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Efficient H₂O₂/CH₃COOH 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 H₂O₂/CH₃COOH 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 ppm, N ≤ 1 ppm). Our studies confirm that high-throughput US applications benefit greatly from flow-reactors.

Keywords: Ultrasound flow-reactors; Clean fuels; Oxidative desulfurization; Oxidative denitrification; Green technology

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, the last few hundred ppm of *S*-compounds in diesel, mainly dibenzothiophene (DBT) alkyl 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) (7,000, 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 stock, (S and N content 241 ppm and 161 ppm 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[®] 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 (gaschromatograph Agilent 6890 with mass detector Agilent Network 5973).

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[®] Multipuls 3, <http://www.gilson.com>, France).

a) The Sonotube[®] (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 (Figure 1).

- b)** 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 x 325 x 0.9 mm), volume 400 ml (Figure 2).
- c)** A 4-horn horizontal flow-reactor (Danacamerini – Torino, Italy), where a digital generator drives four transducers (21.0 ± 0.06 kHz), volume 350 ml (Figure 3).
- d)** A single horn flow system (Sonics and Materials - USA), working at 20 kHz and 750 W in a stainless steel reactor with a 40 ml volume (Figure 4).

Figures 1-4.

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:H₂O₂:CH₃COOH 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. Analytical 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 (3x10 ml) and with a brine solution (3x10 ml), then dried with anhydrous Na₂SO₄, 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:H₂O₂:CH₃COOH 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 (3x10 ml) and then purified either by filtration on a silica gel cartridge [silica (3 g)/diesel (5ml)] 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) Sonotube®

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 minutes for sulfur and nitrogen content. The DBT solution in toluene

(425 ml) was oxidized with a mixture of H₂O₂ (5.71 ml) and CH₃COOH (73 ml). The diesel sample (300 ml) was oxidized with a mixture of H₂O₂ (25.5 ml) and glacial acetic acid (325 ml).

The total energy consumption for the sonication protocol in the Sonotube[®] [H₂O₂ (25.5 ml), CH₃COOH (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).

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

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

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

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

(IV) The energy to sonicate the mixture for 1 h at 170 W was:

$$L = P \cdot t = 170 \text{ W} \cdot 1 \text{ h} = 170 \text{ Wh}.$$

The overall energy consumption of the process was 192.53 Wh.

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 H₂O₂ (11.42 ml) and CH₃COOH (146 ml). The diesel sample (600 ml) was oxidized with a mixture of H₂O₂ (51 ml) and CH₃COOH (650 ml).

The total energy consumption for the emitting plate sonication protocol [H₂O₂ (51 ml), CH₃COOH (650 ml), diesel (600 ml)] is the sum of four components:

(I) The energy to heat the hydrogen peroxide (0.051 l) from 20 °C to 80 °C (dT = 60 K).

$$L = C_s \cdot m \cdot dT = 2620 \text{ (J/kg K)} \cdot 0.051 \text{ (l)} \cdot 1.48 \text{ (kg/l)} \cdot 60 \text{ (K)} = 11.86 \text{ kJ} = 3.29 \text{ Wh (1 Wh = 3.6 kJ)}.$$

(II) The energy to heat the glacial acetic acid (0.650 l) from 20 °C to 80 °C (dT = 45 K).

$$L = C_s \cdot m \cdot dT = 2053 \text{ (J/kg K)} \cdot 0.650 \text{ (l)} \cdot 1.05 \text{ (kg/L)} \cdot 60 \text{ (K)} = 84.07 \text{ kJ} = 23.35 \text{ Wh (1 Wh = 3.6 kJ)}.$$

(III) The energy to heat the diesel (0.600 l) from 20 °C to 80 °C (dT = 45 K).

$$L = C_s \cdot m \cdot dT = 2130 \text{ (J/kg K)} \cdot 0.600 \text{ (l)} \cdot 0.8658 \text{ (kg/l)} \cdot 60 \text{ (K)} = 66.39 \text{ kJ} = 18.44 \text{ Wh (1 Wh = 3.6 kJ)}.$$

(IV) The energy to sonicate the mixture for 1 h at 380 W was:

$$L = P \cdot t = 380 \text{ W} \cdot 1 \text{ h} = 380 \text{ Wh}.$$

The overall energy consumption of the process was 425.08 Wh.

2.6. c) Multi-horn reactor

Exactly the same conditions, volumes, power and flow rates as 2.5 were used.

The total energy consumption for the multi-horn sonication protocol [H_2O_2 (51 ml), CH_3COOH (650 ml), diesel (600 ml)] is the sum of four components:

(I) The energy to heat the hydrogen peroxide (0.051 l) from 20 °C to 80 °C ($dT = 60$ K).

$$L = C_s \cdot m \cdot dT = 2620 \text{ (J/kg K)} \cdot 0.051 \text{ (l)} \cdot 1.48 \text{ (kg/l)} \cdot 60 \text{ (K)} = 11.86 \text{ kJ} = 3.29 \text{ Wh (1 Wh = 3.6 kJ)}.$$

(II) The energy to heat the glacial acetic acid (0.650 l) from 20 °C to 80 °C ($dT = 45$ K).

$$L = C_s \cdot m \cdot dT = 2053 \text{ (J/kg K)} \cdot 0.650 \text{ (l)} \cdot 1.05 \text{ (kg/L)} \cdot 60 \text{ (K)} = 84.07 \text{ kJ} = 23.35 \text{ Wh (1 Wh = 3.6 kJ)}.$$

(III) The energy to heat the diesel (0.600 l) from 20 °C to 80 °C ($dT = 45$ K).

$$L = C_s \cdot m \cdot dT = 2130 \text{ (J/kg K)} \cdot 0.600 \text{ (l)} \cdot 0.8658 \text{ (kg/l)} \cdot 60 \text{ (K)} = 66.39 \text{ kJ} = 18.44 \text{ Wh (1 Wh = 3.6 kJ)}.$$

(IV) The energy to sonicate the mixture for 1 h at 750 W was:

$$L = P \cdot t = 750 \text{ W} \cdot 1 \text{ h} = 750 \text{ Wh}.$$

The overall energy consumption of the process was 795.08 Wh.

2.7. d) Single horn flow system

A loop flow rate of 60 ml/min was used for 80 min at 80 °C. An aliquot of the reaction mixture was collected every 10 min for sulfur and nitrogen content monitoring. The DBT solution in toluene (425 ml) was oxidized with a mixture of H_2O_2 (5.71 ml) and CH_3COOH (73 ml). The diesel sample (300 ml) was oxidized with a mixture of H_2O_2 (25.5 ml) and CH_3COOH (325 ml).

The total energy consumption for the single-horn sonication protocol [H_2O_2 (25.5 ml), CH_3COOH (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).

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

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

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

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

(IV) The energy to sonicate the mixture for 1 h at 31 W was:

$$L = P \cdot t = 31 \text{ W} \cdot 1 \text{ h} = 31 \text{ Wh}.$$

The overall energy consumption of the process was 53.53 Wh.

3. Results and discussion

The synergistic combination afforded by the simultaneous application of continuous flow processing and US technologies tools will enhance the synthetic capabilities of tomorrow's chemists still further.

However, significant technological problems are encountered in attempting to scale beyond these modest levels, especially when moving towards production scales.

The design of reliable reactors for an efficient scale up of sonochemical process is a key requirement for practical applications in sonochemistry. This study shows that only accurate experimental investigation enables an optimal set up to be found. Optimal mass transfer rates and uniform liquid/liquid mixture distributions may be achieved via the combination of a suitable flow system and liquid microjet producing acoustic cavitation.

Hydrogen peroxide and acetic acid were used to obtain a peroxyacid which acts as the reactive oxidant in this flow US oxidation of the undesirable *S*-compounds in diesel. The oxidative protocol was first developed on a model solution of DBT and after that was applied to the diesel sample. Table 1 shows the results of DBT oxidation performed in the Sonotube[®] loop reactor (inclined 45°, working at 35 kHz) using two different oxidant molar ratios S:H₂O₂:CH₃COOH : 1:28:557 and 1:56:1114. The latter enables good conversion in 1 hour and was used in a series of experiments with the aim of comparing different US loop reactors (table 1, fig. 1). All US devices (fig. US devices) gave at least 80% DBTO₂ conversion in 80 min. Once more, with sonochemical flow-reactors we could confirm the promoting effect of US on ODS. The same oxidation procedure used for DBT solution (2.3.1) was performed with a high-speed stirrer (6,000 and 9,000 rpm) in a thermostatted bath at 80°C, in which the horn was replaced by a mechanical mixer. In all cases the conversion yields were lower than 45%.

Table 1. DBT oxidation with H₂O₂:CH₃COOH in the four different US loop reactors.

US flow-reactor	Conversion (%) ^(a, b)							
	(c) 5	28	34	36	38	40	42	42
Sonotube [®]	7	25	51	71	85	96	100	100
	0	2	8	20	43	67	83	89
Emitting plate	0	4	7	20	35	58	73	82
Multi-horn	3	21	46	66	78	86	88	91
Single horn	10	20	30	40	50	60	70	80
Time (min)								

^a DBTO + DBTO₂ (determined by GC-MS analysis)

^b Molar ratio (S:H₂O₂:CH₃COOH) = 1:56:1114

^c Molar ratio (S:H₂O₂:CH₃COOH) = 1:28:557

Figure 5.

This protocol was also applied to semi-continuous diesel oxidation to achieve low sulfur and nitrogen content. Excellent results were achieved in the oxidation of diesel feedstock with efficient desulfurization/denitrification after the removal of the polar oxidized products by filtration on a silica cartridge (table 2) or by MeOH washing (table 3). Diesel mass loss was evaluated for both procedures (< 14% silica gel, < 4% MeOH). Best results were obtained when the adsorption of the oxidized sulfur and nitrogen compounds was performed over silica gel at ambient temperature (table 2).

Furthermore, a continuous experiment using these optimal parameters was performed to determine the adsorbent breakdown point at which the material is saturated and can no longer adsorb oxidized molecules (i.e. determination of the maximal quantity of feed that can be efficiently treated with a given quantity of adsorbent). The total sulfur content in the diesel oil was easily decreased after oxidation/adsorption to less than 5 ppm using peracetic acid, generated in situ with hydrogen peroxide, and a feedstock to adsorbent ratio of less than 2, in only 10 min. This value of 5 ppm is much lower than the maximum sulfur content that will be imposed by international legislation. In other words, acceptable desulfurization levels can be maintained even in the face of the strictest regulations [17]. A thorough process analysis highlights that the Sonotube[®] reactor offer the best compromise between performance and energy consumption.

Table 2. Residual N and S content in diesel feedstock after oxidation in the four different US loop reactors and after silica gel filtration. ($X \pm n$; n=3). (Feedstock diesel: N=161 \pm 0.54 ppm; S=241 \pm 0.33 ppm).

Time (min.)	N residual (ppm)*				S residual (ppm)*			
	Sonotube	Emitting plate	Multi-horn	Single horn	Sonotube	Emitting plate	Multi-horn	Single horn
10	4.48 \pm 0.82	2.01 \pm 0.14	2.28 \pm 0.13	1.60 \pm 0.09	4.89 \pm 2.64	3.21 \pm 0.52	4.87 \pm 0.62	3.03 \pm 0.26
20	4.04 \pm 1.25	1.44 \pm 0.11	2.25 \pm 0.14	0.68 \pm 0.05	4.02 \pm 0.36	1.78 \pm 0.17	4.74 \pm 0.19	0.86 \pm 0.06
30	3.11 \pm 0.18	1.07 \pm 0.16	2.22 \pm 0.18	0.86 \pm 0.08	2.22 \pm 0.41	1.66 \pm 0.65	4.74 \pm 0.45	0.28 \pm 0.03
40	2.74 \pm 0.29	1.06 \pm 0.06	2.13 \pm 0.31	0.53 \pm 0.05	1.64 \pm 0.44	1.42 \pm 0.22	4.30 \pm 0.27	0.13 \pm 0.02
50	1.80 \pm 0.34	1.04 \pm 0.12	2.07 \pm 0.54	0.55 \pm 0.04	1.64 \pm 0.33	1.25 \pm 0.45	3.98 \pm 0.43	< 0.1
60	1.71 \pm 0.03	1.03 \pm 0.07	2.07 \pm 0.25	0.50 \pm 0.04	1.55 \pm 0.12	1.03 \pm 0.13	3.44 \pm 0.32	< 0.1
70	1.65 \pm 0.11	1.03 \pm 0.15	1.95 \pm 0.19	0.67 \pm 0.05	1.44 \pm 0.46	0.83 \pm 0.36	3.44 \pm 0.39	< 0.1
80	1.62 \pm 0.27	1.02 \pm 0.23	1.82 \pm 0.16	0.54 \pm 0.03	0.64 \pm 0.19	0.64 \pm 0.05	3.30 \pm 0.10	< 0.1

* Mass loss (diesel) less than 14%.

Table 3. Residual N and S content in diesel feedstock after oxidation in the four different US loop reactors and after MeOH extraction. ($X \pm n$; n=3). (Feedstock diesel: N=161 \pm 0.54 ppm; S=241 \pm 0.33 ppm).

Time (min.)	N residual (ppm)*				S residual (ppm)*			
	Sonotube	Emitting plate	Multi-horn	Single horn	Sonotube	Emitting plate	Multi-horn	Single horn

10	21.52 ± 0.25	31.45 ± 0.35	21.16 ± 0.34	12.34 ± 0.64	67.64 ± 0.25	54.90 ± 1.56	83.58 ± 0.28	33.95 ± 1.17
20	10.28 ± 0.20	24.86 ± 0.16	20.92 ± 0.52	11.98 ± 0.83	33.17 ± 3.21	46.15 ± 2.48	79.24 ± 0.32	33.10 ± 0.90
30	7.67 ± 0.09	21.16 ± 0.12	20.32 ± 0.28	10.69 ± 0.75	32.55 ± 0.95	35.14 ± 1.22	74.22 ± 0.59	31.97 ± 1.13
40	7.20 ± 0.39	15.28 ± 0.24	19.75 ± 0.19	9.26 ± 0.62	32.32 ± 0.39	30.76 ± 0.67	68.93 ± 0.18	32.39 ± 0.86
50	7.17 ± 0.14	12.44 ± 0.04	19.75 ± 0.47	8.22 ± 0.60	31.83 ± 0.22	26.06 ± 2.03	66.47 ± 0.37	33.32 ± 1.12
60	7.09 ± 0.36	6.94 ± 0.19	18.83 ± 0.35	7.13 ± 0.72	31.61 ± 0.23	23.03 ± 1.60	63.42 ± 0.49	31.06 ± 0.92
70	7.06 ± 0.06	5.17 ± 0.36	18.73 ± 0.17	6.80 ± 0.49	31.44 ± 0.48	21.54 ± 2.22	59.81 ± 0.24	31.11 ± 1.50
80	7.03 ± 0.39	4.18 ± 0.71	17.37 ± 0.49	6.66 ± 0.57	31.16 ± 0.15	18.90 ± 0.98	58.45 ± 0.15	32.87 ± 1.13

* Mass loss (diesel) less than 4%.

Figure 6.

4. Conclusion

The application of US to chemical process intensification hinges on the development of large-scale multiple transducer sonochemical reactors which can operate in loop mode. We have developed an efficient flow process for the oxidative desulfurization/denitrification of liquid fuels in high-power sonochemical reactors using H₂O₂/CH₃COOH as the oxidant. Although this protocol is superior than any other batch process, a general drawback of two-phase ODS and ODN is the remarkable mass loss encountered in lab scale, which currently makes this approach uncompetitive compared to classic catalytic hydrorefining. Nevertheless, the experimental process proposed in the present study appears to be an excellent solution to the future environmental challenges that will soon be imposed by the new regulations. Indeed, it is possible to decrease the sulfur and the nitrogen contents of diesel down to values of lower than 5 and 1 ppm respectively, which is quite remarkable. In addition, we are now aiming at further improving the present process in order to reduce the mass loss and achieve final S concentrations of less than 1 ppm and current results are extremely encouraging.

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