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Abstract

We investigated a technology that enables the distributed decomposition of biogenic (lignin, cellulose) and synthetic (plastic) polymers into renewable or low-carbon-emission chemicals and fuel intermediates that can substitute fossil hydrocarbons for energy, chemical, and fuel production. The specific goal of this project is to (1) selectively convert biogenic polymers such as lignin and synthetic polymers such as polyethylene into hydrocarbons via electrocatalytic and thermocatalytic processes, and (2) optimize (electro)catalyst composition and reaction conditions to mitigate deactivation and control product selectivity.

Summary

In this study, we investigated a technology that enables distributed use of biogenic (lignin, cellulose) and synthetic (plastic) polymers into renewable or low-carbon-emission chemicals and fuel intermediates that can substitute fossil hydrocarbons for energy, chemical, and fuel production. In particular, we investigated the use of our Clean Sustainable Electrochemical Treatment (CleanSET) for decomposing biogenic and synthetic polymers (Polymer Sustainable Electrochemical Treatment [PolySET]) at room temperature and atmospheric pressure. We compared the performance against traditional thermochemical and electrocatalytic routes such as the Fenton reaction, thermocatalytic cracking, and catalytic hydrothermal gasification. The Fenton process achieved ≈90% conversion of treated synthetic plastics such as polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinylchloride (PVC) with 30,000 ppm of exogeneous hydrogen peroxide (H_2O_2), but it generated a wide array of liquid products. However, the PolySET process using the electro-Fenton reaction with 10 ppm of in situ generated H_2O_2 was >90% selective toward oxalic acid production for PE and PVC. Additionally, we demonstrated >180 h of stable PolySET performance for lignin oxidation, in which we achieved >70% chemical oxygen demand (COD) removal and current efficiency (CE). On the other hand, thermocatalytic hydrogenolysis of PE at 300 °C and 4.0 MPa H_2 only achieved 12% PE conversion. Additionally, thermocatalytic lignin oxidation via catalytic hydrothermal gasification (CHG) using Catalyst A resulted in ≈70% COD removal, but was only stable for 60 h.

Acknowledgments

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Acronyms and Abbreviations

CE	current efficiency
CHG	catalytic hydrothermal gasification
COD	chemical oxygen demand
CleanSET	Clean Sustainable Electrochemical Treatment
PolySET	Polymer Sustainable Electrochemical Treatment
H2O2	hydrogen peroxide
ppm	parts per million
H2	hydrogen
RuO2	ruthenium dioxide
Ni	Nickel
MMT	million metric tons
Mo	molybdenum
PE	polyethylene
PNNL	Pacific Northwest National Laboratory
PP	polypropylene
PS	polystyrene
PVC	polyvinylchloride
RHE	reversible hydrogen electrode
TC	total carbon

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1.0 Introduction

Plastic-derived products, valued for their low cost and stability, are infrequently recycled due to economic inefficiencies, leading to landfill disposal. In 2018, the United States generated 292 million metric tons (MMT) of waste, with plastics (mainly polyethylene, polypropylene, polystyrene, and polyvinylchloride) composing 35.6 MMT. Of the total waste, only 23.6% was recycled, with plastics accounting for a mere 4.5%. Globally, 9–15 MMT/year of plastic ends up in aquatic ecosystems, and 13–25 MMT/year in terrestrial environments.[1] By 2040, plastic waste is expected to more than double.[2] Effective recycling technologies are critical to address the environmental and health impacts.

Lignin-derived products, valued for their structural and biofunctional properties, are often underutilized due to economic and processing complexities, leading to significant waste. The annual global production of lignin from pulp and paper industries is about 50 MMT of which only 2% is utilized for lignin-derived products.[3] This underutilization results in 98% of produced lignin ending up in landfills or incinerated, posing environmental hazards.[3]

Currently, thermochemical routes like pyrolysis and gasification operating at high temperatures (300 °C to 1,000 °C) are used for upcycling these biogenic and synthetic plastics into a crude oil, methane, syngas, or char.[4] However, these processes require extensive downstream processing, exogeneous H_2, and generate significant greenhouse gas emissions, limiting their sustainability and application for distributed polymer conversion. Therefore, the development of renewable and sustainable conversion methods is essential to mitigate the environmental impacts of biogenic and synthetic waste. Electrochemical processes are being developed to operate under milder conditions and aim to produce high-value products like dicarboxylic acids and H_2, offering a cleaner and more efficient alternative.[4]

1.1 Electrochemical decomposition of biogenic and synthetic polymers

Electrocatalytic technologies allow for the conversion of biogenic and synthetic polymers at room temperature and atmospheric pressure, making polymer degradation (or upcycling) technology more amenable for distributed manufacturing. The Fenton process is an indirect reaction that uses exogeneous H_2O_2 and a Fenton reagent (e.g., Fe^{2+}) in the solution to generate hydroxyl radicals (•OH), which are highly reactive and capable of breaking down plastic polymers.[5] However, in situ electro-Fenton reactions generate H_2O_2 and regenerate the Fenton reagent.[6] The •OH radicals (instead of the electrodes directly) attack the polymer chains, leading to their decomposition into chemicals or full oxidation into carbon dioxide.[7]

Direct electrocatalytic oxidation uses an anode to directly oxidize the biogenic and synthetic organic compounds at the anode while the cathode simultaneously produces H_2.[8] The organic compound solubilized in the liquid (e.g., lignin, or short-chain carboxylic acids and alcohols found in wastewater) adsorbs onto the anode surface and loses electrons (e^-) and protons (H^+), gains oxygen groups (O^-), and eventually fully oxidizes into CO_2 and H_2O.

In this work, we evaluated Polymer Sustainable Electrochemical Treatment (PolySET) performance via the indirect electro-Fenton process to decompose treated insoluble polymers (e.g., polyethylene [PE], polypropylene [PP], polystyrene [PS], and polyvinylchloride [PVC]).[5] Furthermore, we evaluated the direct decomposition of soluble lignin using our standard RuO_2 to yield value-added products. RuO_2 is an active anode already demonstrated in the original

Clean Sustainable Electrochemical Treatment (CleanSET) process for full oxidation of biomass-derived organic compounds found in wastewater and fermentation broths.[9] The electrochemical experiments were carried out at room temperature and atmospheric pressure. Additionally, we performed chronopotentiometry experiments for >100 h to test the stability of the PolySET process.

1.2 Thermocatalytic conversion of biogenic and synthetic polymers

Thermocatalytic hydrogenolysis is a chemical process that involves the cleavage of single carbon–carbon (C–C) bonds using H_2 in the presence of a catalyst.[10] This method has proven effective for converting synthetic plastics such as PE and PP into fuels, lubricants, and waxes. Pacific Northwest National Laboratory's (PNNL's) recent work demonstrated the remarkable performance of a low-loading Ru metal catalyst for PP and PE conversion.[11] However, waste plastics can contain contaminants like sulfur, which reduce the effectiveness of metal catalysts. Therefore, developing more sulfur-resistant catalysts, such as transition metal sulfides, is beneficial.

Thermocatalytic hydrothermal gasification (CHG) is a process that breaks down organic matter in wastewater or biomass slurry into gaseous products like methane and H_2 using high-temperature and high-pressure liquid phases.[12] It can be conducted under sub- or super-critical water conditions across various temperatures, pressures, and feedstocks. PNNL has developed a proprietary Ru-based, sulfur-resistant catalyst (Catalyst A) that converts sulfur-containing wastewater feedstocks into CH_4 via CHG. This process shows great potential for upgrading challenging sulfur-containing waste biogenic polymer feedstocks, such as alkaline lignin.

In this work, we performed PE hydrogenolysis and lignin CHG using Catalyst A and compared their performance with Ru/C and NiMo sulfide catalysts. Furthermore, the degradation conversion and stability of the thermocatalytic (hydrogenolysis, CHG) and electrocatalytic (PolySET) processes were compared to determine which process is more amenable for decentralized polymer decomposition.

2.0 Experimental Approach

2.1 PolySET of synthetic polymers

We demonstrated the PolySET performance by evaluating its half-cell potential at room temperature and atmospheric pressure in batch electrolyzers. The electrochemical parameters such as cathode half-cell potential, current, and reaction time were controlled and recorded using a Biologic SP-150 potentiostat.

The synthetic polymers were pretreated with sulfonate groups and iron (III), resulting in a pretreated polymer named in this work as Polymer-SO_3-Fe. We characterized these pretreated polymers using total carbon (TC) analysis and inductively coupled plasma mass spectrometry (ICP-MS). The resulting products were analyzed using TC and high-performance liquid chromatography. A suitable cathode metal on carbon felt was developed to facilitate the electrochemical generation of H_2O_2.

2.2 PolySET of biogenic polymers

We demonstrated the baseline performance of a RuO_2 thin film system for direct lignin oxidation in NaOH media at room temperature and atmospheric pressure. We evaluated the effect of varying lignin concentrations and anode half-cell potential. The alkaline lignin was used as received, and the electrochemical performance was recorded using a Biologic SP-150 potentiostat.

The composition of the products after lignin electrochemical oxidation was analyzed using high-performance liquid chromatography, TC, and Hach analysis for chemical oxygen demand (COD).

2.3 Thermocatalytic conversion of synthetic polymers

We evaluated the thermocatalytic hydrogenolysis of PE using Catalyst A and compared its performance with Ru/C and NiMo sulfide catalysts to evaluate the reaction performance and understand the reaction pathways. The experiments were conducted in a batch reactor at 300 °C in H_2 at 4.0 MPa. The reaction products were analyzed using gas chromatography-flame ionization detection and gas chromatography-mass spectrometry.

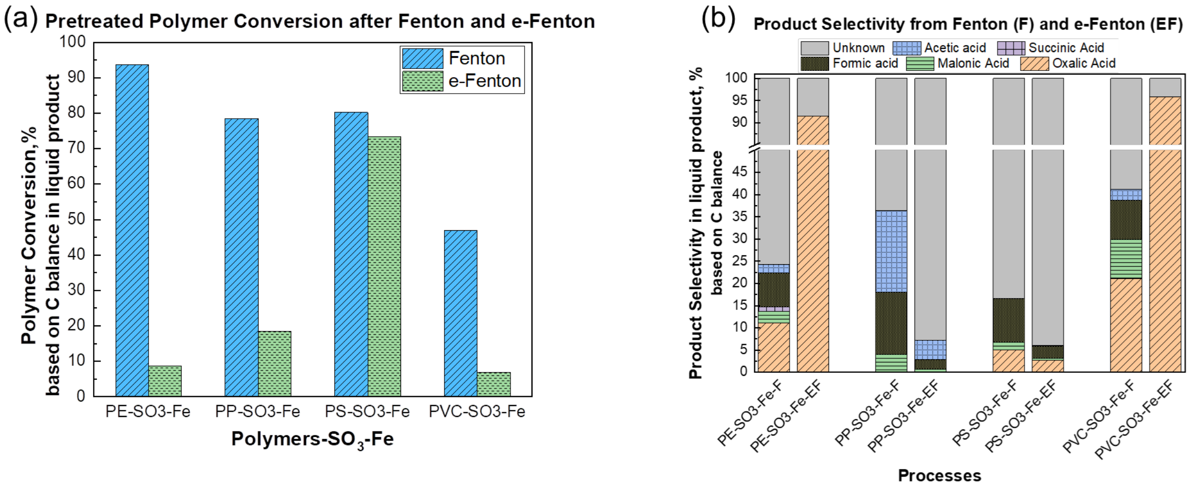
2.4 Thermocatalytic conversion of the biogenic polymer lignin

Experiments were performed using commercially available alkali lignin (containing sulfur) in a continuous-flow fixed-bed CHG reactor at 300–350 °C and 19 MPa.

3.0 Results and Discussion

3.1 Electro-Fenton degradation of synthetic polymers

The PolySET performance for synthetic polymer decomposition—PE, PP, PS, and PVC—was systematically tested using both the Fenton and electro-Fenton processes. As shown in **Figure 1**, polymer conversion ranged from 50% to 95% using the Fenton process with ≈30,000 ppm of exogeneous H_2O_2; however, 9% to 70% conversion was demonstrated with the electro-Fenton process in which H_2O_2 was electrochemically produced in situ at 10 ppm. Notably, the electro-Fenton process demonstrated high selectivity for oxalic acid production, achieving 92% from pretreated PE and 96% from pretreated PVC, while the Fenton process generated product mixtures. These results indicate that while the Fenton reaction generally achieves higher polymer conversion due to the high initial concentration of H_2O_2, PolySET favors the selective generation of valuable products (e.g., oxalic acid) without the need for exogeneous H_2O_2, thus enabling distributed and safer processing of waste synthetic polymers. Future work will focus on improving the PolySET performance with real waste synthetic polymers.



$$\boldsymbol{Conversion},\% = \frac{Total\ C\ mass\ in\ liquid\ product}{Initial\ C\ mass\ in\ solid\ substrate} \times 100$$

$$\boldsymbol{Selectivity},\% = \frac{C\ mass\ in\ specific\ product}{Total\ C\ mass\ in\ liquid\ product} \times 100$$

Figure 1. PolySET performance for the oxidation of treated (-SO_3-Fe) synthetic polymers via the electro-Fenton compared to the Fenton reaction with 30,000 ppm of H_2O_2. (a) Conversion based on carbon balance and (b) product selectivity after reaction at room temperature and atmospheric pressure. The untreated synthetic polymer was inert under reaction conditions.

3.2 Electrocatalytic oxidation of biogenic polymers

We tested the PolySET performance of the baseline RuO_2 system for low-temperature decomposition of lignin in a batch cell at 2.0 V vs. reversible hydrogen electrode (RHE). **Figure 2a** shows the linear sweep voltammetry of RuO_2 in 1 M NaOH with varying lignin concentrations ranging from 100 to 10,000 ppm, indicating that the presence of lignin decreases the current density due to its inherently lower reaction rates compared to the undesirable oxygen evolution reaction (OER). **Figure 2b** illustrates the performance of the baseline RuO_2 for lignin oxidation with a COD of 12,000 ppm (lignin concentration ≈6,500 ppm) in 1 M NaOH at 2.0 V vs RHE.

The anode remained stable for ≈100 h, corresponding to ≈15,000 C. By the end of 170 h, ≈70% COD removal was achieved. The current efficiency (CE) for COD removal was ≈71% at 5,000 C. However, the CE decreased with the charge passed to ≈30% at 25,000 C due to the consumption of lignin and the system becoming more preferential toward the undesirable oxygen evolution reaction.

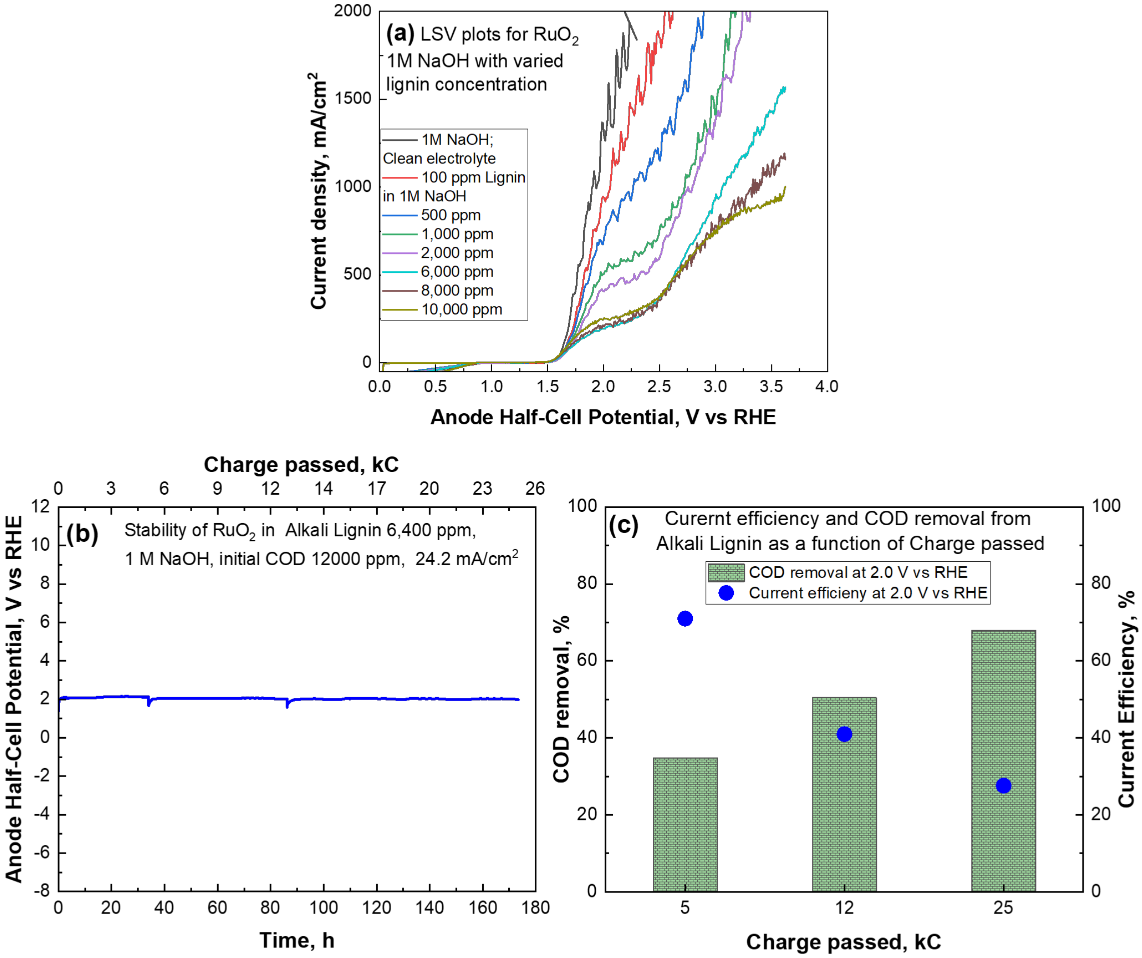


Figure 2. PolySET performance for the decomposition of lignin at 12,000 ppm COD in 1 M NaOH at 2.0 V vs. RHE using a baseline RuO_2-based anode. The experiments were performed in a batch cell at room temperature and atmospheric pressure. (a) Linear sweep voltammetry for the RuO_2-based anode in 1 M NaOH with varied lignin concentration from 100 to 10,000 ppm, (b) anode half-cell potential as a function of time and charge passed, and (c) COD removal and CE for COD removal.

3.3 Thermocatalytic conversion of synthetic polymers

We tested sulfide catalysts for the thermocatalytic hydrogenolysis of PE to identify a sulfur-tolerant catalyst system for processing contaminated waste plastic. We compared our recently developed Catalyst A against a low Ru-loading bimetallic catalyst, a Ru/C catalyst known for excellent activity in reduced form without sulfur, and a commercial NiMo sulfide hydrotreating catalyst. All three catalysts showed low conversion around 10%, with Catalyst A exhibiting slightly higher activity (**Figure 3**). Surprisingly, the Ru-based catalyst did not demonstrate significantly greater activity than the NiMo catalyst, warranting further investigation.

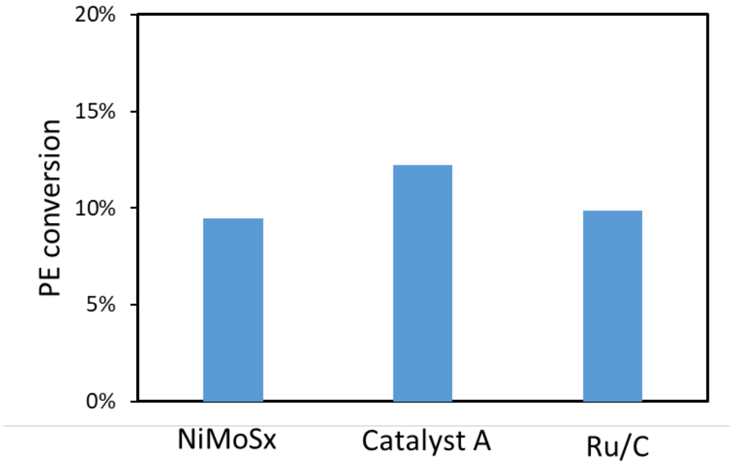


Figure 3. Thermocatalytic conversion of PE over different catalysts at 300 °C, 4.0 MPa H_2, and ~16 h in a batch reactor.

3.4 Thermocatalytic conversion of biogenic polymer lignin

Direct processing of aqueous feed containing whole alkali lignin, with or without an alkaline medium, under CHG conditions (300–350 °C, 19 MPa) using a Ru-based catalyst was unsuccessful due to reactor plugging caused by the formation of high molecular weight species in the catalyst bed. To address this, we developed a lignin pretreatment process at ambient conditions, successfully extracting approximately 50% of the lignin into an aqueous solution. CHG testing with this aqueous solution did not result in reactor plugging over an ~100-hour test (**Figure 4**). However, this pretreatment method needs further optimization to enhance lignin utilization and increase lignin concentration in the final aqueous solution for greater throughput. Additionally, a detailed analysis of the lignin fractions is required to gain insights into the lignin fractionation process. CHG testing of the pretreated lignin aqueous solution using the baseline Ru/C catalyst and the newly developed Catalyst A showed a conversion (measured by COD change) of 50 to 70% at steady state. While the Ru/C catalyst exhibited high initial activity (>95%), but it rapidly deactivated due to sulfur poisoning. The comparable performance of both catalysts at steady state indicates the potential of using the new catalyst for lignin CHG. Further research is needed to close the mass balance, optimize reaction parameters and catalysts for higher lignin conversion, and test other pretreated lignin feedstocks.

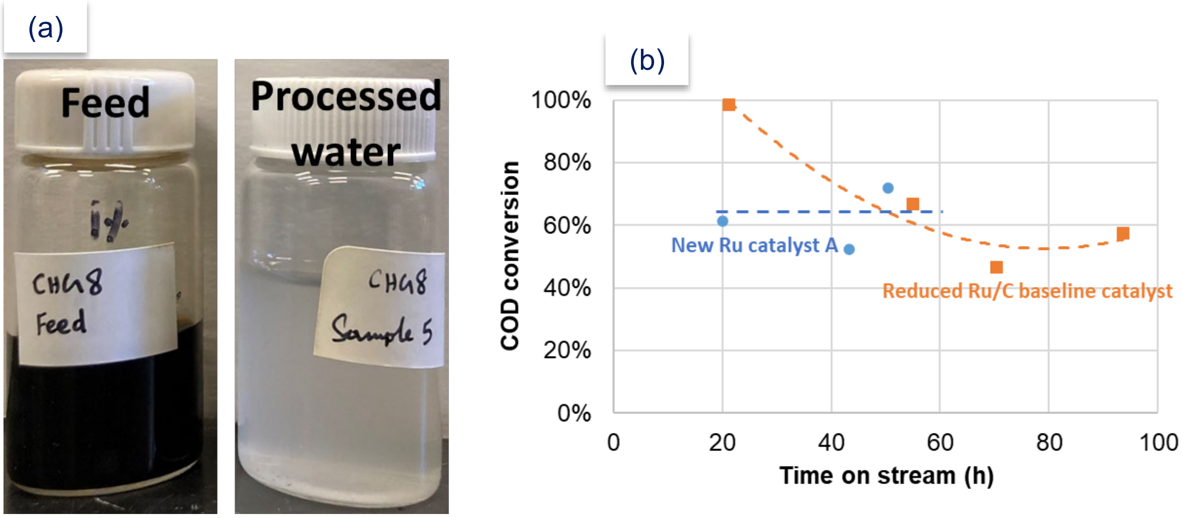


Figure 4. Thermocatalytic hydrothermal gasification of an aqueous feed containing a fraction of alkali lignin over different catalysts. (a) Pictures of the aqueous feed before and after CHG reaction; (b) COD conversion at different times on stream for Catalyst A and baseline catalyst Ru/C.

4.0 Conclusions

In this work, we demonstrated that PolySET can process both biogenic and synthetic polymers at room temperature and atmospheric pressure without apparent deactivation in the presence of sulfur. PolySET exhibited >90% selectivity for oxalic acid from pretreated PE and PVC and up to >70% conversion for pretreated PS. We also reached >160 h of stable performance during the oxidation of alkaline lignin, achieving ≈70% COD removal with ≈71% CE. However, thermocatalytic hydrogenolysis of PE at 300 °C and 4.0 MPa H_2 only accomplished ≈10% PE conversion. Direct thermocatalytic CHG of alkali lignin was unsuccessful due to reactor plugging—a lignin pretreatment process mitigated this issue but required optimization. The new Ru-based, sulfur-tolerant catalyst showed a promising steady state for 60 h, indicating the potential for efficient lignin conversion.

Future work will focus on optimizing the performance of the PolySET process and demonstrating its application with real waste biogenic and synthetic polymers as well as mixtures. The thermocatalytic processes need additional research and development to mitigate catalyst deactivation by sulfur poisoning.

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