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How to design silent control experiments for ultrasound-assisted oil sands extraction and upgrading: A computational study

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ABSTRACT

The major concern in estimating sonochemical yield and efficiency in ultrasound-assisted processes is in defining a "silent" control experiment, without cavitation effects. To estimate the potential benefit of the ultrasonic treatment as compared to conventional heating, we propose that the effects should be compared at the same power input, when the energy in a silent experiment is dissipated as heat. Our calculations of possible temperature increase under the silent conditions for oil sands extraction and upgrading showed necessity of such approach.

1. Introduction

Ultrasonic (US) treatment (UST) in the oil sands extraction and upgrading has drawn considerable attention in the past decade due to the US unique physical and chemical effects originating from cavitation (Mason and Lorimer, 2002; Wayne, 2002; Shedid, 2004; Abramov et al., 2009; Matouq et al., 2009; Mello et al., 2009; Ye et al., 2010; Dai et al., 2011; Zhao et al., 2011). The hot-spot theory is the widest accepted theory explaining the effects of acoustic cavitation (Mason, 1991). Theoretical calculations of adiabatic bubble collapse indicate that temperatures of 4200 K and pressures of 975 atm (depending on the conditions) may be reached within the bubble at the moment of collapse (Mason and Peters, 2002). Stable bubbles containing mainly gas and some vapour oscillate for many acoustic cycles, during which, in contrast with the transient bubbles, mass and heat transfer may occur. US chemical effects have been widely discussed in the literature as well (Mason, 1991; Crum et al., 1999; Suslick et al., 1999; Mason and Lorimer, 2002; Mason and Peters, 2002), where a cavitation bubble is considered as a microreactor with four possible reaction sites: hot gas phase inside the bubble, liquid shell around the bubble, liquid medium surrounding the bubble and liquid droplets inside the bubble. The generation of radicals at hot spots and occurring radical reactions is the most commonly used explanation of sonochemical effects of ultrasound (Lorimer et al., 1991).

The ultrasonic system transforms electrical power into mechanical energy, which is transmitted to the sonicated medium. Part of it is lost to produce heat, and another part produces cavitation, but not all the cavitation energy produces chemical and physical effects. Some energy is reflected and some is consumed in sound re-emission. The sonochemical yield SY may be defined then as the ratio of the measured effect to the input power in Watts (Mason, 1991). For chemical reactions, it is important to know whether the use of ultrasound can improve the reaction yield, for which sonochemical enhancement SE can be calculated as the ratio of the product yield with sonication to the product yield without sonication (Mason and Peters, 2002). Great care must be taken in the definition of what constitutes the control or "silent" reaction. Mason and Peters (2002) proposed that the reference should be submitted to stirring precisely under the same conditions and medium composition, but in the absence of sonication (Mason and Peters, 2002). Magnetic stirrers, in this case, may not fulfill the requirement as they can produce hydrodynamic cavitation. Moreover, heating of a sonicated medium is a common phenomena during UST. Calorimetric efficiency of ultrasonic equipment (defined as energy dissipated as heat per power input) can vary from as low as 2% (Sawarkar et al., 2009) to as high as 53% (Semagina et al., 2000). For example, in the latter case 25 mL of water–ethanol solution was heated from 26 °C to 70 °C after only 7 min of UST (Semagina et al., 2000).

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Clearly, ensuring adequate stirring in the control experiments is necessary, but not sufficient to compare sonochemical efficiency and yield of the reactions and other processes (e.g., extraction) occurring under UST and without it, since both the reaction rate and extraction efficiency increase with increasing temperatures. Some studies do attempt to eliminate the temperature influence by cooling the sonicated medium, however, when a cavitation bubble collapses, temperatures of several thousand K are generated, resulting in radical formation and high reaction rates. The sonicated medium cannot be considered spatially uniform and isothermal on a micro level with temperature gradients of several thousand K, which obstructs comparison of the reaction or extraction yields between the reactions without and with UST.

Unfortunately, data on silent control experiments are not always reported in publications and patents on the use of ultrasound for extraction and upgrading of bitumen and oil fractions; and the UST effect is most often evaluated based on the properties of the raw material. Only small fraction of the reported studies uses stirring in control experiments without UST. Providing adequate stirring is an important issue due to mass transfer problems, e.g. in dimethyldibenzothiophene oxidative desulfurization even under ultrasound the process was found to be diffusion-limited (Kim et al., 2001).

Very few studies include both stirring in control experiments and temperature control/measurement. Positive acoustic effect was found when the same temperatures were used for the control and acoustic experiments, e.g., (Kang et al., 2006; Yang et al., 2009). In contrast, when crude oil rheology was studied after UST and compared to the oil treated at the same temperatures, UST was claimed not to alter the crude oil rheology as a function of temperature (Gunal and Islam, 2000). A representative study of heavy oil upgrading under UST (Gopinath et al., 2006) revealed that the temperature of the sonicated medium increased by 50 °C from the room temperature. For sure, the observed changes in the oil composition would not arise if the oil was simply heated by 50 °C, but the reactions must have occurred due to hot spots forming at the cavitation bubble collapse.

With the above discussed difficulties of finding appropriate conditions for "silent" control experiments, we propose that the fair control experiments should be performed under adequate non-magnetic stirring with such heating that the amount the energy introduced under the silent conditions is the same as the energy introduced during UST. The amount of energy under silent condition will not produce the same local temperatures, and it will likely result in a higher mean temperature, but this approach seems more viable from the viewpoint of estimating the advantage of the use of ultrasonic treatment vs. traditional stirring and heating using the same amount of introduced energy. As a quantitative proof of the necessity to redefine the "silent" control experiment as the one with the same energy input as during the acoustic experiments, below we show several examples of heat transfer calculations, assuming that the introduced US energy is 100% dissipated as heat, based on the reported data for oil sands extraction and upgrading (Gopinath et al., 2006; Okawa et al., 2010). The two cases were selected arbitrarily, only with the purpose of obtaining reasonable, experimentally applicable conditions to be used for the computation. The objective is to estimate the sample temperature rise and the pure thermal effect, if the acoustic energy were introduced as heat from conventional sources.

2. Computational methods

Heat transfer calculations for the amount of introduced power were performed using numerical integration for the reported experimental results in oil sands extraction (Okawa et al., 2010) and upgrading (Gopinath et al., 2006). The assumptions are the following: 100% energy dissipation as heat; atmospheric pressure; no phase changes for bitumen and heavy gas oil, but water vaporization was approximated by keeping the sample temperature constant during vaporization; absence of chemical reactions with the temperature rise. These assumptions are clearly oversimplified but the magnitude of obtained values may indicate the validity of our hypothesis.

To estimate maximum sample temperature, Eq. (1) was integrated over the given period

$$(mC_P)_{eff}\int_{t_i}^{t_f} dT/dt = Q \tag{1}$$

where m=sample mass in kg, C_p=thermal heat capacity in J/kg K, T=temperature in K, t=time in s, and Q=thermal power input in W. Using Euler Explicit time discretization, each new time level i was calculated as

$$T_i = T_{i+1} + (\ Q/(mC_P)_{eff})_{i-1}\Delta t \tag{2}$$

The effective thermal capacity was found as mass balanced contribution of the components, using temperature dependent formulas given in Cengel (2002) and Gray and Masliyah (2005). The specific heat formulas based on T^{-2} were required to avoid negative values of C_p at high temperatures. The oil sands heat capacity was determined based on 14 wt% bitumen content, using specific heats of bitumen and Athabasca coarse solids, mostly $SiO_2 \gg 44$ μm (Gray and Masliyah, 2005). The specific heats of the solids were calculated in J/kg K as

$$C_P = 168 + 2442\times10^{-3}T - 1611\times10^{-6}T^2 \tag{3}$$

$$\text{or } C_P = 914 + 331\times10^{-3}T - 2415\times10^{4}T^{-2} \quad \text{for } 300 < T < 700\ \text{K} \tag{4}$$

The specific heat for bitumen was calculated as (Gray and Masliyah, 2005)

$$C_P = 55 + 6818\times10^{-3}T - 4464\times10^{-6}T^2 \tag{5}$$

$$\text{or } C_P = 1763 + 1542\times10^{-3}T - 4884\times10^{4}T^{-2} \quad \text{for } 300 < T < 600\ \text{K} \tag{6}$$

Water vaporization was approximated by keeping the sample temperature constant during vaporization and calculating the fraction vaporized with

$$x = m_{vapour}/m_{water} = \Sigma Q\Delta t/(h_{fg}m_{water}) \tag{7}$$

where h_{fg}=enthalpy of vaporization in J/kg. After all water vaporized, the calculation continued with specific heat of water vapour. All calculations were performed using Matlab™ and GNU Octave.

3. Results and discussion

3.1. Case 1: extraction (Okawa et al., 2010)

Okawa et al. (2010) compared bitumen extraction from Alberta oil sands treated with 28 kHz and 200 kHz ultrasound (US) (200 W), with the extraction assisted by a mechanical stirrer (750 rpm). The samples, 2.97 g of oil sand, .03 g NaOH, 60 mL of water, were sonicated for 15 min under a hot water flow in the reactor jacket (45 °C and 75 °C). Sonication at 28 kHz for both conditions resulted in very similar bitumen recovery, ~5–8 wt%, as compared to ~1 wt% with a mechanical stirrer at 75 °C. The study does not report the temperature rise in the reactor during sonication, and the reactor is unlikely to be isothermal as no