Ultrasonics - Sonochemistry 69 (2020) 105276

Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Evaluation of different cavitational reactors for size reduction of DADPS

Sarvesh S. Sabnis[a], Rakshit Raikar[b], Parag R. Gogate[a,*]

[a] Chemical Engineering Department, Institute of Chemical Technology, Matunga, Mumbai 40019, India
[b] Chemical Engineering Department, Siddaganga Institute of Technology, Tumkur 572101, Karnataka, India

ARTICLE INFO

Keywords:
Diamino Diphenyl Sulfone
Size reduction
Recrystallization
Cavitation
Particle size analysis
Power intensity

ABSTRACT

The present study deals with the size reduction based on the recrystallization (antisolvent approach using water) of 3,3′-Diamino Diphenyl Sulfone (DADPS) using different types of cavitational reactors as an alternative to the conventional process of mechanical size reduction, which is an energy intensive approach. Ultrasound was applied for fixed time specific to the reactors namely ultrasonic probes at different power dissipation levels and also ultrasonic bath. A High Speed Homogenizer was also used at varying speeds of rotation to establishing the efficacy for size reduction. The processed sample was analysed for particle size and morphology using particle size analyser and optical microscopy respectively. The final yield of recrystallization was also determined. The power density in W/L and power intensity in W/m^2 calculated for each equipment has been used to establish efficacy for size reduction since all devices had dissimilar configurations. Based on the studies of varying power intensity of the different US equipment, it was established that larger the power intensity and power density, smaller was the resultant final particle size after treatment for same time. Among the various ultrasonic devices used, Sonics VCX750 probe yielded the best size reduction of 85.47% when operated at 40% amplitude for 60 min for a volume of 200 ml. A High Speed Homogenizer used at 7000 rpm gave 92.35% of size reduction in 15 min operation and also demonstrated the best energy efficiency. The work has elucidated the comparison of different cavitational devices for size reduction for the first time and presented the best reactors and conditions for the desired size reduction.

1. Introduction

3,3′-Diamino diphenyl sulfone, also known as DADPS or DDS, is a curing agent in epoxy resins and a crystalline organic compound having molecular formula of $C_{12}H_{12}N_2O_2S$ and a molecular weight of 248 with white to light yellow colour and melting point range between 168 °C and 175 °C [1]. It is also an intermediate in the production of heat-resistant resins, polysulfones and other polymers. The range of applications also require the particle of DADPS to be within a specific size range directing the use of reprocessing approaches for achieving the desired size reduction. It is also required to reduce the particle size of DADPS because, particulate nature of DADPS creates difficulty in proper dispersion in the host resin/polymer (resulting in a non-homogenous situation), and this can result into non-uniform behaviour of the resin/polymer.

The term 'size reduction' is applied wherever solid particles are cut or broken in to smaller pieces. Most of the mechanical methods used for size reduction fall into one of the following categories based on mechanism: compression (for coarse reduction of hard solids, to give relatively few fines); impact (gives coarse, medium or fine products); attrition (yields very fine products from soft, nonabrasive materials); and, cutting (gives a definite particle size and sometimes a definite shape, with few or no fines) [2]. A major drawback is that all these approaches are highly energy intensive and may not yield desired size distribution, and there may be large variations in particle sizes and shapes. Also, when it comes to size reduction in a solid-liquid mixture or a slurry, the above mentioned methods may not be able to yield expected outcomes. Also, the aim in any reprocessing is not to hamper the crystalline structure and any kind of mechanical operations would disturb this structure, hence are not the best choice.

DADPS recrystallization and size reduction using antisolvent approach wasn't reported until very recently. Antisolvent crystallization approach offers an inherent advantage in the elimination of thermal energy required in evaporative crystallization and hence avoids any negative effects on heat sensitive materials. DADPS changes its colour (from pale yellow to light brown) when heated beyond 80 °C and in any crystallization or reprocessing it is always advisable to not heat this compound or its solution beyond 70 °C. In our earlier work [3], ultrasound was effectively used for size reduction of DADPS during its reprocessing based on antisolvent crystallization, though using a fixed

* Corresponding author.
E-mail address: pr.gogate@ictmumbai.edu.in (P.R. Gogate).

https://doi.org/10.1016/j.ultsonch.2020.105276
Received 27 February 2020; Received in revised form 25 June 2020; Accepted 21 July 2020
Available online 24 July 2020
1350-4177/

geometry of ultrasound equipment. It was reported that the size of DADPS was reduced to about one third original size due to US treatment under best treatment conditions. XRD analysis also confirmed an improvement in percent crystallinity accompanying with reduction in crystal size. Further literature analysis revealed that no work has been reported on size reduction of the same material using ultrasonic equipment of different configurations. There are multiple studies available on ultrasound assisted size reduction or ultrasound assisted crystallization using a fixed configuration of US source. For example, Dennehy [4] explained that sonocrystallization is technique within the 'Toolbox' and one of the few methods available for chemists and engineers for exerting control over particle size using generally applied configurations of horn or bath [4]. Franco et al. [5] reported that ultrasound is an effective way for reducing the particle size of kaolinite in the size range of 0.1 μm to 30 μm to a size mostly lower than 5 μm after sonication of 10 h using an US horn along with retention of crystallinity and lamellar morphology. Łoś et al. [6] studied the cleavage and size reduction of graphite crystals using ultrasound and reported beneficial results of reduction in the size of final processed samples. In an another study, it was reported that carbon black pigment, used in UV inks, of an initial size of 10 μm was reduced to an order of 50 nm using ultrasonic horn between the frequency range 20–30 kHz [7]. Sumari et al. [8] treated a slurry of 1% (w/v) of cellulose fibres with ultrasonic horn operated at 300 W and 28 kHz and found that the fibre length reduced from 80–120 μm range to 30–50 μm after 1 h sonication. Yamaguchi et al. [9] used different ultrasound probes over the frequency range of 43–480 kHz for size reduction of liposome and concluded that short durations of low frequency and high power ultrasound is more efficient than long-duration of high frequency operation. The observed results were attributed to the fact that small number of cavitation events with stronger physical effects of disturbance (at low frequency operation) are more efficient than the large number of cavitation events with weaker physical effects. The analysis clearly revealed that studies have dealt with same configuration of the ultrasonic reactors confirming the novelty of the current work.

Use of ultrasound for improving the antisolvent crystallization has also been demonstrated mainly for pharmaceutical compounds [10,11]. Ultrasound is a proven way of achieving faster and uniform primary nucleation at lower supersaturation levels and also leads to reduction of agglomeration. Due to the use of ultrasound, a destruction of boundary layers between the liquid–solid interface occurs at faster rates with improvements in mass and heat transfer, which promotes the onset and progress of crystallization. The cavitation bubble collapse induced by ultrasound releases high amount of energy in terms of pressure, temperature and shock wave. Local release of energy helps in attaining supersaturation favourably inducing primary nucleation [12]. Cavities implode near the formed crystals, due to which the solid agglomerates break and result into smaller particles. Patil et al. [13] studied the effect of ultrasonication on the antisolvent crystallization of high energy explosive materials and reported that ultrasound (ultrasound bath of 120 W and 20 kHz frequency) can be successfully applied to control the mean size and size distribution with an increase in the final mass yield. Work has also been reported for obtaining drug particles with optimized size and morphology from the melt and also from solution by applying sonocrystallization [14]. Sonocrystallization was also shown to enable significant reductions in the processing times and result in the generation of better quality crystals [15].

Hydrodynamic cavitation is the process of cavitation bubble generation and growth that occurs in a flowing liquid as a result of a decrease and subsequent increase in local pressure based on alterations of geometry [16]. In pipe systems, cavitation typically occurs either as the result of an increase in the kinetic energy (through an area constriction) or an increase in the pipe elevation. Traditionally, hydrodynamic cavitating devices such as various types of venturies, orifices are not used for solid handling because of blockage problems. Even though a high speed homogenizer works on the principle of hydrodynamic cavitation, it has not been reported for solid handling operations to the best of our knowledge. The present work explored the use of high speed homogenizer based on this finding and the fact that configuration was able to handle solids.

In this work, ultrasonic (especially probe based) devices operated individually and in combinations have been used and based on the analysis of the same, dependency between ultrasonic power intensity and size reduction is established. Also, a High Speed Homogenizer (HSH), employing hydrodynamic cavitation is evaluated for size reduction feasibility. The only use of hydrodynamic cavitation (orifice) for size reduction has been reported in the case of natural cellulose fibres [17]. The application of HSH in the current work is based on the hypothesis that comparatively larger slits in the homogenizer (due to a certain arrangement of rotor and stator) than venturi/orifice type devices may not create blockage problems. An overview of the literature showed that comparison of different ultrasonic equipment for their effectiveness in size reduction and antisolvent crystallization hasn't been evaluated. Most studies have dealt with using a fixed configuration and focused on understanding the effects of operating conditions. Overall, the novelty of current work dealing with the use of different ultrasonic reactors and HSH as hydrodynamic cavitation device is clearly established. In addition for each reactor, important operating parameters were varied to study the effect on the size reduction, also enabling establishing the best treatment conditions.

2. Materials

DADPS was procured from The Dharamsi Morarji Chemical Company Limited, Mumbai, India. Methanol (LR grade), obtained from Thomas Baker Pvt. Ltd, Mumbai was used as the solvent. Distilled water was used as antisolvent to crystallize DADPS from its solution in methanol. Distilled water was prepared freshly in the laboratory using Borosil distillation apparatus.

3. Experimental methodology

3.1. Energy efficiency, power density and power intensity

One of the most important aspect to be addressed for every sonochemical process with potential industrial application is the efficiency in terms of transfer of applied energy into net effects. Cavitational intensity is strongly influenced by the physical and chemical properties of the solvent, treatment conditions and ultrasonic irradiation characteristics [18,19]. From the concept of true and false sonochemical processes, there are two types of applications of ultrasound, namely, those based on the chemical effect (sonochemistry) and those based on the physical effects generated by bubble collapse (sonoprocessing) [20]. The energy conversion (from electrical to acoustic) being a critical factor in industrial applications, makes it indispensable for reduction of electricity requirements for the scaled-up version of sonochemical reactors by evaluating their energy balance. But, this is a bit complicated because of a simultaneous occurrence of mechanical and chemical energy forms in the reaction medium during sonication [21]. It is even more rigorous to realistically characterize the energy consumed to produce cavitation coupled with the thermal, viscous and radiation losses. Instead, the energy efficiency concept is being generally applied to determine the energy conversion in terms of the calorimetrically measured acoustic energy dissipated into the sonicated medium [22]. This seems to be a reliable method to express the performance of sonoreactors and compare different ultrasonic systems.

Effectiveness of any sonochemical rector is governed by ultrasonic power dissipated in the reactor. Also, the important ultrasonic parameters are not independent, and hence a complex procedure must be followed for an efficient optimization [23]. In this connection, the two important parameters that are found to be crucial in the ultrasonic optimization study are power density i.e. the amount of power

Table 1
List of ultrasonic equipment with details.

Sr No	Manufacturer	Type	Specifications			Experiment details				
			Dimensions	Frequency	Maximum power output	Total treated volume	Initial methanol volume	Amount of antisolvent added	Antisolvent addition flowrate	Time required for antisolvent addition
1	Dakshin	Probe	Diameter of 13 mm	20 kHz	200 W	200 ml	100 ml	100 ml	400 (ml/min)	0.25 min
2	Dakshin	Cascade probe	Diameter of 15.6 mm with 4 radiating surfaces	20 kHz	250 W	400 ml	200 ml	200 ml	800 (ml/min)	0.25 min
3	Sonics (VCX 750)	Probe	Diameter of 13 mm	20 kHz	750 W	200 ml	100 ml	100 ml	400 (ml/min)	0.25 min
4	Sonics (VCX 1500HV)	Cascade probe	Diameter of 25 mm with 6 radiating surfaces	20 kHz	1500 W	2000 ml	1000 ml	1000 ml	4000 (ml/min)	0.25 min
5	Roop Telesonic Ultrasonix	Bath with resonating probe	Bath–7 L capacity (350 mm × 120 mm × 200 mm); Resonator- diameter: 50 mm, Length: 200 mm	25 kHz	1000 W	4000–6000 ml	2000 ml	2000 ml	8000 (ml/min)	0.25 min

dissipated per ml of given solution, W/L and power intensity which is the amount of power dissipated per emitter area, W/m^2. The power must be optimized in any case, even when the chemical evolution of the system seems simple. As a general approach, the ultrasonic power shouldn't be mechanically turned to a maximum limit, because, at sufficiently high power, there is no further increase in the desired output, may be in terms of the observed chemical or physical effects for the specific application as reported in the literature [24]. Thus, there is a best condition of power dissipation that exists at which a given process has to be executed in order to avoid needless loss of energy.

Energy efficiency information alone, is insufficient while comparing different ultrasonic equipment with different configurations and varying operating volumes. As the present experimental work involved varying minimum operational volumes of the equipment from 50 ml to 5 l, and also the output power and the cavitation generated,it was thought essential to find out the intensity of dissipated power into the system which would have a great significance on the size reduction results.

3.2. Quantification of dissipated ultrasonic power, energy efficiency, power density and power intensity

The procedure adopted for acoustic power measurements is the calorimetric method. Based on assumption that the mechanical energy generated by the ultrasonic waves is finally converted to heat, the dissipated ultrasonic power U_p is calculated from the rate of temperature increase as per the following equation:

$$U_p = MC_p\frac{dT}{dt} \tag{1}$$

where C_p is the heat capacity of the liquid at constant pressure (J/kg.K), M is the mass of liquid in kg, and dT/dt is the temperature rise per second [25]. Despite some of the reported drawbacks (the convective cooling , the heating of transducer and the sensor that may disturb the measurements), calorimetry is a universal, and precise method for quantifying the acoustic power [26].

The energy efficiency of any ultrasonic device (η) is calculated as,

$$\eta = \frac{Up}{Ip} \times 100 \tag{2}$$

where, I_p is the input electric power to the ultrasound generator and U_p is the actual power dissipated into the system.

The operating power density (W/L) is given by,

$$PD = \frac{U_p}{V} \tag{3}$$

where, PD is the power density is W/L, U_p is actual power dissipated in W and V is the volume in litre for the specific reactor under consideration

The ultrasonic power has been estimated calorimetrically from the initial temperature rise (dT/dt) that gives a reasonable indication of the quantity of energy effectively dissipated into the sonicated liquid.

Power intensity is defined as the ratio of actual power dissipated into the system and radiating surface area [27] as given by the following equation.

$$PI = \frac{U_p}{A} \tag{4}$$

where, PI is the power intensity in W/m^2, U_p is actual power dissipated measured calorimetrically and A is the radiating surface area.

All the measurements (U_P, η, PD) for each US equipment were carried out at fixed condition of final volume (after the addition of antisolvent) for the specific reactor in question.

3.3. Antisolvent crystallization of DADPS

The method followed for antisolvent crystallization has been described in details in our earlier work of Sabnis and Gogate [3]. The solubility of DADPS in methanol was found to be 6 g in 100 ml at 30 °C, and this concentration was used as the saturated solution for all experiments with distilled water as antisolvent. The addition rate of the antisolvent in different cavitational reactors (constant for the specific reactor) was different owing to variation in their capacities as highlighted in Table 1. The value of the flow rate used was 4 times the value of the methanol volume (only considering the numerical values), for example antisolvent addition rate of 400 ml/min was applied for Dakshin 200 W reactor and Sonics 750VCX reactor since 100 ml methanol was taken as starting solutions. This addition rate was decided such that the antisolvent required equal time intervals to enter the DADPS-methanol solution for each reactor. The idea behind using a varying flow rate is to maintain the levels of supersaturation constant based on the varying initial methanol content in the reactor.

In a typical experiment, the solution was initially sonicated for 1 min and with sonication in progress; distilled water was added as antisolvent to crystallize out DADPS. The applied treatment time was fixed as 60 min (unless specified otherwise) after trying multiple sonication durations from 10 to 90 min in the preliminary studies. While using ultrasonic horn, a recommended method is to provide a pulsed input so as to avoid any negative effects (overheating and possible decoupling/erosion after prolonged use) on the transducer and achieve a cost savings. Therefore, pulsed input was applied with duty cycle kept constant at 50% i.e. ultrasound in ON condition for 5 s and OFF for 5 s in a 10 s cycle for the entire sonication period (the actual irradiation time will be half of the mentioned overall treatment time). The effect of power dissipation on particle size was also studied. In the case of HSH, experiments were performed at varying speed of rotation. After the crystallization in the presence of ultrasound or HSH for the required duration, obtained crystallized DADPS was filtered, dried in hot air oven at 80 °C and subsequently used for characterization.

3.4. Equipment configurations

3.4.1. Ultrasonic probes (horns)

The schematic representation of the horn assembly used in the study has been depicted in Fig. 1. As mentioned earlier, various ultrasonic devices such as horns of different power rating and bath with longitudinal horn were used in the current study . Ultrasonic horns purchased from two different manufactures namely Dakshin (Mumbai, India) and Sonics, USA were used. A detailed information regarding these equipment is given in Table 1whereas the geometry of the probes is illustrated in Fig. 2 for a better understanding. The obtained energy efficiencies for ultrasonic horn type configurations were typically low in the range of 6 to 15%.

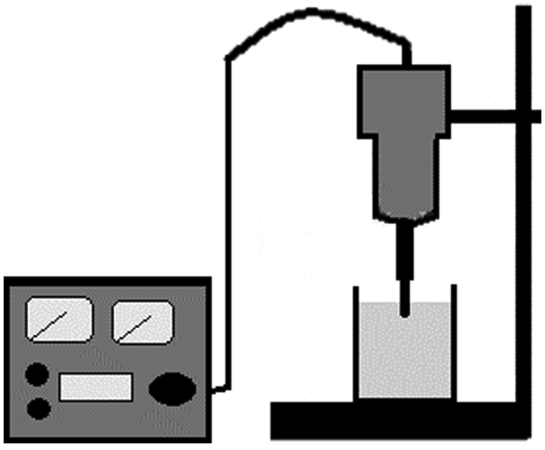


Fig. 1. Schematic representation of the experimental setup for recrystallization of DADPS using a ultrasonic Horn with generator.

3.4.2. Roop Telesonic Ultrasonix bath

Roop Telesonic Ultrasonix bath having tank dimensions of 350 mm × 120 mm × 200 mm used in the work operates at a rated power of 1000 W and a frequency of 25 kHz. The resonator dimensions are diameter of 50 mm and resonator length of 200 mm. The experimentally determined energy efficiency was 23.75%. The actual power density and intensity were 47.5 W/L and 5932 W/m^2 respectively.

3.4.3. High speed homogenizer (HSH)

The high speed homogeniser (Snowtech, Process equipment, Mumbai, India) used in this study has power consumption of 105 W and is depicted schematically in Fig. 3. It consists of a stainless steel rotor with 13 blades and a stator with 9 blades which are 3 mm apart. The rotor is driven by a variable voltage motor having a maximum operating voltage of 30 V or current of 3.5A. It can be operated at varying rotational speeds in the range 1000–12,000 rpm. The gap between the outer diameter of the rotor and the inner diameter of the stator is about 2 mm. The cavitation events are expected to occur downstream of the stator essentially in all the vertical planar jets i.e. slots between the stator blades. Energy efficiency of this HSH has been reported as 43% at 8000 rpm in a previous study [28]. Here, the total volume of DADPS-methanol solution + water was 400 ml taken in a 1000 ml beaker for treatment at different rotation speeds of 3750, 7000 and 10,000 rpm for 15 min (preliminary studies with 30 min indicated that there was no further size reduction beyond 15 min and hence 15 min was fixed as the treatment time). As hypothesized earlier, no blockage issues persisted during the operation.

3.5. Operational details for cavitational reactors

For experiments involving ultrasonic horn 1 (Table 1), the tip was dipped to 5 mm (about 6 cm from bottom of beaker) into solution of known concentration of DADPS dissolved in methanol taken in a glass beaker of 250 ml capacity. No agitation was provided as ultrasound can sustain the required mixing at this operating volume. For ultrasonic horn 2 (Table 1), the tip was dipped up to a 2 cm from the bottom of the reactor of volume 500 ml. Sonics VCX 1500HV probe (horn number 3) being much bigger, and could process larger volumes, was used in a 2.5 l reactor and was fixed at a height of 5 cm from the bottom.

In the experiments conducted using ultrasonic bath (Roop Telsonic Ultrasonix), the total volume used was 4 l and 5 l with agitation using a single pitched blade turbine impeller with four blades and 40 mm diameter operated at 500 rpm. Stirring was used so that the entire mixture could come in the vicinity of the resonator by proper mixing. For the combination approach involving both ultrasonic horn and bath as shown in Fig. 4, the reactor was kept in such a way that the level of the coupling fluid i.e. water was well above the level of mixture . During this, the probe depth was same as mentioned above for horn number 3. Another experiment was conducted at the same operating conditions, but without using the horn to evaluate the effect of indirect sonication in the case of ultrasonic bath.

For the experiments involving HSH, a 1000 ml beaker was used which contained 400 ml of mixture. HSH was dipped into the mixture up to the level of submergence of the stator, so that the vertical liquid jets could produce the desired effects.

3.6. Analysis of particle characteristics

Shimadzu SALD 7500 particle size analyser (measurement range of 10 nm–800 μm) was used for the particle analysis. This particle size analyzer uses laser diffractometry based on the principle that laser beam when incident on the particle, gets diffracted at a specific angle

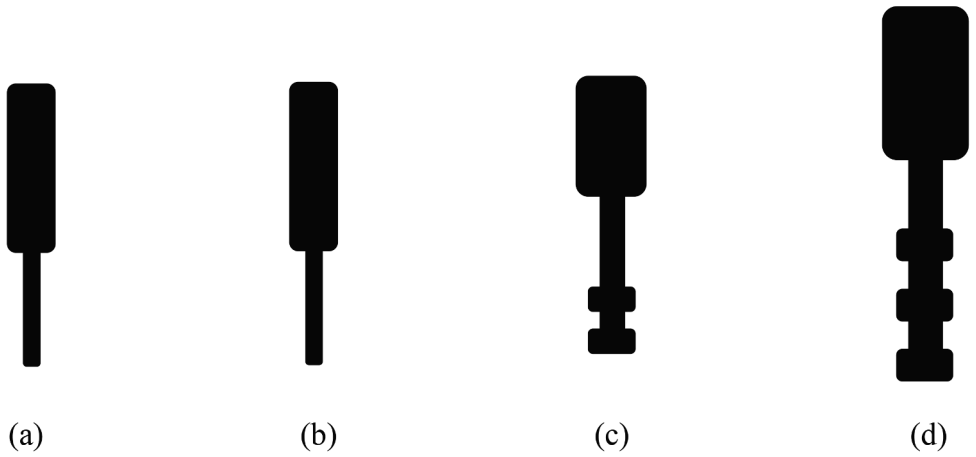


Fig. 2. Schematic representation of geometries of ultrasonic horns used for the study- Dakshin (200 W), (b) Sonics VCX 750, (c) Dakshin 250 W (cascade probe), (d) Sonics VCX 1500 HV (cascade probe).

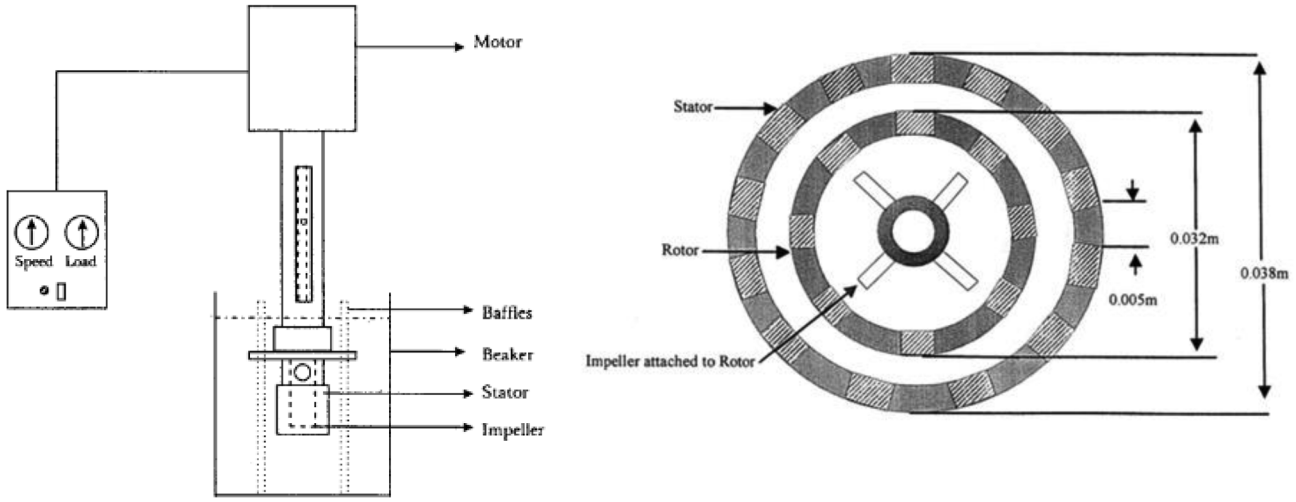


Fig. 3. Schematic diagram of setup and crosssectional view of High Speed Homogenizer (HSH) applied for recrystallization of DADPS.

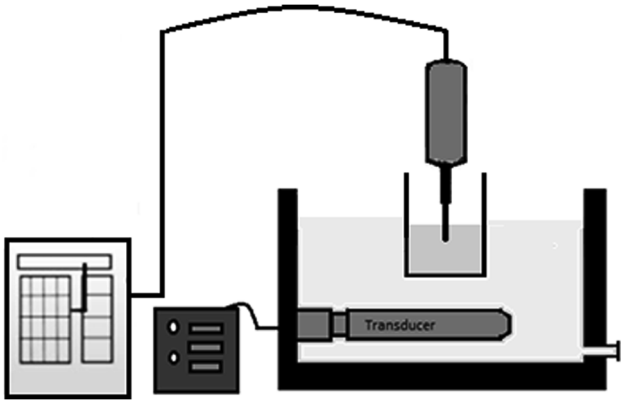


Fig. 4. Schematic representation of the experimental setup for treatment using a combination of ultrasonic bath and horn.

depending on the size of the particle.

Olympus 51X-TF optical microscope was used to study the crystal shape and morphology of the DADPS crystals obtained after treatment using different cavitational reactors. Analysis of untreated DADPS was also performed for the sake of comparison. Objective lenses of 4X, 10X, 40X and 100X magnification were used for the analysis, though only the best results have been illustrated in the form of figures in the discussion.

4. Results and discussions

4.1. Results for energy efficiency, power density and power intensity

Besides the obtained particle shape and size, energy efficiency and power intensity are the main parameters to quantify the efficacies of different ultrasonic devices. The obtained results for the energy efficiency, power density and power intensity as calculated from Eqs. (2)–(4) are depicted in Table 2. For the sake of uniformity, all the experiments for calorimetric power dissipation studies were performed at a duty cycle of 50%, except ultrasonic bath, where no such provision was available.

The calculated energy efficiencies, energy densities and power intensities of all the US equipment are tabulated in Table 2. Energy density has been calculated in terms of the volume of mixture taken for each ultrasonic reactor that has yielded the best size reduction. Accordingly, reactors that can handle lager volumes in a single experiment have lower energy densities than those handling lesser volumes. It can be seen that the equipment with single radiating surfaces (1 and 3) have greater power intensity because of a smaller surface area. The ultrasound bath with the longitudinal resonator has the least power intensity because of large surface area of the resonator. The equipment numbered 2 and 4 are cascading probes i.e. with multiple radiating surfaces. This results into an increase in the radiating surface area resulting into a somewhat lower power intensity. It is also important to note that both

Table 2
Energy efficiency and power intensity of the ultrasonic equipment used.

Sr No	Equipment	Calorimetric Efficiency, η (%)	Power Density, PD (W/L)	Power Intensity, PI (W/m^2)
1	Dakshin (200 W)	6.9	43.12	64.996×10^3
2	Dakshin (250 W)	14.7	54	57.203×10^3
3	Sonics VCX 750 (750 W)	7.71	115.65	174.303×10^3
4	Sonics VCX 1500HV (1500 W)	13.4	80.4	105.442×10^3
5	Roop Telesonic Ultrasonix (1000 W)	23.75	47.5	5.932×10^3

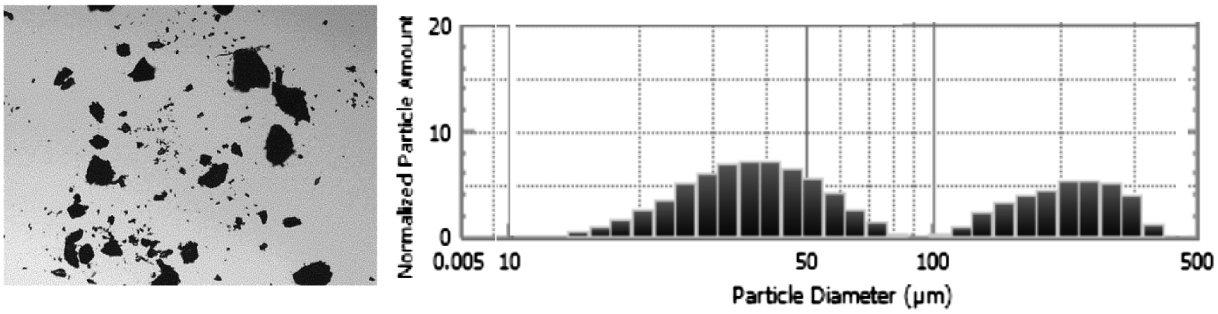


Fig. 5. Microscopic image of original untreated DADPS sample at 4X and its Particle size distribution (PSD).

Table 3
Particle size analysis of original/untreated DADPS.

Sample	Mean (µm)	25% (µm)	50% (µm)	75% (µm)	SD (µm)
DADPS	67.03	39.84	65.86	122.34	0.32

power density and the power intensity play a role in deciding the net effects as also reported by Sivakumar and Pandit [23] for the degradation of Rhodamine B.

4.2. Particle size characterization

4.2.1. Original DADPS sample

The 4X image of the original DADPS sample obtained using optical microscope is given in Fig. 5 along with its particle size distribution. The crystal structure of the captured DADPS sample is found to be non-uniform and uneven as established by the microscopic image. The mean particle size of DADPS sample was found to be 67.029 µm (Table 3) with a wide particle size distribution as evident from Fig. 5. Also, the presence of particles of different shapes and sizes makes the PSD multimodal.

4.2.2. Treatment using Dakshin horn (200 W as rated power)

For the use of Dakshin horn (200 W), single batch volume used was 200 ml in a 250 ml beaker with dimensions (diameter × height) of 60 mm × 120 mm. Initial methanol volume taken for the study was 100 ml and subsequently antisolvent as water was added. The ultrasound parameters and obtained particle size results are shown in Table 4. The minimum particle size obtained was 13.5 µm at 140 W power and duty cycle of 50%. When compared to original DADPS sample, the percent size reduction was found to be 79.86%.

4.2.3. Dakshin horn (250 W as rated power)

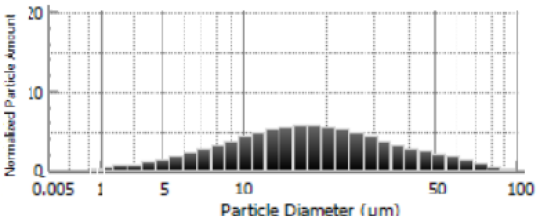
As this was a cascading type of probe, it was operated at relatively larger total volume of 400 ml in a 500 ml beaker with dimensions of 75 mm × 142 mm with 200 ml as initial methanol volume. The horn was operated at the conditions mentioned in Table 4 along with the obtained particle size results. The minimum particle size obtained was 13.93 µm at 190 W power and duty cycle of 50%. When compared to original DADPS sample, the percent size reduction was found to be 79.21%. The particle size distribution obtained in this case is wide as illustrated in Fig 6b. The PSD of the sample and the microscopic image at 40X magnification are shown in Figs. 6 and 7 respectively.

4.2.4. Sonics VCX750 probe (750 W)

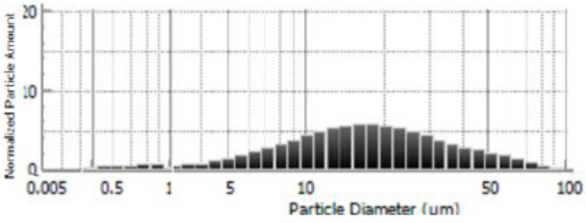
Sonics VCX750 probe operates at a rated power of 750 W and can be operated at a maximum amplitude of 40% as instructed by the manufacturer. A 250 ml beaker with dimensions of 60 mm × 120 mm was used. Initial methanol volume was 100 ml. The observed energy efficiency was 7.71% and power density was 115.65 W/L at 200 ml operational volume. The horn was operated between 30% − 40%

Table 4
Particle size analysis of DADPS treated using various horns.

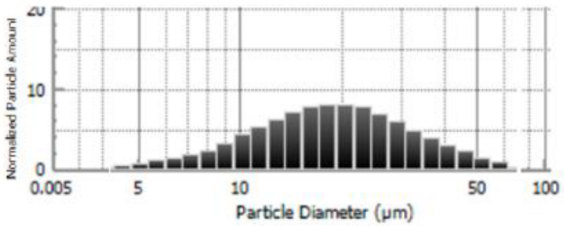
US Equipment	Time (min)	Power (W)	DC (%)	Yield (%)	Mean (µm)	10% (µm)	50% (µm)	90% (µm)	SD (µm)
Dakshin horn (200 W rated power)	60	100	50	77.25	22.02	6.14	25.21	30.51	0.26
	60	120	50	77.25	19.37	5.73	23.49	28.54	0.26
	60	140	50	79.3	13.5	7.52	17.69	32.65	0.28
Dakshin horn (250 W rated power)	60	150	70	78.21	23.74	7.71	26.12	29.89	0.29
	60	180	50	76.07	19.04	12.04	24.24	31.39	0.25
	60	190	50	75	13.93	8.97	16.03	27.29	0.45
Sonics VCX 750 horn	60	240	50	80.5	28.42	13.92	27.89	31.79	0.24
	60	300	50	77	9.74	6.72	10.67	17.34	0.23
Sonics 1500HV horn	20	900	50	82.3	25.08	7.38	21.01	45.91	0.24
	20	1050	50	81	20.83	12.75	20.16	34.87	0.36
	20	1200	50	80.6	11.30	8.28	13.11	19.08	0.36
Bath + Horn	60	800 + 300	50	77.87	17.31	12.27	18.24	26.68	0.28



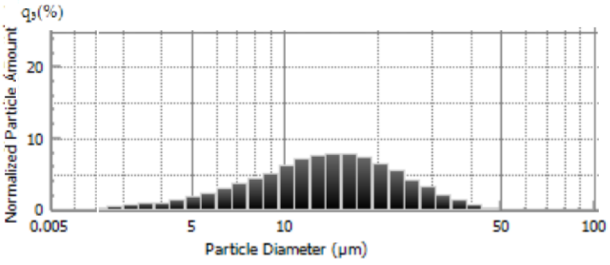
(a) PSD obtained from treatment of DADPS using Dakshin horn (200 W)



(b) PSD obtained from treatment of DADPS using Dakshin horn (250 W)



(c) PSD obtained from treatment of DADPS using Sonics VCX 750 horn



(d) PSD obtained from treatment of DADPS using Sonics VCX 1500HV horn

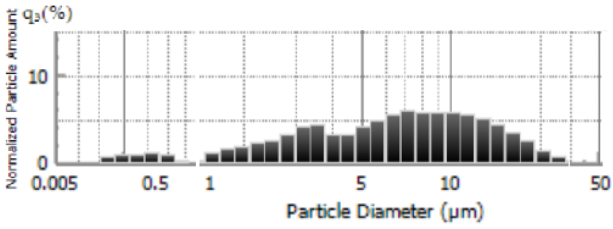


Fig. 6. (a–e): Particle size distribution of DADPS after treatment using different equipment.

amplitude which totals to around 225 W − 300 W input power. The power intensity calculated was 174303 W/m^2 at 40% amplitude i.e. 300 W power. The obtained particle size results are given in Table 4. The average particle size obtained was 9.74 μm at 300 W power and duty cycle of 50%. When compared to original DADPS sample, the percent size reduction was found to be 85.47%. The particle size distribution is shown in Fig. 6c. In this case, higher power led to lower particle size. Similar trend was also reported in the literature [3,29].

4.2.5. Sonics 1500 V probe (1500 W)

Sonics 1500HV probe can process 2000 ml of volume, at which the calculated power density amounted to 80. 4 W/L. 1000 ml of methanol was taken in a 3000 ml beaker (152 mm × 210 mm) for treatment. The horn was operated at different amplitudes as 60%, 70% and 80% at a fixed duty cycle of 50% for 20 min and the obtained results are mentioned in Table 4. It can be seen from presented results that as the amplitude increased, the particles were reduced to lesser size. The particle size obtained was 11.30 μm at 80% amplitude or 1200 W power and duty cycle of 50%. The obtained trends are similar to that reported by Kumar et al. [30]. When compared to original DADPS sample, the percent size reduction was found to be 83.13%. The particle size distribution obtained in this case has been depicted in Fig. 6d. Unlike other ultrasonic devices, this probe was not operated for 60 min because of excess heating observed during the operation.

4.2.6. Roop Telesonic ultrasonicx bath (1000 W)

The operating conditions and particle size results for ultrasonic bath are mentioned in Table 5. Particle size obtained was 32.8 μm at 800 W power for a processed total volume of 5 l. When compared to original DADPS sample, the percent reduction was found to be 51.06%, much lower to that obtained in other configurations of horns. If this volume were to be reduced to 4 l, at same input power, the final size obtained reduced to 14.81 μm with a net size reduction of 77.9%. This is a clear indication that larger processing volumes lower the power density and hence the observed cavitational effects. The power densities calculated for 4 l and 5 l as the processing volumes are 47.5 W/L and 38 W/L respectively. *PD* for 4 l volume being better, is considered hereafter. It is worth mentioning that, even though the bath has the highest calorimetric efficiency at 23.75%, its dissipated power doesn't show the expected outcomes due to its lower power density, clearly illustrating the importance of power density.

4.2.7. Combination of SONICS VCX750 probe and Telesonic bath

A beaker containing DADPS sample was suspended in the bath and it was ensured that the water in the bath, which acts as coupling fluid, completely surrounds the solution taken in beaker. Additionally, ultrasonic horn was dipped into the mixture. The ultrasonic irradiation was carried out for 60 min and the particle size results are mentioned in the Table 4. The mean particle size obtained was 17.31 μm at power input of 300 W from horn and 800 W from bath. A similar reactor with same volume when treated using only Sonics 750 horn, gave a mean size of 9.74 μm with a size reduction of more than 85%. In another experiment, size reduction was assessed with indirect sonication in the bath, with the help of coupling fluid i.e. water. Here, after treatment of 60 min with 800 W power the final obtained mean size was 35.38 μm. This undoubtedly indicates that indirect sonication is unproductive as compared to the direct approach for size reduction. When compared to original DADPS sample, the percent size reduction was found to be only 74.18%. It can be thus inferred that the combination approach hasn't worked well enough in comparison with only Sonics horn when it comes to particle size. Here again, the main cause could be the indirect mode of irradiation. On the contrary to the direct use of ultrasonic bath, the mixture was not in direct contact of the resonator, but the transfer of energy is by means of a coupling fluid i.e. water. Therefore, the cavitation effects and shockwaves may not be adequate to cause desired particle breakage. It can be thus established that direct irradiation gives better results compared to indirect mode of operation.

4.2.8. High speed homogeniser (HSH)

The DADPS sample solution of 400 ml was treated in a 500 ml beaker having dimensions as 80 mm × 115 mm using High Speed Homogeniser over a speed range of 3700–10,000 rpm. The obtained particle size results are given in Table 6. The particle size obtained was 5.13 μm at 7000 rpm and at 10,000 rpm the obtained mean particle size was 8.13 μm. The particle size was about 38.86 μm when the HSH was operated at 3750 rpm. Thus, 7000 rpm could be stated as the optimum speed of rotation for size reduction using a HSH in which a maximum reduction of 92.35% was found. In a HSH, at very high operation

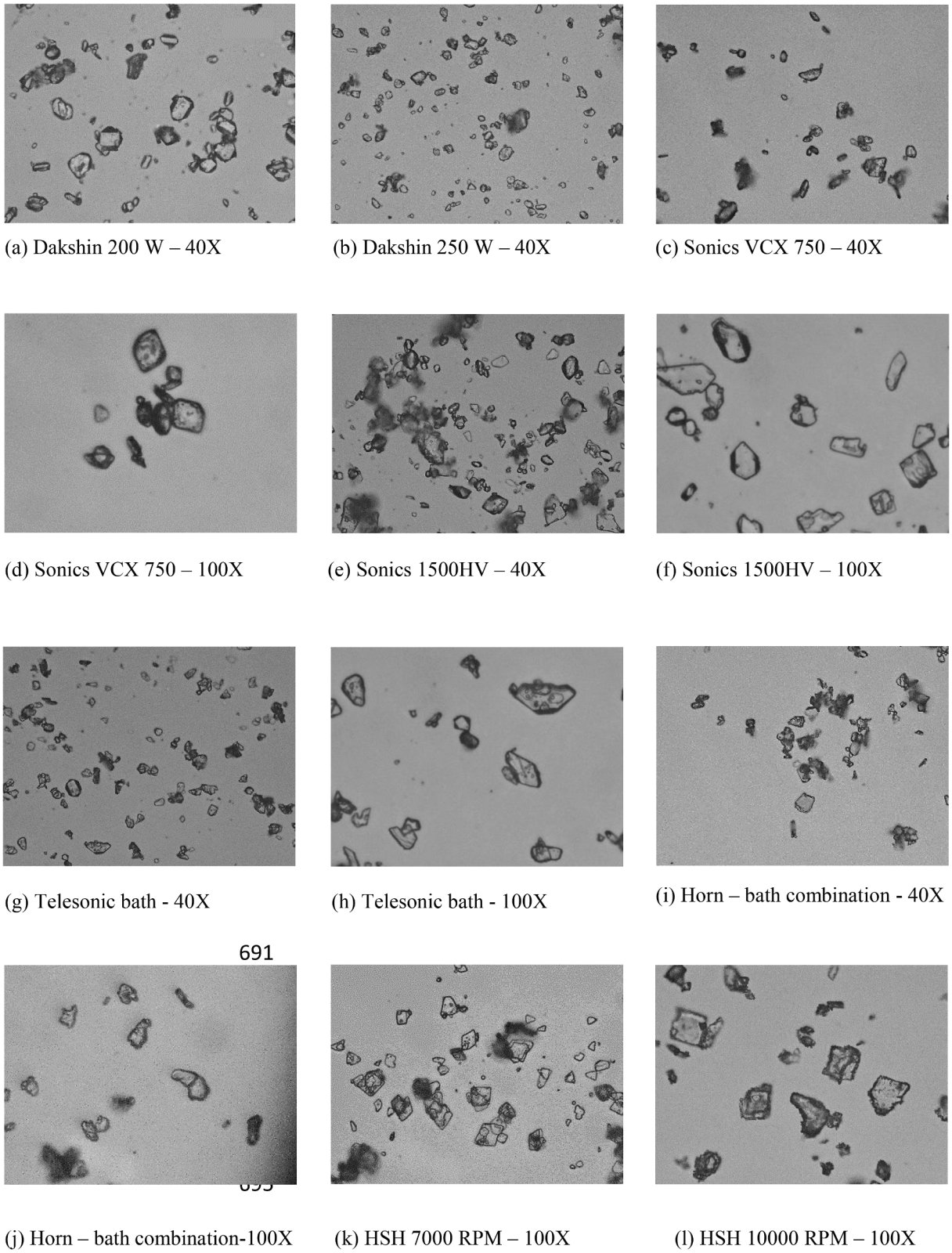


Fig. 7. Microscopic images of treated DADPS samples.

speeds, the pressure of the liquid flowing through the openings nears the vapour pressure of liquid [31], possibly yielding too much cavitation events leading to cushioning effects and reduces the cavitational effects. The size distribution obtained is wide and multimodal in this case as shown in Fig. 6e. The vertical liquid jets generated at high speed along with abrasion due to rotor-stator surfaces are responsible for driving lower mean sizes at the optimum speed of rotation as 7000 rpm.

4.3. Effect of ultrasonic power on particle size and shape

The present work also depicts the effect of ultrasonic power on the final mean particle size over the range of 50 W to 1200 W using

Table 5
Particle size analysis of DADPS treated using Roop Telesonic Ultrasonix bath.

Time (min)	Volume (ml)	Power (W)	Yield (%)	Mean (μm)	10% (μm)	50% (μm)	90% (μm)	SD (μm)
60	4000	800	84.7	14.81	3.99	13.99	26.41	0.29
60	5000	800	85.93	49.16	34.02	51.28	72.69	0.25
60	5000	800	84.22	32.80	25.49	29.68	49.57	0.19

Table 6
Particle size analysis of DADPS treated using High Speed Homogeniser.

Time (min)	RPM	Yield (%)	Mean (μm)	10% (μm)	50% (μm)	90% (μm)	SD (μm)
15	3750	79	38.61	28.86	39.47	52.83	0.19
15	7000	82.7	5.13	3.26	6.48	10.66	0.41
15	10,000	79.25	8.13	9.75	29.06	57.41	0.44

Table 7
Summary of the best particle size reduction results for DADPS using various US equipment with their power density and intensity.

US Equipment	Time (min)	Power (W)	Yield (%)	Mean Size (μm)	Size reduction (%)	Power intensity (W/m^2)	Energy density (W/L)
TU Bath	60	800	84.7	14.81	77.91	5932	47.5
Dakshin 250 W	60	190	76.07	13.93	79.21	57,203	54
Sonics 1500 W	20	1200	80.6	11.30	83.13	105442.6	80.4
Dakshin 200 W	60	140	80.1	13.5	79.86	64,996	43.12
Sonics 750 W	60	300	77	9.74	85.47	174,303	115.65

different configurations of ultrasonic equipment. As depicted in the Table 4, it can be seen that generally higher power input is responsible for giving better size reduction. It can also be interpreted that, there is a best power dissipation condition for each US reactor such that a minimum particle size is obtained effectively. In their analysis of sonochemical reactors, Kumar et al. [30] inferred that the intensity of cavitation is directly proportional to the power dissipated or the amplitude of oscillation. Thus, higher the power (amplitude), more intensive is the cavitation, acoustic streaming and turbulence which results in lower size [3,32] based on particle breakage and reduced agglomeration. Wilhelm et al. [29] studied the effect of power of ultrasound in the crystallization of potash alum and reported that higher power resulted into a lower average crystal size. But, it was also reported that the best power for the desired objective was not the 'maximum power' that can be dissipated into the system, meaning an optimum power specific to equipment exists.

A minute observation of microscopic images presented in Fig. 7, reveals that low power irradiation for ultrasound yielded a slightly better crystal shape. This can be clearly seen in Fig. 7 (a, b) which are the results of power irradiation in the range 100 W–190 W. It is observed that uniform shape crystals are obtained at lower power ranges whereas, in Fig. 7 (f, g, h, i), distorted shapes with wide size distribution are visible for higher ultrasonic powers between 300 W and 1200 W. Such an observation is also reported by Wilhelm et al. [29] attributed to the fact that enhanced ultrasonic power created more abrasion due to higher number of cavitation events and hence lesser uniformity was obtained in crystals of potash alum. Thus, it is important to understand that the selection of best power will strongly depend on the final requirement in terms of the lower mean size or the uniformity of shape of crystals and type of size distribution.

4.4. Analysis based on microscopic images

Microscope image comparison shows differences in the morphology of the crystals. The obtained images for untreated sample and the treated samples using different approaches have been depicted in Figs. 5 and 7 respectively. It can be seen that untreated DADPS constitutes of large irregular shapes without any uniformity whereas DADPS crystallized using antisolvent based approach in presence of ultrasound shows uniform elongated hexagonal geometry particles (uniformness depends on the type of equipment and operating conditions) without substantial agglomerations. The crystal edges are also quite clear and sizes seem to be more or less uniform for the processed DADPS compared to original DADPS. It was clearly established that there is clear deagglomeration occurring due to ultrasound. It has to be also noted that the original DADPS sample at 4X magnification is much bigger than treated samples at higher resolutions, say 40X and 100X. It can be also seen that, the samples treated using ultrasonic horns at low power (100 W–190 W), Fig. 7 (a, b) have a well-defined shape, more or less hexagonal. A more or less similar shape, but with a wider size distribution is found for Fig. 7 (c–f) for the DADPS treated using ultrasonic horns at higher power. DADPS treated in ultrasonic bath has distorted shapes (Fig. 7 g,h). These crystal shapes can be attributed to simultaneous sonication and agitation and lower power density of the bath. The crystals obtained from high speed homogenizer have a quadrilateral geometry (Fig. 7 k,l) with a wide distribution as also evident from the size distribution plot (Fig. 6 e). A minute observation established that 7000 rpm has given better size reduction compared to 10,000 rpm since both the images are at same magnification. The wide size distribution in the case of HSH may be a result of intense throttling effect due to high speed rotor and immobile stator assembly. Such an assembly does also reduce the time spent by the crystals in the cavitation zone at high rotation speeds leading to lower efficacy.

5. Conclusions

The particle size obtained after treatment of DADPS using different ultrasonic reactors has been clearly demonstrated to depend on the type of equipment used. Ultrasonic power intensity and power density were used as unification criteria for comparison to avoid variations based on power outputs and geometries of the devices. It was established that higher power intensity has yielded higher percent size reduction of DADPS as demonstrated in summary Table 7. In other words, greater the power intensity, lower is the mean particle size for the processed DADPS. Also, the microscopic images showed a crystalline structure for ultrasound treated samples. Another noteworthy aspect of the work is that, it was clearly established larger ultrasonic power (> 250 W) resulted into to a certain degree of distorted crystals mainly due to

abrasion. Effect of destructive interference of ultrasound is also observed for the bath-horn combination approach which yields lower size reduction. Experiments conducted using the High Speed Homogeniser (HSH) gave the best results if the criteria was only percent size reduction. Moreover, it has the highest energy efficiency and can process more amount of sample in a single experiment and also requires lesser operating duration. Sonics VCX750 and Dakshin 200 W probes prove to be the best because the treated DADPS crystals have uniform shape and narrower size distribution coupled with smaller particle size. Of course, these reactors will have some problems in going for scale up. The ultrasonic bath, too, has given some decent results which can be an alternative to US horns for scale-up if the desired size reduction is in with final size around 15 μm range. Overall, HSH is the best approach for only size reduction in antisolvent crystallization while ultrasonic horn at the established best power condition is superior when it comes to obtaining desired crystal properties in terms of morphology and size distribution.

CRediT authorship contribution statement

Sarvesh S. Sabnis: Methodology, Investigation, Writing - original draft. **Rakshit Raikar:** Investigation, Writing - original draft. **Parag R. Gogate:** Conceptualization, Supervision, Writing - review & editing, Funding acquisition, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The authors would like to thank DMCC Ltd., Mumbai, India for providing the samples and also Department of Atomic Energy, India for funding the research work.

References

[1] J.Q. Qiao, J.H. Zhao, W.Q. Zhou, H.Z. Lian, Synthesis and quality control of 3,3'-diamino diphenyl sulfone by high performance liquid chromatography, Asian J. Chem. 26 (2014) 8291–8294.
[2] W.L. McCabe, J.C. Smith, P. Harriot, Unit Operations Of Chemical Engineering, 5th ed., McCabe And Smith, McGraw Hill Inc, 1993.
[3] S.S. Sabnis, P.R. Gogate, Ultrasound assisted size reduction of DADPS based on recrystallization, Ultrason. Sonochem. 54 (2019) 198–209, https://doi.org/10.1016/j.ultsonch.2019.01.037.
[4] R.D. Dennehy, Particle engineering using power ultrasound, Org. Process Res. Dev. 7 (2003) 1002–1006, https://doi.org/10.1021/op034124i.
[5] F. Franco, L.A. Pérez-Maqueda, J.L. Pérez-Rodríguez, The effect of ultrasound on the particle size and structural disorder of a well-ordered kaolinite, J. Colloid Interface Sci. 274 (2004) 107–117, https://doi.org/10.1016/j.jcis.2003.12.003.
[6] S. Łoś, L. Duclaux, L. Alvarez, Ł. Hawełek, S. Duber, W. Kempiński, Cleavage and size reduction of graphite crystal using ultrasound radiation, Carbon N. Y. 55 (2013) 53–61, https://doi.org/10.1016/j.carbon.2012.12.005.
[7] K. Hielscher, Ultrasonic milling and dispersing technology for nano-particles, Mater. Res. Soc. Symp. Proc. 1479 (2012) 21–26, https://doi.org/10.1557/opl.2012.1592.
[8] S. Sumari, A. Roesyadi, S. Sumarno, Effects of ultrasound on the morphology, particle size, crystallinity, and crystallite size of cellulose, Sci. Study Res. Chem. Chem. Eng. Biotechnol. Food Ind. 14 (2013) 229–239.
[9] T. Yamaguchi, M. Nomura, T. Matsuoka, S. Koda, Effects of frequency and power of ultrasound on the size reduction of liposome, Chem. Phys. Lipids 160 (2009) 58–62, https://doi.org/10.1016/j.chemphyslip.2009.04.002.
[10] L.S. de los Castillo-Peinado, M.D. Luque de Castro, The role of ultrasound in pharmaceutical production: sonocrystallization, J. Pharm. Pharmacol. (2016) 1249–1267, https://doi.org/10.1111/jphp.12614.
[11] C.S. Su, P.Y. Wu, W. De Jheng, Recrystallization of phenacetin and sulfathiazole using the sonocrystallization process, J. Taiwan Inst. Chem. Eng. 59 (2016) 106–112, https://doi.org/10.1016/j.jtice.2015.08.009.
[12] A.H. Bari, A. Chawla, A.B. Pandit, Sono-crystallization kinetics of K_2SO_4: estimation of nucleation, growth, breakage and agglomeration kinetics, Ultrason. Sonochem. 35 (2017) 196–203, https://doi.org/10.1016/j.ultsonch.2016.09.018.
[13] M.N. Patil, G.M. Gore, A.B. Pandit, Ultrasonically controlled particle size distribution of explosives: a safe method, Ultrason. Sonochem. 15 (2008) 177–187, https://doi.org/10.1016/j.ultsonch.2007.03.011.
[14] R. Ambrus, N.N. Amirzadi, P. Sipos, P. Szabó-Révész, Effect of sonocrystallization on the habit and structure of gemfibrozil crystals, Chem. Eng. Technol. 33 (2010) 827–832, https://doi.org/10.1002/ceat.200900568.
[15] N.S. Deora, N.N. Misra, A. Deswal, H.N. Mishra, P.J. Cullen, B.K. Tiwari, Ultrasound for improved crystallisation in food processing, Food Eng. Rev. 5 (2013) 36–44, https://doi.org/10.1007/s12393-012-9061-0.
[16] Y.T. Shah, A.B. Pandit, V.S. Moholkar, Cavitation Reaction Engineering, 1st ed., Springer Science + Business Media, LLC, New York, 1999. doi: 10.1007/978-1-4615-4787-7.
[17] D.V. Pinjari, A.B. Pandit, Cavitation milling of natural cellulose to nanofibrils, Ultrason. Sonochem. 17 (2010) 845–852, https://doi.org/10.1016/j.ultsonch.2010.03.005.
[18] E.A. Neppiras, Acoustic cavitation, Phys. Rep. 61 (1980) 159–251, https://doi.org/10.1016/S0076-695X(08)60338-5.
[19] L.H. Thompson, L.K. Doraiswamy, Sonochemistry: science and engineering, Ind. Eng. Chem. Res. 38 (1999) 1215–1249, https://doi.org/10.1021/ie9804172.
[20] M. Toma, S. Fukutomi, Y. Asakura, S. Koda, A calorimetric study of energy conversion efficiency of a sonochemical reactor at 500kHz for organic solvents, Ultrason. Sonochem. 18 (2011) 197–208, https://doi.org/10.1016/j.ultsonch.2010.05.005.
[21] J. Berlan, T.J. Mason, Sonochemistry: from research laboratories to industrial plants, Ultrasonics 30 (1992) 203–212, https://doi.org/10.1016/0041-624X(92)90078-Z.
[22] S. Koda, T. Kimura, T. Kondo, H. Mitome, A standard method to calibrate sonochemical efficiency of an individual reaction system, Ultrason. Sonochem. 10 (2003) 149–156, https://doi.org/10.1016/S1350-4177(03)00084-1.
[23] M. Sivakumar, A.B. Pandit, Ultrasound enhanced degradation of Rhodamine B: Optimization with power density, Ultrason. Sonochem. 8 (2001) 233–240, https://doi.org/10.1016/S1350-4177(01)00082-7.
[24] M.V. Bagal, P.R. Gogate, Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: a review, Ultrason. Sonochem. 21 (2014) 1–14, https://doi.org/10.1016/j.ultsonch.2013.07.009.
[25] T.J. Mason, J.P. Lorimer, D.M. Bates, Quantifying sonochemistry: on a 'black art,' Ultrasonics. 30 (1992) 40–42. doi: 0041-624X/92/010040-03.
[26] C.J. Martin, A.N.R. Law, The use of thermistor probes to measure energy distribution in ultrasound fields, Ultrasonics 18 (1980) 127–133, https://doi.org/10.1016/0041-624X(80)90026-8.
[27] T.J. Mason, J.P. Lorimer, Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry, Ellis Horwood Publishers, Chichester, 1988 10.1016/0160-9327(89)90104-x.
[28] K.K. Jyoti, A.B. Pandit, Water disinfection by acoustic and hydrodynamic cavitation, Biochem. Eng. J. 7 (2001) 201–212, https://doi.org/10.1016/S1369-703X(00)00128-5.
[29] N. Amara, B. Ratsimba, A. Wilhelm, H. Delmas, Crystallization of potash alum: effect of power ultrasound, Ultrason. Sonochem. 8 (2001) 265–270.
[30] A. Kumar, P.R. Gogate, A.B. Pandit, H. Delmas, A.M. Wilhelm, Gas–liquid mass transfer studies in sonochemical reactors, Ind. Eng. Chem. Res. 43 (2004) 1812–1819, https://doi.org/10.1021/ie0341146.
[31] P.S. Kumar, A.B. Pandit, Modeling hydrodynamic cavitation, Chem. Eng. Technol. 22 (1999) 1017–1027, https://doi.org/10.1002/(SICI)1521-4125(199912)22:12<1017::AID-CEAT1017>3.0.CO;2-L.
[32] C. Gillespie, How Does Temp Affect the Growth Rate of Crystals?, (2018). https://sciencing.com/temp-affect-growth-rate-crystals-6318908.html (accessed May 31, 2018).