LONG-TERM LIME PRETREATMENT OF POPLAR WOOD

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Introduction

Lignocellulosic biomass (e.g., poplar wood) provides a unique and sustainable resource for environmentally safe organic fuels and chemicals. Hybrid poplar is rated among the most promising species for the United States because it easily grows on marginal lands requiring minimal fertilization, it may be mechanically harvested, it exhibits high growth rates (average 10 to 17 Mg/(ha yr)), and it is easily propagated from either stem cuttings or tissue culture (Wright, 1994; Wayman, 1990).

Using proper processes, lignocellulosic biomass (e.g., poplar wood) can be converted to a wide variety of fuels and chemicals. The first step in these processes is pretreatment. It is required to realize high yields vital to commercial success in biological conversion to ethanol and chemicals (Chang *et al.*, 2000; Mosier *et al.*, 2005). Alkaline pretreatments are effective and produce fewer degradation products than acidic pretreatments. Two types of lime treatment that show high total sugar yields have been awarded a US Patent (Patent number 5,865,898) and are currently used in our laboratory: short term and long term. Short-term lime pretreatment involves boiling the biomass with a lime loading of 0.1 g $Ca(OH)_2$/g dry biomass at temperatures of 85−135°C for 1−3 hours (Chang *et al.*, 1997, 1998). Long-term pretreatment involves using the same lime loading at lower temperatures (40−55°C) for 4−6 weeks in the presence of air (Kim, 2004, Sierra, 2005).

The main purpose of this work is to explore the effect of different conditions of long-term lime pretreatment on the digestibility of poplar wood. A recommended condition of long-term lime pretreatment was found.

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Materials and Methods

Hybrid poplar wood (var NM6), kindly provided by NREL in two different batches, was the feedstock for this study. Its composition is summarized in Table 1. Because the two batches were very different in the amount of lignin, they were called "Low-Lignin Batch" (LLB) and "High-Lignin Batch" (HLB). The amount of poplar in the HLB was large and the amount in the LLB was small. Due to this restriction, fewer pretreatment conditions were tested for the LLB.

Pretreatment conditions:

It has been shown that strategic variables in long-term lime pretreatment of biomass are: temperature, time, oxidation, lime concentration, and water loading (Kim, 2004; Chang *et al.*, 1997; Kaar *et al.*, 2000). On that basis, the experimental conditions for this study were selected as shown in Table 2.

Table 1. Composition of the Feedstock as Measured by TAMU

Component	HLB(1)	LLB(2)
Glucan	42.89	44.09
Xylan	16.26	20.30
Mannan	3.34	NF
Lignin	26.79	21.92
Galactan	NF	NF
Arabinan	NF	NF
Extractives	3.31	3.87
Ash	1.45	1.31
Acetyl	3.35	5.80
TOTAL	97.39	97.29

(1)HLB: High Lignin Batch
(2)LLB: Low Lignin Batch

Table 2. Experimental conditions for pretreatment

Variable	**Conditions tested HLB**	**Conditions tested HLB**
Oxidation	Air present – Air absent	Air present
Temperature	25, 35, 45, 55, 65, 75 ºC	55, 65 and 65ºC
Pretreatment time	0 (raw biomass), 1, 2 and 4, 6, 7, 8 and 12 weeks	0 (raw biomass), 1, 2, 3, 4, 6 and 8 weeks
Lime loading	0.5 g lime/g dry biomass (excess)	0.5 g lime/g dry biomass (excess)
Water loading	10 g water/g dry biomass	10 g water/g dry biomass

Pretreatment System

The pretreatment was performed in 40 packed-bed reactors, which were hand made using PVC pipe. To maintain the desired operation temperature, the reactors were jacketed with a larger diameter PVC pipe and water was pumped from a temperature controlled tank as shown in Figure 1. In the case of the oxidative pretreatment, compressed air, previously scrubbed of carbon dioxide was preheated to the reaction temperature and saturated with air. It was continuously bubbled at a flow rate of about 3.5 mL/min.

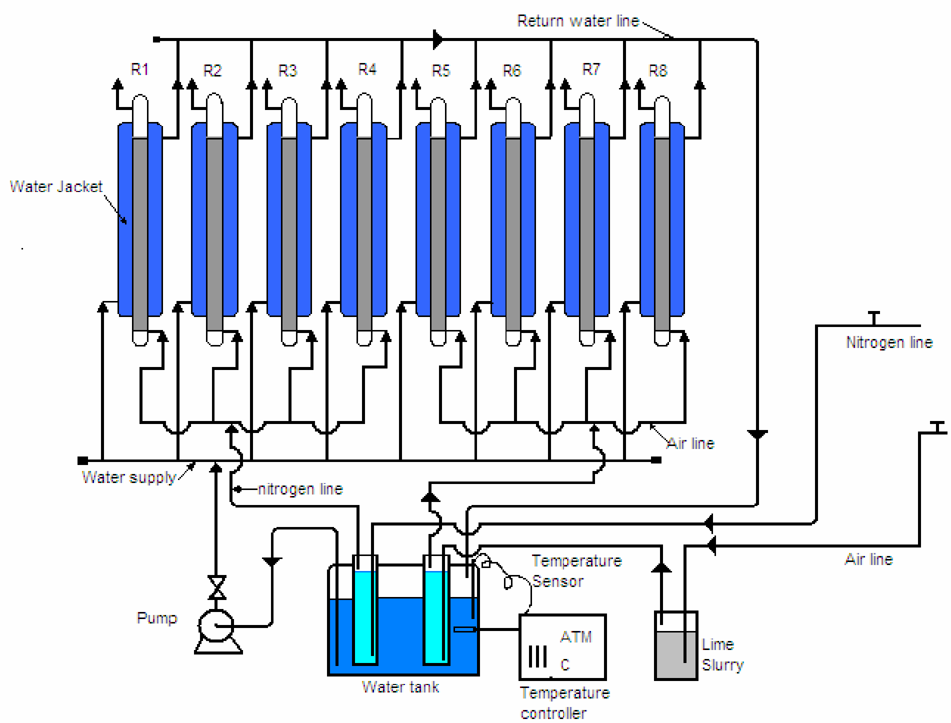


Figure 1. Diagram of a set of eight reactors in the reactor system for lime pretreatment.

Results

Mass Balances

As a result of the lime pretreatment, some poplar wood components were solubilized or degraded. The mass balances before and after pretreatment are presented in Figures 2 and 3.

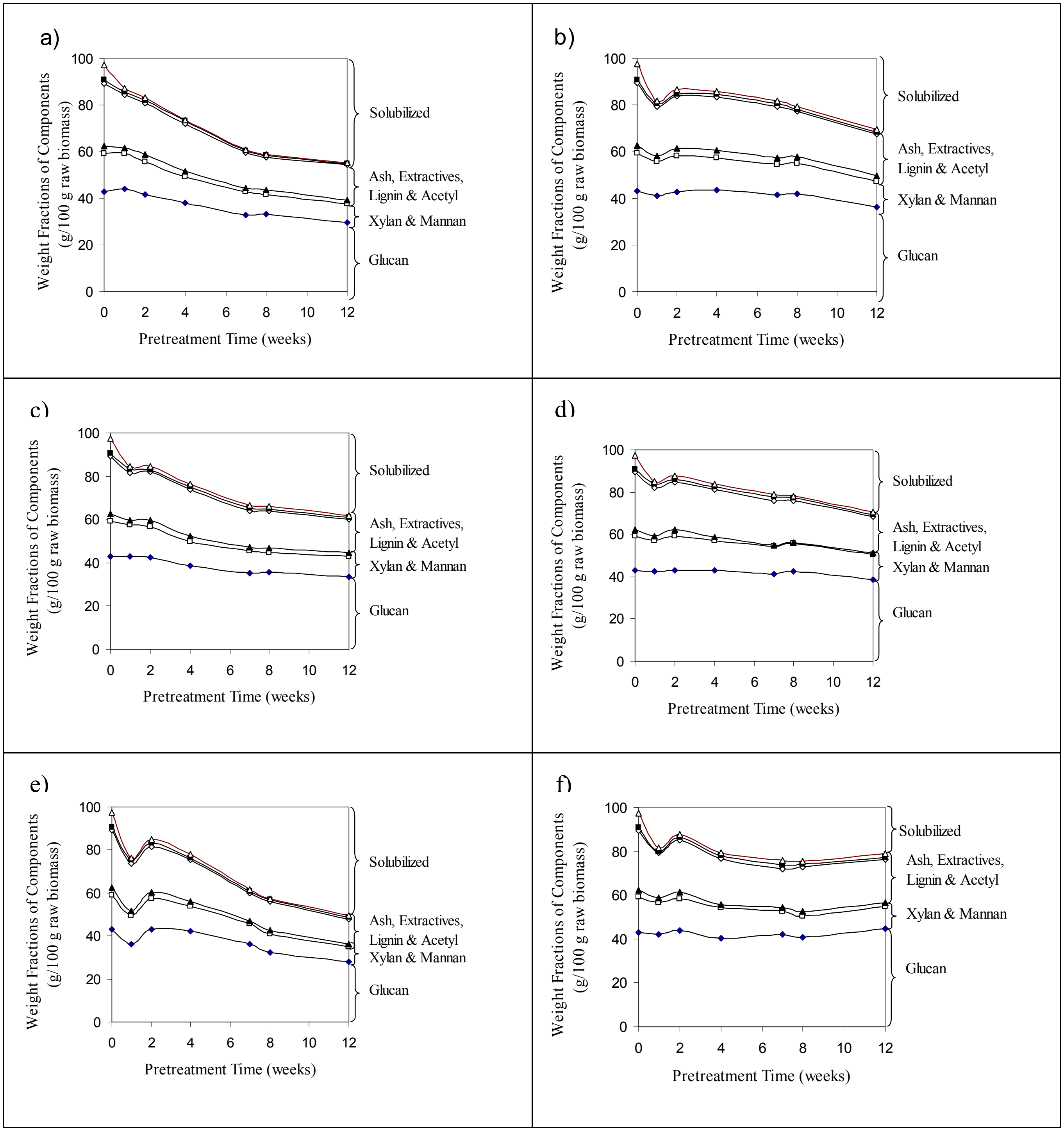


Figure 2. Mass balances after pretreatment for the High-Lignin Batch at the following conditions: a) 25ºC and oxidative, b) 25ºC and non-oxidative, c) 35ºC and oxidative, d) 35ºC and non-oxidative, e) 45ºC and oxidative, g) 45ºC and non-oxidative.

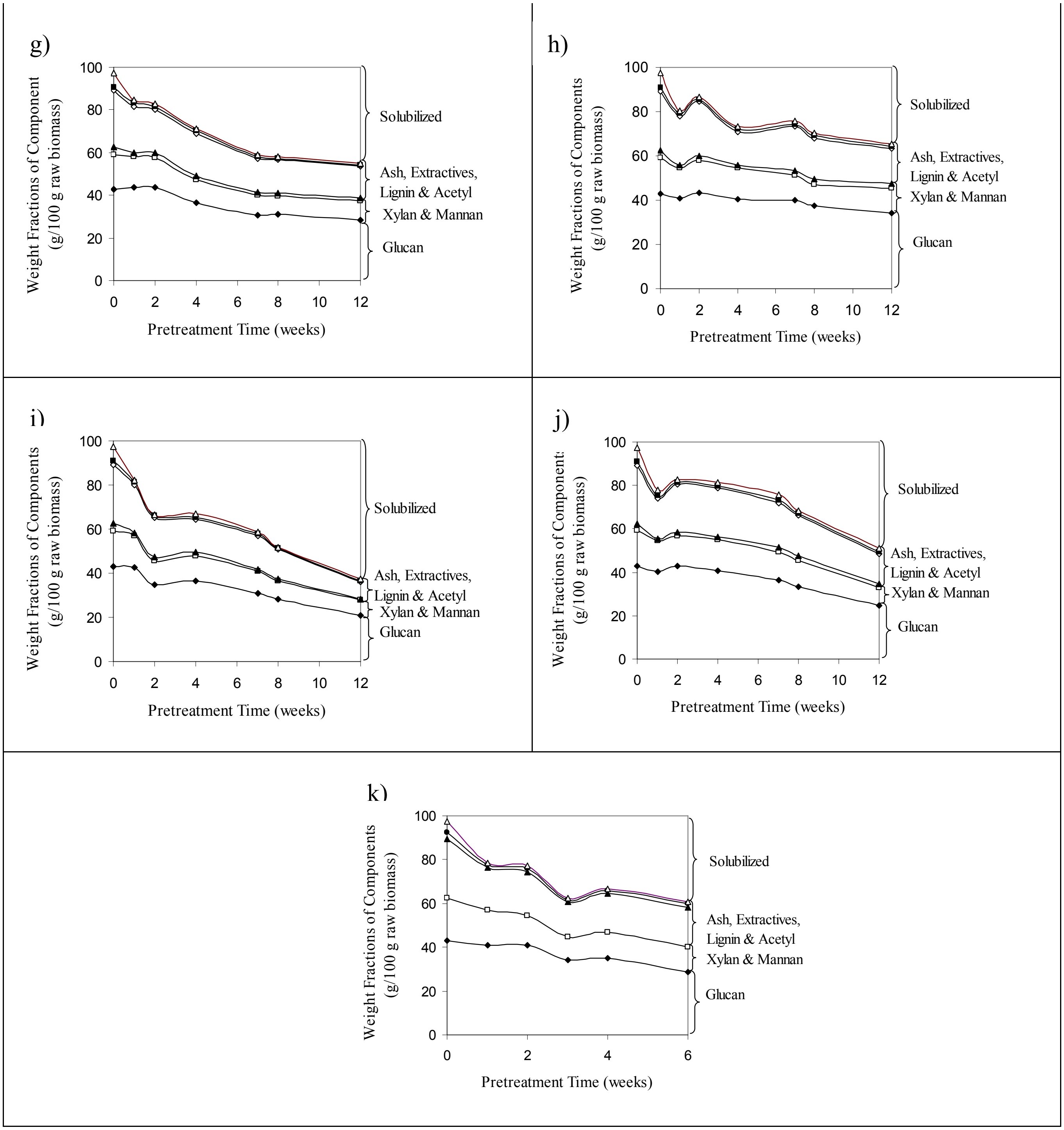


Figure 2. (*Continued*). Mass balances after pretreatment for the High-Lignin Batch at the following conditions: g) 55ºC and oxidative, h) 55ºC and non-oxidative, i) 65ºC and oxidative, j) 65ºC and non-oxidative, k) 75ºC and oxidative.

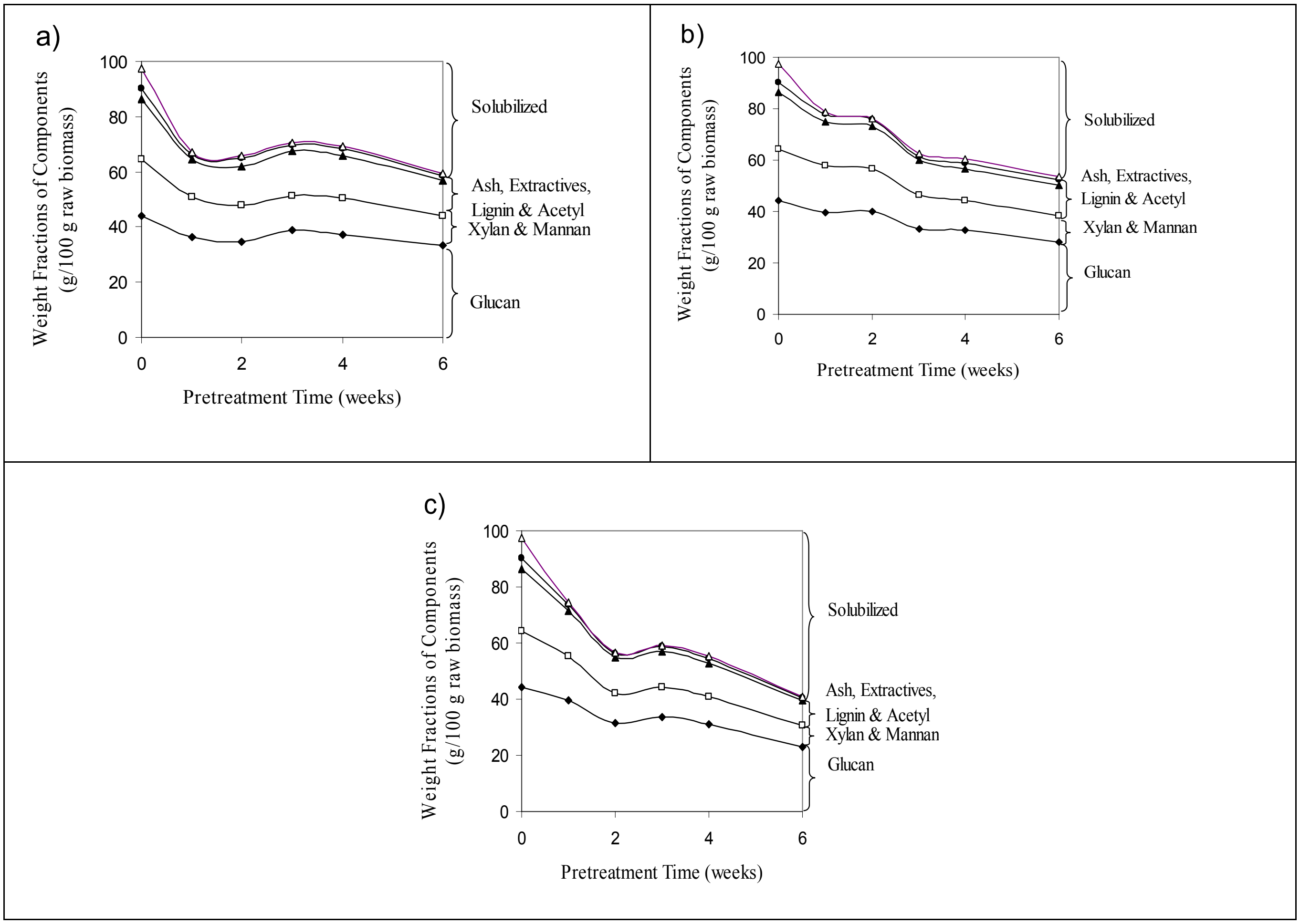


Figure 3. Mass balances after pretreatment for the Low-Lignin Batch at the following conditions: g) 55ºC and oxidative, a) 55ºC and non-oxidative, b) 65ºC and non-oxidative, c) 75ºC and oxidative.

Enzymatic Hydrolysis

After pretreatment, the poplar wood was submitted to enzymatic hydrolysis using Spezyme ® CP Genecor® Cellulase, lot # 301-04075-054. This was to assess the effectiveness of the pretreatment method. The enzyme loading was 15 FPU/g cellulose in raw biomass. The enzymatic hydrolysis was allowed to proceed during 72 hours, after which, the carbohydrates composition was measured by HPLC. The hydrolysis yields of glucan after enzymatic hydrolysis are presented in Figures 4 and 5 for all pretreatment conditions. Similar results were obtained for the enzymatic yield of xylan (these are not shown here).

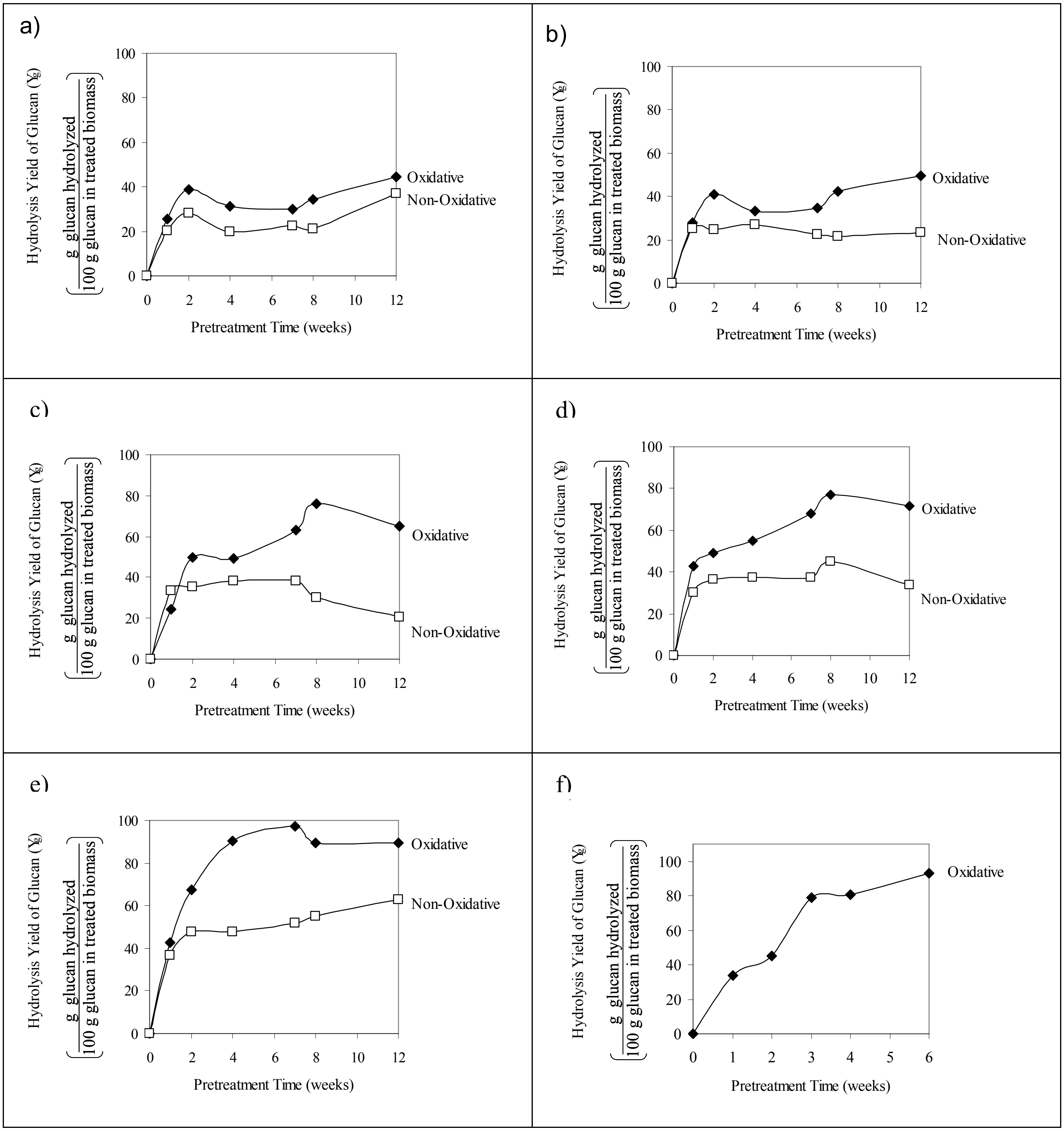


Figure 4. Enzymatic hydrolysis yield of glucan for poplar wood (HLB) pretreated at the following conditions: a) 25ºC b) 35ºC c) 45ºC d) 55ºC e) 65ºC f) 75ºC

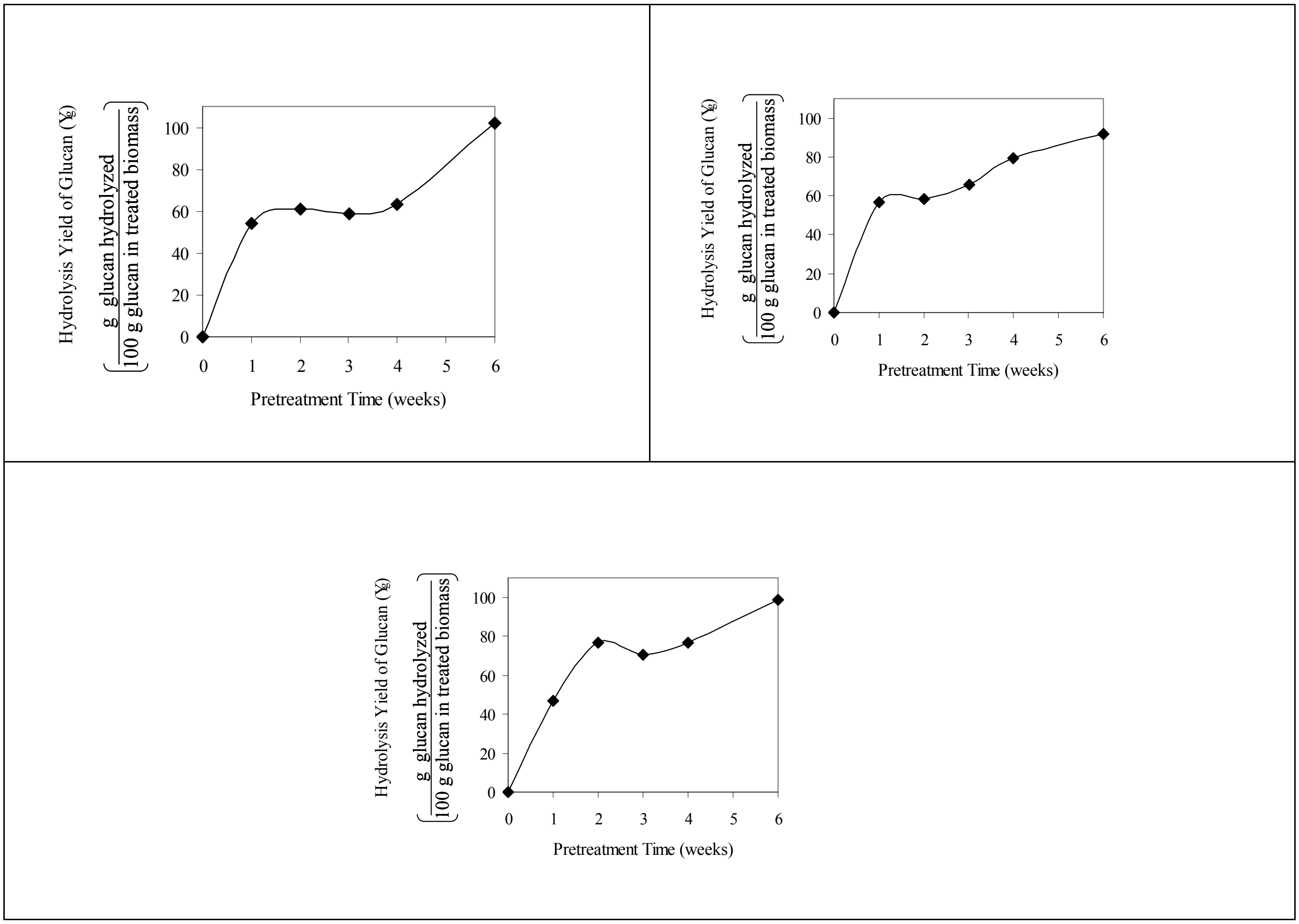
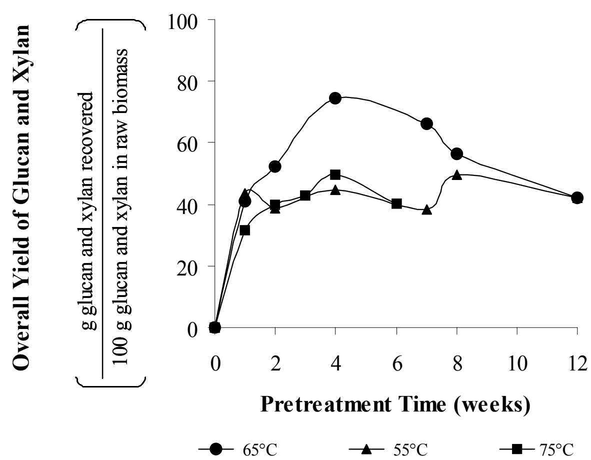


Figure 5. Enzymatic hydrolysis yield of glucan for poplar wood (LLB) pretreated at the following conditions: a) 55ºC b) 65ºC and c) 75ºC

Overall yields and optimum of pretreatment

Considering both the conversion of glucan and xylan after pretreatment and enzymatic hydrolysis, it was found that among all tested conditions of long-term lime pretreatment, it is best to pretreat poplar wood at 65ºC with air and for 4 weeks, because the material pretreated this way shows the highest overall yield (Figure 6).



Conclusion

Yields strongly depend on the lignin content of the raw material. For the high-lignin batch, the optimum enzymatic hydrolysis yield of glucan was 97 g glucan hydrolyzed/g glucan in treated biomass for pretreatment conditions of 7 weeks, oxidative, 65°C. However, the optimum overall yield of glucan was only 73 g glucan hydrolyzed/g glucan in raw biomass and was obtained for pretreatment conditions of 4 weeks, oxidative, at 65°C. This is due to the degradation of cellulose observed during pretreatment.

References

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