The effect of reaction parameters on the synthesis of 5-arylidene barbituric acid derivatives in planetary ball mills.

Supporting Information

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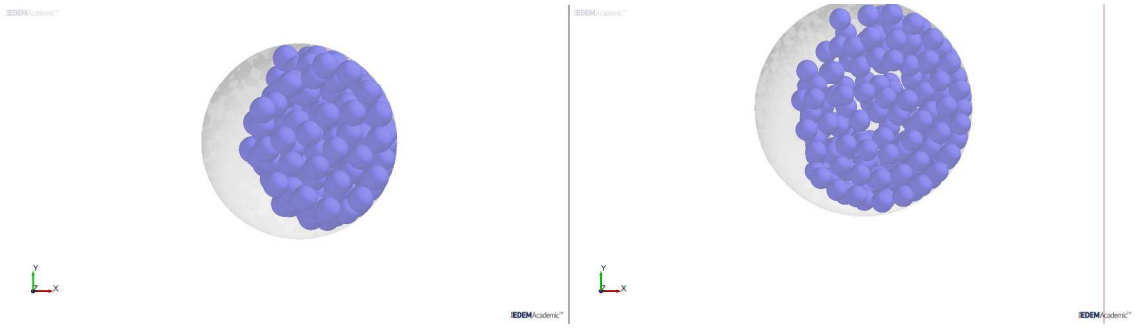

Figure 1. Bulk of the milling balls in 330 mL milling beakers with d_{MV} = 75 mm (left) and d_{MV} = 100 mm (right). Simulation conditions: PBM P6, 330 mL steel beaker, ZrO_2-balls, Φ_{MB} = 0.30, Φ_{GS} = 0.30, d_{MB} = 10 mm, v_{rot} = 650 min^{-1}.

DEM simulations show that for milling beakers with same volume but larger diameter, the packing of the milling balls is less dense with higher d_{MV}. Furthermore the milling ball bulk changes from an ordered to an unordered packing and the velocity of the milling balls is higher.


(a)

(b)

(c)

Figure 2. Pictures of thermal-assisted grinding (TAG). (a) System used for TAG. (b) TAG after 10 min. (b) TAG after 30 min. Conditions: rotary evaporator with water bath, 250 mL round bottom flask, 75 g glass balls, v_{rot} = 100 min^{-1}, d_{MB} = 2 mm, 40 mmol of **1a**, 40 mmol of **2a** (Φ_{MB} = 0.098, Φ_{GS} = 0.12).

TAG reactions were performed in a water bath at 45 and 75 °C using a rotary evaporator as reactor. Mixing of the reactants was ensured by 2 mm milling balls made of glass and rotation of the round-bottom flask at 100 min^{-1}. In order to evaluate the effect of grinding in TAG, reactions were performed under the same conditions but without glass milling balls. The substrates were mixed before reaction and then treated at 75 °C. Without any movement of the glass flask a yield of 9% was observed after 60 min. Especially in the bulk volume the yield was lower and higher yield (16%) was observed in a thin layer at the substrate-glass contact zone. The importance of

mixing becomes apparent when the glass flask was rotated at 100 min^{-1}. The yield increased to 15% and a homogenous mixture was observed. For comparison, TAG with glass bals led to yield of 75% after 60 min.

Simply mixing of the crude substrates in a vial delivered a yield of 10% after 7 d at room temperature. If the substrates were milled before mixing, the yield increased to 25%. These results illustrate the positive effect of the glass balls and milling that based on intense mixing, particle refinement and supply of "new" surfaces.


(a)


(b)


(c)

Figure 3. Pictures of microwave-assisted grinding (MAG). (a) System used for MAG. (b) MAG after 10 min. (b) TAG after 30 min. (c) Inhomogeneous product composition after MAG. Conditions: Rotaprep microwave reactor, 2000 mL vessel, 220 g glass balls, d_{MB} = 2 mm, 800 W, v_{rot} = 25 min^{-1}, 100 mmol of **1a**, 100 mmol of **2a** (Φ_{MB} = 0.035, Φ_{GS} = 0.04).

Due to the necessity to add water in MAG, the glass milling balls improve homogenization of the reaction mixture by distributing the water in the mixture. Nevertheless, an inhomogeneous product composition is still received. Especially in large scale experiments the milling balls are necessary, as they improve mixing and homogenization of the reaction mixture.

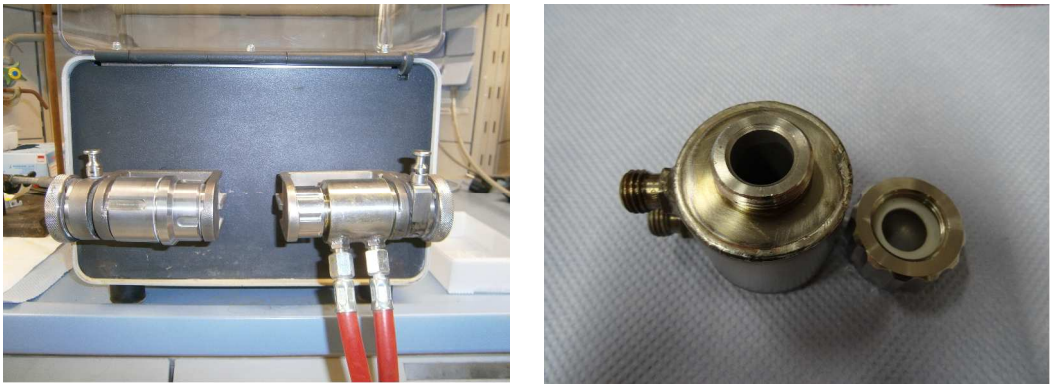

Figure 4. Picture of custom-made double-walled stainless steel milling beaker (V_{MV} = 8 mL, d_{MV} = 14 mm, h_{MV} = 60mm) with tubes for heating fluid.

The left milling beaker acts as counterweight. The internal temperature of the milling beaker was approximately 2 K below thermostat temperature. This internal temperature was constant and no temperature increase was measured after milling.