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Ultrasound assisted oxidative desulfurization of marine fuels on MoO₃/Al₂O₃ catalyst.

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Abstract

Oxidative desulfurization (ODS) was applied to three marine fuels with viscosities between 380 and 700 cSt (centistokes) and sulfur contents between 0.79 and 3.27 wt.%, using a MoO₃/Al₂O₃ catalyst. H₂O₂ was chosen as oxidizing agent with a low oxidant to sulfur ratio of 3, for economic and environmental reasons. Global sulfur removal was obtained after extraction of sulfones by dimethylformamide. Oxidation efficiency was evaluated by monitoring the conversion of alkyl-benzothiophenes and dibenzothiophene molecule by gas chromatography (GC) with a sulfur specific detector. Applying ultrasounds prior to oxidation was found to significantly enhance conversions and sulfur removal, the effect being more pronounced when initial efficiency was low, that is for more refractory molecules and heavier fuels. Ultrasound assisted ODS (UAOD) was effective on raw fuels with initial viscosity below 700 cSt. Indeed, dilution decreased the viscosity of the fuels, allowing reaction to be effective even on initially very heavy fuels. The presence of asphaltenes dissolved or precipitated in the feed did not affect the conversion of Cx-BTs and DBT significantly, with only slight variations of global sulfur removal rates. Global desulfurization rates between 60 and 80% were obtained, clearly showing the efficiency of UAOD applied to complex matrices such as marine fuels.

Keywords: Oxidative desulfurization, marine fuels, ultrasounds, extraction

1 Introduction

Stricter environmental regulations for transportation fuels, including marine fuels, have been implemented, particularly regarding their sulfur content. In 2015, the International Maritime Organization (IMO) announced in MARPOL Annex VI a reduction of the maximum permitted sulfur content in marine fuels and heavy fuel oil: in Sulfur Emissions Control Areas (SECAs), the maximum sulfur mass content permitted is limited to 0.1% since 2015, while for ships operating outside these designated areas the limit for sulfur content is still 3.5% but will be reduced to only 0.5% in 2020 [1]. In order to comply with these limits, the most viable technique that would keep the use of residual

fractions without further change in the technology of the vessels is via the upgrade of marine fuel through desulfurization. Even though hydrodesulfurization (HDS) is the most commonly used process for upgrading fractions to better quality fuels, more severe conditions of temperature and pressure and increasing hydrogen consumption compared to diesel application would be required for the treatment of heavy fuels, with an important financial impact [2]. Among the non-hydrogenation desulfurization processes, oxidative desulfurization (ODS) is considered as a promising alternative or complementary method to conventional HDS [3]. In the ODS reaction, the sulfur containing molecules are oxidized in sulfones, which, due to their polar properties, can be further separated from the reaction mixture by extraction or adsorption [4–6]. The main advantages of this method are related to the economic benefit obtained due to the mild operating conditions: low temperatures and atmospheric pressure. In addition, this process has received attention because of the high oxidative reactivity of 4,6-dimethyldibenzothiophene (DMDBT), known as a refractory molecule in the HDS of diesel feed [7–9]. Despite an increasing number of papers regarding oxidative desulfurization in recent years, most of them focus on the ODS of model molecules and light real feeds such as low sulfur diesel [10–16]. A recent review dedicated to oxidative desulfurization of heavy oils with sulfur content higher than 0.5 wt.% [17] showed that most of the reactions reported for these fuels were carried out using homogeneous catalysis [5,18–22], in some cases assisted by ultrasounds that proved to increase the process efficiency [23–25]. Indeed, heterogeneous catalysis may be preferred, for its advantageous catalyst recovery. However only one study by Tang et al. focused on marine fuels oxidation with a heterogeneous system, a molybdenum oxide powder, the process being assisted by ultrasounds [26]. Final desulfurization rate was only 30%, decreasing total sulfur content from 3.2 wt.% to 2.6 wt.%, therefore not efficient enough for new regulations. Moreover, in most papers on real feed treatment, desulfurization rates are obtained by measuring global sulfur content after oxidation and extraction steps thus without evaluation of the conversion rate of sulfides to sulfones. Gas chromatography technique has been used for quantitative monitoring of the evolution of sulfides concentrations after oxidation, often in the case of model molecules [27–29] but also in the case of prehydrotreated diesel [14] and LGO (Light Gas Oil) [30]. For high sulfur content fuels (>0.5 wt.%S) this method has never been reported in the literature.

In this work, we intend to apply the ODS process to different marine fuel oils: two intermediate fuel oils (IFO) and one high sulfur fuel oil (HSFO) obtained from different origins, with viscosities ranging from 380 to 700 cSt. At first, taking into account that a precise structural characterization and identification of marine fuel sample is unconceivable at the level of description for distillate fractions, the characterization of these fuels will be assessed concerning sulfur containing species in particular. Then, the effect of reaction parameters such as time, catalyst amount, extraction solvent, oxidizing agent nature and quantity, use of ultrasounds, will be further studied and parameters optimized to operate with the best suitable ODS conditions for marine fuels. Subsequently, using the optimum conditions, ODS reaction will be tested on IFO380, IFO500 and HSFO700 samples. Influence of the presence of

asphaltenes, in solution or precipitated, will also be studied. Reaction efficiency will be evaluated by measuring global sulfur content after extraction but oxidation reaction will also be monitored by tracking the evolution of alkyl-BTs and DBT molecule quantities using gas chromatography with a specific sulfur detector.

2 Experimental methods

IFO380, IFO500 and HSFO700 used in this study were provided by SEGULA. Hydrogen peroxide (30 wt.% in water), Ammonium molybdate tetrahydrate (puriss., $\geq 99\%$), Butyrolactone $>99\%$ (GC) were purchased from Sigma Aldrich. Acetonitrile (Environmental Grade, 99.7+%, Alfa Aesar™), 2-ethoxyethanol (99%, extra pure, ACROS Organics™), N,N-Dimethylformamide, (99.8+%, ACS reagent, ACROS Organics™) and n-Dodecane ($\geq 99\%$, Alfa Aesar™) were purchased from Fisher Scientific.

2.1 Catalyst preparation

MoO₃/Al₂O₃ catalysts are reported as efficient in ODS reaction [4,11,31,32]. The MoO₃/Al₂O₃ catalyst used for the ODS of marine fuels in this study was obtained by incipient wetness impregnation of an industrial alumina (176 m²·g⁻¹) with a solution of ammonium heptamolybdate. The maturation step of 3h in a humid atmosphere was followed by drying at 90°C overnight and calcination at 480°C for 3 h under air flow (0.3 L·min⁻¹) with a temperature rate of 1°C·min⁻¹. Final loading in the calcined catalyst was set at 20 wt.% of MoO₃. Raman analysis confirmed the presence of well-dispersed polymolybdates, with only some grains showing the characteristic lines of MoO₃ crystals (not shown here).

2.2 Analysis of the fuels

Elemental C, H, N and S contents of the marine fuels were determined by CHNS analysis on an EA1110 Thermo Fisher Flash instrument. Global sulfur content was also measured by UV fluorescence (Sulf-UV) on an ANTEK 9000S analyzer, the samples being stirred at 80°C for an hour prior to injection.

Sulfur containing species were monitored by gas chromatography on a Varian 3800 coupled with a specific sulfur detector Sievers SCD 355 (Sulfur Chemiluminescence Detector). A high temperature range column was chosen, a Phenomenex ZB-5HT. Because of the heavy nature of the marine fuels used, an integrated guard column was added. Optimized analysis conditions correspond to an initial temperature of 50°C and a final temperature of 260°C with an increase in temperature of 5°C·min⁻¹.

2.3 Dilution and centrifugation of the fuels

Raw marine fuels were diluted 5 times in dodecane. In order to separate precipitated particles, fuels were centrifuged for 20 min at 8000 rpm. Samples nomenclature is R for raw, D for diluted and DC for the liquid phase recovered after dilution and centrifugation.

2.4 Oxidative desulfurization protocol

The ODS tests were carried out on the different marine fuel oil samples in a 100 mL glass batch reactor at atmospheric pressure. The mass of catalyst to mass of charge ratio was taken equal to 0.1, with 6 g of raw sample R or 30 g of D or DC phase introduced into the reactor together with 600 mg of catalyst. The system was heated to 80°C under reflux. The oxidant H₂O₂ was then incorporated with the chosen oxidant to sulfur ratio. Particular interest was devoted to the choice of mixing system as well as to optimization of mixing conditions, due to the heavy nature of the feed. In the case of ultrasound assisted oxidative desulfurization, a probe type ultrasound apparatus VCX-500 purchased from Sonics and Materials with a fixed frequency of 20 kHz was used. The input ultrasonic power to the solution was operated at 40% amplitude, which was determined as optimal. The ultrasound power per fuel oil volume was 6.7 W·mL⁻¹. According to the literature study, the ultrasonication power applied in the case of heavy and high sulfur fuel oil samples fluctuated in the range of 2 to 20 W·mL⁻¹, most of the papers operating around 8 W·mL⁻¹ [23-26].

At the end of the ODS reaction, the catalyst was recovered by filtration. The catalyst was washed first with 50 mL of pentane to remove DBT and dodecane and then with 50 mL of butyrolactone. This second step, due to polar properties of butyrolactone, solubilized the sulfones precipitated or retained on the catalyst. The filtrate and washing solutions were weighed and analyzed by Fluorescence UV (Sulf-UV) to determine their overall sulfur content (sulfides and sulfones). The calculated sulfur balances were found to be above 90% for the different marine fuels. The percentage of retained sulfur on the catalyst was calculated as the difference of the sulfur content in the initial solution and in the reaction solution after filtration and did not exceed 2%. Indeed, the high aromatic content in the real feed may have facilitated the solubility of sulfones rather than their precipitation [30]. Therefore, we considered neglecting the quantity of sulfur retained on catalyst when calculating conversion rates.

2.5 Extraction

The extraction of sulfones from the oxidized fuel was performed by mixing a given volume of oxidized fuel with N-dimethylformamide or butyrolactone. The two phases were allowed to settle and recovered in a separating funnel. The global sulfur removal after extraction was evaluated as the percentage of sulfur content determined by Sulf-UV in the solution after extraction compared to the initial concentration of sulfur in the marine fuel oil. Marine fuel yield after extraction was calculated on the basis of volume change before and after extraction.

3 Results and discussion

The International Maritime Organization (IMO) has proposed a classification of marine fuels in categories according to their sulfur content and viscosities in ISO 8216 and ISO 8217 standards. High Sulfur Fuel Oils (HSFO) are highly viscous residual fuel oils with viscosities as high as 700 cSt (at 50°C) and a sulfur content up to 3.5 wt.%. These characteristics may be modified by blending residual fuels with lighter fractions, and resulting mixtures are referred to as Intermediate Fuel Oils (IFO). Low Sulfur Fuel Oils (LSFO) correspond to residual fuel oils with an overall sulfur content lower than 1 wt.% and are usually marine fuels IFO180 or IFO380 which have been hydrodesulfurized (180 and 380 corresponding to their viscosity value in cSt at 50°C). In this study, three marine fuels with various properties have been selected: IFO380, IFO500 and HSFO700, with viscosities of 380, 500 and 700 cSt respectively. Characterization and ODS tests were performed on raw (R) and diluted (D) samples, as well as on the liquid phase recovered after centrifugation (DC). Dilution in n-dodecane (C12) enabled to simplify manipulations and mixing conditions of fuels, and led to asphaltenes precipitation that could be further separated by centrifugation.

3.1 Characterization of marine fuels

Marine fuel is a very complex mixture to analyze unlike lighter petroleum cuts for which a complete detailed composition is available in the literature. Indeed, few publications report the composition of marine fuels or residuals [33–36]. In this study we have focused on the determination of sulfur and nitrogen contents by CHNS, as well as the distribution of sulfide species by GC-SCD.

3.1.1 Elemental composition of the fuels

Elemental N and S compositions of the fuels are presented in Table 1. A total sulfur content of 0.76 wt.% was measured for IFO380, while a higher value of 3.27 wt.% was obtained for IFO500. The sulfur content in IFO depends on the respective quantities of intermediate and heavy refining fractions that have been mixed to obtain the fuel, thus explaining the different S content in these two IFO samples. The HSFO presented a high value of S content, 2.95 wt.%, in agreement with the heavy character of this feed. The nitrogen mass contents were close in the three samples, varying between 0.37 and 0.49 wt.%. Such high N contents have been reported in HFO, with a value of 0.36 wt.% for a heavy fuel oil with a sulfur content of 2.63 wt.% [35]. This amount is significantly higher than in lighter fractions like diesel and SRGO (Straight Run Gas Oil), where total nitrogen content is not higher than several hundreds of ppm [15,37,38]. Similar H/C ratios were obtained in the three samples, with values varying between 1.45 and 1.52. Such low H/C ratios are commonly reported for heavy fuels, in accordance with their high aromaticity [2,39].

Centrifugation of the diluted samples D allowed to remove the precipitated particles and the sulfur content of the liquid phase recovered after centrifugation (DC) was determined (Table 1). For

IFO380 with low viscosity and low sulfur content, 75% of the sulfur present in the fuel was recovered in the liquid phase. Contrariwise, for fuels with higher viscosity and higher sulfur content, only 43 and 35 % of the sulfur were present in the liquid phase IFO500-DC and HSFO700-DC, respectively. In parallel, the mass of solid obtained after centrifugation increased only slightly with the fuel viscosity, from 12% of the total mass of the fuel for IFO380-D to 14% for IFO500-D and 16% for HSFO700-D. This indicates that in the case of these two latter fuels, precipitated asphaltenes and/or solids particles present in the feed represent a slightly higher mass but more importantly contain more sulfur than in the case of IFO380.

Table 1 : CHNS elemental analysis in the raw (R), diluted (D) and diluted centrifuged (DC) samples, percentage of initial sulfur contained in the DC samples and weight percent of solid phase recovered after centrifugation.

| Marine fuel | H/C(R) | N(R) | S(R) | S(D) | S(DC) | S | M(solid) |
|--------------------|---------------|---------------|---------------|---------------|---------------|----------------|-----------------|
| | ratio | /wt. % | /wt. % | /wt. % | /wt. % | in DC/% | /wt. % |
| IFO380 | 1.52 | 0.49 | 0.76 | 0.76 | 0.65 | 75 | 12 |
| IFO500 | 1.45 | 0.37 | 3.27 | 3.27 | 1.60 | 43 | 14 |
| HSFO700 | 1.47 | 0.39 | 2.95 | 2.95 | 1.60 | 35 | 16 |

3.1.2 Analysis of sulfur containing compounds by GC SCD

Marine fuels can be made of residues from different refining processes consisting of heavy hydrocarbons with high sulfur accumulation. Their complete analysis becomes problematic due to the huge number of isomers present with increasing boiling point and carbon number. Co-elution problems and difficulty in separating very similar components thus occur. Choice of the appropriate column and optimization of the analysis parameters are thus more complex than in the case of lighter feedstocks. The obtained chromatograms for diluted centrifuged samples are presented in Figure 1, together with that of a SRGO with 10000 ppmS diluted with dodecane. Alkyl-benzothiophenes (Cx-BTs) were identified by their retention times between 15 to 27 min, and alkyl-dibenzothiophenes (Cx-DBTs) between 27 to 40 min. Surprisingly we can observe C1-BTs around 15 min that are not present in SRGO fraction. Above 40 min, larger molecules were eluted in resolved peaks. In the literature, analysis by 2D GC coupled with SCD detector revealed the presence of benzonaphthothiophene type molecules in various fuel oils [40–43]. In this range of retention times, an important raise of the baseline due to co-eluting compounds was observed in the chromatograms of the marine fuels, designated as Unresolved Complex Mixture (UCM). UCM is also present on the chromatogram of the SRGO, however in a range of lower retention times (below 40 min), in agreement with the heavier quality of the marine fuel oils. As demonstrated by

2D GC, this UCM seems to correspond to sulfides and thiols of high molecular weight, that could co-elute with dibenzothiophenes and naphthobenzothiophenes present in small quantities [44,45].

Quantification of the different families shows similar repartition for the three fuels, with between 10 and 12% of Cx-BTs, between 35 and 37% of Cx-DBTs and between 53 and 54% of UCM and sulfur containing compounds eluting after 40 min. All diluted centrifuged samples thus appear to present similarities in composition regarding sulfur families.

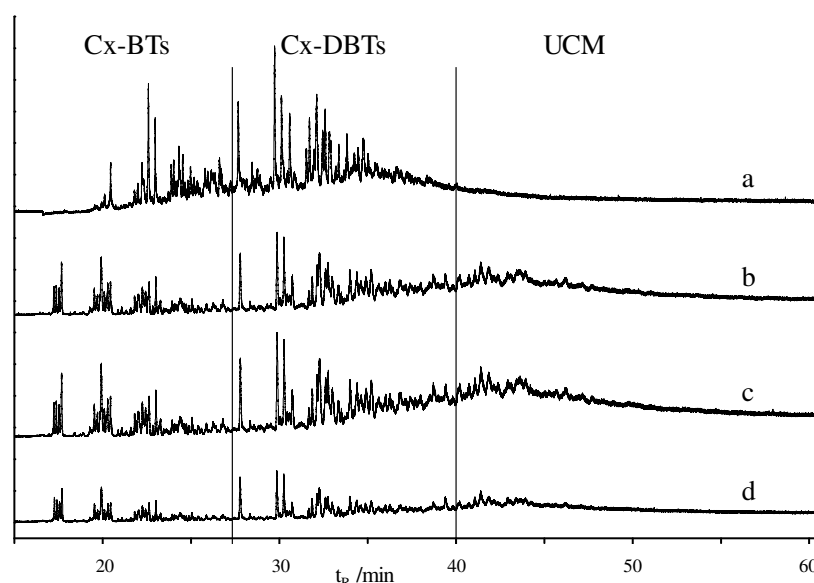


Figure 1: Chromatograms of SRGO (a) and of diluted centrifuged samples HSFO700-DC (b), IFO500-DC (c) and IFO380-DC (d).

3.2 Oxidative desulfurization of IFO500-DC

To study the evolution of the reaction medium during ODS as well as the influence of reaction parameters, the diluted centrifuged sample IFO500-DC was selected, IFO500 presenting intermediate viscosity and high sulfur content.

3.2.1 Conversion of sulfur species during ODS

ODS of IFO500-DC was performed with a H_2O_2/S ratio of 3 and chromatograms of the reaction mixture were registered at 5, 15, 30, 45, 60 and 120 min (Figure 2). After 5 min of reaction, the peaks corresponding to sulfur species began to decrease, with simultaneous appearance of peaks attributed to sulfones in the retention time region above 28 min. By integration on the chromatograms, it is thus possible to follow the conversion of the Cx-BTs compounds as no sulfone peaks interfere in the range of their retention times. However, peaks of Cx-BTs sulfones appear in the region of Cx-DBTs, with

overlapping of peaks from both families. We can only monitor the evolution of the DBT molecule upon ODS, as its corresponding peak, at the beginning of the alkyl-DBT retention time range, does not present any overlapping with sulfones peaks. Evolutions of Cx-BTs and of DBT molecule conversions are thus presented in Figure 3. The conversion of the DBT molecule appears to be higher than that of the BTs family, which has already been noted in the literature. Indeed, the lower electron density on the sulfur atom of BT (5.739) makes it less reactive than DBT and its derivatives with higher density (5.758 for DBT and 5.760 for 4,6-DMDBT) [5,28,46]. ODS reaction evolved quickly in the first minutes, with Cx-BTs conversion of 21% and DBT conversion of 46% at 15 min, increasing to 33% and 54% respectively at 30 min. Only a slight increase was noted afterwards, conversions remaining almost constant after 60 min of reaction for both Cx-BTs (35.6%) and DBT (59.8%). In further experiments, conversions will thus be given as results after 1 hour of reaction.

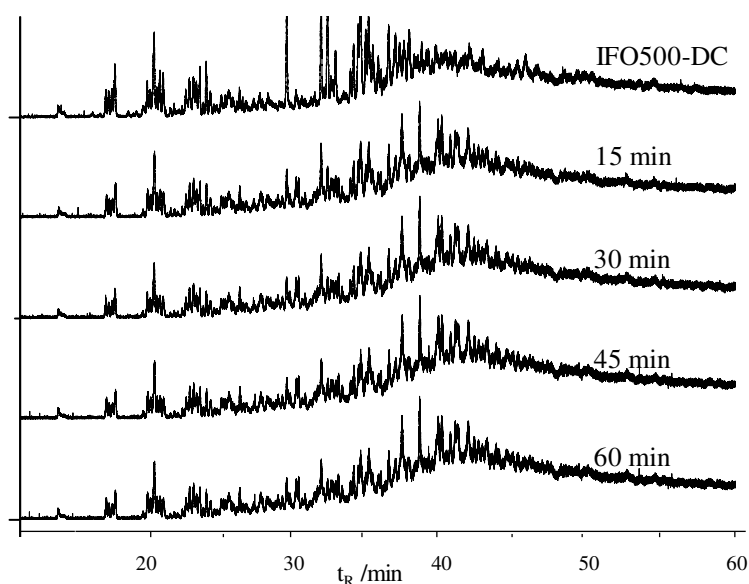


Figure 2: Chromatograms of the reaction mixture in the ODS of IFO500-DC, $H_2O_2/S = 3$, at 0, 15, 30, 45 and 60 min.

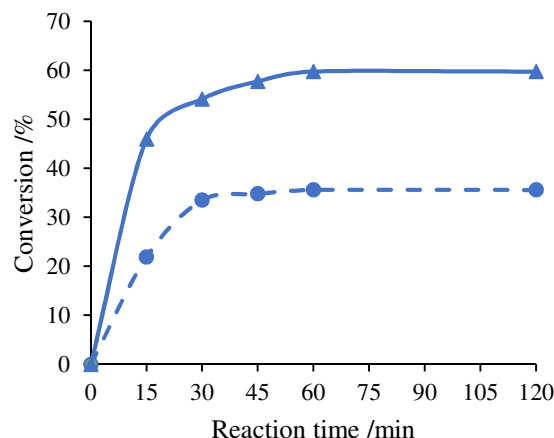


Figure 3: Conversion of Cx-BTs (- -) and DBT (-) in the ODS of IFO500-DC, $H_2O_2/S = 3$.

3.2.2 Effect of oxidizing agent in the ODS of IFO500-DC

In this study, we focused on H_2O_2 as oxidizing agent, as it is a cheap and green compound, with a low Ox/S ratio of 3, in order to optimize the cost and the volume to be treated. The oxidant/sulfur ratio is usually slightly above the stoichiometric ratio of 2 when the ODS of model feeds is concerned [47–49], while much higher ratios above 15 are reported in the ODS of real feeds [4,50,51], due to possible secondary oxidation reactions of aromatics or nitrogen compounds present in these feeds.

To investigate the effect of oxidant amount on activity in the ODS of marine fuels, ODS of IFO500-DC was carried out using H_2O_2 with oxidant to sulfur ratio (Ox/S) of 3 and 25 (Figure 4). Only slight increases of both BTs (from 32 to 48%) and DBT (from 59 to 72%) conversions are noticed when H_2O_2/S ratio increases from 3 to 25, even though in the last case the quantity of oxidant was exceeding the stoichiometric ratio more than 10 times. Indeed, when increasing the quantity of oxidizing agent, contact with the fuel may become an issue in the biphasic medium obtained with H_2O_2 . This confirmed our choice to work with H_2O_2 at low Ox/S ratio, for economic and environmental reasons, as higher quantity does not improve the performance.

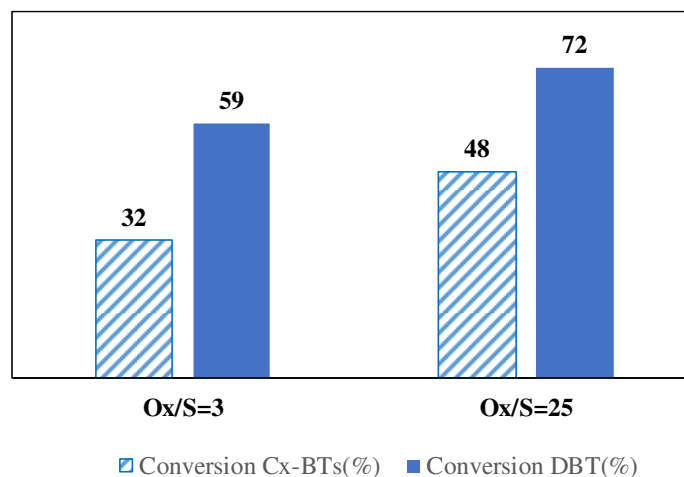


Figure 4: Conversion rates (in %) of Cx-BTs and DBT using H₂O₂ in the ODS of IFO500-DC with Ox/S=3 and 25.

3.2.3 Global sulfur removal: effect of extraction solvent nature and quantity

After oxidation, liquid-liquid extraction is frequently used for the separation of sulfones. Solvent capacity and its selectivity towards sulfones are considered as the main parameters for highly efficient extraction. The solvent should have high capacity to solubilize sulfones and hydrocarbon mixture low solubility to avoid loss of fuel fraction in the solvent. Different types of solvents have been reported in the literature for sulfones extraction [19,22,27,32,52–56]. According to the mentioned publications, it was possible to limit the list of solvents that may be of interest to acetonitrile (ACN), N-Dimethylformamide (DMF), 2-ethoxyethanol and butyrolactone (Bul). Preliminary experiments showed that among these solvents, ACN and 2-ethoxyethanol frequently used in the extraction of oxidized diesel were soluble in the oxidized marine fuel and dodecane fraction, thus making the extraction impossible in our case. Extraction was then performed on non-oxidized fuel IFO500-DC with both DMF and Bul, with a volumetric ratio of solvent/fuel (S/F) of 1. Sulfur reduction rates using DMF and Bul were the same, 30%, leading to a sulfur content in the fuel of 1.2 wt.% after extraction. Some sulfide compounds do migrate to the solvent phase showing that extraction is thus not entirely selective to sulfones.

Global sulfur removal rates after ODS of IFO500-DC and extraction by DMF or butyrolactone are presented in Figure 5, for two solvent/fuel volumetric ratios of 0.5 and 1. Similar desulfurization rates were measured with both solvents, 46 and 49% at a 0.5 ratio, and 58 and 60 at a ratio of 1, showing that extraction after ODS of IFO500-DC allows to double the desulfurization rates when comparing with simple extraction of the fuel. Similarly to literature [57,58], an increase in S/F ratio enhances extraction efficiency; this is related to a better homogenization of the medium that promotes migration of species to the polar phase when using a larger quantity of solvent. Marine fuel yield (percentage of fuel recovered after extraction and solvent removal) reached 90% in the case of DMF with a ratio equal to 1 and 80% with butyrolactone with the same ratio. In order to minimize fuel loss and for economic

considerations for the overall ODS process, DMF with a ratio S/F of 1 has thus been kept for all further experiments.

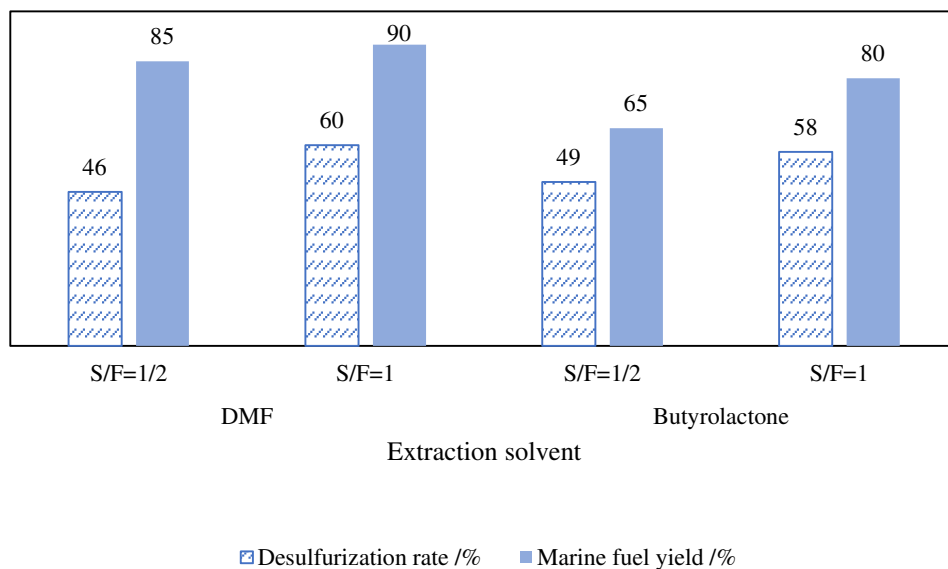


Figure 5: Desulfurization rate and marine fuel yield after extraction of oxidized fuel using DMF and Bul.

3.2.4 Ultrasound assisted ODS

Ultrasound assisted ODS (UAOD) has been reported to be beneficial for the treatment of fuels with high sulfur content [23,24,26,57,59–62]. Use of ultrasounds was thus considered for the ODS of IFO500-DC, the ultrasonication being first used without mechanical stirring. Initial studies focused on optimization of ultrasonication time. The evolution of Cx-BTs and DBT quantities was monitored after 5, 10 and 20 min, with 5 and 10 min of ultrasonication. Conversion of both compound types increased, from 20% to 35% for Cx-BTs and from 50% to 65% for DBT, when ultrasonication time increased from 5 to 10 min. However, after 10 min, overall desulfurization rates remained the same. So as an optimum in terms of energy, we chose to work with 10 min of ultrasonication.

Comparison of performances under ultrasounds (US) or mechanical stirring (MS) was then performed. Conversion results of the Cx-BTs and DBT under both mixing conditions are indicated in Figure 6. The ODS reaction was effective in the case of ultrasounds, with a slight improvement of the conversion after 10 min of the Cx-BTs family from 35 to 38% and the DBT molecule from 60 to 65% with an $O_x/S=3$ ratio compared to mechanical stirring. However, this difference being very small, it could be more energy-effective to use conventional ODS. Then optimized time of 10 min ultrasonication followed by mechanical stirring (US+MS) was applied to the IFO500-DC sample. Experiments with US followed by conventional ODS demonstrated higher conversion of sulfides, from 30% with conventional stirring to 44% for Cx-BTs and from 60 to 70% for DBT. Hence, after extraction by DMF, a higher

desulfurization rate of 76% was obtained with US followed by conventional stirring ODS compared to experiments with US or conventional stirring only.

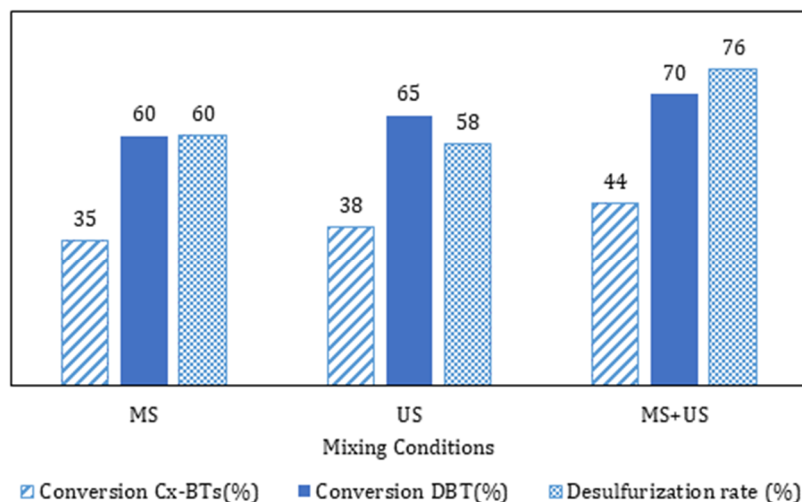


Figure 6: Conversion of Cx-BTs and DBT and desulfurization rates of oxidized fuel IFO500-DC using mechanical stirring (MS), ultrasounds (US) and ultrasounds followed by mechanical stirring (US+MS) ($\text{MoO}_3/\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}_2/\text{S}=3$, $T=80^\circ\text{C}$).

Several effects may account for the observed enhancement. First energy produced from ultrasound can provide an extremely fine emulsion of immiscible liquids (like in the case of the biphasic medium of fuel and H_2O_2). Cavitation created from ultrasound creates micro bubbles that further grow and reach a critical size causing their collapse. Shock waves are formed producing high temperatures and pressures thus promoting chemical oxidation and increasing chemical reactivity [63]. Moreover, ultrasonication is also used as an upgrading method lowering feed viscosity and preventing asphaltene flocculation thus facilitating oxidative desulfurization of heavy crudes [64,65].

3.3 Oxidative desulfurization of IFO380, IFO500 and HSFO700.

The behavior of three marine fuels IFO380, IFO500 and HSFO700 has been evaluated in ODS reaction with increasing complexity of the matrix, that is in diluted centrifuged (DC), diluted (D) and raw (R) states. Indeed, in the centrifuged fuel, the precipitated asphaltenes obtained by dilution with dodecane have been separated, and a less viscous liquid phase is retained for catalytic testing; this also results in significantly lower sulfur content in the case of IFO500 and HSFO700. Diluted fuels without centrifugation, more viscous than the centrifuged ones, have also been tested to evaluate the effect of the presence of precipitated particles. Finally, raw fuels without any dilution or centrifugation have been considered in ODS, in more difficult conditions indeed, as viscosity of the fuels is very high, especially in the case of HSFO700. Results with combined ultrasound assisted system (US+MS) were compared with conventional stirring experiments (MS) in the ODS of all diluted centrifuged phases.

3.3.1 ODS of diluted centrifuged fuels (DC): comparison of the three fuels and effect of US.

IFO380 diluted centrifuged samples with initially 0.79 wt.% S contains 70% of the sulfur present in the fuel, whereas for IFO500-DC and HSFO700-DC containing higher initial sulfur contents around 3 wt.% S, 40% of the total sulfur is present in liquid phase of the fuels, after removal of the solid particles initially present in the fuel or precipitated asphaltenes after dilution with dodecane.

Extraction was performed on the centrifuged fuels and it was found that part of the sulfide compounds migrated to the solvent, with a desulfurization rate of 43% for IFO380-DC and around 20% for IFO500-DC and HSFO700-DC, leading to sulfur contents in the extracted fuels of 0.4 % for IFO380-DC and 1.2% for IFO500-DC and HSFO700-DC. Extraction after ODS reaction will thus not be fully selective to sulfones, evidencing that the sulfur removal determination is not representative of efficiency of oxidation but of the overall oxidation and extraction process.

Sulfur content before and after ODS and extraction are collected in Table 2 for the diluted centrifuged samples of the three fuels; the conversions of Cx-BTs and DBT are also mentioned, for ODS with mechanical stirring (MS) and with the combined system of ultrasounds followed by mechanical stirring (US+MS). After ODS with mechanical stirring and extraction, the total sulfur content decreased to 0.28 wt.% for IFO380-DC, 0.64 wt.% for IFO500-DC and 0.90 wt.% for HSFO700-DC, corresponding to desulfurization rates of 60% for IFO380-DC and IFO500-DC and of 40% for HSFO700-DC, which appeared to be most difficult to desulfurize. Conversion rates of Cx-BTs and DBT were the highest for IFO380-DC (58 and 76% respectively) while similar values were obtained for IFO500-DC (35 and 60%) and HSFO700-DC (25 and 60%), both presenting the same initial sulfur content (1.6 wt.%). It seems that conversions of Cx-BTs and DBT are higher in the lowest sulfur content fuel. Indeed, when increasing the sulfur content in the feed to be treated while keeping the same amount of catalyst, the ratio Mo/S decreases, less active sites are then available for oxidation [24]. Regarding global sulfur removal, total desulfurization rate is higher for IFO500-DC than for HSFO700-DC, whilst they initially contained the same amount of sulfur and conversion rates of Cx-BTs and DBT are similar. This indicates that some specific sulfur compounds present in HSFO700-DC are more difficult to convert or do not migrate to the extracting solvent phase in comparison with IFO500-DC.

The application of ten minutes of ultrasonication prior to ODS with mechanical stirring was found to improve the reaction efficiency: the same trends were observed with the 3 samples. Conversion of DBT increased by 5%, 17% and 25% for IFO380 DC, IFO500-DC and HSFO700-DC respectively, the effect becoming more pronounced when increasing the complexity of the feed. The beneficial effect is even more marked on the conversions of the most refractory compounds Cx-BTs, with an increment of 20%, 26% and even 80% for IFO380 DC, IFO500-DC and HSFO700-DC respectively. Global desulfurization rates also increased very significantly, from 60, 60 and 40% to 80, 77 and 64% for IFO380-DC, IFO500-

DC and HSFO700-DC respectively. These values correspond to final sulfur contents of 0.13, 0.37 and 0.54 wt.%. The use of ultrasounds is definitely beneficial, on sulfide molecules conversion and on global sulfur removal, the effect being more pronounced when initial efficiency is low, that is for more refractory molecules and heavier fuels. This process will therefore be applied to all further experiments.

3.3.2 ODS of diluted fuels (D).

ODS reaction on diluted fuel samples was performed using the optimized combined system of ultrasounds followed by mechanical stirring (US+MS).

To evaluate the influence of the presence of precipitated asphaltenes during ODS, results obtained with diluted samples (D) were compared to those with diluted centrifuged samples (DC). On IFO380, conversions after oxidation of diluted sample D decreased compared to that of diluted centrifuged sample DC: from 70 to 50% (Cx-BTs) and from 80 to 70% (DBT). In addition, global desulfurization rate decreases, from 81 to 65%, with sulfur content increasing from 0.13 to 0.28 wt.% in the final phase. Solid phase removed by centrifugation contains little sulfur, the sulfur content being 0.79 wt.% in IFO380-D and 0.70 wt.% in IFO380-DC. The IFO380 compounds removed by centrifugation after dilution (DC sample) may be detrimental to sulfur compounds oxidation when present in the reaction medium (D sample).

Contrariwise, conversions of Cx-BTs and DBT remain similar in the D and DC samples for IFO500 and HSFO700 (around 45% for Cx-BTs and around 75% for DBT). For these two samples, the desulfurization rate increases, from 77 to 80% for IFO500 and from 64 to 73% for HSFO700. For diluted fuel IFO500-D total sulfur content decreased from 3.27 to 0.63 wt.% and for HSFO700, from 2.95 to 0.79 wt.%. Fuel recovery values around 70% were lower than recovery for DC samples that varied between 80-90 %; this indicates that not only oxidized sulfur compounds are extracted but also other polar compounds present in the fuel, thus lowering recoverability of hydrocarbons. We assume that higher sulfur removal rates obtained for HSFO700 and IFO500 with diluted phase D compared to centrifuged phase DC can be attributed to extraction of more polar species or to oxidation of some sulfur compounds present in the solid phase occurring when applying ODS on diluted phase.

3.3.3 ODS of raw fuels (R)

Our objective is to be able to achieve ODS directly on raw marine fuels, despite high viscosity and sulfur content, to reduce the number of steps and reagents incorporated in the process. ODS on IFO380, IFO500 and HSFO700 was carried out using the same conditions of catalyst and oxidant but with Ox/S=10 since initial experiments showed that ODS of raw fuels with Ox/S=3 was not effective. Even in these conditions, no conversion could be measured for HSFO700. During the reaction, an increase in viscosity was observed for all fuels and this change was much more pronounced in the case of HSFO700, turning the reaction mixture into a pasty formula. Therefore, conversions and sulfur contents after ODS

and extraction could not be evaluated for this fuel. The viscosity change could be attributed to condensation and aggregation of high molecular weight molecules via their oxidation and through free radical reaction and side reactions caused by the complex nature of the fuels [66].

Table 2: Sulfur content of the fuels before and after ODS and extraction, desulfurization rate and conversion rates of Cx-BTs and DBT after ODS (US+MS, except *: only MS) for IFO380, IFO500 and HSFO700, in raw (R), diluted (D) and diluted centrifuged (DC) samples.

| Fuels Performance | IFO380 | | | IFO500 | | | HSFO700 | |
|---|--------|------|------------|--------|------|------------|---------|------------|
| | R | D | DC | R | D | DC | D | DC |
| S before ODS (wt.%) | 0.79 | 0.79 | 0.7 | 3.27 | 3.27 | 1.60 | 2.95 | 1.50 |
| S after ODS & extraction (wt.%) | 0.27 | 0.28 | 0.28*/0.13 | 0.52 | 0.63 | 0.64*/0.37 | 0.79 | 0.90*/0.54 |
| Desulfurization rate (%) | 65 | 65 | 60*/81 | 84 | 80 | 60*/77 | 73 | 40*/64 |
| Cx-BTs conversion (%) | 43 | 50 | 58*/70 | 50 | 44 | 35*/44 | 45 | 25*/45 |
| DBT conversion (%) | 73 | 70 | 76*/80 | 70 | 73 | 60*/70 | 70 | 60*/75 |

Results concerning IFO380 and IFO500 are presented in Table 2. Conversion rates of Cx-BTs and of DBT were found similar in diluted and raw fuel for IFO380 and IFO500 (around 44-50% for Cx-BTs and around 70-73% for DBT). Conversions are thus not affected by the presence of asphaltenes, precipitated or dissolved in the liquid phase. Similarly, viscosity, different in raw and diluted samples, did not have a significant effect on desulfurization efficiency. For IFO380, total sulfur removal after extraction remained the same for raw and diluted samples, equal to 65% and with final sulfur content of 0.27 wt.%. For IFO500, the sulfur removal increased slightly from 80% for diluted to 84% for raw sample, decreasing the final sulfur content to 0.52 wt.% in the treated raw IFO500 fuel. For this fuel, some more species could be extracted from the raw sample than from the diluted sample.

4 Conclusions

Three marine fuels IFO380, IFO500 and HSFO700 were considered for ODS, their viscosity varying between 380 and 700 CSt and their sulfur content between 0.79 and 3.27 wt.%. Dilution by dodecane led to asphaltenes precipitation that could be further separated by centrifugation. In the case of the fuels with higher viscosity and sulfur content, precipitated asphaltenes contained a larger amount of sulfur while similar composition in Cx-BTs, Cx-DBTs and UCM were evidenced by GC-SCD for the three diluted centrifuged samples of the fuels.

Determination of the sulfur removal after reaction and extraction by DMF gave an evaluation of the global process efficiency, which is commonly used in the literature. Oxidation reaction in itself was monitored by GC-SCD by assessing the evolution (presence and quantity) of alkyl benzothiophenes and of dibenzothiophene molecule, for which there is no overlapping with peaks of formed sulfones. H₂O₂ as oxidant with low O/S ratio of 3 was chosen for economic and environmental reasons. Applying ultrasounds prior to ODS reaction with conventional stirring was however found significantly beneficial, both on sulfide molecules conversion and on global sulfur removal. The effect was observed to be more pronounced on the conversion of more refractory molecules and in the ODS of heavier fuels.

ODS was effective on all samples, except on HSFO700 without dilution, for which a very high viscosity mixture appeared during reaction. Except for IFO380, similar values of Cx-BTs and DBT conversions were obtained whatever the fuel and whatever the treatment; this shows that sulfur content, varying from 0.79 to 3.27 wt.%, viscosity, quantity of asphaltenes, have had no impact on the conversion of these sulfide compounds. Concerning IFO380, the compounds that were removed by dilution and centrifugation appeared to be detrimental to sulfides oxidation. After ODS and extraction, and thus taking into account the efficiency of the extraction step, the global sulfur content was significantly decreased, from 0.79% to 0.27% and 0.13% in the raw and diluted centrifuged IFO380 respectively, from 3.27% to 0.52% and 0.37% in the raw and diluted centrifuged IFO500, from 2.95% to 0.79% and 0.54% in the diluted and diluted centrifuged HSFO700. These results, despite the difficulty of implementation of ODS on viscous samples, proved the efficiency of ODS on marine fuels, with final sulfur content close to the values imposed by the MARPOL regulations. Further optimization of catalyst formulation may still enable to improve the obtained results with a conventional MoO₃/Al₂O₃ catalyst.

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