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A critical review on biofuels generation from pulp-paper mill sludge with emphasis on pretreatment methods: renewable energy for environmental sustainability

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Abstract

The pulp and paper mills generates substantial amounts of sludge, posing significant environmental challenge. Addressing this issue, this review explores the dual objective of renewable energy generation and mitigating the environmental impact of pulp-paper mill sludge (PPMS), filling a critical gap in the existing literature. PPMS is recognized as a promising source of fermentable sugars, mainly glucose, and holds potential as a feedstock for biorefinery applications to produce various renewable biofuels, such as biomethane, biohydrogen, bioethanol, biobutanol, and biodiesel, using biorefining concepts. These efforts align with the the United Nations Sustainable Development Goals (UN SDGs) by resource recovery and reducing environmental impact. The present article provides insights on renewable energy generation from PPMS. Despite its promise for bioenergy production, numerous bottlenecks have been identified, including high ash content and the presence of toxic inhibitors, such as phenolics, lignin, chlorolignin, and ligno-carbohydrate complexes which impact the hydrolysis of cellulosic fibers and limit the amount of energy recovery. Various pretreatment methods, such as mechanical, thermal, thermochemical, chemo-mechanical, enzymatic, and microbial are emphasized for their ability to enhance sludge solubility by modifying its structure, thereby releasing fermentable sugars. Pretreatment can decrease crystallinity of cellulose, increase accessible surface area, reduce lignin content, and improve bioenergy recovery in the form of oil and gases from PPMS. Finally, the article suggested future research directions in feedstock pretreatment, catalyst development, and optimization of the overall production system. These areas could address existing gaps in the literature and make the process more feasible and practical for real-world applications. In conclusion, bioenergy recovery from PPMS not only helps reduce the demand for fossil fuels in the near future but also provides a sustainable solution for managing paper sludge, in alignment with the principles of a circular economy.

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Highlights

- PPMS is a low-cost substrate of fermentable sugars to produce, biomethanol, bioethanol, butanol.
- Thermal pre-treatment positively impacted biomethane production from PPMS.
- PPMS contains inhibitors like phenolics, sulfite, wood extracts, organic acids, phenols, furfural, and lignosulfonates, which significantly affect process efficiency and recovery yield.
- Acid pretreatment are promising method to remove ash ($CaCO_3$) from PPMS.
- Ligno-carbohydrate complexes in pulp-paper sludge hindering microbial valorization.

Keywords Biohydrogen, Waste Valorization, Pulp-Paper Mill, Secondary Sludge, 5-Hydroxymethyl furfural

Introduction

The diminution of non-renewable fossil fuels and the increasing impact of climate change demand an immediate shift towards sustainable energy sources. In this scenario, lignocellulosic waste, including pulp and paper industry, has emerged as as a promising alternative due to its abundance and potential for bioconversion into clean fuels [1–4]. Renewable energy has emerged as a significant catalyst for economic and social progress in recent years, playing a vital role in safeguarding communities from the impacts of climate change [5, 6].

Globally, pulp and paper mills (PPM) are the largest contributor to the economy, generating paper products and employment opportunities [7–10]. At the same time, PPM produces substantial amounts of pulp-paper mill sludge (PPMS) – a heterogeneous waste stream containing cellulose fibers, minerals, and organic compounds [11–14]. Due to global demands of paper, paperboard and other paper products, the rapid growth of PPM increases day by day. In 2021, around 417.3 million metric tonnes of paperboard and paper were globally manufactured (https://www.statista.com/). This number is predicted to reach 700–900 million tonnes by 2050 [15, 16]. Approximately 300–350 million tonnes of pulp and paper are produced annually worldwide [17, 18]. The increased manufacturing of paper and paper products is expected to result in a simultaneous increase in PPMS formation by 48–86% compared to the current rates [19]. According to the Working Group report of the 12th Fifth Year Plan (2017) of the Government of India, the PPM in India annually produces approximately 10.92 million tonnes of paper. Interestingly, for every tonne of paper produced, it generates 40–50 kg of sludge, with 70% being primary sludge [20].

PPMS is a concentrated solid or semi-solid residual waste inevitably generated by the wastewater treatment plants (WWTPs) facilities of the PPM [21, 22]. It consists of a heterogeneous mixture of cellulose pulp fibers, minerals, and additional paper developing elements and organic compounds [23, 24]. The mineral content typically includes substances such as calcium carbonate, kaolin, and titanium dioxide, which are commonly used as fillers or coating materials in paper development. Additionally, PPMS contains microplastic fragments, with polyethylene and polypropylene being the most prevalent polymer types [25].

The composition and physical–chemical characteristics of PPMS differ depending on the pulping method and wastewater treatment techniques employed [26]. Typically, PPM facilities produce a wide variety of sludge, categorized into four main types: (i) primary sludge, which is produced in the primary clarifier [26, 27] (ii) secondary sludge, also referred as activated or biosludge, comes from secondary clarifier [12, 28]; (iii) de-inking paper sludge (DPS), which is generated by eliminating inks from post-consumer fiber of recycled papers [29, 30]; (iv) mixed sludge, which is a blend of primary and secondary sludges produced from the WWTPs [31, 32]. The enormous quantities of these different types of sludge produced by PPM pose a significant disposal problem for the PPM [33, 34].

To tackle this issue, various traditional approaches, such as landfilling, incineration, and composting, have been widely practiced for the management and disposal of PPMS. However, these approaches are environmentally sensitive due to their potential for groundwater, soil, and air pollution, as well as formation of toxic leachate and greenhouse gases [35]. To mitigate the adverse effects associated with conventional disposal practices, researchers worldwide have been exploring eco-sustainable methods for solid waste disposal [20, 36, 37].

To fully harness this resource without inducing environmental pollution, several strategies, including hydrothermal liquefaction [38], hydrothermal carbonization [39], gasification [40], pyrolysis [41, 42], torrefaction [43], and combustion [44] have been widely studied by the scientific community for the recycling and management of PPMS. However, these treatment approaches have some notable drawbacks including ineffective treatment, high operational cost, huge consumption of energy, and

noxious gases emissions [45, 46]. In response to these challenges, bioenergy recovery through the valorization of high-moisture-content PPMS has been considered as an alternative solution, aiming to enhance revenue through the production of renewable fuels like bioethanol, biomethane (Bio-CH_4), Bio-hydrogen (Bio-H_2), butanol, and biodiesel [47] that address critical energy challenges while reducing the environmental footprint of the PPM [2]. The valorization of waste from PPM for renewable bioenergy recovery offers an opportunity to increase profitability, boost local economic activity, and enhance the energy efficiency of PPM, all of which contribute to a circular economy.

According to an initial literature survey conducted by the authors indicates only two review articles have been published on the resource recovery and management of PPMS. In a comprehensive review published by Kumar and Verma [48], it was noted that several thermo-chemical technologies had been employed for platform chemicals synthesis, manufacturing of cardboard and supercapacitors, and the generation of high-value products like nanocellulose, cellulose, lactic acids, biofuels, and more. However, these articles remains lack of detailed information on inhibitors and their influence on resource recovery, as well as the utilization of various pretreatment methods. Kaur et al. [49] examined the pretreatment of activated sludge from pulp and paper industries, addressing inhibitory effects and proposing decontamination approaches for its biovalorization in fermentation processes aimed at producing value-added products.

The present study addresses the critical need to develop sustainable energy alternatives by exploring biofuel generation from PPMS, a largely untapped resource. Following this, the primary aim of this review article is to provide an in-depth discussion on the energy recovery from PPMS. While offering a solution for waste management and renewable energy production, this process faces limitations due to the presence of inhibitors like lignin and phenolics that hinder the conversion of cellulose into fermentable sugars.. Strategies to overcome these challenges include various pretreatment methods, such as mechanical, thermal, thermochemical, chemo-mechanical, enzymatic, and microbial. These methods enhance the accessibility of fermentable sugars by modifying the structure of PPMS. Furthermore, the review identifies key areas for future research, including the optimization of pretreatment processes, the development of robust bioconversion technologies, and the exploration of novel microbial strains for efficient biofuel production. By addressing these research gaps, the sustainable valorization of PPMS can be realized, leading to a circular bioeconomy and a reduced reliance on fossil fuels.

The present article begins with a general introduction, followed by an overview of traditional sludge management practices described. Subsequently, the generation of different kinds of sludge during the WWTP in the PPM and their detailed characterization has been briefly discussed. Next, next section explores the recovery of renewable energy from PPMS. Furthermore, the major challenges of the work are discussed. The future perspectives of the work are discussed. Finally, the concluding remarks of the study are presented. In conclusion, the study addresses literature gaps and provides direction for future research to enhance biofuels productivity, aiming to improve commercial feasibility and environmental sustainability. Aspects of the presented knowledge can be applied to develop a biorefinery.

Conventional sludge management approaches: why resource recovery is essential

Sludge disposal represents a substantial financial cost, accounting for approximately 60% of the total operating expenses of WWTPs in numerous mills. For this reason, in PPM, sludge is typically managed by landfilling [50], spreading in agricultural fields as a soil amendment [51, 52], composting [53, 54] or incineration [55] (Fig. 1). These practices are widely utilized to overcome this problem worldwide.

Landfilling is the preliminary method for disposing of PPMS. In several countries, PPMS is unfortunately still disposed of alongside household waste in landfills. Landfilling contributes to carbon footprints due to the decomposition of organic waste, releasing methane—a potent greenhouse gas. In addition, leachate generated from landfills can contaminate water and soil, posing ecological risks [56]. Moreover, upon deposition in landfills, the sludge undergoes anaerobic digestion, resulting in the production of excessive acids and the seepage of organic substances into the soil or runoff. However, utilization of these methods may become unsuitable in the future due to the high cost of disposal, new stringent environmental regulations, and decreasing potential with landfill space becoming scarce and expensive. When landfills, the potential value of these raw feedstocks is lost.

Land applications are the second most widely used method for disposing of PPMS [57, 58]. Applying PPMS to land as soil amendments could serve as an effective strategy to enhance soil physico-chemical quality and promote the growth of native vegetation [59–62]. In addition, it may also stimulate the growth of forest plants, contributing to ecosystem restoration efforts on industrial sites [63–66]. However, the presence of heavy metals and refractory organic contaminants in PPMS can adversely affect aquatic ecosystems, These contaminants

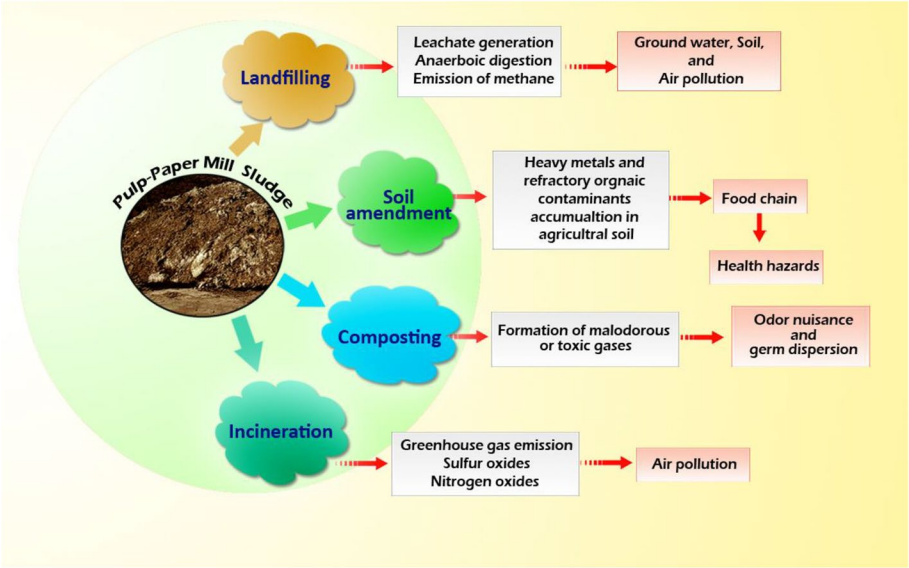

Fig. 1 Conventional pulp-paper mill sludge (PPMS) management approaches and their impact into the environment

may enter food chains and impact higher life forms through biomagnification [4]. Improper accumulation and management of PPMS not only consumes significant land resources but also poses severe threats to the environment. Therefore, the potential risks of soil pollution and hindered crop growth resulting from heavy metals and pathogens in PPMS cannot be ignored [67].

Composting and vermicomposting offer alternative methods for disposing of solid waste, which can reduce harmful substances in PPMS and recycle it for agricultural use [68–70]. Although composting and vermicomposting are considered viable biological waste management practices, they require additional energy inputs and may lead to noxious odor and the dispersion of pathogenic microbes. On the other hand, PPMS with high organic content is mostly incinerated to minimize its burden on the environment. This practice has been used for a long time for the permanent disposal of PPMS by mills. However, incineration is an uneconomic, and highly energy-intensive step. Incineration frequently demands supplemental fuel [71–73]. Secondary fiber paper mills heavily depend on energy, including electricity and heat, to operate machinery and dry paper sheets. Given the continual growth in energy production costs, numerous mills face increasing difficulties in maintaining profitability. Consequently, while incineration of sludge may seem like a viable solution, its feasibility is hindered not only by high moisture content but also by the presence of ash [74, 75]. The high ash and moisture content in PPMS diminishes its overall calorific value, promotes equipment corrosion, and results in residual waste that requires disposal [75, 76]. In addition, incineration of sludge leads to the emission of greenhouse gas (GHG), SOx, and NOx [77]. The expense of both capital-intensive may render incineration unfeasible for many low-income countries.

All of these practices not only lead to a substantial depletion of valuable bioenergy resources but also present challenges to energy security and environmental safety. These challenges encompass environmental contamination [2].

Types of sludge

Worldwide, PPM produces a considerable volume of solid waste, which is subjected to primary, secondary, or tertiary treatment to make it suitable for appropriate disposal [78]. Figure 2 displays an outline of the pulp and paper manufacturing process and the generation of sludge from numerous stages.

Primary sludge

Primary sludge is the residual lignocellulosic solid waste collected from the wastewater treatment plants (WWTPs) in both virgin and recycled PPM. It mainly consists of organic materials and some inorganic substances, posing an environmental challenge [70, 79]. Typically, primary pulp-paper mill sludge (Pri-PPMS) comprises the primary suspended solid collected via gravity settling in the primary clarifier. It constitutes around 3 to 4% of the whole paper product (dry weight) when processing virgin fiber and between 15 to 30% of the overall product when processing recycled fibers [80, 81]. The primary clarifier serves as the main unit for collecting precipitated particles, producing

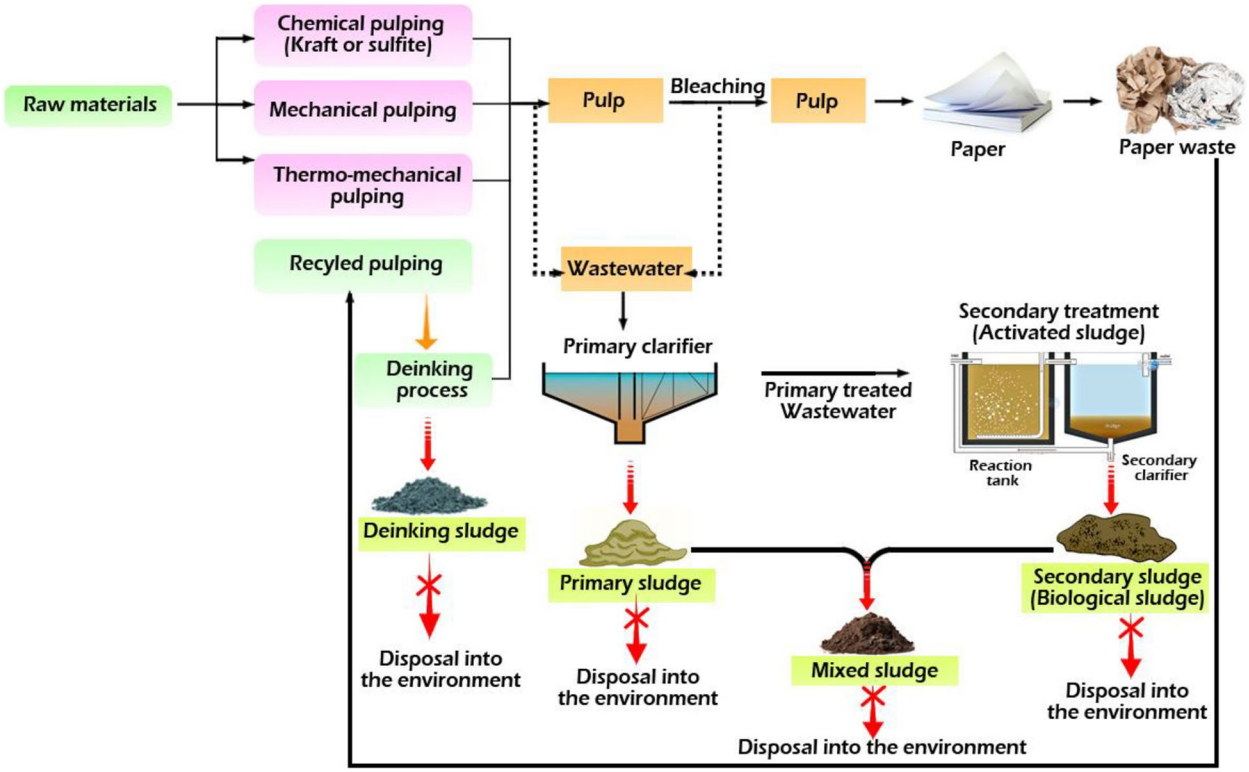

Fig. 2 Paper sludge occurrence in the pulp and paper mills

concentrated Pri-PPMS. Pri-PPMS mainly consists of high fiber materials, contaminants, and inorganic paper fillers (e.g., calcium carbonate ($CaCO_3$), kaolin (Al_2O_3, SiO_2), pitch, and titanium dioxide), as well as lignin by-products and ash. These components are often lost due to incomplete separations at numerous stages like pulp washing, bleaching, and other operations of pulp and paper manufacturing processes [48, 78, 82].

$CaCO_3$ fillers are an important component in Pri-PPMS. $CaCO_3$ is widely used in PPM due to its ability to enhance the whiteness, opacity, and ink absorption efficiency of the finished paper, while also reducing production cost. Moreover, $CaCO_3$ has different effects on dewatering performance [83]. Pri-PPMS typically exhibits greater dewaterability compared to biosludge, and the proportion between these two types of sludge significantly influences the overall dewaterability of the sludge mixture [84]. Furthermore, Pri-PPMS generally exhibits a moisture content ranging from 55 to 75%, which varies based on the dewatering techniques employed [85]. In contrast to secondary sludge, primary sludge typically contains higher solid residues and lower inherent moisture [49]. Research by Kim et al. [86] revealed that primary sludge from kraft pulp mills comprises approximately 58% cellulose, 12% hemicellulose, and 20% Klason lignin by weight. Cellulose, the main component of Pri-PPMS, is composed of cellobiose repeating units linked by 1,4-β-glycosidic bonds [87]. It can be enzymatically hydrolyzed into monomeric sugars, which can then undergo additional valorization processes.

Table 1 shows the composition of Pri-PPMS generated from a typical mill. Pri-PPMS represents a highly promising feedstock for large-scale biorefinery applications, aligning with the concept of the circular bioeconomy [88]. Pri-PPMS derived from PPM with varying in composition from 5–20% of lignin, 35–50% of ash, and 45–60% of carbohydrates (hemicelluloses and cellulose), on a dry basis. The pH of Pri-PPMS is between 8 and 10, higher than the optimal pH of around 5 for cellulase activity. However, the high content of ash, mainly $CaCO_3$ hinders the bioconversion of cellulose fibers [84].

Secondary sludge

Secondary sludge is the main solid waste stream emanated in the WWTP within the PPM [92, 93]. Broadly, the activated sludge process is a widely employed secondary treatment method for diminishing the organic content of pulp and paper mill wastewater (PPMW). However, this process also yields an inevitable byproduct called biological sludge. Secondary pulp paper mill sludge (Sec-PPMS) has a high moisture and ash content,

Table 1 Analysis of different types of sludge generated from various pulp-paper mills [29, 70, 78, 89–91]

Types	Primary sludge [70, 78]	Secondary Sludge [90]	Deinking sludge [29]	Types	Primary sludge [70, 78]	Secondary sludge [90]	Deinking sludge [29]
Parameters	**Values**	**Values**	**Values**	**Parameters**	**Values**	**Values**	**Values**
pH	7.3 ± 0.2	6.90 ± 0.28	7.83	Lignin	–	915 ± 38.70 (mg g^{-1})	9.10%
EC	0.69 ± 0.14	4.95 ± 0.10	–	Chlorophenol	–	462 ± 17.83 (mg g^{-1})	–
Organic matter	–	–	75.4%	Chloride	–	199.938 ± 489.85 (mg g^{-1})	–
Moisture content	63 ± 10 (%)	–	–	Total Elemental	–	–	–
Volatile solids	40 ± 3 (%)	–	–	Phosphorus	151 (mg kg^{-1})	–	0.02%
Total Nitrogen	–	-	0.36 (%)	Potassium	243 (mg kg^{-1})	23.75 ± 0.82 (mg g^{-1})	0.04%
Total organic carbon	23.00 ± 5.63 (%)	–	35.3 (%)	Calcium	12,300 (mg kg^{-1})	–	27%
C/N ratio	50 ± 10	–	73.03	Magnesium	657 (mg kg^{-1})	–	0.37%
TKN	0.35 ± 0.27 (%)	448 ± 18.86 (mg g^{-1})	0.29%	Sodium	1013 (mg kg^{-1})	398 ± 10.95 (mg g^{-1})	–
Ammonical nitrogen	15.00 ± 2.63 (mg kg^{-1})		0.002%	Cadmium	< 1 detectable limit	–	0.08 (mg g^{-1})
Sulfate	–	349 ± 12.25 (mg g^{-1})	–	Chromium	13 (mg kg^{-1})	4.31 ± 0.20 (mg g^{-1})	8.05 (mg g^{-1})
Sulfide	–	0.1428 ± 0.003 (mg g^{-1})	–	Cobalt	< 2 (mg kg^{-1})	0.089 ± 0.004 (mg g^{-1})	< 10 (mg g^{-1})
Soluble BOD	4.20 ± 0.40 (g kg^{-1})	–	–	Copper	123 (mg kg^{-1})	1.91 ± 0.025 (mg g^{-1})	51.4 (mg g^{-1})
Soluble COD	6.70 ± 0.80 (g kg^{-1})	–	–	Iron	852	8.17 ± 0.23 (mg g^{-1})	–
Total Phosphorus	300 ± 67 (mg kg^{-1})	–	–	Nickel	24	0.571 ± 0.03 (mg g^{-1})	2.01 (mg g^{-1})
Available Phosphorus	112 ± 15 (mg kg^{-1})	–	76.7 (mg kg^{-1})	Lead	< 20	–	< 10 (mg g^{-1})
Phosphate	–	4.95 ± 0.10 (mg g^{-1})		Zinc	35	7.771 ± 0.31 (mg g^{-1})	102 (mg g^{-1})
Available K		–	1.3 (mg kg^{-1})	Selenium	–	–	< 0.5 (mg g^{-1})
Water	55.0 (wt. %)	–		Manganese	–	8.80 ± 0.43 mg g^{-1}	–
Cellulose Quantity	14.5 (wt. %)	–	10.10%	Arsenic	–	–	< 1.5 mg g^{-1}
Hemicellulose (%)		–	6.49	Mercury	–	–	< 0.20 (µg kg^{-1})
Kaolin	11.0% (wt. %)	–	–	Dioxins and furans (ng EQT kg^{-1})	–	–	3.3
Calcite (calcium carbonate)	11.5% (wt. %)	–	–	–	–	–	–
Organic compounds and heavy metals Quantity	8.0% (wt. %)	–	–	–	–	–	–
Bulk density	1.476 (g/cm^3)	–	–	–	–	–	–
Specific density	2.260 (g/cm^3)	–	–	–	–	–	–
Water content	88.29 (wt. %)	–	–	–	–	–	–
$CaCO_3$ content	40.5 (%)	–	–	–	–	–	–

BOD Biochemical Oxygen Demand, *COD* Chemical Oxygen Demand, *TKN* Total Kjehdahl Nitrogen, $CaCO_3$ Calcium Carbonate, EC Electrical Conductivity, C/N Carbon/Nitrogen

primarily composed of $CaCO_3$ with low calorific value. It comprises biodegradable and recalcitrant organic compounds, chlorinated organics, sulfide, sulfate, phosphate, Na^+, K^+, Cl^-, lignin, and trace amount of heavy metals [90, 94, 95]. In addition, Sec-PPMS consists of lignin by-products, cell-decay products, and ubiquitous biomass of culturable and unculturable microbial communities [96]. The characteristics and quantity of Sec-PPMS vary depending on the feedstock, manufacturing processes, and the specific WWTP utilized [78]. Due to the significant costs associated with sludge disposal, WWTPs often optimize secondary treatment processes to minimize sludge production. However, this optimization typically leads to enhanced demand for aeration, which constitutes over 50% of the electricity consumption in a WWTP [97]. In many PPM, Sec-PPMS is commonly combined with Pri-PPMS to facilitate removal of water during the sludge dewatering process. Subsequently, it is thickened and disposed of through landfilling or incineration [32, 98]. The calorific values of all the PPMS samples were insufficient to recover energy through thermal processing. However, the elevated ash content of PPMS was suitable for biocomposites, with the potential to enhance their strength using fillers present in PPMS [99].

Mixed sludge

In PPM, the mixed sludge that consists of primary and secondary waste activated sludge is also generated [32, 77]. The ratio of primary to secondary sludge in mixed sludge varies among mills, often maintained at levels such as 50:50, 40:60, or 67:33. This mixture facilitates improvement in dry solids content from 2–3% to 25–40%. The final dry solids content typically ranges from approximately 10% to 50%, influenced by the type of sludge and the dewatering unit employed [100].

Deinking paper sludge

Recycled paper mills utilize a de-inking process to eliminate inks, clay fillers, and coatings from used paper. Deinking sludge is a residue that comes from the deinking process as a paper recycling process for old newsprint paper or old used paper to collect the pulp by removing ink from post-consumer fiber [30, 101]. The generation of deinking sludge can reach levels as high as 150 kg of dry solids per tonne of paper manufactured [102, 103]. Deinking sludge has an extremely complex composition that consists of some fibers, fillers, chemical additives, minerals, lignin, cellulose, and hemicellulose. Additionally, the ash content in deinking sludge typically comprises a significant portion, ranging from 50 to 70% of the total mass, leading to a lower heating value. Deinking sludge typically comprises around 30% organic materials and 70% inorganic metal salts, including ferric, magnesium, calcium, and zinc salts, with calcium predominating as $CaCO_3$ [104]. Deinking sludges are generated during the processing of waste paper consist of ink residues, surfactants, fibers, carbonates, and additives [105]. The study of potentially inhibiting elements indicates that the concentrations of mineral oil, chlorolignin compounds, and metallic elements are the highest concentrations in deinking sludges [101, 103].

Renewable energy generation

Bioenergy holds a crucial position within renewable energy sources, offering substantial potential to meet our energy requirements. Lignocellulosic biomass, in particular, serves as a versatile feedstock for the generation of various biofuels, including Bio-CH_4, Bio-H_2, biomethanol, bioethanol, butanol, and biodiesel [106].

Biomethane

Anaerobic digestion (AD) has been widely considered as an economic and eco-friendly sustainable technology for treating enormous quantities of PPMS and simultaenosuly generating biofuels in the form of Bio-CH_4 (50–75%) [107]. Despite the renewable energy recovery, this technology helps to reduce potentially toxic compounds, decrease sludge volume, and reduce the overall treatment plant operating costs [10]. In addition to generating Bio-CH_4, AD yields a stabilized product that can be utilized as a soil conditioner to improve the quality of degraded soil [108, 109]. In general, AD is a microbial process that operates under oxygen-free conditions (anoxic) to convert organic matter found in PPMS into biogas. This biogas primarily comprises CO_2 and Bio-CH_4, along with minor traces of other impurities like water vapor, ammonia (NH_3), hydrogen sulfide (H_2S), and water vapor. AD, including methanogenesis, is performed by anaerobic microbial communities and takes place in four successive stages, each requiring its characteristic group of microorganisms: (i) hydrolysis, in which hydrolytic bacteria and fungi break down complex organic macromolecules including cellulose and hemicellulose into its smaller components through their enzymatic mechanisms (ii) acidogenesis, during which hydrolysis products are transformed to intermediate volatile fatty acids, and other products like NH_3, H_2S, and Bio-H_2 by the activity of acidogenic bacteria (iii) acetogenesis, in which acetate, CO_2, and Bio-H_2 are generated from fermentation products and (iv) methanogenesis, producing Bio-CH_4 from acetate or CO_2 and Bio-H_2 by a group of obligate anaerobic archaea called methanogens [110–113]. Figure 3 illustrates a flow diagram of the generation of Bio-CH_4 and its four digestion stages.

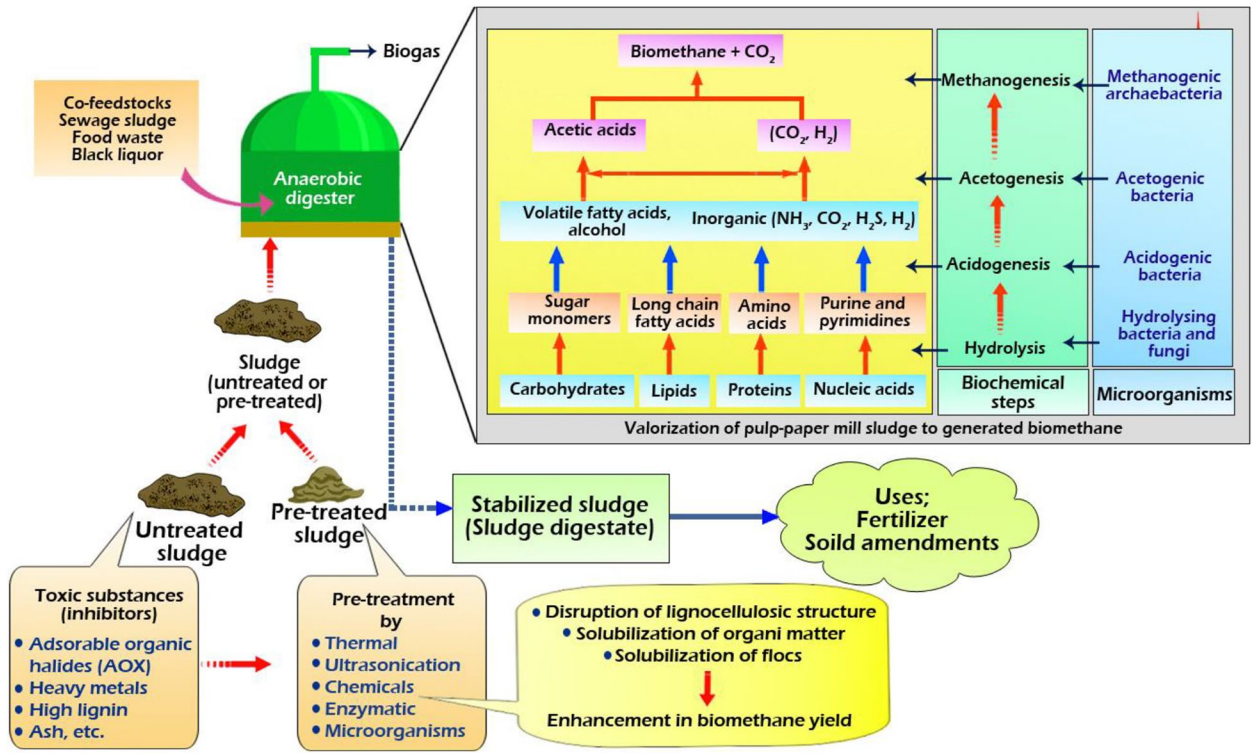

Fig. 3 Schematic representation of anaerobic digestion process of pulp-paper mill sludge

AD has been utilized for decades to stabilize lignocellulosic sludge waste discharged from wastewater treatment plants (WWTPs). Moreover, the use of AD technology for PPMS has not been industrially established because of low biomethane yield (BMY) and long digestion times [101, 114, 115]. Limited findings have been published on the AD of PPMS. Bayr et al. [116] carried out semi-continuous AD trials in a continuous stirred-tank reactor (CSTR), observing Bio-CH_4 production of 190–240 NL Bio-CH_4 per kg volatile solids (VS) for primary sludge over a 23–32 day hydraulic retention time (HRT). The BMY decreased to 150–170 NL Bio-CH_4 per kg VS when a blend of secondary and primary sludge was used and the HRT was reduced to 14–16 days. Authors recommended that Pri-PPMS is more promising to produce biogas compared to Sec-PPMS. Lopes et al. [117] combine lab-scale experiments with mathematical modeling to investigate the Bio-CH_4 generation under thermophilic conditions utilizing the primary and secondary sludges of kraft pulp mills. The anaerobic digestion model based on process simulation developed by Rajendran et al. [118] was adjusted for kraft pulp mill sludge using the biomethane potential (BMP). With a few simple modifications to the Rajendran et al. model, the secondary sludge achieved the highest BMY (46.9 NmL Bio-CH_4 /g VS in 30 days) [117]. The energy balance showed that, because the heat generated by the Bio-CH_4 is insufficient, the AD process under thermophilic conditions for secondary sludge of the kraft mill remains impractical on a large scale [117]. Bio-CH_4 generation potential of lignocellulosic waste depends mainly on its water and organic matter content [101]. Studies on the AD of various Sec-PPMS suggest that these materials typically exhibit low organic matter content, resulting in lower BMP and BMY [115, 119]. The lower BMY and reduced rates of Bio-CH_4 generation of PPMS attributed to the presence of high concentrations of possibly toxic substances like chlorolignin chemicals, mineral oil, and certain metallic elements, coupled with the high ash content, during the AD of PPMS [120]. The presence of toxic chemicals has been identified as the key factor influencing the BMPs of paper sludges [101]. Moreover, the inherent recalcitrant nature of the sludge, characterized by its high lignin content, poses a challenge for bioconversion to Bio-CH_4. In addition, the ligno-carbohydrate complexes present in the PPMS create a barrier for microbial conversion, hindering the efficient production of Bio-CH_4 [121, 122]. The intricate structure necessitates a slow degradation process, thus demanding larger reactor volumes and long HRT for the AD of such wastes at a large scale, consequently resulting in higher

capital costs. Furthermore, the occurrence of sludge flocs makes PPMS hard to be hydrolyzed. According to the report, the majority of the organic substance in waste activated sludge primarily attached with microbial flocs, lowering the organics' bioavailability for AD. Therefore, hydrolysis stands out as the major rate-limiting step impacting the break down of organics during AD of sludge [120].

Microbial cell walls form a semi-rigid structure, protecting the cell from osmotic lysis and rendering them resistant to biodegradation. Through the deflocculation of sludge, rupturing microbial cells, and solubilizing organic matter, sludge pretreatment can effectively break down lignocellulosic biomass and release organic materials. These pretreatment methods can enhance the subsequent enzymatic hydrolyzability of lignocellulosic waste by altering its structure and/or composition to varying degrees. Sludge pretreatments hold the potential to induce cell disruption by dismantling the floc structure and breaking down cell walls into smaller particles, thereby facilitating further hydrolysis [123].

Various sludge pretreatment methods, such as thermal [119, 120], electro-hydrolysis [124], microwave, ultrasonic and chemo-mechanical [125], enzymatic [126], and microbial [127] have been investigated for improving the feasibility of AD of PPMS. The efficacy of three pre-treatment strategies to boost the rate of anaerobic bioconversion of Sec-PPMS—obtained from a kraft pulp mill and a sulfite pulp mill—to Bio-CH_4 was demonstrated by Wood et al. [128]. Pretreatment methods that were employed included: (i) thermal pretreatment at 170 °C; (iii) sonication at 20 kHz and 1 WmL^{-1}; and (iii) thermochemical (caustic) pretreatment at 140 °C and pH 12. The greatest effect on the biodegradability of sludge was caused by thermal pretreatment. Consequently, Bio-CH_4 production rate from kraft sludge and BMY improved by 300 times and 280%, respectively. Moreover, the Bio-CH_4 production rate from sulfite sludge and BMY improved by 50% and 10 times, respectively.

The anaerobic bioconversion of Sec-PPMS to Bio-CH_4 can be greatly increased by the heat and caustic pre-treatment. Pretreatments contribute to the disruption of the lignocellulosic structure, thereby rendering the cellulose more readily available to acidogens [115, 129]. Kinnunen et al. [120] explored mesophilic AD of biosludge of the PPM, focusing on long-standing efficiency of the reactor and the impact of thermal pretreatment. Hydrolysis was identified as the limiting step, but autoclaving the biosludge (20 min at 121 °C) improved hydrolysis, enabling digestion with a shortened HRT of 10 days. This resulted in a BMY of 138 NL CH_4 kg^{-1} VS and allowed for an organic loading rate (OLR) of 2.2 kg VS m^{-3} d^{-1}, whereas untreated biosludge digestion failed with a 10-days HRT due to slow hydrolysis. Long-term mesophilic anaerobic digestion (365 days) showed stable operation with HRTs of 20 and 14 days, however biosludge led to an unstable AD process when the solid content was low (1.5% TS) compared to biosludge with a higher solid content (2.5 to 4.3% TS). Thermal pretreatments resulted at temperatures ranging from 105 °C to 134 °C increased BMPs by 39–88%, while pretreatment at 80 °C showed no significant effect on the final BMP.

Granström and Montelius [130] explored enhancing BMY from PPMS using thermal and chemical pretreatments. Thermal pre-treatment at 140 °C positively impacted Bio-CH_4 production, while 70 °C treatment showed no significant difference. Among the 70 °C treatments, pH 2 was most effective, while $Ca(OH)_2$ at pH 9 had minimal impact. However, at 140 °C, both acid and NaOH treatments decreased Bio-CH_4 production, while $Ca(OH)_2$ showed no significant difference. Overall, thermal pre-treatment at 140 °C alone substantially improved BMY by 170%, rendering additional chemical pre-treatments unnecessary [130]. The effectiveness of PPMS hydrolysis was evaluated by Veluchamy and Kalamdhad [115] using a variety of thermal pretreatment techniques, including a water bath, autoclave, hot air oven, and microwave. The solubilization of organic materials improved with each pretreatment technique. According to Velukhamy and Kalamdhad [115], the hot air oven pretreatment produced the best results in terms of solubilization rates, soluble chemical oxygen demand (sCOD), and volatite fatty acids (VFA) among various pretreatment techniques.

Bayr et al. [116] investigated the effects of various pretreatment methods on the chemical composition and BMY of Sec-PPMS in batch assays at 55 °C. These methods included ultrasound, enzymatic, hydrothermal, and chemical pretreatment (used alone or in combination). The results revealed that hydrothermal pretreatment at 150 °C for 10 min, either alone or in combination with ultrasound pretreatment and/or enzymatic, had the most significant impact on solubilization of sludge and BMY. This treatment led to a notable 31% increase in BMY. Enzymatic pretreatment also showed improvements in BMY, particularly when coupled with pretreatment at 150 °C. However, pretreatment with ultrasound alone did not yield improvements in BMY. Moreover, alkaline and acid pretreatments resulted in lower BMY than the control [116].

To enhance the BMY, Lin et al. [123] established an alkali pretreatment procedure employing various NaOH solution concentrations prior AD of PPMS. 8 g NaOH/100 g TS_{sludge} was the ideal concentration of NaOH for solubilizing organics during the pre-treatment

stage. In this case, the PPMS flocs structure was severely disrupted, which led to a drop in the fiber size and void rate during pretreatment, an increase in VFA concentration during AD of 1040 mg acetic acid/L, and sCOD of up to 83%. The highest BMY ($0.32 m^3$ $CH_4/kgVS_{removal}$) was detected under optimal pretreatment conditions.

Preethi et al. demonstrated that calcium peroxide (CaO_2) induced mechanical disintegration under acidic conditions enhances biopolymer and biogas production from PMS [10]. Optimal floc fragmentation occurred with a CaO_2 dosage of 0.06 g/g SS at pH 5. Anaerobic biodegradability assays showed an increased biogas yield of 167 mL/g COD, compared to 52 mL/g for the crude sample.

Black liquor (BL), a by-product of soda pulping, can increase Bio-CH_4 generation from excess PPMS while reducing treatment costs [131]. NaOH was found to be effective as other thermochemical pretreatment methods for dissolving flocs and solubilizing sludge. Nevertheless, the addition of BL resulted in a 7–30% enhancement in the BMY as well as an increase in the background COD and VFA concentration. Study recommended that using BL instead of NaOH for the thermal process was cost-effective [131].

The rate and extent of the AD of PPMS were examined using the BMP method with various food/microorganisms (F/M) ratios, as detailed in the study by Veluchamy and Kalamdhad [114]. The highest BMY (3.4 L) occurred at F/M ratio of 2.0, followed by 3.3 L at F/M ratio of 1.5 and 2.9 L at F/M ratio of 2.5. The optimal Bio-CH_4 production rate was observed to be 3.66 L. Lower F/M ratios may affect biomass activity due to high substrate concentration during BMP testing, while F/M ratios greater than 2.0 resulted in reduced BMY due to improved VFA generation, lowering reactor pH and inhibiting methanogen activity [114]. Pretreating raw material with the active microbial consortium OEM1 and concurrently degrading lignocellulose and chlorophenols enhanced the BMY by 1.4 times, with a maximum BMY of 429.19 mL/gVS recorded [127]. Moreover, following the active OEM1 pretreatment, the AD system became more stable with a pH range of 6.1–7.5 and without VFA inhibition.

Hagelqvist [132] investigated how to increase the potential of Bio-CH_4 generation from Sec-PPMS by combining batch-wise mesophilic anaerobic co-digestion with municipal sewage sludge (MSW). During a 19-days batch AD process, when up to 50% of the VS were substituted with Sec-PPMS, the generation of Bio-CH_4 for MSW remained largely unchanged. Moreover, it was demonstrated that the solid byproduct of the AD of the Sec-PPMS from the forest industry should be appropriate for use in enhancing the quality of soil in areas not utilized for food production.

Biohydrogen

Biohydrogen (Bio-H_2) has gained widespread recognition as a clean and renewable energy source in the twenty-first century, characterized by zero pollutant emissions from combustion. Bio-H_2 generation from the conversion of sludge, through fermentation and saccharification, has been considered an environmentally friendly and less energy-intensive process of waste management. It allows the use of industrial sludge for obtaining cleaner and greener bioenergy, with a high calorific value [133]. The generation of Bio-H_2 would give a new direction to PPMS management and contribute positively to climate change adaptation and circular economy [134].

Anaerobic fermentation and dark fermentation are two common methods widely employed for the generation of Bio-H_2 from organic waste. In this context, Wu and Zhou [135] studied the anaerobic Bio-H_2 production from paper mill sludge (PMS) under optimized conditions, such as sludge reaction time (SRT) of 32 h and OLR of 3000 mg $COD{\cdot}L^{-1}{\cdot}d^{-1}$. Bio-$H_2$ was produced within a biohydrogen yield (BHY) of 620.8 mL H_2/g COD, and the organic material utilized was 31.8% [135]. Lin et al. [133] demonstrated the co-digestion of food waste (FW) and pulp-paper sludge (PPS) under anaerobic conditions for Bio-CH_4 and Bio-H_2 co-production in two-stage mesophilic–thermophilic process in batch reactors. The maximum BHY of 64.48 mL g^{-1} VS_{fed} and BMY of 432.3 mL g^{-1} VS_{fed} were achieved with a 1:1 VS ratio of PPS to FW as feedstock. No VFA accumulation, NH_3–N, or Na^+ inhibition occurred during Bio-H_2 and Bio-CH_4 fermentation, with 71%–87% elimination efficiencies of sCOD [133]. Yadav and Mohanty [136] highlighted the utilization of PMS as biomass for Bio-H_2 generation from steam gasification by optimizing the steam flow rate (SFR) to analyze syngas characteristics. The optimal SFR was determined as 0.75 mL/min, with corresponding syngas characteristics: $1.4 m^3$/Kg (syngas yield), 11.92 MJ/m^3 (high heating value; HHV), and 58% (Bio-H_2 fraction). The highest cold gas efficiency (CGE) reached approximately 96% at the optimal SFR [136].

PPMS appeared to be a readily usable substrate for *C. thermocellum,* which hydrolyzes the amorphous cellulose of PPMS yielding both potential biofuels (Bio-H_2 and bioethanol) as well as active cellulases [137]. An et al. [138] achieved the highest Bio-H_2 production of 64.32 mM with 7.4% paper sludge under thermophilic conditions. Using high-throughput sequencing (HTS) technology, they investigated the dominance of the orders Clostridiales and Thermoanaerobacterales during Bio-H_2 generation. *Thermoanaerobacterium* and *Ruminiclostridium* were identified as key players in the hydrolysis of paper sludge and subsequent Bio-H_2 generation. Furthermore, the study indicated that supplementing

with *Clostridium thermocellum* significantly improved holocellulose degradation rate and Bio-H_2 yield by 32.95%, and 96.80%, respectively. Moreover, inoculation with *C. thermocellum* shortened the lag phase of Bio-H_2 production and enhanced VFA generation. However, Bio-H_2 production through anaerobic fermentative methods encounters a fundamental limitation of low BHY.

Dark anaerobic fermentation presents an intriguing substitute for generating Bio-H_2 due to its cost-effectiveness and the availability of diverse organic substrates. This process, which operates under anaerobic conditions without light or oxygen constraints, is facilitated by microorganisms capable of utilizing a wide array of feedstock, including various waste types and lignocellulosic materials, for Bio-H_2 production. Pulping sludge, rich in cellulosic substrate holds promise for Bio-H_2 production via dark fermentation. The use of paper sludge in the fermentative generation of Bio-H_2 by the extreme thermophile *Caldicellulosiruptor saccharolyticus* was discussed by Kádár et al. [139]. Paper sludge hydrolysate added to the medium was promising to produce Bio-H_2, acetate, and lactate as the only carbon and energy source. The medium's carbon balance and lactate production were factors that affected the BHY. In comparison to the generation rate in media containing xylose, glucose, or a mixture of these sugars, the maximum volumetric Bio-H_2 generation rate was 5 to 6 mmol/ ($L \bullet h^{-1}$). The lowest rate of Bio-H_2 production indicates that the paper sludge hydrolysate contains inhibitory substances [139].

The primary component of PPMS is cellulose, a linear polysaccharide polymer composed of cellobiose units tightly connected by β-1,4-glycosidic bonds. The remarkable tensile strength of microfibrils arises from the interconnection of cellulose chains via van der Waals forces and hydrogen bonds. In PPMS, hemicellulose binds the cellulose microfibrils, while lignin complexes encase them. Due to its complex and specialized structure, cellulose is resistant to chemical and biological attacks. Hemicellulose polymers, heterogeneous polysaccharides made of hexoses, pentoses, and acids, are branched, random, and amorphous. The interaction of hemicellulose's short, branching chains with lignin, amidst the cellulose microfibril network, forms a rigid cellulose-hemicellulose-lignin matrix. Similar to lignocellulosic substrates, pulping sludge is resistant to enzymatic and microbiological processes and consists of multifaceted components like lignin, hemicellulose, and cellulose. Sugars derived from PPMS can serve as a source of carbon feedstocks by microbes to produce Bio-H_2 and other biochemicals. However, high ash content in PPMS, particularly $CaCO_3$, impact the enzymatic hydrolysis of cellulosic fibers by enhancing their surface area [87].

Pretreatment breaks down the crystalline structure of cellulose and disrupts the lignin structure, which improves the hydrolysis efficiency of the lignocellulosic substrate. Lin et al. [133] studied the optimal starting pH, the ideal carbon-to-nitrogen (C/N) ratio, and the pulping sludge proportion for the generation of Bio-H_2 from anaerobic sludge pretreated with NaOH at high temperatures. The best yield of reducing sugar production (229.68 ± 2.09 mg/gTVS) was obtained by pretreating the sludge with a 3% NaOH solution at 121 °C for 2 h in an autoclave, followed by hydrolyzing it with 5 filter paper unit (FPU) crude cellulase at 50 °C and maintaining pH 4.8 for 24 h. For the generation of Bio-H_2, a C/N ratio of 40 and an initial pH of 6 were ideal. Furthermore, the addition of paper waste to the pulping sludge increased the overall output of Bio-H_2 production. The greatest BHY was 151.70 ml/gTVS, and the continuous Bio-H_2 synthesis was carried out in a glass reactor with nylon fragments serving as supporting media.

Pre-washing of PMS with diluted hydrochloric acid (HCl) converts insoluble ash, such as $CaCO_3$, into soluble $CaCl_2$, typically improving enzymatic hydrolysis of the sludge [140]. To improve PMS digestibility, Rorke et al. [141] developed a promising surfactant-coupled green liquor dregs pretreatment strategy. Following pretreatment, a considerable decrease in aluminum, chromium, cobalt, arsenic, lead, and copper and improve substrate digestibility. The maximum reducing sugar release under optimized conditions was 16.38 g/L. The comparative study of Bio-H_2 production in simultaneous saccharification and fermentation (SSF) and separate hydrolysis and fermentation (SHF) showed that SSF demonstrated a 36.26% enhancement in BHY from pretreated PMS, with a 3.72 mL/g. Bio-H_2 production from paper industry wastes was conducted using SSF in batch reactors with anaerobic biofilms [142]. Results showed that without pretreatment, optimal conditions for maximizing Bio-H_2 production were pH 5 and an enzyme load of 70 FPU, yielding 31.188 mmol/h × gSV. With 2.5% H_2SO_4 pretreatment, optimal conditions were 70 FPU enzyme load and pH 4, resulting in the highest BHY of 55.844 mmol/h × gSV.

Bioethanol

Bioethanol production from the PPMS has emerged as a highly promising feedstock, offering a viable contribution to renewable processes that can be used to generate sustainable clean energy generation [143]. Moreover, it helps to avert the disposal of these wastes through landfilling [144]. Sludge from PPM, containing cellulose, hemicellulose, lignin, and ash, serves as a promising feedstock for fermentable sugars, primarily glucose. The extensive

surface area of fine PPMS fibers enhances enzymatic hydrolysis efficiency [145]. It can be repurposed for microbial fermentation to produce bioethanol, thereby enhancing its valorization [146]. The study illustrated that utilizing PPMS for bioethanol production enables both the valorization of this waste and a reduction in its final volume simultaneously [147]. Specialized software for economic analysis in the pulp and paper industry showed that producing bioethanol from fractionated PPMS was significantly more profitable [148]. Converting PPMS into bioethanol involves two key steps. Firstly, the polysaccharide component undergoes hydrolysis to yield fermentable sugars, such as L-arabinose, D-xylose, and D-glucose, dissolved in hydrolysate. Secondly, these lignocellulosic hydrolysate containing the fermentable sugars ferment into ethanol by microbial process [149]. Moreover, the fermentable sugars can be utilized for the synthesis of biopolymers, biochemicals, and biofuels,

Bioethanol production commonly employs SHF and SSF processes. Figure 4 represents the experimental setup for the production of bioethanol from PPMS by SHF and SSF processes. Separate hydrolysis, conducted separately from the fermentation step, mainly involves the use of extracellular enzymes and refers to the process of breaking down lignocellulosic material, typically found in lignocellulosic biomass, into simple sugars like D-glucose and D-xylose, and other fermentable sugars, such as D-galactose, D-mannose, and D-arabinose. Enzymes, usually cellulases and hemicellulases, are added to the pretreated biomass to catalyze the hydrolysis reaction, breaking down the hemicellulose and cellulose into fermentable sugars. The resulting simple sugars can be used in fermentation to produce platform chemicals like succinic, citric, and lactic acid, and biopolymers, such as polyhydroxybutyrates (PHBs) and polyhydroxyalkanoates (PHA). Cellulases, comprising a cocktail of enzymes-namely β-glucosidases, endoglucanases, and exoglucanases, are widely employed in separate hydrolysis and plays a substantial role in the transformation of cellulose into fermentable sugars. Once the hydrolysis is complete

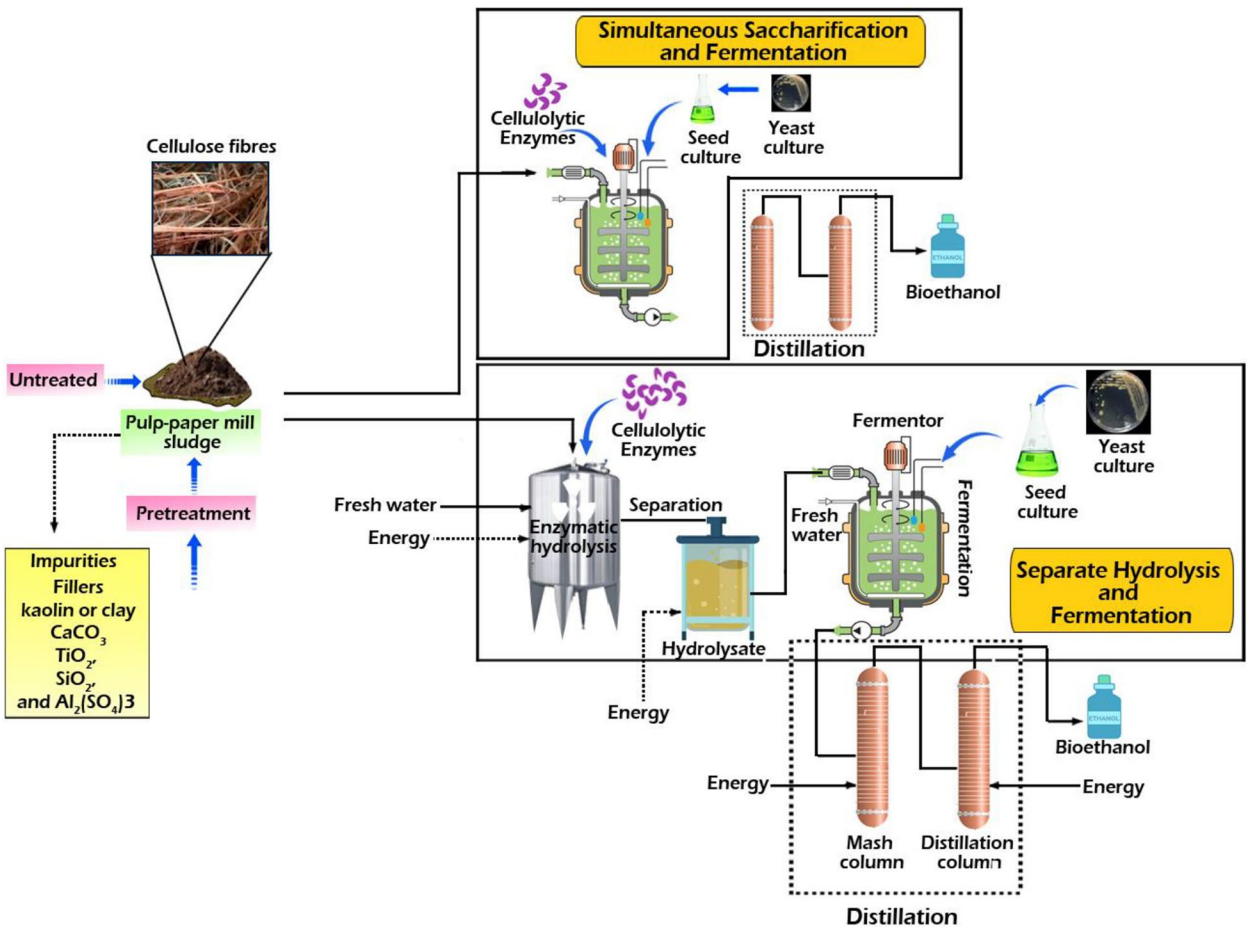

Fig. 4 Diagrammatic presentation of the overall process of the production of ethanol from pulp-paper mill sludge by separate hydrolysis and fermentation and simultaneous saccharification and fermentation processes

and the sugars are released, they are separated from the solid biomass, and the resulting sugar solution, known as hydrolysate, is fermented by yeast or bacteria to produce bioethanol [146].

Zambare and Christopher [88] developed an integrated biorefinery approach utilizing PPMS to produce value-added products, such as lipids, biofuels, additive materials, and fermentable sugars, that have various usages in numerous industries. They hydrolyzed primary sludge using a commercially available cellulase enzyme (Cellic® CTec2) alongside non-ionic surfactants, particularly polyethylene glycol 4000. The use of surfactants resulting in a two-fold increase in hydrolysis efficiency, reaching 74.4%. Response surface methodology revealed that solids and enzyme loadings significantly enhanced enzymatic hydrolysis. The fermentability of the hydrolysate was also evaluated by using *Saccharomyces cerevisiae*, which produced 9.7 g/L of bioethanol with a 92% bioethanol yield, and *Cutaneotrichosporon oleaginosum*, an oleaginous yeast, which yielded 37.8% biolipids at a C/N ratio of 40. However, the use of commercial enzymes to hydrolyze PPMS has limitations due to its high cost and requirement of distinct optimal conditions for the hydrolysis of particular substrates by enzymes. Apart from this, enzymatic sugar recovery is hindered by the inorganic material, lignin, and lignin monomers found in PPMS. In addition, fillers, high ash content, and impurities like clay orkaolin, SiO_2, $Al_2(SO_4)_3$, and TiO_2 related to cellulosic fibers inhibit cellulase activity, thus making PPMS a challenging substrate for biofuel generation [150].

The high ash content in PPMS is mainly due to the occurrence of $CaCO_3$, a major filler, derived from lime kiln and paper manufacturing waste streams. This negatively impacts the enzymatic hydrolysis process in PPMS, as ash creates alkaline conditions and tends to bind with enzymes more readily than the fibers. Ash showed higher enzyme affinity than fibers, with approximately 3–5 mg of enzyme loss per gram of acid insoluble ash [80, 151]. Dyk et al. [143] demonstrated increased bioethanol synthesis from paper sludge waste using cellulase-producing *S. cerevisiae* strains. Ethanol Red® and genetically engineered strains Cellusec® 1.0 and 2.0 utilizing xylose and producing cellulase and produced bioethanol.

Cao et al. [152] highlighted that enzymatic hydrolysis of PMS has been ineffective due to poor cellulase binding by $CaCO_3$ and clay. This reduces the digestibility of cellulose fibers in PMS, resulting in low hydrolysis yields (8–32% glucose per gram of cellulose). However, the cellulose crystalline structure hampers accessibility to chemicals and enzymes. The ash content can vary by weight from 10 to 50%, depending on the mill type. Due to interference of ash in enzymatic hydrolysis of PPMS, it is essential to undertake pretreatment procedures to minimize or eliminate ash components before advancing to enzymatic hydrolysis and bioconversion processes [146, 153]. These steps are crucial for neutralizing the alkalinity of sludge and lowering the pH level. Doing so enhances fiber hydrolysis, ensuring a significant yield of sugars [146]. A study by Chen et al. [80] revealed that enzyme hydrolysis produced higher sugar yields from fractionated material. Gurram et al. [150] explored a wide array of methods for the elimination of $CaCO_3$ from PMS. The promising method involved removing $CaCO_3$ as calcium chloride ($CaCl_2$). In this method, 1 M HCl was employed that successfully converted the insoluble $CaCO_3$ to soluble $CaCl_2$. The soluble $CaCl_2$ could be separated from the sludge with washing. $CaCO_3$ removal occurs according to the following reaction.

$$\underset{\text{Calcium carbonate}}{CaCO_3} + \underset{\text{Hydrochloric acid}}{2HCl} \rightarrow \underset{\text{Calcium chloride}}{CaCl_2} + \underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Water}}{H_2O}$$

Gurram et al. [150] stated that $CaCO_3$ concentration was reduced from 27% to 0.5% w/w (dry weight basis) when using HCl. The pretreatment of PPMS eploying HCl plays a crucial role in removal of ash content. Gurram et al. [150] investigated the bioconversion of paper mill sludge (PMS) into bioethanol using either cationic polyelectrolyte (as an accelerant) or hydrogen peroxide (H_2O_2) pretreatment. Ash and $CaCO_3$ are eliminated from PMS during pretreatment using accelerants and H_2O_2. This enhances enzymatic hydrolysis, leading to quicker and more efficient cellulose conversion and increased ethanol fermentation. The de-ashed sludge further boosts hydrolysis yields by 16% and 25% (g glucose/g cellulose). Within 9 h, the fermentation of the formed sugars yields up to 95% of the theoretical optimal bioethanol production, resulting in higher bioethanol productivity.

Mendes et al. [154] investigated the elimination of ash from paper sludge using various acids (acetic acid, HCl, nitric acids (HNO_3), sulfuric acid (H_2SO_4), or spent acid). Concentrated acids allow the hydrolysis of hemicelluloses and cellulose. HCl and HNO_3 were found to be most effective, reducing the ash content from 35% to 1.8% and 1.9%, respectively. This enhancement led to improved enzymatic hydrolysis of primary sludge. The

pretreatment of sludge with HCl enhanced sugar conversion yields by the enzymatic action from 20 to 88% while the treatment with spent acid enhanced sugar conversion yields from up to 72%.

Duncan et al. [149] explored the conversion of PPMS to sugars and then fermentated it to either ethanol or isoprene. Chemical profiling of sludge showed that the $CaCO_3$, including hemicellulose, ranged respectively from 0.4 to 34%, 8.4 to 10.7%, and 28 to 68%. The existence of $CaCO_3$ led to low hydrolysis rates. To address this, HCl was employed in sludge washing, which neutralized the $CaCO_3$, and improved hydrolysis rates by 50 to 88%. However, the generation of isoprene was "very low" (190 to 470 nmol). In fermentation, the highest conversion efficiency occurred when an industrial yeast strain was used, with productivity ranging from 0.18 to 1.64 g L^{-1} h^{-1}. While fractionation improves carbohydrate conversion, the highest sugar recovery was achieved with sludge containing 20% ash [155]. It is recommended to use a high-shear process with more acid to prevent the harmful effects of ash and improve cellulase accessibility to fibers [155]. Fiber separation, essentially a washing procedure, isolates pure cellulosic materials from additives and fillers. Thus, the recovery of fibers is essential for the optimal functionality of microbes and enzymes and for mitigating any inhibitory effects [144]. The conversion of PPMS to bioethanol conversion in the SHF process is shown in Fig. 4.

The SHF process, while offering advantages in certain contexts, also comes with several disadvantages, such as time-consuming, additional equipment and space requirements, high energy consumption, lower yield of the desired products, high operational complexity, and high production cost. Unlike SHF, SSF presents the advantage of integrating saccharification and fermentation processes. This integration reduces the need for enzymes and lowers production costs. In addition, SSF has the potential to decrease energy consumption and shorten processing time, and overall expenses, possibly eliminating the necessity for sterilization [82]. In this context, Mendes et al. [82] utilized *S. cerevisiae* ATCC 26602 for SSF to demonstrate the integrated bioconversion of Pri-PPMS into second-generation bioethanol. This process involves an enzymatic hydrolysis stage to convert carbohydrates into monosaccharides, followed by fermentation to produce bioethanol. Despite initial mixing challenges, batch conditions achieved higher bioethanol productivity, yield, and concentration (0.78 g L^{-1} h^{-1},, 48.9%, and 41.7 g L^{-1}, respectively) with an enzyme dosage of 5 FPU gCH^{-1}, surpassing fed-batch results. These metrics further improved to 1.02 g L^{-1} h^{-1}, 64.0%, and 54.6 g L^{-1} when the dosage of enzyme was enhanced to 15 FPU gCH^{-1} in SSF.

Enzymatic saccharification is often preferred to acid hydrolysis as it combines cellulose hydrolysis with bioethanol fermentation. Boshoff et al. [156] evaluated the use of virgin and recycled mill sludge in high solids fermentation with low enzyme dosages during SSF for bioethanol production. They noted that when solid loadings are high, both water-holding capacity and viscosity have a crucial impact on bioethanol generation. The elevated viscosity of PMS limited the maximum solid loading attainable to 18% (w/w) for virgin PMS and 27% (w/w) for recycled PMS, with enzyme dosages of 20 FPU/g dry paper sludge and 11 FPU/g dry paper sludge, respectively. The bioethanol yield and concentration for recycled paper sludge and virgin pulp were 45.5 g/L at 78.2% and 34.2 g/L at 66.9%, respectively.

The effectiveness of enzymatic saccharification in lignocellulosic substrate depends on the chosen pretreatment method, including factors, such as the specific physiological conditions (like mixing, temperature, and pH), the level of preserved lignin, as well as the concentrations of inhibitors, enzymes, and substrate. To enhance the efficiency of converting sludge into chemicals, various pretreatment methods were employed to decrease the $CaCO_3$ content and adjust the pH levels. A fed-batch semi-simultaneous saccharification and fermentation method was employed to explore an advanced enzymatic pre-hydrolysis technique for the effective transformation of PPMS into bioethanol [157]. The highest yield of reducing sugars, 45 ± 3.75% (w/w), was achieved in validation experiments under optimal conditions, which included a surfactant concentration of 0.16%, (w/w), a solid loading of 6% (w/w), and enzyme loading of 158 FPU/gm. The fed-batch saccharification with an 18% (w/w) PPS solid loading yielded a maximum of 8.65 g/L xylose and 79.56 g/L glucose after 60 h. Furthermore, fermentation with a Baker's yeast (*S. cerevisiae*) and co-culture of *Pichia stipitis* NCIM 3499 at 18% (w/w) solid loading produced 42.34 g/Lbioethanol, with a yield of 0.53 g/g. To advance sustainable energy, Alkasrawi et al. [158] conducted a techno-economic study and developed an innovative evaluation method for converting PMS into bioethanol. The study found that de-ashing alters the surface morphology and increases the sugar yield to nearly 86%, compared to just 2.2% in sludge sample. Using Aspen PLUS, the conversion of PMS to biofuel was modeled, revealing a significant reduction in energy usage by around 13,320 MJ/h. The simulation also indicated that producing bioethanol from PMS is 20% more cost-effective compared to corn stover. The life cycle assessment of bioethanol generation from PPMS was conducted by Sebastião et al. [147]. They employed a cradle-to-gate approach to evaluate an ethanol plant designed to process 5400 tonnes of dry sludge per year.

The environmental hotspots identified were the hydrolysis and neutralization of $CaCO_3$. The study demonstrated environmental benefits through the use of recombinant yeast capable of co-fermenting glucose and xylose, as well as by reducing the quantity of HCl in the neutralization process.

To effectively remove lignin and hemicellulose, PPS material was first treated with a series of pre-treatment techniques, including steam explosion and NaOH treatment. Das et al. [159] isolated a potential cellulolytic bacterium strain, *Arthrobacter woluwensis* TDS9, that efficiently convert cellulosic content of primary PMS into reducing sugar employing carboxymethyl cellulose (CMC) as the sole source of carbon. An alkaline pH (8.0) improved sugar production to 1100.09 µg/mL in a medium with CMC of 1.5% and beef extract 1.25% after 72 h at 25 °C. Potassium ions (K^+) boosted carboxymethyl cellulase (CMCase) activity upto 1.06 U/mL at pH of 8 and temperature 50 °C, using CMC as a substrate for 30 min. Strain TDS9 yielded 433.33 µg/mL reducing sugar from 1% pretreated PMS. Beta(β)-glucosidase II (53 KDa) and endoglucanase IV (33 KDa) were detected in crude protein. Microscopic examination revealed structural alterations in cellulose fibers post-chemical treatment, enhancing enzymatic hydrolysis saccharification. These ultrastructural changes facilitated the release of the cellulose fibers and enhanced the saccharification for enzymatic hydrolysis.

Energy conservation, economic efficiency, and waste stream management are crucial in producing bioethanol from PPMS. A study explored the potential of reusing effluent from the PMS de-ashing method for bioethanol production, rather than adding fresh water [160]. De-ashing is the removal of organic and inorganic materials from fiber cellulose, essentially a purification process using water and diluted base or acid to cleanse the fiber's impurities. The study found that up to 30% of the process effluent could be reused without adversely affecting the fermentation of bioethanol or enzymatic hydrolysis. Consequently, there is a 30% reduction in the volume of effluent requiring treatment, leading to a 22.5% cost saving. Furthermore, the recycling effluent decreases the energy needed in the evaporation and distillation units by 1206 kJ/kg.

To maximize saccharification and subsequent sugar production, process parameters must be optimized for effective saccharification of the selected feedstock. Utilizing a Box–Behnken design (BBD), Pri-PPMS with a glucan content of 51% was employed to optimize the enzymatic saccharification process for bioethanol synthesis [161]. Nonionic surfactants have been demonstrated to enhance enzymatic hydrolysis of cellulosic biomass in several studies. Borjesson et al. [162] reported that the addition of surfactants (polyethylene glycol 4000; PEG-4000) enhanced the enzymatic conversion rate of steam-pretreated spruce significantly from 42 to 78%. Interestingly, this improvement was not observed when spruce was delignified, suggesting that PEG 4000 enhanced hydrolysis by binding to lignin. Alkasrawi et al. [163] showed that adding 2.5 g/L of Tween 20 reduced the amount of enzymes required by half while maintaining the same yield of bioethanol using spruce chips as the substrate in SSF. The addition of surfactant (PEG-4000) increased the enzymatic saccharification efficiency of dried primary sludge (DPS) by 12.8%. Solid enzyme loading and saccharification duration had notable impacts on DPS saccharification. Despite a projected saccharification efficiency discrepancy of 56.76%, the experimentally validated optimal conditions—1% (w/w DPS) PEG-4000 loading 2.03% enzyme loading (10 FPU/g DPS), and 10.4% w/w DPS solid loading—achieved a saccharification efficiency of 57.66%. Moreover, *S. cerevisiae* fermented the saccharified sugars into bioethanol (9.35 g/L), greater the theoretical maximum sugar-to-bioethanol conversion yield by 91.6%. This approach could minimize the need for sludge disposal, promoting a circular economy and offering an eco-friendly solution. Zhu et al. [18] demonstrated that autoclaving and washing had limited impact on improving enzymatic hydrolysis of PMS. However, washing reduced ash content, thereby decreasing the amount of acid needed for neutralization. The addition of nonionic surfactants, such as PEG-8000, Tween 80, and Triton X-100 enhanced PMS conversion rate. The optimal rates of 55.4% and 56.3% were achieved using 5% PEG-8000 and 1% Triton X-100, respectively. The supplementation with 5% PEG-8000 achieved the maximum conversion rate of 74.7% with 10% PMS and 3% enzymes [18].

Typically, fermentable reducing sugars are derived from lignocellulosic biomass through hydrolysis using alkali-acid reagents. However, this method of acid/alkali hydrolysis presents several challenges, including difficulties in product separation, equipment corrosion, catalyst recyclability, and post-treatment waste disposal. These limitations have driven the search for alternative methods. In addition, these methods disrupt the intracellular redox balance, affecting the fermentation capabilities of yeast. By-products, such as acetaldehydes, furfural, and 4-hydroxybenzoic acids can act as growth inhibitors for yeast.

Aviation fuel

The production of sustainable aviation fuel (SAF) from PPMS offers a promising pathway for renewable energy generation. PPMS is rich in organic matter, which can be processed through thermochemical or biochemical

methods to produce bio-oil. This bio-oil can then be upgraded and refined into SAF, providing a low-carbon alternative to fossil-based aviation fuel. Lan et al. conducted a life-cycle assessment (LCA) on converting paper sludge contaning high-ash to SAF utilizing a catalytic sugar upgrading system [164]. This process yields a carbon intensity of 35.7–41.8 $gCO_2eq\ MJ^{-1}$ SAF (−636 to −584 gCO_2eq per dry kg paper sludge) when acetone is used as a solvent. Recycling ash for cement substitution can further reduce this to 5.1–11.1 $gCO_2eq\ MJ^{-1}$ (−925 to −873 gCO_2eq per dry kg). Producing SAF from paper sludge (−925 to −584 gCO_2eq) is more climate-friendly than landfilling, with the potential to yield over 330 million gallons of SAF annually and cut emissions by 2–7 million tCO_2eq [164].

Biodiesel

Biofuels, such as bioethanol and biodiesel, generated from the chemical or biological conversion of lignocellulosic waste of PPM, are currently considered a promising approach to reduce the environmental impact of PPMS and address the depletion of fossil fuels [165, 166]. PMS offers a low-cost carbon source for oleaginous microorganisms to produce lipid production in fermentation process. Deeba et al. [167] utilized *Cryptococcus vishniaccii* to convert PMS into neutral lipids for biodiesel production. Ultrasonication was employed as a pretreatment device to obtain paper mill sludge extract (PMSE). This sludge extract yielded higher intracellular lipid content (53.40%) and lipid production (7.8 ± 0.57 g/L) compared to the glucose synthetic medium (5.5 ± 0.8 g/L, 40.44%). Following transesterification of the triglycerides in the lipid droplets into biodiesel and subsequent GC–MS analysis, the biodiesel exhibited improved oxidative stability and quality, attributed to increased levels of oleic, palmitic, linoleic, and stearic acid.

Butanol

Bio-based butanol is considered a promising next-generation fuel due to its advantage over bioethanol, such as lower vapor pressure, reduced corrosiveness, and greater energy density. In this context, PMS was utilized for biobutanol synthesis. A novel bioprocess for production of butanol from industrial wastes was developed by Cao et al. [168]. Their study highlighted the co-valorization of PMS and 5% corn steep liquor (CSL) using a strain of *Clostridium tyrobutyricum* cat1::adhE2. During the SHF, PMS demonstrated a yield of over 80% when hydrolyzed into monosugars, allowing for the production of 16.5 g/L butanol.

Challenges

PPMS is inevitably generated in huge volumes by the WWTPs facilities of PPMs. There is an urgent need for sustainable methods to manage these large volumes of sludge. The use of PPMS production as a potential renewable energy feedstock still faces several challenges. One significant hurdle in utilizing sludge as a feedstock in microbial fermentation processes lies in managing its high ash content, primarily stemming from filler materials like clay, TiO_2, $Al_2(SO_4)_3$, SiO_2, and $CaCO_3$ associated with cellulosic fibers. Ash significantly hinder enzymatic hydrolysis, thus hampering efficient bioconversion. Thus, the removal of ash becomes imperative for optimal bioconversion. Moreover, the high water holding capacity of PPMS frequently results in an extremely viscous fermentation medium, thereby diminishing adequate mixing. Consequently, a range of physical, chemical, or physicochemical pre-treatment processes has been employed to eliminate ash from PPMS. However, these methods utilize huge quantities of toxic chemicals and high energy inputs and are not affordable on large scale. Thus, the high cost associated with the requisite pre-treatment procedures pose another challenge in producing biofuels at modest cost compared to traditional fossil fuels. To unlock the potential of PPMS as a renewable energy source, a deeper understanding of PMS biomass chemistry and feasible valorization technologies are require. The important challenges of fermentation are the inconsistent yield and low productivity of value-added products from the PPMS hydrolysate. The key challenge so far has been the absence of data concerning pilot-scale systems and the transition to industrial applications of using PPMS as a substrate for generation of bioenergy in microbial processes. These challenges provides a road map for future research. Figure 5 shows the major obstacles in valorization of PPMS for bioenergy and biofuel generation.

Future perspectives

Pulp and paper industry generates millions of tonnes of waste annually, becoming a major environmental burdens worldwide. This critical review identified the gaps that lead to the following research directions;

- ➢ The heterogeneity of the PPMS presents challenges in developing standardized receovry and yield processes for bioenergy. Future research is required to comprehend the detailed chemistry of PPMS, aiming to develop more effective methodologies.
- ➢ Solubilization of solids in fermentation media is essential to release nutrients from PPMS and promote microbial growth. Future studies should

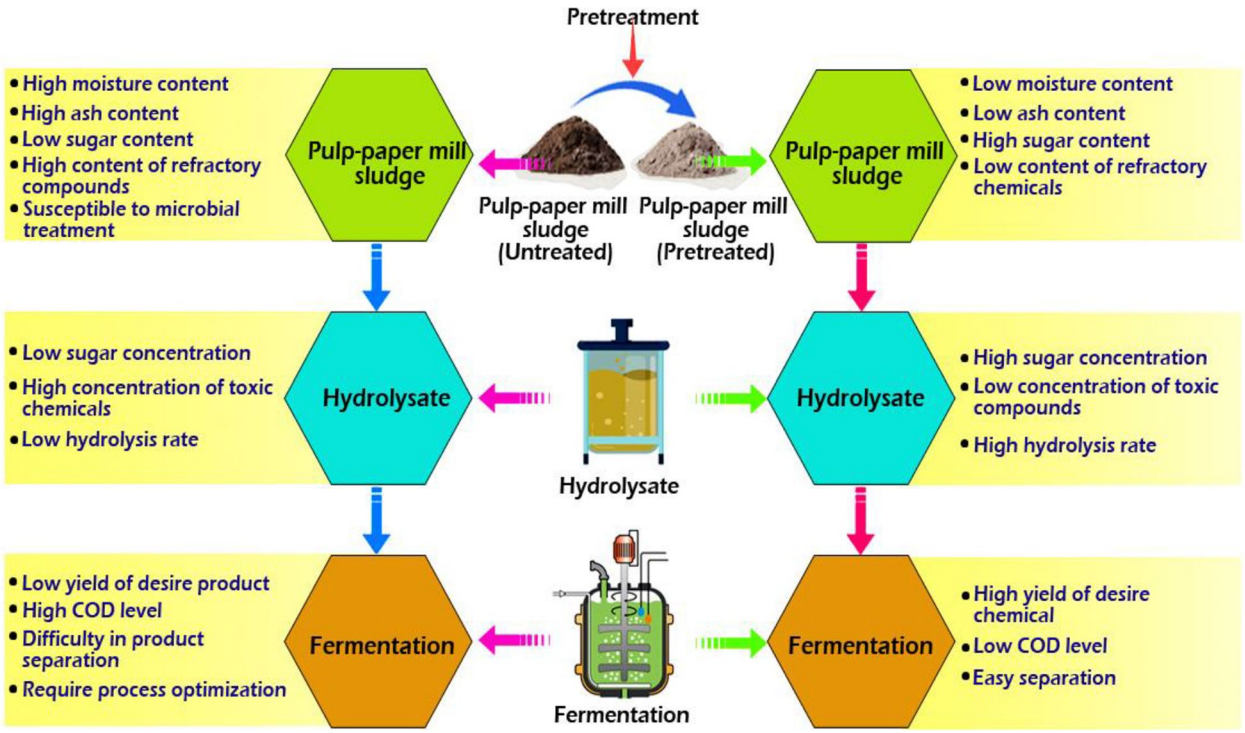

Fig. 5 Schematic shows some of the major challenges associated with the valorization of pulp-paper mill sludge which hider the product yield and recovery processes

emphasis on improving the release of nitrogenous and carbon compounds in fermentation media.

➢ Cocktail of microbial enzymes plays a vital role in biotransforming and degrading organic content in PPMS to generate biofuels. Research is needed to understand the detailed mechanism and identify enzymes involved in degradation and/or biotransformation of lignin and other co-contaminants present in PPMS.

➢ PPMS contains high quantities of inhibitor that hinder microbial growth during fermentation. Rigorous investigation is still essential to identify robust microbial strains that can endure the high variability of organic content in PPMS.

➢ Optimizing the nutritional and environmental process parameters is crucial for maximizing bioenergy recovery from PPMS through microbial valorization. Further investigation is required in this area.

➢ Most PPMS valorization research focuses on lab-scale experiments with great potential for renewable bioenergy production and environmental impact reduction. Pilot and field studies are needed to demonstrate the effectiveness of microbe-based valorization technology and increase its acceptance.

➢ Future investigation should address technological challenges, such as inconsistent yield, downstream operation, and bioreactor setup to enhance the bioenergy recovery for commercialization.

➢ Future research is needed to optimize valorization technologies, aiming to improve the yield and recovery of bioenergy and biofuels from PPMS.

Overcoming these challenges requires developing effective techniques for pretreatment and valorization of PPMS. This approach will integrate circular economy principles and sustainability practices in thePPM, particularly relevant when using PPMS as a feedstock.

Conclusion

The sustainable management of PPMS produced by the paper manufacturing industry is becoming a matter of public concern due to their potential environmental and human health impacts. PPMS can be used as a value added renewable feedstock for the fermentation industry due to its high content of monosaccharides or even in polysaccharides,. Recovering renewable energy from PPMS is a promising waste management approach aligns with the Unite Nations Sustainable Development Goal 7 (Clean and affordable energy) and promotes environmental sustainability. This review highlights the use of PPMS as a sustainable feedstock for Bio-CH_4, Bio-H_2, bioethanol, biobutanol, and biodiesel generation. However, the

high ash content in PPMS, primarily from materials like kaolin or clay and $CaCO_3$, adversely affects enzymatic hydrolysis, posing challenges for bioenergy recovery. Pretreatment methods such as accelerant, steam explosion, and chemical treatments (H_2O, HCl, NaOH, HNO_3) have been crucial for reducing inhibitor concentrations and enhancing conversion efficiency. Thermal techniques such as ultrasonication, microwaves, hot air ovens, and autoclaving have shown potential to improve biomass accessibility, enhance sludge solubilization for enzymatic hydrolysis, and boost biofuel production. However, due to their energy-intensive nature, further research is needed to develop more cost-effective approaches to improve biogas yields. Nonetheless, achieving high yields remains a challenge, more studies are needed to optimize biofuel synthesis through the removal of maximum concentration of inhibitors from PPMS. Moreover, most of the PPMS valorization studies have been conducted at the laboratory scale to generate Bio-CH_4, Bio-H_2, and other renewable fuels. Ongoing research still faces numerous challenges that must be addressed to achieve scaled production and commercialization. There should be a focus on in-depth pilot-scale and field-scale analyses of both technical and socio-ecological aspects, including biodegradability, toxicity, environmental emissions, energy balance, and cost issues, rather than focusing solely on laboratory-scale studies. This approach will help assess the relevance of bioenergy production for commercial applications. In addition, future research should focus on modelings, simulations, as well as sustainability, and techno-economic analysis. In conclusion, the utilization of PPMS holds substantial promise to produce bioenergy, contributing to reducing environmental impacts and promoting a circular economy and should be recommended.

Abbreviations

PPM	Pulp-paper mills
Pri-PPMS	Primary pulp-paper mill sludge
WWTP	Wastewater treatment plant
PPMS	Pulp-paper mill sludge
AD	Anaerobic digestion
HRT	Hydraulic retention time
BMY	Biomethane yield
BMP	Biomethane potential
VFA	Volatile fatty acid
F/M	Food/microorganisms
PMS	Paper mill sludge
PPS	Pulp-paper sludge
SHF	Separate hydrolysis and fermentation
Bio-CH_4	Biomethane
Bio-H_2	Biohydrogen
SSF	Simultaneous saccharification and fermentation

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Authors' contributions
VK conceptualized this study and drafted the manuscript. VK was a major contributor in writing, reviewing, and editing this manuscript. He also revised it critically before initial submission. Authors PV, FA de F, PKS, AV, JHPA-P contributed substantially to writing, reviewing, editing, and commented on the initial draft of the manuscript. All authors read and approved the final manuscript.

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Declarations

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Competing interests
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