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Comparison of batch and continuous ultrasonic emulsification processes

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ABSTRACT

Batch and continuous ultrasonic emulsification processes on both lab and pilot scales were investigated using Tween 80 or milk protein isolate (MPI) as emulsifiers. The process parameters of processing volume, residence time and ultrasonic amplitude, as well as emulsion formulations, emulsifier type and concentration, were studied for the effect on emulsion droplet size. Emulsions prepared with ultrasound yielded submicron droplets, ~200 nm, with Tween 80 and MPI, utilising all processing methodologies. Inverse power laws were obtained correlating emulsion droplet size with respect to energy density, highlighting the efficiency of the continuous over batch processing. This efficiency is ascribed to the smaller processing volumes, associated with continuous ultrasonic emulsification. Longer processing times were required for MPI to achieve submicron droplets (<200 nm) in comparison to Tween 80 as greater times are necessary for interfacial adsorption and surface stabilisation, shown by interfacial tension measurements.

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1. Introduction

Low frequency (≤ 100 kHz) high power (>10 W cm⁻²) ultrasound is a versatile technology widely utilised within the food industry for the alteration and generation of microstructures (McClements, 1995; O'Sullivan et al., 2015a,b). It is a long established technique for the preparation of emulsions (Bondy and Söllner, 1935). Sonication readily produces submicron droplets when using low molecular weight surfactants (Abismaïl et al., 1999; Kentish et al., 2008). Submicron dispersed phase droplets confer several advantages over larger droplets, including an increase in the bioavailability of lipophilic components and a surface area for controlled release. Increased emulsion stability due to reduced creaming or sedimentation which limits aggregation and coalescence enhances the commercial shelf life (McClements, 2011; O'Sullivan et al., 2014a,b).

Ultrasound treatment of liquid media operates through the generation of cavitation bubbles due to pressure differentials during acoustic wave propagation (Servant et al., 2001). Cavitation bubbles disperse and attenuate ultrasonic waves due to the acoustic impedance differential between the liquid and gaseous phases, resulting in either partial or complete scattering of the acoustic

waves (McClements, 1995). Systems containing many bubbles exhibit multiple scattering as the bubbles behave like mirrors, causing reflection of the acoustic wave and an effective increase in the absorption of acoustic energy (Juliano et al., 2011; McClements and Povey, 1989). Cavitations are concentrated in the volume at the tip of the sonotrode, this localisation results in high levels of energy input (Martini, 2013; Trujillo and Knoerzer, 2011). Given the high number of cavitations within the vicinity of the tip of the sonotrode, higher attenuation (*i.e.* gradual loss of intensity) levels are observed and are dominated by acoustic scattering. The acoustic intensity decays exponentially with increasing distance from the sonotrode tip, effectively dissipated at distances as low as 1 cm from the tip (Chivate and Pandit, 1995). Ultrasonic cavitations are highly unstable entities prone to rapid collapse creating highly localised regions of hydrodynamic shear (O'Donnell et al., 2010). These acoustically induced cavitations result in the disruption of micron sized dispersed phase droplets and facilitate the formation of submicron emulsion droplets (Gogate et al., 2011).

Emulsification utilising ultrasonic technologies has been a field of growing interest over the past decade, with extensive investigations conducted upon the process parameters (*i.e.* contact time with the acoustic field, ultrasonic power, volume processed, etc.), in addition to emulsion formulations (Jafari et al., 2007; Kentish et al., 2008). Low molecular weight emulsifiers (*i.e.* surfactants) have predominantly been utilised as part of these studies. To date,

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there is a lack of literature on the use of industrially relevant high molecular weight emulsifiers (*i.e.* proteins). The work of Kaltsa et al. (2013) on whey protein and Heffernan et al. (2011) on sodium caseinate show that the formation of submicron emulsions via batch ultrasonic emulsification is possible. No systematic investigations of process parameters or continuous methods using proteins as emulsifiers with ultrasound are currently available.

The objective of this research was to understand the influence of ultrasonic process parameters and emulsion formulation, emulsifier type and concentration, on the droplet size of oil-in-water emulsions (*i.e.* Sauter mean diameter, $d_{3,2}$). The efficacy of batch and continuous process configurations for the production of submicron emulsions with food grade industrially relevant ingredients (*i.e.* multi-fraction proteins) using low frequency high power ultrasound was assessed. Comparisons between batch and continuous processing were explored in terms of processing time within the acoustic field, acoustic power and processing volume. The effect of emulsifier type, was investigated with a low molecular weight surfactant (Tween 80) and high molecular weight biopolymer (milk protein isolate), over a range of concentrations to assess the performance of these ingredients as emulsifiers during the sonication process.

2. Materials and methods

2.1. Materials

Milk protein isolate (MPI; Ultramor™ 9075), a composite mixture of ~80% micellar casein and ~20% whey protein (Fox, 2008), was kindly provided by Kerry Ingredients and Flavours (Listowel, Ireland), whereby the protein content was 86 wt.%. Tween 80 and sodium azide was purchased from Sigma Aldrich (UK). The oil used in this study was commercially available rapeseed oil and was tested for surface active impurities using interfacial tension measurements (*cf.* Section 2.2.2.4.) as described in Section 3.2. The water used in all experiments was passed through a double distillation unit (A4000D, Aquatron, UK).

2.2. Methods

2.2.1. Preparation of emulsifier solutions

The continuous phase of emulsion were prepared by dispersing Tween 80 and MPI in water at 40 °C to obtain to obtain solutions at concentrations in the range of 0.1–3 wt.%. Tween 80 and MPI are completely soluble at these concentrations. Sodium azide (0.02 wt.%) was added to the solutions to diminish the microbial activity.

2.2.2. Emulsion preparation and characterisation

10 wt.% of dispersed phase (rapeseed oil) was to added to the aqueous continuous phase containing either Tween 80 or MPI at concentrations, ranging from 0.1 to 3 wt.%. A coarse pre-emulsion was prepared via high shear mixing at 8000 rpm for 2 min for lab and pilot scale trials, utilising SL2T and AXR Silverson mixers, respectively (Silverson, UK).

2.2.2.1. Batch configuration for ultrasonic emulsification. Lab scale batch ultrasonic processing (Viber Cell 750, Sonics, USA) was undertaken with the ultrasonic probe centrally located with an immersion depth of 3 mm in the pre-emulsion, with volumes ranging from 3.02 to 151.13 mL, sonication times from 1 to 300 s and ultrasonic amplitudes of 20–40%.

2.2.2.2. Continuous configuration for ultrasonic emulsification. Lab scale continuous processing (Viber Cell 750, Sonics, USA) was

carried out by positioning the ultrasonic probe orthogonal to the path of flow of the pre-emulsion, using a brass tee junction with an internal diameter of 4 mm. The ultrasonic probe was positioned 4 mm from the base of the tee junction (*cf.* Fig. 1a) and surrounded by ice to mitigate against heat gain. The pre-emulsion was pumped peristaltically (Masterflex L/S Digital Pump System with Easy-Load II Pump Head, Cole-Parmer, UK) with volumetric flow rates of 25–250 mL/min and an ultrasonic amplitude of 20–40%.

Pilot scale continuous processing (UIP1000hd, Hielscher Ultrasonics GmbH, Germany) had the flow path of pre-emulsion in the same plane as the ultrasonic probe. The ultrasonic probe was positioned 20 mm from the inlet of the coarse emulsion and the outlet was positioned perpendicular to the sonotrode (*cf.* Fig. 1b). The pre-emulsion was pumped centrifugally (Millipore, UK) with volumetric flow rates ranging from 2700 to 5700 mL/min (163–343 L/h) with ultrasonic amplitudes of 50–100%.

The residence time, t , which the pre-emulsion is within the acoustic field for both continuous processing methodologies is controlled by variation of the volumetric flowrate (Q), and is determined from Eq. (1):

$$t = V/Q \quad (1)$$

where t is the residence time (s), V is the volume under the influence of the acoustic field (m^3) and Q is the volumetric flowrate

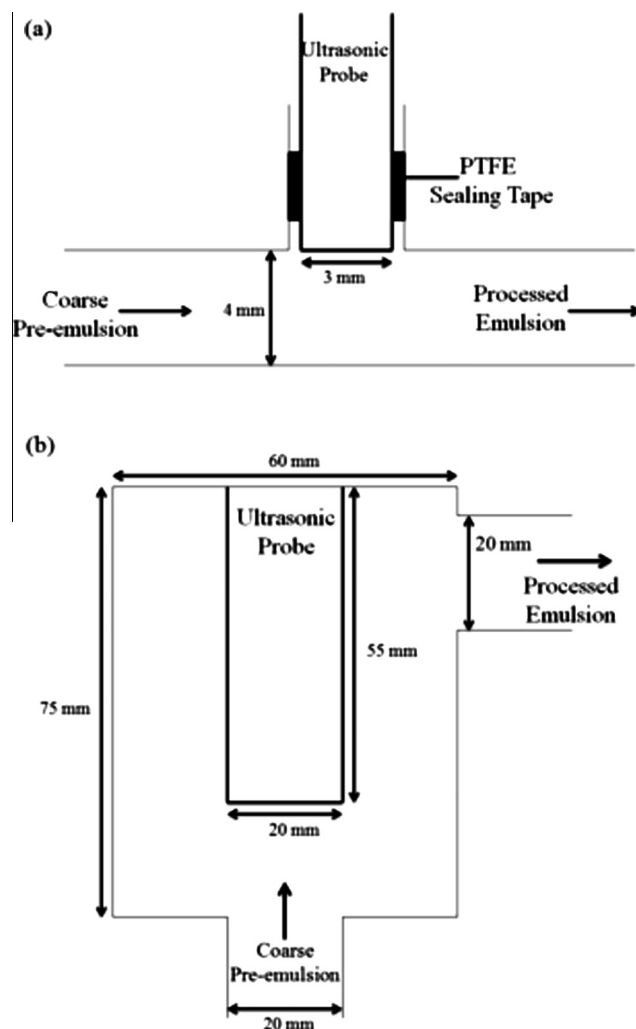


Fig. 1. Schematic of continuous ultrasonic emulsification for (a) lab scale and (b) pilot scale trials.

Table 1
Acoustic power (P_a) and acoustic intensity (I_a) for lab (Viber Cell 750) and pilot (UIP1000hd) scale ultrasonic processors.

Ultrasonic processor	Amplitude (%)	Acoustic power (W)	Acoustic intensity (W cm^{-2})
Viber Cell 750	20	8.5 ± 0.2	120.3 ± 2.8
	30	19 ± 0.6	269.1 ± 8.5
	40	32 ± 0.9	453.3 ± 12.8
UIP1000hd	50	78 ± 1.3	20.5 ± 0.3
	60	98 ± 1.2	25.7 ± 0.3
	70	131 ± 2.3	34.4 ± 0.6
	80	164 ± 4.2	43.2 ± 1.1
	90	208 ± 3.7	54.7 ± 0.9
	100	234 ± 5.4	61.6 ± 1.4

Table 2
Residence times (t) of pre-emulsion within acoustic field for lab (Viber Cell 750) and pilot (UIP1000hd) scale ultrasonic processors with respect to volumetric flowrate (Q).

Ultrasonic processor	Volumetric flowrate (mL/min)	Contact time (ms)
Viber Cell 750	25	120
	50	60
	100	30
	150	20
	200	15
	250	12
UIP1000hd	2700	140
	4500	84
	5700	66.3

($\text{m}^3 \text{s}^{-1}$). The volumes under the influence of the acoustic field for the lab and pilot scale continuous processes are $5 \times 10^{-8} \text{ m}^3$ and $6.3 \times 10^{-6} \text{ m}^3$, respectively. The residence times for pre-emulsions within the acoustic field for continuous processing in both lab and pilot scale ultrasonic processors are provided in Table 2.

2.2.2.3. Droplet size measurements. The droplet size of the emulsions was measured by laser diffraction using a Mastersizer 2000 (Malvern Instruments, UK) immediately after emulsification. Emulsion droplet size values are reported as the surface mean diameter (Sauter mean diameter; $d_{3,2} = \sum n_i d_i^3 / \sum n_i d_i^2$), where n_i is the number of droplets of diameter d_i .

2.2.2.4. Interfacial tension measurements. The interfacial tension between the aqueous phases (pure water, low molecular weight surfactant, or high molecular weight biopolymer solutions) and the oil phase (rapeseed oil) was measured using a tensiometer K100 (Krüss, Germany) with the Wilhelmy plate method, as detailed by O'Sullivan et al. (2015a,b). The interfacial tension values and the error bars are reported as the mean and standard deviation, respectively, of three repeat measurements.

2.2.3. Ultrasonic processing, acoustic intensity and energy density determinations

A lab scale ultrasonic processor (Viber Cell 750, Sonics, USA) with a stainless steel microtip ($d = 3 \text{ mm}$; $S_A = 0.07 \text{ cm}^2$) was used for the preparation of emulsions using batch and continuous configurations, operating at 20 kHz. Continuous emulsification was further investigated with scale up trials utilising a pilot scale ultrasonic processor (UIP1000hd, Hielscher Ultrasonics GmbH, Germany) with a titanium tip ($d = 20 \text{ mm}$; $S_A = 3.8 \text{ cm}^2$).

Emulsions were sonicated at different amplitudes to vary the acoustic power transmitted, whereby the lab and pilot scale ultrasonic processors operated within amplitude ranges of 20–40% (maximum amplitude of 108 μm) and 50–100% (maximum amplitude of 57 μm), respectively. The acoustic intensity (I_a) was

determined calorimetrically by measuring the temperature rise of the sample as a function of time, under adiabatic conditions. The acoustic intensity, I_a (W cm^{-2}), was calculated using Eq. (2) from Margulis and Margulis (2003):

$$I_a = \frac{P_a}{S_A}, \text{ where } P_a = mc_p \left(\frac{dT}{dt} \right) \quad (2)$$

where P_a is the acoustic power (W), S_A is the surface area of the tip of the sonotrode (cm^2), m is the mass of ultrasound treated medium (g), c_p is the specific heat of the medium ($\text{J g}^{-1} \text{K}^{-1}$) and dT/dt is the rate of temperature change with respect to time of the medium (K s^{-1}), starting at $t = 0$. The temperature was measured by means of a digital thermometer (TGST3, Sensor-Tech Ltd., Ireland), with an accuracy of $\pm 0.1 \text{ K}$. The acoustic power (P_a) and acoustic intensity (I_a) for the lab scale and pilot scale ultrasonic processors are provided in Table 1, for the ultrasonic amplitudes employed during emulsification.

Acoustic intensity (I_a) data was converted to energy density (E_v ; J m^{-3}), relating acoustic intensity to both processing volume and time, using Eq. (3):

$$E_v = \frac{I_a S_A t}{V} \quad (3)$$

where t is residence time (s or ms) and V is processing volume (m^3).

2.3. Mathematical models

Emulsion droplet size data was correlated to energy density using inverse power laws, yielding a linear trend, with logarithmic plot axes this can be fitted by Eq. (4):

$$f(x) = \frac{a}{x^b} \quad (4)$$

where $f(x)$ is emulsion droplet size ($d_{3,2}$; μm), x is energy density (E_v ; MJ m^{-3}), a is the value of $f(x)$ when $x = 1$ and b is the gradient of the fit.

2.4. Statistical analysis

Student's t -test with a 95% confidence interval was used to assess the significance of the results obtained. t -test data with $P < 0.05$ were considered statistically significant.

3. Results and discussions

3.1. Comparison of lab scale batch and continuous configurations for effect of processing time and ultrasonic power

The effect of processing volume for lab batch configuration for a fixed ultrasonic amplitude and emulsifier concentration upon emulsion droplet size was initially investigated. Fig. 2 shows pre-emulsions prepared with 1.5 wt.% Tween 80 sonicated with an ultrasonic amplitude of 40% (i.e. 453.3 W cm^{-2}). Droplet size measurements as a function of processing time, from 0 to 300 s, and processing volume, from 3.02 to 151.13 mL.

Increasing the processing time of batch ultrasonic homogenisation results in a decrease in the resultant emulsion droplet size regardless of processing volume, this has also been reported by Abismail et al. (1999) and Jafari et al. (2007). The time required to achieve the minimum droplet size is a function of the processing volume, larger processing volumes require prolonged processing times to achieve the minimum droplet size which has been shown by Maa and Hsu (1999). Ultrasonic processing of smaller volumes is more efficient as the acoustic energy emanated from the tip of the sonotrode is absorbed more intensely resulting in more rapid size reduction. This volume effect arises from the complete

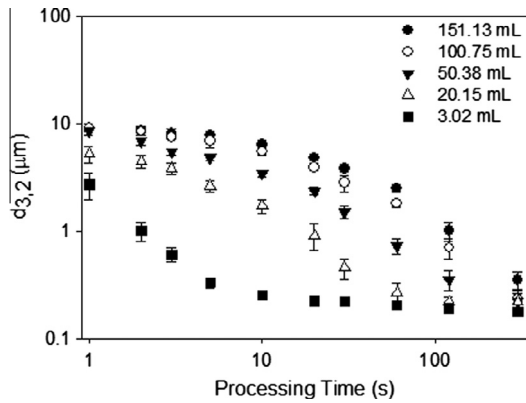


Fig. 2. Effect of batch volume and ultrasonic processing time on droplet size ($d_{3,2}$) of emulsions stabilised with 1.5 wt.% Tween 80 prepared employing lab scale batch ultrasonic homogenisation.

dissipation of acoustic intensity at distances as low as 1 cm from the tip (Chivate and Pandit, 1995) highlighting the importance of ultrasonic tip location for effective processing (Gogate et al., 2011).

The effect of residence time of pre-emulsion within the acoustic field at the lab scale with respect to continuous processing is presented in Fig. 3. This was achieved by variation of the volumetric flow rate to alter the acoustic residence time. Pre-emulsions with 1.5 wt.% Tween 80 were sonicated with an ultrasonic amplitude of 40% (i.e. 453.3 W cm^{-2}). Droplet size changes as a function of residence time for lab scale continuous ultrasonic processing is shown in Fig. 3.

Similar to the behaviour shown in Fig. 2 for batch processing, increasing the residence time of pre-emulsions within the acoustic field for continuous processing increases energy transmission to the pre-emulsion, enhancing droplet size reduction (Freitas et al., 2006; Kentish et al., 2008). However, the timescale for emulsification utilising continuous ultrasonic processing is milliseconds in comparison to seconds for batch processing, this is due to the flow rates of pre-emulsion through the system. Submicron emulsion droplet sizes are achieved with the continuous configuration in milliseconds owing to the smaller processing volume ($5 \times 10^{-2} \text{ mL}$) by comparison to those of batch processing ($\geq 3.02 \text{ mL}$). The smaller volumes considered for residence times with continuous processing allow for a greater increase in the volume effect seen with batch systems. This allows the entire flow path to be subject to acoustic energy which improves transmission

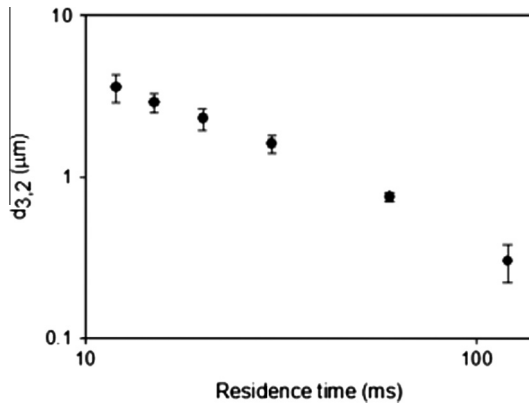


Fig. 3. Effect of acoustic processing time on droplet size ($d_{3,2}$) of emulsions stabilised with 1.5 wt.% Tween 80 prepared employing continuous lab scale ultrasonic processor (40% amplitude).

of acoustic energy to generate smaller emulsion droplets and increases the efficacy of this process.

The effect of energy transmission to the pre-emulsion (i.e. different acoustic amplitudes) upon resultant emulsion droplet size was also investigated. 1.5 wt.% Tween 80 pre-emulsions were sonicated with ultrasonic amplitudes of 20–40% for both lab scale batch and continuous configurations, with a 50.38 mL volume of pre-emulsion for lab scale batch processing. Fig. 4 shows droplet size measurements as a function of processing time and ultrasonic amplitude for both batch and continuous processing.

Increasing the acoustic amplitude yields greater ultrasonic energy transmission to the pre-emulsion (cf. Table 2), decreasing the time required to achieve the minimum emulsion droplet size which is determined by the emulsion formulation, $\sim 200 \text{ nm}$ (cf. Fig. 4a). The acoustic power imparted to a liquid system controls the number of bubbles, with a higher power (i.e. amplitude) generating more bubbles (Trujillo and Knoerzer, 2011). The unstable nature of ultrasonically generated bubbles results in the number of cavitation events being related to the number of bubbles present. The cavitation events result in high levels of hydrodynamic shear which acts upon the pre-emulsion reducing droplet size, so more power more rapidly reduces droplet size.

Similar trends were exhibited with the lab scale continuous configurations (cf. Fig. 4b), whereby increasing the ultrasonic amplitude reduced the processing time required to decrease emulsion droplet size, for comparable reasons as previously discussed. Given the lower residence times associated with the continuous processing methodology, it appears emulsions with smaller droplet sizes can be achieved more effectively due to more efficient utilisation of acoustic energy with this configuration. Furthermore, operating at higher acoustic energies (i.e. greater

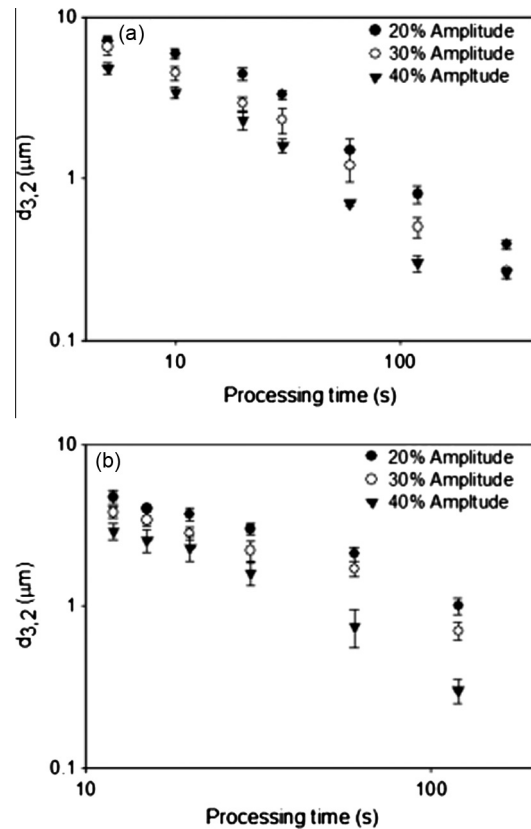


Fig. 4. Effect of ultrasonic amplitude and processing time (t) with the acoustic field upon droplet size ($d_{3,2}$) of emulsions fabricated with 1.5 wt.% Tween 80 prepared utilising (a) lab scale batch (50 mL) and (b) lab scale continuous configurations.

ultrasonic amplitudes) predominately decreases the timescale by which smaller emulsion droplets are formed. In order to test these hypotheses, the effect of energy with respect to volume processed, energy density (E_v ; MJ m^{-3}), was subsequently determined for the assessment of the efficiency of energy utilisation of each of the configurations investigated.

Emulsion droplet size data for all configurations (cf. Fig. 4) was normalised with respect to energy density, as described in Section 2.2.3. Droplet size measurements ($d_{3,2}$) as a function of energy density (E_v) are shown in Fig. 5 for both lab scale configurations. Normalisation of the emulsion droplet size data yielded a linear trend, with logarithmic plot axes, an inverse power law as detailed in Section 2.3. (cf. Eq. (4)).

For both lab scale configurations, master curves were obtained which predict emulsion droplet size with respect to energy density for all ultrasonic amplitudes investigated. Similar coefficient values (a and b) were obtained for the batch and continuous process configurations (cf. Eqs. (5) and (6)), but significant differences ($P < 0.05$) in energy density between batch and continuous process were observed, whereby the energy density for the continuous configuration is lower than the batch configuration by approximately 50%. The energy density differential between configurations is predominately attributed to the difference in processing volume, for which continuous processing has a chamber volume 1000 times less than that of the batch configuration, allowing for more effective transmission of acoustic energy to the pre-emulsion. Additionally, the effect of acoustic amplitude yields no difference on the obtained predictive curves for the determination of emulsion droplet size at a given energy input, highlighting that the energy provided, a combination of acoustic power and processing time, are the determining factors of emulsion droplet size for lab scale ultrasonic emulsification processes.

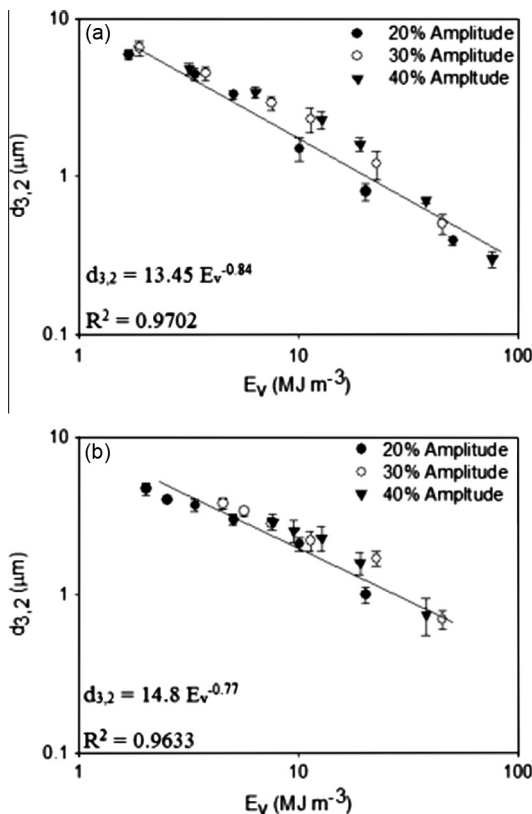


Fig. 5. Effect of energy density (E_v) upon emulsion droplet size ($d_{3,2}$) utilising (a) lab scale batch ultrasonic processing and (b) lab scale continuous ultrasonic processing for 1.5 wt.% Tween 80 stabilised emulsions, 20–40% amplitudes for both configurations.

$$\text{Lab scale batch configuration : } d_{3,2} = \frac{13.45}{E_v^{0.84}} \quad (5)$$

$$\text{Lab scale continuous configuration : } d_{3,2} = \frac{14.8}{E_v^{0.77}} \quad (6)$$

3.2. Effect of emulsifier concentration and type on emulsion formation

Emulsion droplet size ($d_{3,2}$) as a function of emulsifier type and concentration is shown in Fig. 6. Emulsion droplet sizes were measured immediately after emulsification. Regardless of emulsifier type or the processing methodology employed, increasing the emulsifier concentration allows for the formation of smaller emulsion droplets with slower processing times. This is due to when emulsifier concentration is increased, more emulsifier molecules are present within the continuous phase allowing reduced times for adsorption to the newly formed interface. This allows for more rapid formation of submicron emulsion droplets (Beverung et al., 1999). A minimum surfactant concentration is required to stabilise the emulsion interface, if this is reached submicron emulsion droplets can be produced. At emulsifier concentrations >0.5 wt.%, for both emulsifier types and processing methodologies, the difference in the emulsion droplet size is not statistically significant ($P > 0.05$). This shows that once sufficient emulsifier is present to stabilise interfaces an excess of emulsifier is present within the continuous phase. The statistically insignificant differences ($P > 0.05$) in emulsion droplet size at emulsifier concentrations >0.5 wt.% are in agreement with those of O'Sullivan et al. (2014a,b) for emulsions fabricated with Tween 80 and MPI, prepared utilising high pressure valve homogenisation, whereby emulsion droplet sizes of ~ 200 nm were obtained. Comparable emulsion droplet sizes to those of O'Sullivan et al. (2014a,b) were acquired in all instances except for emulsions prepared with MPI employing continuous ultrasonic processing (cf. Fig. 6d), whereby micron-sized droplets were achieved ($\sim 1 \mu\text{m}$). These observed significant differences ($P < 0.05$) in emulsion droplet size are ascribed to disparities in processing methodology employed between the two studies. Comparable emulsion droplet sizes were obtained for Tween 80 for both processing methodologies owing to the significantly lower ($P < 0.05$) molecular weight in comparison to MPI.

At lower emulsifier concentrations (≤ 0.5 wt.%) rapid emulsion coalescence was exhibited for batch and continuous methodologies at processing times >60 s and >60 ms, respectively, for both emulsifiers investigated (cf. Fig. 6). This re-coalescence of emulsion droplets is attributed a combination of insufficiency of emulsifier to stabilise the interface within the respective formulations and over processing of the emulsions. Back coalescence of emulsion droplets is commonly exhibited in systems where insufficient emulsifier is present, and over processing occurs. Jafari et al. (2008) detail the factors involved in the re-coalescence behaviour of emulsions prepared utilising ultrasonic equipment. The predominant rationale ascribed to the observed re-coalescence phenomena is a combination of the low adsorption rate of emulsifier, due to the low concentrations present, and the high energy density associated with ultrasonic processing, whereby the likelihood of droplet collision is increased within the area of emulsification (i.e. proximity to the tip of the sonotrode).

As previously discussed for emulsion formulations prepared with Tween 80, the residence time during which the pre-emulsion in the acoustic field is of the order of milliseconds for continuous processing in comparison to batch processing, where the timescale is an order of magnitude greater, that of seconds. Emulsions prepared with Tween 80 form smaller emulsion droplets in shorter residence times in the acoustic field in comparison to the high molecular weight emulsifier, MPI, for all emulsifier

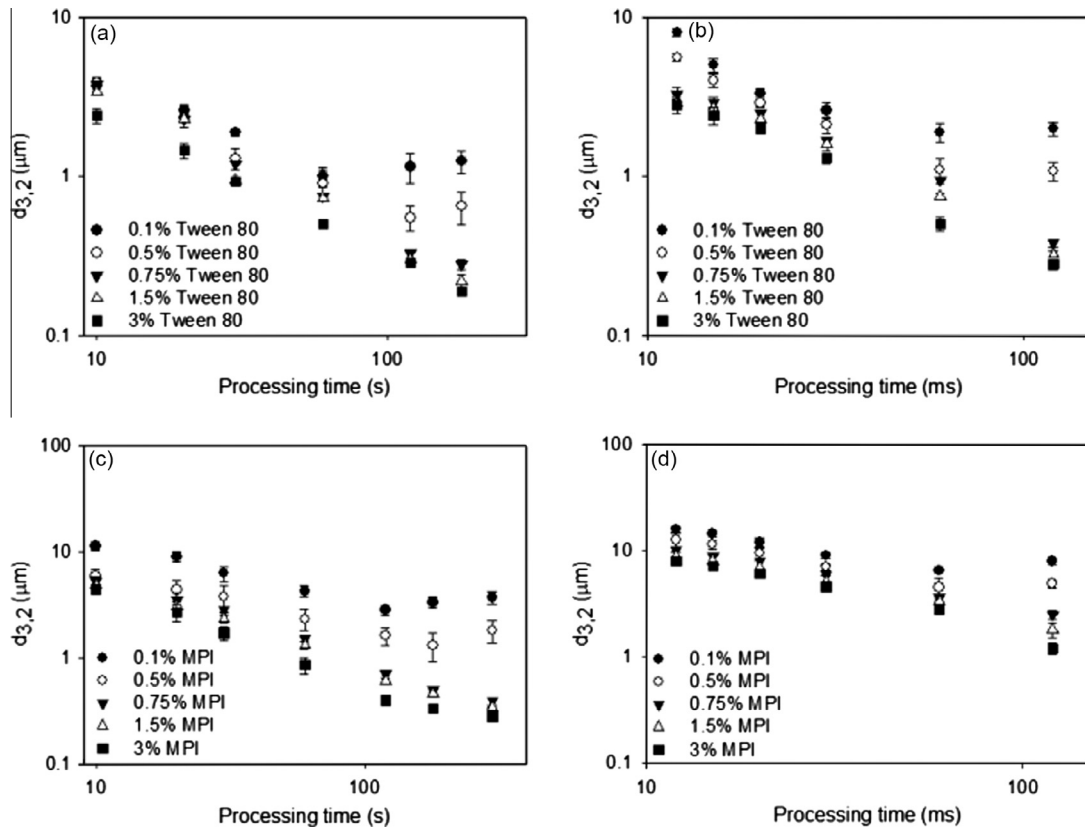


Fig. 6. Effect of emulsifier type and concentration upon emulsion droplet size ($d_{3,2}$) of Tween 80 for (a) batch and (b) continuous ultrasonic processing, and MPI for (c) batch and (d) continuous ultrasonic processing. All data is for lab scale methodologies (ultrasonic amplitude of 40%) and the batch size utilised is 50 mL.

concentrations and processing configurations. This behaviour is ascribed to a combination of lower diffusion rates for the higher molecular weight species, and longer surface denaturation times required for stabilisation of emulsion droplets with proteins, whereby surface denaturation refers to the conformational rearrangement of proteins upon adsorption at oil–water interfaces (Beverung et al., 1999).

The rate of diffusion of an emulsifier to an interface and the time required for conformational changes upon adsorption was probed with studies of interfacial tension. Fig. 7 presents the interfacial tension between rapeseed oil and water, 0.1 wt.% Tween 80 and 0.1 wt.% MPI solutions. The presence of naturally present surface active surface impurities within the dispersed phase was assessed by measuring the interfacial tension of distilled water and rapeseed oil. The interfacial tension decreases continually with

respect to time (cf. Fig. 7), and this behaviour is attributed to the nature of the dispersed phase and to a lesser extent the type of emulsifier utilised. Gaonkar (1989, 1991) described how the time dependant nature of interfacial tension of commercially available rapeseed oils with pure water was due to the presence of surface active impurities present within the oils. Furthermore, after purification of these oils the time dependant nature of the interfacial tension was no longer exhibited demonstrating that the time dependant nature of interfacial tension is due to surface active impurities within the commercially available rapeseed oil.

The initial interfacial tension value for 0.1 wt.% Tween 80 is significantly ($P < 0.05$) lower than that of 0.1 wt.% MPI (cf. Fig. 7), demonstrating how the lower molecular weight emulsifier is capable of adsorbing to the oil–water interface more rapidly, accounting for the increased rate of droplet breakup for Tween 80 in comparison to that of MPI. The equilibrium value of interfacial tension differs significantly between Tween 80 and MPI due a combination of molecular weight differences, the average molecular weight of Tween 80 and MPI are 1.3 and ~24 kDa (O'Sullivan et al., 2014a,b) and required surface denaturation for interfacial stabilisation. This demonstrates that lower molecular weight emulsifiers (i.e. Tween 80) have enhanced interfacial packing in comparison to higher molecular weight entities (i.e. MPI).

The effect of emulsifier concentration upon the previously discussed correlative models relating emulsion droplet size ($d_{3,2}$) with respect to energy density (E_v) was consequently assessed. Fig. 8 shows emulsion droplet size as a function of energy density for emulsions prepared with a range of Tween 80 and MPI concentrations utilising lab scale batch (50.38 mL) and continuous ultrasonic processing, with an ultrasonic amplitude of 40%.

Increasing the Tween 80 and MPI concentration above the 0.5 wt.% limiting concentration yields a marginal reduction in emulsion droplet size with respect to energy density, indicating

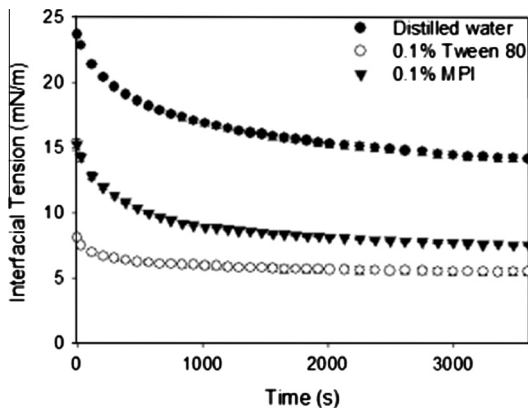


Fig. 7. Comparison of interfacial tension between distilled water (●), Tween 80 (○) and MPI (▼) with rapeseed oil. The concentration for both emulsifiers was 0.1 wt.%.

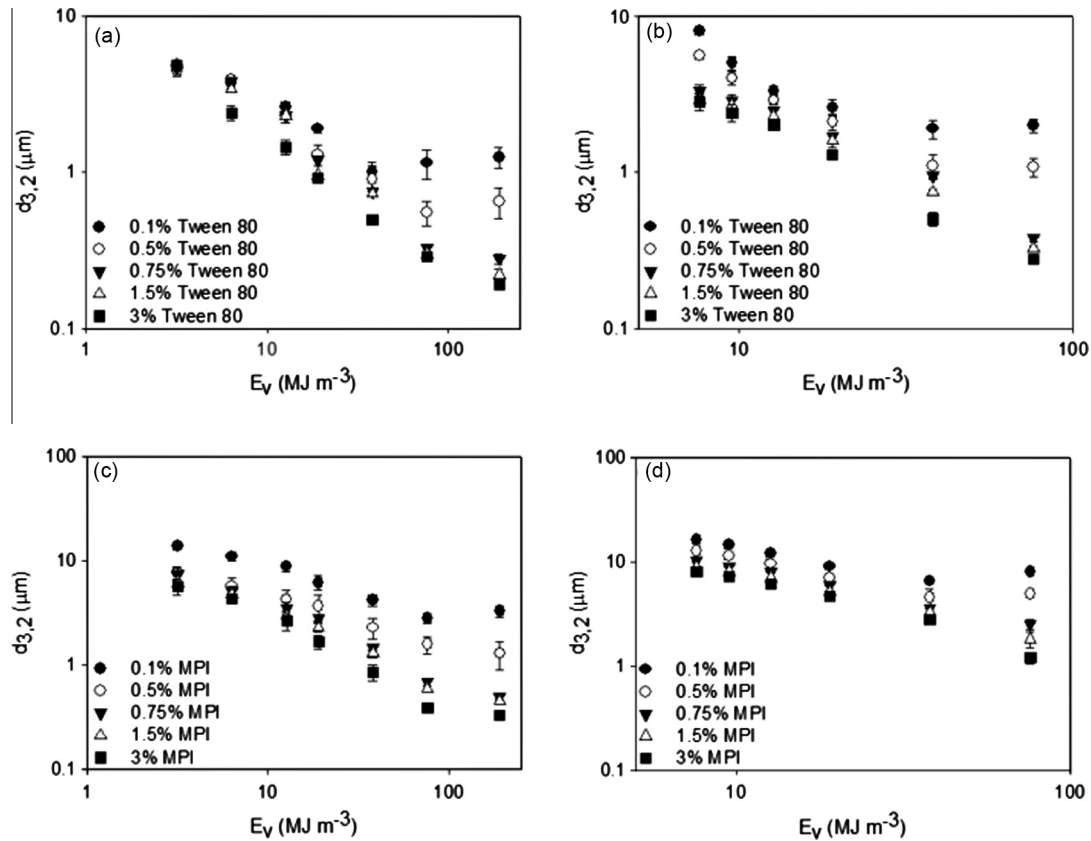


Fig. 8. Effect of energy density (E_v) upon emulsion droplet size ($d_{3,2}$) for emulsions prepared with Tween 80 utilising (a) batch and (b) continuous ultrasonic processing, and with MPI utilising (c) batch and (d) continuous ultrasonic processing. All data is for lab scale methodologies (ultrasonic amplitude of 40%) and the batch size utilised is 50 mL.

that increased emulsifier concentrations allows for a marginally more efficient utilisation of acoustic energy. Regardless of emulsifier type or processing configuration (batch or continuous), no significant differences were observed with respect to emulsifier concentrations. The inverse power law model for $d_{3,2}$ and E_v did not accurately predict the behaviour of sonicated emulsions with no excess emulsifier (<0.5 wt.%).

3.3. Effect of energy density on pilot scale continuous ultrasonic emulsification

The effect of energy density on pilot scale continuous ultrasonic homogenisation and the emulsion droplet size ($d_{3,2}$) produced was assessed. Pre-emulsions prepared with 1.5 wt.% Tween 80 were processed at ultrasonic amplitudes of 50% and 90%. Droplet size measurements as a function of energy density are shown in Fig. 9.

Pilot scale processing yields two distinct fits for emulsion droplet size with respect to energy density, unlike lab scale they are dependent on the ultrasonic amplitude (Eqs. (7) and (8)). The significant difference in gradient (*i.e.* b) between the fits demonstrates that processing of emulsions at higher ultrasonic energies yields more efficient utilisation of energy for emulsion droplet breakup.

$$\text{Pilot scale continuous configuration @ 50\% amplitude: } d_{3,2} = \frac{17.7}{E_v^{0.19}} \quad (7)$$

$$\text{Pilot scale continuous configuration @ 90\% amplitude: } d_{3,2} = \frac{41.07}{E_v^{1.019}} \quad (8)$$

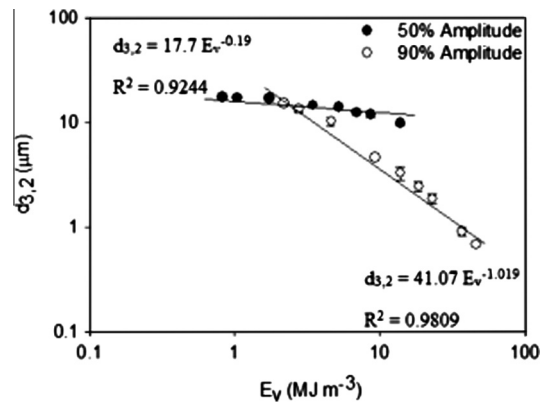


Fig. 9. Effect of energy density (E_v) upon emulsion droplet size ($d_{3,2}$) utilising pilot scale continuous ultrasonic processing (ultrasonic amplitudes of 50% and 90%) for 1.5 wt.% Tween 80 stabilised emulsions.

There is a disparity between the results obtained for the lab scale (*cf.* Fig. 5a and b) and that of the pilot scale predictive models, whereby for the lab scale configurations all fall onto one master curve independent of ultrasonic amplitude, whilst the pilot scale processing exhibits two distinct slopes based on ultrasonic amplitude. This is attributed to the configuration of the pilot scale in comparison to the lab scale setups, whereby the tip of the sonotrode is located 2 cm from the entrance to the chamber (*cf.* Fig. 1). It is therefore possible that the ultrasonic cavitations which instigate emulsification are sufficiently distanced from the entrance to the chamber allowing some elements of pre-emulsion to bypass the acoustic field either partially or

completely. Increasing the ultrasonic amplitude results in the ultrasonic cavitations occurring closer to the entrance of the chamber, allowing for improved emulsification efficiency. Thus, operating at higher acoustic intensities provides more efficient use of acoustic energy for the fabrication of submicron droplets, as is exhibited by the difference in gradients between processing at 50% and 90% amplitudes (cf. Fig. 9). The lab scale continuous configuration is more efficient in size reduction at all amplitudes investigated due to the narrow distance between the tip of the sonotrode and the base of the tee-junction (3 mm) inhibiting the bypassing effect exhibited in the pilot scale configuration, highlighting the importance of adequate ultrasonic processor design for efficient emulsification (Gogate et al., 2011).

4. Conclusions

Ultrasound is capable of forming submicron emulsion droplets at both lab scale (batch and continuous) and pilot scale (continuous). Efficient formation of submicron droplets is achieved at higher ultrasonic amplitudes and lower processing volumes, as acoustic energy is utilised more efficiently in lower processing volumes. Prolonged residence times allow for greater droplet breakup. The timescale of emulsification for continuous processing is milliseconds in comparison to seconds for batch processing, yet submicron emulsions are achieved in both instances due to the intense utilisation of acoustic energy.

Inverse power law models relating emulsion droplet size ($d_{3,2}$) to energy density (E_v) were obtained. These fits were independent of emulsifier concentration (>0.5 wt.%) and ultrasonic amplitude for the lab scale methodologies, whilst the pilot scale continuous configuration is dependent upon the ultrasonic amplitude due to bypassing of pre-emulsion at lower amplitudes. Additionally, the fittings were unable to predict the re-coalescence behaviour exhibited for both emulsifiers at low emulsifier concentrations (i.e. <0.5 wt.%). The high molecular weight biopolymer (i.e. MPI) achieved submicron droplets at a slower rate than that of the low molecular weight surfactant (i.e. Tween 80), owing to the molecular weight differences of proteins in comparison to that of small molecule surfactants.

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