CO_2-SWITCHABLE SURFACTANTS ENHANCE THE WATER RESISTANCE OF LATEX-BASED COATINGS

RAZ ABBASI

Carbon dioxide (CO_2) has emerged as an innovative "trigger" for stimuli-responsive materials. Compared to other triggers such as light, acids, and oxidants, CO_2 has the advantages that is inexpensive, nonhazardous, non-accumulating in the system, easily removed, and it does not require the material to be transparent. CO_2-switchable surfactants are a class of responsive materials for which CO_2 is a trigger used to reversibly switch the surfactant properties from surface-active ("on") to less surface-active ("off") form.

Driven by environmental and health concerns with volatile organic compounds (VOCs), there has been a significant shift toward water-based (latex) coatings produced via emulsion polymerization. Surfactants are known to be a "necessary evil" in emulsion polymerizations, crucial for dispersing monomers, stabilizing polymer particles, and prolonging shelf life. However, their ionic nature and incompatibility with the polymer matrix can negatively affect coating performance.

In current work, latex formulations have been designed using a CO_2-switchable surfactant, which switches from being ionized to neutral upon application to a substrate. During film drying, as water and CO_2 evaporate, the surfactant spontaneously transitions from a charged state to a neutral, hydrophobic state. The lack of a functioning surfactant in the dried coating enhances its resistance to moisture, water, and corrosion. These latexes exhibited excellent storage stability in the presence of CO_2, maintaining consistent particle size and high zeta-potential values over time. Films made from these latexes exhibited significantly lower water and moisture absorption compared to those made with permanently charged surfactants. Additionally, this water-based coating demonstrated corrosion resistance comparable to solvent-based formulations, but without the use of any VOCs.

THERMO-ALKALINE PRETREATMENT FOR ENHANCED ANAEROBIC DIGESTION OF BIOPLASTICS

FARIMAH AMINFAR

Microplastic (MP) pollution has become a significant environmental challenge, even with the increasing use of bioplastics such as polylactic acid (PLA) and polyhydroxyalkanoates (PHA). While these bioplastics have more affinity towards biodegradation, their persistence in anaerobic digestion (AD) systems limits their potential for effective waste treatment. To address this issue, this study investigates the impact of thermo-alkaline pretreatment on the degradation of PLA and PHA in AD. The MPs were sized between 200 and 500 µm through a standardized meshing procedure with 35, 45, 75 mesh size sieves and underwent thermo-alkaline pretreatment using a bench-top pressure-sealed microwave reactor. The pretreatment process involved exposure to sodium hydroxide (NaOH) at the concentrations of 1%, 2%, and 3% (w/w) combined with heat at 60°C, 90°C, and 120°C. The microwave reactor heating rate was set at 3°C/min, and the samples were held at the target temperature for 60 minutes.

The pretreated MPs were subsequently subjected to batch biochemical methane potential (BMP) tests at mesophilic conditions (37°C) for 65 days to evaluate biogas yield and MP degradation. The structural and chemical changes in the MPs were analyzed using Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM), revealing significant polymer breakdown and surface changes. The results indicate that thermo-alkaline pretreatment enhances the hydrolysis of PLA and PHA, facilitating microbial assimilation and leading to increased biogas production. Pretreatment improved biogas yield from 437 mL/g COD in the untreated PLA-added digesters to 641 mL/g COD in the digester fed with pretreated PLA under 3% NaOH and 60°C. The maximum biogas yield of 713 mL/g COD was obtained from PHA pretreated under 1% NaOH and 120°C, 44% higher than that of control (untreated) PHA digesters.

Fourier-transform infrared spectroscopy (FTIR) analysis revealed significant chemical changes, including reduced carbonyl (C=O) and ester (-COO-) bond intensities, indicating polymer chain scission. Scanning electron microscopy (SEM) images showed increased surface roughness, cracks, and fragmentation, confirming physical degradation of the MPs. After the thermo-alkaline pretreatment, the surface was corroded, and clear cracks and pore structure formed. By increasing the surface area and porosity, the enzyme binding sites are increased, and the hydrolysis of the plastics is accelerated, thereby promoting biodegradation. This study demonstrates the effectiveness of thermo-alkaline pretreatment in enhancing the biodegradability of PLA and PHA microplastics in anaerobic digestion. Optimizing pretreatment conditions can improve organic waste management while increasing biogas recovery from biodegradable plastics. These findings offer valuable insights for developing sustainable strategies for bioplastic waste management in wastewater treatment plants and anaerobic digestion systems. Future research will focus on microbial community dynamics and the long-term operational impacts of integrating pretreated microplastics into continuous anaerobic digestion systems, further advancing the sustainability and practicality of bioplastic waste management.

COMPARATIVE STUDY OF BIOCHAR-AMENDED AND UNAMENDED ANAEROBIC DIGESTION UNDER VARIOUS ORGANIC LOADINGS

FATEMEH SADAT ARGHAVAN

Anaerobic digestion (AD) is a sustainable method for treating organic waste while producing valuable products such as biogas and fertilizer. The AD process consists of three main stages: hydrolysis, acidogenesis, and methanogenesis. Pretreatment techniques and co-digestion are commonly applied to AD feedstocks to enhance the efficiency of the hydrolysis. Thus, the concentration of soluble organic materials is increased, leading to the rapid production of volatile fatty acids (VFA). However, due to the slower growth rate of methanogenic archaea (0.02–0.06 1/d) compared to acidogenic bacteria (0.6–1.0 1/d), VFAs are produced faster than consumed. This imbalance can delay biogas production or even result in system failure due to acidification.

To address this issue, the addition of carbon-based materials with porous structure and electron transfer capabilities is considered a promising strategy. In this study, wood-derived biochar (BC) was selected for this purpose.

Batch anaerobioc digesters were set up with food waste and thermally pretreated sludge and supplemented with 15 g/L of biochar. These were operated under three different food-to-microorganism ratios (F/M) of 1, 3, and 5 (g/g volatile solids) representing low (L), medium (M), and high (H) organic loading conditions. Control digesters without biochar were also operated under the same conditions. Soluble organics and VFA concentrations were monitored over the first 16 days.The two-phase Gompertz model was used to calculate the kinetics of biogas production.

In the digesters, The performance of control digesters declined as F/M increased. The high F/M, no biochar (H-CO) reactor produced 285 mL biogas/g total chemical oxygen demand (TCOD) at a rate of 4.2 mL/gTCOD·d, which is lower than the 344 mL/gTCOD with a rate of 6.9 mL/gTCOD·d values observed in the low F/M, no biochar (L-CO) reactor. The lag phase was also 70% longer in H-CO (17 d) compared to L-CO (10 d), indicating delayed microbial activity under high organic loading.

When comparing digesters with and without BC, the greatest improvement was observed under the highest F/M condition. The high F/M with biochar (H-BC) reactor achieved a significantly higher biogas yield of 367 mL/gTCOD compared to 285 mL/gTCOD in the H-CO reactor ($p < 0.001$). Furthermore, the H-BC reactor recovered four days earlier and exhibited a higher biogas production rate (5.5 vs. 4.2 mL/gTCOD·d). This improved performance in H-BC is likely attributed to lower VFA concentrations, which decreased from 5600 mg/L on day 3 to 2300 mg/L on day 7. The used BC has a porous structure (pore volume of 0.23 cm^3/g) that can adsorb VFA and release them gradually, allowing methanogenic archaea sufficient time to utilize VFA effectively.

In conclusion, the addition of 15 g/L of biochar improved AD performance by 28% in terms of biogas yield under high organic loading conditions. For the next step in the present research, the focus will be on estimating the effects of BC on biogas composition, to maximize the methane content and reduce impurities.

INTEGRATION OF THERMAL AND THERMO-ALKALINE PRE- AND INTER-TREATMENT WITH TWO-PHASED SLUDGE ANAEROBIC DIGESTION

FLORENCE BULLEM

Primary sludge (PS) is a product of primary treatment in municipal wastewater treatment plants (WWTPs). Anaerobic digestion (AD) is commonly used for converting sludge into biomethane. Thermal hydrolysis (TH) is a widely used pre-treatment technique for breaking down sludge structure at high temperatures (160-180℃), increasing the bioaccessibility of soluble organics in the subsequent AD process, improving biogas production yield and rate. Thermo-alkaline hydrolysis (TAH) is more effective than TH for protein-rich feedstocks like sludge, as it can denature proteins at high pH by disrupting the external layer of sludge and releasing its organic contents. Consequently, it is anticipated that the combined impacts of TH and alkaline treatments will significantly boost the yield of biogas. However, PS contains biodegradable organics which are readily converted to biogas with or without pretreatment. Upon depletion of these organics, the less degradable portion of the sludge remains, and the mechanism of biogas production shifts towards microbial lysis. In this case, applying TH or TAH after a first anaerobic digestion becomes an inter-treatment which targets this recalcitrant fraction of sludge. In this research, TH and TAH were used as an inter-treatment step of a two-phased sludge AD process to target the less degradable portion of sludge remaining from the first stage of AD (**AD-TH-AD** and **AD-TAH-AD**). The experimental design also included a conventional two-stage AD process (**AD-AD**), a single-stage AD process (**AD**), and a

single-stage AD following TH pre-treatment (**TH-AD**). A Biochemical Methane Potential (BMP) test was used to study the effect of TH as a pre- and inter-treatment, and the potential improvement of TAH as an inter-treatment over TH inter-treatment. A Box-Behnken Design (BBD) was used to generate the experimental runs with varying pH (10 – 12), temperature (90 -170℃), and holding time (10 – 60 mins). The performance metrics were evaluated using soluble chemical oxygen demand (SCOD) and ultimate biogas yield (UBY). AD and AD-AD had UBY of 138 $\text{mL/gVS}_{\text{added}}$ and 169 $\text{mL/gVS}_{\text{added}}$, respectively. TH-AD at 170℃ showed the highest UBY of 182 $\text{mL/gVS}_{\text{added}}$ from all pre-treatment scenarios. TAH as an inter-treatment (**AD-TAH-AD**) increased UBY linearly with pH and temperature ($p < 0.05$), while holding time had a negligible effect on UBY ($p > 0.05$). The highest soluble COD concentration (38,437 mg/L) and COD solubilization (21%) from AD-TAH-AD were realized at pH 12 and 170℃, but the highest biogas yield (277 $\text{mL/gVS}_{\text{added}}$) was at pH 11 and 170℃. Also, AD-TH-AD at 170℃ had an 11% COD solubilization but a comparable UBY (250 $\text{mL/gVS}_{\text{added}}$), 11% less than the optimal yield from AD-TAH-AD. This suggests that soluble but non-biodegradable compounds which possibly affect AD are produced at high pHs and temperatures. Overall, the results show that TH, as an inter-treatment improves biogas production compared to TH as a pre-treatment, but including alkaline treatment does not provide a further significant increase.

HYBRID OBSERVER FRAMEWORK FOR BIOREACTORS WITH ASYNCHRONOUS MEASUREMENTS AND HUMAN-IN-THE-LOOP DELAYS

BASSEY EYO

In this paper, a novel hybrid observer design framework for continuous Bioreactor systems with asynchronous measurements and human-in-theloop (HITL) delays is hereby proposed. We adopt the standard Bioreactor system model with biomass and substrate concentrations, where we only measure biomass concentration available at discrete, aperiodic sample intervals. The proposed hybrid observer framework should handle both continuous (flow) dynamics and discrete (jump) conditions when measurements become available. We employed a Lyapunov function with a cross-term, to proof uniform global asymptotic stability(uGAS) for both delayed and undelayed measurement instances. Lyapunov-Krasovskii functional approach is employed to account for history effects for the delayed case. We, therefore, derived specific conditions for observer gains, Dilution rate bounds, and maximum allowable time (Tmax) between measurements to ensure uGAS. We performed simulation on a continuous stirred tank reactor (CSTR) to validate our theoretical findings, thereby demonstrating the observer's effectiveness in estimating the unmeasured substrate concentration even with significant (HITL) delays. Our findings will contribute immensely to the ever-growing field of hybrid systems theory for bioprocess monitoring, solving practical problems such as asynchronous measurement and delays caused by human interactions in the process.

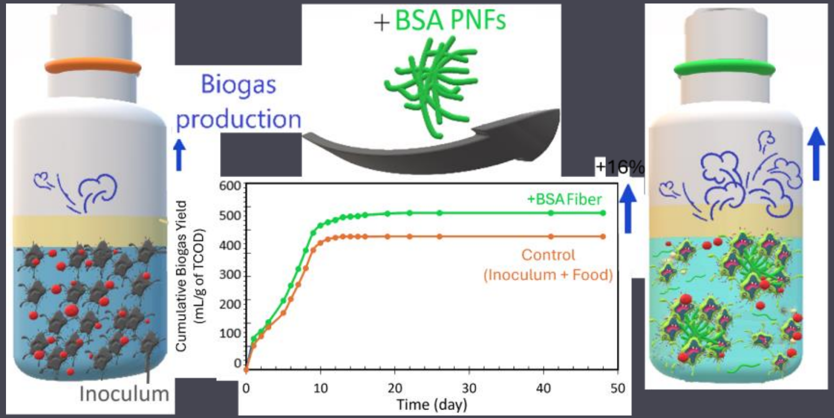
BOOSTING ANAEROBIC DIGESTION PERFORMANCE WITH PROTEIN NANOFIBER ADDITIVES

ROMINA HAJMOHAMMADTAGHISHIRAZI

Anaerobic digestion (AD) plays a critical role in organic waste management and wastewater treatment. AD converts organic waste into methane-rich biogas and biofertilizers through microbial decomposition under oxygen-free conditions. However, the performance of AD, particularly hydrolysis—the rate-limiting step—can drop drastically when faced with complex feedstocks such as wastewater sludge. This is largely due to the complex structure of sludge, which negatively impact enzymatic hydrolysis. To over come this limitation, AD microbes produce extracellular polymeric substances (EPS), composed of various organic and inorganic compounds, promoting microbial interactions. Recent advancements have showcased that nanomaterials can mimic the EPS structure and enhance AD performance by promoting microbial attachment, improving enzymatic activity.. In this research, we demonstrate that protein nanofibers (PNFs), specifically derived from bovine serum albumin (BSA), hold considerable promise as novel bio-additives in AD owing to their environmentally friendly nature, high surface area, and biomimetic properties that mimic EPS functions.

This study investigates the application of BSA-derived PNFs to enhance AD efficiency, focusing on methane production, EPS composition, microbial granulation, and digestate characteristics. Biochemical methane potential (BMP) assays were performed using powdered milk substrates (as control substratre) inoculated with mesophilic municipal AD digestate. Incorporating BSA nanofibers at an optimal dosage of 900 mg/L increased methane production significantly by 16 ± 4%. Enhanced methane yield was linked to improved microbial granulation and microbial community stability, whereby BSA addition increased tightly bound protein content (from 0.6 to 1.4 g/L) and decreased loosely bound protein (from 0.6 to 0.45 g/L), and soluble protein (from 1.2 to 0.2 g/L), resulting in stronger microbial aggregates.

Advanced characterization techniques, including atomic force microscopy (AFM), Thioflavin T (ThT) fluorescence, and Fourier-transform infrared spectroscopy (FTIR), revealed protein structural changes during digestion. Microscopic analyses illustrated improved floc and granule formation in the presence of BSA nanofibers, correlating positively with enhanced microbial interactions and microbial community stability. Furthermore, integrating BSA nanofibers improved sludge dewaterability, reflected by reduced Sludge Volume Index (SVI) and increased total solids (TS) of dewatered digestate cake. These improvements suggest practical operational benefits, including lower sludge handling costs and increased reactor stability. This research provides insights into how BSA-derived nanofibers can enhance AD performance, potentially enabling more stable, cost-effective, and sustainable wastewater treatment practices.



TUNING IONOMER DISTRIBUTION IN CATALYST LAYERS FOR EFFICIENT ETHYLENE ELECTROSYNTHESIS WITH DILUTED CO_2 FEEDSTOCK

ANH-DAO HO

The electrochemical CO_2 reduction (CO2R) into valuable chemicals, such as ethylene, is a promising approach to alleviate carbon emissions while transitioning emissions into renewable carbon-based feedstocks. Cu catalysts have shown their significant potential in electrochemical CO_2 conversion into multicarbon products, particularly into C_2 products such as ethylene. It has been reported that the selectivity of Cu catalysts depends on the microenvironment near active sites. Introducing ionomers, such as Nafion, to Cu catalyst layer is one of the effective methods to enhance CO2R selectivity and suppressing competing hydrogen evolution reaction (HER). The Nafion ionomer basically an ionic polymer with a hydrophobic backbone and charged heads which facilitate CO_2 accessibility and proton transport at ionomer/Cu interfaces. In addition, the formation of C_2H_4 can be regulated by feeding diluted CO_2 feedstock. In this study, we explore the effect of ionomer distribution and CO_2 concentration in the feedstock on ethylene selectivity. We first optimized Cu:Nafion ratio to achieve a maximum ethylene Faradaic efficiency (FE) of 28% at the current density of 220 mA/cm^2 and 100% CO_2 concentration. We found that coating another layer of ionomer on top of Cu:Nafion catalyst layer further increases ethylene FE to 37% at the current density of 360 mA/cm^2 . When combining this catalyst with diluted CO_2 feedstock (20% CO_2 in Argon), ethylene FE was increased to 50% at the same current density of 368 mA/cm^2 . Our results point out the importance of Nafion distribution in catalyst layer on CO2R to multiple carbon products.

Key words: electrochemical CO_2 reduction, ionomer coating, ethylene selectivity, CO_2 concentration

AOTEMPO-MEDIATED CROSSLINKING OF POLYPROPYLENE BY MIXED PEROXIDES AND PHOTO INITIATORS

JEROME JOSEPH

4-acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl (AOTEMPO) can be employed to modulate the onset, rate, and yield of radical-mediated crosslinking of polypropylene (PP) using dicumyl peroxide (DCP). AOTEMPO forms alkoxyamine intermediates with propagating radicals, enabling controlled radical release and providing pendant acrylate functionalities. To replicate the controlled dynamics achieved with AOTEMPO, mixed peroxide formulations comprising DCP and 1,1-Bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane (L-231) are investigated. In addition, the pendant acrylate groups allow for a secondary UV-curing mechanism. This alternative chemistry has been studied using a suitable photoinitiator 2-Hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (I2959) and subsequent yield has been quantified.

FREE RADICAL COPOLYMERIZATION OF BIO-BASED ITACONATE MONOMERS

SARA MOHEBBI

Monomers based on itaconic acid are a promising bio-based alternative to petroleumderived monomers in the production of commercial acrylic resins. Our group has recently shown that although itaconate homopolymerization suffers from low rates of monomer conversion and decreased polymer molar masses, copolymerization with acrylates is a means to successfully introduce bio-content of up to 50%. However, a better understanding of the radical copolymerization kinetics is needed to optimize synthesis conditions and ensure that itaconate monomers can match the current range of physical properties and chain functionalities offered by petroleum-derived monomers. Thus, we use in-situ nuclear magnetic resonance (NMR) spectroscopy to systematically study polymerization rates and copolymer composition in systems containing itaconate acids and butyl acrylate. We also measure molar mass distributions in the resulting copolymers through size exclusion chromatography (GPC) analysis. The investigation focuses on determining how the itaconate monomers' functionality influences the polymerization process. By examining these factors, we aim to pave the way for more sustainable polymer production without compromising on quality or performance.

A-OPTIMAL MODEL-BASED DESIGN OF EXPERIMENTS FOR PROCESSES WITH UNCERTAIN INPUTS

BRIGHT OFORI

Model-based design of experiments (MBDoE) techniques are effective tools for selecting experimental conditions that enable the development of accurate fundamental models. Existing MBDoE methods assume that the selected experimental conditions will be implemented perfectly, without any uncertainties. Unfortunately, some chemical processes have independent variables with significant uncertainties. Neglecting important input uncertainties may result in sub-optimal experimental designs that influence the accuracy of parameter estimates and associated model predictions. In this study, we propose a new MBDoE approach that accounts for input uncertainties when selecting experimental runs for estimating model parameters. Using an updated A-optimality criterion, we design experiments for a batch pharmaceutical process with an uncertain initial reactant concentration. The selected conditions are compared with corresponding conditions obtained using traditional A-optimal design where input uncertainties are neglected. Preliminary results suggest that the proposed method yields superior experimental designs and smaller parameter confidence intervals than traditional methods.

STRATEGIES TO DESIGN HIGH-PERFORMANCE ZINC-BASED BATTERIES USING GRAPHENE: NEW VANADIUM GRAPHENE HYDROGEL CATHODE AND ANODE DENDRITE MITIGATION DUE TO GRAPHENE COATINGS

ANDREW SELLATHURAI

Aqueous batteries utilizing zinc are considered as a potential technology for stationary energy storage systems due to zinc's high theoretical capacity, favorable reduction potential, safety, and affordable costs. However, both electrodes of the Zn-based are facing challenges. The utilization of zinc anodes in mildly acidic electrolytes remains challenging, partly because of dendrite formation during charge and discharge cycling. The first part of this talk presents the influence of reduced graphene oxide surface coatings and electrolyte additives on the stripping/electroplating performance of zinc anodes. Partially and fully coated electrodes are investigated and compared to the performance of a bare zinc surface. The results show that the coatings, in combination with a suitable background electrolyte, greatly improve the reversibility and stability of the zinc plating/stripping. Likewise, zinc battery performance is often limited by as suitable cathode materials. In recent years, aqueous zinc/vanadium pentoxide battery chemistry has been of great interest owing to its high safety, material abundance, cost, and energy density. Vanadium pentoxide has a unique layered structure that allows for the reversible intercalation of many multivalent ions, zinc included. We show a novel a two-step synthesis process for producing highly interconnected self-assembled vanadium pentoxide-graphene cathode for efficient/reversible intercalation of zinc between the cathode and a graphene coated zinc anode. A very high specific capacity of 502 mAh g^{-1} at a current density of 0.1 A g^{-1} is obtained and 184 mAh g^{-1} at a current density of 5 A g^{-1} .

ADVANCED FUNDAMENTAL MODELLING AND PARAMETER ESTIMATION TECHNIQUES FOR POLYMERIZATION PROCESSES

JAKOB STRAZNICKY

The physical properties of commodity polymers such as polyethylene (PE) and polypropylene (PP) vary greatly depending on the chemical structures of the polymer molecules. The wide range of physical properties exhibited by these polymers makes them versatile for applications in many different end-use products. Microstructure characteristics that influence the polymer's physical properties include average chain length, molecular weight distribution (MWD), copolymer composition distribution (CCD) and tacticity. Mathematical models are powerful tools that chemical engineers can use to control these microstructure characteristics, thereby producing polymer grades with targeted physical properties. Accurate values of model parameters, which are often estimated using experimental data, must be available for fundamental models to provide accurate predictions. Unfortunately, numerical difficulties are often encountered when estimating model parameters in polymerization models due to the large number of parameters required to predict detailed polymer characteristics. Fortunately, these difficulties can be alleviated using subset-selection and/or Bayesian parameter estimation methodologies that help stabilize otherwise ill-conditioned estimation problems. Use of these methodologies lead to improved parameter estimates and model predictions, which is crucial when models are used to select reactor operating conditions or to scale-up novel processes.

HYBRID RECYCLING OF POLYVINYL CHLORIDE AND POLYETHYLENE TEREPHTHALATE: A LIFE CYCLE AND TECHNO-ECONOMIC ASSESSMENT

ABDUL YAEESH YAISH

With global plastic waste accumulation continuously growing, effective recycling approaches are increasingly in demand. In this study, we propose a recycling system capable of recovering polyvinyl chloride (PVC), diisononyl phthalate (DINP), and polyethylene terephthalate (PET) from mixed waste consisting of tarpaulins and wire harnesses. The system combines selective dissolution to extract PVC and DINP and enzymatic hydrolysis to reduce PET to monomers terephthalic acid and ethylene glycol which are then re-polymerized. We show through life cycle assessment that the system has lower environmental impacts than virgin production in several categories including acidification (28% lower), ozone depletion (94% lower), land use (95% lower), and freshwater eutrophication (48% lower). Despite these improvements, the hybrid system was shown to lack performance in some key metrics such as climate change (48% higher), energy demand (26% higher), and carcinogenic toxicity (1,105% higher). Steam production for distillation is the primary contributor to most impact categories, followed by residual PVC waste treatment and electricity demand. Scenario analysis indicates that ameliorating these impacts depends on utility sourcing and alternative waste disposal practices. Techno-economic analysis reveals that the system cannot achieve price parity with virgin PVC, primarily due to high wire harness feedstock procurement. Although the system currently lacks environmental and economic sustainability, this study offers opportunities for process optimization and establishes a foundational methodology for developing hybrid recycling systems.