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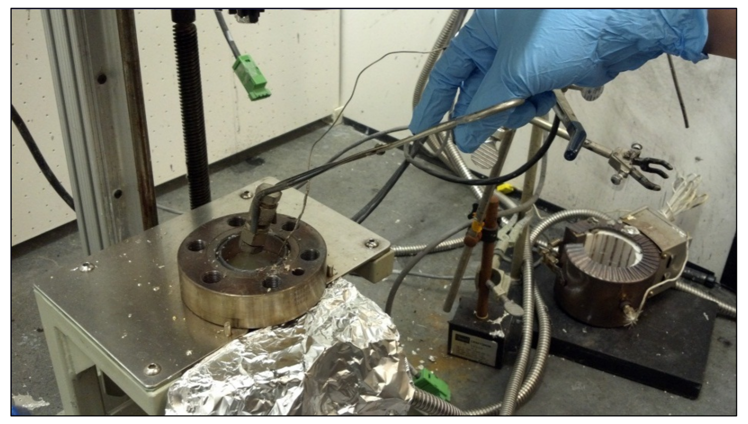
The Role of Acid Pretreatment in Solvolysis of Switchgrass

Introduction

Thermochemical conversion technologies like fast pyrolysis and solvolysis are able to rapidly depolymerize whole lignocellulosic feedstocks into liquid products which include sugars, phenols. Both are attractive as deconstruction processes for the production of fuels. While pyrolysis of untreated biomass usually yields very little sugars, both acid washing/water rinse and acid infusion have been observed to dramatically increase the production of anhydrosugars during fast pyrolysis of lignocellulosic biomass, a phenomenon attributed to passivation of alkali and alkaline earth metals (AAEM) that otherwise catalyze scission of pyranose and furanose rings in plant polysaccharides. However, problems like char agglomeration during fast pyrolysis of acid infused biomass, and the tendency of levoglucosan to polymerize and subsequently dehydrate to char may limit the potential for maximizing sugar production. We hypothesize that solvolysis of biomass may be able to migrate these problems and therefore improve sugar production.

Experimental Methods



- **Materials**

Feedstocks: Untreated switchgrass, acid-washed/water rinsed (AWWR) switchgrass, acid-infused (AI) switchgrass (with 2wt% of sulfuric acid), levoglucosan, xylose, glucose

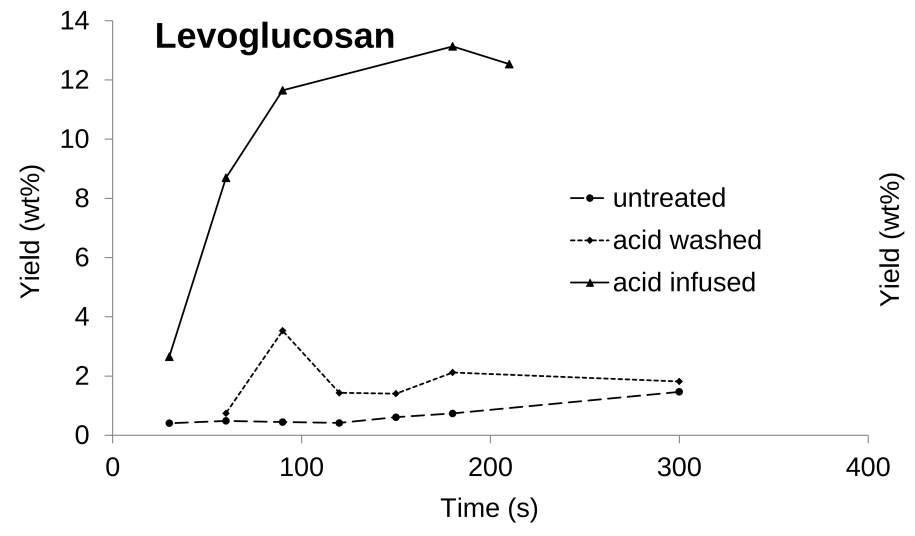
Solvents: 1, 4-dioxane, water, and the mixture of 1, 4-dioxane and water (9: 1 ratio)

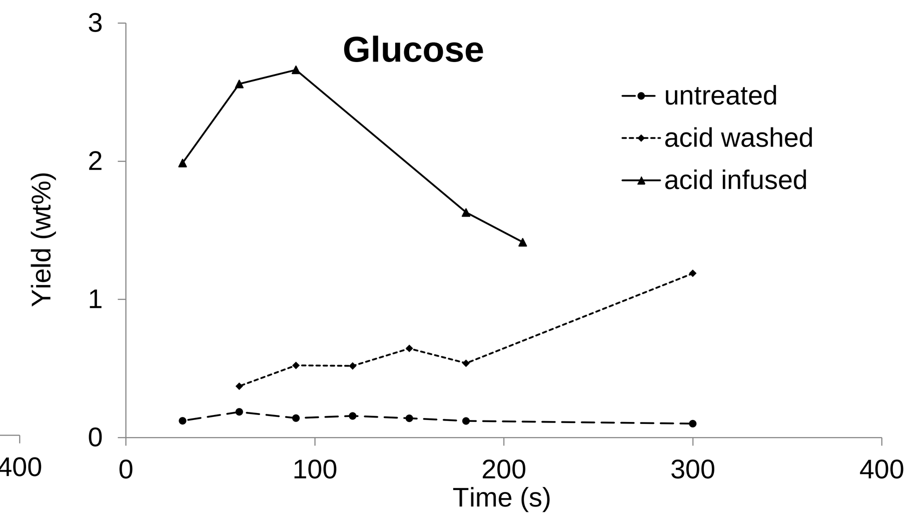
- **Apparatus**

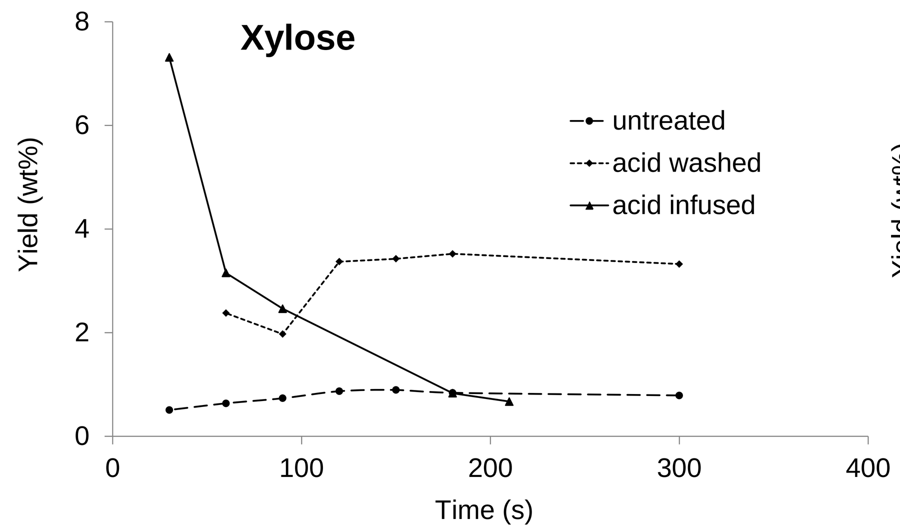
Reactors: assembled with two, 3/8 inch Swagelok cap and connector

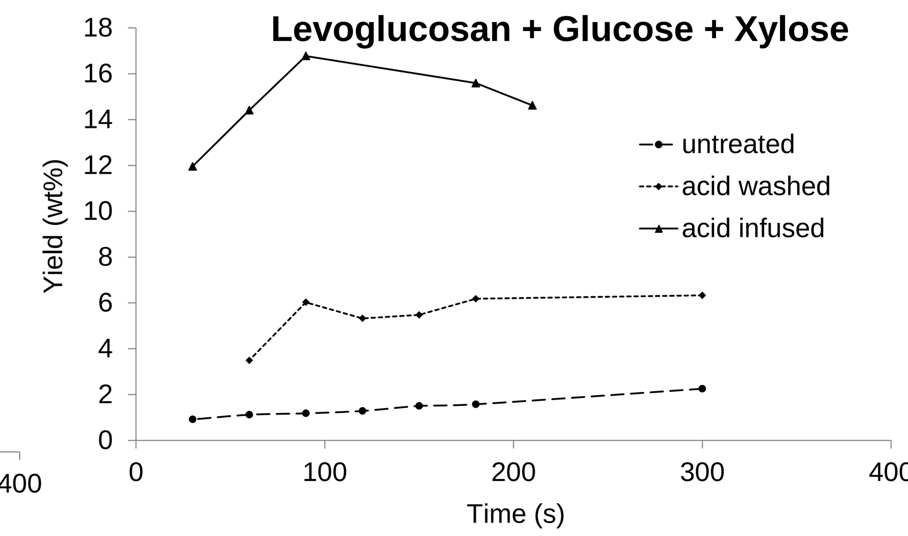
Heating mechanism: Molten tin bath

Sugar Production Under Different Acid Pretreatments Using 1, 4-dioxane as Solvent





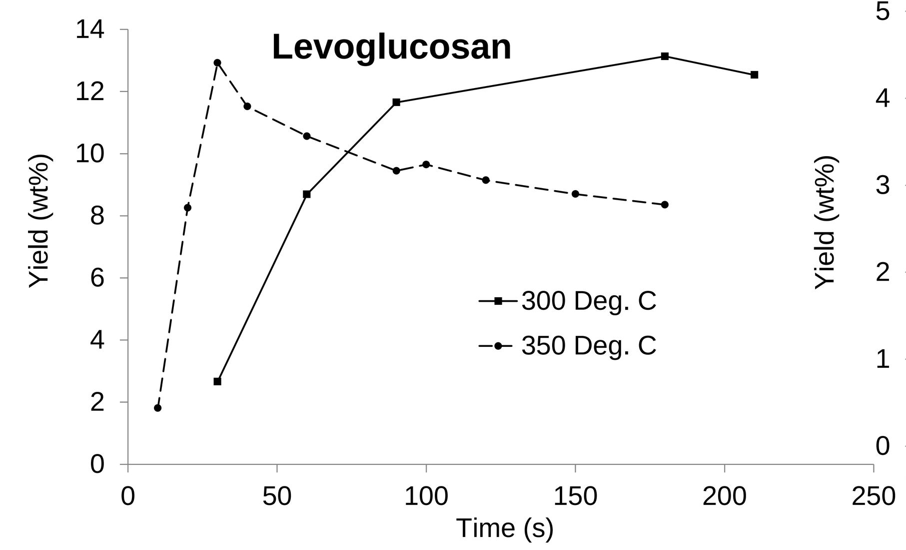


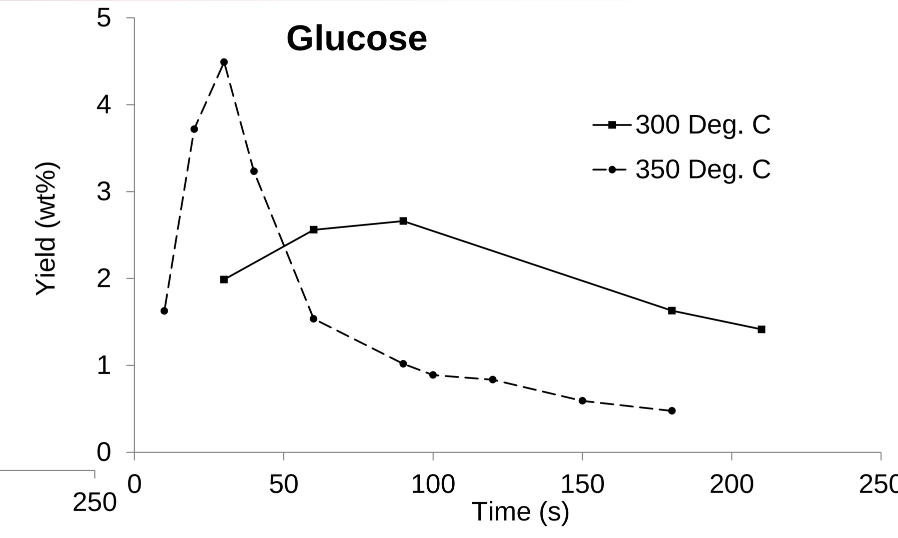


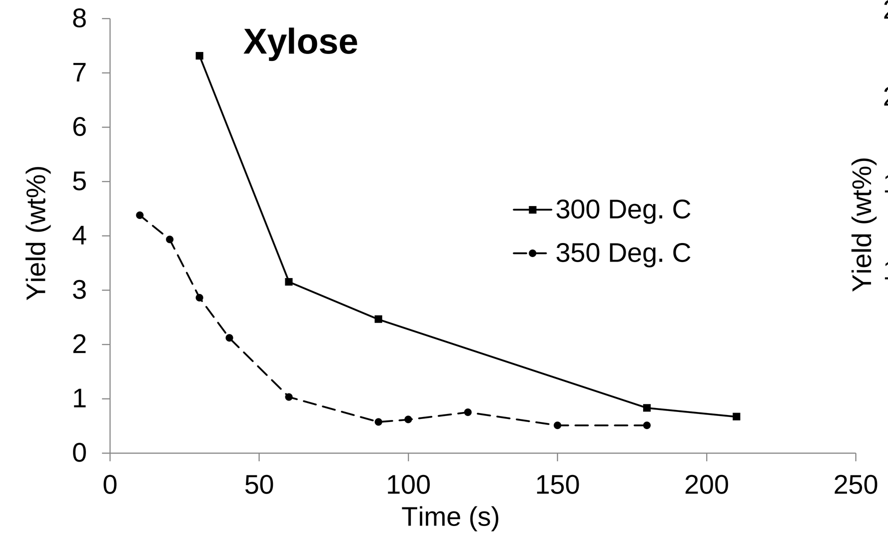
❑The presence of AAEM did not significantly affect the deconstruction of polysaccharides during solvolysis. The presence of solvent appears to mitigate the catalytic effect of AAEM.

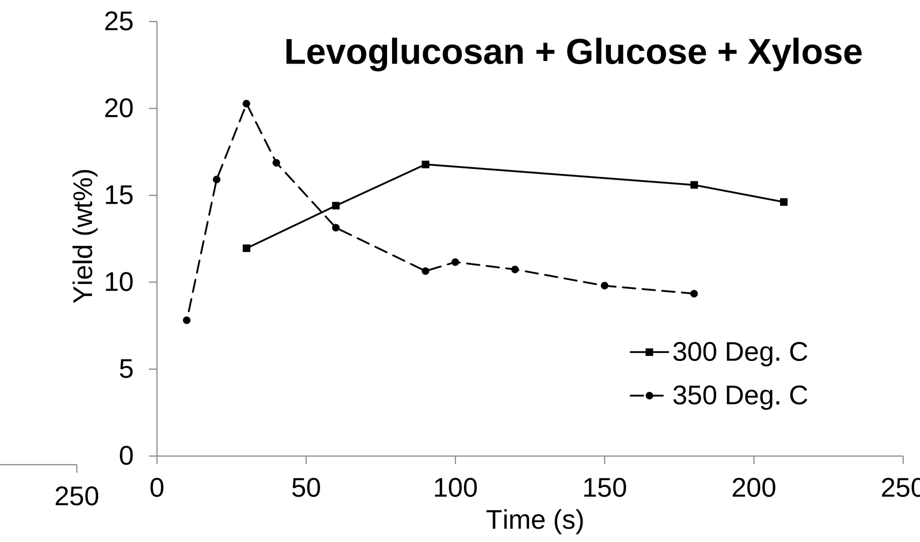
❑The yields of sugars increased significantly for acid infused switchgrass with acid acting as a strong catalyst for the depolymerization and hydrolysis of polysaccharides. Acid also catalyzes dehydration reactions that lead to the formation of furfural, hydroxymethylfurfural, levoglucosenone, etc.

Effect of Temperature on Solvolysis of Acid Infused Switchgrass in 1, 4-dioxane









❑Higher reaction temperature leads to higher maximum yields of levoglucosan, glucose and total sugar monomers, but lower maximum yield of xylose.

❑ Thermal stability of the sugars decreases with increasing temperature. The yield of total sugar monomers is lower at higher temperature after stabilization due to decomposition.

Effect of Water as Co-solvent on Sugar Production from Acid-infused Switchgrass

❑Pressurized water is known to be an excellent solvent for solvolysis reactions.

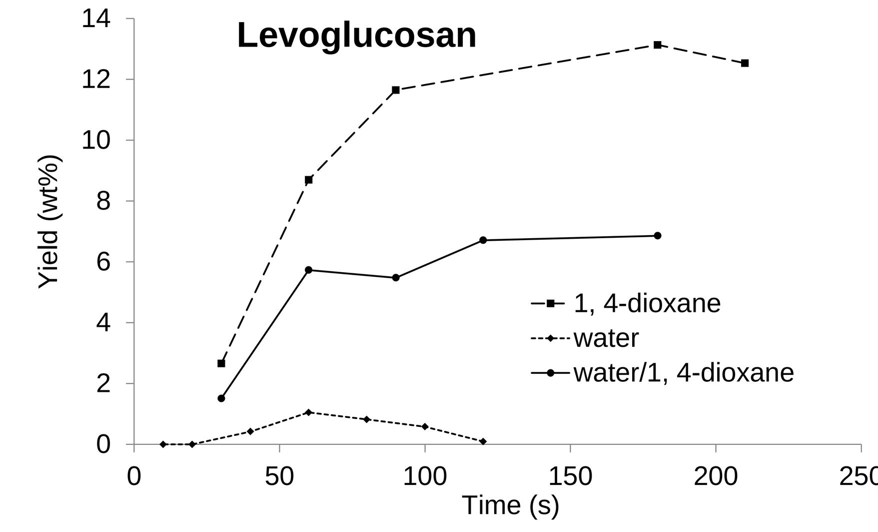
❑Fresh switchgrass contains up to 60% of water.

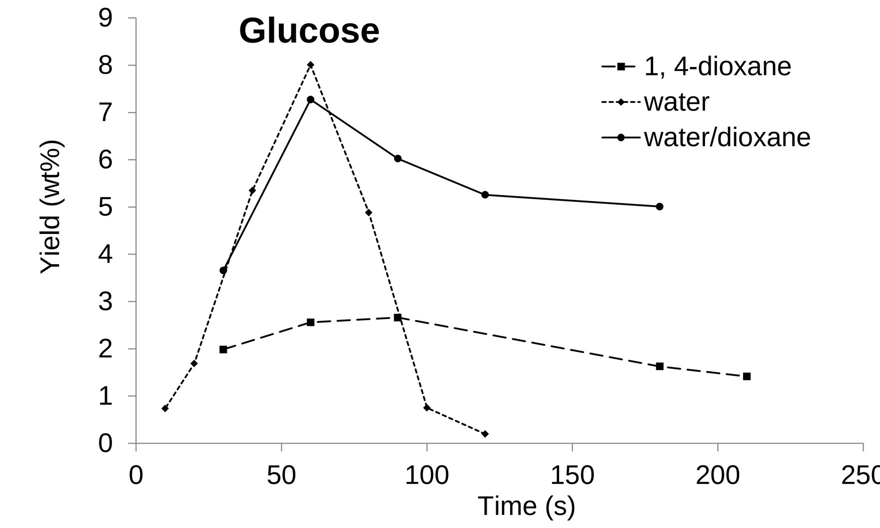
❑While levoglucosan is the major sugar when 1, 4-dioxane is the solvent, glucose becomes the major sugar when water is the solvent.

❑Glucose formed is extremely unstable in water medium.

❑Partial hydrolysis of levoglucosan to glucose is observed when water is co-solvent.

❑Both glucose and levoglucosan are thermally stable in the mixture solvents compared to water as the single solvent.





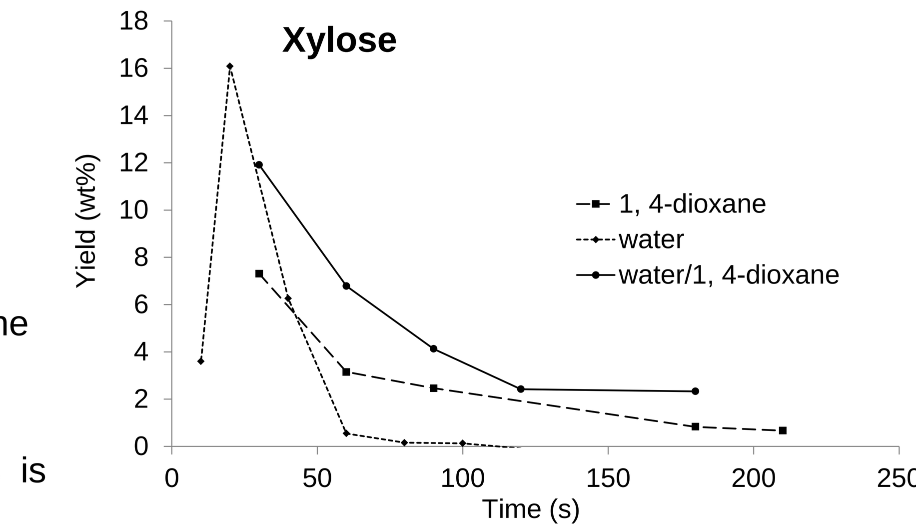
Effect of Water as Co-solvent (continued)

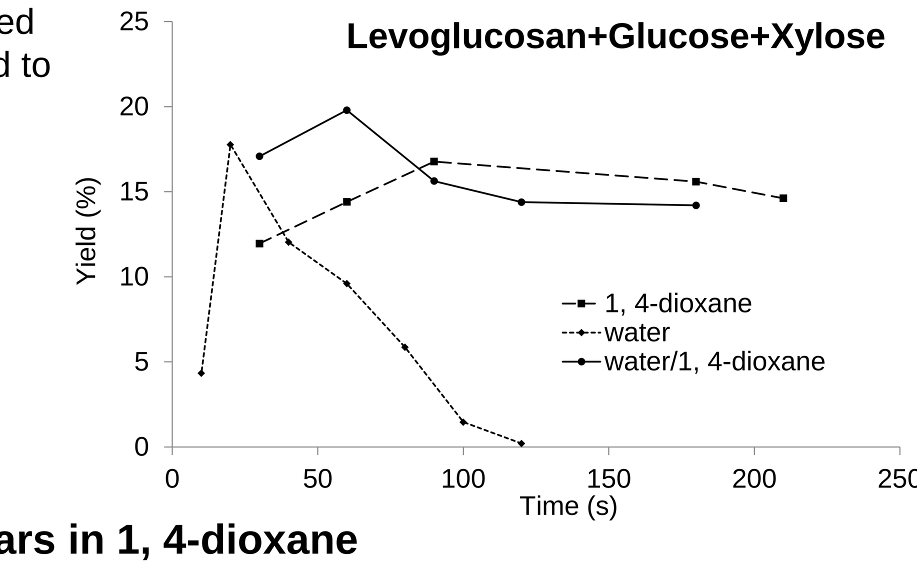
❑ Higher maximum yield of xylose is produced when water is the solvent. However, xylose rapidly degrades.

❑Using water as co-solvent improved the yield of xylose compared to pure 1, 4-dioxane system.

❑ Higher maximum yield of total sugars is obtained from the solvent mixture.

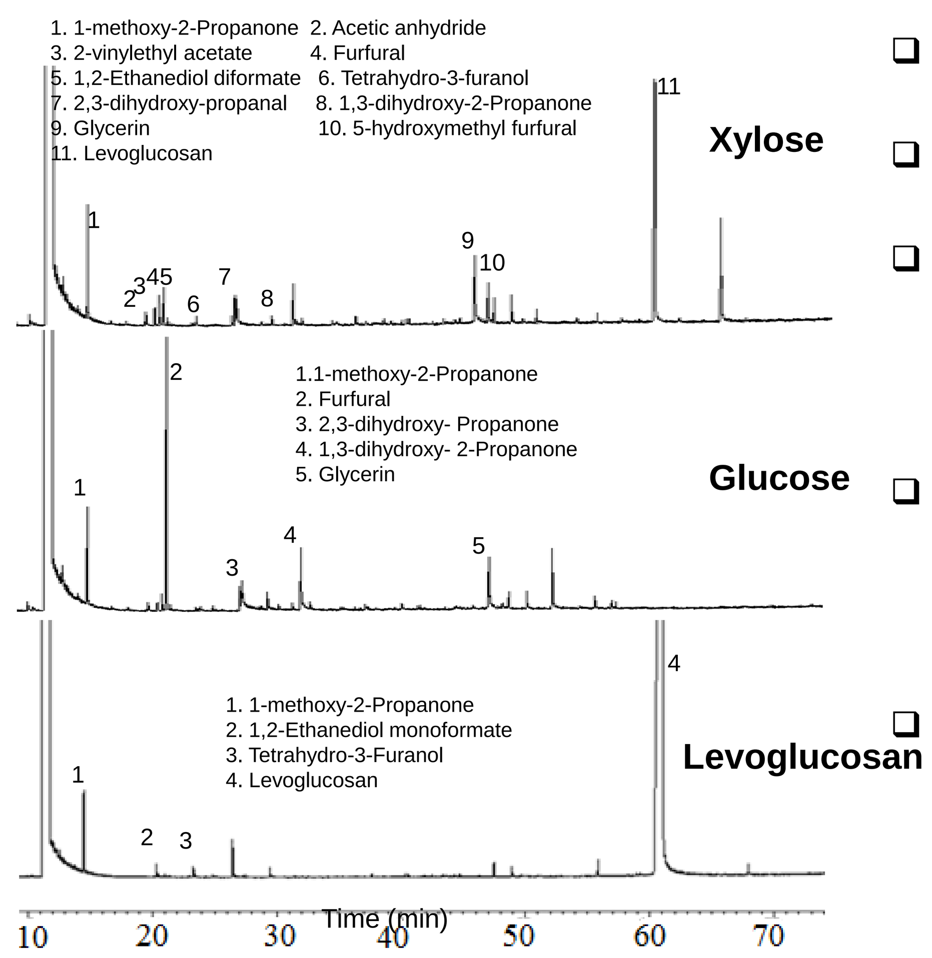
❑Thermal stability of the sugars improved greatly in the solvent mixtures compared to water alone.





Degradation of Monomeric Sugars in 1, 4-dioxane

GC/MS chromatogram of decomposition products



- Levoglucosan is relatively stable to thermal decomposition.
- Levoglucosan is the major decomposition product of glucose.
- Cellulose and levoglucosan can both hydrolyze in the presence of water to glucose, while glucose can dehydrate to levoglucosan when 1, 4-dioxane is the solvent.
- Conversion between glucose and levoglucosan, although not completely reversible, could greatly improve stability of levoglucosan and glucose in 1, 4-dioxane.
- The choice of solvent impacts not only primary products but also secondary products of solvolysis.

Conclusions

❑ Although AAEM is known to catalyze ring scission of pyranose and furanose in cellulose and hemicellulose during fast pyrolysis, the presence of AAEM did not significantly affect the deconstruction of polysaccharides during solvolysis.

❑ A small amount of acid infused into biomass prior to solvolysis strongly catalyzes the depolymerization of polysaccharides.

❑The sugars produced were more stable in a mixture of 1, 4-dioxane and water compared to pure water, resulting in a maximum yield of total sugars of 19.8wt%.

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