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Sustainable poplar biorefinery producing butanol-rich solvents, furfural, and lignin-derived compounds with environmental and economic benefits

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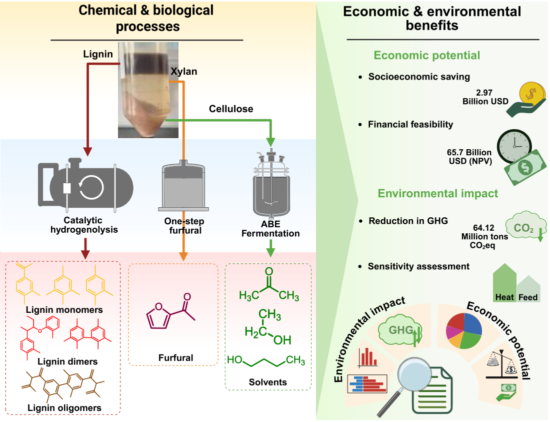
HIGHLIGHTS

- ➢Mild biphasic pretreatment enabled efficient biomass fractionation with one-pot furfural production.
- ➢*Clostridium* fermentation yielded 16.2 g/L of solvents, with 10.5 g/L of butanol as the major product.
- ➢Lignin hydrogenolysis yielded 46.4% monomeric lignin with high selectivity.
- ➢Scale-up could reduce 64.12 Mt $CO_{2\text{-eq}}$ and save USD 2.97 billion annually.
- ➢Feedstock supply and energy use are identified as key factors in the biorefinery process.

GRAPHICAL ABSTRACT



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ABSTRACT

The transformation of poplar biomass into bio-based chemicals, fuels, and lignin-derived products through an integrated biorefinery is essential for realizing its full potential as a sustainable and economically viable feedstock. This study presents a poplar biorefinery approach using mild biphasic pretreatment (*p*-toluenesulfonic acid/pentanol + $AlCl_3$, 110°C, 40 min) to produce bio-based platform multiple products. The pretreatment achieved efficient fractionation, with 83.2% delignification, 95.2% xylan removal, and minimal cellulose loss (7.8%), enabling high-yield one-pot furfural production (68.5%, 11.3 g/L). Enzymatic hydrolysis of the cellulose-rich residue, combined with fermentation by *Clostridium acetobutylicum*, produced a bio-solvent mixture of 16.2 g/L, including 10.5 g/L butanol. Depolymerized lignin was recovered and subjected to catalytic hydrogenolysis, yielding 46.4% monomers, 9.3% dimers, and 17.4% oligomers. Processing 140 Mt of poplar biomass annually at scale could deliver substantial environmental and economic gains, avoiding approximately 64.12 Mt of $CO_{2\text{-eq}}$ emissions and generating an estimated USD 2.97 billion in annual socioeconomic benefits. Sensitivity analysis confirmed biomass availability as the dominant factor influencing emission reduction. Economic evaluation demonstrated strong financial viability, with an aggregate net present value of USD 65.7 billion projected for full national implementation. This work establishes a holistic and economically compelling biorefinery strategy for the sustainable production of bio-based chemicals and fuels.

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Contents

Abbreviations

ABE	Acetone-Butanol-Ethanol
BET	Brunauer–Emmett–Teller
CrI	Crystallinity index
CAPEX	Initial capital expenditure
Et-S	4-ethyl syringol
Et-G	4-ethyl guaiacol
GC	Gas chromatography
GHG	Greenhouse gas
HMF	Hydroxymethylfurfural
HPLC	High-performance liquid chromatography
IRR	Internal rate of return
MWL	Milled wood lignin
Mt	Million tonne
NPV	Net present value
OPEX	Operational expenditures
Pr-S	4-propyl syringol
Pr-G	4-propyl guaiacol
SEM	Scanning electron microscopy
TsOH	*p*-toluenesulfonic acid
TRL	Technology Readiness Level
USD	United States dollar
XRD	X-ray diffraction

1. Introduction

The growing reliance on fossil fuels over the past few decades has significantly increased greenhouse gas (GHG) emissions, exacerbated climate change, and threatened global energy security (Marzban et al., 2025). These escalating challenges have driven renewed efforts to transition toward renewable energy sources. Lignocellulose, derived from plant materials such as wood, grasses, and agricultural residues, has emerged as a promising renewable feedstock for biofuels and bio-based chemicals (Zhou et al., 2021). It is abundant, inexpensive, and carbon-neutral, making it a critical component of a bioeconomy focused on reducing GHG emissions and promoting sustainability (Madadi et al., 2025c). However, the structural recalcitrance of lignocellulose poses a significant barrier to its efficient conversion, particularly in the hydrolysis of cellulose and hemicellulose into fermentable sugars (Wang et al., 2025). The complex lignin structure further complicates biomass fractionation, limiting the commercial viability of biofuel production (Zhou and Tian, 2022).

To address these challenges, pretreatment technologies are essential for breaking down the biomass structure and improving the accessibility of its components. Biphasic solvent systems, utilizing immiscible alcohols (e.g., butanol and pentanol) in combination with acids, demonstrate promise in biomass fractionation (Zhan et al., 2023). When combined with catalysts like *p*-toluenesulfonic acid (TsOH) and sulfuric acid (H_2SO_4), these systems operate under milder conditions (lower temperatures and shorter reaction times) compared to traditional methods, making them more energy-efficient and economically feasible (Tongtummachat et al., 2022). The biphasic system separates lignocellulose into three fractions: cellulose-rich solids, an aqueous phase rich in xylan-derived compounds, and an organic phase containing lignin. Recovering high-quality fractions and reusing solvents (*i.e.*, pentanol, >84% after four cycles) and catalysts (*i.e.*, TsOH, >96% after four cycles) enhances process efficiency and sustainability (Islam et al., 2021; Madadi et al., 2022).

Recent advancements in biorefinery development focus on maximizing the value of all biomass fractions. Lignin can be selectively converted into low-molecular-weight monomers and dimers through catalytic hydrogenolysis (Madadi et al., 2023a). This conversion provides a renewable source of aromatic compounds, which are crucial for the production of a wide range of chemicals, including those utilized in the pharmaceutical, polymer, and aerospace industries. Furthermore, lignin oligomers can be converted into high-value chemicals, such as phenols and catechols, which serve as precursors for various industrial applications, thereby further improving the economic viability of the biorefinery (Kouris et al., 2020).

In addition to lignin valorization, the pentose-rich aqueous phase obtained during pretreatment offers an opportunity for one-pot production of furfural and hydroxymethylfurfural (HMF), key platform chemicals. Conventional furfural production involves multi-step processes, including dilute-acid pretreatment followed by catalytic dehydration at elevated temperatures (>150°C) (Bao et al., 2024). These processes are energy-intensive and often lead to sugar degradation, resulting in reduced yield and increased costs. Recent advances in one-pot strategies using solid acid catalysts, such as TsOH and aluminum chloride ($AlCl_3$), enable the direct production of furfural from the pentose-rich phase in a more energy-efficient manner, operating at lower temperatures and eliminating the need for additional separation steps (Jiang et al., 2018). The combination of TsOH and $AlCl_3$ is particularly effective in breaking down the

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lignocellulose structure, where TsOH promotes hydrolysis and $AlCl_3$ enhances hemicellulose dissolution and xylose conversion into furfural (Sajid et al., 2021). The cellulose-rich fraction from biphasic pretreatment can also be converted into biofuels through microbial fermentation, such as acetone-butanol-ethanol (ABE) fermentation by *Clostridia* species (Karimi et al., 2024). This process produces bioalcohols with high energy density and industrial relevance.

Integrating these diverse valorization pathways in a single biphasic pretreatment system enhances efficiency and resource circularity. Co-producing furfural, bioalcohols, and lignin-derived monomers improves overall process sustainability. Efficient recovery of high-purity intermediates streamlines downstream processing, reduces operational complexity, and enhances scalability (Madadi et al., 2025b). Despite advancements, the industrial viability of integrated systems necessitates a comprehensive evaluation that extends beyond laboratory-scale performance. Socioeconomic analysis and GHG quantification are essential tools for assessing the environmental and economic impacts of biorefinery systems (Brandão et al., 2022). These analyses help identify trade-offs and optimization opportunities, ensuring the long-term success of bioenergy technologies (Madadi et al., 2025a).

This study reports an integrated biorefinery approach utilizing a biphasic pretreatment of poplar biomass under mild conditions with a pentanol/TsOH solvent system, employing $AlCl_3$ as a co-catalyst. The role of $AlCl_3$ in promoting one-pot furfural production, effective biomass fractionation, and subsequent enzymatic hydrolysis and fermentation of the cellulose-rich fraction to produce ABE is demonstrated. The recovered lignin fraction is further valorized through catalytic hydrogenolysis, yielding valuable aromatic monomers and dimers. The environmental and economic sustainability of this system is evaluated through comprehensive GHG analysis, socioeconomic assessment, and sensitivity analysis, offering insights into its potential for industrial-scale implementation.

2. Experimental

2.1. Materials and chemicals

The poplar wood chip samples were collected from an agricultural site associated with Guangxi University, China. The composition of the poplar biomass included 45.9% cellulose, 27.1% hemicellulose, and 25.6% lignin. The wood chips were ground using a 50-mesh screen and subsequently dried at 40°C overnight. The TsOH was procured from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China), while $AlCl_3$ and alkaline lignin were obtained from Shanghai Chengjie Chemical Co., Ltd. (Shanghai, China). The pretreatment solvent, pentanol, was supplied by Zibo Nalcohol Chemical Co., Ltd. (Shandong, China). All experiments in this study were performed in three replicates.

2.2. Process of biphasic pretreatment

The biphasic pretreatment system consisted of 60% v/v pentanol and 20 wt% TsOH, along with varying concentrations of $AlCl_3$ at 4, 6, 8, and 10 wt% (based on the weight of the raw substrate). In each experiment, 10 g of biomass was added to 100 mL of the catalyst-solvent mixture, maintaining a solid-to-liquid ratio of 1:10 (w/v). The mixture underwent thermal treatment in a controlled autoclave reactor (CY-1100X, Zhengzhou, China) at temperatures of 90, 110, 130, and 150°C for 40 min. After cooling to ambient temperature, the system separated into three distinct phases: an organic phase rich in lignin, an aqueous phase containing dissolved xylan-derived compounds, and a solid residue primarily composed of cellulose. The solid residue was washed repeatedly with distilled water until a neutral pH of 7.0 was achieved. Afterward, it was prepared for chemical composition analysis and subjected to further hydrolysis and fermentation. Lignin was recovered from the organic phase through precipitation using a 90:10 (v/v) water–ethanol mixture, followed by centrifugation and freeze-drying (Madadi et al., 2023b).

2.3 Enzymatic hydrolysis and ABE fermentation processes

The dried, pretreated solid residues were mixed with citrate buffer (50 mM, pH 4.8) and then subjected to enzymatic hydrolysis at a 10% (w/v) solid loading (Adney and Baker, 2008). The hydrolysis was carried out by Cellic® CTec 2 at an enzyme dosage of 10 $FPU/g_{biomass}$. The mixture was incubated at 50°C and 180 rpm for 72 h. After hydrolysis, the resulting hydrolysate was separated by centrifugation (8000 rpm, 5 min).

ABE fermentation was applied using the *Clostridium acetobutylicum* 1201 strain. The cryopreserved spores were first revived in 25 mL of cooked meat medium (containing 60 g/L cooked meat and 10 g/L glucose). They were then activated via heat shock at 75°C, followed by rapid cooling on ice. The culture was incubated at 37°C for 16–18 h at 170 rpm (Heidari et al., 2025).

The activated culture (6% v/v) was transferred to pepton-glucose-yeast medium enriched with 1% (v/v) P2 stock solution. P2 contained buffering agents (50 g/L KH_2PO_4, 50 g/L K_2HPO_4, 220 g/L CH_3COONH_4), minerals (20 g/L $MgSO_4{\cdot}7H_2O$, 1 g/L $MnSO_4{\cdot}H_2O$, 1 g/L $FeSO_4{\cdot}7H_2O$, 1 g/L NaCl), and vitamins (0.1 g/L thiamine, 0.1 g/L para-aminobenzoic acid, 0.001 g/L biotin). The fermentation was carried out under anaerobic conditions at 37°C and 160 rpm for 18 h. The pH of the 50 mL hydrolysate was adjusted to 6.8, then supplemented with 1 g/L yeast extract and 3 g/L peptone in 118 mL serum bottles. The bottles were sealed, flushed with nitrogen for at least 5 min, and sterilized at 115°C for 15 min. After sterilization, a 1% (v/v) P2 solution was added, and inoculation was performed at a 6% (v/v) concentration. Fermentation proceeded at 37°C with shaking at 160 rpm for 72 h (Zhang et al., 2022a).

2.4. Lignin catalytic hydrogenolysis

The depolymerization of several lignin samples—including the lignin from this study, milled wood lignin (MWL) obtained through ball milling of raw poplar, and an extensive enzymatic hydrolysis process (Xie et al., 2024a), and commercial alkaline lignin—was carried out in a high-pressure autoclave reactor (CY-1100X, Zhengzhou, China). For each reaction, 100 mg of lignin was mixed with 30 mL of methanol and 100 mg of a 5 wt% Ru/C catalyst. The reactor was pressurized with hydrogen gas to 3 MPa and heated to 250°C for 180 min. After the reaction and subsequent cooling to room temperature, the resulting oil products were analyzed for lignin-derived compounds (monomers, dimers, and oligomers) based on our previous work (Madadi et al., 2025c).

2.5. Analysis of the chemical components

The contents of cellulose, hemicellulose, and lignin in both raw and pretreated samples were determined following the standard NREL protocol. Glucose and xylose levels were measured using high-performance liquid chromatography (HPLC) with a Bio-Rad Aminex HPX-87H column (9 µm, 7.8 × 300 mm), employing 5 mM H_2SO_4 as the mobile phase at a flow rate of 0.6 mL/min and a column temperature of 60°C (Sluiter et al., 2008).

Quantification of furfural and HMF in the liquid fraction of the biphasic system, HPLC analysis was carried out using an Aminex HPX-87H column (300 × 7.6 mm) at 60°C with 5 mM H_2SO_4 as the mobile phase at a flow rate of 0.5 mL/min.

The crystallinity index (CrI) of raw and pretreated samples was assessed *via* X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer. CrI was calculated based on the intensity of the crystalline peak (I_{002}) at $2\theta \approx 22.5°$ and the amorphous background (I_{am}) at $2\theta \approx 18.5°$. Morphological changes in the pretreated solids and extracted lignin were examined *via* scanning electron microscopy (SEM, JSM-IT500, Japan) (Madadi et al., 2023a). Specific surface area, pore volume, and pore size distribution were evaluated using a surface area analyzer (Autosorb-IQ, Micromeritics, USA). The Brunauer–Emmett–Teller (BET) method was applied for quantitative estimation.

Acetone, butanol, and ethanol concentrations were determined using a gas chromatography (GC) TRACE 1300 (Thermo, USA) equipped with a hydrogen flame ionization detector and a packed column (PorapaQ, 80/100 mesh) (Cai et al., 2016). The analysis of phenolic monomers derived from lignin depolymerization was performed using GC with the following settings: injector temperature at 275°C, split ratio 50:1; oven temperature increased from 50°C (held 5 min) to 280°C at 10 °C/min and maintained at 280°C for 10 min (Madadi et al., 2025c).

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The cellulose recovery, xylan removal, delignification, CrI, severity factor, furfural yield, and HMF yield were calculated based on **Equations S1-S7** in **Table S1**.

2.6. Economic potential and environmental impacts analysis

2.6.1. Socioeconomic analysis

The experimental data obtained in this study were used for socioeconomic analysis. **Equations 1–5** were applied to evaluate the positive effects of converting poplar biomass into acetone, butanol, ethanol, furfural, as well as lignin-derived compounds (monomers, dimers, and oligomers) on GHG emissions reduction and related social costs. The annual production capacity for acetone, butanol, ethanol, furfural, and lignin-derived compounds was quantified using **Equation 1**, based on the premise of a 140 million tonnes (Mt) annual supply of poplar biomass (F_{BP}) in China (Zhao et al., 2022).

$$F_{bi} = Y_i \times F_{BP} \qquad \text{Eq. 1}$$

where, F_{bi} (tonne) is the annual output of each product, and Y_i (tonne/tonne) signifies the corresponding yield for each process. This analysis assumes that each product targets a distinct market, including lignin monomers, dimers, and oligomers, which are intended to replace fossil-based phenol as an eco-friendly alternative, whereas acetone, butanol, ethanol, and furfural substitute their conventional commercial counterparts.

This reduction in GHG emissions is calculated by comparing baseline emissions ($F_{bi} \times C_i$) associated with the annual consumption of conventional or fossil-based products with the emissions caused by the respective biorefinery products (Ritchie et al., 2018). The GHG reduction of each product (Δ_{GHGi}, tonne $CO_{2\text{-eq}}$) was determined *via* **Equation 2**, which compares baseline emissions ($F_{bi} \times C_i$) from the industry consumption annual of conventional products to emissions from biorefinery products.

$$\Delta_{GHG_i} = F_{b_i} \times (R \times C_i - C_{b_i}) \qquad \text{Eq. 2}$$

In this equation, F_{bi} (tonne) represents the quantity of biochemical products produced in the biorefinery. C_{bi} and C_i denote the farm-to-gate GHG emission factors (kg $CO_{2\text{-eq}}$/kg bioproduct) for the biorefinery products and conventional products, respectively. R is the conversion factor of biochemical products to fossil-based products. The total GHG reduction achieved by introducing all biorefinery products to the market was calculated using **Equation 3**.

$$\Delta_{GHG} = \sum \Delta_{GHG_i} \qquad \text{Eq. 3}$$

The social cost reduction (Δ_{SCC}, USD) associated with the decrease in carbon emissions was calculated using **Equations 4** and **5**;

$$\Delta_{SCC} = \sum \Delta_{SCC_i} \qquad \text{Eq. 4}$$

$$\Delta_{SCC_i} = \Delta_{GHG_i} \times SCC \qquad \text{Eq. 5}$$

where Δ_{SCCi} denotes the social cost reduction achieved by introducing each product. *SCC* (USD/t CO_2) corresponds to the social cost of carbon, which is an estimate of the total economic damage caused by emitting one more tonne of CO_2, including costs related to environmental damage, public health, and economic disruption. *SCC* values are determined by governments based on factors such as time horizon, socioeconomic conditions, climate sensitivity, discount rate, and emission pathways. Following previous work, the average SCC in China ranges from 31.0 to 76.0 USD/t CO_2. This study used the average value of 46.33 USD/t CO_2 to compute the associated SCC (Wang et al., 2022b).

2.6.2. Farm-to-gate GHG emissions analysis

A farm-to-gate analysis, based on a 1-tonne poplar biomass reference unit (**Fig. 1**) and the mass balance flow of the optimal biorefinery process (**Fig. S1**), was conducted to comprehensively assess the environmental impacts of the system. This approach quantifies total GHG emissions across the defined system boundary, including all energy usage, process inputs, waste generation, and logistics. Laboratory-scale data were extrapolated to industrial scale following the methodology proposed by Piccinno et al. (2016). GHG emission from farm-to-gate (C_{total}, kg $CO_{2\text{-eq}}$) was estimated using **Equation 6**, by summing the product of the quantity of each consumed resource ($Q_{consumed\ resource}$) and its respective emission factor ($C_{consumed\ resource}$), with emission factors obtained from Ecoinvent 3 (**Table S3**).

$$C_{total} = \sum Q_{consumed\ source} \times C_{consumed\ resource} \qquad \text{Eq. 6}$$

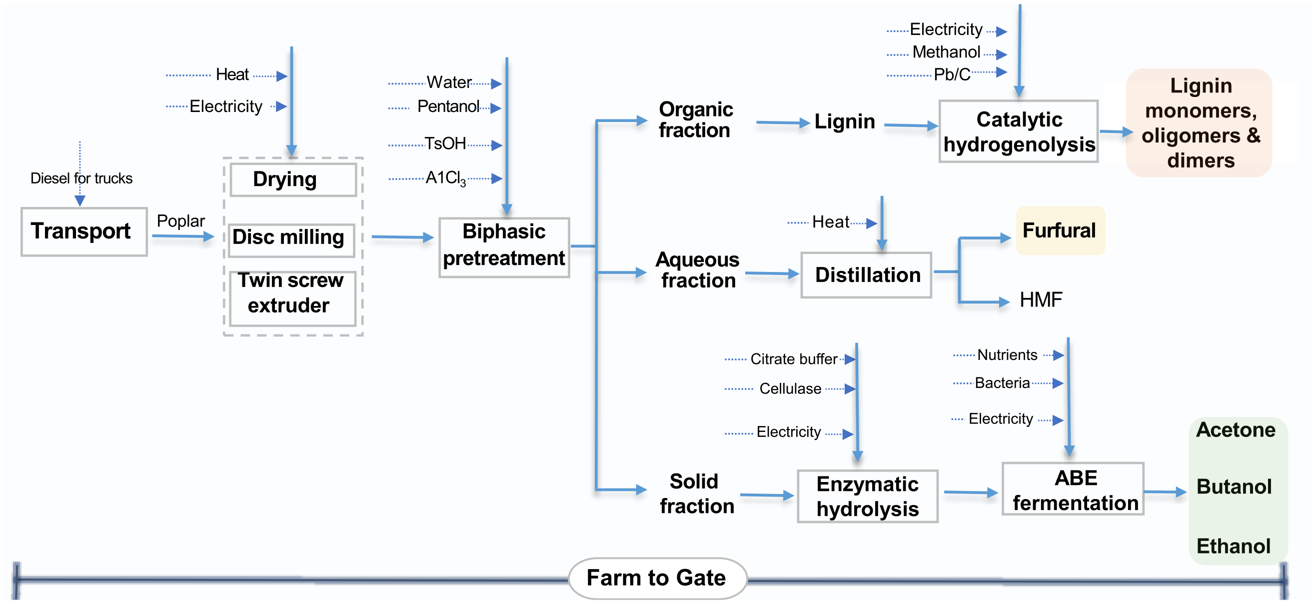

Fig. 1. Process diagram used for farm-to-gate analysis of poplar wood biorefining into acetone, butanol, ethanol, furfural, and lignin-derived compounds.

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2.6.3. Sensitivity analysis

The reliability of socioeconomic results was evaluated through sensitivity analysis to reduce uncertainty and potential over- or under-estimation of the positive environmental outcomes. This assessment examined the impact of ±30% and ±50% variations in key parameters, including biomass supply, energy consumption, and material inputs, on the reduction of GHG emissions (Madadi et al., 2025c).

2.6.4. Feasibility analysis

Investment decisions for new industrial processes or plants rely on anticipated economic returns. The financial feasibility of the proposed biorefinery was evaluated using the Net Present Value (NPV) and Internal Rate of Return (IRR) methods. NPV (**Eq. 7**) calculates the present value of future cash flows derived from the initial capital expenditure (CAPEX), where a positive NPV indicates profitability and a negative NPV implies financial unviability. IRR (**Eq. 8**) represents the discount rate at which NPV equals zero; the project is considered profitable if IRR exceeds the applied discount rate.

$$\mathrm{NPV} = \sum_{t=1}^{n} \frac{\mathrm{CF_t}}{(1+\mathrm{i})^{\mathrm{t}}} \text{-CAPEX} \qquad \text{Eq. 7}$$

$$0 = \sum_{t=1}^{\mathrm{n}} \frac{\mathrm{CF_t}}{(1+\mathrm{IRR})^{\mathrm{t}}} \text{-CAPEX} \qquad \text{Eq. 8}$$

The net cash flow in year t (CF_t) is determined as discounted annual revenues minus operational expenditures (OPEX). A 15% discount rate (i) was applied for present value estimation. The analysis incorporates the initial CAPEX in year 0 and assumes a project lifespan of 20 yr (n) to assess long-term financial viability.

Estimating CAPEX for emerging projects is challenging due to uncertain scaling factors and limited cost data. Accordingly, total equipment costs for a 730,000 tonne/yr capacity were derived from the literature (Baral and Shah, 2016), with sub-module cost allocation detailed in **Table S3**. Annual OPEX, encompassing manufacturing and sales costs, is also provided in **Table S4**. Revenue streams (**Table S4**) include acetone, butanol, ethanol, and furfural, priced at current market rates in China, as well as lignin-derived compounds, assumed to be USD 1,750 per tonne, representing the midpoint of the USD 1,500–2,000 range for phenol-formaldehyde resin.

3. Results and Discussion

3.1. Effect of $AlCl_3$ concentration in pentanol/TsOH system on lignocellulose fractionation

Building on our previous study, where 20 wt% TsOH and 60% v/v pentanol were identified as optimal pretreatment conditions (Song et al., 2025). We further examined the effect of incorporating $AlCl_3$ (4–10 wt%) at temperatures ranging from 90 to 150°C for 40 min. The fractionation efficiency was evaluated in terms of cellulose recovery, xylan removal, and delignification (**Fig. 2**).

Cellulose recovery gradually declined with increasing $AlCl_3$ dosage and temperature (**Fig. 2a**). Degradation ranged from 2% under the mildest condition (4 wt%, 90°C) to 32.2% at the most severe (10 wt%, 150°C). At 110°C, cellulose loss remained below 15% when $AlCl_3$ was ≤ 6 wt%, suggesting that moderate conditions largely preserved cellulose. The enhanced degradation observed under harsher conditions reflects acid-catalyzed hydrolysis of β-1,4-glycosidic bonds, promoted by the combined Brønsted acidity of TsOH and the Lewis acidity of Al^{3+} (Sun et al., 2024). In contrast, xylan was highly susceptible to solubilization across all tested conditions (**Fig. 2b**). Xylan was far more susceptible to removal. Solubilization increased from 61.6% (90 °C, 4 wt%) to nearly complete (>99%) under higher severities. At 130°C, removal exceeded 98% with 8 wt% $AlCl_3$ and approached 100% with 10 wt%. Complete solubilization was achieved at 150°C across all concentrations. This efficiency is attributed to strong acid-catalyzed cleavage of hemicellulosic linkages, with Al^{3+} ions further enhancing hydrolysis (Sun et al., 2024). Pentanol likely aids by stabilizing dissolved sugars in the organic phase, preventing reprecipitation (Fernández-Bautista et al., 2024). Delignification was strongly temperature dependent (**Fig. 2c**). At 90°C, removal did not exceed 53% even with 10 wt% $AlCl_3$, whereas increasing the temperature to 110°C boosted lignin dissolution to over 80%. The highest delignification (88.7%) occurred at 150°C with 10 wt% $AlCl_3$. This improvement reflects Al^{3+} assisted cleavage of ether and ester linkages in lignin–carbohydrate complexes, together with TsOH-driven protonation of lignin structures. Elevated temperatures accelerated these reactions, enabling more extensive solubilization.

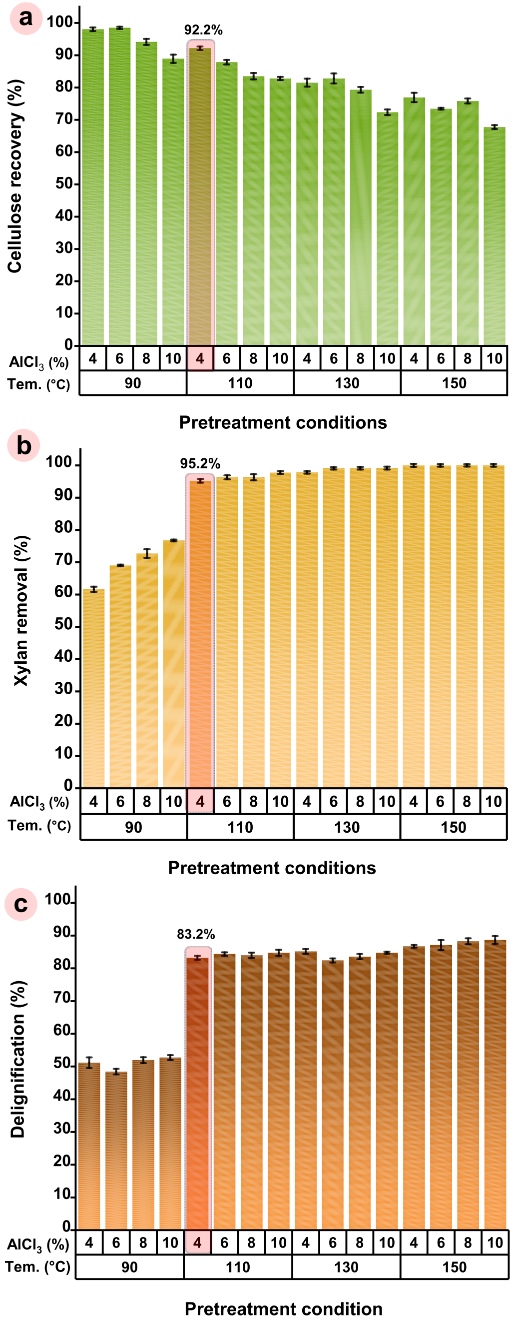

Fig. 2. Effect of $AlCl_3$ concentration (4–10 wt%) and temperature (90–150°C) on poplar biomass fractionation in the TsOH/pentanol biphasic system (20 wt% TsOH, 60% v/v pentanol, 40 min). Shown are **(a)** cellulose recovery, **(b)** xylan removal, and **(c)** delignification. Data are presented as mean ± SD (n = 3).

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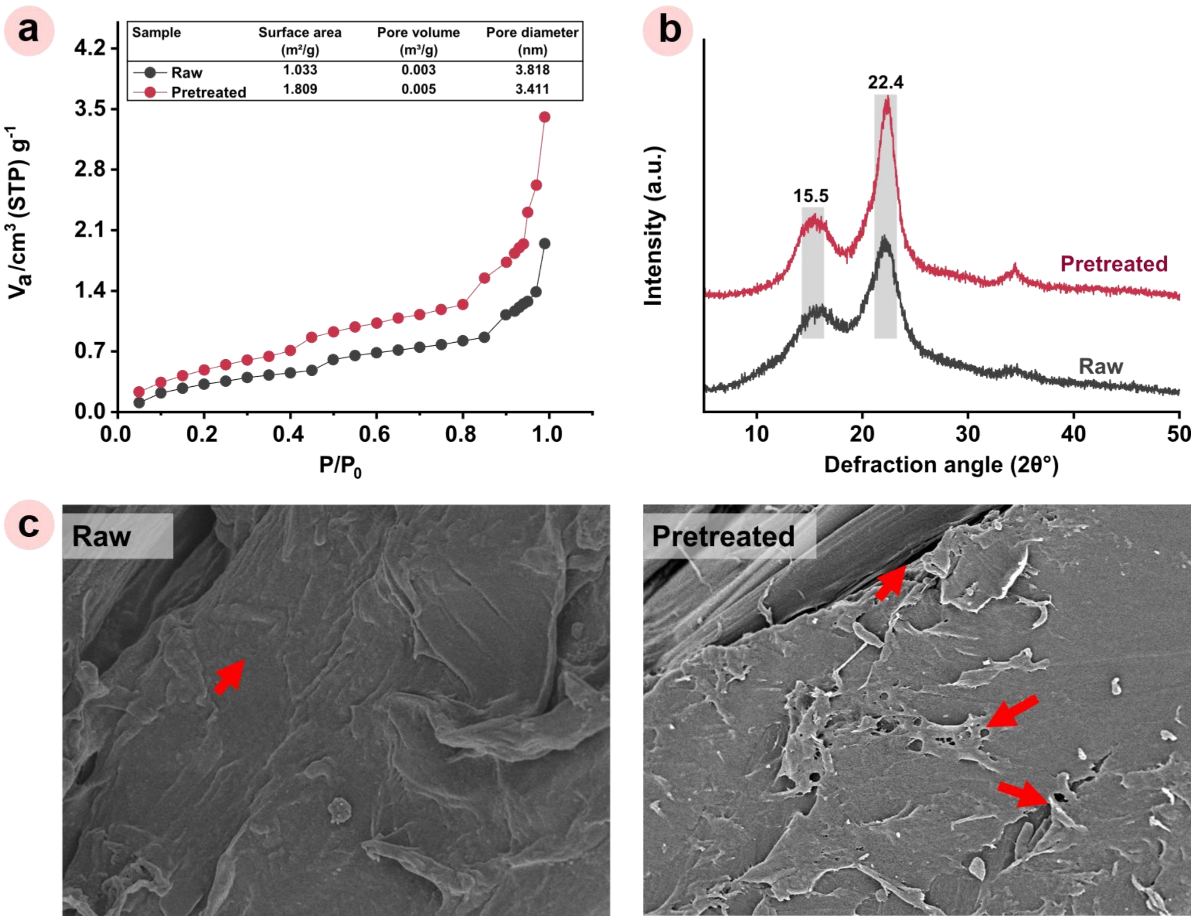
The optimal condition was identified as 110°C with 4 wt% $AlCl_3$, achieving 83.2% delignification and 95.2% xylan removal while limiting cellulose degradation to 7.8% (cellulose recovery 92.2%). Based on the severity factor (**Eq. S4**), this condition corresponds to a mild pretreatment (severity factor 1.90), indicating low thermal input. Notably, this performance matched that of the TsOH/pentanol system alone at 140°C, highlighting the role of $AlCl_3$ in reducing thermal severity without sacrificing efficiency. In summary, the synergistic action of TsOH, $AlCl_3$, and pentanol enabled effective lignocellulose fractionation. Higher $AlCl_3$ concentrations and temperatures enhanced the removal of hemicellulose and lignin, but also promoted cellulose loss. Moderate conditions, however, allowed selective fractionation with minimal cellulose degradation, offering a promising route for energy-efficient biomass pretreatment.

The structural changes induced by TsOH/pentanol + $AlCl_3$ at the optimum condition (110°C, 4 wt% $AlCl_3$) were evaluated in comparison with raw poplar biomass using BET, XRD, and SEM analyses (**Fig. 3**). BET results showed that the raw biomass had a specific surface area of 1.033 m^2/g, pore volume of 0.003 m^3/g, and average pore diameter of 3.818 nm. After pretreatment, the surface area increased to 1.809 m^2/g and the pore volume rose to 0.005 m^3/g, while the average pore diameter decreased slightly (**Fig. 3a**). The increase in surface area and pore volume can be attributed to the removal of hemicellulose and partial delignification, which created additional voids and exposed internal structures (An et al., 2020). At the same time, the smaller pore diameter suggests that the fiber bundles collapse or fragment, leading to narrower but more numerous pores. These changes collectively reflect a substantial structural rearrangement of the biomass matrix (Wan et al., 2010).

XRD analysis revealed further evidence of structural alteration (**Fig. 3b**). Both raw and pretreated samples displayed typical cellulose I diffraction peaks at 2θ ≈ 22.4° and a broad peak near 15°. The CrI increased from 38.3% in raw biomass to 56.2% after pretreatment. This rise in CrI is consistent with the preferential removal of amorphous components such as hemicellulose and lignin, which increases the relative proportion of crystalline cellulose (Saleknezhad et al., 2025). While higher CrI is often interpreted as reduced accessibility, in this case, the enhanced porosity and disrupted morphology (confirmed by BET and SEM) offset this effect, ensuring that the cellulose remains more accessible to subsequent enzymatic or catalytic attack (Azad et al., 2024). SEM imaging corroborated these findings. The raw biomass exhibited a compact, smooth surface with intact fiber bundles, characteristic of a dense lignocellulosic network. In contrast, the pretreated sample showed extensive disruption, with visible cracks, pores, and surface roughness (**Fig. 3c**). These morphological changes indicate loosening of the cell wall structure and breakdown of lignin–carbohydrate complexes (Zhang et al., 2022b), consistent with the observed increase in porosity and relative crystallinity. Overall, these structural analyses confirm that TsOH/pentanol + $AlCl_3$ pretreatment enhances biomass fractionation by increasing surface area and pore volume, selectively removing amorphous components, and disrupting cell wall integrity. Together, these modifications improve substrate accessibility despite the higher apparent crystallinity.

The presence of Al^{3+} in the TsOH/pentanol system can significantly influence the delignification pathway due to its Lewis acid characteristics (**Fig. S2**). The Al^{3+} center coordinates with the oxygen atoms of ether and ester groups in lignin and lignin–carbohydrate complexes, withdrawing



Sample	Surface area (m²/g)	Pore volume (m³/g)	Pore diameter (nm)
Raw	1.033	0.003	3.818
Pretreated	1.809	0.005	3.411

Fig. 3. Physicochemical properties of raw and pretreated poplar biomass. **(a)** Surface area, pore volume, and pore diameter were determined by BET analysis. **(b)** XRD patterns collected in the 2θ range of 5–50° at a scanning rate of 2°/min. **(c)** SEM micrographs at 5 µm magnification showing surface morphology before and after pretreatment.

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electron density from the oxygen and increasing the electrophilicity of the neighboring carbon atoms (Song et al., 2026). This interaction facilitates the cleavage of β–O–4 and C–O–C linkages, thereby accelerating lignin depolymerization (Saleknezhad et al., 2025). Furthermore, the polarization induced by Al^{3+} lowers the energy barrier for C–O bond scission and enhances the selectivity of delignification (Madadi et al., 2025a). The cooperative Brønsted–Lewis acid interaction between TsOH and $AlCl_3$, therefore, plays a crucial role in enhancing lignin removal efficiency and preserving carbohydrate integrity during pretreatment (Madadi et al., 2025a).

In conclusion, the TsOH/pentanol + $AlCl_3$ pretreatment led to significant structural modifications in poplar biomass. Increased surface area, enhanced porosity, and the selective removal of hemicellulose and lignin improved cellulose accessibility, while most of the cellulose remained intact despite the increased crystallinity. The cooperative action of catalysts facilitated selective cleavage of lignin–carbohydrate linkages, promoting delignification without substantial cellulose degradation. The biphasic system further enhanced lignin solubility in the organic phase, preventing redeposition and maintaining the integrity of the solid substrate. Together, these structural and mechanistic effects underpin the observed high enzymatic digestibility and efficient biomass fractionation, providing a clear explanation for the improved sugar release and conversion achieved under mild pretreatment conditions.

3.2. Integrated production of bio-based platform chemicals

3.2.1. Furfural production

The TsOH/pentanol + $AlCl_3$ system fractionated poplar into three distinct streams, in which, during pretreatment, part of the solubilized xylose was dehydrated to furfural, while a smaller fraction of glucose was converted to HMF (**Fig. 4**).

Furfural production was strongly influenced by both temperature and $AlCl_3$ concentration (**Fig. 4a**). At 90°C, furfural titers remained below 6.0 g/L regardless of catalyst loading. Raising the temperature to 110°C significantly increased furfural levels, reaching 11.3 g/L at a 4 wt% $AlCl_3$ concentration. Further increases to 130–150°C provided only marginal improvements, with a maximum of 12.5 g/L at 150°C and 10 wt% $AlCl_3$. However, this condition caused severe cellulose degradation (31.1 g/L glucose release) (**Fig. 4b**), compromising process selectivity. Therefore, 110°C and 4 wt% $AlCl_3$ were identified as the optimal conditions, balancing high furfural production (68.5%, 11.3 g/L) with minimal cellulose loss. HMF production followed a similar temperature and catalyst-dependent trend but remained at much lower concentrations (**Fig. 4b**). It was not very important at 90 °C (< 0.1 g/L), increased modestly at 110°C (0.19 g/L at the highest $AlCl_3$), and peaked at 2.95 g/L at 150°C and 10 wt% $AlCl_3$. Under the optimal condition (110°C, 4 wt% $AlCl_3$), HMF reached only 0.04 g/L, with limited cellulose solubilization (3.6 g/L) and substantial xylan extraction (25.8 g/L). These results indicate that moderate severity favors the selective conversion of hemicellulose to furfural, while suppressing undesired side reactions (Qiao et al., 2025).

Yield-based analysis (**Fig. 4c**) reinforced these findings. Furfural yields increased steadily with temperature, reaching ~68–70% at 130°C, while HMF yields were more sensitive to $AlCl_3$ loading, peaking at 13.6% at 150°C and 10 wt% $AlCl_3$ when furfural yields were ~72%. These results highlight the system's ability to couple aldose–ketose isomerization with ketose dehydration in a one-pot process, enabling efficient conversion of xylose, xylan, and hemicellulose to furfural. The formation of HMF was negligible (1.34 g/kg_{poplar}), indicating that glucose degradation was low (<10%) under the mild conditions (110°C, 40 min). Under these conditions, most glucose remained in the cellulose fraction and only a small amount was released into the aqueous phase, which limited its participation in dehydration reactions to HMF.

Mechanistically, $AlCl_3$ functions as a Lewis acid, with Al^{3+} coordinating to the carbonyl oxygen of xylose, thereby promoting isomerization to xylulose, a ketopentose that is more susceptible to dehydration (Wang et al., 2022a). TsOH contributes Brønsted acidity, catalyzing the dehydration of xylulose to furfural as well as glucose-to-fructose isomerization, followed by dehydration to HMF (Saleknezhad et al., 2025). The combined Lewis–Brønsted acid environment lowers the activation barrier for xylose conversion (**Fig. S2**), resulting in high furfural selectivity under comparatively mild conditions (Jiang et al., 2018). Temperature further modulates this synergy. At 90 °C, reaction rates are too low to achieve efficient conversion. At 110°C, sufficient thermal energy facilitates $AlCl_3$-driven isomerization and TsOH-catalyzed dehydration, resulting in high furfural yields with minimal cellulose degradation. At 130–150°C, furfural yields plateau, but cellulose hydrolysis accelerates, undermining overall selectivity and carbon efficiency.

Compared with earlier one-pot processes, which typically required temperatures of 150–170°C and long reaction times (>360 min), the $AlCl_3$–TsOH/pentanol system enabled efficient furfural production at a lower temperature and shorter reaction times (**Table 1**). Such performance underscores the system's strong potential for selective hemicellulose valorization in integrated biorefineries.

3.2.2. ABE production

Enzymatic hydrolysis of the pretreated solid residue using Cellic® CTec 2 under optimized conditions yielded 49.3 g/L glucose (**Fig. 5**). The presence of $AlCl_3$ during pretreatment facilitated delignification under mild conditions, generating a cellulose-rich substrate that was highly amenable to enzymatic hydrolysis.

ABE fermentation was then performed under two setups: (i) non-supplemented nutrient medium (control, **Fig. 5a**) and (ii) nutrient-supplemented medium (**Fig. 5b**), to evaluate the effect of nutrient availability on glucose utilization and solvent production. Initial glucose concentrations were comparable between the two systems: 49.3 g/L in the nutrient-supplemented condition and 48.3 g/L in the control. In the nutrient-

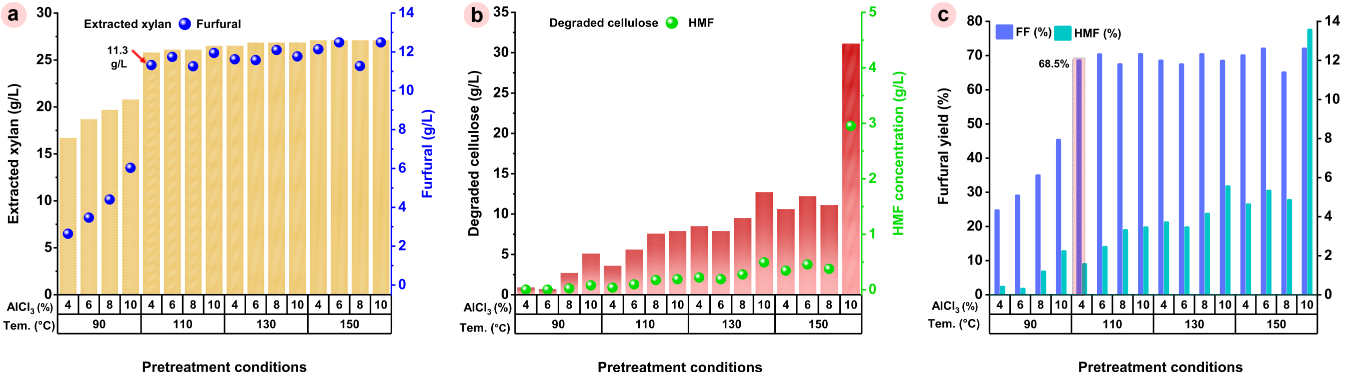

Fig. 4. Effect of $AlCl_3$ concentration (4–10 wt%) and temperature (90–150°C) on xylan and cellulose conversion to furfural and HMF, respectively. **(a)** Furfural concentration relative to extracted xylan (g/L). **(b)** HMF concentration concerning cellulose degradation. **(c)** Yields of furfural and HMF under different pretreatment conditions. Data are presented as mean ± SD (n = 3).

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Table 1.
Comparison of recent one-pot furfural production yields from various biomass feedstocks using different catalysts, solvents, and reaction conditions.

Substrate	Catalyst	Solvent	Condition	Furfural Yield (%)	Ref.
Corncob	$AlCl_3$	HCl/DMC	100 °C, 360 min	93.3	Ariyanti et al. (2025)
Sugarcane bagasse	$H_3PO_4/AlCl_3$	Water/acetone	170 °C, 5 min	72.2	Sun et al. (2024)
Olive stone Almond hull	$AlCl_3.6H_2O$	Me-THF/ KBr	150 °C, 10 min	42 39	Salgado-Ramos et al. (2024)
Dry pellet pomace Olive virgin pomace	$NbOPO_4$	Water	180 °C, 210 min	57 67	Lima et al. (2024)
Corncob	Zeolite	Water/LiBr	170 °C, 360 min	29.9	Zhu et al. (2023)
Corn cob	CX_4SO_3H	Butyl acetate/NaCl	160 °C, 60 min	56	Castro et al. (2023)
Corncob	$AlCl_3$/NaCl/LiCl	Water/MIBK	150 °C, 40 min	83.2	Nzediegwu and Dumont (2023)
Grass	H_2SO_4	Water	180 °C, 20 min	42.3	Santos et al. (2023)
Sugarcane bagasse	H_2SO_4	DESs/DMSO	140 °C, 40 min	28.4	Amesho et al. (2022)
Corncob	SO_4^{-2}/CX-DMSn	Water	180 °C, 300 min	65.7	Cai et al. (2021)
Switchgrass	H_2SO_4	ChCl/MIBK	170 °C, 60 min	84	Chen et al. (2019)
Poplar	**$AlCl_3$/TsOH**	**Water/pentanol**	**110 °C, 40 min**	**68.5**	**This Study**

supplemented fermentation, complete glucose consumption occurred within 120 h, whereas 9.6 g/L of glucose remained unutilized in the control, highlighting the improved substrate assimilation that occurred when nutrients were provided. At 120 h, solvent titers in the nutrient-supplemented condition reached 2.1 g/L acetone, 3.6 g/L ethanol, and 10.5 g/L butanol, yielding a total ABE concentration of 16.2 g/L. In contrast, the control condition produced 0.96 g/L acetone, 0.96 g/L ethanol, and 9.23 g/L butanol, totaling 11.15 g/L ABE. The glucose-to-ABE conversion yield was 0.329 g/g in the nutrient-supplemented system, compared with 0.304 g/g in the control.

The superior solvent production observed under nutrient-supplemented conditions can be attributed to enhanced microbial growth and metabolism, as well as the alleviation of NADH limitation during solventogenesis. Nutrient supplementation provides essential cofactors, vitamins, and nitrogen sources that support enzymatic activities in glycolysis and solventogenic pathways (Diez-Antolínez et al., 2016). Central enzymes catalyze the conversion of pyruvate to acetyl-CoA and butyryl-CoA, and aldehydes are subsequently reduced to ethanol and butanol by their respective dehydrogenases (Zhou et al., 2023). Since 1 mol of butanol synthesis requires 4 mol of NADH, whereas glycolysis produces only 2 mol per mol of glucose, NADH availability constitutes a limiting factor in solventogenesis (Liao et al., 2019). Nutrient supplementation thus increases intracellular NADH and ATP levels, accelerates the transition from acidogenesis to solventogenesis, mitigates premature acid accumulation, and results in higher solvent titers (Woo et al., 2018). These mechanistic considerations explain the observed improvements in ABE production and carbon conversion efficiency in nutrient-supplemented cultures, consistent with previous studies in *C. acetobutylicum* (Dziemianowicz et al., 2022). These results align with previous reports (Amiri et al., 2014; Rezaei et al., 2021), which indicate that nutrient supplementation increases ABE titers to 10–14 g/L.

A comprehensive mass, carbon, and energy balance was performed, focusing on the sugar fraction of 1 kg of poplar biomass, which consisted of 459 g of cellulose and 271 g of hemicellulose. The mass balance quantified the distribution of these sugar-based components among the main sugar-based products (acetone, butanol, ethanol, furfural, and HMF). The carbon yield in these products was approximately 62.4%, while the energy yield reached 72.8%, calculated based on the standard enthalpy of combustion of each compound (**Table S2**). These results confirm the efficiency of carbon conversion and provide a quantitative assessment of the energetic performance of the sugar-based fraction of the process.

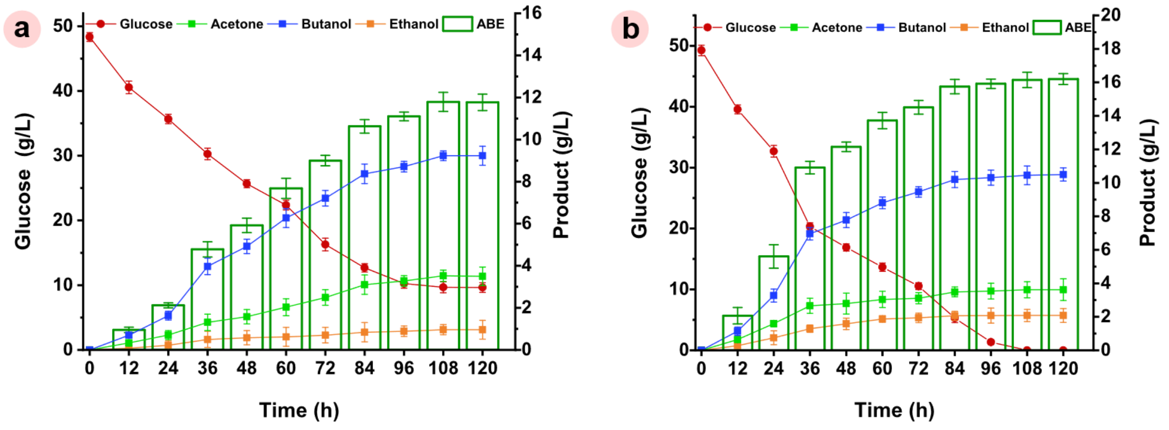

Fig. 5. ABE production potential of the pretreated cellulose-rich substrate. Glucose fermentation to acetone, butanol, and ethanol by the *C. acetobutylicum* strain at 37°C for 120 h and 160 rpm. **(a)** Fermentation without nutrient supplementation (control). **(b)** Fermentation with nutrient supplementation. Data are presented as mean ± SD (n = 3).

3.2.3. Production and selectivity of lignin-derived compounds

The recovered lignin, subjected to optimized conditions, was then treated with Ru/C-catalyzed hydrogenolysis at 250°C, yielding aromatic monomers, dimers, and oligomers. Quantitatively, biphasic lignin from TsOH/pentanol + $AlCl_3$ pretreatment achieved the highest monomer yield at 46.4 wt%, accompanied by 9.3 wt% dimers and 17.4 wt% oligomers. MWL displayed a slightly lower monomer yield (45.3 wt%) and dimers/oligomers (19.4 wt%), while alkaline lignin produced only 28.1 wt% monomers and 17.8 wt% dimers/oligomers (**Fig. 6a**).

The types of dimers and oligomers produced varied significantly with lignin type, reflecting differences in structural integrity and bond preservation (Obrzut et al., 2023). MWL predominantly generated β-O-4, β-5, and β–β dimers, along with S–G and G–G linkages, consistent with its well-preserved native structure. Its oligomers were mainly linear β-O-4 trimers and β-β-β-O-4 hybrids, indicating limited condensation and retention of labile ether bonds, which favors selective monomer production (Xie et al., 2024a). Alkaline lignin, in contrast, contained a higher proportion of condensed linkages, including 5–5, 4–O–5, and β–5 with C–C bonds, reflecting significant structural degradation during alkaline pretreatment. Correspondingly, its oligomers were branched and contained more C–C linkages, which reduces susceptibility to hydrogenolysis and results in lower monomer yields and selectivity. Biphasic lignin exhibited a combination of β-O-4, β–β, and β-5 dimers, mostly uncondensed, and short linear oligomers rich in β-O-4 and resinol structures (Madadi et al., 2025c). This composition supports the observed high monomer yields and syringyl selectivity, as the preservation of these linkages facilitates targeted cleavage under Ru/C-catalyzed hydrogenolysis. Overall, the distribution of dimers and oligomers directly correlates with the degree of bond preservation and condensation, explaining the differences in monomer yield and selectivity among the lignin types (Chen et al., 2023). The superior performance of biphasic lignin is attributed to Ru-catalyzed self-transfer hydrogenolysis, in which lignin itself serves as a hydrogen donor, generating active species that efficiently cleave ether bonds with minimal external hydrogen input, supporting atom economy and a reduced carbon footprint (Shen et al., 2022). Notably, lignin obtained from TsOH/pentanol pretreatment was previously reported to yield only 33.9% phenolic monomers, substantially lower than the current work (Xie et al., 2024b).

The biphasic lignin exhibited remarkable selectivity toward syringyl-type monomers, with 4-propyl syringol (Pr-S) and 4-ethyl syringol (Et-S) accounting for 53.9% and 43.3% of total monomers, respectively. Guaiacyl-type products, such as 4-propyl guaiacol (Pr-G) and 4-ethyl guaiacol (Et-G), were minimal (0.8% and 1.0%), and unidentified compounds contributed only 1.2% (**Fig. 6b**). This preferential release of S-type phenolics is linked to the well-preserved β-O-4 linkages in biphasic lignin, which favor selective cleavage during hydrogenolysis (Madadi et al., 2025c). MWL exhibited a similar monomer profile, with Pr-S (40.8%) and Et-S (45.1%) dominating, alongside moderately higher guaiacyl fractions (Pr-G 6.0%; Et-G 5.5%). The comparable selectivity to biphasic lignin indicates that retention of β-O-4 linkages and structural integrity is key for efficient monomer production (Zijlstra et al., 2019). In contrast, alkaline lignin produced a heterogeneous distribution with lower syringyl monomers (Pr-S 23.9%, Et-S 20.7%), higher guaiacyl monomers (Pr-G 13.8%, Et-G 10.3%), and a substantial fraction of unidentified compounds (31.7%). The reduced selectivity arises from structural degradation during alkaline pretreatment, which breaks β-O-4 and other ether linkages, limiting the formation of specific monomers (Min et al., 2017).

3.3. Environmental impacts and economic potential of biomass biorefinery

The environmental performance of the poplar biomass biorefinery was rigorously assessed through a farm-to-gate lifecycle analysis. The annual processing of 140 Mt of biomass yields a substantial output of bioproducts, including 4.5 Mt of acetone, 2.5 Mt of ethanol, 12.9 Mt of butanol, 25.7 Mt of furfural, and 29.8 Mt of lignin-derived compounds (**Table 2**). The process itself generates a total of 916.33 kg $CO_{2\text{-eq}}$/tonne of poplar biomass processed, equivalent to 0.92 kg $CO_{2\text{-eq}}$/kg of biomass (**Table S5**). A critical finding is the dominant contribution of energy consumption to the facility's operational footprint, which accounts for 71.0% of total emissions. Within this category, heat generation is the most significant factor (67.6%). This high contribution of heat consumption is mainly due to the energy-intensive

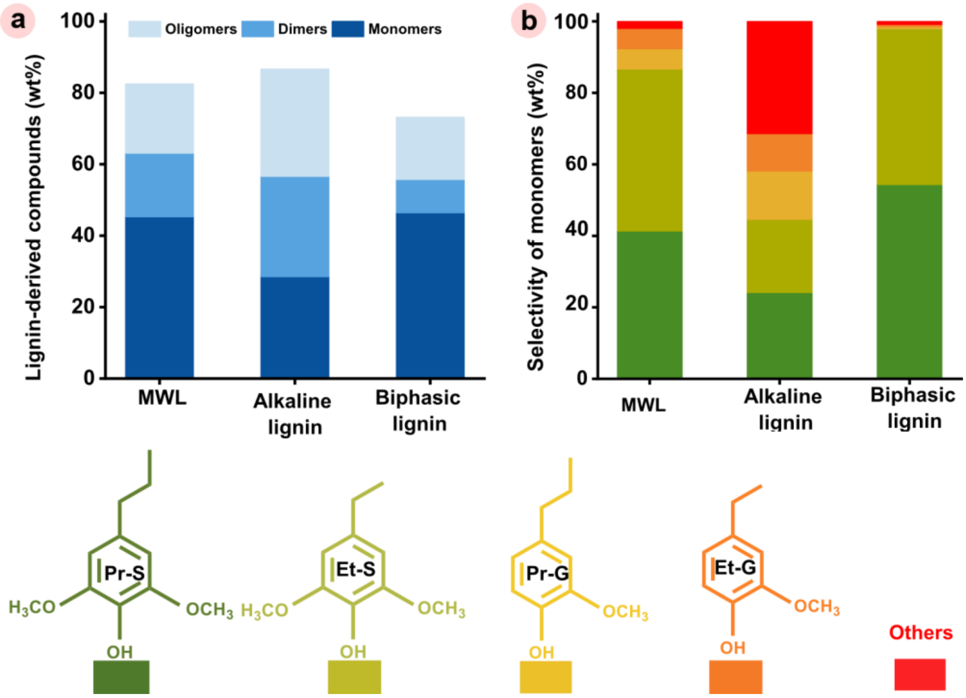

Fig. 6. Lignin depolymerization to derivatives with Ru/C, 3 MPa, 250°C, 180 min. **(a)** Yields of monomers, dimers, and oligomers. **(b)** Lignin monomer selectivity. Biphasic lignin refers to the lignin obtained in this study.

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nature of solvent recovery and biomass pretreatment operations. Notably, a two-phase system needs considerable thermal energy to maintain phase separation and solvent recovery, while downstream distillation of ABE further increases the thermal load. These process units contribute most to the energy consumption, highlighting that process integration strategies, such as vapor recompression, heat recovery, or coupling with renewable heat sources, could significantly reduce the GHG impact of biorefinery. Material inputs and transportation contribute 25.8% and 2.8%, respectively (**Fig. 7a**).

The net environmental benefit, however, is profound. As detailed in **Table 2**, several key biorefinery products exhibit markedly lower farm-to-gate emissions than their fossil-based analogues. For example, the production of 1 kg of lignin-derived compounds emits 1.32 kg $CO_{2\text{-eq}}$, which is 56.1% lower than the 3.01 kg $CO_{2\text{-eq}}$ associated with producing an equivalent quantity of phenol. Similarly, bio-based furfural and butanol demonstrate reductions of 25.4% and 10.3%, respectively, compared to their fossil-derived counterparts. Ethanol shows a particularly notable advantage: its farm-to-gate footprint of 2.76 kg $CO_{2\text{-eq}}$/kg is 31.6% lower than that of gasoline (4.04 kg $CO_{2\text{-eq}}$/kg), reflecting the benefit of displacing fossil transportation fuels with cellulosic ethanol. In contrast, acetone exhibits no significant benefit, with nearly identical GHG emissions compared to its fossil-based equivalent (2.73 *vs*. 2.40 kg $CO_{2\text{-eq}}$/kg), underscoring that not all products achieve climate gains under current process conditions. The lower GHG emission of compounds derived from lignin compared to phenol is primarily due to the avoidance of fossil-based benzene oxidation processes and the utilization of renewable carbon feedstocks, which recycle biogenic CO_2 within the system boundary (Meijer et al., 2022). Conversely, the comparable emissions of acetone indicate that its bio-based production pathway remains constrained by high energy demands, primarily due to the need for distillation, which offsets the potential carbon savings. Importantly, because lignin-derived compounds and furfural together constitute over 70% of the product portfolio by weight, their substantial reductions significantly contribute to the overall GHG savings of the biorefinery, underscoring the climate mitigation potential of valorizing both carbohydrate- and lignin-derived streams.

The large-scale substitution of conventional products drives substantial avoided emissions (Δ_{GHG}) and associated reductions in socioeconomic costs (Δ_{SCC}), as quantified in **Fig. 7b**. The replacement of phenol with lignin-derived compounds delivers the most significant benefit, avoiding 50.47 Mt of $CO_{2\text{-eq}}$ and approximately USD 2338 million in social costs. Collectively, the biorefinery's product portfolio enables a total of 64.12 Mt of $CO_{2\text{-eq}}$ reduction and USD 2971 million in *SCC*. This finding is consistent with other studies emphasizing the potential of biorefineries to reduce GHG emissions. Three factors primarily dictate the mitigation potential: the availability of feedstock, biorefinery placement, and the number of products generated. For example, valorising corn stover into bioethanol, biodiesel, biomethane, and value-added byproducts resulted in a 4.3 Mt decrease in $CO_{2\text{-eq}}$ emissions (Alavijeh et al., 2023). In another case, refining one tonne of apple pomace into biogas and mycoprotein was projected to decrease $CO_{2\text{-eq}}$ emissions by 2.5 tonnes (Abbasi-Riyakhuni et al., 2024) More recently, an analysis showed that refining 140 Mt of poplar biomass into ethanol, lignin oil, and furfural (*via* a two-step process) could reduce CO_2 emissions by 75.3 Mt and provide socioeconomic savings of USD17.3 billion (Madadi et al., 2025a). The integrated biorefining process presented

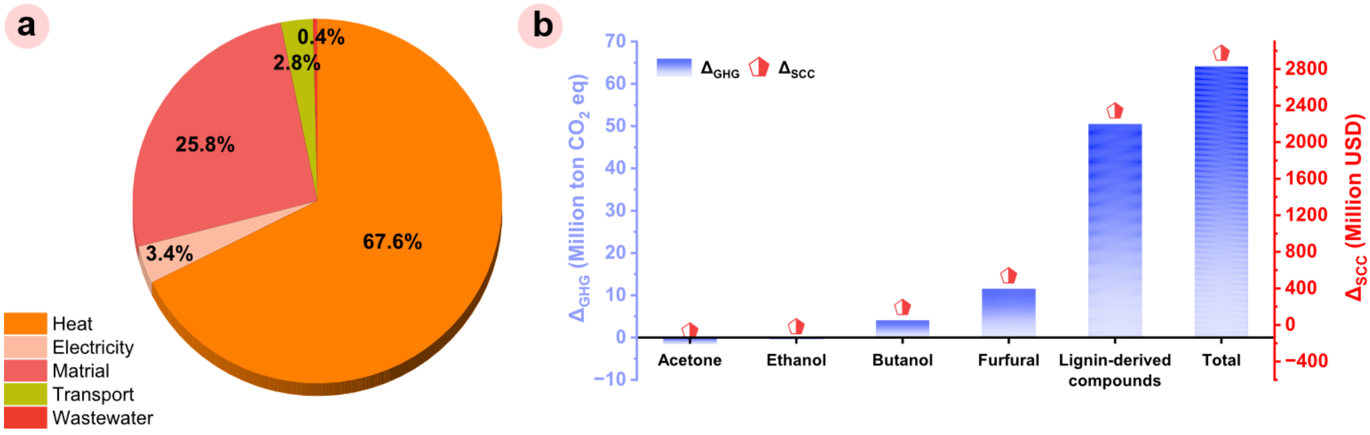

Fig. 7. **(a)** The relative share of individual resource inputs contributing to the facility's comprehensive farm-to-gate carbon footprint. **(b)** The overall reduction in greenhouse gas emissions (Δ_{GHG}) and its calculated economic benefit (Δ_{SCC}) achieved through byproduct utilization.

Table 2.
Annual production of multiple products from 140 Mt of available poplar biomass and the associated farm-to-gate GHG emissions.

Products	**Annual Production, F_i (Mt)**	**Weight Fraction, X_i (kg/kg)**	**$C_{\text{bioproducts}}$ (kg $CO_{2\text{-eq}}$/kg Product)**	**$C_{\text{fossil-based products}}$ (kg $CO_{2\text{-eq}}$/kg Fossil-Based Product)**	**R (kg/kg)**
Acetone	4.5	0.06	2.73	2.40[a]	1
Ethanol	2.5	0.03	2.76	4.04	0.64[b]
Butanol	12.9	0.17	2.78	3.10	1
Furfural	25.7	0.34	1.31	1.77[c]	1
Lignin-derived compounds	29.8	0.40	1.31	3.01[a]	1
Total products	75.4	1.00		-	

[a] According to the Ecoinvent 3 database.
[b] Estimated by dividing the specific energy of cellulosic ethanol by the specific energy of gasoline, with the numbers 29.70 MJ/kg and 46.5 MJ/kg, respectively.
[c] Hong et al. (2015)

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in this study, with its broader product slate, achieves a significant mitigation impact of 64.12 Mt, underscoring the trade-offs between product diversification and maximum emission savings. This comparison highlights the capability of tailored biorefinery configurations to generate substantial environmental and socioeconomic benefits.

A sensitivity analysis (**Fig. 8**) reveals that the net GHG saving is most sensitive to biomass availability. A 30% and 50% increase in feedstock supply results in a 38.5% and 52.2% increase in Delta GHG, respectively, while equivalent decreases result in a 25.6% and 41.4% decrease. The result is also negatively sensitive to energy input, with 30% and 50% higher heat consumption resulting in a 22% and 37.4% reduction in net benefit, respectively. These findings confirm that securing a robust biomass supply and optimizing energy efficiency are paramount to maximizing the environmental return. The economic potential of the biorefinery is directly derived from its environmental performance, as reflected in the *SCC*. The significant avoidance of GHG emissions translates into considerable economic value by mitigating future climate-related damages. The total Δ_{SCC} of USD 2971 million represents the projected economic benefit accrued from avoiding environmental damage by displacing 64.12 Mt of $CO_{2\text{-eq}}$ emissions. This figure quantifies the substantial positive externality of the biorefinery operation. The substitution of phenol with lignin-derived compounds alone accounts for the majority of this benefit (USD 2338 million), highlighting the exceptionally high economic potential of valorizing lignin, which is traditionally a low-value stream. These results demonstrate that the integrated biorefinery model not only mitigates carbon emissions but also generates significant societal economic value, providing a powerful economic rationale for its development from a policy perspective.

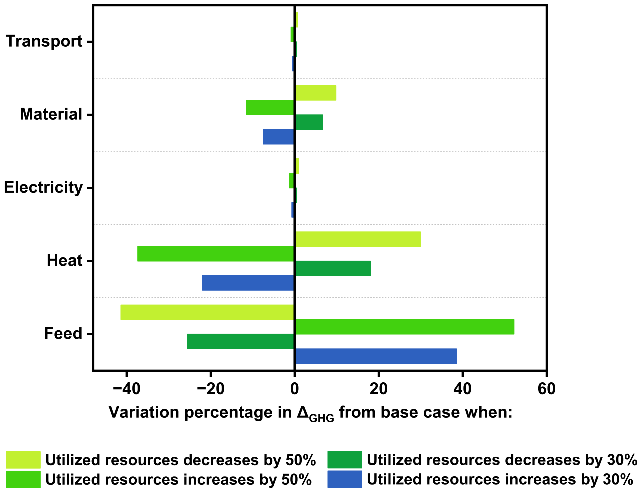

Fig. 8. Impact of ±30% and ±50% resource availability fluctuations on the system's GHG reduction potential (Δ_{GHG}). The central value represents the base-case mitigation of 64.12 Mt $CO_{2\text{-eq}}$.

The financial viability of this biorefinery concept is primarily evaluated for a commercial-scale plant with an annual processing capacity of 730,000 tonnes of biomass. Establishing this operation requires a considerable CAPEX of USD 387.0 million, encompassing total plant direct costs (USD 235.3 million), total plant indirect costs (USD 93.7 million), and working capital. Annual OPEX is projected at USD 416.7 million, with major cost drivers being raw materials (poplar, pentanol, TsOH), energy, labor (USD 50.0 million), maintenance (USD 16.5 million), and fixed charges (USD 41.7 million). Despite these significant costs, the plant achieves a robust net annual cash flow of USD 116.5 million. The compelling financial attractiveness is definitively demonstrated by key investment metrics: a Net Present Value (NPV) of USD 342.2 million at a 15% discount rate—significantly exceeding the initial CAPEX—and a high IRR of 29.9%. The high IRR is primarily due to the concurrent production of a range of bioproducts derived from biomass, which diversifies revenue streams and minimizes waste generation. The main feedstock of this biorefinery is also inexpensive and classified as a waste product. To estimate the financial potential at the national scale, as presented in the environmental analysis (140 Mt of biomass annually), a direct scaling approach based on the number of equivalent biorefineries was employed. This scale of operation would require approximately 192 individual facilities of the same capacity (730,000 tonnes/yr). Assuming each plant achieves a similar financial performance, the aggregate NPV for the entire system is projected to be approximately USD 65.7 billion (192 plants × USD 342.2 million per plant).

These metrics confirm strong profitability and a compelling financial rationale for the investment, indicating a high likelihood of full capital recovery coupled with substantial returns over the project's operational lifetime. It is essential to note that this aggregate estimate is a theoretical projection that assumes the successful replication of the base-case financial model across all facilities, without accounting for potential economies of scale, regional cost variations, or market price effects resulting from such a large volume of output. Nonetheless, this robust financial profile de-risks the substantial upfront investment and underscores the potential for commercially viable, sustainable industrial operations at a transformative national scale.

4. Conclusions and future direction

This study presents a comprehensive and integrated biorefinery strategy that converts poplar biomass into a range of high-value, bio-based products. At its core is a mild biphasic pretreatment system that efficiently fractionates biomass, enabling direct furfural production with a yield of 68.5%, the fermentation of cellulose residue into a butanol-rich solvent mixture, and the catalytic conversion of lignin into monomers with a yield of 46.4%. The environmental and economic potential of this multi-product strategy is substantial. Scaling the model to the nation's available biomass could reduce GHG emissions by more than 64.12 Mt of $CO_{2\text{-eq}}$ annually, while generating socioeconomic savings of USD 2.97 billion. Among all product streams, the substitution of fossil-based phenol with lignin-derived compounds emerged as the single largest contributor to these benefits. Equally important, this environmental promise is matched by strong economic performance. The process is both technically feasible and financially attractive, with a projected net present value of USD 342.2 million for a standard facility and an exceptional rate of return. These results demonstrate that sustainable biorefining can be both a profitable investment and an environmental imperative.

This work provides a validated and sustainable blueprint for lignocellulosic biorefineries, bridging the gap between laboratory-scale innovation and industrial-scale implementation. By integrating process efficiency, product diversification, and rigorous economic and environmental metrics, it charts a practical pathway for reducing dependence on fossil resources and advancing a circular bioeconomy. To fully realize this potential, future efforts should focus on pilot-scale validation, with particular attention to optimizing energy integration and strengthening biomass supply chains—two factors identified as most critical to long-term environmental and economic success.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Information

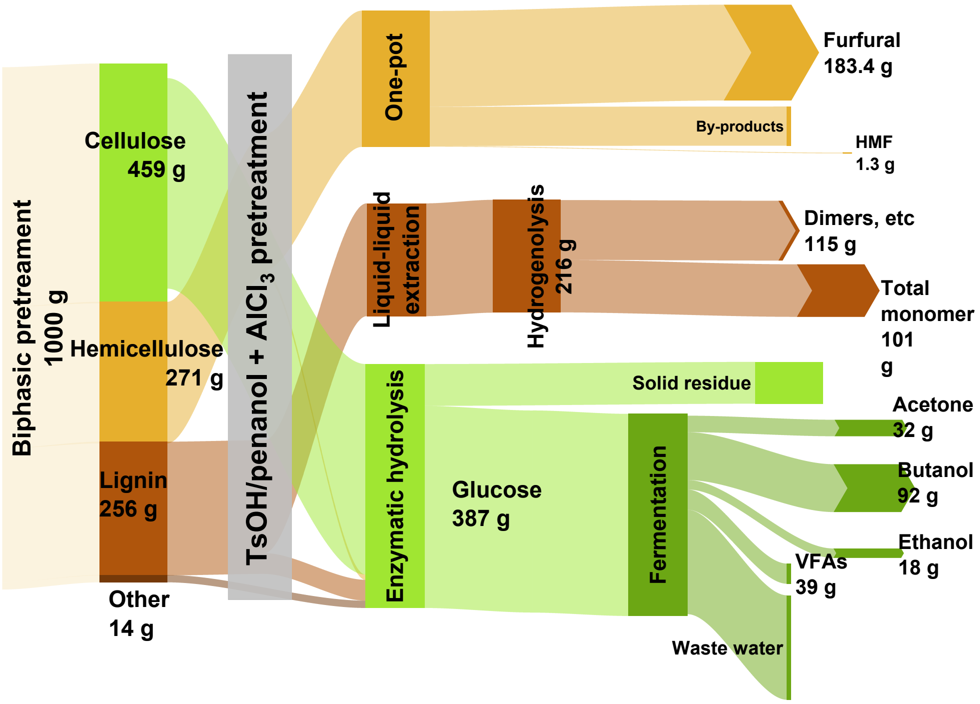

Fig. S1. Mass balance flow of the poplar biorefinery to acetone, butanol, ethanol, furfural, and lignin-derived compounds (monomers, dimers, and oligomers) based on 1000 g of biomass. **Pretreatment conditions**: 10% (w/w) biomass loading, 60% pentanol, 20 wt% TsOH, 4 wt% $AlCl_3$ (based on the weight of the raw substrate), 110 °C, 40 min. **Enzymatic hydrolysis conditions**: 10% biomass loading, 10 FPU/g Cellic® CTec 2, 50 °C, 72 h. **ABE fermentation conditions**: *Clostridium acetobutylicum* 1201 strain, 37 °C, 160 rpm for 18 h. **Catalytic hydrogenolysis conditions**: 100 mg lignin, 30 mL methanol, 100 mg 5 wt% Ru/C, 3 MPa, 250 °C, 180 min.

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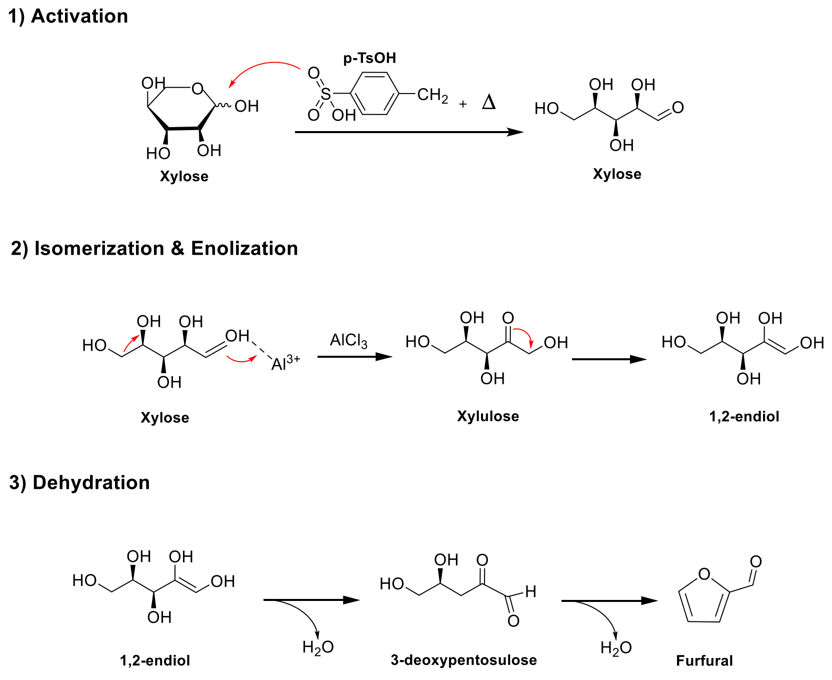

Fig. S2. Proposed influence of $AlCl_3$ on the furfural production pathway in the TsOH/pentanol system.

Table S1.
Equations used in this study.

No.	Equation
Eq. S1	$\text{Cellulose recovery (\%)} = \dfrac{\text{Cellulose in pretreated substrate (g)}}{\text{Cellulose in raw biomass (g)}}$
Eq. S2	$\text{Xylan removal (\%)} = 1 - \dfrac{\text{Hemicellulose in pretreated substrate (g)}}{\text{Hemicellulose in raw biomass (g)}}$
Eq. S3	$\text{Delignification (\%)} = 1 - \dfrac{\text{Lignin in the pretreated substrate (g)}}{\text{Lignin in raw biomass (g)}}$
Eq. S4	$\text{Severity factor} = \log R_0 = e^{\left(\frac{T-100}{14.75}\right)} \times t$
Eq. S5	$\text{CrI (\%)} = \dfrac{I_{002}-I_{am}}{I_{002}} \times 100$
Eq. S6	$\text{Furfural yield (\%)} = \dfrac{\text{Furfural produced (g)}}{\text{Initial xylose in raw biomass (g)}} \times \dfrac{132}{96} \times 100$
Eq. S7	$\text{HMF yield (\%)} = \dfrac{\text{HMF produced (g)}}{\text{Initial cellulose in raw biomass (g)}} \times \dfrac{162.14}{126.11} \times 100$

Table S2.
Mass, carbon, and energy yields of ABE solvents, furfural, and HMF from 1 kg of poplar under optimum pretreatment conditions.

	Feed		Main Sugar-based Products					Overall Yield (%)
	Cellulose	Xylan	Acetone	Butanol	Ethanol	Furfural	HMF	
Mass (g)	459	271	31.59	91.60	18.14	183.46	1.34	44.67*
Carbon (g $_{\text{Carbon}}$)	203.80	123.06	19.60	59.37	9.46	114.66	0.77	62.7**
ΔH° Combustion (kJ/mol)	-2828	-2342.2	-1790	-2676.1	-1367	-2339	-2781.5	-
Energy (kJ)	8005	4801	974	3307	538	4468	29.5	72.7***

* g product/kg poplar
** g Carbon product/kg Carbon poplar
*** kJ energy product/kJ energy feed

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Table S3.
Modules used in collecting data from Ecoinvent 3.

Inputs From Technosphere: Energy/Materials/Transportation	**Module on SimaPro**
Electricity	Electricity, high voltage {RoW}| electricity production, solar tower power plant, 20 MW | Conseq, S
Heat	Heat, district or industrial, natural gas {RoW}| market for heat, district or industrial, natural gas | Conseq, S
Transportation	Transport, freight, lorry >32 metric tonne, EURO5 {RoW}| transport, freight, lorry >32 metric tonne, EURO5 | Conseq, S
Pentanol	1-pentanol {GLO}| market for | Conseq, S
$AlCl_3$	Aluminium chloride {GLO}| market for aluminium chloride | Conseq, S
Tap water	Tap water {BR}| market for tap water | Conseq, S
Phenol	Phenol {GLO}| market for | Conseq, S
Ethanol	Ethanol fermentation plant {GLO}| market for | Conseq, S
Butanol	1-butanol {GLO}| market for | Conseq, S
Methanol	Methanol {GLO}| market for | Conseq, S
Wastewater	Wastewater, average {RoW}| market for wastewater, average | Conseq, S

Table S4.
CAPEX, OPEX, and annual revenues for a capacity of 730 kt/yr.*

CAPEX **Process unit**	**Cost (Million USD)**
Total plant direct cost	235.3
Total plant indirect cost	93.7
Working capital	58.0
Total	**387.0**

OPEX **Items**	**Cost (USD/tonne)**	**Cost (Million USD for 730 kt/yr)**
Material cost		
Poplar	95.61	69.8
Pentanol	1000	24.1
TsOH	1611	16.5
Catalyst	-	29.2
$AlCl_3$	1600	3.5
Nutrient Medium	-	5.9
Enzyme	-	6.2
Methanol	302.1	1.0
Inoculum	-	0.7
Water	-	0.7
Electricity & heat	-	67.6
Operating labor	-	50.0
Maintenance	-	16.5
Fixed charge	-	41.7
Plant overhead cost	-	20.8
General expense	-	62.5
Total		**416.7**

Annual revenues **End-products**	**Cost (USD/tonne)**	**Product yield (kg/tonne biomass)**	**Million USD/yr**
Acetone	771	32.0	18.0
Ethanol	753	18.0	9.9
Butanol	884	92.0	59.4
Furfural	1299	183.4	173.9
Lignin-derived compounds	1750	213.0	272.1
Total			**533.3**

* Source: Peters et al. (2003); Baral and Shah (2016); Liao et al. (2020); Tschulkow et al. (2020); Stone (2021); Fastmarkets; Made-in-China; Shanghai Metals Market (SMM); SunSirs.

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Table S5.
Material and energy inputs, as well as their GHG emissions, for biorefining 1 tonne of poplar.

Process Stage	Inputs	Value	Unit	GHG Emissions to the Air (Kg $CO_{2\text{-eq}}$)
Biomass transport	Average distance	180	km	16.67
Biomass preparation	Electricity	202	kWh	9.89
	Water	500	kg	0.32
	Heat	435	MJ	33.45
Pretreatment	Heat	640	MJ	49.22
	TsOH	14.0	kg	22.54
	$AlCl_3$	3.0	kg	16.14
	Water	2000	kg	1.27
	Pentanol	33	kg	155.76
Pentanol recovery	Heat	3920	MJ	301.45
TsOH recovery	Heat	885	MJ	68.06
Enzymatic hydrolysis	Electricity	185	kWh	9.06
	Heat	655	MJ	50.37
	Cellulase	3.63	kg	10.76
	Water	4100	kg	2.61
Fermentation	Electricity	240	kWh	11.75
	Heat	241	MJ	18.53
	Nutrients	23.98	kg	22.57
Distillation	Heat	1125	MJ	86.51
Lignin catalytic hydrogenolysis	Methanol	4.5	kg	4.73
	Heat	43	MJ	3.31
Furfural production	Heat	113	MJ	8.69
Wastewater treatment	-	6.6	m^3	3.70
Product transport	Average distance	180	km	8.97
Total				**916.33**

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