The way towards a CL-20/HMX Cocrystal scale-up

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ABSTRACT

A variety of techniques to produce the CL 20/HMX cocrystal have been published, since its discovery in 2012. However, their capability of producing the cocrystal in a size region and production scale suitable for its use in polymer bonded explosives (PBX) has as of yet neither been tried nor assessed. In the corresponding presentation that is based on previously published work (10.1002/prep.201800332) the systematic process of selecting suitable solvents and crystallisation methods as well as optimisation thereof with a focus on the efficient production of high-quality cocrystals for use in PBX is illustrated.

SUMMARY

The following parameters were devised to identify a suitable solvent and crystallisation process.

- Compact crystal morphology are produced
- Cocrystals in the region of 200 µm must be obtainable
- Cocrystals of good quality must be reliably obtainable
- Crystallisation process must either exhibit a good CL-20 efficiency or CL-20 must be easily recyclable from solution

Of all testes solvents only acetonitrile and cyclohexanone were capable of producing compact cocrystals. And only acetonitrile was suitable for all tested crystallisation

methods. In Table 1 the results of the crystallisation experiments in acetonitrile are summarised.

Table 1: Summary of crystal quality, crystal size, CL 20 efficiency and solution recyclability for different crystallisation methods and conditions.

crystallisation method	200 µm possible	crystal quality	CL-20 efficiency	solution recyclability
antisolvent at 60°C	Yes	+	25 %	-
cooling from 60 °C to 20 °C	Yes	+	14 %	+
batch RC[a)] at 60 °C	No	-	>75 %	+
batch RC at 20 °C	yes	+/-	>70 %	++

a) Reaction cocrystallization (RC) utilises the solubility difference between CL-20 and HMX, and the cocrystal.

While the capability to produce 200 µm cocrystals is categorical and the CL-20 efficiency, which is defined as ratio of CL 20 found in the cocrystal divided by the used CL-20, can be quantified, the crystal quality and solution recyclability cannot be as precisely specified. For crystal quality and solution recyclability a qualitative representation was therefore chosen, where – connotes bad, + good and ++ very good. +/- for RC at 20 °C stands for varying crystallisation results. Generally, at 20 °C slow transformation into the cocrystal occurred and HMX or CL-20 impurities are likely to occur in crystallisation experiments. This behaviour was seen as a sign for a low energy benefit of the cocrystal compared to crystallising the pure components at 20 °C. Poor crystal quality and no control over the particle size are the result of the high supersaturation during batch RC and the fast nucleation in acetonitrile at 60 °C. Antisolvent and cooling crystallisation are capable of producing high quality cocrystals in adjustable size. Because of the solubility difference of CL-20 and HMX however only a poor CL-20 efficiency can be achieved. It can be seen from table 1 that none of the crystallisation methods are capable to satisfy all the proposed specifications. Most likely the application of semibatch RC can remedy that fact, because it combines the supersaturation control of antisolvent/cooling crystallisation with the CL-20 efficiency of batch RC.