



## Efficient H<sub>2</sub>O<sub>2</sub>/CH<sub>3</sub>COOH oxidative desulfurization/denitrification of liquid fuels in sonochemical flow-reactors



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### ABSTRACT

The oxidative desulfurization/denitrification of liquid fuels has been widely investigated as an alternative or complement to common catalytic hydrorefining. In this process, all oxidation reactions occur in the heterogeneous phase (the oil and the polar phase containing the oxidant) and therefore the optimization of mass and heat transfer is of crucial importance to enhancing the oxidation rate. This goal can be achieved by performing the reaction in suitable ultrasound (US) reactors. In fact, flow and loop US reactors stand out above classic batch US reactors thanks to their greater efficiency and flexibility as well as lower energy consumption. This paper describes an efficient sonochemical oxidation with H<sub>2</sub>O<sub>2</sub>/CH<sub>3</sub>COOH at flow rates ranging from 60 to 800 ml/min of both a model compound, dibenzothiophene (DBT), and of a mild hydro-treated diesel feedstock. Four different commercially available US loop reactors (single and multi-probe) were tested, two of which were developed in the authors' laboratory. Full DBT oxidation and efficient diesel feedstock desulfurization/denitrification were observed after the separation of the polar oxidized S/N-containing compounds (S ≤ 5 ppmw, N ≤ 1 ppmw). Our studies confirm that high-throughput US applications benefit greatly from flow-reactors.

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### 1. Introduction and background

Economics, industrial competitiveness, demand and regulatory constraints have driven the development of greener reaction paths and the intensification of chemical processes to the point where it has become a key research area and one that has widely exploited non-conventional energy sources such as power ultrasound (US) [1,2]. The collapse of cavitation bubbles generates a host of physical and chemical phenomena which are particularly evident in heterogeneous systems in which liquid microjets disperse and break up particles and droplets. In recent years, chemistry in flowing systems and often in loop reactors, has become more prominent as a method of carrying out chemical transformations as it can easily be scaled up to kilogram-scale. The design and optimization of sonochemical flow apparatuses are not trivial tasks. Typical flow systems have been applied in sonocrystallization [3], water treatment processes [4] and in the production of biodiesel [5]. An increase in reactor volume leads to a simultaneous increase in the ultrasonic power needed to maintain the same power density and owing to the power limitation of each single transducer, a

large-scale reactor requires several ultrasonic transducers [6]. Apart from the fundamental technical parameters studied by physicists and engineers, one of the main limitations in the scale up of this equipment is the energy consumption. This problem was encountered when a scale up of water decontamination processes that gave outstanding results in the laboratory was attempted [7,8]. Sonochemical flow processes involving a fluidic biphasic system strongly improve heat and mass transfer as well as the control of temperature, pressure and concentration. The present work illustrates the use of four different sonochemical flow-reactors for the intensification of oxidative desulfurization/denitrification of liquid fuels.

There is a stringent need for new methods of reducing the sulfur and nitrogen content in fuel oils in order to satisfy upcoming legislation that will limit their content ever more drastically. Since 2006, almost all of the petroleum-based diesel fuel available in Europe and North America is of ultra-low-sulfur diesel (ULSD) type.

To achieve these goals with current hydrodesulfurization (HDS) technology, the use of higher temperature, higher pressure, larger reactor volume and more active catalysts (Co–Mo or Ni–Mo sulfide alumina) is indispensable but costly. Nevertheless, some refractory S-compounds in diesel, mainly dibenzothiophene (DBT) alkyl

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derivatives, are very difficult to remove even under harsh hydrodesulfurization conditions [9]. Of the new strategies developed, oxidative desulfurization (ODS) and denitrification (ODN) appear to be particularly promising [10]. In such processes, S-compounds are oxidized into sulfones that can be subsequently easily removed by conventional separation operations (solvent extraction, adsorption, distillation etc.) because they are much more polar than the hydrocarbons that constitute most of the fuel oils. [11].

Although these processes are widely described and discussed in scientific and patent literature, technical hurdles caused by the high volumes of reagent solution and solvents have hampered a cost effective application [10].

The US-assisted oxidative desulfurization has been thoroughly investigated and compared with silent conditions under efficient stirring or mixing [11,12]. In a previous study some of the authors showed a specific ODS enhancement due to the sonochemical effect [13]. The reaction with peroxyacid generated *in situ* by hydrogen peroxide and acetic acid, was performed both under US (20 kHz) and under high-speed stirring (HSS) (7000, 12,000 and 16,000 rpm). Having all parameters constant the higher efficiency of US was evident: 95% desulfurization after only 9 min (US) vs 70% even after more than 30 min (HSS).

In general the bottlenecks encountered in batch processes require for scaling up the development of automated flow processes by means of fixed-bed flow-reactors [14], microreactors [15] or flow sonochemical reactors [16] followed by simple extraction to remove the oxidized material and residual reagents.

## 2. Experimental

### 2.1. Materials and methods

All reagents and solvents were purchased from Sigma–Aldrich – Italy. The liquid fuel sample was provided by Petrobras – Brazil. It is a hydrotreated diesel feedstock, (S and N content 241 ppmw – part per million by weight – and 161 ppmw, respectively).

Silica gel 60 (0.063–0.200 mm) for column chromatography was purchased from Merck.

Sulfur and nitrogen elemental analyses were performed in the Multi EA<sup>®</sup> 5000 Analytik Jena – Germany, in accordance with national and international standards (ASTM D 5453 and D 4629). The treated samples were analyzed by GC–MS (gas-chromatograph Agilent 6890 with mass detector Agilent Network 5973). A mechanical stirrer model MA 102 by Marconi, Piracicaba, Brazil, was used for tests under high speed stirring.

### 2.2. Sonochemical flow-reactors

In this piece of work, we performed the oxidation reactions in four different sonochemical flow-reactors in which a peristaltic pump (Masterflex L/S Digital Drive, power 70 W) circulated the two-phase (liquid/liquid) reacting mixture in systems “a”, “b” and “c”. Mixing in system “d” was performed by a multi-channel peristaltic pump (Gilson<sup>®</sup> Minipuls 3, France).

- The Sonitube<sup>®</sup> (Synetude – Chambéry, France) a US-reactor with a classic “T” shape in a slanting, 45° position and one transducer working at 35 kHz, volume 70 ml (Fig. 1).
- A cup-horn like emitting plate (Danacamerini – Torino, Italy), a flow US-reactor made up of three transducers (21.5 kHz) lodged in the bottom of the chamber and cemented to a titanium alloy plate (100 × 325 × 0.9 mm), volume 400 ml (Fig. 2).
- A 4-horn horizontal flow-reactor (Danacamerini – Torino, Italy), where a digital generator drives four transducers (21.0 ± 0.06 kHz), volume 350 ml (Fig. 3).

- A single horn flow system (Sonics & Materials Newtown, USA), working at 20 kHz and 750 W in a stainless steel reactor with a 40 ml volume (Fig. 4).

### 2.3. General procedures

#### 2.3.1. Oxidation of DBT solution

A DBT solution (0.5 mg/ml in toluene) was oxidized with hydrogen peroxide (35 wt.%) and glacial acetic acid. Two molar ratios S:H<sub>2</sub>O<sub>2</sub>:CH<sub>3</sub>COOH were tested: (1) = 1:28:557 and (2) = 1:56:1114. The liquid/liquid mixture was circulated through the different US reactors by a peristaltic pump. Samples were taken every 10 min, up to 90 min of irradiation time. The reaction mixture was recovered in a separating funnel. The organic phase (10 ml) was washed with water (3 × 10 ml) and with a brine solution (3 × 10 ml), then dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered on paper and analyzed by GC–MS.

#### 2.3.2. Oxidation of diesel samples

Diesel samples were oxidized with a solution of hydrogen peroxide (35 wt.%) and glacial acetic acid. The molar ratio S + N:H<sub>2</sub>O<sub>2</sub>:CH<sub>3</sub>COOH was 1:56:1114 and the liquid/liquid mixture was circulated by the peristaltic pump. The reaction mixture was recovered in a separating funnel and an aliquot of the diesel sample (10 ml) was washed with water (3 × 10 ml) and then purified either by filtration on a silica gel cartridge [silica (3 g)/diesel (5 ml)] or by liquid–liquid extraction with MeOH (1:1 v/v). The recovered sample was analyzed for total S and N content using an elemental analyzer.

### 2.4. (a) Sonitube<sup>®</sup>

A loop flow rate of 130 ml/min was used for 80 min, at 80 °C and the average power was 200 W. The reactions were monitored every 10 min for sulfur and nitrogen content. The DBT solution in toluene (425 ml) was oxidized with a mixture of H<sub>2</sub>O<sub>2</sub> (5.71 ml) and CH<sub>3</sub>COOH (73 ml). The diesel sample (300 ml) was oxidized with a mixture of H<sub>2</sub>O<sub>2</sub> (25.5 ml) and glacial acetic acid (325 ml).

The total energy consumption for the sonication protocol in the Sonitube<sup>®</sup> [H<sub>2</sub>O<sub>2</sub> (25.5 ml), CH<sub>3</sub>COOH (325 ml), diesel (300 ml)] is the sum of four components:

(I) The energy to heat the hydrogen peroxide (0.0255 l) from 20 °C to 80 °C (dT = 60 K).

$$L = Cs \cdot m \cdot dT = 2620 \text{ (J/kg K)} \cdot 0.0255 \text{ (l)} \cdot 1.48 \text{ (kg/l)} \cdot 60 \text{ (K)} = 5.93 \text{ kJ} = 1.64 \text{ W (1 W = 3.6 kJ)}$$

(II) The energy to heat the glacial acetic acid (0.325 l) from 20 °C to 80 °C (dT = 60 K).

$$L = Cs \cdot m \cdot dT = 2053 \text{ (J/kg K)} \cdot 0.325 \text{ (l)} \cdot 1.05 \text{ (kg/L)} \cdot 60 \text{ (K)} = 42.03 \text{ kJ} = 11.67 \text{ W (1 W = 3.6 kJ)}$$

(III) The energy to heat the diesel (0.300 l) from 20 °C to 80 °C (dT = 60 K).  $L = Cs \cdot m \cdot dT = 2130 \text{ (J/kg K)} \cdot 0.300 \text{ (l)} \cdot 0.8658 \text{ (kg/l)} \cdot 60 \text{ (K)} = 33.19 \text{ kJ} = 9.22 \text{ W (1 W = 3.6 kJ)}$ .

(IV) The energy to sonicate the mixture for 1 h at 170 W was:  
 $L = P \cdot t = 170 \text{ W} \cdot 1 \text{ h} = 170 \text{ W}$ .

The overall energy consumption of the process was 192.53 W.

### 2.5. (b) Cup-horn like emitting plate

A loop flow rate of 400 ml/min was used for 80 min, at 80 °C and the average power was 400 W. The reaction was monitored every 10 min for sulfur and nitrogen content. The DBT solution in toluene (850 ml) was oxidized with a mixture of H<sub>2</sub>O<sub>2</sub> (11.42 ml) and CH<sub>3</sub>COOH (146 ml). The diesel sample (600 ml) was oxidized with a mixture of H<sub>2</sub>O<sub>2</sub> (51 ml) and CH<sub>3</sub>COOH (650 ml).

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