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Review

A review on potential of green solvents in hydrothermal liquefaction (HTL) of lignin

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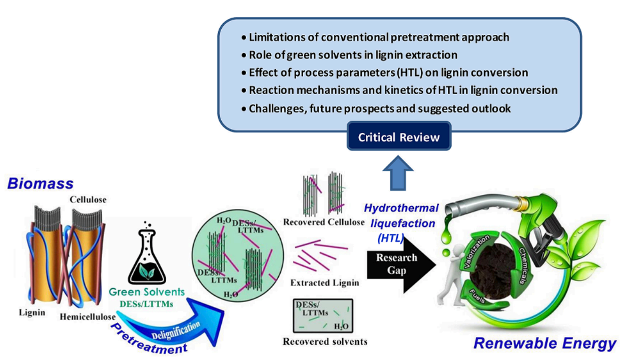
HIGHLIGHTS

- Highlighted the limitations of conventional biomass pretreatment methods.
- Discussed role of green solvents in extraction and HTL of lignin from biomass.
- Identified the most ideal process parameters for HTL of lignin.
- Reviewed the reaction mechanism and kinetic for HTL of lignin.
- Existing challenges of green solvents in HTL of lignin are emphasized.

GRAPHICAL ABSTRACT



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ABSTRACT

One of the greatest challenges in biorefinery is to reduce biomass' recalcitrance and enable valorization of lignin into higher value compounds. Likewise, green solvents and hydrothermal liquefaction (HTL) with feasible economic viability, functionality, and environmental sustainability have been widely introduced in extraction

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Process parameters
Renewable energy

and conversion of lignin. This review starts with the underscore of disadvantages and limitations of conventional pretreatment approaches and role of green solvents in lignin extraction. Subsequently, the effect of process parameters along with the reaction mechanisms and kinetics on conversion of lignin through HTL were comprehensively reviewed. The limitations of green solvents in extraction and HTL of lignin from biomass were discussed based on the current advancements of the field and future research scopes were also proposed. More details info on HTL of biomass derived lignin which avoid the energy-intensive drying procedures are crucial for the accelerated development and deployment of the advanced lignin biorefinery.

1. Introduction

The growing world populace has led to a global society which is presently over reliant on fossil fuels as a primary source of energy. However, the rapid consumption of this non-renewable energy increases the environmental impacts such as global warming and pollution as well as brings substantially more harm to human health. Therefore, to mitigate this problem, researchers have been progressively exploring cheap, economical and renewable energies as an excellent approach to provide a continuous supply of energy for the future generations without the use of fossil fuels (Breyer et al., 2022). In this context, lignocellulosic biomass is regarded as the most abundant renewable source worldwide (Kucharska et al., 2018) while it is a great alternative for replacing fossil feedstocks to obtain biofuels and bio-based materials to achieve environmental sustainability (Clauser et al., 2021).

The bioconversion of lignocellulosic biomass is complex and incompetent due to biomass recalcitrance, complication in the lignocellulosic matrix, cellulose crystallinity and lignin inhibition (Vélez-Mercado et al., 2021). Almost 70 % of the total biomass is obtained from cellulose and hemicellulose that are strongly connected to the lignin component via hydrogen and covalent bonds which strengthens the rigidity of the plant cell wall and make it robust (Ufodike et al., 2020). Lignin is a 3D unstructured polymer which comprises of methoxylated phenylpropane units and their by-products (Huang et al., 2018). It makes up 15–35 wt% of lignocellulosic biomass and is a profuse sustainable resource for the manufacture of fuels chemicals and fuels. In contrast with cellulose and hemicellulose, lignin is a non-saccharide macromolecular material with a complex structure. Various conventional methods for dissociating biomass into their major components, such as lignin, cellulose and hemicellulose have been investigated by several research works. Methods like steam pre-treatment, steam explosion, acidic and alkaline pre-treatment, and supercritical fluids which disintegrate the complex materials in biomass into monomeric units have been introduced and investigated over the recent years (Ashokkumar et al., 2022). Nonetheless, these methods appear to be less effective, expensive and non-environmentally friendly (Tan et al., 2021) which calls for alternative pre-treatment methods that are rapid and cost-and-energy effective.

Vast advancements in the field of solvent development focus on formulating environmentally friendly and safer solvents of any kind that satisfies the green chemistry metrics and sustainable development goals. Green solvents encompass those which are non-toxic, non-volatile, recyclable, biodegradable, which the synthesis should not incur high cost and preferably made from materials that are readily available (Das et al., 2017). Solvents of current interest that are recognized as green solvents include water, supercritical fluids, organic carbonates, ionic liquids (ILs), deep eutectic solvents (DESs), and bio-based solvents (Welton, 2015). Recently, DESs have been extensively acknowledged as analogues of ILs and developed as the new representative for green solvents (Hussin et al., 2020). DESs can easily be synthesized from readily available natural sources, simply by mixing two solid starting materials, hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) at moderate temperature without the need for further purification steps to form liquid eutectics by hydrogen bond interactions. DES constitutes of a group of easily tuneable eutectic mixtures that are adjustable to suit for specific applications, ascribed to their high number of HBDs present in the mixture (Bernasconi et al., 2017). Lignin is one of the main products from biomass pretreatment using DESs. Nevertheless, valorization of lignin still require further research and development since the recalcitrant nature of lignin limits its ability in generation of valuable products (Banu et al., 2019).

In recent years, thermochemical conversion of biomass for bio-oil production has attracted extensive research attention as a significant source of renewable. In this regard, hydrothermal liquefaction (HTL) of biomass for bio-oil production offers several advantages as compared to other thermochemical conversion technologies whereby the acquirement of 30 % liquefaction was favourable as to the energy and cost benefit ratios of 0.956 and 1.02, respectively (Banu et al, 2018). HTL is a thermochemical liquefaction process using water as the main reaction medium at sub- or supercritical states for depolymerization of biomass to form bio-oil (Arturi et al., 2019). The liquid (bio-oil) yield and the product distribution are dependent on various process conditions such as reaction temperature, pressure, residence time, heating rate, solvent and catalyst used (Gollakota et al., 2018). During HTL, various decomposition reactions are involved, such as depolymerization, repolymerization, cleavage of ether bond, demethoxylation and hydrolysis (Ciuffi et al., 2021).

Biomass delignification using green solvents is still an underdefined process as many researchers mainly studied the efficiency of lignin extraction from biomass and their thermal stability without considering the potential of value-added products that can be produced from the green solvents-extracted lignin through HTL technology since lignin is an important source of phenolic and aromatic compounds (Déniel et al., 2016). As such, this review aims to close this gap by providing a comprehensive picture of the HTL behaviour in conversion of biomass derived lignin. This review starts with the highlight of disadvantages and limitations of conventional pretreatment approaches and role of green solvents in extraction of lignin from biomass followed by the effects of HTL process parameters on conversion of lignin as well as reaction mechanisms and kinetics of HTL in converting lignin. The limitations and future perspectives of green solvents in extraction and HTL of lignin are also presented.

2. Conventional pretreatment approaches in extraction of lignin from biomass

Mechanical pre-treatment methods including milling, microwave irradiation, ultrasound irradiation, and extrusion are commonly used to increase the surface area of the lignocellulosic materials by reducing and minimising the particle sizes. This method usually leads to reduction in degree of polymerisation and crystallinity. In general, mechanical pre-treatment methods alone are insufficient and ineffectively to hydrolyse hemicellulose and extract lignin from the lignocellulosic biomass. Thus, they are normally incorporate with chemical pre-treatment methods to enhance the overall downstream conversion and yield (Tu & Hallett, 2019).

Chemical pre-treatment methods such as acid pre-treatment, alkaline pre-treatment and organosolv pretreatment are generally relied on the superior lignin dissolvability of the organic or inorganic chemicals. The utilization of the organic and inorganic solvents helps to dislocate and loosening the recalcitrant structure of the lignocellulosic materials with the chemical interactions between the intrapolymer or interpolymer