A New Planetary Ball Mill Device with Adjustable Speed Ratio for Enhanced Mechanochemical Processes

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Introduction

Pluto Mills planetary ball mill prototype (Figure S1) is designed to be an adaptable modular design for mechanochemical investigations. The design was inspired by the planetary gear box, however, instead of gears we used a synchronous belt system where the belt acted as the ring gear and a fixed pulley in the centre as the sun. As the belt system is constructed using standard parts, changing the speed ratio between the sun disc and vial rotation can be done quickly and cheaply by replacing the vial pulleys with different Pitch Centre Diameters (PCD). Vials are made of 316 stainless steel and clamped with cams at the base and a tapered securing ring on the top. This ensures that the vial remains aligned to the centre of the shaft. The belt is secured by meshing with the fixed pulley at the centre, the tensioning arm presses the belt against this pulley ensuring that it cannot slip.

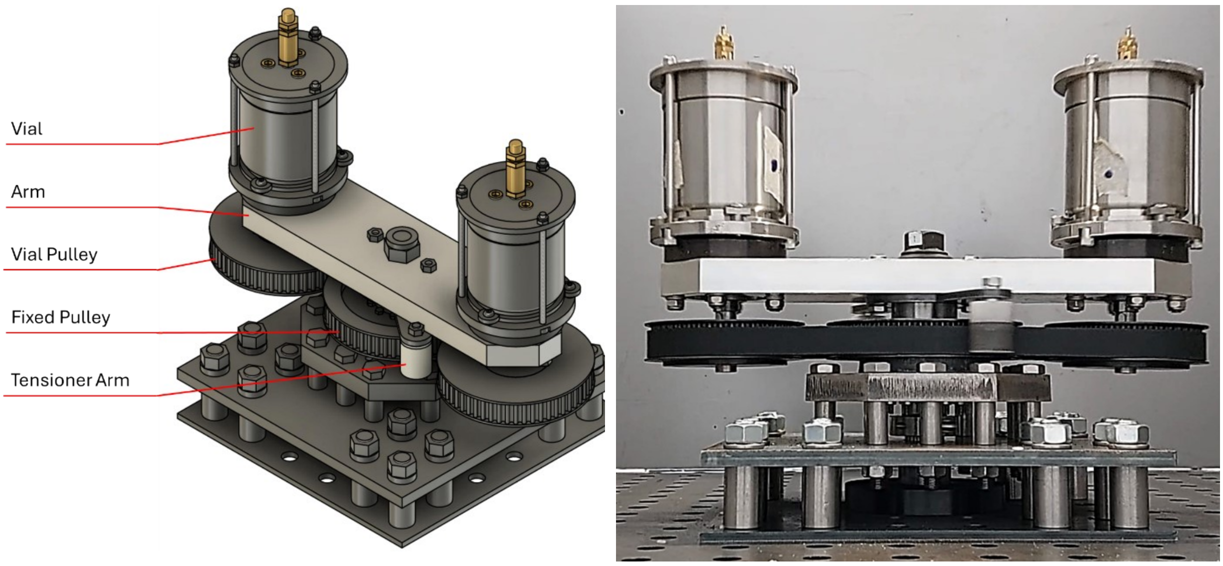


Figure S1: General construction of Pluto Mill Prototype using belt drive.

Subassemblies

The device can be broken down into subassemblies:

1. The main shaft
2. Vials and their platform/shafts
3. Electronics/Safety Enclosure.

The detail of their assembly and utility is shown in this document.

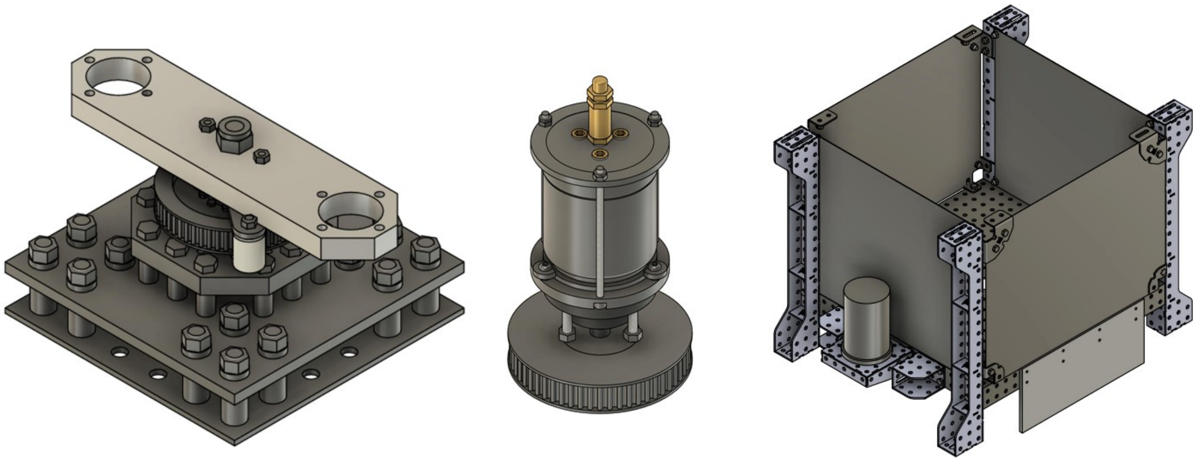


Figure S2: Subassemblies of Pluto Mills prototype: 1 The main shaft [Left], 2 vial and shaft [centre], 3 safety enclosure [right].

Main Shaft Assembly

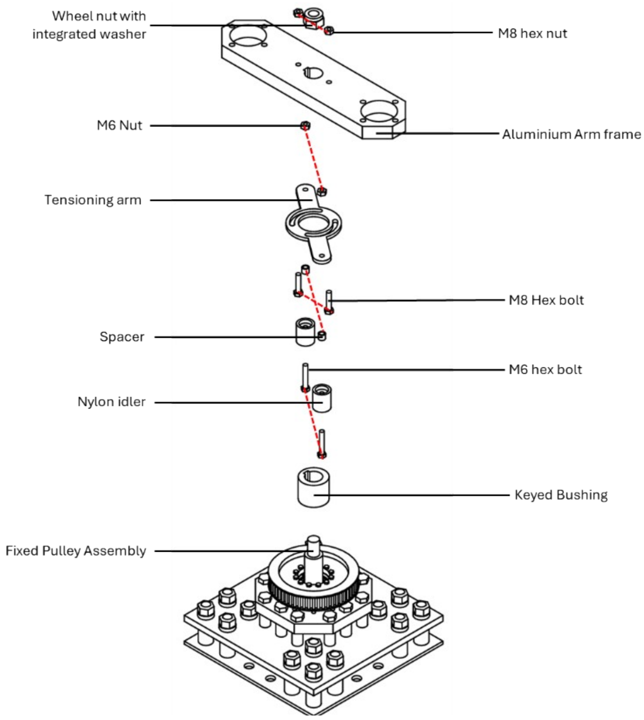


Figure S3: Exploded isometric of arm-frame assembly.

Arm Construction

The aluminium arm frame is made from 25 mm thick aluminium plate, cut using a CNC machine. 6 mm mild steel plate was laser cut for the tensioner arm. Two nylon idlers were selected to hold the synchronous belt in place. The tensioner arm assembly was held in place using two M8 bolts going through the arm frame. When loosened, the tensioning arm can swing back and forth. Once tightened, the steel on aluminium interaction prevented the arm from moving at all. This also applies to the shaft, making the removal of the arm difficult without a bearing puller. The shaft key is shared between the keyed bushing and the arm frame ensuring arm assembly remains secure.

Fixed Pulley Construction

The fixed pulley is made from a pulley with a pilot bore. Once the hub was removed, a hole was made for the bushing and an array of small holes for M4 bolts that hold the assembly together. A roller bearing was used to steady the shaft. However, to address the potential alignment issue the bearing selected had a spherical outer race that would compensate for any initial misalignment. The bearing was nested in a 20 mm steel plate and restraining ring. A shim was used to act as a bridge between the parts for when the bearing was pressed into position. The inner race rested on another inner race sleeve being suspended by a split shaft collar. All this was suspended above the main shaft assembly using M12 connector nuts.

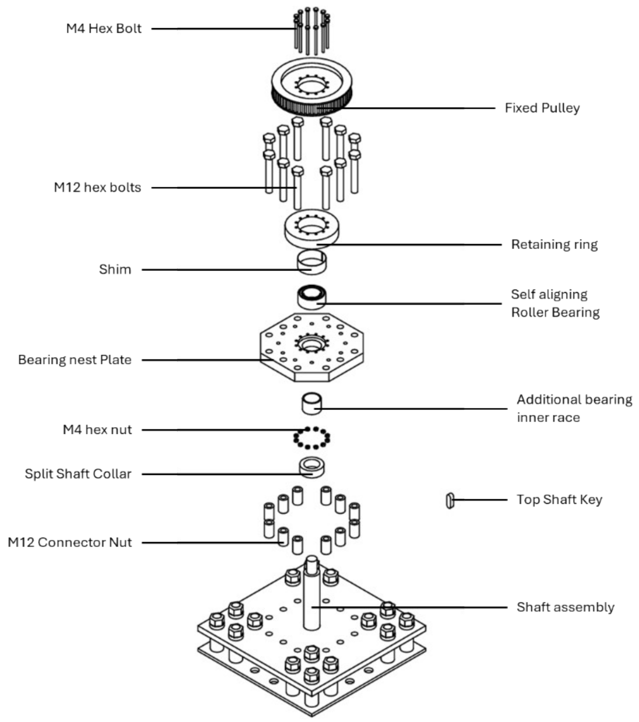


Figure S4: Exploded isometric of fixed pulley and roller bearing housing.

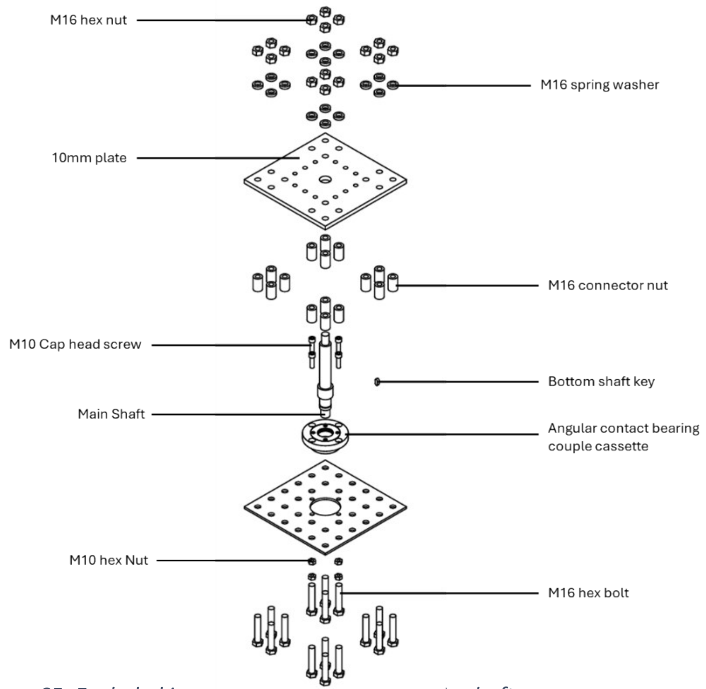


Figure S5: Exploded isom n shaft.

Base Construction

30 mm diameter main shaft bearing cassette was bolted to a 6mm steel welding table using M10 cap head screws. To ensure rigidity an additional 6 mm steel reinforcing plate was added. The locating bearing was a set of back-to-back angular contact bearings that had an interference fit making it impossible to be disassembled without destroying the bearings. The washer, tab-washer and lock nut used to lock shaft to bearings is not shown (please refer to the vial construction diagram). The 10 mm steel cover plate was suspended using M16 connector nuts.

Vial Assembly

The vials are secured using a set of cams that lock into a groove cut into the vial wall's base and a clamp ring that presses against a taper on the vial lid which is secured with long M6 cap head screws. The mill generates a lot of heat and thus the sealed vial could build up a significant amount of pressure. To address this potential safety hazard a calibrated safety pressure valve was installed to vent the vial if pressure proves to be too great. It was planned to install additional monitoring devices hence the additional holes in the lid. These holes were sealed with brass plugs. The platform for the vial has a 30° taper that mates with the base of the vial walls. The 20 mm diameter shaft that protrudes from the platform is held by a pair of back-to-back angular contact bearings similar to that of the main shaft arrangement with the shaft being secured with a washer, tab washer and bearing locknut. Not shown is the shaft key that used standard sizing and was 30 mm long, this holds the taper lock bushing in place. The bearing cassette is then bolted to the aluminium arm frame with M8 cap head screws and Nyloc nuts. A taper lock bushing is used to secure the vial pulley to the shaft.

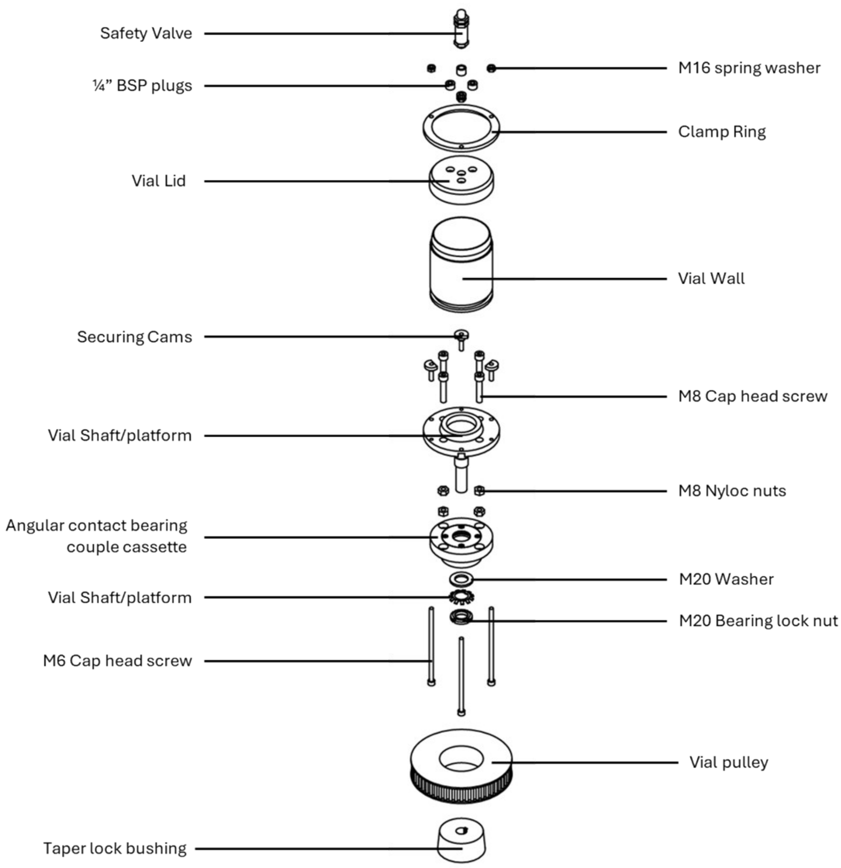


Figure S6: Exploded isometric of vial, its platform and pulley.

Safety Enclosure and Motor Slide

A 1 m x 1 m welding table was modified, allowing the ball mill to be mounted to its centre. The safety enclosure is composed from 1 mm laser cut mild steel. Not shown is a 10 mm polycarbonate roof panel that was later attached to the enclosure. The panels were supported with 1 m standard mild steel struts that were sold as standard laser cut templates also made from 6 mm thick mild steel. A modified laser cut squared faced bracket was used to mount the 2.2 kW 2 pole AC motor. 25 mm chipboard was mounted to the side of the table using M8 hex bolts and nuts, on which the electronics were secured. The enclosure panels were secured using M16 bolt and Nyloc nuts. Unused sections of the support struts were removed and then used to construct the motor slide.

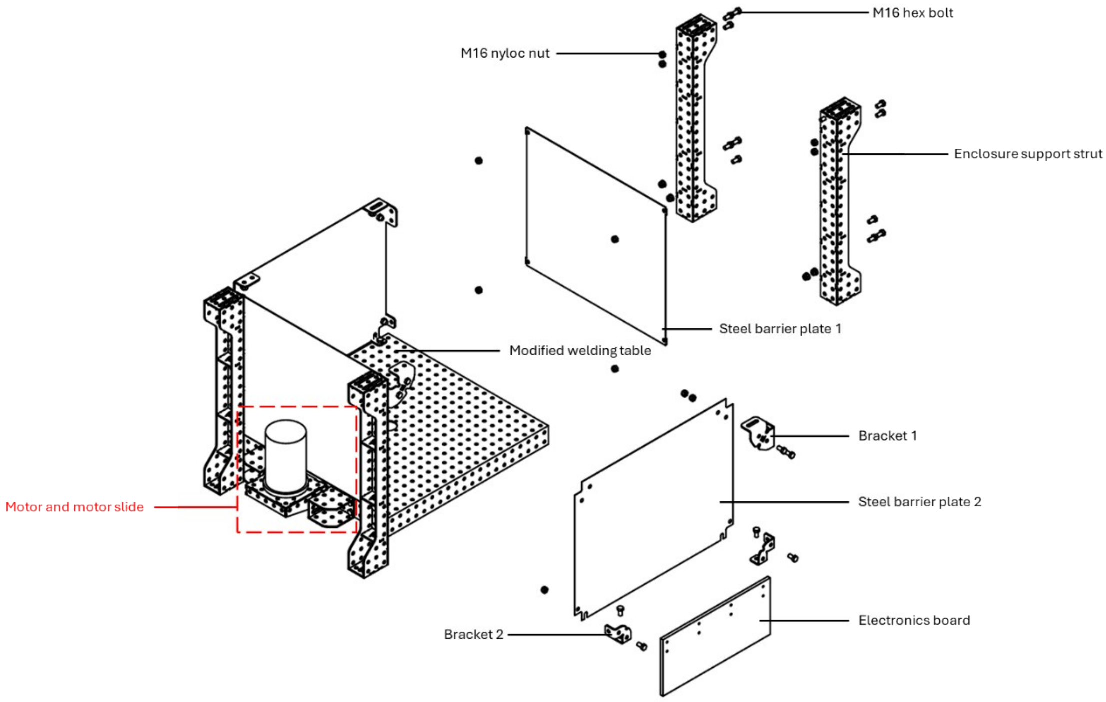


Figure S7: Exploded Isometric showing safety enclosure construction.

The main shaft is connected to the motor using a wedge belt. A 5:1 ratio was used to allow the motor to operate between 400-600 rpm. Long M16 bolts holds the motor bracket. These bolts were clamped using a double hex nut which presses against the head of the bolt and the Nyloc nut on the other end. When loosened the bolts can glide along the I-holes to tighten the wedge belt.

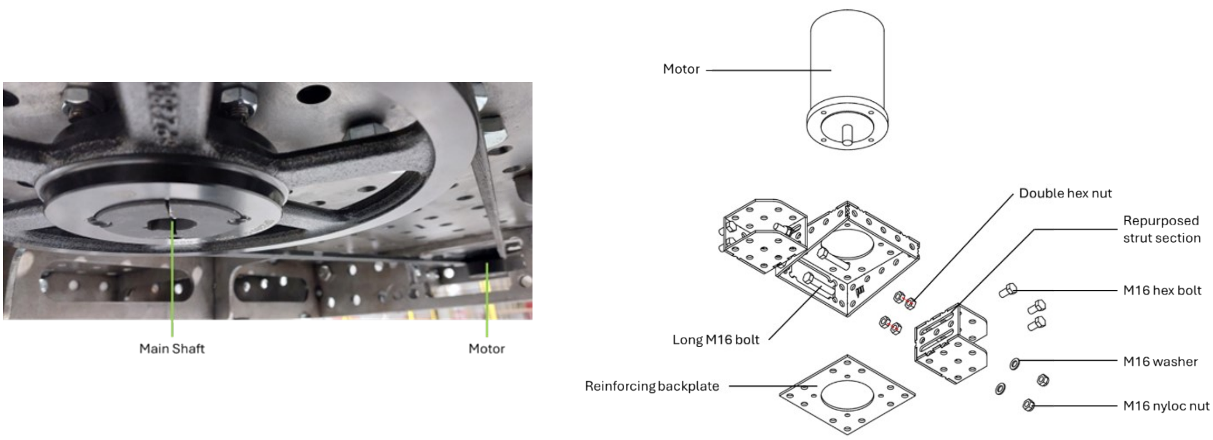


Figure S8: Photograph of main shaft belt drive arrangement (Left). Exploded isometric of motor slide.

Control Panel

A simple analogue manual control system was devised for testing using a potentiometer to regulate the Variable Frequency Drive (VFD) inverter. The other controls are simple start/stop buttons for easy operation using and an emergency stop serving as a safety switch to prevent accidental activation.

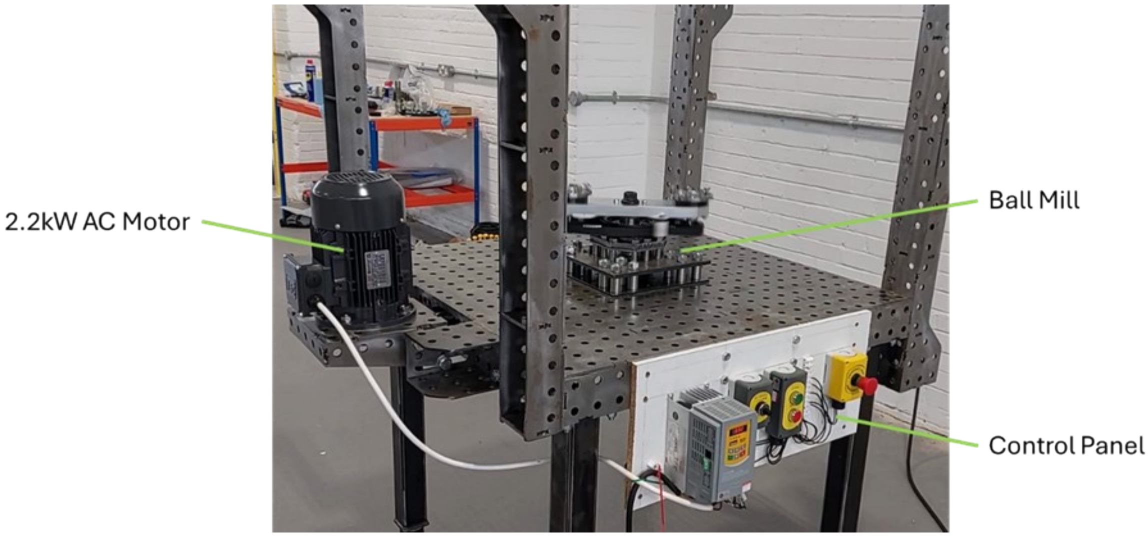


Figure S9: Photograph of ball mill without enclosure during initial testing of drive system.

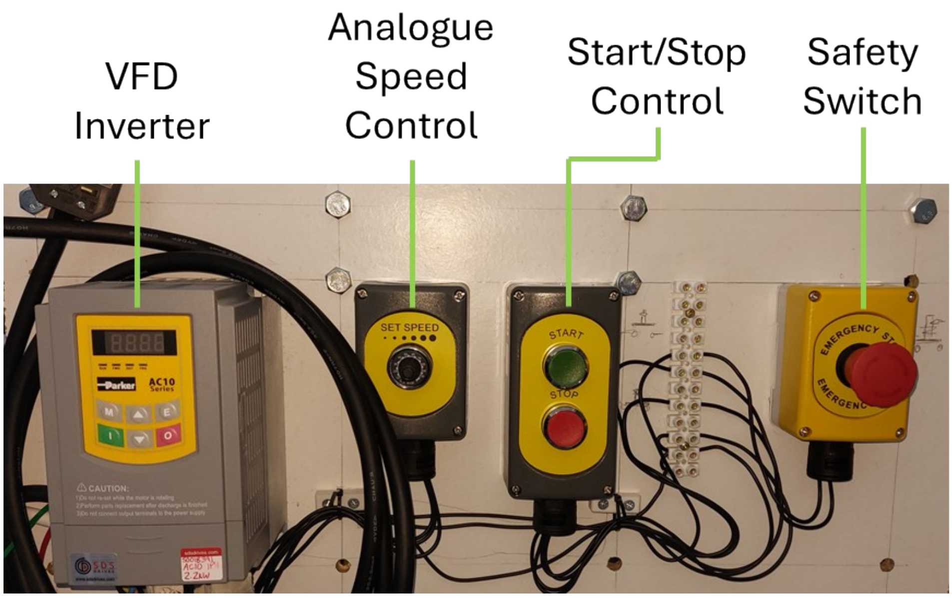


Figure S10: Photograph of control panel.

Device Comparison Table

Table S1: Comparison between Pluto PBM and other similar PBM devices

Milling device	Max Vial Volume (mL)	Sun Disk Radius (mm)	Internal Diameter (mm)	Speed Ratio (-400 RPM)	RCF (-400 RPM) (g)
Pluto Mill Belt Drive	**500**	**152**	**82**	**1-3**[a]	**27.19**
Activator-2S	250	104	80	0-3.75	18.60
Retsch PM 300	250	150	76	2	26.83
Fritsch Pulverisette 5	225	90	65	2	16.10

a: When using a High Torque Drive (HTD) 8M belt modulus the speed ratio is limited to approximately 3 for taper lock bushings. However, if the modulus were to be reduced this could reach above 5. As this was a first attempt it was thought best to use 8M to reduce chances of slipping when testing at higher speeds.

Table S2: Online resources for each of the milling devices

Milling device	Website
Pluto Mill Belt Drive	https://plutomills.com/; https://github.com/PlutoMills/OpenMill/ [a]
Activator 2S	http://www.activator.ru/engl/foto2S.html
Retsch PM 300	https://www.retsch.com/products/milling/ball-mills/planetary-ball-mill-pm-300/
Fritsch Pulverisette 5	https://www.fritsch-international.com/sample-preparation/milling/planetary-mills/details/product/pulverisette-5-premium-line/

a: Both the website and Github repository are currently under development

Experimental Section

General Methods and Materials

All chemicals were commercially available (Sigma-Aldrich, Fluorochem, Apollo Scientific, TCI UK). Anhydrous $MgSO_4$ was used for drying organic extracts and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by TLC using commercial glass backed thin layer chromatography (TLC) plates (Merck Kieselgel 60 F254). The plates were observed under UV light at 254 and 365 nm. The technique of flash chromatography was used throughout for all non-TLC scale chromatographic separations using Merck Silica Gel 60 (less than 0.063 mm). For the collection of high-performance liquid chromatography (HPLC) data a Shimadzu LC-2040C 3D Plus instrument was used, equipped with a C18 column.

β-Pinene Oxidation Experiments

The Al_2O_3 (42.2 g), β-pinene (3.02 g), $KMnO_4$ (10.5 g), and Water (1.11 g) were all combined in a milling vial (stainless steel, V = 500 mL) with 1/3 of the vial's internal volume occupied by milling balls (stainless steel, d = 8 mm). Subsequently, the vial was then closed, secured to the PBM and the contents were milled at 400 RPM for 10 minutes under air. Following that, the vial was dismounted, and the resulting slurry was removed using water (22 mL) and ethyl acetate (EtOAc) (33 mL). The aqueous solution was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried under $MgSO_4$, and then the solvent was removed under reduced pressure. Thin layer chromatography (TLC) was then ran using EtOAc/Hexane (1:3) eluent mixture, to qualitatively assess the outcome of the reaction. For the HPLC analysis, 10 mg of the crude solid were suspended to 1 mL of EtOAc. The mixture was then filtered through a membrane syringe filter (pore size 0.45 µm, diam. 33 mm) and the resulting solution was injected to the HPLC instrument (injection volume 2 µL). The above procedure was repeated three times for each speed ratio setting.

Figure S11: Photographs of the loaded reaction vial before (a) and post (b) milling.

Theoretical Vs Experimental Result

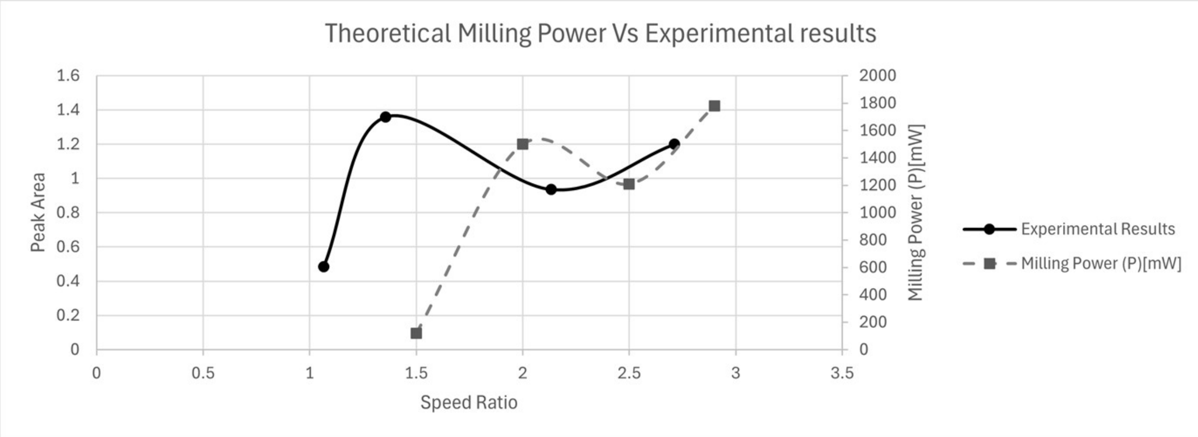
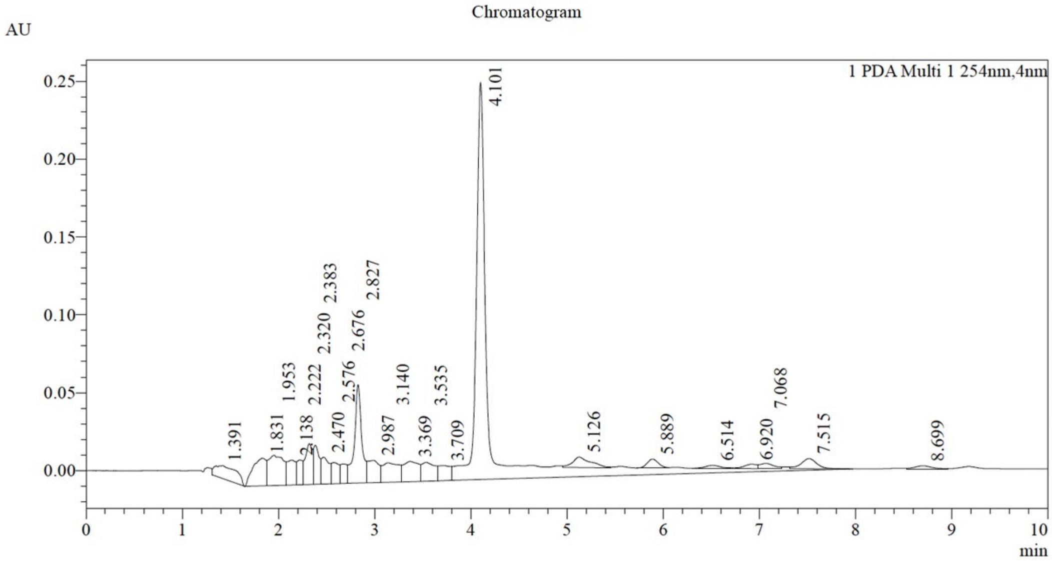


Figure S12: A shape comparison between the experimental results and the theoretical milling power based on a validated mathematical model. These are the same results that are shown in figure 2b at 400rpm. Peak Area is given in A.U. (absorbance units).

HPLC Chromatograms



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height
1	1.391	135993	7556
2	1.831	171912	17743
3	1.953	210192	19359
4	2.138	96012	15930
5	2.222	66905	15899
6	2.320	135436	26165
7	2.383	101728	24979
8	2.470	95615	17250
9	2.576	75080	13636
10	2.676	58978	12540
11	2.827	336547	62768
12	2.987	114267	14258
13	3.140	148696	12455
14	3.369	142105	12930
15	3.535	114209	12076
16	3.709	81150	9685
17	4.101	2451992	254107
18	5.126	87523	6645
19	5.889	48270	5749
20	6.514	22551	1945
21	6.920	25822	2725
22	7.068	34051	3289
23	7.515	74641	6501
24	8.699	23170	1938
Total		4852843	578128

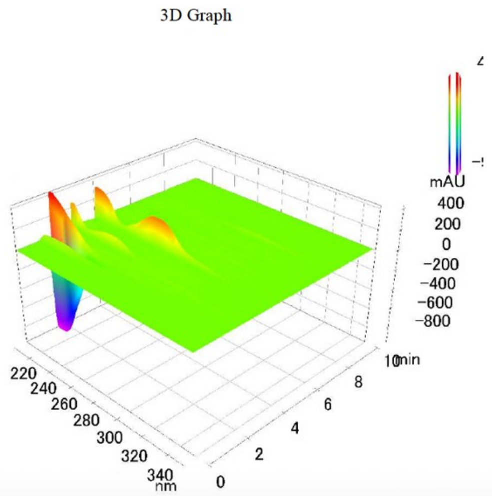
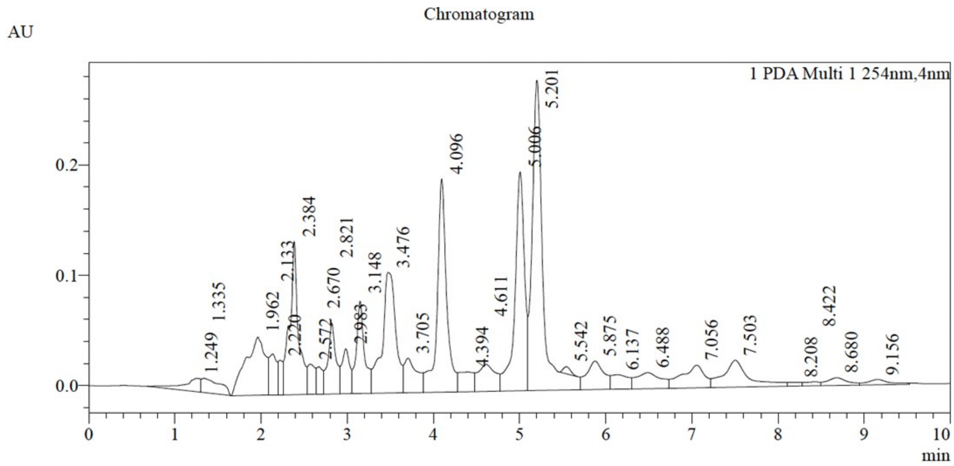


Figure S13: Chromatogram showing the degradation of β-pinene after 10 min of milling at a speed ratio of 1.066.



Peak Table

PDA Ch1 254nm

Ret. Time	Area	Height
1.249	169742	12106
1.335	196772	13086
1.962	832723	52620
2.133	213395	37153
2.220	118003	31379
2.384	996397	137371
2.572	161099	27507
2.670	123491	24731
2.821	413552	64131
2.983	265817	40550
3.148	554989	83405
3.476	1211770	109212
3.705	325750	31294
4.096	1475754	192574
4.394	210316	17778
4.611	347832	24480
5.006	1540046	198211
5.201	2451834	280100
5.542	37496	6386
5.875	367071	25784
6.137	177428	13065
6.488	284780	14482
7.056	378469	20543
7.503	503633	24374
8.208	35503	3367
8.422	43667	3538
8.680	114722	7014
9.156	85333	4709
	13637385	1500951

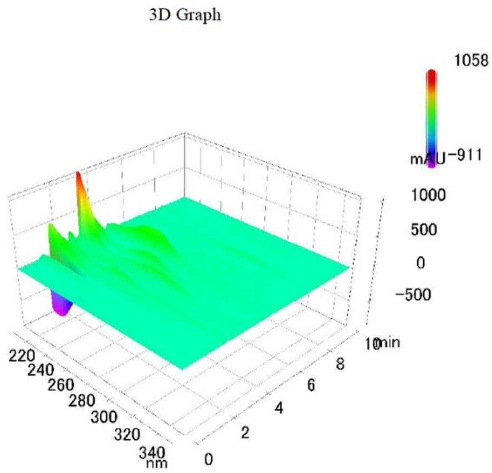
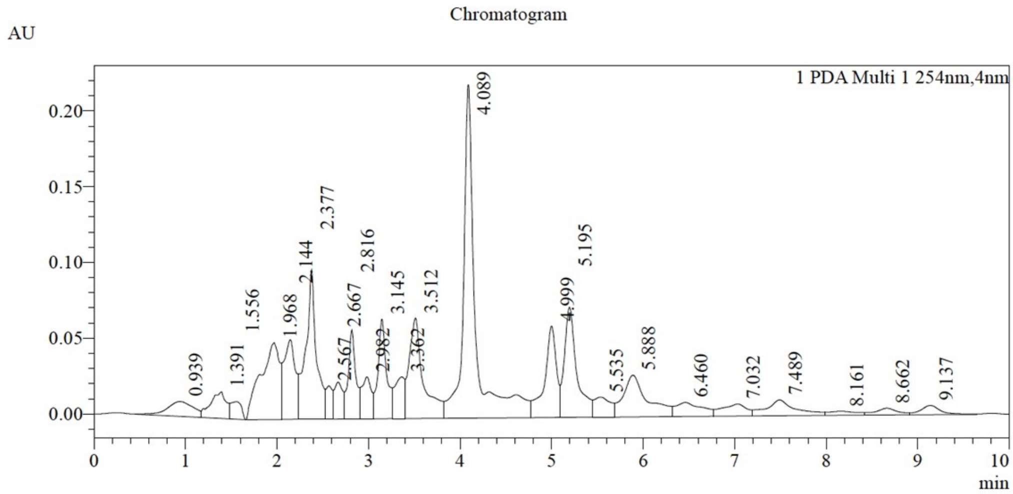


Figure S14: Chromatogram showing the degradation of β-pinene after 10 min of milling at a speed ratio of 1.357.



Peak Table

PDA Ch1 254nm

Ret. Time	Area	Height
0.939	192532	9734
1.391	207884	17363
1.556	93130	11443
1.968	722327	50577
2.144	455174	52431
2.377	803008	97562
2.567	108021	21847
2.667	152416	24335
2.816	335346	58233
2.982	205310	27678
3.145	431411	65117
3.362	202446	27402
3.512	721546	66085
4.089	2009837	218617
4.999	550777	60161
5.195	688591	72461
5.535	164315	13267
5.888	509417	27486
6.460	185336	9260
7.032	150031	7987
7.489	237607	10474
8.161	57640	2692
8.662	77430	4509
9.137	94871	6124
	9356404	962844

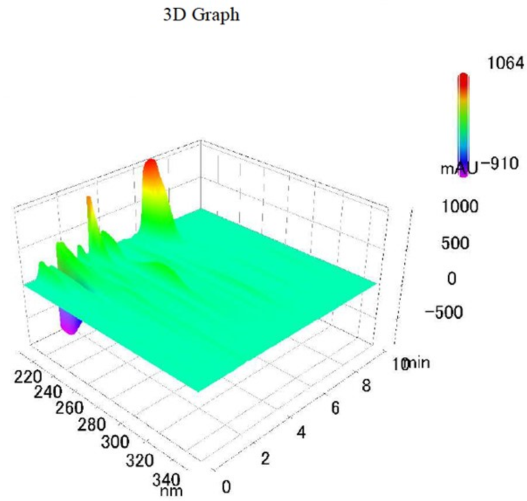
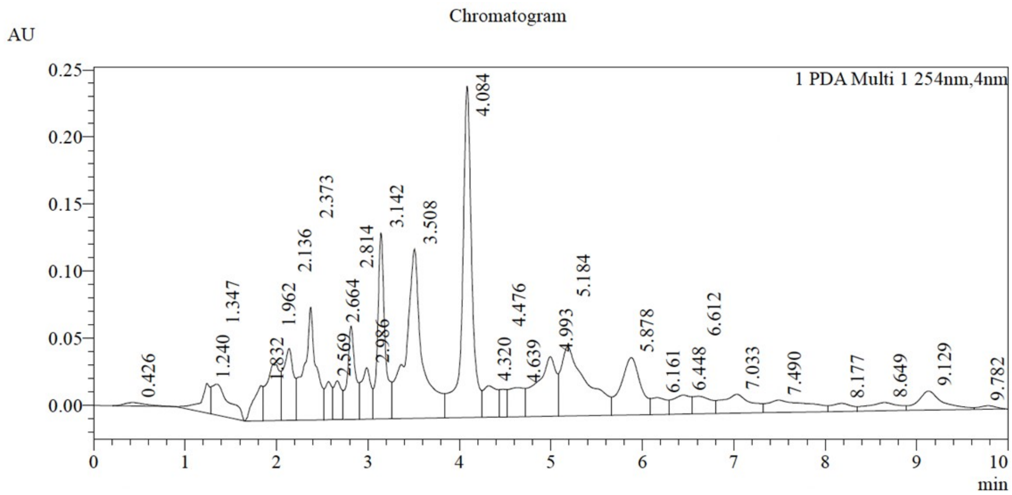


Figure S15: Chromatogram showing the degradation of β-pinene after 10 min of milling at a speed ratio of 2.132.



Peak Table

PDA Ch1 254nm

Ret. Time	Area	Height
0.426	43368	2584
1.240	157081	21994
1.347	307469	23069
1.832	189025	26133
1.962	408286	41775
2.136	422841	53333
2.373	775949	83769
2.569	148900	28222
2.664	171294	28845
2.814	424438	69417
2.986	277350	38069
3.142	773990	138038
3.508	1598181	125682
4.084	1776179	246408
4.320	239096	23301
4.476	108158	20583
4.639	253897	21623
4.993	656948	44198
5.184	1018231	51695
5.878	641182	42674
6.161	141063	12517
6.448	194593	14008
6.612	180007	13073
7.033	312235	14002
7.490	290819	9177
8.177	96357	5997
8.649	146032	6163
9.129	264364	14146
9.782	32416	2539
	12049749	1223033

3D Graph

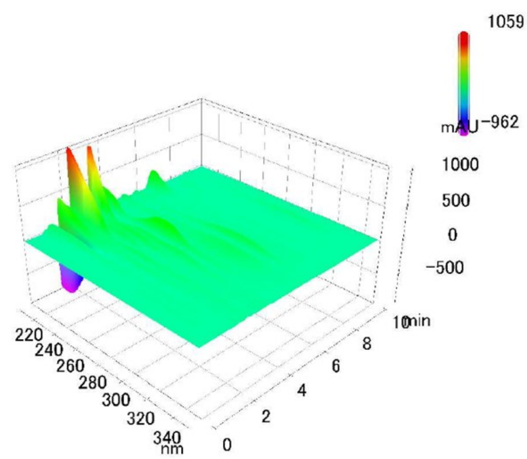


Figure S16: Chromatogram showing the degradation of β-pinene after 10 min of milling at a speed ratio of 2.713.