope 23.561) of the absorbance with respect to concentration of Indulin AT in ethylene glycol at about 280 nm. The estimated detection limit of this method was found to be about 3 g/L (or about 23 mg/g_{dry wood}), and the concentrations of lignin in all the samples fell below this limit.

3. Results and discussion

Preliminary testing showed that the addition of formic acid increased the hemicellulose hydrolysis to xylose and furfural (Fig. 1). It was also found that a liquid-to-wood-ratio (LtW) of 8 yielded a higher extraction level per unit mass than a LtW of 4 (17 wt% higher at 150 °C); these values of LtW were chosen as they have been used for solid-liquid biomass reactions (Li *et al.* 2016, Peleteiro *et al.* 2016, Watkins *et al.* 2015) . Additionally, the preliminary results showed that the xylose extraction could be improved at temperatures below 150 °C and concentrations of formic acid above 4.85 wt%. Moreover, it was found that lower temperatures favored a higher extraction yield ratio. Three temperatures were ultimately chosen for the experimentation: a ‘high’ temperature of 170 °C as it has been used previously in water extraction (Li *et al.* 2013), and two lower temperatures below 150 °C (130 and 140 °C). To assess the effect of increased formic acid present in the reaction medium, concentrations of 7.24, 14.52, and 21.76 wt% with respect to the solvent mass were used. Additionally, experiments without added formic acid were carried out for comparison.

The main advantages of formic acid aided hot water extraction over its uncatalyzed counterpart are the lower reaction temperature and shorter contact times which, in continuous process, would translate to smaller equipment. Due to the lower process temperature, lower pressure steam could be used at 130-140 °C (e.g. 4 barg, 151 °C) than at 170 °C (e.g. 10 barg, 184 °C). Recovery of formic acid is well established in the industry, which would be arguably easier to achieve than neutralization or recovery when using sulfuric acid as catalyst.

3.1. Xylose and furfural yields

Fig. 2 shows the xylose and furfural yields as percentages of the total estimated moles of hemicellulose. The trend clearly indicates a remarkable increase in the xylose extraction at lower temperatures (130, 140 °C) with formic acid. However, this effect was less significant at higher concentrations of formic acid. The maximum xylose yield without added formic acid was 27 mol% of the total hemicellulose at 3 hours reaction time and 170 °C. At the lower temperatures the extraction yield remained below 3 %. On the other hand, when 7.24 wt% of formic acid was used, the xylose yield increased to a maximum of 54 mol% at 2 hours reaction time and 140 °C. At 170 °C, the xylose yield decreased with time, likely due to dehydration of xylose into furfural and degradation of xylose into side-products (e.g. humines). Increasing the formic acid concentration to 14.52 and 21.76 wt% did not have any major effect, other than an apparent faster extraction at the lowest temperature (130 °C) and a decrease in maximum xylose yield (47 mol%). The shapes of the curves at 170 °C suggest that the xylose yield becomes increasingly time-sensitive as the concentration of acid increases. With the highest formic acid concentration (21.76 wt%), the xylose yield decreases dramatically between 0.5 and 1 hour reaction times (46 to 22 mol%).

Furfural is obtained through the dehydration of xylose. The furfural yield varied significantly with respect to temperature and formic acid concentration, with furfural yield being favored by both longer times and higher acid concentrations. Without added formic acid, at 3 h reaction time and at the highest temperature (170 °C) the yield of furfural was 20 mol%. At lower temperatures, the yield remained below 0.4 mol% (140 °C) and 0.1 mol% (130 °C). With formic acid, the furfural yield increased at all temperatures, particularly at 170 °C. The dehydration of xylose into furfural is likely favored at higher temperatures. In all cases, the lowest amount of furfural was

obtained at the lowest temperature (130 °C) and shortest reaction time (0.5-1 h). With formic acid at 14.52 and 21.76 wt%, the trial runs at 170 °C showed a decrease in the furfural amount, likely due to the degradation and polymerization of furfural (Lamminpää *et al.* 2014).

3.2. Xylose & furfural combined yield

Fig. 3 shows the total yield of hemicellulose products (xylose and furfural). Without formic acid, the lower temperatures yielded below 2 and 3 mol% at 130 and 140 °C respectively. At 170 °C, the maximum yield (47 mol%) was achieved at the longest reaction time (3 h). With formic acid, a remarkable increase in the yield (particularly at 130 and 140 °C) can be seen in all cases with respect to the case without formic acid. However, the maximum yield achieved (70 mol%) was with the highest concentration of formic acid (21.76 wt%) at the highest temperature (170 °C) for the shortest reaction time (0.5 h). With formic acid, the yield trend at the lower temperatures was to increase with time (particularly at 7.24 wt% of formic acid). In contrast, at 170 °C, the yield decreased with time. This decrease in yield can be explained by the uncontrollable degradation of hemicellulose and its hydrolysis products at higher temperatures (i.e. 170 °C). Xylose dehydrates to furfural and can polymerize to water insoluble humins. Furfural, in turn, can also degrade to humins. The HPLC chromatograms showed the presence of possible oligomers (such as cellobiose) and higher order sugars (polysaccharides). It is possible that these higher order polysaccharides are the unreacted hemicelluloses in the form of glucuronoxylan, as it is typically the dominant hemicellulose in birch (Testova *et al.* 2009). Nevertheless, the chromatogram peaks were significantly smaller than the main compounds which would suggest a relatively small amount of these oligomers and sugars. The data at 170 °C suggests that the local maximum of hemicellulose extraction could be below the 0.5 h reaction time and thus a very short reaction time (<0.5 h) could suffice to reach this maximum.

3.3. Glucose & HMF yield

The cellulose yield in the liquid product was desired as low as possible. An indicator of the cellulose extraction yield was the combined amount of glucose and HMF (hydroxymethylfurfural). HMF is obtained by the acid-hydrolysis of cellulose and subsequent dehydration of glucose. Without added formic acid, the lowest yield

of glucose + HMF was obtained at the lowest times at all temperatures, as seen from Fig. 4. The addition and increase of formic acid concentration yielded a higher amount of glucose and HMF. This trend was more drastic at 170 °C than at the lower temperatures. At 130 °C, the glucose + HMF yield remained below 5 mol% of the total cellulose content for all acid concentrations. At 140 °C, the yield remained below 7 mol%. At 170 °C, the yield at 3 h reaction time was the highest, with yields of 12 % (7.24 wt% HCOOH), 15 mol% (14.52 wt% HCOOH), and 17 mol% (21.76 wt% HCOOH).

3.5. Extraction yield ratio

The extraction yield ratio (EYR) was calculated as the ratio of the combined yield of xylose and furfural to the combined yield of glucose and HMF. Thus, not only was a high yield of extraction desired, but also a high extraction yield ratio. When no formic acid was added, the EYR increased with reaction time at 130 and 140 °C, whereas at 170 °C it decreased. In the runs with added formic acid, the lowest temperature (130 °C) exhibited higher maximum EYR than at 140 and 170 °C. The maximum EYR without added formic acid was obtained at 1 h reaction time and 170 °C (14). For the lower temperatures, the extraction yield ratio remained below 3. With 7.34 wt% formic acid in the reaction medium, the highest EYR (14) was achieved at 2 h at 130 °C, as well as at 1 h at 140 °C. The extraction yield ratio at the earliest sampling point (0.5 h) at 170 °C for the cases with formic acid, was smaller with increasing formic acid concentration: 9 (7.24 wt% HCOOH), 8 (14.52 wt%), and 7 (21.76 wt%). Using lower temperature kept the extraction yield ratio in the product relatively high. The temperature-dependent behavior of the EYR could be linked to the activation energies of the hydrolysis of cellulose and hemicellulose. If the activation energy of the hydrolysis of cellulose were larger than the activation energy of the hydrolysis of hemicellulose, then lower temperatures would favor hemicellulose products, which is the case in this study. Additionally, as the formic acid concentration increased, the reaction favored the cellulose extraction. This may have been caused by the rapid extraction of hemicellulose, leaving the cellulose more vulnerable to extraction in a shorter time. It is possible that a higher maximum EYR could be found at times below 1h and 140 °C.

Formic-acid-aided hot water extraction could find its major utility in pretreatment of lignocellulosic feedstock before delignification and cellulose processing. The possible mild process conditions would allow the cellulose and lignin to remain mostly in the solid residue, while most of the hemicellulose with traces of cellulose and lignin would be separated into the soluble phase.

4. Conclusions

Hemicellulose was extracted from birch sawdust by hot water extraction. Formic acid increased the extraction of hemicellulose at all temperatures (130, 140, 170 °C). A mild (130 °C) and long (2h) treatment proved beneficial for xylose yield. A higher hemicellulose yield with higher proportion of furfural was possible at 170 °C and 0.5 h. Formic-acid-aided hot water extraction is a feasible technique for hemicellulose extraction from wood, keeping the cellulose degradation low. The solid product retains most of its cellulose, with decreased hemicellulose content. This solid product can be delignified, leaving a cellulose-rich, low-hemicellulose, low-lignin product with high added value.

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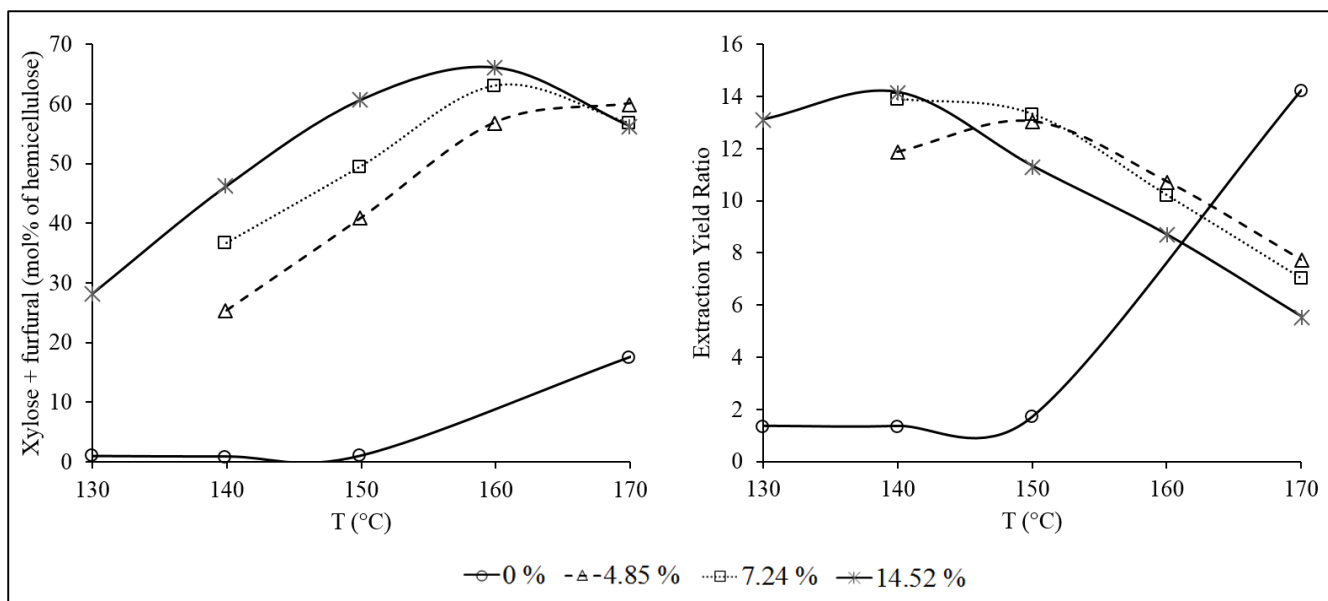


Fig. 1. Preliminary experiments. All runs were carried out for 1 hour at a LtW of 8. Percentages in legend are wt% of formic acid

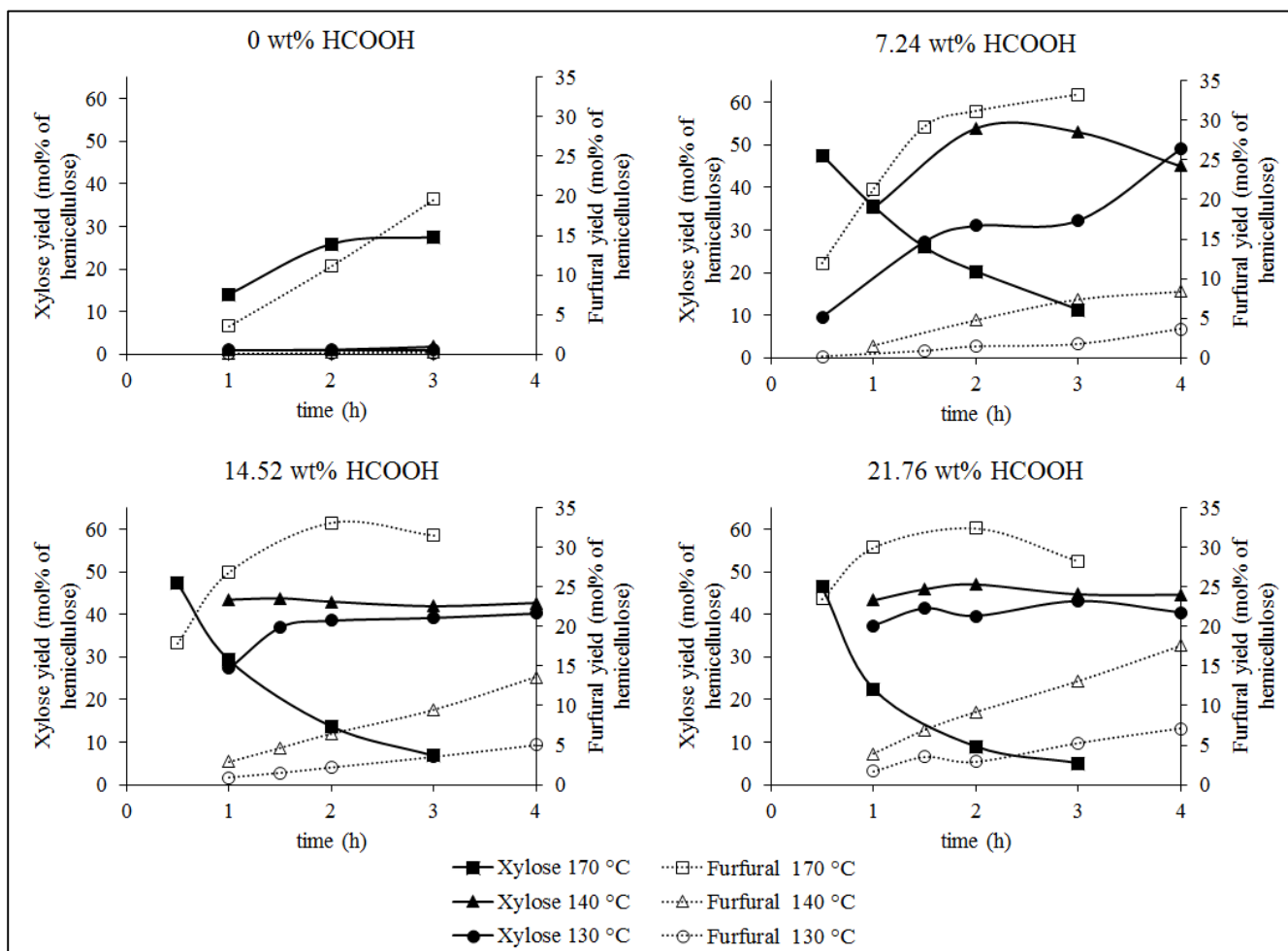


Fig. 2. Xylose and furfural yields as mole percentages of total hemicellulose.

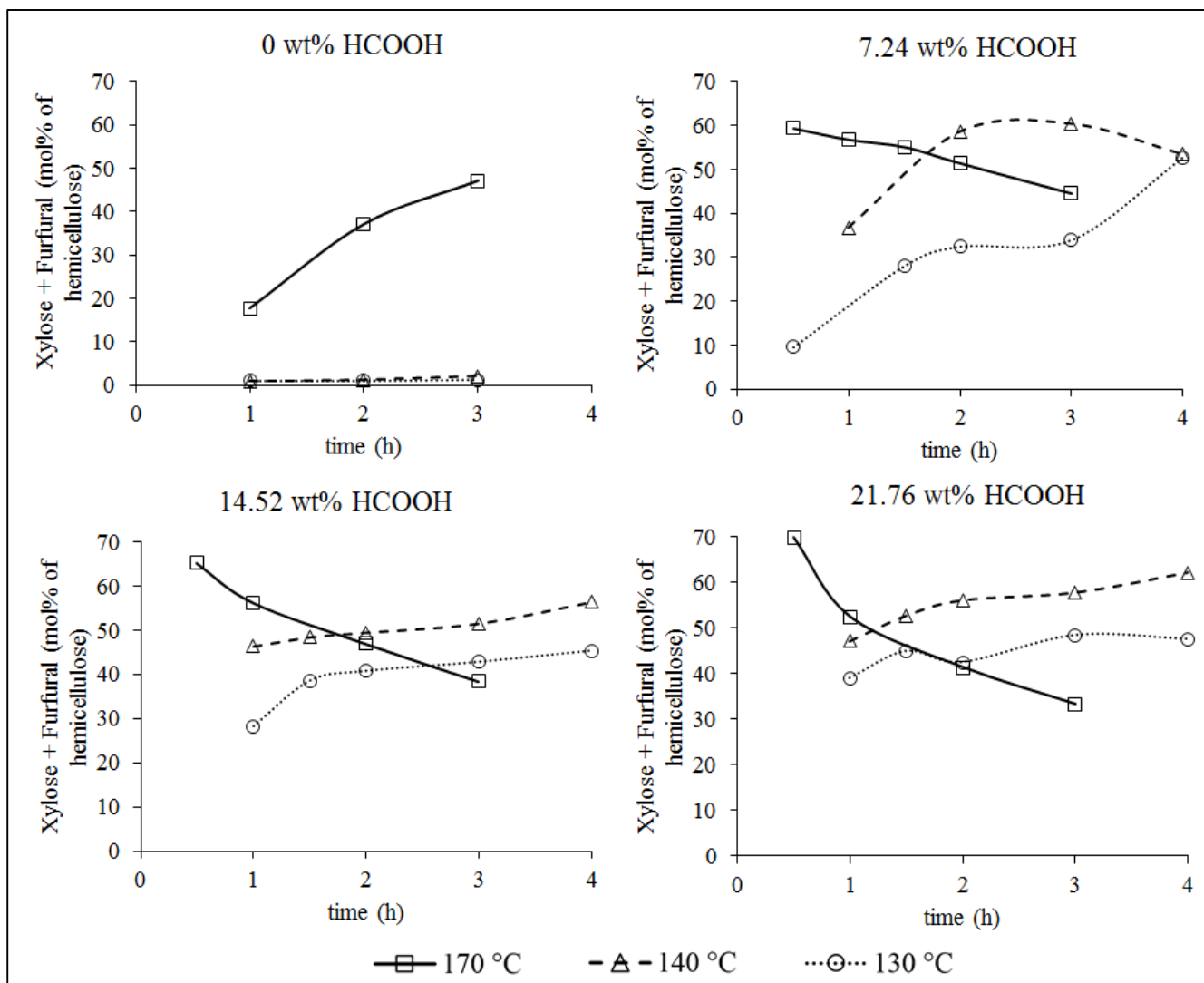


Fig. 3. Xylose and furfural combined yield as a mole percentage of total hemicellulose

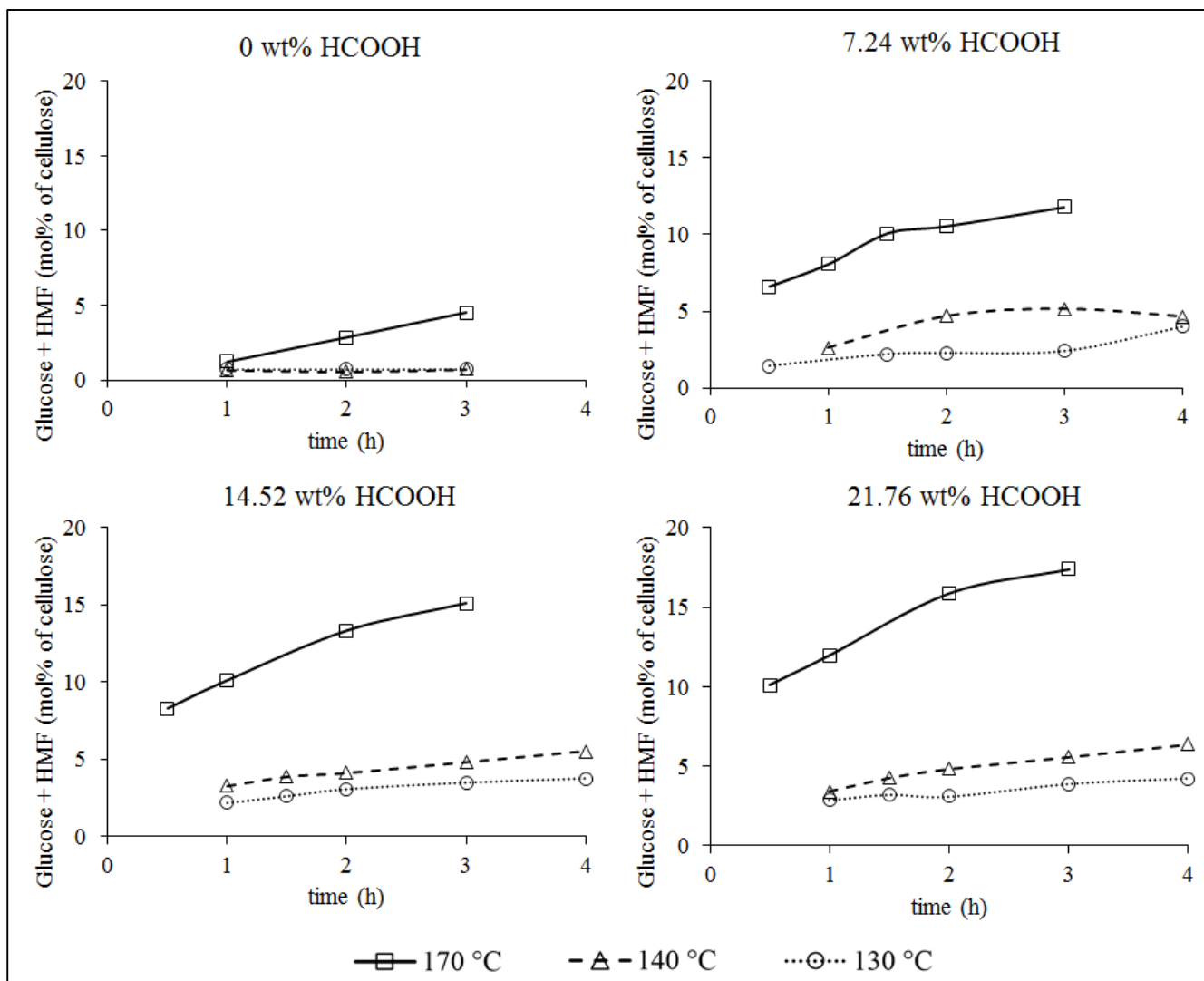


Fig. 4. Glucose and HMF combined yield as a mole percentage of total cellulose.

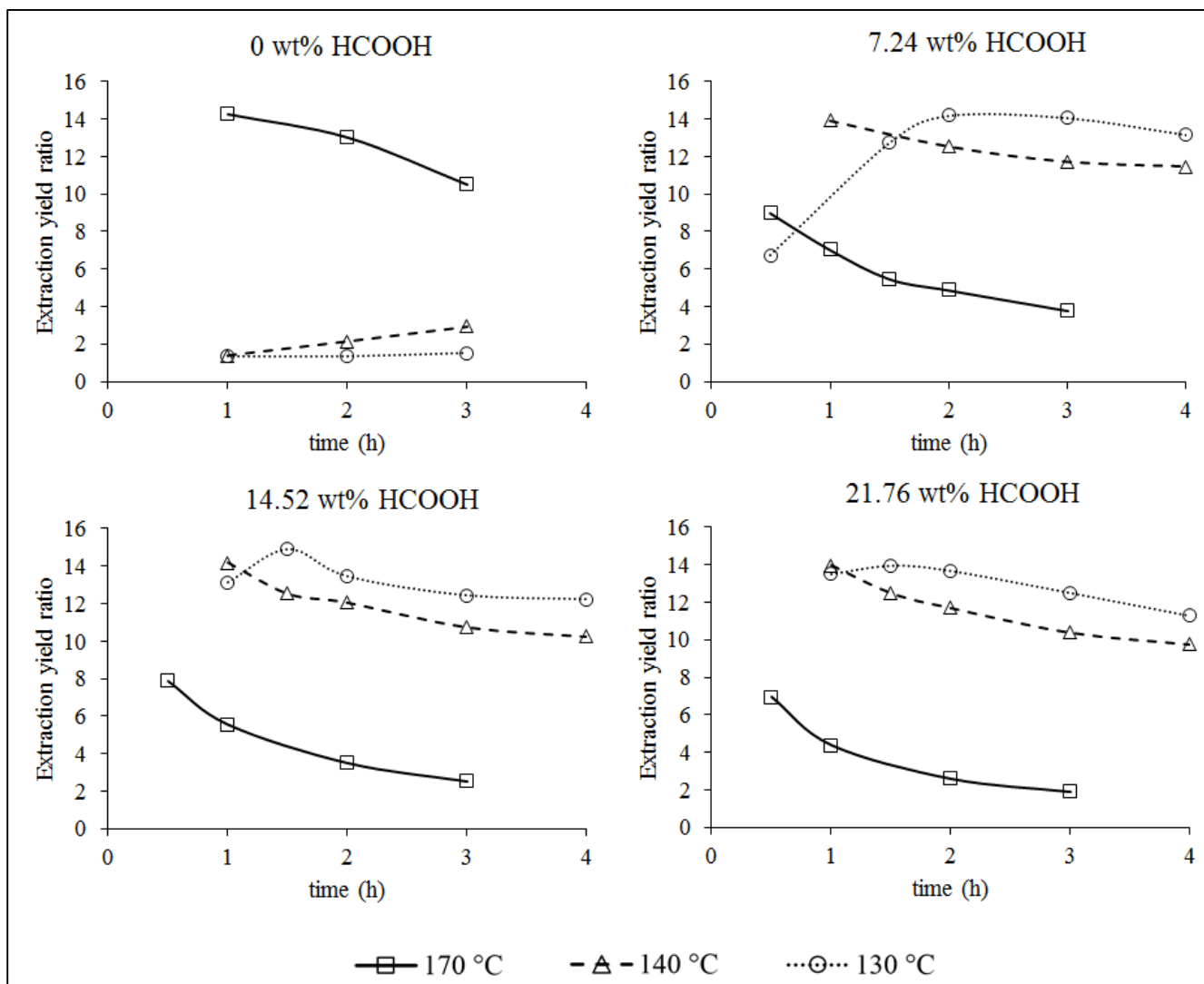


Fig. 5. Extraction yield ratio ([Xylose and Furfural combined yield] / [Glucose and HMF combined yield]).