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# Quantitative comparison of the efficiency of mechanochemical reactors

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A simple method is proposed for the comparison of the mechanical dose rates of different mills, based on measuring the ignition time of a mechanically-induced self-propagating reaction (MSR). Specifically, a SPEX 8000 Mixer Mill with round-ended and flat-ended milling vials and a Fritsch Pulverisette-6 planetary mill are compared, using the ignition of MSR between Zn and S powders as the test reaction. The method facilitates the comparison of reaction kinetics data obtained by using different milling equipment.


## 1. Introduction

Mechanochemical processing has been utilized in inorganic and organic synthesis, the preparation of alloys, ceramics, and nanocomposites, and the activation and disordering of alloys and compounds [1–4]. If the reaction between the reactant powders is highly exothermic, milling can initiate a self-propagating thermal reaction after some activation time [5]. Mechanochemical reactions are usually carried out in high-energy milling devices, such as shaker mills, planetary mills, attritors, and vibration mills [2, 3, 6]. Several factors affect the efficiency of a mill, including its type, speed or frequency, the shape, size and material of the milling bodies, temperature, atmosphere, etc. [7]. Consequently, predicting the kinetics of a mechanochemical process is a challenging task.

Even comparing reaction kinetics data on the same reaction but obtained using different equipment or mill parameters is difficult. For example, the synthesis of $ZnFe_2O_4$ from ZnO and $Fe_2O_3$ took about 2 h using an AGO-2 planetary mill [8] and 4 h with a Fritsch Pulverisette-7 mill [9]. Direct comparison of the reaction kinetics would be possible, if the relative efficiencies of the two mills were known. The kinetics of the formation of AlFe alloys from a mixture of elemental powders was studied by Nasu *et al.* [10] and Wang *et al.* [11]. Their results could be compared directly, if the time scales of the two experiments could be normalized to each other. The mechanically induced cation redistribution in $NiFe_2O_4$ was studied using an EI 2 × 150 planetary mill [12, 13] and a Fritsch Pulverisette-7 mill [14]. An independent measurement of the relative milling intensities would be beneficial again. In many cases, the milling conditions influence the reaction route and the obtained products, not only the rate of the reaction. For example, complete amorphization and the formation of intermetallic compounds are observed in the Ni-Zr system, depending on the processing parameters [15]. But even in such complex cases, it is useful to match the time scales using the relative milling intensities before searching for further effects.

A mechanically-induced self-propagating reaction (MSR) is possible, if a highly exothermic powder mixture, such as Ti-C [16], CuO-Fe [17] or Ni-Al [18], is processed in a milling device. Ignition takes place at a "hot spot" between the colliding milling tools and propagates through the activated powder as an SHS (self-propagating high-temperature synthesis) reaction [5]. In high-energy mills such as shaker and planetary mills, hot spots are always present, and ignition takes place when propagation becomes possible due to sufficient mechanical activation, i.e., the reactants have received a critical amount of mechanical dose (absorbed energy per unit mass) [5, 19]. The time it takes to reach the critical dose, i.e., the ignition time ($t_{ig}$) of a given MSR is inversely proportional to the milling efficiency as measured by the rate of mechanical dose. Comparing the ignition times obtained for the same reaction but using different mills provides a simple means to compare the efficiencies of the mills. Moreover, the dose rate achieved with a particular mill is usually proportional to the ball-to-powder mass ratio for a broad range of powder masses and combinations of milling balls. This is expected, if the balls move independently

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and their impact velocity depends only on the motion of the milling container. The influence of the ball-ball collisions can be considered negligible, if the ignition time is found to be proportional to the powder-to-ball mass ratio, $p$. In this case the mechanical dose rate is an appropriate way to characterize the milling efficiency and it is inversely proportional to the slope of the ignition time versus powder-to-ball mass ratio plot. The same trend is suggested by the milling maps derived by Suryanarayana *et al.* [20] for the mechanical alloying of Ti and Al.

## 2. Experimental results

We have chosen the ignition of MSR in a mixture of fine Zn and S powders to measure the relative milling efficiencies of a SPEX 8000 Mixer Mill with round-ended and flat-ended steel vials and a Fritsch Pulverisette-6 (P-6) planetary mill. The formation of ZnS from a mixture of elemental powders is one of the oldest and most studied examples of MSR [21].

Two sets of experiments were carried out with the SPEX 8000 Mixer Mill, one using a round-ended hardened steel vial and the other using a flat-ended steel vial. Several combinations of steel balls were employed, from ten 6.35-mm diameter balls to a mixture of three 12.7-mm, six 9.5-mm and twelve 6.35-mm balls. The charge ratio was varied from $p = 0.024$ to $p = 0.48$, the powder mass from 1 to 10 g. The vial was closed under argon to avoid the possible effects of atmospheric oxygen and humidity. The temperature of the milling vial was measured with a $K$-type thermocouple pressed against its surface and the abrupt temperature increase was used as the signal of ignition. The results are shown by "$\times$" and "$+$" for the flat- and round-ended vials in Fig. 1. The points are reasonably close to two straight lines through the origin, the best fits give $t_{ig} = 220p$ (min) for the round-ended and $t_{ig} = 140p$ (min) for the flat-ended vial. The milling intensity is inversely proportional to these slopes and it is proportional to the ball-to-powder mass ratio.

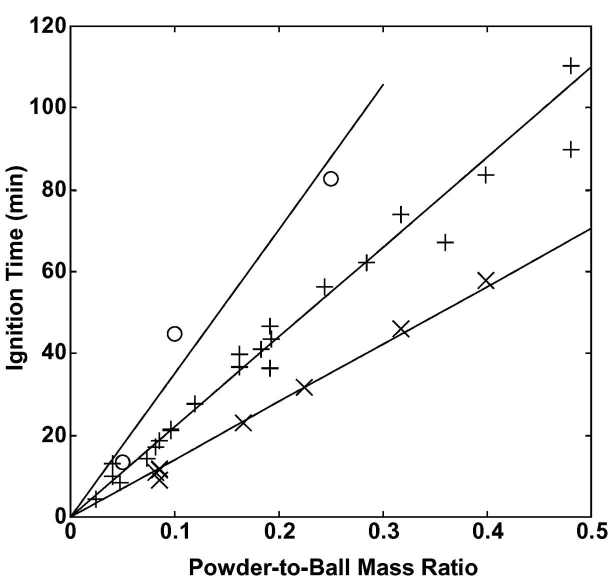


*Figure 1* Ignition time as a function of the charge ratio for the MSR between Zn and S. Results obtained with a SPEX 8000 Mixer Mill and flat- and round-ended vials and with a Fritsch P-6 mill are shown by "$\times$", "$+$", and "o", respectively.

The experiments with the P-6 planetary mill employed a 150 cm$^3$ stainless steel bowl and 5-mm steel balls. The temperature of the grinding chamber was monitored using a GTM (gas pressure and temperature measuring) system (Fritsch, Idar-Oberstein) [22]. The experiments were performed by milling 10 g of powder in air at 550 rpm. The ignition times are shown by the open circles in Fig. 1. They are close to a straight line through the origin as anticipated, the best fit gives $t_{ig} = 350p$ (min).

In summary, the ignition time is proportional to the powder-to-ball mass ratio for each equipment. The SPEX 8000 Mixer Mill with flat-ended vial delivers the largest dose rate, about $220/140 = 1.57$ times larger than the same mill with round-ended vial. The efficiency of the Fritsch P-6 planetary mill is about $350/140 = 2.5$ times lower under the applied conditions.

## 3. Discussion

It must be emphasized that although the above comparison is based on the ignition time of an MSR, the result is equally valid for comparing mechanochemical processes with continuous kinetics, such as gradual reactions, the disordering of alloys or oxides, etc. The time scale of the kinetics obtained with the P-6 mill and the one obtained with a SPEX 8000 mill and the round-ended vial has to be compressed 2.5-fold and 1.57-fold, respectively, in order to compare the results directly to the kinetics measured with a SPEX 8000 mill and flat-ended vial. Further correction is needed if the ball-to-powder mass ratios are different.

The magnitude of the difference between the flat-ended and round-ended vials is somewhat surprising, although it is clear that the balls usually travel the entire length of the flat-ended vial between collisions and they impact the ends almost head-on, while the same is not the case for the round-ended vial. This result calls attention to the importance of reporting the type and size of the milling container, along with other details of the milling conditions, if comparison with results from other laboratories is to be made possible.

The efficiency of any other high-energy mill can be compared to the mills used in this study employing the same procedure: The ignition time of the combination reaction between Zn and S powders has to be measured for a few combinations of balls and powder masses. If the ignition time is proportional to $p$ within reasonable limits, the assumptions of the above analysis are valid and the efficiency of the mill is inversely proportional to the slope of the $t_{ig}$ versus $p$ line. By comparing this slope to the slope found for a mill in this study and correcting for the different ball-to-powder ratios, any kinetics measured with that mill can be compared directly to results obtained using the SPEX 8000 Mixer Mill or the Fritsch P-6 planetary mill.

The behavior of low-energy mills—such as vibratory mills—may be different. If the impacts are not always energetic enough to provide sufficient hot spots, the ignition time may not correlate well with the activation dose. Therefore, care must be exercised when attempting the application of this calibration scheme for low-energy mills. In particular, the proportionality between the ignition time and the powder-to-ball mass ratio has to be established.

The above evaluation is based on a simplified picture, with assumptions that are not strictly valid in many cases. For example, some reactions depend on the energy of the individual impacts, not only on the total energy input. Relaxation may be important, differentiating between the effects of long, low intensity and short, high intensity milling. Nevertheless, matching the time scales of the reaction kinetics as closely as possible facilitates the investigation of more subtle differences.

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