

Pentanol-water biphasic pretreatment facilitates energy-efficient fractionation of lignocellulose

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ABSTRACT

The pretreatment is the most important step for biomass conversion which alters the structure of lignocellulosic biomass to make the substrate accessible enzymatic saccharification and fractionates biomass into the major components for complete utilization of biomass. The fractionation of major biomass components after traditional organosolv pretreatment is tedious and energy-intensive especially when solvent recovery is crucial. In this study, pentanol/water biphasic pretreatment of acacia wood was carried out to investigate energy benefits of the process, pretreatment efficiency, and lignin potential to produce value-added chemicals. The two completely immiscible phases facilitated the separation of biomass fractions which reduced about 46.5% of the total energy consumption for pretreatment and fractionation process. Besides, the lower distribution co-efficient of acid in the organic phase preserved approximately 26.4% of β -aryl ether (β -O-4) linkage in lignin which further increased the energy benefits of the pretreatment process by increasing lignin valorization potential.

Keywords: Energy consumption, Biphasic pretreatment, 1-Pentanol, Hydrolysis, Lignin

NOMENCLATURE

Abbreviations

$P_w C_x t_y S_z$	Identity of pretreated sample
P_w	Pentanol composition (%)
C_x	Acid concentration (mM)
t_y	Retreatment time (min)
S_z	Liquid to solid ratio
mM	Millimolar
SED	Substrate enzyme digestibility
HSQC	Heteronuclear single quantum coherence

1. INTRODUCTION

Lignocellulosic biomass has been regarded as a renewable and sustainable source of energy and chemicals that can be used as an alternative to fossil fuel to combat environmental hazards and global warming potential. The conversion of biomass to bioenergy and chemicals encounters a lot of technological challenges [1]. Pretreatment is the most important and energy-intensive process for biomass conversion which determines the efficiency of the later conversion steps and downstream processing [2, 3]. Due to the lignin recyclability, organosolv fractionation among other chemical methods is getting more attention in biorefinery production [4, 5]. In organosolv pretreatment, lignocellulose is fractionated by dissolving hemicellulose and lignin in the water-organosolv mixture leaving cellulose as an insoluble pulp. The separation of fractionated lignin and hemicellulose is crucial for efficient valorisation of biomass which is accomplished by the addition of water to the pretreatment liquor [6]. On the other hand, the addition of water increases the energy consumption of distillation for solvent recovery since distillation energy is directly proportional to the volume of distillation solution.

The physical separation of cellulose, hemicellulose, and lignin fractions in three different phases during pretreatment can facilitate fractionation and effective valorisation of major biomass components [7]. A one-pot chemo catalytic n-butanol/water biphasic system was investigated to convert eucalyptus sawdust into a cellulose pulp, hemicellulose-derived polyols, and lignin-derived phenolics [8]. The effective valorisation of hemicellulose and lignin was achieved at 200°C temperature in presence of Ru/C catalyst and hydrogen pressure. The phase separation at lower temperature offers a facile strategy to separate lignin-derived chemicals in butanol and polyols in water. H₂SO₄ acid catalysed water /n-butanol biphasic system

promoted separation of biomass components in three different phases of which recovered lignin and cellulose with 96% enzyme digestibility [9]. However, no other studies have been investigated the energy benefits of biphasic pretreatment for effective valorisation of biomass components. Besides, the solubility of butanol (7-8%) in water [10] at room temperature showed a high solvent loss during physical separation. On the other hand, pentanol has the lower solubility in water (2%) which may facilitate more efficient solvent recovery by physical separation of hemicellulose and lignin fractions (as shown in **fig.1**).

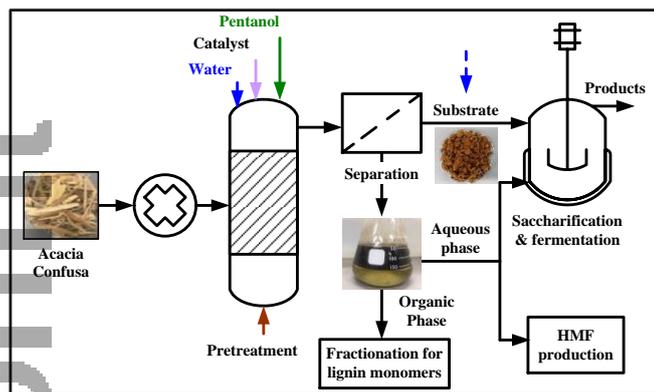


Fig 1 Conceptual diagram of pentanosolv pretreatment of lignocellulose biorefinery for energy-efficient fractionation.

In this study, pentanol/water biphasic pretreatment of acacia wood was investigated to evaluate the energy benefits of this process will be compared with water-miscible traditional organosolv pretreatment of biomass. The pretreatment efficiency, substrate digestibility, lignin purity will also be investigated to clarify the efficiency of the process to produce bioethanol and high-value lignin.

2. MATERIALS AND METHODS

The pretreatment of *Acacia Confusa* wood was carried out at 170°C temperature in a metallic cylinder with varying time, solvent, and catalyst concentration [6]. The energy consumed in the pretreatment and fractionation was calculated based on enthalpy change of the respective system [11]. Chemical composition of raw and pretreated substrate was determined by the NREL procedure [12]. Pretreated pulp was separated from liquor for the determination of enzyme digestibility of substrate and liquor was allowed to separate hemicellulose rich aqueous and lignin-rich organic phases. The lignin was recovered from organic phase by evaporation, followed by washing several times with ethanol and water. 2DHSQC NMR analyses were conducted to evaluate the purity and potential of recovered lignin [6].

3. RESULTS AND DISCUSSION

The pretreatment efficiency, energy consumption in pretreatment and fractionation, hydrolysis efficiency, and characteristics of fractionated lignin will be discussed in this section.

3.1 Pretreatment efficiency

The chemical composition of raw and pretreated acacia wood residues was demonstrated in Fig 2(a). The pretreated substrate experienced hemicellulose and lignin solubilization in the solvent and resulted in an insoluble fraction with high cellulose content of about 73.3% (at 60 mM acid concentration). The hemicellulose removal increased with the acid concentration in the pretreatment liquor and complete hemicellulose removal was obtained (> 60 mM of acid). Lignin removal also increased with the addition of acid in the liquor but decreases at a high acid concentration (≥ 85 mM acid) due to lignin condensation [6]. Instead, very high catalyst concentration in the pretreatment liquor decreased cellulose recovery due to the strong hydrolyzing effect of acid to degrade cellulose sugars.

3.2 Energy consumption

The energy consumption was calculated for pretreatment and fractionation of 1 kg of dry wood. The total energy consumption in the pretreatment is a function of solvent volume and pretreatment temperature as shown in table 1. The energy consumption of pentanol pretreatment (2.4 MJ) was almost similar to that of conventional ethanol process (2.5MJ). However, the almost complete immiscibility of pentanol in water resulted in physical separation of lignin and hemicellulose. It reduced about 46.5% of the total energy consumption for pretreatment and fractionation due to no energy requirement in the fractionation and solvent recovery.

Table 1 Energy consumption for pentanosolv and conventional ethanosolv pretreatment.

Process	Energy Consumption (MJ/Kg)			
	Cooking	Milling	Recovery	Net
Pentanol	2.39	0.36	-	2.75
Ethanol	2.47	0.36	2.30	5.14

3.3 Enzymatic hydrolysis

To investigate the effect of pentanol-water pretreatment on digestibility of insoluble cellulosic fraction of substrate, enzymatic hydrolysis was carried out at 3% solid loading and 15 FPU/gm of enzyme loading. The hydrolysis yield at 72 hrs (fig 2(b)) showed that the enzyme digestibility strongly depends on the hemicellulose and lignin content of the substrates.

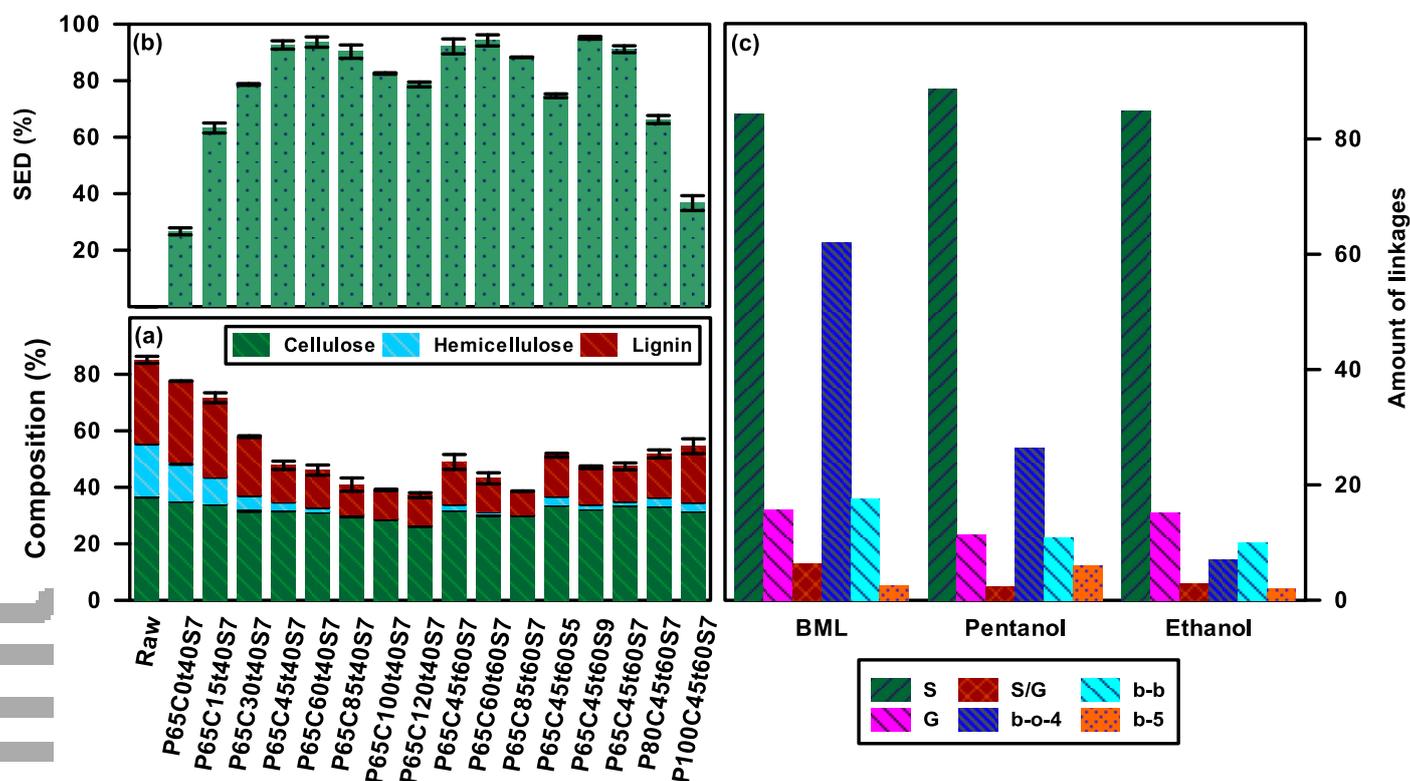


Fig 2 The efficiency of pentanol-water treatment system; (a) chemical composition of the raw and pretreated *Acacia Confusa* wood at 170 °C with varying solvent and catalyst compositions; (b) enzyme digestibility of the substrates at 72 hrs; (c) properties of fractionated lignin in terms of major subunits and chemical linkages.

Results also demonstrated that almost complete hemicellulose removal and around 60% removal of lignin can result in high (more than 90%) enzyme digestibility due to much lower binding strength of organosolv lignin with enzyme [13, 14].

3.4 2D-HSQC NMR analysis

The quantitative values of different subunits and inter-unit linkages in fractionated lignin were determined by using aromatic subunits ($S_{2/6}$ at δ_C/δ_H 105.0/6.6 ppm and G_2 at δ_C/δ_H 112.7/6.9 ppm) as the internal standard. The amount of β -aryl ether (β -O-4), phenylcoumaran (β -5), and resinols (β - β) linkages were determined from their integral values of α position at δ_C/δ_H 71.9/4.1 ppm, δ_C/δ_H 85.6/4.6 ppm, and δ_C/δ_H 86.1/4.1 ppm respectively. Pentanol pretreatment can preserve 26.4% of β -O-4 linkages in the fractionated lignin which was much higher than the conventional ethanol pretreatment (7.05%) as shown in fig 2(c). The reduced acid severity on lignin due to the physical separation of acid and lignin was responsible to preserve the higher proportion of the most important β -O-4 linkages.

4. CONCLUSION

Pentanol can be a budding candidate for pretreatment of lignocellulose in the biorefinery, which saved 46.5% of the energy consumption for pretreatment and solvent recovery. It resulted in

approximately 75% lignin removal and more than 90% enzyme digestibility of substrates except for very high and low catalyst (H_2SO_4 acid) concentration. Pentanol pretreatment preserved up to 26.4% beneficiary lignin linkages (β -O-4) due to the auto separation of lignin from a vulnerable acidic environment. Thus, the use of pentanol as a pretreatment solvent is possible, thereby can achieve the objectives of high energy output and saccharification yield in the biorefinery.

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REFERENCE

- [1] Islam MK, Wang H, Rehman S, Dong C, Hsu H-Y, Lin CSK, Leu S-Y. Sustainability metrics of pretreatment processes in a waste derived lignocellulosic biomass biorefinery. *Bioresour. Technol.*, 2020. **298**: p. 122558.
- [2] Islam MK, Dong C, Hsu HY, Lin CSK, Leu SY. Valorisation of Woody Biomass. *Waste Valorisation: Waste Streams in a Circular Economy*. Wiley, 2020: p. 87-108.
- [3] Zhao X, Li S, Wu R, Liu D. Organosolv fractionating pre-treatment of lignocellulosic biomass for efficient

enzymatic saccharification: chemistry, kinetics, and substrate structures. *Biofuel Bioprod Bior*, 2017.

[4] Salapa I, Katsimpouras C, Topakas E, Sidiras D. Organosolv pretreatment of wheat straw for efficient ethanol production using various solvents. *Biomass Bioenergy*, 2017. **100**: p. 10-16.

[5] Tang C, Shan J, Chen Y, Zhong L, Shen T, Zhu C, Ying H. Organic amine catalytic organosolv pretreatment of corn stover for enzymatic saccharification and high-quality lignin. *Bioresour. Technol.*, 2017. **232**: p. 222-228.

[6] Dong C, Meng X, Yeung CS, Ho-Yin T, Ragauskas AJ, Leu S-Y. Diol pretreatment to fractionate a reactive lignin in lignocellulosic biomass biorefineries. *Green Chem.*, 2019. **21**(10): p. 2788-2800.

[7] Zimmermann CJ, Bollar NV, Wettstein SG. Liquid phase conversion of lignocellulosic biomass using biphasic systems. *Biomass Bioenergy*, 2018. **118**: p. 163-171.

[8] Renders T, Cooreman E, Van den Bosch S, Schutyser W, Koelewijn S-F, Vangeel T, Deneyer A, Van den Bossche G, Courtin C, Sels B. Catalytic lignocellulose biorefining in n-butanol/water: a one-pot approach toward phenolics, polyols, and cellulose. *Green Chem.*, 2018. **20**(20): p. 4607-4619.

[9] Schmetz Q, Teramura H, Morita K, Oshima T, Richel A, Ogino C, Kondo A. Versatility of a dilute acid/butanol pretreatment investigated on various lignocellulosic biomasses to produce lignin, monosaccharides and cellulose in distinct phases. *ACS Sustain. Chem. Eng.*, 2019. **7**(13): p. 11069-11079.

[10] Liu F, Liu L, Feng X. Separation of acetone–butanol–ethanol (ABE) from dilute aqueous solutions by pervaporation. *Sep. Purif. Technol.*, 2005. **42**(3): p. 273-282.

[11] Cambero C, Sowlati T. Incorporating social benefits in multi-objective optimization of forest-based bioenergy and biofuel supply chains. *Appl. Energy*, 2016. **178**: p. 721-735.

[12] Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D, Crocker D. Determination of structural carbohydrates and lignin in biomass. *LAP.*, 2008. **1617**: p. 1-16.

[13] Yoo CG, Li M, Meng X, Pu Y, Ragauskas AJ. Effects of organosolv and ammonia pretreatments on lignin properties and its inhibition for enzymatic hydrolysis. *Green Chem.*, 2017. **19**(8): p. 2006-2016.

[14] Leu S-Y, Zhu J. Substrate-related factors affecting enzymatic saccharification of lignocelluloses: our recent understanding. *Bioenergy Res.*, 2013. **6**(2): p. 405-415.

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