Ultrasound-induced emulsification of subcritical carbon dioxide/water with and without surfactant as a strategy for enhanced mass transport ☆

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A B S T R A C T

Pulsed ultrasound was used to disperse a biphasic mixture of CO_2/H_2O in a 1 dm^3 high-pressure reactor at 30 °C/80 bar. A view cell positioned in-line with the sonic vessel allowed observation of a turbid emulsion which lasted approximately 30 min after ceasing sonication. Within the ultrasound reactor, simultaneous CO_2-continuous and H_2O-continuous environments were identified. The hydrolysis of benzoyl chloride was employed to show that at similar power intensities, comparable initial rates ($1.6 \pm 0.3 \times 10^{-3}$ s^{-1} at 95 W cm^{-2}) were obtained with those reported for a 87 cm^3 reactor ($1.8 \pm 0.2 \times 10^{-3}$ s^{-1} at 105 W cm^{-2}), demonstrating the conservation of the physical effects of ultrasound in high-pressure systems (emulsification induced by the action of acoustic forces near an interface). A comparison of benzoyl chloride hydrolysis rates and benzaldehyde mass transport relative to the non-sonicated, 'silent' cases confirmed that the application of ultrasound achieved reaction rates which were over 200 times faster, by reducing the mass transport resistance between CO_2 and H_2O. The versatility of the system was further demonstrated by ultrasound-induced hydrolysis in the presence of the polysorbate surfactant, Tween, which formed a more uniform CO_2/H_2O emulsion that significantly increased benzoyl chloride hydrolysis rates. Finally, pulse rate was employed as a means of slowing down the rate of hydrolysis, further illustrating how ultrasound can be used as a valuable tool for controlling reactions in CO_2/H_2O solvent mixtures.

1. Introduction

One way of improving the separation between immiscible species following synthetic procedures, is to use a biphasic system involving an organic solvent and an aqueous phase [1,2]. Owing to its low critical point (31.1 °C/73.8 bar) and ease of separation upon depressurisation, subcritical or supercritical CO_2 may be employed usefully as a replacement for the organic phase [3,4]. Moreover, as the solvating power of CO_2 is confined to small, relatively non-polar compounds, the presence of a second aqueous phase can greatly increase the accessibility of hydrophilic species (e.g. salts), that are commonly employed in many organic chemistry reactions. Additionally, the reaction of CO_2 with water leads to the formation of carbonic acid, providing an intrinsic proton source (pH 3–4) [5,6], which may be advantageous for several processes [7].

Due to the presence of a liquid–liquid interfacial barrier, mass transfer rates in biphasic systems may be improved by increasing the interfacial area through the formation of an emulsion [8]. Emulsions of CO_2/H_2O (C/W) have the distinct advantage over conventional organic-phase emulsions of allowing the complete reversal to the biphase upon depressurisation of the system. Furthermore, the droplet size and stability of the emulsion may be controlled by specially-designed surfactant molecules allowing greater fine-tuning of the reaction system [9]. Dispersions of CO_2 and water, as emulsions or microemulsions [10], have been developed for a range of synthetic processes, including hydrogenations [11–14], hydroformylations [15], the synthesis of metal nanoparticles [16], and polymerisations [17]. Due to its favourable properties, *pulsed* ultrasound may also be used to generate emulsions and therefore increase the rate of reactions. Ultrasound may also be considered as a tool for green chemistry, by allowing the use of benign conditions and enhancing energy efficiency [18]. The use of ultrasound in high-pressure systems has been reported for several extraction processes in CO_2 [19–21].

A previous study by Timko et al. investigated the hydrolysis of benzoyl chloride in a CO_2/H_2O biphase under ultrasonication in a reactor of 87.2 cm^3 volume [22]. In the present study, we have designed a 1 dm^3 high-pressure ultrasound reactor and used this

to emulsify a dense CO_2/H_2O solvent system. Scaling up the hydrolysis of benzoyl chloride, we show that the efficiency is not lost at this scale-up factor, highlighting the conservation of the positive physical effects of ultrasound. Emulsion formation and subsequent breakdown was observed by passing the emulsions through a 30 cm^3 view cell and monitoring the change in turbidity over time. The advantages of ultrasound were further demonstrated for the hydrolysis reaction in the presence of Tween 80, a bio-compatible surfactant, able to stabilise a uniform C/W emulsion with estimated surface areas greater than 480 m^2 kg^{-1}. The combined effects of ultrasound and Tween 80 resulted in faster reaction rates than those reported for a pre-formed H_2O in CO_2 (W/C) microemulsion [23], with higher energy efficiency than without the use of surfactant. Overall, the results demonstrate the potential utility of this reactor methodology for industrial applications.

2. Materials and methods

2.1. Reagents

Benzaldehyde (>99%) [100-52-7], benzoyl chloride (>99%) [98-88-4], benzoic acid (>99%) [65-85-0], octane [111-65-9] and polysorbate [9005-65-6] (Tween 80), were purchased from Sigma–Aldrich UK, and used without further purification. Liquid carbon dioxide was obtained from BOC UK, CP grade, and had a given purity of 99.995%.

2.2. System configuration (Fig. 1)

A high-pressure, cylindrical 1 dm^3 stainless-steel vessel (Parr, USA I.D. = 9.5 cm, H = 16 cm) was designed to incorporate an ultrasound probe and manufactured for use in the present study. CO_2 was delivered to the vessel via a high-pressure pump (Thar Instruments), electronically connected to a PC. The amount of CO_2 entering the reactor was recorded via a mass flow meter positioned in-line before the pump. The vessel was insulated by an electric heating jacket, and the temperature was controlled by a temperature controller (Parr 4838) coupled to a J type thermocouple, positioned in an immersed thermowell. The pressure was recorded to within ±0.1 bar using a transducer (Druck PTX 1400; Druck Ltd, Leicester, UK) with dedicated display. Ultrasound was introduced from a 20 kHz VCX-1500W processor (Sonics & Materials, CT, USA), coupled with a titanium alloy horn of tip diameter 2 cm. Tip amplitude (20–100%) was manually selected and related to the energy transferred to the fluid, while the pulse rate could define the ratio of ultrasound ON/ultrasound OFF based on a sonication cycle (e.g. 25%, 1 s ON/3 s OFF). A calibration between delivered and dissipated power was undertaken using the calorimetric method [24]. Power density values reported here (W cm^{-3}) were obtained by dividing the total energy per pulse time (J s^{-1}) by the vessel volume. When comparing vessels of different sizes, power intensity (W cm^{-2}) may also be encountered. Here power intensity values were calculated by dividing the power by the irradiating surface area of the tip. As a consequence of high amplitude settings resulting in a rapid ~3 °C rise in the temperature of the vessel, water cooling was employed to keep the vessel temperature constant during experiments. A dual piston HPLC pump (Jasco PU-2087) with a maximum flow rate of 20 cm^3 min^{-1} was used to recirculate the vessel contents. Connections to the vessel were made by 1/4″ and 1/8″ stainless steel Swagelok tubing, while connections to the pump were made in 1/16″ tubing.

2.3. General method for sonication of the CO_2/H_2O biphase

The vessel was initially heated until the desired temperature (30 °C) was reached. Water was then added to give a volume be-
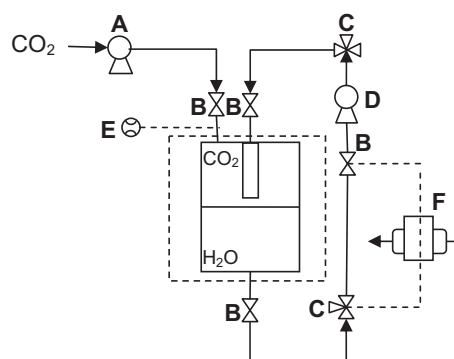

Fig. 1. Schematic showing the experimental setup utilised for sonication of CO_2/H_2O in the 1 dm^3 reactor A: CO_2 pump; B: high-pressure valve; C: 3-way sampling valve; D: circulation pump; E: 6-port valve for injecting compounds into the CO_2 stream; F: bypass of the H_2O recirculating line for visualisation through the 30 cm^3 view cell.

tween 400 and 650 mL. CO_2 was supplied to the sealed vessel at a flow rate of ~40 g min^{-1}, until the desired pressure was reached. Following 30 min of equilibration/recirculation, sonication was initiated and continued for a known time.

2.4. Observation of emulsion stability

A 30 cm^3 high-pressure stainless-steel view cell I.D. = 2.5 cm, H = 5.7 cm (Parr Instruments, Moline, IL, USA) fitted with two in-line sapphire windows (D = 1.5 cm), was used to visualise the dispersion generated in the ultrasound reactor (Fig. 1F), at 30 °C/80 bar. Heating was provided by two electric heating plates connected to a dedicated controller, and monitored by an immersed J type thermocouple. Emulsion stability was assessed by measuring the increase in light intensity (Visilight I-Led) over time, following termination of a 10-min sonication/circulation period. Time-lapse recordings were carried out using a Photron high-speed camera at 10-s time intervals, and the digital images transferred to a PC, using a dedicated interface. The images were analysed with ImageJ for the sum of the greyscale pixel values (integrated density) inside a defined area, and each time-point value divided by the maximum density recorded in the absence of turbidity. Experiments were also performed under conditions above the CO_2 critical point in order to minimise any effect associated with phase transition.

2.5. Compound injection, sampling and analysis

For greater precision, hydrophobic compounds were added to the CO_2 phase via a 6-port valve positioned in-line with the CO_2 feed, and connected by 1/16″ Swagelok tubing. A standard 1 mL bypass loop was used to inject a known amount of each compound. Following equilibration of the reactor contents at 30 °C/70 bar, either benzaldehyde or benzoyl chloride was injected into the flowing CO_2 feed, while final pressurisation to 80 bar was achieved. Aliquots (2 mL) were taken from the recirculating H_2O line at the specified time intervals and analysed immediately by gas chromatography (Shimadzu GC-2010, combined with autosampler and injector AOC-20, and equipped with a DB-5 column and an FID). Four or five aliquots were taken over the course of each experiment at different time points. For the same set of conditions, experiments were repeated three times, generating aggregated data of non-overlapping time points. The final concentration was obtained from a standard calibration line. The H_2O recirculating line originated from a 14-cm 1/4″ stainless steel dip tube immersed in the reactor. The sampling point was therefore positioned 8 cm below the probe tip. Aliquots from the CO_2 phase on the other hand were