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Comparison of Staged and Biphasic Organosolv Pretreatment to Facilitate the Production of Lignin-Based Sustainable Aviation Fuel (SAF) from Pelletized Urban Wood Product Wastes

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ABSTRACT

High-yield fractionation and depolymerization to convert woody waste-derived lignin into cycloalkane hydrocarbons is an essential subject to complete the function of sustainable aviation fuel (SAF). However, the biorefinery process needs to be carefully designed to produce small molecular weight monolignol at significant quantity. Our recent studies demonstrate that in comparison to one-pot catalytic transfer hydrogenolysis (CTH), in which large quantity of cellulosic fibers are forming into low value chars, lignocellulosic biomass could produce a higher quantity of SAF after mild fractionation. To upgrade the organosolv induced C-O-C protection during acid catalyzed biomass pretreatment process for treating municipal woody waste, this study performed 24 sets of pretreatment experiments followed by CTH to produce cycloalkane hydrocarbons SAF. We compared the types and yield of SAF precursors after the conventional, staged pretreatment, and biphasic pretreatment over the one-pot CTH approach with detailed lignin-lignin characterization and regression analysis. The results confirmed that all organosolv pretreatment strategies could benefit lignin-lignin dissociation and increase its solubility before CTH. Preservation of β -O-4 linkages up to 42% can benefit the monomer yield by 30% in the downstream process.

INTRODUCTION

Significant developments in the conversion of lignocellulosic biomass through biorefinery processes have been sparked by the rising need for renewable fuels, chemicals, and materials as a result of growing concern about global climate change and continuous reliance on petroleum (Tuck et al., 2012). The aviation industry being the major consumer of fuels, is a major target for reducing the carbon footprint by shifting the paradigm toward sustainable production of aviation fuel. Today, the majority of commercially available sustainable aviation fuel (SAF) is generated by deoxygenating the lipid feedstocks obtained from plants and animals to create iso- and n-alkane hydrocarbon blends (Schutyser et al., 2018). Conspicuously, cycloalkanes and aromatics account for 30 to 70% of current aviation gasoline and cannot be replaced by n-alkane, thereafter limit the percent blend of SAF in the jet fuel. Jet fuel consists primarily of n-paraffins (20%), aromatics (18%), cycloparaffins (31%), isoparaffins (29%), naphthenes and other hydrocarbons with a carbon distribution number of C8-C16 (Okolie et al., 2023). To meet the sustainability goals of aviation industry, SAF needs to be blended with the conventional jet fuel as SAFs typically include linear paraffins, cycloparaffins, olefins and aromatic compounds, in the range of Carbon 8-16. ASTM Standards 7566 demands that SAF need to be blended with at least 50% of the fossil-based kerosene (Eswaran et al., 2021). The average carbon number of lignin based SAF is 15 whereas conventional Jet fuel has average carbon number of 11 (Yang et al., 2022). Presently, various SAF production pathways have been developed and

the standards for the specification of these oils have been developed. The various approved pathways are described briefly (Okolie et al., 2023).

- i. Fischer-Tropsch synthesis of Synthetic Paraffinic Kerosene (FT-SPK) which includes making SAF from Municipal solid waste (MSW) and forestry wastes. The blending ratio is up to 50%.
- ii. Fischer-Tropsch synthesis of SPK with aromatics (FT-SPK/A). The blending ratio is up to 50%.
- iii. Hydro-processing of esters and fatty acids (HEFA) from triglyceride-based feedstocks such as vegetable oils, waste oil, algae, and animal fat. The blending ratio is up to 50%.
- iv. Hydro-processing of Fermented sugars to Synthetic Iso-paraffins (HFS-SIP) from sugars like cellulose, carbohydrates, and starch. The blending ratio is up to 10%.
- v. Alcohol-to-Jet synthesis of SPK using iso-butanol and ethanol (ATJ-SPK). The blending ratio is up to 30%.
- vi. Catalytic hydro-thermolysis jet fuel (CHJ) from biomass. The blending ratio is up to 50%.
- vii. Hydro-processing of high hydrogen content hydrocarbons, esters, and fatty acids to SPK (HC-HEFA-SPK) which include SAF production from oils retrieved from biologically derived hydrocarbons like algae. The blending ratio is up to 10%.

The effective production of valuable products from lignin, a complex, aromatic heteropolymer that makes up to 15-30 wt. % of biomass and has a greater energy density than polysaccharides, is a major challenge in the biorefinery process (Anderson et al., 2017). Lignin serves as the biggest source of renewable aromatic compounds available in nature (Schutyser et al., 2018). During biosynthesis, arbitrary radical coupling processes polymerize lignin from three monolignols (*p*-coumaryl, coniferyl, and sinapyl alcohols), resulting in a three-dimensional amorphous structure. The lignin monomers are connected by an array of C-C and C-O-C linkages, including β -5, β -O-4, β - β , β -1, 5-5, and 4-O-5, with the β -O-4 linkage being the most abundant (Li et al., 2015). Lignin monomers or dimers, which naturally contain 7-18 carbon atoms, can be swiftly deoxygenated and transformed into jet fuel range hydrocarbons. As a result, removing the surplus oxygen from lignin monomers becomes the primary goal. Hydrodeoxygenation (HDO) is commonly employed to convert lignin and its derivatives to hydrocarbons (Stone et al., 2022). Catalytic transfer hydrogenolysis (CTH) is one such mechanism widely used to extract oxygen from depolymerized lignin using hydrogen donors. The CTH of lignin via alcohols has received a lot of consideration in the literature (Li et al., 2015). Primary and secondary alcohols (like supercritical methanol and tetrahydrofuran) can both work as hydrogen donors in the process (Huang et al., 2022).

Several barriers must be compressed before lignin can be effectively transformed into aviation fuel. One of the major complications of lignin selective conversion is its recalcitrancy and heterogeneous structure (Wang et al., 2017) and usually dealt with using pretreatment mechanisms which are mainly focused on fractionating and removing the lignin to increase the biotransformation of the biomass into products. Traditional biomass pretreatment techniques are essentially carbohydrate-focused approaches that intend to eliminate lignin to enhance cellulose accessibility to cellulase enzymes (Li et al., 2018). The technical lignin extracted as a by-product of these operations are usually deteriorated or condensed. This study focuses on improving these methods of pretreatment to extract lignin in the purest possible form with maximum retention of the β -O-4 linkages. To this, organosolv pretreatment using 1,4-butanediol (BDO) and biphasic pretreatment using 1-pentanol are opted to obtain the high-quality lignin by preserving the β -O-4 bonds, followed by the CTH process to convert it into lignin monomers.

METHODOLOGY

Feedstock and Pretreatment Plan

The biomass feedstock used in this study was composed of urbanized wooden pellets falling under the category of softwood with a length of around 5cm and a diameter of 2cm. The biomass consisted of 35 \pm 2% cellulose, 14 \pm 1% hemicellulose (consisting of xylose, arabinose and mannose), and 28 \pm 2% lignin. Around 40g of wooden pellets were fed into a hydrothermal reactor at a liquid-to-solid ratio of 6. A total of 8 reactors were put inside a large stainless-steel rotating digester in which pretreatment solvent was added and then the reactor was closed and made airtight. The digester was mounted on a shaft for rotation at a constant speed to mix the contents of the reactors, continuously. The whole system was heated at a controlled temperature of 160°C. After the reaction, the reactor was cooled down to room temperature and treated biomass was filtered out, air dried for chemical composition analysis, and the filtrate containing dissolved lignin was employed for the CTH process. The structural carbohydrates (cellulose and hemicelluloses) and lignin in the raw and treated biomass were assessed through two-stage acid hydrolysis according to the National Renewable Energy Laboratory (NREL) protocol (Sluiter et al., 2008). Before analysis, the samples were dried. The moisture content was determined by calculating the loss in weight of the wood sample by drying in hot air oven at 105°C. The samples were mixed with 72% H₂SO₄ and hydrolyzed at 30°C temperature in a water bath for 60 minutes. The solution was diluted to 3.97 % H₂SO₄ (w/w) and autoclaved at 121°C for another 60 minutes for complete hydrolysis. During primary hydrolysis, polysaccharides are completely separated from the lignin whereas secondary hydrolysis depolymerizes oligomers to monomer sugars. The autoclaved masses were filtered to separate lignin residue and filtrate containing cellulose and hemicellulose sugars. The

dissolved structural sugars using high-performance liquid chromatography (HPLC, Shimadzu-20A) fitted with a CHO-782 Transgenomic sugar column, while lignin was gravimetrically determined from the dried mass of the residue.

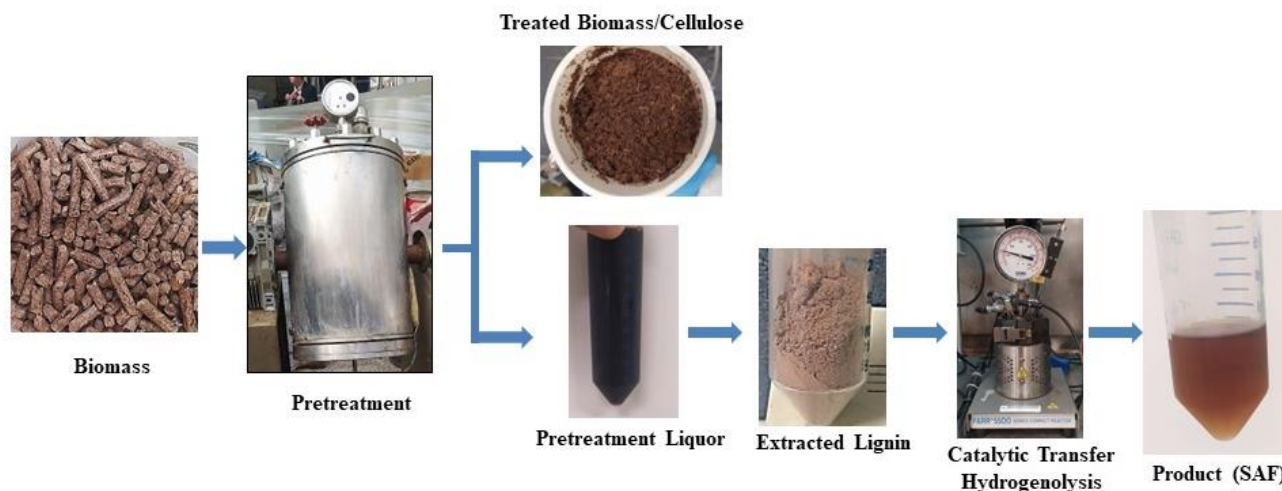


Figure 1: Schematic representation of the organosolv pretreatment of wood pallets and one-pot CTH process of the extracted lignin into monomers.

Pretreatment Conditions

The overall experimental plan and the methodology followed during the process have been shown in **Figure 1**. The solvents used and various pretreatment conditions are reflected in **Table 1**. Experiment 1-8 are designed to test the pretreatment performance at single cook using a mixture of organic solvent and dilute acid. The results of the process will serve as a benchmark in comparing with other experiments that include different approaches which are being mentioned. The next set of experiments from 9-16 includes a biphasic system in which Pentanol is mixed with dilute acid to compare the extraction capability of lignin in a separate phase and finally, a staged process in which the biomass is treated with an organic solvent first and then treated with dilute acid to perceive the quality of obtained lignin in a staged process which is believed to be better because most of the lignin should get extracted in the first cook using organic solvent. Different pretreatment conditions (**Table 1**) were employed to fractionate the wood pellets into its components and then lignin extraction. A series of experiments were performed, and results are described in the following sections.

At first acid-catalyzed single step organosolv (DA+Organosolv) pretreatment was performed and the total biomass

Table 1: Experimental setup for the staged and biphasic organosolv pretreatment

Exp. No.	Mode	L/S Ratio	1 st Cook			2 nd Cook		
			Temp	Time	Solvent	Temp	Time	Solvent
1	Dilute Acid (DA) + Organosolv	6	160	60	BDO (50%)+DA (150mM)	n/a		
2		6	160	60	BDO (50%)+DA (100mM)			
3		6	160	60	BDO (50%)+DA (50mM)			
4		6	160	60	BDO (65%)+DA (150mM)			
5		6	160	60	BDO (65%)+DA (100mM)			
6		6	160	60	BDO (65%)+DA (50mM)			
7		6	160	60	BDO (80%)+DA (150mM)			
8		6	160	60	BDO (80%)+DA (100mM)			
9	Biphasic	6	160	60	Pentanol (50%)+DA (150mM)	n/a		
10		6	160	60	Pentanol (50%)+DA (100mM)			
11		6	160	60	Pentanol (50%)+DA (50mM)			
12		6	160	60	Pentanol (65%)+DA (150mM)			
13		6	160	60	Pentanol (65%)+DA (100mM)			

14		6	160	60	Pentanol (65%)+DA (50mM)			
15		6	160	60	Pentanol (80%)+DA (150mM)			
16		6	160	60	Pentanol (80%)+DA (100mM)			
17	Staged	6	160	30	BDO (50%)	160	30	DA (150mM)
18		6	160	30	BDO (50%)	160	30	DA (100mM)
19		6	160	30	BDO (50%)	160	30	DA (50mM)
20		6	160	30	BDO (65%)	160	30	DA (150mM)
21		6	160	30	BDO (65%)	160	30	DA (100mM)
22		6	160	30	BDO (65%)	160	30	DA (50mM)
23		6	160	30	BDO (80%)	160	30	DA (150mM)
24		6	160	30	BDO(80%)	160	30	DA (100mM)

Catalytic Transfer Hydrogenolysis (CTH)

After pretreatment, dissolved lignin from the pretreatment liquor was precipitated out using DI water. The precipitated lignin was then stored at -20°C for 12 hours. Afterwards, the lignin was freeze-dried to get powdered lignin. A 0.5g of prepared lignin was mixed with 0.1g of catalyst (Ruthenium on carbon) and put into a CTH reactor. Tetrahydrofuran (20 mL) was added to act as a hydrogen donor. The reactor was tightly closed, and hydrogen gas was purged into the reactor and air purged out simultaneously. The reaction was run for 5 hours at 225°C and a pressure of 40 bar. After reaction and cooling down, the sample was filtered to remove the catalyst, and the filtrate containing lignin monomers was analyzed using Gas Chromatography with Thermal Conductivity Detector (GC-TCD, Agilent 7890B) and Gas Chromatography with Mass Spectrometry (GC-MS, Agilent 5977B).

RESULTS AND DISCUSSION

Effect of organosolv pretreatment on lignin

The weight loss and chemical composition of the pretreated biomass has been depicted in **Figure 2**. After the pretreatment, cellulose recovery (95 – 99%) was maximal in the pretreated solids at all the tested conditions. These results are also in line with our previous organosolv pretreatment studies (Islam et al., 2021, Dong et al., 2019). Whereas the hemicellulose removal efficiency was found to be higher with the increasing dosage of the dilute acid catalyst. The lignin extracted from the pretreatment liquor was about 5g of dry lignin from 40g of biomass. The overall lignin removal efficiency was 65±3% for the sample in which BDO proportion was 80%. Though the hemicellulose removal was relatively higher at increased acid dosage, the lignin removal was comparatively lower among all samples. and the NMR data revealed less β -O-4 bond linkages which might be due to lignin condensation, hence the combined organosolv + DA pretreatment may not be a promising option as a high-yield SAF additive, as the primary objective of the study is lignin extraction rather than hydrolysis of the pretreated substrates.

Another pretreatment approach, staged-organosolv (BDO > DA) was carried out at different experimental conditions by varying the BDO and DA quantities and ratio. Results demonstrated that at the first stage of the BDO > DA process, condensation effects were not observed. This may be because lignin acidolysis tended to occur less frequently and lignin carbocation was stabilized by organosolv (Islam et al., 2021). With the cleavage of the ether bonds by the (H⁺) ions produced by the solvolytic cleavage of organosolv, about 50% of the lignin was removed during the BDO process. The elimination of the lignin-hemicellulose complex may have been the primary cause of the second step of the lignin removal that took place during the DA process. This method could result in lignin condensation, which would lower the quality of the fractionated lignin. Contrarily, the extracted lignin was characterized as a reactive-lignin as the interunit linkages at α - positions of β -O-4, β -5, and β - β in the residual lignin could not be identified in the aliphatic region, while preserving 42% of the β -O-4 linkages, analyzed via 2DHSQC NMR spectra (data will be shown later). Hence, staged-organosolv pretreatment can be a favourable option to obtain the cyclohexane fraction of the SAF additive after catalytic reduction.

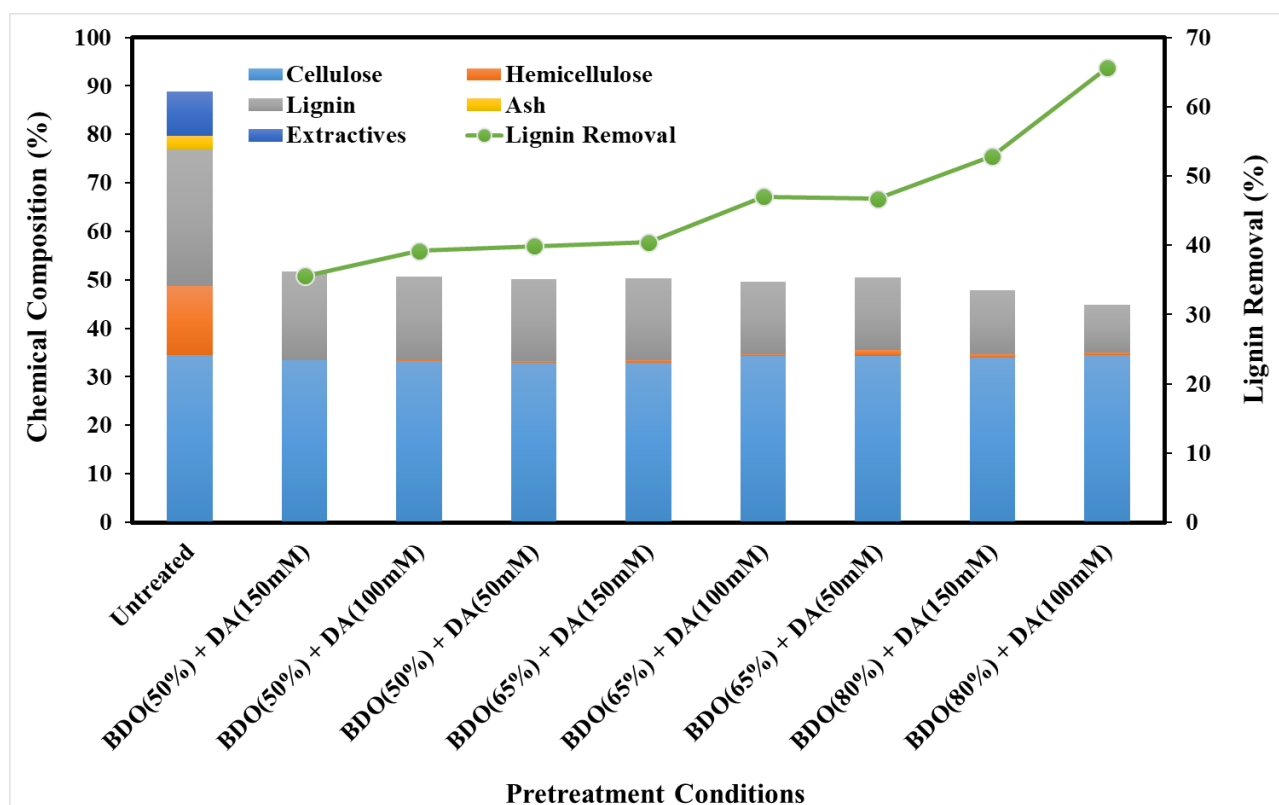


Figure 2: Chemical composition and lignin removal efficiency of the untreated (raw) and DA + organosolv pre-treated wood pellets.

Effect of biphasic pretreatment

Biphasic pretreatment resulted in highest cellulose recovery as an insoluble solid residue and 70.3% of the lignin dissolving in the organic phase. The removal of lignin was found to be similar to the removal of hemicellulose, and the lignin solubility increased with the organosolv (pentanol) composition, enhancing the hydrophobic interaction between lignin and solvent. However, because lignin dissolution is so dependent on hemicellulose dissolution, lignin removal began to decline after 65% of the solvent concentration. Lignin condensation reaction (condensed C=C bonds) led to a reduction in lignin removal from the solid pulp at very high acid concentrations (85 mM acid) or pretreatment severity, thereby reducing the overall lignin removal efficiency (data will be shown later).

Lignin depolymerization

Further to the pretreatment, lignin extraction, and characterization, depolymerization of the extracted lignin will be performed via CTH process. The expected yields of lignin depolymerization are depicted in **Table 2**. Among all the tested procedures, staged-organosolv was outperformed in producing a high-quality reactive lignin, yielding a higher depolymerization yield (30%) over other organosolv pretreatment efficiencies.

Table 2. Overall yields (obtained + expected) during processes involved in lignin extraction and monomer production

Pretreatment approach	Lignin Extraction	Lignin Depolymerization
DA + Organosolv	65%	24%
Organosolv > DA	50%	30%
Biphasic	70%	27%
CTH	-	15%

The obtained SAF was analyzed using GC-MS to observe the depolymerization products and the collective yield. Figure 3 shows the GC-MS results of the product. The internal standard was set at retention time of 6 and hence all the monomers identified after the set parameters can be seen in the figure. The major portion of the SAF was obtained at retention time of 7.8 to 8.6 which corresponds to 4-ethyl-2-methoxyphenol and 2,6-dimethoxyphenol having carbon number of 9. The other products detected at retention time 8-10 are the monomers with carbon number 10 and 11.

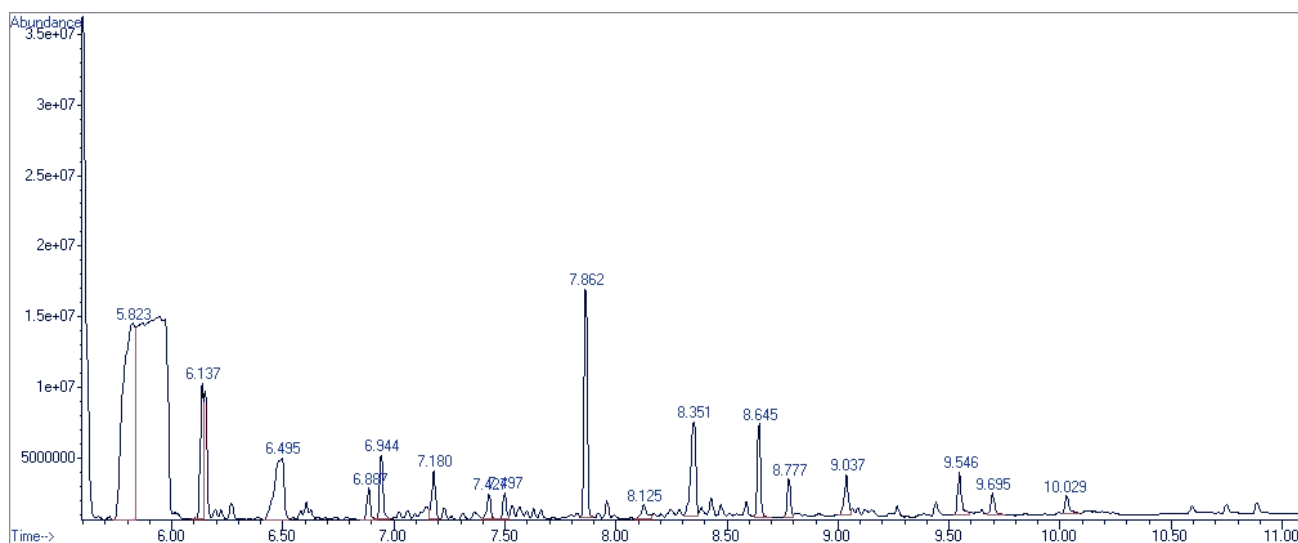


Figure 3: GC-MS results of the product/SAF

CONCLUSIONS

The goal of this study is to maximize the production of reactive lignin by comparing different pretreatment approaches for lignin extraction as the basic measure to enhance the monomer yield. The staged-organosolv outcompeted the single-stage and biphasic pretreatment approaches by preserving the β -O-4 linkages. The monomer yield of the reactive lignin was also higher among three processes, and further compared with the one-pot CTH as a standard protocol. With the same monomers after OS > DA, the resulted cyclohexane may present as an SAF additive to help in decarbonizing the aviation industry.

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