



## Review article

# Linking mechanochemistry with the green chemistry principles: Review article

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## ABSTRACT

The need to explore contemporary alternatives for industrial production has driven the development of innovative techniques that address critical limitations linked to traditional batch mechanochemistry. One particularly promising strategy involves the integration of flow processes with mechanochemistry. Three noteworthy technologies in this domain are single-screw extrusion (SSE) and twin-screw extrusion (TSE) and Impact (Induction) in Continuous-flow Heated Mechanochemistry (ICHeM). These technologies go beyond the industrial production of polymers, extending to the synthesis of active pharmaceutical ingredients, the fabrication of (nano) materials, and the extraction of high-added value products through the valorisation of biomass and waste materials. In accordance with the principles of green chemistry, ball milling processes are generally considered greener compared to conventional solvothermal processes. In fact, ball milling processes require less solvent, enhance reaction rates and reaction conversion by increasing surface area and substituting thermal energy with mechanochemical energy, among others. Special attention will be given to the types of products, reactants, size of the milling balls and reaction conditions, selecting 60 articles after applying a screening methodology during the period 2020–2022. This paper aims to compile and analyze the cutting edge of research in utilizing mechanochemistry for green chemistry applications.

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## 1. Introduction

In recent decades, both the scientific community and society have heightened awareness regarding the impact of human activities on the environment. This increased awareness has exerted pressure on authorities and spurred efforts to find solutions to environmental challenges. Chemistry has emerged as a focal point of concern, given that many traditional chemical processes are not sustainable in the long term, leading to detrimental effects on the environment and overall quality of life, leading to well-known problematics such as climate change. As defined by International Union of Pure and Applied Chemistry (IUPAC), mechanochemistry involves chemical reactions induced by the direct absorption of mechanical energy. This mechanical energy can be applied through various means such as by shearing, stretching, grinding, or milling [1]. Impact is typically achieved through processes such as a jet mill, a falling hammer, and a disintegrator, while shear occurs in a mortar and pestle as well as in an extruder. Simultaneous application of both impact and shear forces is achieved in devices like a vibrating mill, an attritor, and a planetary mill (Fig. 1).

Mechanochemistry has been established, as a part of the chemistry, since the 1880s [2]. But it was not until 1990s that it has become a recognized field [3], with examples of such reactions occurring in commonplace devices like pestles or mortars. However, more comprehensive devices were developed, both at the laboratories or pilot level, such as ball milling, single-screw extrusion (SSE) or twin-screw extruders (TSE) [3]. Recent advancements in synthetic and purification techniques have elevated mechanochemistry's potential as a promising avenue for clean production processes [4–8]. Noteworthy examples include patents such as WO2016156749A1 “Method for manufacturing calcium zincate crystals, and the uses thereof” for the so-called IMPACT reactor, a ball milling reactor employing micro-sized zirconia oxide beads, which has been utilized in diverse applications and products development [9–11].

Mechanochemistry constitutes one of the four primary fields of chemistry, alongside thermochemistry, electrochemistry, and photochemistry. However, its applications have garnered increased attention from the scientific community in recent decades, owing to its numerous advantages. Notably, these advantages include the environmentally friendly nature of mechanochemical processes, the significant reduction or complete elimination of hazardous solvents, the ability to configure the reactor under milder conditions without requiring external heat, and the achievement of high yields in less time compared to other technologies [4,7,12,13]. This is attributed to the reduction in particle size, resulting in an increased surface area, enhanced contact between reactants, minimized mass transfer limitations, and accelerated reaction rate [7,14,15]. Despite the notable progress, mechanochemistry's development is still in its early stages when compared to its potential in advanced chemical synthesis [4,16]. Positioned between chemistry and mechanical engineering, mechanochemistry emerges as an indispensable tool for various applications within sustainable chemistry. Mechanochemical technologies are employed either independently or in conjunction with other technologies – such as when its used to help activating the reaction before a conventional solvothermal reactor – to design and synthesize advanced chemical materials with added value [17].

For instance, metal-organic frameworks (MOFs) have received special interest due to their properties, including extraordinary porosity, adjustable pore sizes, and extensive possibilities for varying organic-inorganic compositions. Extensive studies of MOFs thus far underscore their significant potential, particularly in catalysis, gas adsorption, drug delivery, water treatment, and energy storage. However, the large-scale production of MOFs faces limitations primarily due to uneconomical, environmentally unfriendly, and complex synthesis methods. Mechanochemistry is an alternative solution for the efficient and environmentally friendly synthesis of various MOFs [4,10,18,19]. Regarding thermoplastics recycling, the mechanical forces generated in mechanochemical processes can induce chain scission and the formation of free radicals [20–22]. Furthermore, mechanochemistry proves capable of synthesizing chalcogenides in the form of nanoparticles, such as sulfides and selenides. These materials are significant contenders for application in thermoelectric and photovoltaic systems, transforming thermal and solar energy into electrical energy without generating hazardous by-products [23–25]. Furthermore, the application of mechanochemical treatment in biomass research has drawn significant attention from researchers. This method effectively reduces the particle size, crystallinity, and degree of polymerization of lignocellulosic materials, influencing the structural characteristics of lignin, cellulose, and hemicellulose [26]. A major advantage is that this process is physical, meaning that, as the degree of polymerization decreases, toxic compounds typical of chemical depolymerizations are not produced [27]. Consequently, the ultimate objective of employing these mechanochemical processes is to facilitate the separation of components within lignocellulosic waste, leading to their valorisation. This involves producing chemical compounds with high added value using enzymes or heterogeneous catalysts [28,29].

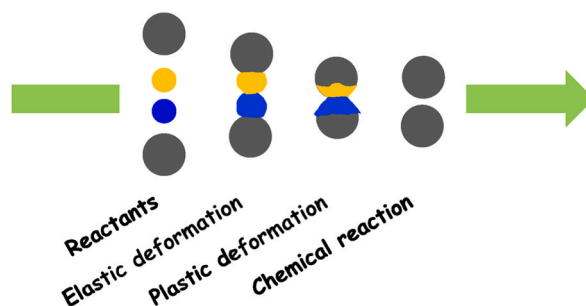


Fig. 1. Basic concept for ball impact energy in mechanochemical synthesis.

Other relevant areas of research has garnered significant attention in recent years. For instance, the development of asymmetric organocatalysis and the mechanoenzymology under ball milling activation. Avila-Ortiz et al. (2019) highlight this trend in their study, "Recent Applications of Mechanochemistry in Enantioselective Synthesis," where they emphasize advantages such as the elimination of solvents from reaction media [30]. The study presents the application of small dipeptides as chiral organocatalysts under solvent-free and high-speed ball milling conditions, with a focus on the asymmetric aldol addition reaction. Pérez-Venegas et al. (2020 and 2021) discuss the use of mechanochemistry in the synthesis of pharmacology active compounds [31,32]. Their work emphasizes the evaluation of biocatalytic protocols mediated by the combination of mechanical activation and enzymatic catalysis, representing an innovative and promising "green" approach in chemical synthesis in a high carbon emitting sector such as pharmacology.

Micro-ball-milling (beads) is widely used in mechanochemistry to grind powders into tiny particles. In these processes, mechanical forces are generated by the impact of the micro-milling balls (0.5–1 mm of diameter) with the reactants. Solvent-free processes or those using catalytic quantities of solvent, such as in the case of liquid-assisted grinding (LAG), are relatively uncommon in chemical synthesis. However, in the past decade, this approach has gained popularity with the use of ball milling because of its ease of use, low cost, environmental friendliness, and potential to yield extremely high yields [7,33].

The objective of this paper is to compile and analyze the cutting edge of research in the utilization of ball milling for green chemical syntheses. For the sake of clarity, special attention will be given to the types of products and reactants, the material of the milling balls, and the utilized reaction conditions, among others.

## 2. Methodology

The present review follows the principles of systematic reviews [34] to avoid common biases affecting traditional literature reviews [35]. Initially, we conducted a search for papers on mechanochemical ball milling reactions that provided information on reaction conditions, materials, yield, and selectivity. The search string was applied to titles, abstracts, and keywords on the ScienceDirect scientific database: ("ball milling") AND (reaction OR synthesis) AND temperature AND time AND (conversion OR yield) AND selectivity AND flow. Only paper in English, published in peer-reviewed journals, were considered. The search yielded 9797 articles, which were screened for publications from January 2020 to February 2022 within the Environmental Science category. The remaining 354 articles underwent a manual screening process at progressively greater levels of detail (e.g., titles, abstracts, and full text) [35]. Eligibility criteria were applied to ensure alignment with the scope and goal of the present study. Additionally, 7 articles meeting the specified criteria were identified during the course of this work. These articles came to the authors' attention through references of other papers, in the preparation of unrelated studies, or through papers related to the work of the present review. The resulting set of scientific papers (60 articles) underwent detailed study and analysis. They were compiled and summarized in an Excel table, which included information such as the corresponding authors, title, keywords, year of publication, journal, number of pages, location, details on chemicals, and reaction conditions, and the materials used. The ROSES flow diagram [36] illustrates the process followed in screening and synthesizing the scientific articles (Fig. 2).

The ScienceDirect database has been used as one of the leading and prominent scientific repositories worldwide. However, the authors of the present article wish to caution that certain works dealing with innovative reactions, mechanisms, and system development may be absent in this review, especially if they have been published in other scientific databases.

To address this potential gap, the authors suggest complementing the present review with additional research from reputable sources comparable to ScienceDirect in reliability and comprehensiveness. For instance, we wish to acknowledge the recent relevant review from Juaristi and Ávila-Ortiz (2023) [38].

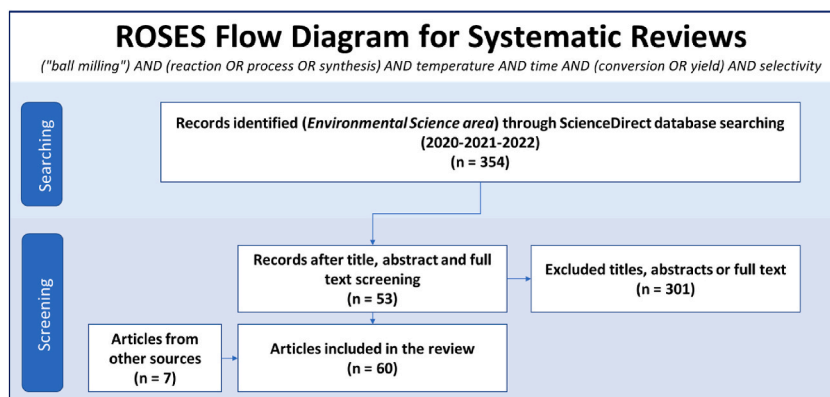


Fig. 2. ROSES flow diagram for this systematic review [37].

### 3. Articles review results and discussion

#### 3.1. Generalities and principles

Publications on ball-milling processes exhibit a year-by-year growth (Fig. 3), reflecting a rising interest in this field. For instance, the number of articles published in the first month of 2022 accounts for 31 % of those published throughout the entirety of 2021, surpassing the total number of articles published in 2017.

Grinding, in a general context, refers to a mechanical action involving hard surfaces on a material, with the primary goal of disintegration and size reduction. The commonly used pestle and mortar represent a straightforward approach to this process. In contrast, non-manual methods often utilize ball milling, a well-established technique in materials processing. A ball mill, a type of grinder, typically possesses a cylindrical shape extending along a longitudinal axis where the stationary milling chamber is located. This method relies on the transfer of mechanical energy to solids being comminuted by the collisions with the milling agents, which typically are beads in a ball mill. While solid-state processes are prevalent in ball milling applications, there are instances of liquid-assisted grinding (LAG) reactions, such as glycerol valorisation [39].

In general, mechanochemistry commonly categorizes methods into ball milling and extrusion techniques, each with distinct advantages and drawbacks. Ball milling, known for producing finer particle size ( $<10\ \mu\text{m}$ ), proves versatile across a wide array of applications, even for toxic and abrasive materials. However, a potential downside lies in the risk of product contamination due to wear and tear from the milling agents and the casing. In contrast, extrusion, while having certain limitations on the types of products it can handle, scalability and energy demands boasts notable advantages. These include operational flexibility, easy integration into production lines, high mixing efficiency, a continuous operation setup and the ability to handle large product volumes, among other benefits [39].

Based on the papers reviewed in this study – provided in the references of this paper and in the summary table from the supplementary materials –, the materials employed in this chamber consist of metals and ceramics, including the milling balls, which are frequently crafted from the same material as the stationary chamber. This design choice aims to prevent galvanic corrosion and wear-related concerns. Although steel is the most used material, it poses the risk of metal contamination. To address this issue, zirconia, characterized by similar density and comparable impact to steel, can be utilized as an alternative to avoid such contamination (Fig. 4) [4].

For the reviewed articles, the volume proportion between the reactants, typically in powder form, and the milling balls range from 1:3 to 1:30, being the most used the 1:10. There are different shapes and dimensions of agitators. Typically, an agitator shaped in an elongated rod form, where this chamber rotates on its longitudinal axis, providing mechanical energy to the system. The reactants and the milling agents are placed inside the chamber into motion, being prone to collision in this process. On a laboratory scale, the planetary ball mill is the most used technique or equipment, explicitly mentioned in 24 out of the 60 research papers included in the present study. This equipment consists in a jar filled with reactants and balls that vibrates and/or oscillates with a motor.

Of the 60 papers constituting the entire study, 49 % are related to the synthesis of advanced materials such as composites, MOF, nanomaterials, and others. Examples include MIL-101 and ZIF-8 [40], MIL-100(Fe) and CoS [41], MIL-100(Fe) and  $\text{WO}_3$  [42] for contaminant removal from water with advanced oxidation processes (AOP); carbon nanotubes [43], UiO-66- $\text{NH}_2$  and  $\text{Bi}_5\text{O}_7$  composite [44], nano- $\text{FeS}_2$  for pharmaceutical industry wastewater treatment and enhanced degradation of ciprofloxacin [45]; zero-valent iron (ZVI) composites for organic pollutants [46] and chromium removal from water [47]; graphene oxides (GO) and other graphite derivatives for applications such as water treatment [48–50], supercapacitor [51], lithium-ion batteries [52] or bone tissue engineering [53]; and Rh/meso- $\text{Al}_2\text{O}_3$  for chemical storage of hydrogen [54]. About 24 % of the papers employ ball-milled materials for waste recycling, water remediation, or soil remediation, using raw material such as blast-furnace slag [55,56], coal and fly ash landfilled in ash ponds [57,58], halogenated organic pollutants [59], lithium-ion batteries [60,61], cardboard waste [62], or heavy metals [63–65]. Approximately 17 % of the papers utilize biomaterials as starting reactants, including distiller grains [66], peanut shell for biochar

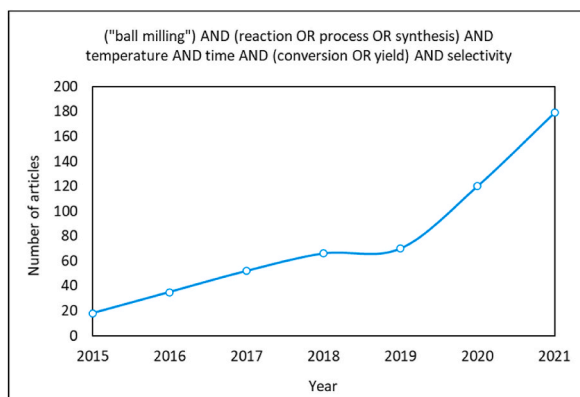


Fig. 3. Articles published yearly related to the search string.

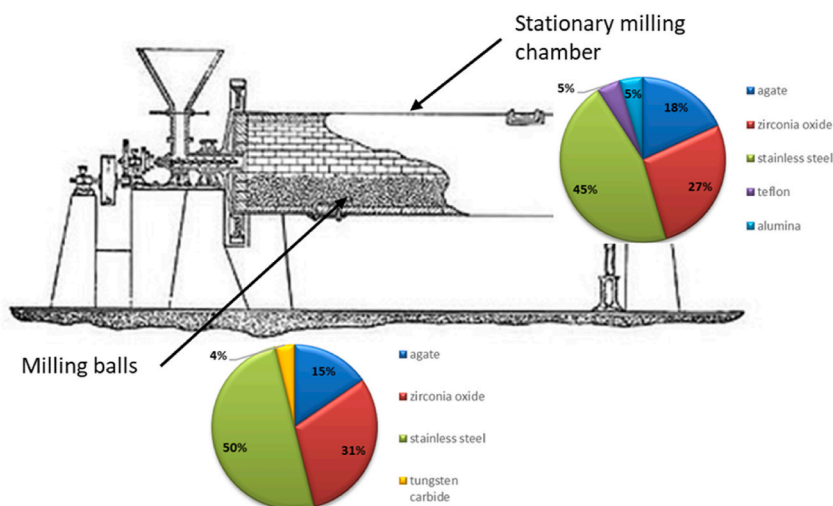


Fig. 4. Ball mill scheme and nature of the milling chamber and balls.

production [67]; corn stover and SnO<sub>2</sub> for bio-H<sub>2</sub> production [68]; Sn-functionalized biochar catalyst for glucose isomeration to fructose and food waste valorisation [69]; natural cellulosic fiber—an abundant, low-cost renewable material with a wide variety of applications, serving as a crucial component for building a sustainable and green society—activation [70]; tannin, which is intensively explored due to its unique properties (e.g., wide pore size, high surface area, large pore volume, excellent chemical stability and adjustable channel structure), with different nitrogen source compounds [71]; milled waste biomass tar as a catalyst for H<sub>2</sub>O<sub>2</sub> decomposition and subsequent methylene blue degradation in aqueous solution [72]. The remaining 10 % are articles that do not fit into the 3 theme described above.

### 3.2. Ball milling processes parametrization

While some studies has explored real time monitoring techniques, such as using highly penetrating synchrotron radiation to monitor mechanochemical transformations by X-ray powder diffraction (XRPD) through the walls of the milling jar [73], or employing Raman spectroscopy [74], and the combination of both [75], the current scientific community lacks the understanding on the operating conditions of reactions done using mechanochemistry, hence most of the published works employing ball milling or other mechanochemical processes do not mention information about the reaction, and kinetics and thermodynamics. This omission arises from the inherent difficulty of monitoring the operating conditions during these processes, treating the reaction as a “black box”. This lack of detailed information makes it challenging to replicate experiments from one laboratory to another. Additionally, mechanochemical reactors generating extreme hotspots along reactions further complicate the control the operating conditions.

Out of the 60-research article evaluated in this study, 10 % do not specify the requiring milling time for completing the reaction, 67 % omit the information on the necessity of thermal input, approximately 22 % fail to present the rotation speed of the miller, and about 78 % do not disclose the maximum yield achieved. Regarding milling equipment details, 80 % do not provide the ball-to-powder weight ratio, 45 % do not mention the milling ball or chamber material, around 55 % do not specify the size of the milling balls used, and 60 % do not offer information on the size of the chamber where the reaction takes place.

Despite the environmental advantages of mechanochemical processes, their optimization requires consideration of a substantial number of parameters, particularly those highlighted into the previous paragraphs. A comprehensive understanding of how mechanochemical processes function, how mechanical energy transforms into chemical energy, and how enhancements can be made is crucial for establishing mechanochemistry as a standard in the field of materials science. In January 2021, Gil-González et al. (2021) published a research article presenting a kinematic-kinetic approach for the parametrization and prediction of mechanically induced reactions [76]. In this study, Gil-González et al. (2021) explored various experimental parameters such as the dimensions of the milling chamber, the grinding medium, and the rotational speed [76]. They utilized the procedure outlined in previous works for the mechanochemical synthesis of CoSb<sub>3</sub> [77,78] in two different planetary mills – the Micro Mill Pulverisette 7 Premium Line and the PM100 – modified to control gas atmosphere with a gas cylinder throughout the milling process [79,80]. The authors proposed an equation to estimate the input power, accumulated energy and impact energy applied to the reactants. These were parametrized by combining theoretical-empirical equations proposed by Burgio et al. (1991) and the most widely used kinetic models for solid state reactions [81].

Specifically, the impact energy (J hit<sup>-1</sup>) was calculated using equation (1):

$$\Delta E = \frac{1}{2} m_b W_p^2 \left[ \left( \frac{W_v}{W_p} \right)^2 \left( \frac{D_v - d_b}{2} \right)^2 \left( 1 - 2 \frac{W_v}{W_p} \right) - 2 R_p \left( \frac{W_v}{W_p} \right) \left( \frac{D_v - d_b}{2} \right) - \left( \frac{W_v}{W_p} \right)^2 \left( \frac{D_v - d_b}{2} \right)^2 \right] \quad (1)$$

$m_b$ : mass of a ball  $d_b$ : diameter of a ball  $D_v$ : diameter of the jars  $R_p$ : distance from the center of the mill to the center of the vial  $W_p$ : angular velocity of the supporting disk  $W_v$ : angular velocity of the jars.

Gil-González et al. (2021) introduce a correction factor to account for the hindering effect when employing multiple balls simultaneously in the milling process, which leads to a reduction in impact energy [76]. By taking into account the total number of balls utilized and the frequency with which balls are propelled against the opposite wall of the jars, it becomes feasible to estimate the total energy transferred per unit weight of powder.

### 3.3. Types of milling

Neat milling, also known as dry milling, is a mechanical milling technique where solid materials are subjected to milling without the use of any additional liquid or solvent. In this process, milling balls or media impact and compress the material, resulting in size reduction and sometimes chemical transformations. Neat milling is often applied in situations where introducing liquids may adversely affect the desired product or where dry conditions are essential. It is commonly used in pharmaceuticals, ceramics, and materials science for producing fine powders and modifying material properties [48,65,82].

The term LAG was initially used in 2006 and involves the addition of small amounts of liquid to enhance the reaction kinetics, optimize yields and mitigate issues of product amorphization found in some neat grinding applications [5]. This technique enhances the milling process by facilitating reactions, improving particle size reduction, and providing a medium for heat dissipation. LAG is particularly useful when a reaction or transformation is promoted by the presence of a liquid medium. It is frequently employed in organic synthesis, pharmaceuticals, and materials research where enhanced reactivity and control over reaction conditions are desired.

Slurry milling involves milling a solid material in the presence of a liquid to create a slurry. The mixture of solid particles and liquid is then subjected to mechanical forces to achieve size reduction and other desired effects. Slurry milling is commonly used in industries such as mining and minerals processing, where the milling of ores is performed in the presence of water or other liquids. It helps in achieving efficient particle size reduction and liberating valuable components from the ore matrix [83].

Solution or wet milling involves milling a solid material in a liquid solution, typically using a solvent. This technique is employed to promote reactions between the solid material and the solvent, leading to the formation of new products. Solution milling is widely utilized in chemistry, particularly in the synthesis of nanoparticles, pharmaceuticals, and fine chemicals. It provides a controlled environment for reactions and allows for the generation of products with specific properties [52,55,65].

The Deasyl group has pioneered the development of various processes utilizing cutting-edge technology from WAB-Group. Among these innovations is the deployment of a highly efficient bead mill, equipped with ZrO<sub>2</sub> micro-milling beads stabilized with 20 % CeO. Specifically, the DYNO®-MILL MULTI LAB, designed for continuous flow wet-milling applications, stands out. This state-of-the-art equipment operates on the principle of leveraging the collision between zirconia microbeads and reactants to activate reactions. Notably, the mechanical energy required for this process is achieved indirectly through the utilization of electricity, which powers the motor responsible for the motion of the rotor and discs within the machine [9]. The milling chamber accommodates microbeads, constituting 55 %–70 % of the chamber's volume relative to its total stationary volume. These microbeads, exhibiting a substantially spherical shape, possess a mean diameter ranging from 0.5 to 1 mm and a Vickers hardness measured in accordance with standard EN ISO 6507–1, typically falling within the range of 1000–1400 HV1 [9]. Despite being an outstanding technique for diverse procedures as already commented, no methodology is perfect. Some limitations that have been encountered involve the use of hazardous solvents, including acids such as HCl or H<sub>2</sub>SO<sub>4</sub>, or even *N,N*-dimethyl formamide. Limitations rely on the composition of certain parts of the instrument. Furthermore, not full-continuous flow processes can be carried out, since some crucial stages in organic chemistry as purification have to be carried out in batch.

### 3.4. Green chemistry principles in ball milling processes

The environmental situation of the last decades has eased the advancement of Green Chemistry (GC), emphasizing the reduction of: i) reaction times, ii) use of solvents, and iii) energy demand. This approach is progressively assimilated and implemented in diverse scientific investigations [16]. The twelve principles of GC provide a framework for evaluating the effectiveness of this implementation in various chemical processes. These principles, as outlined by Anastas (1998) [84] and reiterated by Ardila-Fierro (2021) [85], include: GC1) prevention, GC2) atom economy, GC3) less hazardous chemical syntheses, GC4) designing safer chemicals, GC5) safer solvents and auxiliaries, GC6) design for energy efficiency, GC7) use of renewable feedstocks, GC8) reduce derivatives, GC9) catalysis, GC10) design for degradation, GC11) real-time analysis for pollution prevention, and GC12) inherently safer chemistry for accident prevention [16,84]. Specifically, addressing GC1) prevention, GC5) safer solvents and auxiliaries and GC8) reduce derivatives, ball milling can be conducted with little or no solvent. This is attributed to the fact that the activation energy of the reaction is achieved mechanically, with the milling balls. The impact of the beads with those reactants can reduce the mass transfer limitations and enhance the mixing of them. In contrast, solvothermal processes rely on solvents as heat sinks in exothermic reactions or as heat suppliers in endothermic processes [12,13]. Solvents are sometimes employed to enhance the mixing of reactants, especially when they are immiscible or highly viscous. The milling balls, with a lifespan of approximately 10,000 h, can be continuously reused without experiencing wear or affecting the efficiency of the process [86]. Ball milling reactions often achieve high yields in a short time, mitigating the environmental impact associated with the milling balls. This assumption was notably considered by Arfelis et al. (2023) in their Life Cycle Assessment (LCA) comparing different processes for producing calcium zincate (CAZN) for zinc batteries.

For GC2) atom economy, some mechanochemical-aided reactions [87–89] have demonstrated superior yields and selectivity compared to conventional processes, resulting in a reduction in waste and by-products. For instance, Miranda Júnior et al. (2021) investigated [90], for first time via mechanochemistry, the copolymerization reaction of the biodegradable monomers urea and citric acid, achieving a yield of 82 % compared to the solution condition, which yielded only 70 % in the article from Wu et al. (2020) [91]. For GC3) less hazardous chemical syntheses and GC11) real-time analysis for pollution prevention, using fewer or even avoiding solvents helps reducing toxic or hazardous by-products. Moreover, ball milling is employed for pollution prevention or remediation of hazardous products. Examples include the use of landfilled coal ash in ball milling processes to produce cement binders [57], mechanochemical processes for stabilizing heavy metals in fly ash from municipal solid waste incineration plants [64,65], conversion of furnace waste slag into building material through ball milling [92], mechanochemistry for the pre-treatment of arsenic selective leaching from copper smelter flue dusts [93], and the operation of a high-energy ball miller [94] for synthesizing magnetite nanoparticles with amino-phosphonic functionalized poly(-glycidyl methacrylate) polymer as a sorbent for U(VI) from aqueous solutions. Mechanochemistry is commonly employed in the fabrication of the manufacturing of MOFs for wastewater treatment. MOF are useful for water treatment advanced oxidation processes (AOP) like, such as the Fenton process [40–44,47,48,50,63,72,95,96], as well as the remediation of organic pollutants [46,59,97,98].

The majority of mechanochemical reactions take place without external heat input, aligning with the principle of GC6) design for energy efficiency. Although electricity is required to induce the mechanical forces activating the reaction – here, renewable, or nuclear (not preferred) can be used to reduce the environmental impact of these processes – the environmental impacts of electricity production are generally lower than those associated with steam production for thermal energy. This comparison may vary based on the electricity mix of each country. Considering the European Union Green Deal, it is anticipated that the energy mixes of electricity will become greener over time [99]. Additionally, several applications for energy storage have been observed, such as the manufacturing of electrode materials for batteries [100–104] or MOFs for chemical storage of hydrogen or other gases [105,106].

For the GC7) use of renewable feedstocks, several studies in the field of biomass valorisation have demonstrated the advantages of mechanochemistry [66,68,70], particularly when working with materials such as cellulosic fibers [70], corn stover [68], rice straw, distillers grains and Eupatorium adenophorum [66]. This topic is expanded in section 3.5. Mechanochemical treatments in biomass valorisation. For GC9) catalysis, ball milling serves as a valuable tool in catalyst manufacturing [42,67,107,108]. This method facilitates the production of smaller particle sizes and increased surface area [10], enhancing the catalyst's activity by maximizing contact between catalyst and reactants. Moreover, it introduces rich defects and oxygen-containing functional groups [67]. Notably, catalyst manufacturing can be achieved using biomass wastes such as walnut shell [109]. Addressing GC10) design for degradation involves finding a balance between long lifespan and (bio)degradability capacity. For instance, the prolonged stability of plastics has led to their undesirable accumulation in the environment. Recent efforts have focused on designing functional polymers with adaptable degradability [16]. Additionally, mechanochemical processes have emerged as a new avenue for degrading or recycling existing polymer-based products [45,58,66,87]. Regarding GC12) inherently safer chemistry for accident prevention, some of the risks associated with mechanochemical processes can be easily mitigated: i) certain reactions are conducted under nitrogen or argon atmospheres to avoid prevent the risk of explosion risks [40,110], ii) some authors introduce a small amount of solvent, typically water or ethanol, to decompose the residue of the reaction for the same purpose [63], iii) other intermittently pause the reaction to cool it down, preventing excessive temperature increases [52,59,64,65,72,87,94,111].

Motivated by the principles of GC and mechanochemistry, innovative strategies and technologies are being developed. In this context, a sophisticated and sustainable high-throughput reaction platform has been created through collaboration between Bachofen AG (WAB-Group) and Deasyl S.A. (Patent No. 20220152621). This platform integrates the advantages of mechanical energy, thermal, and pressure activation within a continuous flow system, complemented by an in-situ heating mechanism. The tool employs the cutting-edge I-CHeM (Impact/Induction in Continuous flow Heated Mechanochemistry) technology [112].

### 3.5. Mechanochemical treatments in biomass valorisation

Biomass represents one of the largest waste source globally, estimated at 130 million tonnes per year [29]. Lignin is the most abundant biopolymer after cellulose. The wood industry alone discarded, in 2022, between 50 and 70 million tons of lignin waste worldwide [113]. Typically composed of lignocellulosic, and lignin, biomass waste also includes proteins and extractable compounds like lipids, prompting the international energy agency to target 10 % of the world's energy from biomass by 2050 [114]. The diverse processes biomass can undergo, owing to its complex composition, open up numerous applications, including the production of activated carbons through pyrolysis [114,115], hydrogen production with heterogeneous catalysts [116], nanocellulose generation [26,117], and the synthesis of biodiesel and platform molecules like 5-hydroxymethylfurfural and furfural (HMF) [118,119].

The challenge with many of these processes lies in the energy-intensive reactors they employ, necessitated by high temperatures and pressures. However, mechanochemical pre-treatment has emerged as a solution, enhancing reaction yields and often allowing milder reaction conditions, thereby increasing productivity [120–122]. While many of these processes are dry or slightly wetted by inorganic acids, inorganic bases or solvents, there is a growing trend towards LAG processes for valorisation of biomass-derived products [123].

In the past decade, mechanochemical pre-treatment has gain significant attention, particularly for depolymerizing lignocellulosic materials, leading to improved subsequent treatments [124]. These treatments can yield nanocellulose, primarily nanofibrils (NFC), which, being less crystalline, offer advantages in various applications such as hydrolysis, pharmaceutical, and adsorbents [125–127]. Yu and Wu (2011) conducted ball milling experiments on microcellulose, observing significant changes in cellulose microstructure with just 1 h of milling, reducing particle size. Extended milling (7 h) led to particle agglomeration, proving less effective for further

**Table 1**

Pretreatment of biomass for diferents reactions of biomass valorisation.

Pretreatment			Post-treatment					
Reactor	Catalyst	Biomass	Reaction	Time (h)	Temp. (°C)	Yield (%)	Pression (Mpa)	Ref.
Ball milling	–	MCC	Cellulose → Methyl lactate	10	200	45	0,5	[129]
Ball milling	–	MCC	Cellulose → Glycerine	5	205	41	5	[130]
Ball milling	–	MCC	Cellulose → Glucose	1	200	76.3	–	[131]
Ball milling	–	MCC	Cellulose → HMF	2	170	45.4	–	[132]
Ball milling	–	MCC	Cellulose → H <sub>2</sub>	24	40	–	–	[133]
Pretreatment			Post-treatment					
Reactor	Catalyst	Biomass	Reaction	Time (h)	Temp. (°C)	Yield (%)	Pression (Mpa)	Ref.
Ball milling	NaOH/NH <sub>3</sub> (5%w/w)	Wheat straw	Wheat straw → Glucose	72	50	91,9 %	–	[134]
Ball milling	KOH	Rice straw	Rice Straw → Glucose + xylose	1	200	52.1 % glucose 66.5 % xylose	–	[131]
Ball milling	Ca(OH) <sub>2</sub>	Eucalyptus wood chips	Eucalyptus wood chips → glucose	48	170	90	–	[135]
Ball milling	H <sub>2</sub> SO <sub>4</sub>	Eucalyptus loxophleba	Eucalyptus loxophleba → sugars monomers	0.5	150	94	–	[136]
Ball milling	HCl	Eucalyptus wood	Eucalyptus Wood → glucose	48	50	95.7	–	[137]

MCC: Microcrystalline cellulose.



size reduction [128]. This cellulose pretreatment has been utilized by various research groups to enhance yields for various target compounds, including methyl lactate, ethylene glycol, HMF, and even H<sub>2</sub> as detailed in Table 1.

While most studies employ microcrystalline cellulose (MCC), Table 1 showcases results where biomass undergoes direct treatment using acid or mineral bases. The utilization of these acids/bases significantly enhances the hydrolysis processes of the hemicellulosic and cellulosic fractions. Furthermore, subsequent treatments enable the separation of lignin for individual recovery [138,139].

However, these processes typically involve two stages: an initial impregnation stage with acid or mineral base and a subsequent integration stage in a hydrothermal or continuous flow reactor. Nonetheless, LAG and ICHEM processes could potentially address these challenges and streamline the process into a single step. Biomass is immersed in a liquid medium, where the mechanochemical system reduces particle size, crystallinity, and enhances the reactivity of exposed hemicellulose chains. This is attributed to the reduction in monomers forming the chains and the increased number of chains in solution, rendering them more easily accessible [27–29].

To mitigate the current global warming trend and diversify energy sources, the transformation of biomass into fuels and chemicals is becoming increasingly popular. Traditionally, the industrial production of high-added value products such as vanillin involve non-environmentally friendly processes like the Riedel process [140]. In this regard, when combining mechanochemistry with continuous flow approaches, greener strategies to obtain the desired products can be reached. As reported by Martín-Perales et al. (2023), high yields of vanillin were obtained in the oxidation of biomass-derived platform molecules, such as isoeugenol and vanillyl alcohol. The novelty of this study is that no catalyst is needed, high temperatures are not required and in short times of reaction, with optimal results at 25 °C during 19 min of residence time and 30 mL of H<sub>2</sub>O<sub>2</sub> (35 % v/v) when using isoeugenol as precursor, and 80 °C during 19 min of residence time and 10 mL of H<sub>2</sub>O<sub>2</sub> (35 % v/v) for vanillyl alcohol oxidation.

### 3.6. Life cycle assessments (LCAs) in ball milling processes

When assessing the entire life cycle of products, it is crucial to acknowledge that the precursors used in some cases are obtained through contaminating or less eco-friendly processes. While numerous papers compare innovative ball milling processes with the conventional synthesis methods for producing identical products, highlighting the typically lower environmental impact of mechanical processes [41,43,51,52,54,67,88,141–143], there is limited literature that quantifies these impacts throughout the entire life cycle of the products [10,26,144]. In conducting an overall environmental study, it is essential to consider whether the operation unit for milling balls requires additional pre-treatment or post-treatment processes, such as drying, calcination, size reduction, or other energy-intensive procedures that are not needed in conventional processes.

Morfino et al. (2022), conducted an LCA comparison between zircon and alumina sand applied in the production of ceramic tiles, including the milling processes required for its manufacture. The study results indicated that the main differences between the two processes were influenced by the energy mix used in each process. Mechanochemical processes rely on electricity as an energy supply, whereas solvothermal processes typically use steam (often produced from natural gas) for heat. Arfelis et al. (2023a) conducted an LCA comparing different pre-treatments for cellulose extraction from wood chips. The pre-treatments assessed are: i) mechanical, ii) enzymatic, and iii) TEMPO-mediated oxidation routes. The results of their LCA were allocated considering the different tensile strength obtained for each pre-treatment. This property affects the functionality of the product under comparison and, therefore, the LCA methodology itself obliges to take it into account in the functional unit (FU) of the study. The main output of their study is that both, mechanical and TEMPO-mediated oxidation routes, present lower impacts than the enzymatic pre-treatment. Being the mechanical pre-treatment the one presenting slightly milder contributions to climate change, acidification, eutrophication, and other indicators. Even though, Arfelis et al. (2023a) argued that the fact that TEMPO-mediated oxidation is environmentally unfeasible should be put under question. After all, and despite being disregarded in most assessment publications up to date, it is the only well-known way to selectively oxidize primary hydroxyl groups and thus producing kinds of CNFs that are unthinkable by other ways. Arfelis et al. (2023b) conducted a LCA for the CAZN production for zinc batteries. The study consists in comparing the environmental impact of the wet milling production of CAZN crystals with the traditional production process named hydro-thermal synthesis. In this case, the results were allocated according to the activation rate of the batteries which depended on the particle size of the crystals. Arfelis et al. (2023b) also identified that, in LCAs dedicated to continuous industrial processes, the author must pay attention to the selection of the FU. Despite falling beyond the scope of cradle-to-gate LCA practices, factors such as the particle size of the ultimate product or the residence time of the reaction introduce variability, resulting in the final product having a higher number of service units or functions. Hence, it is crucial to recognize these aspects as valuable supplementary information when evaluating alternative options. Utilizing a functional unit dependent solely on mass in LCA results fails to account for these nuances. Notably, there exist numerous chemical LCA studies that already incorporate flowrate as the functional unit, addressing these intricacies in their analyses [145–148]. Similar approach is taken in the incorporation of Module D within the framework of EN 15804:2012 + A2:2019, which serves to account for information beyond the cradle-to-gate scope in LCAs of construction products [149,150].

In other LCAs conducted by the authors of this paper, it has been demonstrated that the use of mechanochemistry to activate chemical reactions often leads to a greener process with improved conversion and selectivity [10,11,26,151,152].

## 4. Conclusions

Interest in mechanochemical processes has grown within the scientific community due to their environmentally friendly nature. However, a notable challenge lies in the batch nature inherent to mechanochemistry. Recent efforts aim to overcome this limitation by introducing continuous-flow approaches to mechanochemical processes, aligning with the twelve principles of GC.

One innovative strategy that integrates continuous-flow with beads-assisted processes is ICHEM technology, exemplified by the

remarkable high-throughput reactor, IMPA<sup>°</sup>CT. This technology enables the production of various compounds, ranging from high-added value like vanillin [109] or biodiesel [153], to advanced catalysts, including diverse MOFs and CaDG for biodiesel production [9,154–156].

Stainless steel, zirconia oxide, and agate are commonly used materials in the milling chamber and milling balls. Ball milling is frequently employed for synthesizing advanced materials such as MOF and nanomaterials. Moreover, it has found applications in waste recycling, biomaterials production, and water and soil remediation. Emphasizing the need to monitor ball milling reaction conditions is crucial. Avoiding the presentation of processes as a “black box” enhances experiment repeatability and aids in comprehending the reaction kinetics. Ball milling processes offer a pathway to developing more sustainable procedures. This review shows how mechanochemical approaches align with all GC principles. Particularly, ball milling processes are often more environmentally friendly than conventional solvothermal processes, requiring less solvent and substituting thermal energy demand with electricity demand. Despite the benefits, there is a scarcity of LCA papers for ball milling processes. Utilizing this methodology to compare innovative syntheses with conventional processes could contribute significantly to understanding mechanochemistry and its potential to enhance widely used solvothermal processes.

This comprehensive exploration affirms mechanochemical strategies as pivotal in advancing sustainable and eco-friendly chemical synthesis, ultimately propelling the field towards a more efficient and environmentally conscious future.

#### Data availability statement

Data will be made available on request.

#### Ethics approval and consent to participate

We confirm that this is an original work and has not been previously published in any other scientific journal, nor is it under consideration for publication elsewhere. The authors have consulted the Guide for Authors before this submission. The manuscript has been prepared in compliance with the Ethics in Publishing Policy and with the rest of indications described in the aforementioned guide.

#### CRediT authorship contribution statement

**Sergi Arfelis:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis. **Ana I. Martín-Perales:** Writing – review & editing. **Remy Nguyen:** Writing – review & editing. **Antonio Pérez:** Writing – review & editing. **Igor Cherubin:** Writing – review & editing. **Christophe Len:** Writing – review & editing. **Irene Malpartida:** Writing – review & editing, Funding acquisition, Conceptualization. **Alba Bala:** Writing – review & editing, Supervision. **Pere Fullana-i-Palmer:** Writing – review & editing, Project administration.

#### Declaration of competing interest

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

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e34655>.

#### References

- [1] IUPAC, Compendium of Chemical Terminology, second ed., Blackwell Scientific Publications, Oxford, 1997 <https://doi.org/10.1351/goldbook>.
- [2] L. Takacs, Mechanochemistry and mechanical alloying 2003 M. Carey lea, the first mechanochemist 9 (2004) 4987–4993.
- [3] L. Takacs, The historical development of mechanochemistry, Chem. Soc. Rev. 42 (2013) 7649, <https://doi.org/10.1039/c2cs35442j>.
- [4] J.-L. Do, T. Friščić, Mechanochemistry: A Force of Synthesis, 2016.
- [5] D. Tan, T. Friščić, Mechanochemistry for organic chemists: an update, Eur. J. Org. Chem. 2018 (2018) 18–33, <https://doi.org/10.1002/ejoc.201700961>.

- [6] S.L. James, C.J. Adams, C. Bolm, D. Braga, P. Collier, T. Friiç, F. Grepioni, K.D.M. Harris, G. Hyett, W. Jones, A. Krebs, J. MacK, L. Maini, A.G. Orpen, I. P. Parkin, W.C. Shearouse, J.W. Steed, D.C. Waddell, Mechanochemistry: opportunities for new and cleaner synthesis, *Chem. Soc. Rev.* 41 (2012), <https://doi.org/10.1039/c1cs15171a>.
- [7] C. Bolm, J.G. Hernández, Mechanochemistry of gaseous reactants, *Angew. Chem. Int. Ed.* 58 (2019) 3285–3299, <https://doi.org/10.1002/anie.201810902>.
- [8] C. Len, V. Duhan, W. Ouyang, R. Nguyen, B. Lochab, Mechanochemistry and oleochemistry: a green combination for the production of high-value small chemicals, *Front. Chem.* 11 (2023) 1–19, <https://doi.org/10.3389/fchem.2023.1306182>.
- [9] F. Lacoste, J. Thiel, Method for Manufacturing Calcium Zincate Crystals, and the Uses Thereof, WO 2016/156749 A1, 2016.
- [10] S. Arfelis, I. Malpartida, V. Lair, V. Caldeira, I. Sazdovski, A. Bala, P. Fullana-i-Palmer, Life cycle assessment on calcium zincate production methods for rechargeable batteries, *Sci. Total Environ.* 866 (2023) 161094, <https://doi.org/10.1016/j.scitotenv.2022.161094>.
- [11] C. Len, M.R. Khodadadi, J. Thiel, F.R. Lacoste, Procédé De Fabrication Du (2,2-Diméthyl-1,3-Dioxolan-4-Yl)Méthanol, FR3103813, 2019.
- [12] V. Ojijo, S.K. Pillai, Compatibilization of Polymer Blends by Shear Pulverization, Elsevier Inc., 2019, <https://doi.org/10.1016/B978-0-12-816006-0.00009-8>.
- [13] J.L. Howard, Q. Cao, D.L. Browne, Mechanochemistry as an emerging tool for molecular synthesis: what can it offer? *Chem. Sci.* 9 (2018) 3080–3094, <https://doi.org/10.1039/c7sc05371a>.
- [14] F. Delogu, Mechanochemical behavior of surface radicals in ground quartz, *J. Phys. Chem. C* 115 (2011) 21230–21235, <https://doi.org/10.1021/jp206354p>.
- [15] P. Meloni, G. Carcangiu, F. Delogu, Specific surface area and chemical reactivity of quartz powders during mechanical processing, *Mater. Res. Bull.* 47 (2012) 146–151, <https://doi.org/10.1016/J.MATERRESBULL.2011.09.014>.
- [16] K.J. Ardila-Fierro, J.G. Hernández, Sustainability assessment of mechanochemistry by using the twelve principles of green chemistry, *ChemSusChem* 14 (2021) 2145–2162, <https://doi.org/10.1002/cssc.202100478>.
- [17] C. Espro, D. Rodríguez-Padrón, Re-thinking organic synthesis: mechanochemistry as a greener approach, *Curr. Opin. Green Sustainable Chem.* 30 (2021) 100478, <https://doi.org/10.1016/j.cogsc.2021.100478>.
- [18] S. Glowinski, B. Szczęśniak, J. Choma, M. Jaroniec, Mechanochemistry: toward green synthesis of metal–organic frameworks, *Mater. Today* 46 (2021) 109–124, <https://doi.org/10.1016/j.mattod.2021.01.008>.
- [19] V. Caldeira, L. Jouffret, J. Thiel, F.R. Lacoste, S. Obbade, L. Dubau, M. Chatenet, Ultrafast hydro-micromechanical synthesis of calcium zincate: structural and morphological characterizations, *J. Nanomater.* 2017 (2017), <https://doi.org/10.1155/2017/7369397>.
- [20] A. Ghosh, *Resour. Conserv. Recycl.* 175 (2021).
- [21] C.P. Liu, M.K. Wang, J.C. Xie, W.X. Zhang, Q.S. Tong, Mechanochemical degradation of the crosslinked and foamed EVA multicomponent and multiphase waste material for resource application, *Polym. Degrad. Stabil.* 98 (2013) 1963–1971, <https://doi.org/10.1016/j.polydegstab.2013.07.019>.
- [22] S. Yin, R. Tuladhar, F. Shi, R.A. Shanks, M. Combe, T. Collister, Mechanical reprocessing of polyolefin waste: a review, *Polym. Eng. Sci.* 55 (2015) 2899–2909, <https://doi.org/10.1002/pen.24182>.
- [23] M. Baláz, M. Achimovičová, P. Baláz, E. Dutková, M. Fabián, M. Kováčová, Z. Lukáčová Bujňáková, E. Tóthová, Mechanochemistry as a versatile and scalable tool for nanomaterials synthesis: recent achievements in Košice, Slovakia, *Curr. Opin. Green Sustainable Chem.* 24 (2020) 7–13, <https://doi.org/10.1016/j.cogsc.2019.12.007>.
- [24] P. Baláz, M. Baláz, M. Achimovičová, Z. Bujňáková, E. Dutková, Chalcogenide mechanochemistry in materials science: insight into synthesis and applications (a review), *J. Mater. Sci.* 52 (2017) 11851–11890, <https://doi.org/10.1007/s10853-017-1174-7>.
- [25] M. Baláz, O. Dobrozhan, M. Tešínský, R.Z. Zhang, R. Džunda, E. Dutková, M. Rajnák, K. Chen, M.J. Reece, P. Baláz, Scalable and environmentally friendly mechanochemical synthesis of nanocrystalline rhodostannite (Cu<sub>2</sub>FeSn<sub>3</sub>S<sub>8</sub>), *Powder Technol.* 388 (2021) 192–200, <https://doi.org/10.1016/j.powtec.2021.04.047>.
- [26] S. Arfelis, R.J. Aguado, D. Civancik, P. Fullana-i-Palmer, M.À. Pèlach, Q. Tarrés, M. Delgado-Aguilar, Sustainability of cellulose micro-/nanofibers: a comparative life cycle assessment of pathway technologies, *Sci. Total Environ.* 874 (2023) 162482, <https://doi.org/10.1016/j.scitotenv.2023.162482>.
- [27] O. Lomovsky, A. Bychkov, I. Lomovsky, Mechanical Pretreatment, Biomass Fractionation Technologies for a Lignocellulosic Feedstock Based Biorefinery (2016) 23–55, <https://doi.org/10.1016/B978-0-12-802323-5.00002-5>.
- [28] S. Furusato, A. Takagaki, S. Hayashi, A. Miyazaki, R. Kikuchi, S.T. Oyama, Mechanochemical decomposition of crystalline cellulose in the presence of protonated layered niobium molybdate solid acid catalyst, *ChemSusChem* 11 (2018) 888–896, <https://doi.org/10.1002/cssc.201702305>.
- [29] F. Hajiali, T. Jin, G. Yang, M. Santos, E. Lam, A. Moores, Mechanochemical transformations of biomass into functional materials, *ChemSusChem* 15 (2022), <https://doi.org/10.1002/cssc.202102535>.
- [30] C.G. Avila-Ortiz, M. Pérez-Venegas, J. Vargas-Caporalí, E. Juaristi, Recent applications of mechanochemistry in enantioselective synthesis, *Tetrahedron Lett.* 60 (2019) 1749–1757, <https://doi.org/10.1016/j.tetlet.2019.05.065>.
- [31] M. Pérez-Venegas, E. Juaristi, Mechanoenzymology: state of the art and challenges towards highly sustainable biocatalysis, *ChemSusChem* 14 (2021) 2682–2688, <https://doi.org/10.1002/cssc.202100624>.
- [32] M. Pérez-Venegas, E. Juaristi, E. Juaristi, Mechanochemical and mechanoenzymatic synthesis of pharmacologically active compounds: a green perspective, *ACS Sustain. Chem. Eng.* 8 (2020) 8881–8893, <https://doi.org/10.1021/acssuschemeng.0c01645>.
- [33] S. Chaudhuri, A. Ghosh, S.K. Chattopadhyay, Green synthetic approaches for medium ring-sized heterocycles of biological and pharmaceutical interest, *Biol. Synth. Approaches. Heterocycles* (2021) 617–653, <https://doi.org/10.1016/B978-0-12-820792-5.00004-4>.
- [34] A.S. Pullin, G.K. Frampton, B. Livoreil, G. Petrokofsky, Guidelines and standards for evidence synthesis in environmental management VERSION 5.0. <https://environmentalevidence.org/information-for-authors/>, 2018. (Accessed 9 May 2022).
- [35] N.R. Haddaway, P. Woodcock, B. Macura, A. Collins, Making literature reviews more reliable through application of lessons from systematic reviews, *Conserv. Biol.* 29 (2015) 1596–1605, <https://doi.org/10.1111/cobi.12541>.
- [36] N.R. Haddaway, B. Macura, P. Whaley, A.S. Pullin, ROSES Flow Diagram for Systematic Reviews, 2017, <https://doi.org/10.6084/m9.figshare.5897389>.
- [37] N.R. Haddaway, B. Macura, P. Whaley, A.S. Pullin, ROSES Flow Diagram for Systematic Reviews, 2017, <https://doi.org/10.6084/m9.figshare.5897389>.
- [38] E. Juaristi, C.G. Avila-Ortiz, Salient achievements in synthetic organic chemistry enabled by mechanochemical activation, *Synthesis* 55 (2023) 2439–2459.
- [39] A.I. Martín-Perales, A.M. Balu, I. Malpartida, R. Luque, Prospects for the combination of mechanochemistry and flow applied to catalytic transformations, *Curr. Opin. Green Sustainable Chem.* 38 (2022) 100714, <https://doi.org/10.1016/j.cogsc.2022.100714>.
- [40] M. Li, Z. Li, X. Yu, Y. Wu, C. Mo, M. Luo, L. Li, S. Zhou, Q. Liu, N. Wang, K. Lun Yeung, S. Chen, FeN<sub>4</sub>-doped carbon nanotubes derived from metal organic frameworks for effective degradation of organic dyes by peroxymonosulfate: impacts of FeN<sub>4</sub> spin states, *Chem. Eng. J.* 431 (2022) 133339, <https://doi.org/10.1016/j.cej.2021.133339>.
- [41] L. Wu, C.C. Wang, H.Y. Chu, X.H. Yi, P. Wang, C. Zhao, H. Fu, Bisphenol A cleanup over MIL-100(Fe)/CoS composites: pivotal role of Fe–S bond in regenerating Fe<sup>2+</sup> ions for boosted degradation performance, *Chemosphere* 280 (2021) 130659, <https://doi.org/10.1016/j.chemosphere.2021.130659>.
- [42] J.W. Wang, F.G. Qiu, P. Wang, C. Ge, C.C. Wang, Boosted bisphenol A and Cr(VI) cleanup over Z-scheme WO<sub>3</sub>/MIL-100(Fe) composites under visible light, *J. Clean. Prod.* 279 (2021) 123408, <https://doi.org/10.1016/j.jclepro.2020.123408>.
- [43] A.S.G.G. Santos, C.A. Orge, O.S.G.P. Soares, M.F.R. Pereira, 4-Nitrobenzaldehyde removal by catalytic ozonation in the presence of CNT, *J. Water Proc. Eng.* 38 (2020), <https://doi.org/10.1016/j.jwpe.2020.101573>.
- [44] C. Zhao, Y. Li, H. Chu, X. Pan, L. Ling, P. Wang, H. Fu, C.C. Wang, Z. Wang, Construction of direct Z-scheme Bi<sub>5</sub>O<sub>7</sub>/UiO-66-NH<sub>2</sub> heterojunction photocatalysts for enhanced degradation of ciprofloxacin: mechanism insight, pathway analysis and toxicity evaluation, *J. Hazard Mater.* 419 (2021) 126466, <https://doi.org/10.1016/j.jhazmat.2021.126466>.
- [45] E. Aseman-Bashiz, H. Sayyaf, Synthesis of nano-FeS<sub>2</sub> and its application as an effective activator of ozone and peroxydisulfate in the electrochemical process for ofloxacin degradation: a comparative study, *Chemosphere* 274 (2021) 129772, <https://doi.org/10.1016/j.chemosphere.2021.129772>.
- [46] S. Wu, S. Deng, Z. Ma, Y. Liu, Y. Yang, Y. Jiang, Ferrous oxalate covered ZVI through ball-milling for enhanced catalytic oxidation of organic contaminants with persulfate, *Chemosphere* 287 (2022) 132421, <https://doi.org/10.1016/j.chemosphere.2021.132421>.

- [47] W. Wang, B. Hu, C. Wang, Z. Liang, F. Cui, Z. Zhao, C. Yang, Cr(VI) removal by micron-scale iron-carbon composite induced by ball milling: the role of activated carbon, *Chem. Eng. J.* 389 (2020) 122633, <https://doi.org/10.1016/j.cej.2019.122633>.
- [48] M. Sivakumar, S. Yadav, W.S. Hung, J.Y. Lai, One-pot eco-friendly synthesis of edge-carboxylate graphene via dry ball milling for enhanced removal of acid and basic dyes from single or mixed aqueous solution, *J. Clean. Prod.* 263 (2020) 121498, <https://doi.org/10.1016/j.jclepro.2020.121498>.
- [49] Y. Xu, G. Wang, L. Zhu, W. Deng, C. Wang, T. Ren, B. Zhu, Z. Zeng, Desert beetle-like microstructures bridged by magnetic Fe<sub>3</sub>O<sub>4</sub> grains for enhancing oil-in-water emulsion separation performance and solar-assisted recyclability of graphene oxide, *Chem. Eng. J.* 427 (2021) 130904, <https://doi.org/10.1016/j.cej.2021.130904>.
- [50] Y. Xu, G. Wang, L. Zhu, L. Shen, Z. Zhang, T. Ren, Z. Zeng, T. Chen, Q. Xue, Multifunctional superhydrophobic adsorbents by mixed-dimensional particles assembly for polymorphic and highly efficient oil-water separation, *J. Hazard Mater.* 407 (2021) 124374, <https://doi.org/10.1016/j.jhazmat.2020.124374>.
- [51] Y. Wang, H. Meng, Y. Lu, C. Li, Mechanochemical conversion of graphite to highly Cross-linked alkynyl carbon material as excellent mercury (II) sorbent, *Chem. Eng. J.* 415 (2021) 129009, <https://doi.org/10.1016/j.cej.2021.129009>.
- [52] Q.H. Nguyen, H. Kim, I.T. Kim, W. Choi, J. Hur, Few-layer NbSe<sub>2</sub>/graphene heterostructures as anodes in lithium-ion half- and full-cell batteries, *Chem. Eng. J.* 382 (2020) 122981, <https://doi.org/10.1016/j.cej.2019.122981>.
- [53] H. Maleki-Ghaleh, M. Hossein Siadati, A. Fallah, A. Zarrabi, F. Afghah, B. Koc, E. Dalir Abdolahinia, Y. Omid, J. Barar, A. Akbari-Fakhraabadi, Y. Beygi-Khosrowshahi, K. Adibkia, Effect of zinc-doped hydroxyapatite/graphene nanocomposite on the physicochemical properties and osteogenesis differentiation of 3D-printed polycaprolactone scaffolds for bone tissue engineering, *Chem. Eng. J.* 426 (2021) 131321, <https://doi.org/10.1016/j.cej.2021.131321>.
- [54] J. Chen, M. Yao, Q. Zou, P. Chen, F. Liu, T. Zhao, Solvent-free synthesis of Rh/meso-Al<sub>2</sub>O<sub>3</sub> via mechanochemistry for hydrolytic dehydrogenation of ammonia borane, *Int. J. Hydrogen Energy* 47 (2022) 5230–5239, <https://doi.org/10.1016/j.ijhydene.2021.11.137>.
- [55] H. Hou, J. Zhou, M. Ji, Y. Yue, G. Qian, J. Zhang, Mechanochemical activation of titanium slag for effective selective catalytic reduction of nitric oxide, *Sci. Total Environ.* 743 (2020) 140733, <https://doi.org/10.1016/j.scitotenv.2020.140733>.
- [56] X. Lv, K. Song, Y. Xin, X. Lv, Novel process for deep removal of chlorine and recycling of chlorinated tailings from titanium-bearing blast-furnace slag, *Process Saf. Environ. Protect.* 159 (2022) 842–849, <https://doi.org/10.1016/j.psep.2022.01.056>.
- [57] A.M. Balachandra, N. Abdol, A.G.N.D. Darsanasiri, K. Zhu, P. Soroushian, H.E. Mason, Landfilled coal ash for carbon dioxide capture and its potential as a geopolymer binder for hazardous waste remediation, *J. Environ. Chem. Eng.* 9 (2021) 105385, <https://doi.org/10.1016/j.jece.2021.105385>.
- [58] N. Um, T.W. Jeon, Pretreatment method for the utilization of the coal ash landfilled in ash ponds, *Process Saf. Environ. Protect.* 153 (2021) 192–204, <https://doi.org/10.1016/j.psep.2021.07.013>.
- [59] Z. Lou, L. Song, W. Liu, S. Wu, F. He, J. Yu, Deciphering CaO-induced peroxydisulfate activation for destruction of halogenated organic pollutants in a low energy vibrational mill, *Chem. Eng. J.* 431 (2022) 134090, <https://doi.org/10.1016/j.cej.2021.134090>.
- [60] B. Li, J. Li, Z. Xu, Recover lithium and prepare nano-cobalt from spent lithium ion batteries using a one-pot mechanochemical reaction, *Clean Eng Technol* 5 (2021) 100282, <https://doi.org/10.1016/j.clet.2021.100282>.
- [61] J. Liu, X. Bai, J. Hao, H. Wang, T. Zhang, X. Tang, S. Wang, Y. He, Efficient liberation of electrode materials in spent lithium-ion batteries using a cryogenic ball mill, *J. Environ. Chem. Eng.* 9 (2021) 106017, <https://doi.org/10.1016/j.jece.2021.106017>.
- [62] R. Zhang, Z. Zhu, Microwave assisted hydrothermal conversion of waste cardboard, *Process Saf. Environ. Protect.* 156 (2021) 209–218, <https://doi.org/10.1016/j.psep.2021.10.005>.
- [63] L. Xia, Y. Lu, H. Meng, C. Li, Preparation of C-MOx nanocomposite for efficient adsorption of heavy metal ions via mechanochemical reaction of CaC<sub>2</sub> and transitional metal oxides, *J. Hazard Mater.* 393 (2020) 122487, <https://doi.org/10.1016/j.jhazmat.2020.122487>.
- [64] S. Yu, B. Du, A. Baheiduola, C. Geng, J. Liu, HCB dechlorination combined with heavy metals immobilization in MSWI fly ash by using n-Al/CaO dispersion mixture, *J. Hazard Mater.* 392 (2020) 122510, <https://doi.org/10.1016/j.jhazmat.2020.122510>.
- [65] Q. Yuan, Y. Zhang, T. Wang, J. Wang, C.E. Romero, Mechanochemical stabilization of heavy metals in fly ash from coal-fired power plants via dry milling and wet milling, *Waste Manag.* 135 (2021) 428–436, <https://doi.org/10.1016/j.wasman.2021.09.029>.
- [66] Z. Zhao, B. Wang, X. Zhang, H. Xu, N. Cheng, Q. Feng, R. Zhao, Y. Gao, M. Wei, Release characteristics of phosphate from ball-milled biochar and its potential effects on plant growth, *Sci. Total Environ.* 821 (2022) 153256, <https://doi.org/10.1016/j.scitotenv.2022.153256>.
- [67] M. Gao, Z.Y. Wang, Y.R. Yuan, W.W. Li, H.Q. Liu, T.Y. Huang, Ball-milled biochar for efficient neutral electrosynthesis of hydrogen peroxide, *Chem. Eng. J.* 434 (2022) 134788, <https://doi.org/10.1016/j.cej.2022.134788>.
- [68] N. Tahir, F. Nadeem, Q. Zhang, Optimisation of photo-fermentative biohydrogen production from corn stover through the synergetic effect of ultrafine grinding and SnO<sub>2</sub> nanomaterials, *J. Clean. Prod.* 328 (2021) 129631, <https://doi.org/10.1016/j.jclepro.2021.129631>.
- [69] X. Yang, I.K.M. Yu, D.C.W. Tsang, V.L. Budarin, J.H. Clark, K.C.W. Wu, A.C.K. Yip, B. Gao, S.S. Lam, Y.S. Ok, Ball-milled, solvent-free Sn-functionalisation of wood waste biochar for sugar valorisation in food waste valorisation, *J. Clean. Prod.* 268 (2020) 122300, <https://doi.org/10.1016/j.jclepro.2020.122300>.
- [70] L. Huang, Q. Wu, Q. Wang, R. Ou, M. Wolcott, Solvent-free pulverization and surface fatty acylation of pulp fiber for property-enhanced cellulose/polypropylene composites, *J. Clean. Prod.* 244 (2020) 118811, <https://doi.org/10.1016/j.jclepro.2019.118811>.
- [71] J. Zhao, W. Shan, P. Zhang, S. Dai, Solvent-free and mechanochemical synthesis of N-doped mesoporous carbon from tannin and related gas sorption property, *Chem. Eng. J.* 381 (2020) 122579, <https://doi.org/10.1016/j.cej.2019.122579>.
- [72] D. Li, T. Yang, Y. Li, Z. Liu, W. Jiao, Facile and green synthesis of highly dispersed tar-based heterogeneous Fenton catalytic nanoparticles for the degradation of methylene blue, *J. Clean. Prod.* 246 (2020), <https://doi.org/10.1016/j.jclepro.2019.119033>.
- [73] T. Friščić, I. Halasz, P.J. Beldon, A.M. Belenguer, F. Adams, S.A.J. Kimber, V. Honkimäki, R.E. Dinnebir, Real-time and in situ monitoring of mechanochemical milling reactions, *Nat. Chem.* 5 (2013) 66–73, <https://doi.org/10.1038/nchem.1505>.
- [74] D. Gracin, V. Strukil, T. Friscic, I. Halasz, K. Uzarevic, Laboratory real-time and in situ monitoring of mechanochemical milling reactions by Raman spectroscopy, *Angew. Chem. Int. Ed.* 53 (2014) 6193–6197, <https://doi.org/10.1002/anie.201402334>.
- [75] L. Bätzdorf, F. Fischer, M. Wilke, K.J. Wenzel, F. Emmerling, Direct in situ investigation of milling reactions using combined x-ray diffraction and Raman spectroscopy, *Angew. Chem. Int. Ed.* 54 (2015) 1799–1802, <https://doi.org/10.1002/anie.201409834>.
- [76] E. Gil-González, M. del R. Rodríguez-Laguna, P.E. Sánchez-Jiménez, A. Perejón, L.A. Pérez-Maqueda, Unveiling mechanochemistry: kinematic-kinetic approach for the prediction of mechanically induced reactions, *J. Alloys Compd.* 866 (2021) 158925, <https://doi.org/10.1016/j.jallcom.2021.158925>.
- [77] O.L. Arnache, J. Pino, L.C. Sa, Determination of milling parameters useful on the formation of CoSb<sub>3</sub> thermoelectric powders by low-energy mechanical alloying, <https://doi.org/10.1007/s10854-016-4271-5>, 2016.
- [78] J. Yang, Y. Chen, J. Peng, X. Song, W. Zhu, J. Su, R. Chen, Synthesis of CoSb<sub>3</sub> Skutterudite by Mechanical Alloying, vol. 375, 2004, pp. 229–232, <https://doi.org/10.1016/j.jallcom.2003.11.036>.
- [79] A. Perejón, N. Murafa, P.E. Sánchez-Jiménez, J.M. Criado, J. Subrt, M.J. Diánez, L.A. Pérez-Maqueda, Direct mechanosynthesis of pure BiFeO<sub>3</sub> perovskite nanoparticles: reaction mechanism, *J Mater Chem C Mater* (2013), <https://doi.org/10.1039/c3tc30446a>.
- [80] F.K. Urakaev, Mechanism and kinetics of mechanochemical processes, *High-Energy Ball Milling: Mechanochemical Processing of Nanopowders* (2010) 9–44, <https://doi.org/10.1533/9781845699444.1.9>.
- [81] N. Burgio, A. Iasonna, M. Magini, S. Martelli, F. Padella, Mechanical alloying of the Fe-Zr system. Correlation between input energy and end products, *Il Nuovo Cimento D* 13 (1991) 459–476, <https://doi.org/10.1007/BF02452130>.
- [82] C. Loustau-Cazalet, C. Sambusiti, P. Buche, A. Solhy, E. Bilal, M. Larzek, A. Barakat, Innovative deconstruction of biomass induced by dry chemo-mechanical activation: impact on enzymatic hydrolysis and energy efficiency, *ACS Sustain. Chem. Eng.* 4 (2016) 2689–2697, <https://doi.org/10.1021/acssuschemeng.6b00194>.
- [83] Tate Suma, *Lyle Process Technology, Slurry Mill Operating Manual*, 2000.
- [84] P.T. Anastas, J.C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, 1998.
- [85] K.J. Ardila-Fierro, J.G. Hernández, Sustainability assessment of mechanochemistry by using the twelve principles of green chemistry, *ChemSusChem* 14 (2021) 2145–2162, <https://doi.org/10.1002/cssc.202100478>.

- [86] F. Lacoste, J. Thiel, Method for Manufacturing Calcium Zincate Crystals, and the Uses Thereof, WO 2016/156749, 2016.
- [87] E.O. Miranda Júnior, V.H. Rhem Silva, M. Leão, E. Cabral-Albuquerque, S. Cunha, R.L. Lima Fialho, Clean polycondensation through mechanochemistry: catalyst-free production of new urea-citric acid copolymer, *J. Clean. Prod.* 311 (2021), <https://doi.org/10.1016/j.jclepro.2021.127569>.
- [88] P. Wu, Q. Jia, J. He, L. Lu, L. Chen, J. Zhu, C. Peng, M. He, J. Xiong, W. Zhu, H. Li, Mechanical exfoliation of boron carbide: a metal-free catalyst for aerobic oxidative desulfurization in fuel, *J. Hazard Mater.* 391 (2020) 122183, <https://doi.org/10.1016/j.jhazmat.2020.122183>.
- [89] L. Xu, Y. Xiong, G. Zhang, F. Zhang, Y. Yang, Z. Hua, Y. Tian, J. You, Z. Zhao, An environmental-friendly process for recovery of tellurium and copper from copper telluride, *J. Clean. Prod.* 272 (2020) 122723, <https://doi.org/10.1016/j.jclepro.2020.122723>.
- [90] E.O. Miranda Júnior, V.H. Rhem Silva, M. Leão, E. Cabral-Albuquerque, S. Cunha, R.L. Lima Fialho, Clean polycondensation through mechanochemistry: catalyst-free production of new urea-citric acid copolymer, *J. Clean. Prod.* 311 (2021), <https://doi.org/10.1016/j.jclepro.2021.127569>.
- [91] P. Wu, Q. Jia, J. He, L. Lu, L. Chen, J. Zhu, C. Peng, M. He, J. Xiong, W. Zhu, H. Li, Mechanical exfoliation of boron carbide: a metal-free catalyst for aerobic oxidative desulfurization in fuel, *J. Hazard Mater.* 391 (2020) 122183, <https://doi.org/10.1016/j.jhazmat.2020.122183>.
- [92] X. Lv, K. Song, Y. Xin, X. Lv, Novel process for deep removal of chlorine and recycling of chlorinated tailings from titanium-bearing blast-furnace slag, *Process Saf. Environ. Protect.* 159 (2022) 842–849, <https://doi.org/10.1016/j.psep.2022.01.056>.
- [93] L. Guo, Z. Hu, Y. Du, T.C. Zhang, D. Du, Mechanochemical activation on selective leaching of arsenic from copper smelting flue dusts, *J. Hazard Mater.* 414 (2021) 125436, <https://doi.org/10.1016/j.jhazmat.2021.125436>.
- [94] A.A. Galhoum, W.H. Eisa, I. El-Tantawy El-Sayed, A.A. Tolba, Z.M. Shalaby, S.I. Mohamady, S.S. Muhammad, S.S. Hussien, T. Akashi, E. Guibal, A new route for manufacturing poly(aminophosphonic)-functionalized poly(glycidyl methacrylate)-magnetic nanocomposite - application to uranium sorption from ore leachate, *Environ. Pollut.* 264 (2020) 114797, <https://doi.org/10.1016/j.envpol.2020.114797>.
- [95] J. Lan, Y. Dong, Y. Xiang, S. Zhang, T. Mei, H. Hou, Selective recovery of manganese from electrolytic manganese residue by using water as extractant under mechanochemical ball grinding: mechanism and kinetics, *J. Hazard Mater.* 415 (2021) 125556, <https://doi.org/10.1016/j.jhazmat.2021.125556>.
- [96] R. Yang, Q. Chang, N. Li, H. Yang, Synergistically enhanced activation of persulfate for efficient oxidation of organic contaminants using a microscale zero-valent aluminum/Fe-bearing clay composite, *Chem. Eng. J.* 433 (2022), <https://doi.org/10.1016/j.cej.2021.133682>.
- [97] J.E. Naicker, R. Govinden, P. Lekha, B. Sithole, Transformation of pulp and paper mill sludge (PPMS) into a glucose-rich hydrolysate using green chemistry: assessing pretreatment methods for enhanced hydrolysis, *J. Environ. Manag.* 270 (2020) 110914, <https://doi.org/10.1016/j.jenvman.2020.110914>.
- [98] L.P. Turner, B.H. Kueper, K.M. Jaansalu, D.J. Patch, N. Battye, O. El-Sharnouby, K.G. Mumford, K.P. Weber, Mechanochemical remediation of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) amended sand and aqueous film-forming foam (AFFF) impacted soil by planetary ball milling, *Sci. Total Environ.* 765 (2021) 142722, <https://doi.org/10.1016/j.scitotenv.2020.142722>.
- [99] European Commission, Energy and the Green Deal, (n.d.). [https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal/energy-and-green-deal\\_en](https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal/energy-and-green-deal_en).
- [100] B. Li, J. Li, Z. Xu, Recover lithium and prepare nano-cobalt from spent lithium ion batteries using a one-pot mechanochemical reaction, *Clean Eng Technol* 5 (2021) 100282, <https://doi.org/10.1016/j.clet.2021.100282>.
- [101] J. Liu, X. Bai, J. Hao, H. Wang, T. Zhang, X. Tang, S. Wang, Y. He, Efficient liberation of electrode materials in spent lithium-ion batteries using a cryogenic ball mill, *J. Environ. Chem. Eng.* 9 (2021) 106017, <https://doi.org/10.1016/j.jece.2021.106017>.
- [102] I. Moez, D. Susanto, W. Chang, H.D. Lim, K.Y. Chung, Artificial cathode electrolyte interphase by functional additives toward long-life sodium-ion batteries, *Chem. Eng. J.* 425 (2021) 130547, <https://doi.org/10.1016/j.cej.2021.130547>.
- [103] Q.H. Nguyen, H. Kim, I.T. Kim, W. Choi, J. Hur, Few-layer NbSe<sub>2</sub>@graphene heterostructures as anodes in lithium-ion half- and full-cell batteries, *Chem. Eng. J.* 382 (2020) 122981, <https://doi.org/10.1016/j.cej.2019.122981>.
- [104] M. Wu, L. Yang, Y. Zhou, J. Jiang, L. Zhang, T. Rao, P. Yang, B. Liu, W. Liao, BaTiO<sub>3</sub>-assisted exfoliation of boron nitride nanosheets for high-temperature energy storage dielectrics and thermal management, *Chem. Eng. J.* 427 (2021) 131860, <https://doi.org/10.1016/j.cej.2021.131860>.
- [105] J. Chen, M. Yao, Q. Zou, P. Chen, F. Liu, T. Zhao, Solvent-free synthesis of Rh/meso-Al<sub>2</sub>O<sub>3</sub> via mechanochemistry for hydrolytic dehydrogenation of ammonia borane, *Int. J. Hydrogen Energy* 47 (2022) 5230–5239, <https://doi.org/10.1016/j.ijhydene.2021.11.137>.
- [106] Y. Shu, X. Duan, Q. Niu, R. Xie, P. Zhang, Y. Pan, Z. Ma, Mechanochemical Alkali-Metal-Salt-mediated synthesis of ZnO nanocrystals with abundant oxygen Vacancies: an efficient support for Pd-based catalyst, *Chem. Eng. J.* 426 (2021) 131757, <https://doi.org/10.1016/j.cej.2021.131757>.
- [107] Q. Wang, M. Ma, K. Cui, X. Li, Y. Zhou, Y. Li, X. Wu, Mechanochemical synthesis of MAPbBr<sub>3</sub>/carbon sphere composites for boosting carrier-involved superoxide species, *J. Environ. Sci. (China)* 104 (2021) 399–414, <https://doi.org/10.1016/j.jes.2020.12.024>.
- [108] S. Yousef, R. Kalpokaitė-Dickuvienė, A. Baltušnikas, I. Pitak, S.I. Lukošiuaitė, A new strategy for functionalization of char derived from pyrolysis of textile waste and its application as hybrid fillers (CNTs/char and graphene/char) in cement industry, *J. Clean. Prod.* 314 (2021), <https://doi.org/10.1016/j.jclepro.2021.128058>.
- [109] A. Isabel Martín-Perales, D. Rodríguez-Padrón, A. García Coletto, C. Len, G. de Miguel, M.J. Muñoz-Batista, R. Luque, Photocatalytic production of vanillin over CeO<sub>x</sub> and ZrO<sub>2</sub> modified biomass-templated titania, *Ind. Eng. Chem. Res.* 59 (2020) 17085–17093, <https://doi.org/10.1021/acs.iecr.0c01846>.
- [110] S. Jafarirad, M. Kosari-Nasab, R. Mohamadpour Tavana, S. Mahjouri, R. Ebadollahi, Impacts of manganese bio-based nanocomposites on phytochemical classification, growth and physiological responses of *Hypericum perforatum* L. shoot cultures, *Ecotoxicol. Environ. Saf.* 209 (2021) 111841, <https://doi.org/10.1016/j.ecoenv.2020.111841>.
- [111] M.L. Grasso, L. Fernández Albanesi, S. Garroni, G. Mulas, F.C. Gennari, Methane production by mechanochemical processing of MgH<sub>2</sub>-Li<sub>2</sub>CO<sub>3</sub> as sources of H<sub>2</sub> and CO<sub>2</sub> at room temperature, *J. CO<sub>2</sub> Util.* 40 (2020) 101209, <https://doi.org/10.1016/j.jcou.2020.101209>.
- [112] S. Benedikt, M. Guillaume, *Agitator Ball Mill*, 2021 20220152621.
- [113] M. Mujtaba, L. Fernandes Fraceto, M. Fazeli, S. Mukherjee, S.M. Savassa, G. Araujo de Medeiros, A. do Espírito Santo Pereira, S.D. Mancini, J. Lipponen, F. Vilaplana, Lignocellulosic biomass from agricultural waste to the circular economy: a review with focus on biofuels, biocomposites and bioplastics, *J. Clean. Prod.* 402 (2023) 136815, <https://doi.org/10.1016/j.jclepro.2023.136815>.
- [114] S. Wang, G. Dai, H. Yang, Z. Luo, Lignocellulosic biomass pyrolysis mechanism: a state-of-the-art review, *Prog. Energy Combust. Sci.* 62 (2017) 33–86, <https://doi.org/10.1016/j.pecc.2017.05.004>.
- [115] P. Liu, H. Zhuang, Y. Qian, J. Yang, Y. Pan, Z. Zhou, L. Jia, F. Qi, Recent advances in mass spectrometric studies on the reaction process of biomass pyrolysis, *Fuel Process. Technol.* 237 (2022) 107473, <https://doi.org/10.1016/j.fuproc.2022.107473>.
- [116] J.L.C. Fajín, M.N.D.S. Cordeiro, Renewable hydrogen production from biomass derivatives or water on trimetallic based catalysts, *Renew. Sustain. Energy Rev.* 189 (2024), <https://doi.org/10.1016/j.rser.2023.113909>.
- [117] D. Pradhan, A.K. Jaiswal, S. Jaiswal, Emerging technologies for the production of nanocellulose from lignocellulosic biomass, *Carbohydr. Polym.* 285 (2022) 119258, <https://doi.org/10.1016/j.carbpol.2022.119258>.
- [118] I. Pérez-Núñez, C. García-Sancho, J.A. Cecilia, R. Moreno-Tost, L. Serrano-Cantador, P. Maireles-Torres, Recovery of pentoses-containing olive stones for their conversion into furfural in the presence of solid acid catalysts, *Process Saf. Environ. Protect.* 143 (2020) 1–13, <https://doi.org/10.1016/j.psep.2020.06.033>.
- [119] I. Malpartida, P. Maireles-Torres, C. Vereda, J.M. Rodríguez-Maroto, S. Halloumi, V. Lair, J. Thiel, F. Lacoste, Semi-continuous mechanochemical process for biodiesel production under heterogeneous catalysis using calcium diglyceride, *Renew. Energy* 159 (2020) 117–126, <https://doi.org/10.1016/j.renene.2020.05.020>.
- [120] A.M. Pérez-Merchán, G. Rodríguez-Carballo, B. Torres-Olea, C. García-Sancho, P.J. Maireles-Torres, J. Mérida-Robles, R. Moreno-Tost, Recent advances in mechanochemical pretreatment of lignocellulosic biomass, *Energies* 15 (2022), <https://doi.org/10.3390/en15165948>.
- [121] F. Shen, X. Xiong, J. Fu, J. Yang, M. Qiu, X. Qi, D.C.W. Tsang, Recent advances in mechanochemical production of chemicals and carbon materials from sustainable biomass resources, *Renew. Sustain. Energy Rev.* 130 (2020) 109944, <https://doi.org/10.1016/j.rser.2020.109944>.
- [122] J. Huang, Y. Zhu, T. Liu, S. Sun, J. Ren, A. Wu, H. Li, A novel wet-mechanochemical pretreatment for the efficient enzymatic saccharification of lignocelluloses: small dosage dilute alkali assisted ball milling, *Energy Convers. Manag.* 194 (2019) 46–54, <https://doi.org/10.1016/j.enconman.2019.04.078>.

- [123] A. Isabel Martín-Perales, D. Rodríguez-Padrón, A.M. Balu, S. Halloumi, I. Malpartida, R. Luque, Continuous flow catalyst-free mechanochemical conversion of iso Eugenol and vanillyl alcohol for vanillin production: from lab experiments to scaled-up premises, *Ind. Eng. Chem. Res.* 62 (2023) 17545–17552, <https://doi.org/10.1021/acs.iecr.3c02250>.
- [124] K.S. Guiao, C. Tzoganakis, T.H. Mekonnen, Green mechano-chemical processing of lignocellulosic biomass for lignin recovery, *Chemosphere* 293 (2022) 133647, <https://doi.org/10.1016/j.chemosphere.2022.133647>.
- [125] H.K. Pradeep, D.H. Patel, H.S. Onkarappa, C.C. Pratiksha, G.D. Prasanna, Role of nanocellulose in industrial and pharmaceutical sectors - a review, *Int. J. Biol. Macromol.* 207 (2022) 1038–1047, <https://doi.org/10.1016/j.ijbiomac.2022.03.171>.
- [126] P. Shen, Q. Tang, X. Chen, Z. Li, Nanocrystalline cellulose extracted from bast fibers: preparation, characterization, and application, *Carbohydr. Polym.* 290 (2022) 119462, <https://doi.org/10.1016/j.carbpol.2022.119462>.
- [127] R. Si, Y. Chen, D. Wang, D. Yu, Q. Ding, R. Li, C. Wu, Nanoarchitectonics for high adsorption capacity carboxymethyl cellulose nanofibrils-based adsorbents for efficient Cu<sup>2+</sup> removal, *Nanomaterials* 12 (2022) 160, <https://doi.org/10.3390/nano12010160>.
- [128] Y. Yu, H. Wu, Effect of ball milling on the hydrolysis of microcrystalline cellulose in hot-compressed water, *AIChE J.* 57 (2011).
- [129] K. ichi Tominaga, K. Nemoto, Y. Kamimura, Y. Hirano, T. Takahashi, H. Tsuneki, K. Sato, Synthesis of methyl lactate from cellulose catalyzed by mixed Lewis acid systems, *Fuel Process. Technol.* 199 (2020) 106288, <https://doi.org/10.1016/j.fuproc.2019.106288>.
- [130] A.R. Mankar, A. Modak, K.K. Pant, High yield synthesis of hexitols and ethylene glycol through one-pot hydrolytic hydrogenation of cellulose, *Fuel Process. Technol.* 218 (2021) 106847, <https://doi.org/10.1016/j.fuproc.2021.106847>.
- [131] X. Qi, L. Yan, F. Shen, M. Qiu, Mechanochemical-assisted hydrolysis of pretreated rice straw into glucose and xylose in water by weakly acidic solid catalyst, *Bioresour. Technol.* 273 (2019) 687–691, <https://doi.org/10.1016/j.biortech.2018.11.011>.
- [132] Q. Hou, C. Bai, X. Bai, H. Qian, Y. Nie, T. Xia, R. Lai, G. Yu, M.L.U. Rehman, M. Ju, Roles of ball milling pretreatment and titanil sulfate in the synthesis of 5-hydroxymethylfurfural from cellulose, *ACS Sustain. Chem. Eng.* 10 (2022) 1205–1213, <https://doi.org/10.1021/acssuschemeng.1c06936>.
- [133] L. Lan, H. Chen, D. Lee, S. Xu, N. Skillen, A. Tedstone, P. Robertson, A. Garforth, H. Daly, C. Hardacre, X. Fan, Effect of ball-milling pretreatment of cellulose on its photoreforming for H<sub>2</sub> production, *ACS Sustain. Chem. Eng.* 10 (2022) 4862–4871, <https://doi.org/10.1021/acssuschemeng.1c07301>.
- [134] J. Yang, C. Gao, X. Yang, Y. Su, S. Shi, L. Han, Effect of combined wet alkaline mechanical pretreatment on enzymatic hydrolysis of corn stover and its mechanism, *Biotechnol. Biofuels. Bioprod.* 15 (2022) 1–11, <https://doi.org/10.1186/s13068-022-02130-0>.
- [135] M. Ishiguro, T. Endo, Effect of the addition of calcium hydroxide on the hydrothermal-mechanochemical treatment of Eucalyptus, *Bioresour. Technol.* 177 (2015) 298–301, <https://doi.org/10.1016/j.biortech.2014.10.135>.
- [136] Y. Yu, Y. Long, H. Wu, Near-complete recovery of sugar monomers from cellulose and lignocellulosic biomass via a two-step process combining mechanochemical hydrolysis and dilute acid hydrolysis, *Energy Fuel.* 30 (2016) 1571–1578, <https://doi.org/10.1021/acs.energyfuels.5b02196>.
- [137] H.M. Wang, B. Wang, J.L. Wen, S.F. Wang, Q. Shi, R.C. Sun, Green and efficient conversion strategy of Eucalyptus based on mechanochemical pretreatment, *Energy Convers. Manag.* 175 (2018) 112–120, <https://doi.org/10.1016/j.enconman.2018.09.002>.
- [138] X. Cheng, R. Ning, F. Zhang, L. Ji, K. Wang, J. Jiang, Structural conversion and characterization of Camellia oleifera shell lignin based on mechanochemical-assisted pretreatment, *Biomass Bioenergy* 170 (2023), <https://doi.org/10.1016/j.biombioe.2023.106708>.
- [139] C. Sun, L. Zheng, W. Xu, A.V. Dushkin, W. Su, Mechanochemical cleavage of lignin models and lignin via oxidation and a subsequent base-catalyzed strategy, *Green Chem.* 22 (2020) 3489–3494, <https://doi.org/10.1039/d0gc00372g>.
- [140] S. Andini, A. Bolognese, D. Formisano, M. Manfra, F. Montagnaro, L. Santoro, Mechanochemistry of ibuprofen pharmaceutical, *Chemosphere* 88 (2012) 548–553, <https://doi.org/10.1016/j.chemosphere.2012.03.025>.
- [141] T.L. Lambat, S.H. Mahmood, D. Taher, S. Banerjee, Sulfamic acid catalyzed oxonium-ene reactions under ball milling conditions: straightforward access to highly functionalized Oxabicyclo[3.2.1]octenes, *Curr. Res. Green. Sustain. Chem.* 4 (2021) 100118, <https://doi.org/10.1016/j.crgsc.2021.100118>.
- [142] Y. Shu, X. Duan, Q. Niu, R. Xie, P. Zhang, Y. Pan, Z. Ma, Mechanochemical Alkali-Metal-Salt-mediated synthesis of ZnO nanocrystals with abundant oxygen vacancies: an efficient support for Pd-based catalyst, *Chem. Eng. J.* 426 (2021) 131757, <https://doi.org/10.1016/j.cej.2021.131757>.
- [143] T. Leo Jin, X. Liu, Q. Gao, H. Zhu, C. Lian, J. Wang, R. Wu, Y. Lyu, Pyrolysis-free, facile mechanochemical strategy toward cobalt single-atom/nitrogen-doped carbon for highly efficient water splitting, *Chem. Eng. J.* 433 (2022) 134089, <https://doi.org/10.1016/j.cej.2021.134089>.
- [144] A. Morfino, J. Gediga, K. Harlow, B. Mazzanti, Life cycle assessment comparison between zircon and alumina sand applied to ceramic tiles, *Clean Eng Technol* 6 (2022) 100359, <https://doi.org/10.1016/j.clet.2021.100359>.
- [145] F. Battista, Y.S. Montenegro Camacho, S. Hernández, S. Bensaïd, A. Herrmann, H. Krause, D. Trimis, D. Fino, LCA evaluation for the hydrogen production from biogas through the innovative BioRobur project concept, *Int. J. Hydrogen Energy* 42 (2017) 14030–14043, <https://doi.org/10.1016/j.ijhydene.2016.12.065>.
- [146] S. Bello, P. Méndez-Trelles, E. Rodil, G. Feijoo, M.T. Moreira, Towards improving the sustainability of bioplastics: process modelling and life cycle assessment of two separation routes for 2,5-furandicarboxylic acid, *Sep. Purif. Technol.* 233 (2020) 116056, <https://doi.org/10.1016/j.seppur.2019.116056>.
- [147] H. Guzmán, F. Salomone, E. Batuecas, T. Tommasi, N. Russo, S. Bensaïd, S. Hernández, How to make sustainable CO<sub>2</sub> conversion to Methanol: thermocatalytic versus electrocatalytic technology, *Chem. Eng. J.* 417 (2021), <https://doi.org/10.1016/j.cej.2020.127973>.
- [148] H. Taher, A. Giwa, H. Abusabiekeh, S. Al-Zuhair, Biodiesel production from Nannochloropsis gaditana using supercritical CO<sub>2</sub> for lipid extraction and immobilized lipase transesterification: economic and environmental impact assessments, *Fuel Process. Technol.* 198 (2020) 106249, <https://doi.org/10.1016/j.fuproc.2019.106249>.
- [149] J. Albertí, C. Brodhag, P. Fullana-i-Palmer, First steps in life cycle assessments of cities with a sustainability perspective: a proposal for goal, function, functional unit, and reference flow, *Sci. Total Environ.* 646 (2019) 1516–1527, <https://doi.org/10.1016/j.scitotenv.2018.07.377>.
- [150] European Standards, EN 15804 A2 Sustainability of Construction Works - Environmental Product Declarations - Core Rules for the Product Category of Construction Products, 2019. <https://www.en-standard.eu/csn-en-15804-a2-sustainability-of-construction-works-environmental-product-declarations-core-rules-for-the-product-category-of-construction-products/>.
- [151] S. Arfelis, I. Malpartida, A. Bala, V. Lair, R. Xifré, R. Aguado, M. Delgado-Aguilar, J. Parduhn, I. Sazdovski, P. Fullana-I-Palmer, Wood chips components separation with a new wet-milling process compared to chemical depolymerization: a technical, economic, and environmental comparison, *ACS Sustain. Chem. Eng.* (2023), <https://doi.org/10.1021/acssuschemeng.3c07477>.
- [152] S. Arfelis, I. Malpartida, V. Lair, V. Caldeira, I. Sazdovski, A. Bala, P. Fullana-i-Palmer, Life cycle assessment on calcium zincate production methods for rechargeable batteries, *Sci. Total Environ.* 866 (2023) 161094, <https://doi.org/10.1016/j.scitotenv.2022.161094>.
- [153] I. Malpartida, P. Maireles-Torres, C. Vereda, J.M. Rodríguez-Maroto, S. Halloumi, V. Lair, J. Thiel, F. Lacoste, Semi-continuous mechanochemical process for biodiesel production under heterogeneous catalysis using calcium diglycerate, *Renew. Energy* 159 (2020) 117–126, <https://doi.org/10.1016/j.renene.2020.05.020>.
- [154] J. Thiel, F.R. Lacoste, V. Lair, S. Halloumi, I. Malpartida, B. Moevus, Three-Dimensional Crusher, Its Implementation Process And Its Uses, 2018. FR3081732B1.
- [155] F.R. Lacoste, J. Thiel, V. Lair, S. Halloumi, Procédé de production d'esters d'acides gras et de glycérol à basse température, 2018 WO2018002559A1.
- [156] F.R. Lacoste, V. Lair, J. Thiel, S. Halloumi, Method for Manufacturing Calcium Diglycerate, 2018. WO2018060654A1.