SFE540: The Subcritical Water Depolymerization of Lignin Using a Heterogeneous Catalyst

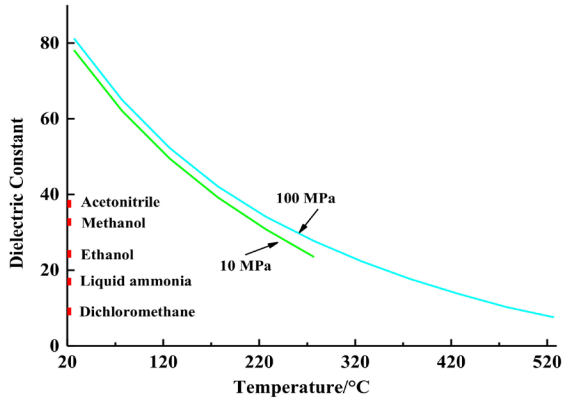
Introduction

Lignocellulosic biomass is a complex biopolymer which is contained in the cell walls of plants. The biopolymer is composed of three different polymers: cellulose, hemicellulose, and lignin. The paper and pulp industries produce millions of tons of lignan polymer waste every year. The conversion of lignin into its phenolic monomers using subcritical water and a catalyst could be a renewable source of value- added materials and industrial products such as binders and epoxy resins.

Existing methods used to depolymerize lignan are expensive, require long processing times, and use toxic chemicals to produce the desired phenolic compounds. This application describes the work of scientists at South Dakota State University to depolymerize lignin using a catalyst and subcritical water. This environmentally friendly technique uses water at a temperature of 240 C to produce phenolic monomers in the minimal processing time of 10 minutes.

Subcritical water

The term subcritical water describes water in the liquid state at a temperature above its boiling point of 100 C and its critical temperature of 374 C. The water is liquified by applying pressure to the system. Liquid water exhibits many changes in its characteristics as it is heated to the subcritical state. The viscosity and surface tension of the liquid water decreases and diffusivity increases. In addition, the dielectric constant of water decreases significantly as it is heated and water behaves like a mixture of water and methanol when in the subcritical temperature range. Thus, subcritical water may be used to extract many organic molecules such as phenolic monomers with substantial environmental benefits compared to the use of conventional organic solvents.



Equipment

Helix - Applied Separations (Allentown, PA, USA).

24-mL stainless-steel vessel

Materials

Lignin – Alkali lignin purchased from Sigma Aldrich

Lignan – Extracted from pine sawdust by pressurized solvent extraction using methyl isobutyl ketone, ethanol, and 0.1 M H2SO4 as solvents. The extracted lignin yield was 18.86% from the pine sawdust. (reference 1)

Ni-Graphene catalyst- Department of Agricultural and Biosystems Engineering

Deionized water
Acetic acid
Ethyl acetate
o-Terphenyl - analytical standard

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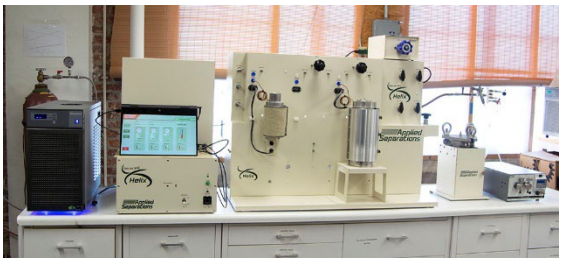
Subcritical Water Application Notes



Method

Catalytic Depolymerization of alkali lignan and lignin samples extracted from pine sawdust

Add 0.025 grams of catalyst (Ni-Graphene) and 0.25 grams of lignan to a 24 ml stainless steel vessel filled with glass beads.

Pressurize vessel with subcritical water to 22.5 MPa (monitored by a pressure transducer placed between the reaction vessel and the exit valve of the supercritical reactor).

Heat to 240 °C for 10 min with constant stirring.
Quickly cool the vessel after the completion of the reaction with ice water.

Separate the liquid products from the lignin residue via vacuum filtration.

Add 0.2 ml of acetic acid to the liquid mixture for the protonation of phenoxide ions.

Extract the organic products from the aqueous medium with ethyl acetate and concentrate the organic layer under N2 gas.

Add 100 ul of o-Terphenyl to 1.5 mL of sample as an internal standard for the quantification of phenolic monomers by GC/MS.

Results

A. Catalytic Depolymerization of Alkali Lignan using Subcritical water

Yield of phenolic monomers in the presence of Ni-graphene catalyst at 240 C with standard deviation of triplicate reactions.

Phenolic Monomer	**mg Monomer/ g Alkali Lignan**	Std. Dev.
Guaiacol	3.70	0.16
Vanillin	9.59	0.34
Isoeugenol	3.26	0.15
Acetovanillone	2.95	0.06
Guaiacylacetone	6.38	0.26
Homovanillic acid	14.96	0.18

B. Catalytic Depolymerization of Pine Sawdust using Subcritical Water

Phenolic Monomer	Abundance (%)
Phenol	0.63
Guaiacol	1.15
Syringol	2.02
m-Hydroxy benzaldehyde	2.23
Vanillin	5.52
Propyl guaiacol	1.95
Syrinzaldehyde	12.82
Methoxy eugenol	2.41
Coniferaldehyde	4.13
Synapyl alcohol	3.85

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Conclusion

Depolymerization of alkali lignin and lignan from agricultural waste products using a subcritical water-based method and Ni-Graphene catalyst achieved high efficiency at mild reaction conditions. The 10 minute reaction time and temperature of 240 C is lower than traditional methods. Overall, this method is greener, eco-friendly, cheaper, and capable of being used on a large scale for the depolymerization of alkali lignin. The catalyst was able to convert the lignin into low molecular weight monomers, such as vanillin, homovanillic acid, guaiacol, and syringaldehyde, in the presence of subcritical water. Depolymerization of alkali lignin with the optimized subcritical water method and Ni-Graphene catalyst could be a highly effective method to obtain clean and value-added phenolic monomers.

References

1. Jadhav B, Roy R, Rahman MS, Raynie DE. Extraction and Depolymerization of Lignin from Pine Sawdust and Pistachio Shells. Biomass. 2022 Nov 28;2(4):348-57.

2. Jadhav B, Roy R, Rahman MS, Amit TA, Subedi S, Hummel M, Gu Z, Raynie DE. Enhancing the Efficacy of the Subcritical Water-Based Alkali Lignin Depolymerization by Optimizing the Reaction Conditions and Using Heterogeneous Catalysts. Biomass. 2022 Aug 24;2(3):178-87.

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