RSC Mechanochemistry

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *RSC Mechanochem.*, 2025, **2**, 20

Received 27th June 2024
Accepted 11th October 2024

DOI: 10.1039/d4mr00069b

rsc.li/RSCMechanochem

A new planetary ball mill device with adjustable speed ratio for enhanced mechanochemical processes†

Frank Yntema,[ab] Cameron Webster[a] and Emmanouil Broumidis *[ab]

In this paper, we introduce a novel planetary ball mill device featuring an interchangeable speed ratio, allowing users to manually adjust this parameter to suit the needs of each reaction. The device's modular design offers unprecedented control over the kinetic energy input, enabling enhanced reaction efficiency, selectivity, and precision.

Mechanochemistry, which utilizes mechanical forces to drive chemical reactions, is commonly conducted using various milling devices such as mixer mills (MM), twin screw extruders (TSE), and planetary ball mills (PBM). As seen in Table 1, these devices share several operational parameters that can be adjusted by users to optimize reaction outcomes.[1] However, a notable limitation of conventional PBMs is their fixed speed ratio $\left(\frac{\text{jar speed}}{\text{disk speed}}\right)$, set by the manufacturer, which constrains the ability to fine-tune the kinetic energy and shear forces for individual reactions. Typically, the default value in commercial PBMs is set at −2. However, these devices have originally been developed for general purpose grinding and metal alloying applications, and not mechanochemistry. As such, we believe that being able to control this parameter is crucial for optimizing mechanochemical reactions, and herein we describe the development of a new device capable of doing that.

PBMs are a cost-effective way to generate a combination of impact and shear forces for mechanochemistry. The balls collide creating a localized point of high pressure and temperature on a microscale and the rubbing between surfaces causes heat due to friction.[2] The fundamental layout of the PBM is shown below (Fig. 1A). The impact energy of a single ball can be estimated by using the travel distance from the point of detachment to the point of impact (Fig. 1B). Such a kinematic model makes it possible to break down the variables that influence the PBM's performance (Fig. 1C). The relationship between these variables can be summarized into three equations:[3,4] (1) The kinetic energy of the ball during the impact, (2) the number of impacts per second, (3) the cumulative energy of the mill for a specified time. Multiple vials are connected and balanced to a disc that spins at a set rotational speed (W_p). These vials have their own gearing to make them rotate relative to the disc (W_v). The behavior of the balls inside these vials are dependent on this ratio. The performance of a PBM is related to the impact energy of the balls (E_b) and the number of impacts over time (ν_t) leading to the cumulative energy during the reaction (E_{cum}). This is dependent on many factors that affect the kinematic properties of the mill including: the diameter of the sun disc (R_p) and vial (D_v); the mass $\rho_b\left(\frac{\pi {d_b}^3}{6}\right)$ and geometry of the balls (d_b), the rotation speed of the sun disc (W_p) and relative rotation speed of the vials (W_v). Using such a kinematic model it is possible to optimize the performance by identifying the parameters which ensure the ball has the greatest amount of travel between detachment and impact for a given sun disc and the specified rotation speed. This will give the maximum possible impact energy for the intended drive specification. One way to achieve this optimal performance is by adjusting the ratio between the rotation speeds for the sun disc and vials (W_v/W_p). However, this also results in a non-linear behavior in the milling power (E_{cum}) due to the increased travel time negatively affecting the milling frequency (ν_t). These observations were supported in previous studies that varied the speed radio and radii ratio and captured the change in the time between the ball's point detachment and impact affecting the resulting milling frequency.[5]

$$\Delta E_b = \frac{1}{2}\left(\rho_b \frac{\pi {d_b}^3}{6}\right) {W_p}^2 \left(\left(\frac{W_v}{W_p}\right)^2 \left(\frac{D_v - d_b}{2}\right)^2 \left(1 - 2\frac{W_v}{W_p}\right) - 2R_p\left(\frac{W_v}{W_p}\right)\left(\frac{D_v - d_b}{2}\right) - \left(\frac{W_v}{W_p}\right)^2 \left(\frac{D_v - d_b}{2}\right)^2\right) \quad (1)$$

[a]*Pluto Mills Ltd, Michelin Scotland Innovation Parc, Baldovie Rd, Dundee, DD4 8UQ, UK. E-mail: m.broumidis@hw.ac.uk*

[b]*Heriot-Watt University, Grid Building, Enterprise Hub, Boundary Road North, Gait 1, Edinburgh, EH14 4AS, UK*

† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d4mr00069b

Table 1 List of operational parameters seen in common commercial milling devices and their adjustability

Operational parameter	Milling device	Adjustable by user?
Milling material	MM/TSE/PBM	Yes
Size, geometry and number of milling balls	MM/PBM	Yes
Milling volume	MM/TSE/PBM	Yes
Filling degree	MM/PBM	Yes
Ball-to-mass ratio	MM/PBM	Yes
Operating frequency	MM/TSE/PBM	Yes
Reaction time	MM/TSE/PBM	Yes
Temperature	MM/TSE/PBM	Yes
Atmosphere	MM/PBM	Yes
Speed ratio	PBM	No

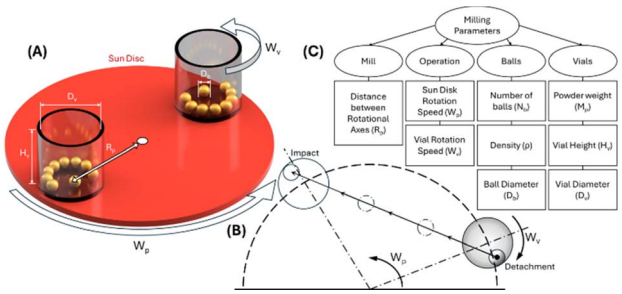


Fig. 1 (A) Layout of conventional PBM. (B) Illustration of the fundamental kinematic model of ball travel within the vial. (C) Diagram of all the variables that influence a PBM's performance. This model is only applicable while the PBM is in avalanche mode.

$$v_t = N_b K(W_p - W_v) \quad (2)$$

$$E_{cum} = \frac{\Delta E_b^* v_t t}{m_p} \quad (3)$$

When impact energy (Fig. 2a) and milling power (Fig. 2b) is plotted against the different speed ratios, this relationship is clear to observe, that at the point of optimal impact energy there is a dip in the milling power. Such nonlinear behavior makes the PBM performance difficult to predict. There is also the fact that this idealized model does not take the influence of ball-to-ball indirect impact interactions, and the friction caused by the presence of the powder. However, mathematical models can classify three distinct behaviors, that being chaotic, avalanche and rolling. These modes are approximated using the speed ratio (i) between the sun disc and vial (W_v/W_p). When below the limit threshold (i_{limit}) ball behavior will be chaotic. When above critical ($i_{critical}$) the balls will roll against the vial wall and little reaction will take place. These thresholds can be calculated by using the ratio of the sun disc (R_p) and internal vial (R_v) radii (eqn (4)). For mechanochemistry most reactions are performed between these thresholds.[2]

$$i_{limit} = 1 - \sqrt{\frac{R_p}{R_v}} \leq i \leq 1 + \sqrt{\frac{R_p}{R_v}} = i_{critical} \quad (4)$$

These unknowns have been assessed using mathematical models,[4,6–9] numerical simulations,[10–12] and experiments.[13–17]

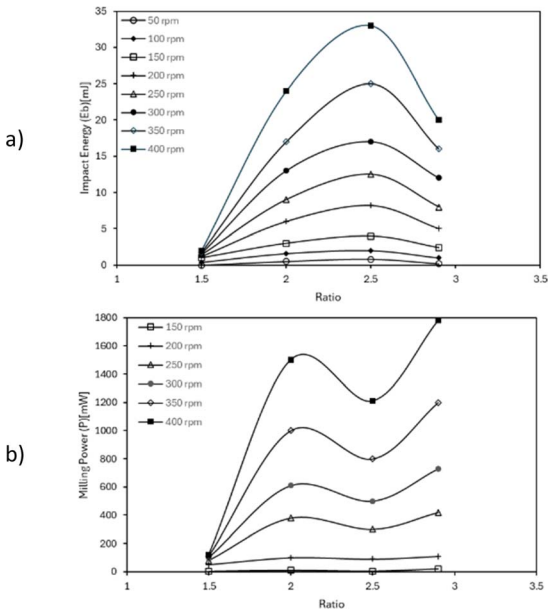


Fig. 2 (a) Impact energy using validated kinematic model[6] with different sun disc speeds and the relationship of the speed ratio between the sun disk and vials. Please note that the rotation of the vials was counter to the sun disk rotation and thus W_v would be negative. (b) Shows how the milling power would change using the same parameters.

However, these investigations are difficult to validate due to how most PBMs have limited variability in speed ratio and sun disc rotation rates making a proper parametric study on the general performance of PBMs costly. This, combined with the difficulties of building reliable monitoring techniques due to the harsh environment within the vials, means there is limited data on how the motion of the ball mill affects the mechanochemical reaction. One study overcomes the lack of monitoring by using an exothermic reaction that has a specific ignition point.[15] By monitoring the temperature, the performance of the reaction can be determined by observing the resulting temperature spike. The findings show that the relative change in performance has a close correlation to the idealized kinematic model. Milling power is not the only aspect of the PBM when it comes to mechanochemistry. The intense friction that is

generated during milling results in a rapid buildup of heat. This means that some reactions have a limited milling time before they decompose. Determining this additional parameter makes the relationship between impact energy and milling frequency important. Impact energy that is higher than needed for the chemical activation will generate unnecessary heat. It will also cause additional wear on the vial walls, introducing more contaminants. These issues are what makes the PBM's performance difficult to predict.

In order to better understand and control the PBM, Pluto Mills designed a new drive system (Fig. 3) that was more modular than those in other PBM designs. This allows for a more feasible means to change milling parameters and assess the resulting changes in performance, making parametric analysis for various mechanochemical experiments easier.

The drive system is a planetary belt drive inspired by the planetary gear box. The design has a two-vial capacity, each with a 500 mL internal volume, much higher (2×) than any other commercial PBM. Each vial assembly has a double clamping system with cams that lock into a slot at the vial's base and a tampered ring that clamps down onto the vial lid. These are secured onto a flanged shaft with an integrated platform that has a 30-degree taper lock acting as a holder. This requires the tapered indent to be machined into the base of the vials. The benefit of doing so means that the vials will maintain their centre at higher speeds. The shafts are connected to a 20 mm thick plate that acts as an arm. The span between the centre of the vial shafts (sun disk diameter) is 304 mm. Synchronous belt pulleys are attached to the shafts. The radius of these pulleys determines the resulting speed ratio. This does mean that partial disassembly is needed in order to change the speed ratio. Thus, taper lock bushings and a modular arm design was used. Changing the pulleys beneath the vials can be done within 5 minutes. This would be less convenient than directly driving each vial using an electric motor like the Activator 2S PBM, which would allow the speed ratio to be changed dynamically. However, electric motors have a limited speed, meaning its maximum speed ratio is reduced when the sun disc rotation speed is higher. For example: when the Activator 2S sun disc speed is 400 rpm, since the maximum vial rotation speed is 1500 rpm, the maximum speed ratio is approximately 3.75. However, when the sun disc speed is doubled to 800 rpm, as the maximum vial speed is constant, the maximum speed ratio is reduced to 1.875. In contrast, our belt pulley design allows consistent speed ratios even at higher sun disc speeds. Table 2 lists the pulleys used, the associated speed ratios and the types of synchronous belts required. The belt surrounds the pulleys acting as a ring gear. The teeth of the belt are held stationary using a fixed pulley located at the main shaft. A second arm with nylon idlers is used to tension the belt. The drive system is designed to operate up to 1600 rpm. These higher speeds meant that more robust bearings were required, thus high precision angular contact bearings were used. However, for the experiments, speeds were limited to 400 rpm for comparison to other commercially available mills. Speed ratios were selected to be between 1–3 as most commercial mills fall into this range (see "Comparison Table" in ESI†). This also allowed us to use a higher tooth modulus for the belt, reducing the chances of slipping.

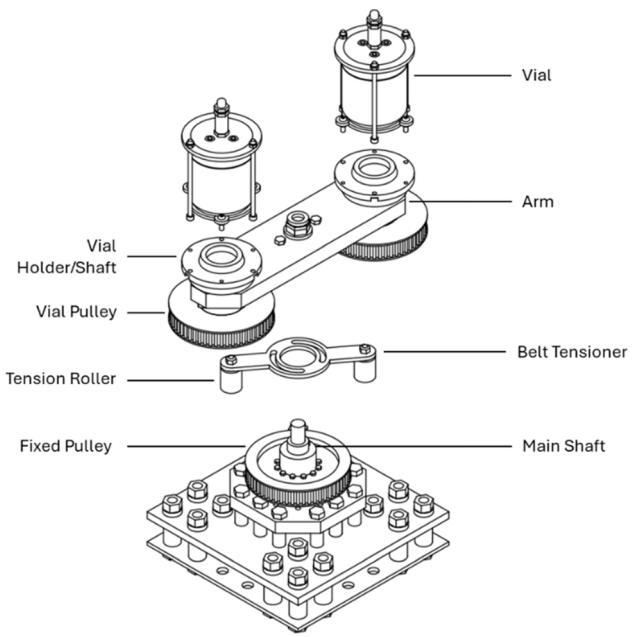
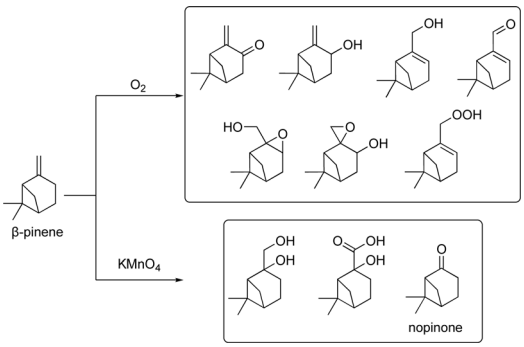


Fig. 3 Exploded isometric diagram of the Pluto Mill's PBM drive system design.

To prove that our PBM works as intended and to validate the previously published theoretical results, we opted to examine the effects of the speed ratio on the oxidative degradation of 6,6-dimethyl-2-methylidenebicyclo[3.1.1]heptane (β-pinene), as a model reaction. Similar to how mechanochemistry has been employed for the degradation of active pharmaceutical ingredients (APIs),[18,19] this study explores the relationship between speed ratio adjustments and the formation of specific degradation products (Scheme 1). β-Pinene, a monoterpene commonly derived from turpentine or the resin of pine trees, was chosen due to its high reactivity and propensity to oxidize under mechanochemical conditions.[20] The resulting outcome was surprising, as although the results have the same characteristics of what would be expected from the theoretical model, the point of optimum performance is closer to a ratio below 1.5 rather than the expected ratio of 2 (ESI "Theoretical *vs.* Experiment"†). Although the milling parameters are different, the theoretical models[6] and Discrete Element Models (DEM)[21] would predict that a larger vial and sun radius would increase the optimum impact ratio and thus also the optimum milling power speed ratio.

Table 2 The pulleys used in the experiment and their resulting speed ratios

No. teeth	Pitch diameter (mm)	Belt no. teeth	Belt length (mm)	Speed ratio
56	142.60	133	1064	1.066
44	112.05	121	968	1.357
28	71.30	107	856	2.132
22	56.02	102	816	2.713



Scheme 1 β-Pinene and some of its oxidation products that have been reported under oxidative ($KMnO_4$ and O_2) conditions.[20,22] 6,6-dimethylbicyclo[3.1.1]heptan-2-one (nopinone), is a common oxidation product of β-pinene that is formed in the presence of potassium permanganate ($KMnO_4$).

The experimental setup (Fig. 4a) was based on the previously developed protocol developed by Hopfe and co-workers.[23] In our case, the procedure was carried out at the gram scale (56.8 g of material per vial, 2 vials per milling session), as the new PBM is designed for accommodating large scale reactions. For each speed ratio the experiment was repeated 3 times in total. After 10 min of milling, the PBM was stopped, the contents of the milling vials were worked up (details in ESI†) and subjected to high-performance liquid chromatography (HPLC) analysis. The outcome of the reaction was evaluated in two ways: the degradation profile of the reaction was determined based on the consumption of the starting material, β-pinene at different speed ratios, and similarly based on the amount of nopinone that was formed during the milling. This was done for each of the four speed ratios that were tested. The effect of the speed ratio on the reaction outcome was profound when compared to Fig. 2b. It was found that the point of highest recorded performance was at a speed ratio of 1.357 instead of being around 2 like the theoretical milling power optimum (Fig. 2b). The following minimum point also changes to 2.132, instead of being close to 2.5 shown in Fig. 2b. A similar discrepancy was observed before, when measuring the ignition time for the formation of TiB_2 with a Pulverisette 4 planetary mill at different speed ratios.[15] They found that the point of highest efficiency was closer to 2.5. This was higher than what was expected in the kinematic model. However, in both cases the same general trend was observed. Finally, it was concluded that other factors like the Ball-to-Powder Ratio (BPR) and the independent vial rotation speed altered the outcome. The fact that, regardless of the reaction, the overall outcome remains consistent could be a way to better understand and optimize mechanochemical reactions.

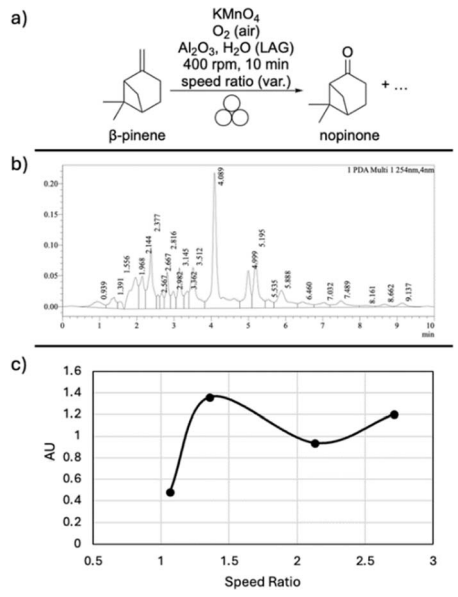


Fig. 4 (a) General reaction scheme for the mechanochemical oxidation of β-pinene in the presence of $KMnO_4$ and atmospheric O_2. Neutral alumina (Al_2O_3) was used as an auxiliary grinding agent. (b) Representative HPLC chromatogram after 10 min of milling, at a speed ratio of 2.132 shows a large number of products, including remaining unreacted β-pinene ($t = 4.089$ min) and product nopinone ($t = 3.362$ min). (c) Cumulative graph showing the relative nopinone production for different speed ratios. Both β-pinene and nopinone HPLC peaks were identified by using pure commercial samples as references.

Conclusions

In summary, this study aims to encourage researchers within the mechanochemical community to take into account all relevant milling parameters when designing their experiments. Mechanochemical setups are highly complex, involving many interdependent factors, and seemingly minor changes can have a dramatic impact on the outcome of a reaction. A good example of this comes from the recent work of Friščić *et al.*,[24] where in a copper-catalyzed reaction, switching from stainless steel to aluminium vials caused mechanoinhibition by preventing copper(I) chloride (CuCl) oxidation, illustrating the intricate interplay of these factors. Another recent example by Haag *et al.* explored the parameter of mass transfer by introducing a corrugated ball-mill medium that enhances efficiency in solvent-free mechanochemical reactions, such as co-crystallization and allotrope conversion.[25] In a similar fashion, in this work we highlight the effect of speed ratio in the oxidation of β-pinene performed using PBMs. We designed, built and tested a new PBM that is able to switch between different speed ratios, thus enabling users to finetune a parameter that has been previously neglected and can affect reaction outcomes substantially. The parts list, computer aided design (CAD) files, and detailed instructions for construction are all available online.[26] The PBM is designed so that it can be assembled and constructed, including sourcing the parts, by most university mechanical/electrical workshops at a cost comparable to or lower than a commercial ball mill, like the Retsch MM400.

Data availability

Data for this article, including CAD files, parts and diagrams for the construction of the device are available at **https://github.com/PlutoMills/OpenMill**.

Author contributions

Frank Yntema (FY): design, assembly, and testing of the PBM, writing of manuscript; Cameron Webster (CW): conducting of mechanochemical degradation experiments; Emmanouil Broumidis (EB): conceptualization, original design of PBM, funding acquisition, supervision of mechanochemical experiments, writing of manuscript.

Conflicts of interest

EB is the director of Pluto Mills Ltd, and holds a patent (WO2024018234A1) that protects the PBM's design that is disclosed herein from commercial use.

Acknowledgements

EB would like to thank Innovate UK for an ICURe fellowship (grant number: 10031020) which funded this study. Moreover, EB thanks Dr Filipe Vilela (Heriot-Watt University, UK) and Dr Gareth O Lloyd (University of Lincoln, UK) for useful scientific discussions and support at the early stages of the development of Pluto Mills Ltd. Finally, EB would like to thank Glenn Bojanov (University of Bern, Switzerland), for valuable insights and proofreading of this manuscript.

Notes and references

1 N. Fantozzi, J.-N. Volle, A. Porcheddu, D. Virieux, F. García and E. Colacino, *Chem. Soc. Rev.*, 2023, **52**, 6680–6714.
2 F. K. h. Urakaev, in *High-Energy Ball Milling*, ed. M. Sopicka-Lizer, Woodhead Publishing, 2010, pp. 9–44.
3 N. Burgio, A. Iasonna, M. Magini, S. Martelli and F. Padella, *Il Nuovo Cimento D*, 1991, **13**, 459–476.
4 M. Broseghini, L. Gelisio, M. D'Incau, C. L. A. Ricardo, N. M. Pugno and P. Scardi, *J. Eur. Ceram. Soc.*, 2016, **36**, 2205–2212.
5 V. I. Molchanov, O. G. Selezneva and E. N. Zhirnov, in *Activation of Minerals during Grinding*, Nedra, Moscow, 1988, pp. 177–189.
6 G. Kakuk, I. Zsoldos, Á. Csanády and I. Oldal, *Rev. Adv. Mater. Sci.*, 2009, 21–38.
7 P. P. Chattopadhyay, I. Manna, S. Talapatra and S. K. Pabi, *Mater. Chem. Phys.*, 2001, **68**, 85–94.
8 F. K. Urakaev and V. V. Boldyrev, *Powder Technol.*, 2000, **107**, 93–107.
9 F. K. Urakaev and V. V. Boldyrev, *Powder Technol.*, 2000, **107**, 197–206.
10 H. Mio, J. Kano and F. Saito, *Chem. Eng. Sci.*, 2004, **59**, 5909–5916.
11 C. C. Doumanidis, H. A. Al Kaabi, A. S. M. Alzaabi, I. E. Gunduz, C. Rebholz and C. C. Doumanidis, *Powder Technol.*, 2016, **301**, 1077–1084.
12 C. Xie and Y. Zhao, *Powder Technol.*, 2022, **398**, 117057.
13 S. Rosenkranz, S. Breitung-Faes and A. Kwade, *Powder Technol.*, 2011, **212**, 224–230.
14 F. Erdemir, *Measurement*, 2017, **112**, 53–60.
15 C. Real and F. J. Gotor, *Heliyon*, 2019, **5**, e01227, Note: the planetary PBM used in this study is no longer commercially available.
16 A. S. Rogachev, D. O. Moskovskikh, A. A. Nepapushev, T. A. Sviridova, S. G. Vadchenko, S. A. Rogachev and A. S. Mukasyan, *Powder Technol.*, 2015, **274**, 44–52.
17 F. K. Urakaev, *Mendeleev Commun.*, 2016, **26**, 546–548.
18 R. P. Kaiser, E. F. Krake, L. Backer, J. Urlaub, W. Baumann, N. Handler, H. Buschmann, T. Beweries, U. Holzgrabe and C. Bolm, *Chem. Commun.*, 2021, **57**, 11956–11959.
19 E. F. Krake, L. Backer, B. Andres, W. Baumann, N. Handler, H. Buschmann, U. Holzgrabe, C. Bolm and T. Beweries, *ACS Cent. Sci.*, 2023, **9**, 1150–1159.
20 P. Liu, X. Liu, T. Saburi, S. Kubota, P. Huang and Y. Wada, *RSC Adv.*, 2021, **11**, 20529–20540.
21 H. Mio, J. Kano, F. Saito and K. Kaneko, *Mater. Sci. Eng., A*, 2002, **332**, 75–80.
22 U. Neuenschwander, E. Meier and I. Hermans, *ChemSusChem*, 2011, **4**, 1613–1621.
23 T. Szuppa, A. Stolle, B. Ondruschka and W. Hopfe, *ChemSusChem*, 2010, **3**, 1181–1191.
24 K. Floyd, L. Gonnet, T. Friščić and J. Batteas, *RSC Mechanochem.*, 2024, **1**, 289–295.
25 O. Bawadkji and R. Haag, *RSC Mechanochem.*, 2024, advance article.
26 **https://github.com/PlutoMills/OpenMill**.