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Abstract: The International Maritime Organization (IMO) has limited marine fuel sulfur content in Sulfur Emission Control Areas (SECAs) from 1 to 0.1 wt.% in 2015 and will limit marine fuel sulfur content from 3.5 to 0.5 wt.% in all maritime areas by 2020. Marine fuels consist of heavy oils characterized by high sulfur content with refractory sulfur compounds difficult to remove using existing conventional high pressure hydrodesulfurization processes. However, these sulfides molecules appeared more reactive in oxidative desulfurization (ODS) process, carried out at mild conditions without hydrogen consumption. The objective of this thesis is to propose an oxidative desulfurization method of marine fuels. Nevertheless, ODS on heavy fuels is still immature and marine fuels are poorly studied with only few publications reported in literature. This work first focused on the development of a reliable methodology for the analysis of sulfur compounds in marine fuels before the study of an appropriate and efficient catalyst for marine fuel ODS reaction with optimized operating conditions. Among a large variety of marine fuels, three marine fuels were chosen with high viscosities that varied from 380 to 700 cSt. The results of chemical analysis revealed high sulfur content ranging from 0.6 to 3.2 wt.% reflecting the variability of the composition of marine fuels. ODS reaction was carried out by heterogeneous catalysis using MoO_3/Al_2O_3-H_2O_2 system in batch reactor. The effects of reaction time, oxidant to sulfur molar ratio (Ox/S) and extracting solvent were investigated. Ultrasound assisted oxidative desulfurization coupled to normal mixing provided better desulfurization rates due to the synergetic effect provided by ultrasounds. Studies on the effects of molybdenum loading, phosphorus and/or vanadium doping and molybdenum precursor type were carried out on the alumina-supported molybdenum catalyst. Others oxide carriers were also employed, remarkably improving catalytic performances. Under the optimum conditions and with the most efficient catalysts, it was possible to oxidize and desulfurize all selected feeds making them compatible with the 2020 new regulations.

Key words: ODS, H_2O_2, extraction, MoO_3/Al_2O_3, ultrasound, marine fuels.

Résumé : L'Organisation Maritime Internationale (OMI) a limité la teneur en soufre des combustibles marins dans les zones de contrôle des émissions de soufre (zones SECA) de 1 à 0,1 % en 2015 et la limitera, d'ici 2020, de 3,5 à 0,5 % dans toutes les zones maritimes. Les fiouls marins sont constitués des résidus lourds caractérisés par une teneur élevée en soufre, la majeure partie du soufre se trouvant dans des molécules dites réfractaires, très difficiles à éliminer par le procédé d'hydrodésulfuration existant, fonctionnant sous haute pression d'hydrogène. Cependant, ces molécules soufrées sont connues pour être plus réactives dans le procédé de désulfuration oxydante ou oxydésulfuration (ODS), réalisé dans des conditions douces sans consommation d'hydrogène. L'objectif de cette thèse est de proposer une désulfuration des fiouls marins par ODS. Toutefois, l'ODS sur les fiouls lourds est encore immature et les fiouls marins restent peu étudiés

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avec peu de publications reportées dans la littérature. Les travaux de cette thèse se sont donc tout d'abord portés sur le développement d'une méthodologie fiable pour l'analyse des composés soufrés dans les combustibles marins, avant une étude pour la détermination d'un catalyseur efficace et approprié, couplée à l'optimisation des conditions opératoires. Parmi une large variété de fiouls marins, trois fiouls ont été choisis, caractérisés par une viscosité élevée variant de 380 à 700 cSt. Les résultats d'analyse chimique ont révélé des teneurs élevées en soufre entre 0,6 et 3,2 % reflétant la variabilité de composition des combustibles marins. La réaction d'ODS a été effectuée par catalyse hétérogène à l'aide du système MoO_3/Al_2O_3-H_2O_2 dans un réacteur batch. Les effets du temps de réaction, du rapport molaire oxydant/soufre (Ox/S) et du solvant d'extraction ont été étudiés. Le couplage des ultrasons avec l'ODS classique a permis d'obtenir de meilleurs taux de désulfuration grâce à l'effet de synergie amené par l'utilisation des ultrasons. Des études sur les effets de la teneur en molybdène, du dopage au phosphore et/ou au vanadium et du type de précurseur du molybdène ont été réalisées sur le catalyseur molybdène sur alumine. D'autres supports oxydes ont également été utilisés, améliorant considérablement les performances catalytiques. Dans des conditions de réaction optimales et avec les catalyseurs les plus efficaces, il a été possible d'oxyder toutes les charges sélectionnées et de les désulfurer pour les rendre compatibles avec les nouvelles normes 2020.

Mots Clés : ODS, H_2O_2, extraction, MoO_3/Al_2O_3, ultrason, fiouls marins.

Les travaux de cette thèse, en collaboration avec SEGULA Technologies (thèse CIFRE), sont confidentielle et ne peuvent être divulgués sans autorisation.

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Symbols, acronyms and abbreviations

SECA	Sulfur Emission Control Areas
LNG	Liquified Natural Gas
HDS	Hydrofesulfurization
ODS	Oxidative desulfurization
ULSD	Ultra-Low Sulfur Diesel
HSFO	High Sulfur Fuel Oil
IFO	Intermediate Fuel Oil
LSFO	Low Sulfur Fuel Oil
ULSFO	Ultra Low Sulfur Fuel Oil
Cx-BTs	Alkyl Benzothiophene
DBT	Dibenzothiophene
DMDBT	4,6-Dimethyldibenzothiophene
tBHP	tert-butylhydroperoxide
H_2O_2	30 wt.% hydrogen peroxide in water
LHSV	Liquid Hour Space Velocity
VGO	Vaccum Gas Oil
SRGO	Straight Run Gas Oil
LCO	Light Cycle Oil
DMF	N,N-Dimethylformamide
ACN	Acetonitrile
NMP	N-methyl pyrrolidone
GC	Gas chromatography
GC-SCD	Gas chromatography coupled to sulfur chemiluminescence detector
GC-NCD	Gas chromatography coupled to nitrogen chemiluminescence detector
HPLC	Polyaromatic hydrocarbon liquid chromatography
Sulf-UV	Sulfur analysis by Ultra-Violet fluorescence
UAOD	Ultrasound Assisted Oxidative Desulfurization
XRF	X-Ray Diffraction
R	Raw fuel
D	Diluted fuel
DC	Diluted Centrifuged fuel
DF	diluted Filtered fuel
cSt	Centistockes
SP	solid Phase
C12	Dodecane
X	Xylene
C12-X	Dodecane-Xylene
C7	Heptane
S/F	Solvent to Fuel ratio
MS	Mechanincal Stirring
US	Ultrasound

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General Introduction

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General Introduction

Fuel oil is an important derivative of crude oil mainly used in the commercial maritime shipping industry. The environmental impact of this energy vector continues to be a major challenge due to its high sulfur content. Sulfur compounds are among the most hazardous deleterious petroleum contaminants. During fuel combustion, sulfur oxides gases (SOx) are emitted and contribute to air pollution. The consequences of this pollution on the environment are becoming increasingly important, leading to the depletion of the ozone layer and climate change in particular. Much attention has been paid to air pollution (lead, NOx, SO_2), and particularly to sulfur dioxide leading to the formation of acid rain, which in turn contributes to soil and forest degradation and causes respiratory problems.

In order to avoid these serious health and environmental consequences, strict regulations have severely limited the sulfur content of fuels. The acceptable level of sulfur in diesel was reduced by the Clean Air Act CAA amendments to 15 ppm from 2006 in Japan and USA and to 10 ppm in Europe in 2009.

In the case of marine fuels containing high levels of sulfur content, regulations concerning pollutant discharges from ships are now evolving with the implementation of the MARPOL Convention, in particular Annex VI concerning emissions of sulfur oxides (SOx) from fuels combustion. Responding to the desire of some coastal nations for further reduction of SO_x emissions from ships in their regions, Sulfur Emission Control Areas (SECAs) have been instituted. SECAs consist of the Baltic Sea area, the North Sea area, the North American region (containing the coastal sector of the United States and Canada), and the United States Caribbean Sea areas (around Puerto Rico and the United States Virgin Islands) (Figure 1) Thus, the maximum sulfur content by mass of marine fuels authorized in these areas was decreased from 1.0 wt.% to 0.1 wt.% on 1 January 2015 (IMO: MARPOL). A decision taken by the international maritime organization in October 2016 will impose the reduction of this sulfur limit in marine fuels from 3.5 to 0.5 wt.% by 2020 for all other areas.

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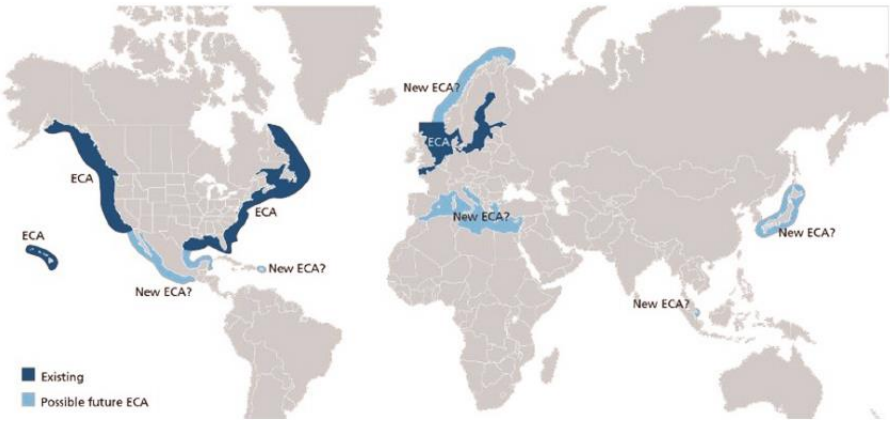

Figure 1: Existing and possible future ECA zones worldwide.

To meet the regulations and reduce these emissions, ship-owners have several options and can currently use lower sulfur fuels such as liquefied natural gas (LNG) or low sulfur marine diesel, or they can apply post combustion treatment where they continue to use sulfur-rich fuels using exhaust gas cleaning systems (scrubbers). However, each solution has its own serious drawbacks and implications. It has been predicted that LNG can account for only 50% of shipping energy demand by 2050 [1,2]. Moreover, the use of LNG entails high capital investments, including the capital cost of new-storage tanks. The function of a scrubber on a seagoing vessel is to use seawater to wash out the sulfur in the exhaust gas. Regulations will also have to change on this point in order to restrict all discharges (liquid, solid or smoke) and these systems alone may not meet the most stringent limitations [3]. In addition, scrubbers may require significant modifications on ships demanding high capacity investments. Furthermore, in the long term and with the expected regulatory changes, the storage of sulfur waste in the hold and the treatment of scrubber washing water may also pose a space problem. The integration of the device into the ship is therefore a key factor. The use of low-sulfur marine diesel is the only current option without significant modification. Nevertheless, an additional cost is associated with the purchase of diesel compared to marine fuel (up to 40 to 60% depending on price quotations). Scenarios of switching to a 50% or 100% distillate marine fuel scenario also show CO_2 emissions 7.5–15 times higher than the low sulfur residual marine fuel case [4]. The model used to obtain these results considers the balance of the entire refinery and economic optimization, so the higher CO_2 emissions also reflect the difficulty of producing distillate marine fuels, which is already a high-demand product.

In this context, SEGULA Engineering France aims at developing a pre-combustion desulfurization process that allows ships to continue to use heavy fuel oil as fuel while complying with MARPOL regulations on sulfur oxide emissions. A desulfurization concept process is proposed, adapted to marine fuel oil and integration constraints in a ship, taking into account the treatment of generated byproducts. Among desulfurization techniques, the conventional refining

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process for desulfurization known as hydrodesulfurization (HDS) cannot be adopted. The ships are not designed for the installation of refining equipment, working under high pressure of hydrogen. Moreover, it requires additional energy and high hydrogen consumption to produce lower-sulfur marine fuels. Thus, researches focused mainly on the non-hydrogenation desulfurization methods [5,6]. Among these methods, oxidative desulfurization (ODS) attracted researchers' attention. It consists of a two-step reaction: first the sulfur molecule is converted by oxidation to its corresponding sulfones in the presence of an oxidant, then, a purification step is applied in which oxidized sulfur compounds are separated mainly using extraction or adsorption method. In addition, this process is attractive because of the high oxidative reactivity of 4,6-dimethyldibenzothiophene (DMDBT), known as a refractory molecule in the HDS of diesel feed.

Oxidative desulfurization is an interesting solution meeting criteria established by SEGULA for future integration into a global desulfurization process: no hydrogen consumption, limited reaction temperature and atmospheric pressure. Moreover, oxidant such as hydrogen peroxide may be produced onboard in the long term and generated coproducts (sulfones) can be further treated to minimize all pollutant releases. A significant number of reviews related to oxidative desulfurization process have been published but were mainly dedicated to model molecules. The technology of heavy fractions ODS is still immature. Moreover, despite the high number of publications related to ODS diesel fractions, it is not currently used in a commercial or refinery stage nor tried for marine fuel oil. The identification of the formed sulfones can be also considered, in order to valorize these compounds on the scale of the global desulfurization process to be developed by SEGULA Engineering France.

The objective of this thesis focuses on the first step of an integrated process, proposing an oxidative desulfurization of marine fuels. The work will have to focus on the development of a reliable methodology for the analysis of sulfur compounds in marine fuels, and on the optimization of an appropriate and efficient catalyst for the reaction of ODS for the fuels with optimized operating conditions for the reaction.

In this manuscript, we will first present in Chapter I the state of the art concerning analysis of marine fuels in addition to oxidative desulfurization reaction applied to different fuel. ODS principle, potential application, different catalytic systems used in the ODS, in particular heterogeneous based catalysts will be developed. Moreover, we will present a review accepted in the thesis dealing with ODS of heavy oils explaining the difficulties and the difference in ODS conditions when heavy samples are considered.

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Chapter II describes the different preparation methods of catalysts, characterization techniques together with test protocols used in ODS of marine fuels along with analytical methods involved in identification and quantification of compounds inside marine fuels.

Chapter III is dedicated to the characterization of marine fuels. Elemental analysis of raw fuels will be fully detailed. Moreover, analysis of total sulfur compounds and nature of sulfur compounds will be presented for the different fractions of fuels. Work is not restricted to sulfur compounds, speciation of aromatics and nitrogen species will be also included. Due to the high viscosity and complexity of marine fuels containing high molecular weight and high boiling point molecules, characterization of marine fuels will include a development and optimization of analytical techniques conditions.

In chapter IV after optimization of the ODS reaction conditions, reactivity of three different marine fuels will be compared with the use of the classical Mo/Al_2O_3 oxide catalyst. Evaluation of the total sulfur elimination after extraction will be also performed.

Finally, Chapter V will study the performance of different catalysts families, allowing to highlight an efficient catalytic system with high reactivity of sulfur molecules. The study will include a large variety of active species and supports with distinctive properties (surface area, oxygen mobility, acid-base properties).

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State of Art

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Chapter I State of Art

This chapter presents a literature review on desulfurization using oxidative desulfurization method.

The first part of this chapter introduces the main properties of marine fuels.

The second part focuses on the oxidative desulfurization reaction (ODS) and develops its principle, its potential application with different oxidant and catalytic systems encountered. Moreover, this part includes a brief introduction of recent technologies (ultrasounds and ionic liquids) coupled to ODS in order to enhance its performance.

The third part of this chapter is devoted to the recent advances in ODS reaction when applied to high sulfur content real fuels and in particular heavy feedstocks. All reaction aspects will be presented in the review attached, published in Catalysts (Catalysts 2018, 8, 344; doi:10.3390).

At the end of the chapter, a conclusion positions the ODS process to be applied on marine fuels and introduces the objective of this thesis work.

I.1. Marine Fuels

I.1.1. Definition

Marine fuels, also known as heavy fuel oils (HFO) [1], Residual Fuel Oil or Bunker fuel, are mainly derived from the residues of various refinery distillation or cracking processes. They are a complex mixture brown to black liquid (solid at room temperature) with a characteristic odor. They are generally mixed with other lighter cuts to meet viscosity and composition specifications that guarantee their performance and limit their impact on the environment.

Heavy fuel oil is the cheapest fuel among the products derived from refining processes. In addition to marine applications (marine fuels), it is still used in power stations in combustion equipment such as boilers, furnaces and diesel engines (maximum sulfur content of 1 wt.% S for these uses).

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I.1.2. Categories

The International Maritime Organization (IMO) has proposed in ISO 8216 and ISO 8217 standards a classification of marine fuels in categories according to their sulfur content and viscosities. **High Sulfur Fuel Oils (HSFO)** are highly viscous residual fuel oils with viscosities as high as 700 cSt (given 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 the 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. Since 1 January 2015, in accordance with MARPOL Annex VI, marine fuels must not contain more than 0.1 wt.% sulfur in these protected areas (SECAs). LSFOs can no longer be used alone (without scrubbers) in these areas and have been replaced by **ultra-low sulfur marine fuel (ULSFO)**, which uses low sulfur marine diesel fuel.

I.1.3. Properties

The knowledge of the properties and composition of the feedstock is primordial to ensure high process efficiency. Important properties that can characterize a residual matrix are the physical properties such as density and viscosity as well as the chemical properties with evaluation of carbon, hydrogen, sulfur and nitrogen given by elemental analysis.

I.1.3.1. Physical Properties

I.1.3.1.1. Density

Density is important criteria for the quality of fuel oils. The hydrogen content is generally related to density and boiling point. Indeed, a high hydrogen content generally implies a low density. The density gives an indication of the ignition quality of the fuel. The density of heavy fuel oils normally varies between 900 and 1000 $kg.m^{-3}$ at 15°C. Fuel oils from catalytic cracking residues are denser than those obtained from atmospheric distillation. In this case the density can increase beyond 1000 $kg.m^{-3}$ which has environmental implications in case of oil spilling into sea water [2].

I.1.3.1.2. Viscosity

Kinematic viscosity is a measure of the fluidity of fuel oil at a certain temperature. The viscosity of an oil decreases with increasing temperature. The high viscosity of fuel oils is a key

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parameter that requires constant heating in order to transport fuels in lines and to maintain them in a physical state adaptable to be injected in engines. The heating temperature before injection into the engine is regulated to obtain the required viscosity. The kinematic viscosity for marine applications is therefore reported at 50°C and 100°C. Expressed in centistokes ($mm^2.s^{-1}$), it characterizes the fuel oils from which the name IFO380 or IFO180 comes. Typically, IFO marine fuels (a mixture of HFO and lighter fractions) have a kinematic viscosity of 380 or 180 cSt at 50°C. Generally speaking, the viscosity of fuel oils at 100°C varies between 6 and 50 cSt.

I.1.3.2. Elemental Analysis

Marine fuel is made from the heaviest and most residual fractions of crude oil. It is a complex mixture of molecules from different sizes, polarities and structures. Their boiling range vary from 350 and can go up to 650°C with carbon range between C20 to C50. It also contains asphaltenes (cf I.1.3.2.4) and smaller amount of heteroatoms (sulfur, nitrogen, oxygen and organometallic compounds) whose contents vary according to the nature of the crude origin. To better understand the nature of this charge, its characterization is crucial.

I.1.3.2.1. Nitrogen and Oxygen

The mass content of nitrogen compounds in heavy fractions can reach up to 1% while for diesel the nitrogen content is not above 0.1%. They have basic or neutral character. The presence of these compounds can lead to the poisoning of catalysts used in heavy-duty conversion processes, and can also be oxidized during ODS process, in competition with sulfur containing compounds.

Oxygenated compounds are present in low concentrations (between 0.05% and 1.5% by weight). These are acidic compounds that can cause corrosion problems in pipes or containers. Figure I.1 provides examples of oxygenates found in crude oil and petroleum cuts [3].

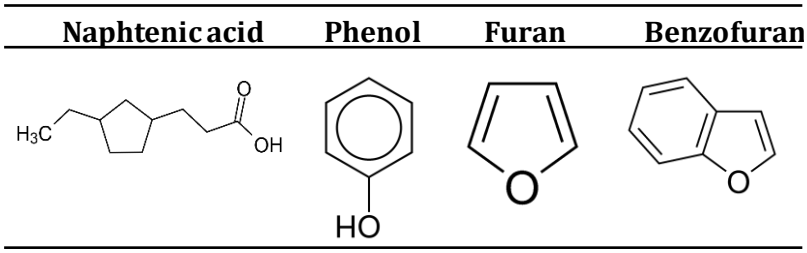

Figure I.1 : Oxygenated compounds present in marine fuels.

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I.1.3.2.2. Metals

Metals in crude oil are mainly nickel and vanadium. Other metal ions reported form crude oils, include copper, lead, iron, magnesium, sodium, molybdenum, zinc, cadmium, titanium, manganese, chromium, cobalt, antimony, uranium, aluminum, tin, barium, gallium, silver and arsenic. But nickel and vanadium are the most abundant. Metals in crude oils are of fundamental interest for better understanding geochemical origin of petroleum source. The information could be useful for catagenetic oil formation, maturation of organic matter, correlation, depositional and environmental studies [4]. They are concentrated in the heaviest residual fractions only. Metals are found as complex organometallic structures, associated with resins and asphaltenes [1,5]. The content of these metals can reach up to 1000 ppm in the case of the heaviest oils. They are responsible of poisoning the catalysts used in heavy-duty conversion processes. Vanadium is of major significance for fuels burned in both diesel engines and boilers because when combined with sodium (perhaps from seawater contamination) and other metallic compounds in critical proportions it can form high melting point ashes which are corrosive to engine exhaust valves, valve seats and super heater elements.

I.1.3.2.3. Sulfur

The old classification of crude oil was based on its sulfur content. Because sulfur is the most common and the least desired heteroatom in petroleum and the various petroleum cuts, the quality and then actually the price of crude oil varies with the sulfur content present. In particular, it has serious environmental impacts with the emission of harmful sulfur oxides following the combustion of fuel oil. In addition, sulfur can lead to the deactivation of catalysts used in refining processes.

Sulfur is naturally present in crude oil. The nature and sulfur composition of petroleum varies depending on the origin of the crude oil. The sulfur content can fluctuate between 0.5 wt.% in the case of light crude oil and up to 10 wt.% in the case of the heaviest crude oil in Venezuela [6].

Sulfur exists in two forms, either inorganic such as elemental sulfur or hydrogen sulfide, or integrated into organic molecules. In these molecules, sulfur is present in the form of the following chemical families:

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- Mercaptans or thiols, R-S-H where the terminal atom is an alkyl chain or paraffin.

- Sulfides R-S-R'. Polysulfides can be obtained depending on the number of sulfur atoms connected.

- Thiophenes, a family characterized by the aromaticity of its compounds. Thiophene is a cyclic molecule with a sulfur atom. It is divided into two groups:

o Benzothiophene (BT) and its alkylated substituents,

o Dibenzothiophene (DBT) and its alkylated derivatives.

The distribution of sulfur compounds varies with the nature of the oil cut: in general, the heavier the cut, the higher the sulfur content and the more complex its structure. According to Uhler *et al*. [7], between 70 and 90% of sulfur compounds are concentrated in the residual fraction of petroleum where cyclic sulfur compounds and high molecular weight sulfur aromatic polys (PASH) are found.

In the case of the diesel, which is the most studied fraction in desulfurization processes, both groups of sulfur compounds BT and DBT are generally present. However, composition in sulfur products depends on the origin of the crude oil and the refining process from which diesel is derived. For example, SRGO mainly contains alkyl-BTs and alkyl-DBTs as well as thiophenes, thio-ethers and thiols, whereas in the case of gas oils such as light cycle oil (LCO) resulting from catalytic cracking, sulfur compounds are limited to BTs and DBTs [4]. In the case of residual fuel oils, which are made of hydrocarbons with the highest boiling points, the nature of the sulfur compounds can be the same as diesel but in different proportions. Thiophene compounds are present in the form of benzo-dibenzonaphthobenzo-thiophenes and various derivatives.

I.1.3.2.4. Resins and Asphaltenes

Asphaltenes and resins are two of the many heavy organic compounds. Their exact molecular structure is generally not known.

Petroleum asphaltenes are high molecular weight fractions that are insoluble in low molecular weight paraffins (n-heptane, n-pentane) but soluble in some aromatic solvents such as toluene, pyridine or benzene. They are poly-aromatic condensed rings with short aliphatic chains and polar heteroatoms. They are considered as the heaviest with very high molecular weight (2000-5000) and most polar fraction of crude oil. Their presence makes the fluid viscous and difficult to handle and transport. Therefore, it is necessary to ensure that these compounds remain in suspension over the normal range of storage temperatures. In addition, during hydrotreating processes, asphaltenes can deactivate catalysts due to their high heteroelement content. In the

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presence of catalysts, the diffusion of compounds to catalytic sites is limited by the presence of asphaltenes, reducing process efficiency. Finally, the severe process conditions (high temperatures and pressures) cause chemical modifications, which can make the system unstable, precipitating asphaltenes and reducing their diffusion properties.

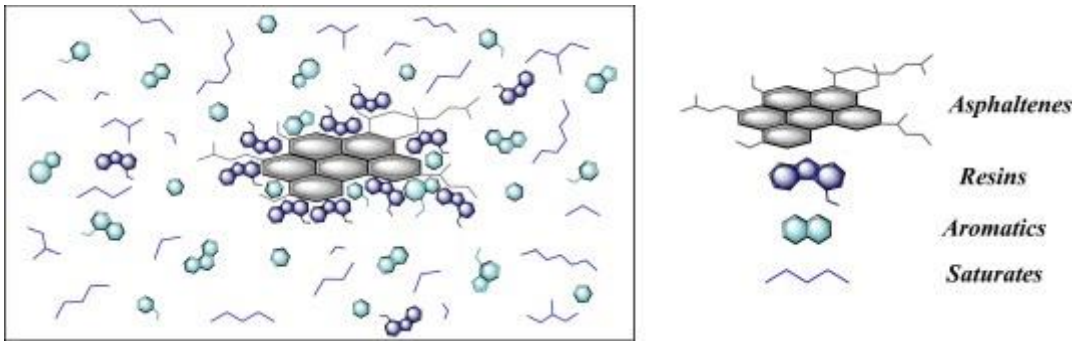

Figure I.2: SARA fractions in crude oil [8].

Asphaltenes are surrounded by maltenes, made up of resins, aromatics and saturated substances (Figure I.2) known in the acronym of SAR. The physico-chemical properties of maltenes may be similar to those of asphaltenes. Resins are a polyaromatic entity containing heteroatoms and metals. Their polarity is intermediate between those of asphaltenes and aromatics. In addition, they are soluble in n-heptane but precipitate in pentane [9]. Associative behavior is less pronounced than that of asphaltenes. They are present in minority in the tailings. This fraction plays a very important role in dissolving asphaltenes in the environment and preventing their precipitation. Maltenes adsorb on the surface of colloidal asphaltene particles and play a role as dispersant because they have an intermediate polarity between the asphaltenes and the rest of oil. However, authors such as Pereira *et al.* [10] believe that resins can also be responsible for both the stability and instability of asphaltenes. They correlated asphaltene stability/instability issue to the resin molecular self-interaction intensity. They suggested that resins with weak self-interaction exhibit a low adsorption tendency and tend to stabilize asphaltenes against flocculation. In contrast, resins that strongly self-interact exhibit high adsorption and produce a thick and sticky adsorbed layer, which favors flocculation of contacting asphaltene particles.

The characterization of marine fuels, which are made up of the heaviest fractions of oil, highlights the complexity of the charge, which contains many highly complex molecules. The publications of Uhler *et al*. [7] report the composition of marine fuels. Chromatography analysis coupled to FID (flame ionization detector) or MS (mass spectrometry) detector of different marine fuels was considered to identify boiling point distribution of hydrocarbons inside marine fuels. The target compounds consisted of selected *n*-alkanes and isoprenoids and chromatographic

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carbon ranges (i.e., C10–C25, C25–C45). GC/MS analysis was also realized to identify 2- through 6- ring aromatic compounds as well as high molecular weight polycyclic aromatic hydrocarbons. Widely used HFO and IFO samples composition was found to be very diverse making it difficult to establish a unique fingerprint for marine fuels. This work gave an idea about the hydrocarbon analysis in marine fuel but with no detailed analysis of heteroatoms inside fuels. Despite the different analytical techniques available, it is very difficult to characterize marine fuels individually at the molecular level. But as with all processes, knowledge of the matrix will be a key step. The study and analysis of sulfur species present in marine fuels will be crucial steps to be completed for a better understanding of catalytic tests.

I.2. Oxidative desulfurization ODS

I.2.1. Generalities

I.2.1.1. Oxidation Reaction

The oxidation reaction takes place in liquid or gas phase. Gas phase oxidation of diesel fractions is presented by a few works. The principle of gas phase ODS consists in selective oxidation of sulfur containing compounds to sulfur dioxide and sulfur trioxide with subsequent trapping of these products by adsorption methods followed by condensation of liquid diesel fuels. The mechanism of oxidation of cyclic sulfur containing compounds was not described in literature, however ODS proceeds via a step of the adsorption of a sulfur containing molecule on the catalyst surface and its subsequent oxidation to sulfur dioxide, with following desorption in gas phase. Gas phase ODS occur at atmospheric pressure but with temperatures 180-250°C and can reach up to 400°C [11].

Liquid phase reaction has been the most studied [12]. ODS in liquid phase is performed at a temperature below 120°C at which light petroleum fractions exist in liquid phase, and at atmospheric pressure. The process is carried out in two steps (Figure I.3) in the presence of an oxidant and a catalyst. At first, sulfur molecules are transformed to sulfoxides and sulfones by oxidation of divalent sulfur, by an electrophilic addition of oxygen atoms to hexavalent sulfur. Sulfoxides are only obtained when using weak oxidizing agent such as sodium periodate that is able to do partial oxidation of sulfides [13]. The formed sulfones which have different physical and chemical properties from hydrocarbons are removed in the second step by a separation technique as extraction, adsorption or thermal decomposition. The strong affinity of sulfur for oxygen, permits selective attachment of oxygen to organic sulfides and thiophene derivatives without rupture of C-C and C-S bonds.

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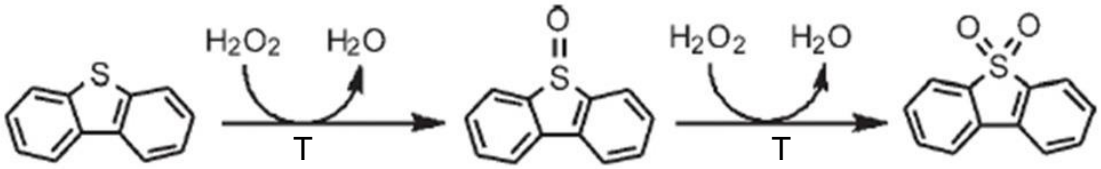

Figure I.3 : Reaction pathway for ODS of DBT molecule.

ODS reaction has been studied on real and model feeds. The advantage of ODS is its low cost, high selectivity, no consumption of expensive hydrogen as in the case of HDS. It was used as a finishing process after HDS for the post treatment of the most refractory sulfur compounds in HDS of diesel fuels [14].

Numerous catalytic systems have been considered in ODS reaction. They are mainly categorized into homogenous or heterogeneous catalysts. The main type of homogeneous catalysts reported in the literature are carboxylic acids as well as homogeneous metallic systems such as polyoxometalates. Formic and acetic acids are considered the most used catalysts in ODS among the carboxylic acids.

Upon the use of homogeneous or heterogeneous metal based catalysts, oxidation reaction mechanism is the same. Metal peroxide intermediate is formed by nucleophilic attack of oxidant on metal of VI-group located on heterogeneous surface or in homogeneous catalyst. Electrons are withdrawn from the peroxyl moiety and the electrophilic character of the peroxidic oxygen is increased. The S-containing compound oxidation proceeds by nucleophilic attack of an active peroxycomplex to form sulfoxide and regenerated metal-species. Then the sulfoxide undergoes further oxidation by metal-species or by metal-peroxycomplex with formation of sulfone. In the case of Mo/Al_2O_3 system, some articles proposed a mechanism [15–17]. For instance, ODS mechanism proposed for the Mo/Al_2O_3 system in the presence of H_2O_2 and Mo/Al_2O_3 in the work of Garcia *et al*. is presented in Figure I.4.

1. The hydroperoxymolybdate group can be formed by nucleophilic attack of hydrogen peroxide on the oxo bridging ligands of the hepta and octamolybdate species on the surface of the alumina.
2. The hydroperoxymolybdate species (2) undergoes a reversible loss of a water molecule to produce the monoperoxo species (3). As a result, the peroxo group is electrophilically activated.
3. In the same way, it is possible to form the diperoxo species. The mono- and diperoxo species are in equilibrium with the original hepta and octamolybdate species.

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4. ODS occurs by nucleophilic attack of the sulfur atom in organosulfide compounds (4) on a peroxo group of the species mono- or diperoxo (3) to form sulfoxide (5). This attack can occur on one (or both) of the peroxo groups present on molybdenum diperoxo species.
5. Subsequently, the sulfoxide (5) is further oxidized by a pe-roxide oxide of the peroxo molybdenum species (3) to form sulfone (6).

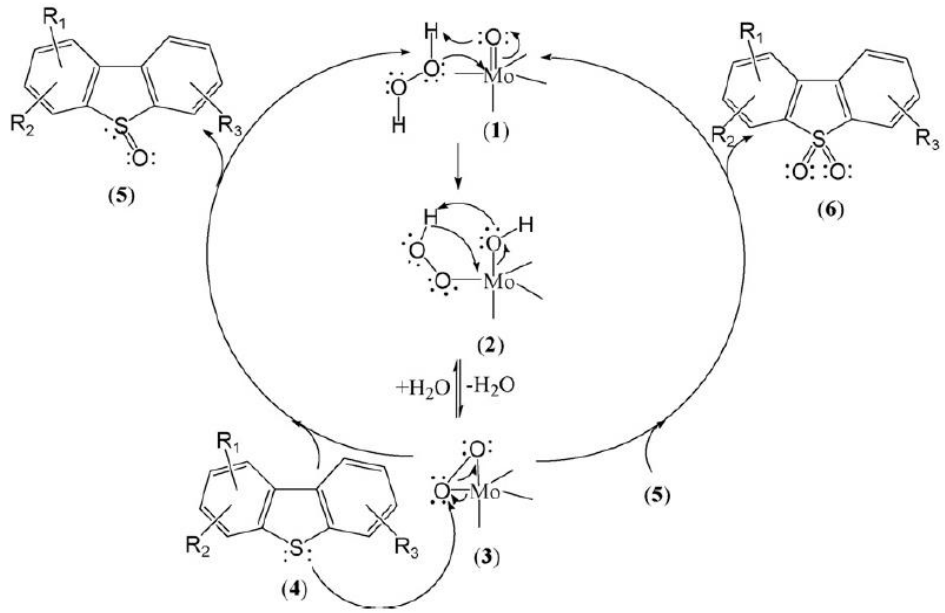

Figure I.4: Proposed mechanism for oxidative desulfurization of sulfur species using Mo/Al_2O_3-H_2O_2 system [17].

The evolution of ODS research has led to industrial processes based on ODS. More than 30 patents have been filed by various companies. Five ODS processes for deep desulfurization of the diesel have reached the demonstrator stage [14] (Stanislaus *et al.*), however none have reached the commercialization stage. Most likely, other parameters, such as the incorporation of additional steps to obtain a suitable final diesel product, have been omitted and have a negative impact on the economic balance sheet. To achieve Ultra-Low Sulfur Diesel, refiners seem to prefer the renovation of existing hydrodesulfurization units rather than installing a new unconventional process [14,18]. Nevertheless, with heavy cuts, ODS remains an advantageous solution that allows the treatment of HDS-refractory molecules, which also requires more severe conditions, with higher pressures and temperatures[19].

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I.2.1.2. Separation of sulfones : Extraction

Among the separation methods, liquid-liquid extraction is mainly used after oxidation of the sulfur compounds. After extraction, the desulfurized feedstock is recovered by distillation and the solvents can be reused for several extraction cycles.

This method is a traditional method for separating the desired components according to their solubility using specific solvents characterized by their polarity and dielectric constant. Although this method seems relatively simple, the use of appropriate solvent is crucial to guarantee effective separation.

Liquid-liquid extraction has been frequently used as a separation method on different model feedstocks. Most studies have reported the use of polar solvents such as acetonitrile[20], DMF, methanol, butyrolactone [17,21], N, N-dimethylpyrrolidone [16]. For model feeds initially containing DBT or 4,6 DMDBT, acetonitrile and methanol have been demonstrated as highly effective extraction solvents [22–27].

Separation techniques are not limited to liquid-liquid extraction; adsorption can also be used [28–30] with different types of adsorbents (alumina, activated carbon, zeolites, polymers). In this method, sulfones are preferentially adsorbed and retained on adsorbent. The adsorbent can be reused after regeneration at high temperature.

Regardless of the separation technique used, most articles offer a desulfurization measurement by a global sulfur analysis after an extraction or adsorption step of the sulfur compounds. The desulfurization rate is mainly assessed by measuring the overall sulfur content after the extraction stage (S_{final}) in relation to the initial sulfur content (S_{init}) with an X desulfurization equal to (S_{init}-S_{final}) / S_{init} x 100 expressed as a %. The reported desulfurization results are actually measured after ODS and therefore result from a combination of oxidation and extraction of sulfur compounds.

However, some articles calculate the conversion of sulfur compounds to sulfones directly after oxidation. This conversion is based on the quantification of sulfur species using the chromatography technique. Quantitative measurements are performed by identifying typical peaks in the chromatogram and integrating them to determine and compare the effectiveness of catalytic systems [31–34].

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I.2.2. Reactivity of sulfur compounds

Various studies have reported the ODS reactivity of sulfur compounds with different catalytic system. The results depend on the oxidant/catalyst system. With hydrogen peroxide as oxidizing agent, the reactivity of the species is highly dependent on the nature of the catalyst used. The reactivity varies also according to the electron density of the sulfur atom and the steric hindrance of the alkyl substituents.

The homogeneous H_2O_2/formic acid catalyst system has been the subject of numerous studies on the reactivity of sulfur molecules [20,35]. Reactivity then seems to increase with the increase in electron density of the sulfur atom. Thus, the reactivity of molecules such as 4,6-DMDBT is higher than that of DBT and BT.

With the H_2O_2/phosphotungustic acid system studied by Ali *et al.* [36], the reactivity of species was also affected by the steric hindrance of substituted alkyl groups with reactivities in the following decreasing order: DBT > 4-methyl, 6-ethyl DBT > BT.

The same parameters can be applied to heterogeneous systems. The study by Jiang *et al.* [37] with a model charge in the presence of H_2O_2, an ionic liquid and a solid catalyst of the dialkylpiperidinium tetrachloroferrate [C_2OHmpip] $FeCl_4$ type, shows that after 60 min of reaction, the reactivity of the sulfur compounds follows the order DBT > BT > 4,6-DMDBT. The study shows the effect of two parameters: electron density and steric hindrance. The authors explain the low reactivity of 4,6-DMDBT by the steric congestion on the sulfur atom, and the lower reactivity of BT compared to DBT by the lower electron density on the sulfur atom (5.739 vs 7.578).

Caero *et al.* [38] demonstrate different reactivity results, with an H_2O_2 system, V_2O_5/TiO_2 catalyst on model molecules with an Ox/S=8 ratio. Reactivity decreased in the order DBT > 4-MDBT > 4,6-DMDBT > BT indicating the steric effect achieved by alkyl substituents. Indeed, for DBT, 4-MDBT and 4,6-DMDBT, the electron densities on the sulfur atom are very close (5.758, 5.759 and 5.760, respectively), and in this case in heterogeneous catalysis, methyl groups become the main obstacle to the sulfur atom's approach to the catalyst's active phase.

However, Sampanthar *et al.* [39] showed that the increased electron density on the sulfur atom in substituted thiophene derivatives compensated for the steric effect of alkyl groups where the oxidation of model thiophene compounds on an 11% MnO_2/Al_2O_3 catalyst in the presence of air varies in the order: 4,6-DEDBT > 4,6DMDBT> 4-MDBT> DBT.

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I.2.3. Oxidant choice

A significant amount of research has been conducted on ODS oxidizing agents, including oxidants such as hydrogen peroxide, organic peroxides, ozone, oxygen, nitrogen oxides, and nitric acid.

Sulfides are more reactive than other hydrocarbons because it has expanded octets and can form additional bonds with other atoms. Nevertheless, finding a selective oxidant is very important.to avoid oxidation of other hydrocarbons like alkane, alcohols or alkene that can occur using transition metal homogeneous catalysts in the presence of organic solvents [40] and to avoid other reactions such as hydrogenation, condensation and polymerization. For instance, in the case of light hydrocarbon fractions like gasoline, the oxidation the olefins present in the feedstock results in a decrease in the octane number. In addition, this oxidation also increases the loss of charge by extraction of oxidized hydrocarbon compounds other than sulfur compounds [41] .

Guth and Diaz [41] demonstrated the oxidation of sulfur compounds with nitrogen oxides like NO_2 and NO_3. The reaction was applied to the residual fuel oils and the separation of the sulfones produced by liquid-liquid extraction using methanol. The desulfurization of residual fuel oil with a sulfur content of 2.2 wt.% S reached 88% in a continuous reactor at a temperature of 150°C for 4 min. Then, Guth *et al.* [27] developed the oxidation of sulfur compounds using nitrogen oxides and oxygen to sulfur trioxide which is absorbed with concentrated sulfuric acid; however, the desulfurization rates obtained were low. Tam *et al.* [42] worked on ODS with nitrogen oxides on different charges with sulfone extraction with different solvents. The desulfurization of shale oil (2.85 wt.% S) into gaseous sulfur oxides reached 62% after one hour of reaction at 60°C. Several patents have been issued on the ODS of automotive fuels using gaseous oxidants such as air and ozone [43,44] . The separation of the sulfones in these processes was carried out by adsorption. The reaction took place at temperatures between 25 and 90°C, LHSV between 0.5 and 10 h^{-1}, the overall sulfur content has decreased to 10 ppm. Sherman [45] patented the use of oxygen for ODS of diesel containing 233 ppm sulfur whose content was reduced to 12 ppm after reaction at a temperature of 160°C and a pressure of 14 atm. The use of ozone has been tried for model feeds. ODS of thiophene was carried using a catalyst based on zirconia sulfate with 100% desulfurization [43]. The different studies showed that desulfurization performed using selective oxidizing agents as air, ozone, or nitrogen oxides presents a main drawback: the emission of the reaction product SO_2 is detrimental to environmental protection by Javadli and De Klerk [46].

Various studies [26,47–50] mention the use of the hydrogen peroxide (H_2O_2)/organic acid system which can be coupled to a catalyst for the ODS reaction. Peracids, highly reactive and

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corrosive, are produced during the reaction. The reaction is carried out according to the following steps: first, H_2O_2 reacts with organic acid to give the peroxide acid, the acid formed then reacts with the sulfur compound to give the sulfones. Petro Star Inc. A process has thus been developed and patented in which diesel fuel is mixed with peroxyacetic acid, the oxidation of sulfur compounds is carried out at 100°C and at atmospheric pressure. After the removal of the sulfones, the sulfur content in the fuel is reduced from 4200 to 10 ppm. However, the main disadvantage of these systems is that they are expensive and difficult to recover [14].

Organic peroxides have shown good oxidation performance of sulfur compounds. The most commonly used hydroperoxide is tert-butylhydroperoxide (tBHP). The main advantage of these systems is that it is soluble in the hydrocarbon-based phase, forming a single miscible phase, which simplifies the design of the reactors used. This oxidant has been used in batch and fixed bed reactors. In the case of the batch reactor, Yan *et al.* [51] reported the ODS of the DBT model molecules using tBHP with an SBA-15 catalyst. This catalyst, being both a catalyst and an adsorbent, has achieved a desulfurization rate of 90%. An ODS process based on this oxidant has been patented [52,53] by Lyondell Chemicals and EniChem/UOP. The Lyondell process used extraction for sulfone separation, while EniChem/UOP removed sulfones by adsorption. Despite the advantage of the miscibility of tBHP with hydrocarbon feed, one major drawback is the waste treatment of the t-butyl alcohol by-product generated. In addition to its high price, another major disadvantage is the low amount of active oxygen per unit mass (17 to 10%), which makes it very expensive to transport. Consequently, it is recommended to install a hydroperoxide production unit in the refineries, which is not profitable given the increase in investments in the capital cost.

The best candidate as an oxidizing agent is hydrogen peroxide. This has a high amount of active oxygen per unit mass (47%). In addition, it is a commercial product at a moderate price often used at the industrial level, a "green" solvent where the resulting by product is only water. Desulfurization of a commercial diesel fuel was carried out and the sulfur content was reduced from 0.2 to 0.05 wt.% after 48 hours of photo-irradiation [54]. However, this reaction is not applicable on an industrial scale due to the long reaction time. Qiu *et al.* [55] prepared $H_3PMo_{12}O_{40}/SiO_2$ catalyst for the ODS of model fuels using hydrogen peroxide. These HPMo / SiO_2 have been very effective for the oxidation of DBT and BT. At a reaction temperature of 70°C, the conversion rate of DBT reached 100% in only 60 min and the conversion rate of BT reached 99.2% in 150 min. Reaction times are still too high to be integrated into a refinery. When using H_2O_2, the main problem is related to the presence of two reaction phases: an oily phase with the sulfur compound and a polar phase containing the oxidant (H_2O_2) which is not soluble in the oily phase. For this reason, some authors have studied the use of phase transfer systems in the presence of H_2O_2. It improves miscibility between phases, thereby increasing the probability of contact

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between reagents and increasing the rate of reaction. Sachdeva and Pant [56] used phosphotungustic acid as a catalyst for the ODS of a real diesel cut with a phase transfer agent which is tetra-traoctylamonium bromide, in the presence of the oxidant H_2O_2. The authors reported that 98% of sulfur was removed.

I.2.3.1. Oxidant/Sulfur ratio

Considering the stoichiometry of the reaction (Figure I.3) the stoichiometry ratio of oxidant molecule to sulfur content designated as Ox/S is 2. Nevertheless, in the case of model molecules, a wide range of Ox/S ratios was used. Same model molecules depending on catalytic systems need sometimes high Ox/S to be 100% oxidized. For instance, Li *et al.* [57], for example, effectively used a ratio that is close to stoichiometry Ox/S=3 to oxidize DBT using supported phosphomolybdic acid immobilized on $ILSiO_2$ and H_2O_2 as oxidant. In another study by Trakarnpruk and Rujiraworawut [47], eventhough that H_2O_2 was also used but an Ox/S ratio of 10 was required for oxidation of the model mixture (BT, DBT and 4,6-DMDBT) in the presence of $Na_2HPW_{12}O_{40}$ catalyst and resulting in desulfurization rates of 95% for DBT and 4,6-DMDBT and 75% for BT.

In the case of real feeds containing complex mixture of molecules and therefore more difficult to oxidize, requiring a higher oxidant/sulfur ratio. Moreover, they may also contain nitrogen molecules that can compete sulfur molecules for oxidation. Yang *et al.* [58] performed the ODS of a diesel cut using phosphotungstic silver supported on silica, with an Ox/S ratio equal to 12. After 4 hours of reaction at 60°C, a change in sulfur content from 1800 ppm to 312 ppm was obtained. In another study using a heteropolyanion catalyst, the sulfur content of a 500 ppm diesel was reduced to 9 ppm with an Ox/S ratio of 20 [59]. In both cases the oxidant used was H_2O_2, the reported Ox/S ratio was very high.

Using the Mo/Al_2O_3 catalyst promoted by bismuth Bi but in the presence of TBHP, in a batch for 180 min, Prasad *et al.* reduced the sulfur content on diesel from 8000 ppm to 237 ppm, with Ox/S=2.5 within 180 min.

The literature reports the study of the effect of the Ox/S ratio on desulfurization results. Studies have shown that increasing this ratio improves conversion, but at a certain threshold (e. g. Ox/S=20) desulfurization performance decreases [16]. The objective is then to develop a catalyst that promotes reaction with a low Ox/S ratio to limit the use of an excess oxidant.

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I.2.4. Catalytic systems

I.2.4.1. Active Phase

I.2.4.1.1. Relevant elements for active phase

Various transition metal in their oxidic form have been reported for ODS applications. The use of molybdenum [17,34,60–64], tungsten [32,47,55,65–68], vanadium [29,69–71] or various oxides was then largely considered in the ODS of liquid fuels.

In studies conducted by Wang *et al.* [31], various metal oxides based on Mo, W, V, Nb, Zr, Cr supported on alumina were tested in the ODS of DBT in a fixed bed reactor using TBHP as oxidant. With an Ox/S=1.5 ratio, the best catalytic activity was observed for molybdenum oxide, with reactivity in the following decreasing order: MoO_3>WO_3>V_2O_5>Nb_2O_5>ZrO_2>CrO_3. They accounted this result to the coordination of hydroperoxide to Mo–O was improved by the increase of $Mo^{\delta+}$-$O^{\delta-}$ polarization of bond when MoO_3 was dispersed on Al_2O_3, and therefore, the electrophilicity of peroxy oxygen generated is enhanced favoring ODS reaction.

The MoO_3/Al_2O_3 catalyst has been tested on model molecules, with ODS reacting on a model charge formed of thiophenes, DBT and 4,6-DMDBT using an Ox/S=4 ratio [64]. Complete desulfurization of the DBT and DMDBT molecules was observed. The effect of molybdenum content was studied on the conversion of a DBT molecule. The conversion of the DBT molecule increased from 40.9% to 86.4% with the increase in Mo content from 10 to 14%. Then, a drop in conversion to 82% was observed with a Mo content of 18%. Apparently, the increase in molybdenum content has led to the agglomeration and growing of MoO_3 crystals, which has led to a decrease in activity.

Metal oxide catalysts derived from Mn, Co, W, Ni, V, Fe and Cu, respectively were tested also tested in ODS. In studies of Sampanthar *et al.*, Nawaf *et al.* and Abu Bakar *et al.* [39,72,73], DBT desulfurization using oxygen in a fixed reactor was evaluated. Among these catalysts, only manganese and cobalt oxides were found to be effective The ODS activity was reported for catalysts loaded with 2 or 5% Co_3O_4. However, in the case of MnO_2/Al_2O_3 catalysts, to have comparable results with 2 or 5% Co_3O_4, higher metal loading catalysts (11 and 13% MnO_2) should be used.

More precious and resistant metals such as palladium Pd-based systems can be used. Zapata *et al.* [74] compared the performance of catalysts based on Pd, Cr_2O_3, Co-Mo supported on alumina for ODS of model mixture (Th, BT, DBT) using H_2O_2 at 60°C. Among the 3 systems, Pd

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exhibited the highest desulfurization efficiency. However, by comparing oxidation results with other literature work, complete desulfurization results can be obtained with less expensive transition based metal such as molybdenum.

I.2.4.1.2. HPA

Catalysis by polyxoxometalates (POMs) also named heteropolyanions (HPAs) or isopolyanions is an increasingly studied field. POM polyoxometalates are a large group of complex inorganic compounds, which composition can be described as an assembly of oxygen polyhedra (octahedra and tetrahedra) of limited extent obtained by sharing one or more oxo (or hydroxo) ligands, the polyhedra being joined at their corners, edges or faces. A large number of structures have been described (Figure I.5), the most common are the Anderson, Keggin and Dawson structures. Keggin structures POMs are the most widely used because of their stability and commercial availability. High activities in homogeneous catalysis using such catalysts have encouraged the heterogenization of such systems and the use of HPAs as an active phase supported in ODS. HPAs have a low specific surface area (<10 m^2/g) but can be dispersed on a suitable support for heterogeneous catalysis applications. Thus, Da Silva and Dos Santos [75] studied the ODS of the model mixture (BT, DBT) with an initial sulfur content of 1000 ppm using Keggin structural POMs supported on alumina. Complete desulfurization was observed after 180 min at 60°C.

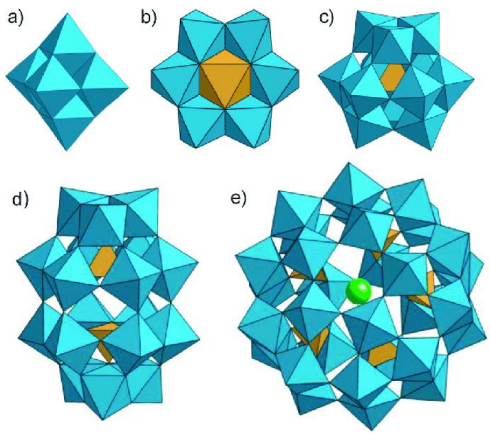

Figure I.5:Polyhedral representation of (a) Lindqvist, (b) Anderson, (b) Anderson, (c) Keggin, (d) Wells–Dawson and (e) Preyssler polyoxoanions. The blue octahedrons conform the metal oxide core [76].

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Yu and Wang [59] focused on heteropolyanion type. Three different polyanions, $Mg_9Al_3(OH)_{24}[PW_{12}O_{40}]$ (MgAl-PW_{12}), $Mg_9Al_3(OH)_{24}[PMo_{12}O_{40}]$ (MgAl-PMo_{12}) and $Mg_{12}Al_4(OH)_{32}[SiW_{12}O_{40}]$ (MgAl-SiW_{12}), were synthesized and characterized to test their effectiveness in the ODS of 500 ppm using hydrogen peroxide. The extraction of sulfur compounds was carried out by acetonitrile. The reaction was carried out at a temperature of 60°C, with an oxidant/sulfur ratio Ox/S of 20 and in the presence of 1 wt% catalyst. The activity of phosphorus-containing catalysts was higher than that of silicon-containing catalysts with DBT conversions; the order of reactivity obtained is as follows: MgAl-SiW_{12} < MgAl-PW_{12} < MgAl-PMo_{12}, with 100% DBT conversion for the last catalyst. In addition, by comparing the two catalysts with the same central atom (MgAl-PMo_{12} and MgAl-PW_{12}), the molybdenum-containing catalyst was more active than the tungsten based catalyst, indicating that the activity is influenced by the central and peripheral atoms. Another advantage of this catalyst is the possibility to recycle it up to 5 times with a conversion of 99.8%. Simply filter it, wash it with acetonitrile and then dry it in an oven.

Various approaches have been proposed for the preparation of polyoxometalate-based materials on silica supports. The conventional method of synthesis by impregnation has been used in the previously reported studies, but the interaction between POM and oxide was low. Other type of synthesis was explored, instead of impregnation that can lead to leaching of active phases and further deactivation. Direct synthesis method has been tried by Capel-Sanchez *et al.* [77] Ion exchange functionalized silica immobilized tungsten and molybdenum catalysts were prepared and tested in ODS for DBT (240 ppm S) with Ox/S=8. The results showed a better performance with the molybdenum based catalyst (88% DBT conversion) compared to the tungsten based catalyst (42% DBT conversion) also the incorporation of polyoxometalates was considered to make the systems more stable because they are less sensitive to leaching of the active phase. Zhang *et al.* [78] prepared $Ti_3(PW_{12}O)_4/SiO_2$-Al_2O_3 catalysts using the sol-gel method for the reaction of DBT at temperature of 70°C, with an Ox/S=3:1. The desulfurization of the DBT (200 ppm S), reached a value of about 98% after 2 hours.

To overcome the leaching problems of the active phase during reaction, polyoxometalates can also be deposited on the modified silicic support in order to immobilize it. In this case, the support is first modified by anchoring amine groups by reaction with $NH_2RSi(OEt)_3$ as proposed by Luo *et al.* [79]. The subsequent reaction with heteropolyacid leads to the protonation of amine groups anchored on the support and promotes the formation of well-dispersed polyoxometalates on the support [79]. HPW-NH_2-MCM-41 catalysts were tested in the DBT ODS in a model solution containing 80 ppm sulfur at a temperature of 60°C in the presence of hydrogen peroxide (Ox/S= 8). After 3 hours of testing, conversions of 100% are obtained for HPW contents of 20%. The HPW–NH_2–MCM-41 could be used for more than five times without significant loss of activity, and

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leaching of tungsten species in the reaction system is 2.1 wt.%. The good stability can be attributed to the strong interaction between the amino groups and the HPW molecules on the surface of MCM-41.

I.2.4.1.3. Effect of promotors on molybdenum based catalysts

The addition of a promoter on the catalyst in heterogeneous catalysis has a beneficial effect on the catalytic activity. It increases dispersion on specific surface area, prevents sintering of particles and can improve mechanical stability [60]. Various promoters such as bismuth [60], tungsten [48,62], phosphorus [16,80,81], iron [16] or vanadium [63,80,82], on a molybdenum based catalyst, have increased desulfurization rates. Others such as nickel, cobalt known as good promotors in HDS and titanium have given an antagonistic result by lowering desulfurization by decreasing the polarization of the Mo-O bond that promotes nucleophilic attack reaction. This polarization is decreased by the strong interaction of metal ions with the spinel type of Al_2O_3 lattice that contributes to the lower elimination of organosulfur [16,48,62].

The addition of 3% bismuth oxide added by the 15% MoO_3/Al_2O_3-SiO_2 catalyst has enhanced the conversion of 4,6-DMDBT from 95 to 100% and reduced total sulfur content in LCO from 8000 ppm S to 237 ppm S [60]. Moreover, addition of bismuth inhibited deactivation of the catalyst due to sulfone adsorption during the ODS reaction.

The effect of phosphorus was reported by Han *et al.* [81] on a MoO_3/SiO_2 catalyst for ODS of dibenzothiophene by cumene hydroperoxide. The fixed-bed reactor, at atmospheric pressure at 50°C, is supplied with a model feed of 1000 ppm of sulfur mixed with the oxidant with a molar ratio Ox/S equal to 5. In the absence of phosphorus, the conversion of DBT on the MoO_3/SiO_2 catalyst is 47.3%. With the increase in the P/Mo ratio to 1, it reaches 92.6%.

The study of a series of bimetallic oxide catalysts, prepared and tested in ODS of model molecules of thiophene, DBT and 4,6-DMDBT showed that catalyst activity decreases in the order W/Mo > Ti/Mo > V/Mo and this is attributed to an improvement in molybdenum dispersion on the support in the presence of tungsten [48]. In addition, a study by Mokhtar *et al.* on the same model feeds using tBHP as oxidant and the presence of dopant W and co-dopant V in Mo-W-V/Al_2O_3 catalyst confirmed these results, suggesting that tungsten acts as a promoter and potentially stabilizes the intermediate Mo oxide by forming M–O bonds.

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I.2.4.2. Effect of supports

The properties of support can highly affect the catalytic efficiency (activity, product distribution, stability) of ODS catalysts. Traditional metal oxide supports like alumina, silica and titania have been widely used as supports mainly due to their low price, easy preparation and high mechanical strength providing high surface area, good pores distribution thus better metals dispersion. Among different active species molybdenum based catalyst showed interesting and promising results, therefore, various kind of supports has been developed and tried as carriers. Wang *et al.* [24] showed that interaction between molybdenum and support can change ODS results. Better desulfurization results were obtained with molybdenum supported on alumina compared to titanium oxides or alumina silica. ODS of light cycle oil containing 0.8 wt.% S with Prasad *et al*. [60] showed that silica-alumina support (Siral) can improve desulfurization compared to silica alone, suggesting that conversion was improved by the acidity of the carrier.

Phosphotungustic acid catalysts supported on various supports were prepared and tested on a set of model molecules. ODS results were gathered in Table I.1. According to the table, various kinds of porous solid materials such as SiO_2; TiO_2; c-Al_2O_3, activated carbon and CeO_2 have been tested. These HPA-supported catalysts showed excellent ODS catalytic activity of thiophene and its derivative. However, despite that work was applied on model feed, considerable quantities of oxidant (6 < Ox/S< 12) and long reaction times (t>120 min) were needed, which limits their industrial application. These results needs to be evaluated on real fractions.

Table I.1 : Conversion of different sulfur molecules in different works using PW supported on various supports.

Catalyst	Feedstock	Conditions (Ox/S, Temperature, Reaction time)	Conversion (%)	REF
PW/TiO_2-SiO_2	DBT 1000 ppm S	12, 70°C, 120’	96	[51]
PW/CeO_2	DBT 1000 ppm S	6, 30°C, 30’, IL	99	[83]
PW/SiO_2	BT, DBT, DMDBT 500 ppm S	12, 60°C, 120’	95	[84]
Ag-PW/SiO_2	DBT 800 ppm S	12, 70°C, 240’	96	[85]
PW/TiO_2	BT, DBT, DMDBT 500 ppm S	12, 80°C, 120’	95	[23]
PW/TUD-1	DBT 500 ppm S	8	98	[25]

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Activated carbon is widely used as adsorbent mainly due to its high surface area, large pore volumes and very uniform pore size distribution. Moreover, activated carbon showed potential application as common catalyst for oxidative desulfurization. It can be used as supports or catalyst by itself because of its physical performance and surface functional groups containing oxygen. Different carbon materials such as activated carbon (AC) [86,87], graphene oxide (GO) [88–90], single wall carbon nanotube (CNT) [91] have been used as supports in ODS reaction. They showed high capacity to remove sulfur compounds using air in the replacement of hydrogen peroxide as an oxidant. For instance, activated carbon was shown to have a high catalytic activity for the oxidative desulfurization of diesel fuel (800 ppm S). The better catalytic performance in the oxidation of DBT was observed for carbon having the higher adsorption capacity. 98% of the sulfur could be removed from diesel oil (8000 ppm S) using the system H_2O_2/activated carbon, with 96.5% oil recovery.

Metal–organic frameworks (MOFs), owing to their porous structure, crystallinity and high stability, have received increasing attention as support to incorporate POMs for ODS reaction [16,67,92–95]. This incorporation was found to increase catalyst stability and recyclability [96]. Various forms of MOF such as molecules MIL-101 [97–100] and UiO-66 [101–103] based supports have been used in ODS of different model molecules.

Catalysts based on mesoporous carrier materials have shown significant desulfurization efficiency in ODS due to their ordered porosity, high surface area-to-volume ratio, controllable pore size and can be easily functionalized, high and controllable porosity and narrow pore size distribution. The ordered pore structure can promote the diffusion reactants and intermediates into the catalyst channel [32,58,63,104–107]. A mesoporous 4A silica catalyst, an economically advantageous carrier, was developed by Yang *et al*. for ODS of DBT. 99% conversion was obtained after 30 minutes with an Ox/S=2.5 ratio. Recently, under optimized conditions (H_2O_2/S molar ratio = 7, 70 °C, acetonitrile as extraction solvent), PW_4/SBA-15 prepared by immobilization of PW_4 in an ordered mesoporous silica (SBA-15) led to complete desulfurization of the model diesel containing benzothiophene, dibenzothiophene and 4,6-dimethyldibenzothiophen within a reaction time of 2 h [108].

Shiraishi *et al.* [50] studied vanadosilicate molecular sieve as a catalyst for oxidative desulfurization of light oil with H_2O_2 as the oxidant. The amount of sulfur was reduced to ultra-low levels of less than 50 ppm from 450 ppm. Nonetheless, recovered vanadosilicate cannot be used further because of the dissolution of the vanadium present on the silica surface into the reaction media.

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Mixed silica-based containing titanium have also been proven to be active catalysts in oxidation reactions [22,109–113]. Jose *et al.* [112] studied the ODS reaction for a thiophene mixture in isooctane using hydrogen peroxide on a microporous titanium-based TS-1 catalyst containing copper. A maximum desulfurization of 93% was obtained with an Ox/S=10 ratio. However, this catalyst is not recommended for large molecules that will not be able to access small pores and active sites, which prevents their oxidation [114]. Therefore, despite the good results given with thiophene, oxidation of larger sulfur molecules such as benzothiophenes, dibenzothiophenes and their derivatives seems impossible.

The catalytic activity of zeolitic materials can be improved by reducing the particle size, which in turn increases its upper surface area [115]. Under the same operating conditions (H_2O_2, Ox/S=10) for ODS of DBT, Maity *et al.* [116] used the microporous Ti-beta catalyst. With the high Ox/S ratio, more than 93.5% of the DBT was oxidized. However, the catalyst recycling study showed a significant reduction in its activity after only one cycle.

Other titanium-based catalyst, such as Ti-HMS [117,118], Ti-MWW [119], Ti-MCM-41 [34], with larger pore sizes, have shown better performances for the oxidation of BT and DBT molecules. However, the main problem with these catalysts is the low stability of their activity, which prevents their use on an industrial scale.

Further interest has been focused on Ti-SBA-15 catalysts containing hexagonal pores [111,113]. However, a low catalytic activity of Ti-S has been reported using hydrogen peroxide [113], most probably due to a low dispersion of titanium in silica. In addition, there was poor accessibility for reagents due to the high film thickness. Instead of SBA-15, SBA-16 was chosen by Rivoira *et al.* [22] because of its high surface area and high thermal stability, but especially because of its three-dimensional mesoporous structure for better mass transfer. This support has given encouraging results in hydrotreating. The ODS on DBT (initial content 2000 ppm S) with an Ox/S=5 ratio and two catalysts Ti-SBA-16 and TiO_2-SBA-16 were tested. After one hour of reaction 90% sulfur removal was reported with TiO_2-SBA16 to be compared to 70% DBT conversion for Ti-SBA-16. With the titanium oxide form, a better dispersion of titanium oxide on the support allowed to further decompose the hydrogen peroxide (justified by the study of the percentage of remaining hydrogen peroxide) for the ODS reaction. Reuse of the catalyst up to four times has been reported.

Anatase or rutile TiO_2 can achieve applications in the decomposition of organic compounds with UV radiation. TiO_2 based photocatalysts have been used in ODS. Wang *et al.* [120] explored the photocatalytic activity of nano-TiO_2 in ODS and found that nano-TiO_2 can be prepared in ionic liquids. Water was mixed with ionic liquid that contained TiO_2 photocatalyst.

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The role of the water was to react with holes to form •OH radicals, which was the oxidant. Total sulfur content was reduced from 465 to 26 ppm in diesel oil, after 10 h of UV irradiation. Titanium oxide loaded with multi-walled carbon nanotubes exhibited also high photochemical activity. The MWNTs/TiO_2 composite was evaluated on the oxidation of model compounds DBT and 4,6-DMDBT (800 ppm total S). Complete conversion after 120 min of photocatalytic reaction using the MWNTs/TiO_2 composite, followed by adsorption was attained.

Commercially available zirconia support did not receive attention in the ODS reaction. Despite its high acidity, it seems that its poor specific surface area and porosity inhibited its further use. However, using non-conventional preparation techniques, attempts were tried to enhance its properties. ZrO_2 surface was enlarged by combining it with materials of good textural characteristics. For instance, the introduction of ZrO_2 in ordered silica allows obtaining ZrO_2 containing solids of high specific surface area [121]. Ramos *et al.* [107] synthetized FeOx/Zr-SBA-15 mesostructured catalyst with a specific surface area of 400 $m^2.g^{-1}$. The presence of zirconia increased surface acidity and promoted Fe_2O_3 formation by inhibiting amorphous iron oxide. The catalytic activity of FeOx/Zr-SBA-15 catalysts was higher than that of the FeOx/SBA-15 catalysts. The best catalysts (30% Fe/Zr-SBA-15) could completely remove DBT (0.1 g catalyst, 300 ppm DBT in 100 ml n-hexadecane) from model fuel at 60 °C within 30 min.

I.2.5. Ultrasound assisted oxidative desulfurization

To optimize the reaction of ODS, researchers worked on the addition of other techniques to increase the contact between the oxidant and sulfur molecules. Ultrasound assisted oxidative desulfurization is based on irradiation with the phenomenon of cavitation created by mechanical vibrations. The shock waves created promote the reaction and reduce the reaction time with the species present. So, with gentle operating conditions, high speeds and better selectivity, ultrasound has attracted attention for ODS application. Despite the addition of the energy consumption cost of ultrasound, ultrasound assisted oxidative desulfurization UAOD remains economical compared to HDS under optimal conditions, and without the use of hydrogen according to Ja'afari *et al.* [90].

The researchers considered that the effectiveness of ODS coupled with ultrasound is based on three main factors: the phase transfer catalyst, the catalyst itself and ultrasounds.

Homogeneous formic/acetic acid systems are generally used for ODS with ultrasound [65,122–127] but heterogeneous catalyst systems have also been tested and have shown good activity and reuse capabilities [25,107,128–130].

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Studies of operating conditions have been carried out to obtain the best results [86,122–124,128,129,131]. The key parameters and optimal values reported in these studied applied to model molecules are as follows:

- Temperature: optimal at 50°C, it should not exceed 60 to 70°C.

- Ultrasound intensity: range between 50-100 $W.cm^{-2}$.

- Ultrasound frequency: range between 20 and 50 kHz, but it should be noted that no ODS tests on fuel oils using higher frequencies have been reported.

As a phase transfer agent, tetraoctyl bromide has been used frequently. The effective transfer agent mass then varies between 0.2 and 50 g/L [124] .

I.2.6. Ionic liquids in ODS

Among the unconventional pathways for ODS, ionic liquids (IL) have emerged and demonstrated potential use. They are not a new class of materials; they are also known as molten salts. However, their use has been widely sought in recent years mainly due to the need for green chemicals that are less harmful to the environment. They are defined as liquids composed entirely of liquid ions at a temperature of 100°C or less. Captivating properties distinguish them such as non-volatility, solubility, high thermal and chemical stability, good catalytic activity and recyclability. These properties induce their use in various fields of catalysis, bio-catalysis, and electrochemistry.

Ionic liquids are composed of organic cations and inorganic anions with different alkyl side chains or functional groups such as alkylsulfates, alkylphosphates or halogen-containing anions. The most studied cations are imidazolium $[C_3H_5N_2]^+$, ammonium $[NH_4]^+$, pyridinium $[C_5H_5NH]^+$ and sulfonium $[SR_3]^+$ (Figure I.6)

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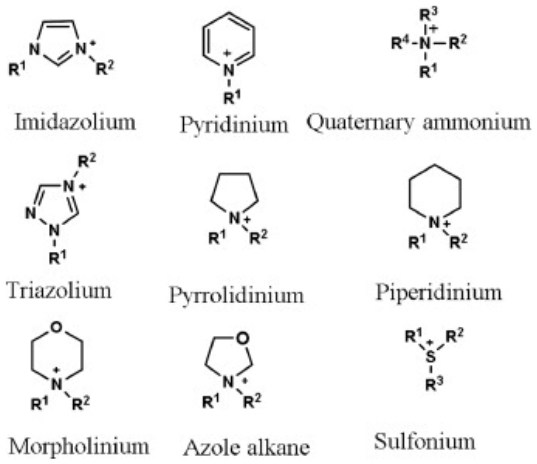

Figure I.6 :Ionic liquids types [40].

The distinctive properties of ionic liquids allow not only multiple applications in different chemical reactions, but also versatile uses for desulfurization.

Ionic liquids can then be used as a catalyst, co-catalyst as a phase transfer agent improving activity or as an extraction solvent during ODS. Extractive desulfurization studies have been performed using neutral ILs such as imidazolium- or pyridium-based ILs or acidic ILs for which it has been proposed that their Lewis acidity helped for better extraction of aromatic model sulfur compounds. It was also found that the IL extraction efficiency was improved when the sulfur compounds were first oxidized. The desulfurization of model feed containing DBT was about 12-22% while a better desulfurization was obtained up to 33–60% when achieving ODS using H_2O_2 (Ox/S = 11) and the same IL [108]. As a drawback, the extraction of sulfur compounds using ILs for extractive desulfurization could be limited by the co-extraction of aromatic compounds of the feed. The main advantages of ionic liquids are their chemical stability and regenerative properties, avoiding the problem of solvent loss.

Efficient desulfurization with complete conversion of DBT and 95% conversion of BT was observed by Zhang *et al.* [78] using a 20% $[BMIN]_3PMo_{12}O_{40}$ silica supported system for ODS of a model feed (DBT, BT) at 60°C. This catalytic activity can be attributed to its amphiphilic character, which improves the adsorption of sulfur compounds on the oxidant.

Other types of ionic liquids such as anions, brönsted acids have been used for a dual function of extraction agent and catalyst. For example, the use of[BMIN][HSO_4] by Gao *et al.*[132] resulted in a 99.6% desulfurization after 90 min using H_2O_2.

Despite the fact that the study of ionic liquids is recent and requires optimization of reaction parameters, their use is in full development for model feeds. Their application is a topic to be addressed in the near future.

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I.3. Review: Oxidative desulfurization of heavy oils with high sulfur content

Despite the high number of reviews attributed to the ODS of diesel fractions showing different catalytic systems and oxidants involved and major progress in process [40,68,133–136], there is no review that is dedicated to the ODS of heavy fractions or diesel fractions with very high sulfur content. In the case of heavy fractions, reviews were limited to listing the advantages and limitations of different desulfurization techniques [46,137,138] when applied on heavy fractions without any further constructive conclusion about ODS of heavy fuels.

Taking into account the use of heavier crude oils and the interest to develop not only a finishing process but a global desulfurization process, our review focuses on the ODS applied to high sulfur content fuels having a sulfur content above 0.5 wt.% S. This review points out ODS of heavy oils that can be suitable for marine fuels for which legislation is currently becoming more and more extreme. Different attractive approaches of the literature towards ODS are reported using homogeneous and heterogeneous catalysis. Recent developments in ODS assisted with ultrasound technology and the use of ionic liquid to enhance ODS efficiency is fully detailed and discussed to better understand their viability when applied to high sulfur content, high viscosity, and high boiling point feeds.

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catalysts

MDPI

Review

Oxidative Desulfurization of Heavy Oils with High Sulfur Content: A Review

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Abstract: The demand for clean fuels is increasing throughout the world, with more stringent environmental regulations for transportation fuels including marine fuels, particularly regarding their sulfur content. Moreover, the quality of crude oil and derived petroleum cuts is getting lower while fossil fuels are still in high demand. Heavy oils are characterized by high sulfur content where most sulfur is found in bulky thiophenic structures difficult to remove using conventional high pressure hydrodesulfurization process. However, they appeared more reactive in oxidative desulfurization (ODS) process, carried out at mild conditions without hydrogen pressure. This review focuses for the first time on the heavy fuels initially containing more than 0.5 wt.%S and upgraded by the ODS process. Different attractive approaches of the literature towards ODS are reported using homogeneous and heterogeneous catalysis. Recent developments in ODS assisted with ultrasound technology and the use of ionic liquid to enhance ODS efficiency will be fully detailed and discussed to better understand their viability when applied to high sulfur content, high viscosity, and high boiling point feeds.

Keywords: oxidative desulfurization; heavy oil; ultrasonic process; ionic liquids

1. Introduction

As reported by the International Energy Agency, global energy requirements have risen more slowly than in the past but are still expected to increase by 30% [1] between today and 2040, with oil demand continuing to grow until 2040 mainly due to the dynamism of China and India. The way that the world meets these growing energy needs is changing with the lead now being taken by natural gas, the rapid rise of renewables, and by energy efficiency. However, the era of oil is not over yet and oil demand growth remains robust in the New Policies Scenario partly due to the rising consumption of road transport, aviation, and shipping. The rapid switch to electric cars pushed by extra policy and infrastructure support is not sufficient to trigger a major turnaround in global oil use.

Among the different petroleum fractions obtained from crude oil (Figure 1), high market demand for light/middle distillates is observed. However, at the same time there is lower availability of light oils yielding high proportion of light/middle distillates used for transportation fuels. Accordingly, the main industrial challenge is to adapt refineries to process heavier crude oils as well as to refine heavier cuts in order to produce light distillates. These crude and residual cuts are mainly known as a complex mixture of high molecular weight hydrocarbons along with impurities such as sulfur, nitrogen,

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aromatics, asphaltenes, and heavy metals. Among these impurities, sulfur is known as the most hazardous undesirable contaminant. EChange in global oil demand by sector in thenvironmental regulations have therefore been introduced in many countries to drastically reduce the sulfur content of transportation fuels (gasoline and diesel) to 10–15 ppm. The International Maritime Organization (IMO) has also proposed a reduction to the maximum permitted sulfur content of marine fuels and heavy fuel oil as described in MARPOL Annex VI. Since 2015, a greatly more regulated shipping emissions sector loomed into view in the Sulfur Emissions Control Areas (SECAs) with a maximum sulfur mass content permitted in marine fuels equal to 0.1%. For ships operating outside designated emission control areas the current limit for sulfur content of ships' fuel oil is still 3.5%, nevertheless a substantial cut will be observed in 2020 where the sulfur content will be limited to only 0.5%. These specifications, beneficial from an environmental point of view, present a major technical and economic challenge for the petroleum refining industry for adapting refineries to process heavier crude oils. Hydrotreatments are the most commonly used processes for upgrading heavy fractions to better quality fuels. To accommodate the increasingly stringent regulations on permissible sulfur levels in fuels more severe conditions of temperature and pressure and increasing hydrogen consumption are required. However, increasing the amount of hydrogen has economic and environmental impacts, notably, by increasing the use of fossil fuel and natural gas reforming and the quantity of CO_2 generated by current hydrogen production technologies.

Significant advances have been made for developing alternative nonhydrogenation processes. Such processes for obtaining ultra-low sulfur diesel (ULSD) include desulfurization by adsorption, reactive adsorption, oxidative desulfurization, extractive desulfurization with solvents or ionic liquids, and biodesulfurization, as detailed in the review of Stanislaus et al. in 2008 [2]**.** Among these methods, oxidative desulfurization forming sulfones from sulfur with the use of an oxidizing agent has received much attention because of its specificity towards sulfur molecules and high oxidative reactivity of 4,6-dimethyldibenzothiophene (DMDBT), known as a refractory sulfur molecule of diesel feed, higher than that of dibenzothiophene (DBT). The sulfone products are further removed mainly by extraction or adsorption. The nature of this process makes it well suited as a finishing process for moderately hydrotreated fuels.

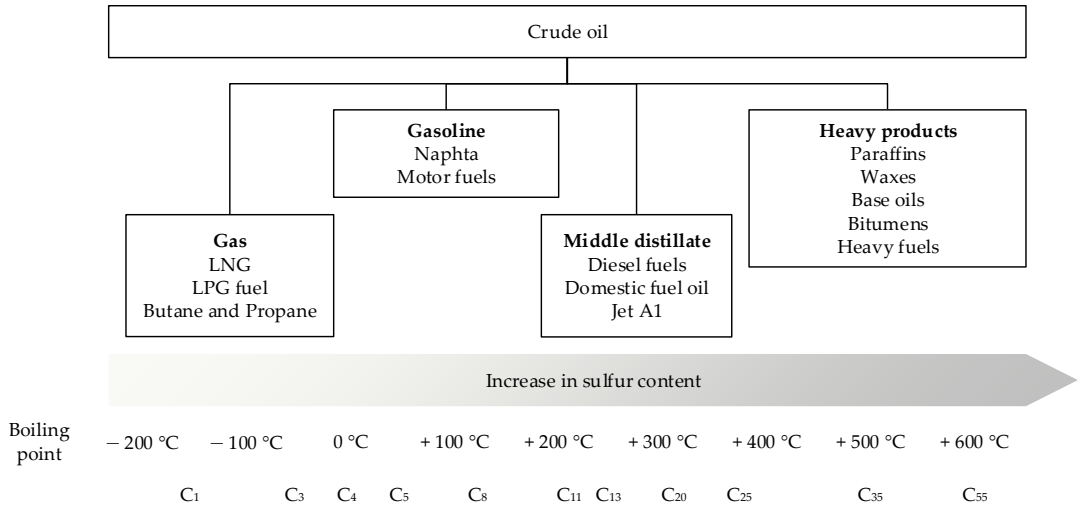

Figure 1. Petroleum fractions from crude oil and properties.

As reported in Figure 2, a large increase in the number of publications related to the oxidative desulfurization (ODS) process is observed since 2007, corresponding to environmental regulations setting up sulfur limitations at 10 ppm for road diesel in Japan and Europe.

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A major part of these publications is dedicated to ODS process performed on model molecules mostly dibenzothiophene (DBT) and dimethyldibenzothiophene (DMDBT). ODS process on real fuels such as diesel has also been investigated starting from hydrotreated diesel containing a low initial sulfur amount (<500 ppmS) for the use of ODS as finishing process. It has indeed been reported that the catalytic behavior may differ in the ODS of model and real feeds [3]. Only one study by Oh et al. in 2017 [4] focused on the ODS of marine diesel. The initial sulfur content was low (230 ppm) and does not match the sulfur content of real feeds. We noticed several recent reviews in the literature dealing with the progress in the technologies for desulfurization of crude oil, but they considered the whole technologies without paying particular attention to the ODS process [5–7].

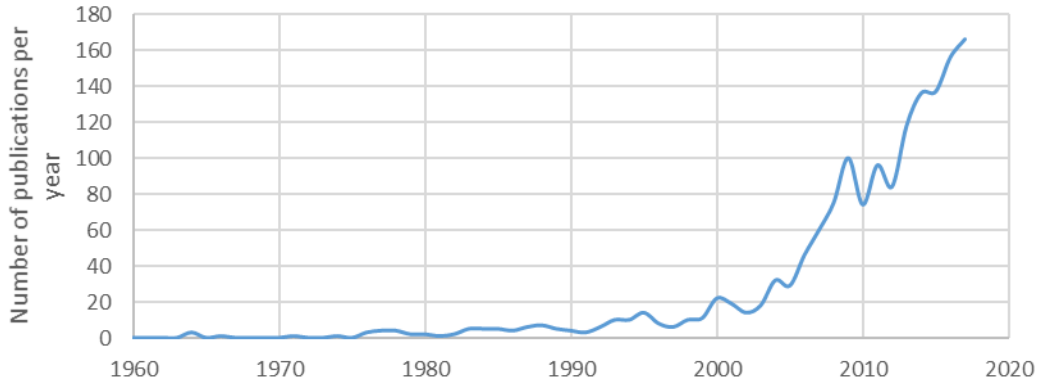

Figure 2. Evolution of the number of papers reporting oxidative desulfurization in bibliographic records. Source: Scopus (keyword: Oxidative desulfurization).

Taking into account the use of heavier crude oils and the interest to develop not only a finishing process but a global desulfurization process without using the expensive hydrogen reactant, this review focuses on the ODS process applied to high sulfur content fuels having a sulfur content above 0.5 wt.%S and highlights the upgrading of heavy fuels by ODS particularly suitable for marine fuels for which legislation is currently becoming more and more extreme. The use of many petroleum fractions are reported in the literature and their denomination in the referenced articles are listed in Table 1, together with their sulfur content.

Table 1. Petroleum fractions referenced in the literature, their denomination in the corresponding article, and their sulfur content.

Fraction	Designation Used in Article	Sulfur Content (%)	References
Gasoline	Naphtha	2.00	Imtiaz et al. 2013 [8]
	Gasoline	1.30	Kulkarni et Afonso. 2010 [9]
Diesel	Light Gas Oil (LGO)	0.005	Estephane et al. 2018 [3]
	SR-LGO	1.33	Otsuki et al. 2000 [10]
	Light Cycle Oil (LCO)	0.80	Prasad et al. 2008 [11]
	Diesel fuel	0.86	Anisimov et al. 2003 [12]
	LCO	0.63	Toteva et al. 2009 [13]
	LGO	1.20	Imtiaz et al. 2013 [8]
	Heavy Gas Oil	4.00	
	Straight Run Diesel Fraction	1.19	Krivtsov et al. 2013 [14]
	Gas Oil	0.57	Trakarnpruk et al. 2009 [15]

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Fraction	Designation Used in Article	Sulfur Content (%)	References
	Gas Oil	2.87	Zannikos et al. 1995 [16]
	Straight Run Gas Oil (SRGO)	1.56	Hassan et al. 2013 [17]
	Marine Diesel	0.02	Oh et al. 2017 [4]
	Crude Diesel	0.83	Mokhtar et al. 2016 [18]
	Diesel Fuel	0.72	Najafi et al. 2011 [19]
	Marine Diesel Oil	0.17	Wan et Yen. 2007 [20]
	Diesel Oil	0.77	Mei et al. 2003 [21]
	Hydrotreated Petroleum Product	3.60	Mello et al. 2009 [22]
Vaccum gas oil	Vaccum Gas Oil (VGO)	2.17	Otsuki et al. 2000 [10]
	Diesel Mixture (VGO+diesel)	0.63	Rakhmanov et al. 2015 [23]
	Vaccum Gas Oil	1.98	Shiraishi et Hirai. 2004 [24]
Heavy fuel oil	Heavy Fuel Oil (HFO)	1.80	Ogunlaja et al. 2017 [25]
	HFO	2.75	Farshi et Shiralizadeh. 2015 [26]
	HFO	3.85	Flores et al. 2004 [27]
Residual Oil	Bunker C Oil	3.17	Tang et al. 2013 [28]
	Residual Fuel	2.86	Kazakov et al. 2016 [29]
	Residual Oil	0.04	Tetrisyanda et al. 2017 [30]
Crude Oil	Crude Oil	1.60	Mohammed et al. 2012 [31]
	Crude Oil	1.12	Abu Bakar et Ahmed. 2016[32]
	Crude Oil	0.10	Rafiee et al. 2016 [33]
	Crude Oil	2.50	Otaibi et al. 2015 [34]
	Crude Oil	5.20	Hosseini et Hamidi. 2014 [35]
	Crude Oil	1.19	Haruna et al. 2018 [36]

2. ODS Technology and Efficiency Evaluation

The oxidative desulfurization process is considered as a two-step reaction. At first, bivalent sulfur is oxidized to the hexavalent corresponding sulfone in the presence of an oxidant: it consists of adding two oxygen atoms to the sulfur without breaking any carbon–sulfur bonds; an intermediate is a sulfoxide compound (Figure 3). With appropriate conditions (i.e., excess of oxidant), sulfones are obtained and no sulfoxide detected. Then, a purification step is performed in which oxidized sulfur compounds are separated from oils due to their different chemical and physical properties from the original sulfur compounds such as boiling point and polarity. In most studies efficiency of the process is evaluated after extraction, and expressed as a global sulfur removal rate.

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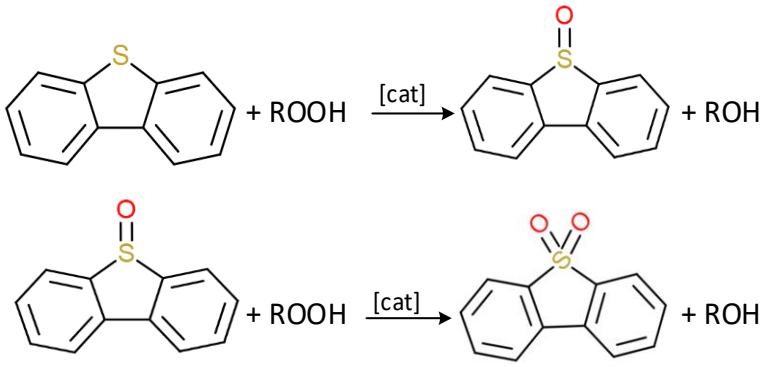

Figure 3. Oxidative desulfurization reaction pathway.

2.1. Sulfones Separation

The purification step can be performed using liquid–liquid extraction, adsorption, precipitation or chemical decomposition. Among separation methods, liquid–liquid solvent extraction is principally used. Extraction solvent can be directly added with the oxidizing agent in the fuel [37–39] or after oxidation of sulfur compounds [40–42]. After extraction, the desulfurized fuel can be obtained by separation of the solvent polar phase and the fuel nonpolar phase, distillation is sometimes used for separation and solvents are often reused for several extraction cycles. Solvent extraction enables separation of desired components based on their variable solubility using specific liquid solvents characterized by their polarity and dielectric constant. Even though this method seems relatively simple, the separation is mainly achieved by the appropriate association of solvent, oil, and selected extracted component. After the oxidative desulfurization reaction, solvent extraction has been applied on a single molecule feed, mixed model feed, as well as real feedstock in particular diesel fraction. The challenge is to maintain a selective extraction of sulfones with high efficiency starting from oxidized real feedstocks with high initial sulfur content.

With the purpose of optimizing extraction of only sulfones from the complex hydrocarbon mixture, several parameters are defined for selecting the best solvent required for sulfones extraction:

- Solvent selectivity toward sulfones
- Solvent capacity: solubility of sulfones in the solvent
- Recoverability of solvent for reuse
- Low solubility of hydrocarbon mixture to avoid loss of fraction in the solvent
- Partition ratio and number of extraction stages.

Solvent capacity and its selectivity toward sulfones are considered as the main parameters for high efficiency. The solvent should have high capacity to solubilize sulfones only. Different types of solvents have been reported in the literature for their sulfones extraction use and are reported in Table 2 with their properties and typical conditions of their use.

Comparison of solvents used for extraction was carried out in several studies and different results were obtained depending on feedstock nature and operating conditions. Most studies used highly polar solvents like acetonitrile, N, N-dimethylformamide (DMF), methanol, butyrolactone, or N, N-dimethylpyrrolidone for extraction. While for the model feed containing initially DBT or 4,6-DMDBT acetonitrile and methanol has been demonstrated as a very efficient extraction solvent [28,43–45], the nature of the feedstock influences the choice of solvent for high sulfur content and heavy feedstock. Acetonitrile was found suitable for the extraction due to its relatively low boiling point at 355 K compared to sulfones (550 to 950 K) which facilitates separation and reuse of solvent. Acetonitrile was chosen for extraction after ODS of diesel oil [21], vacuum gas oil [24], and heavy fuel oil [26]. Methanol was for example selected for extraction of oxidized gas oil by Zannikos et al. [16]. However, the comparison between DMF, acetonitrile, and methanol indicated that the solvent with higher polarity

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extracted more sulfone compounds, thus DMF was the most suitable among them for the extraction of oxidized vacuum gas oil [10]. Complete desulfurization of a 2.17 wt.%S vacuum gas oil was noticed after 10 cycles of extraction with DMF. Similarly, in 2016 Mokhtar et al. [18] chose DMF for extraction of oxidized crude diesel. DMF was also reported as more adapted for extraction from more complex mixtures like crude oil [34]; however, the DMF is classified as a substance of very high concern by the European Chemicals Agency (ECHA) since 2012. Unexpectedly, a nonpolar solvent, n-heptane, was proposed by Mohammed et al. [31] for the extraction of oxidized crude oil. The extraction with this solvent was compared to extraction using methanol. A high percentage of sulfur reduction (85%) from 1.494 wt.%S to 0.217 wt.%S was obtained with n-heptane versus only 31% sulfur removal using methanol. Using n-heptane as a extraction solvent after heavy cuts ODS may precipitate asphaltene molecules further separated from the fuel. To increase the extraction of sulfones from oxidized real feedstock Imtiaz et al. 2013 [8] proposed a two steps extraction with a mixture of solvents: extraction using water–methanol followed by acetonitrile–methanol mixture. After the extraction sequence, the desulfurization rates of the different petroleum fractions (naphtha, light gas oil, heavy gas oil, and bitumen) were respectively 83%, 85%, 69%, and 64% and strongly depended on the nature of the petroleum fraction.

Table 2. Properties of solvents used for extraction and desulfurization rates (D.R.) results.

Extraction Solvent.	Dipole Moment (Debye)	Dielectric Constant	Solvent to Oil Ratio S/O	Petroleum Fraction	Sulfur Content (ppm)	D.R. (%)	Extraction Steps	Reference
N, N-dimethylformamide (DMF)	3.24	36.71	1	VGO + Diesel Fraction	6300	90%	3	Rakhmanov et al. 2015 [23]
Acetonitrile	3.53	35.94	1	HFO	27,500	59%	1	Farshi et Shiralizadeh. 2015 [26]
Acetonitrile + water (80:20) followed by methanol-water (80:20)	-	-	1	Naphtha	20,000	83%	1	Imtiaz et al. 2013 [8]
	-	-	-	LGO	12,000	85%	1	-
	-	-	-	HGO	40,000	69%	1	-
	-	-	-	Bitumen	50,000	64%	1	-
n-Heptane	-	-	2	Crude oil	14,940	85%	1	Mohammed et al. 2012 [31]
Methanol	2.87	32.66	1	Gas oil	24,000	90%	1	Zannikos et al. 1995 [16]
Acetonitrile	3.53	35.94	1	VGO	19,800	89%	1	Shiraishi et Hirai.2004 [24]
DMF	3.24	36.71	1	SR-LGO	13,500	92%	-	Otsuki et al. 2000 [10]
DMF	3.24	36.71	1	VGO	21,700	100%	10	-
Acetonitrile	3.53	35.94	0.5	Diesel	7,744	99%	1	Mei et al. 2003 [21]
Acetonitrile	3.53	35.94	1	HFO	38,500	35%	1	Flores et al. 2004 [27]

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DMF	3.24	36.71	1	Diesel	8,286	90%	4	Mokhtar et al. 2016 [18]

Along with the type of solvent, the heavy nature of hydrocarbons implies restrictions in the operating extraction conditions. A high solvent/feed ratio of 1 could be required. Mohammed et al. [31] have shown that the increase of the solvent/feed ratio from 1 to 3 enhanced the desulfurization rate. Extraction can be carried out at mixing temperature higher (70 °C) than room temperature [10] and several extraction stages, up to 10, can be required to reach the lowest sulfur levels [18,22].

Separation techniques are not exclusively limited to solvent extraction; several studies carried out separation using adsorption. Oxidized sulfur compounds are preferentially adsorbed and removed by the adsorbent compared to nonoxidized sulfur compounds. The adsorbent can be reused by regeneration at high temperatures. Different types of adsorbent have been used (alumina oxides, activated carbon, zeolites, and polymers). It is important to ensure that the sorbent has high affinity toward sulfone molecules leaving nonpolar hydrocarbons (HCs) in the fuel. Comparing adsorption to solvent extraction Chen et al.2010 [46] found that adsorption using alumina of oxidized diesel with 0.88 wt.%S content gave better removal efficiency in comparison with solvent extraction using acetonitrile (68% instead of 28%).

In the work reported by Otsuki et al. for oxidized diesel SRGO solvent extraction was followed by adsorption, considering one method of separation was not sufficient to remove all oxidized compounds [10]. Other works have also noticed the adsorption of sulfones when using a heterogeneous catalyst acting as an absorbent and inducing a washing step to recover the whole quantity of sulfones formed during the ODS process [3,47]. In these studies, different retention rates (sulfones adsorption on the catalyst surface) were observed depending on the nature of the feed and real fuels appeared favorable to sulfone dissolution with lower retention rates observed than with the model fuel.

2.2. Efficiency Evaluation

Despite these works dealing with sulfone adsorption, for real feeds, and in particular high sulfur content feeds, ODS catalytic activity is mainly evaluated measuring the global sulfur content after the extraction step (S_{final}) compared with the initial sulfur content (S_{init}) with conversion (X in %) expressed as $X = (S_{init} - S_{final})/S_{init} \times 100$, this global sulfur content being evaluated by a fluorescence technique. As early as 2001, by using GC-MS and GC-FID equipment, Hulea et al. [48] have also determined the global sulfur removal of kerosene (1310 ppmS) mixed with a suitable solvent (acetonitrile or ethanol) and hydrogen peroxide using Ti-containing molecular sieves. Conversion values in these cases report the oxidation step performance together with the extraction step efficiency. Some studies, such as that reported by Flores et al. [27], have clearly shown that this extraction step could retain sulfide species together with the sulfones indicating that the conversion rate evaluates a global sulfur removal capacity (sulfones and sulfur) rather than ODS conversion. To get around this problem, Flores et al. have initially used acetonitrile for extracting sulfur compounds before oxidation from heavy fuel oil containing 3.85 wt.%S, leading to a 18.4% sulfur reduction, demonstrating the solvent capacity to retain nonoxidized sulfur compounds. It is however clear that higher desulfurization rates are obtained when using oxidized fuels. They are related to the specific affinity between sulfones and solvent. In this case, when catalytic results are based on global sulfur evaluation, they should be considered as a global sulfur removal rate and not an ODS conversion.

Together with the fluorescence method enabling total sulfur evaluation, the gas chromatography method associated with a flame ionization detector (FID) coupled (or not) with a MS detector has already been reported in the literature for qualitative observation of sulfur or sulfone model molecules [49] (Safa et al.2017). For quantitative measurement of sulfur conversion, this technique is often devoted to model feed analysis containing one, or a limited number, of specific sulfur molecules and their corresponding sulfones, characterized by a specific peak easily identified on the chromatogram. The model molecule conversion is calculated from the intensity decrease of the corresponding peak in the chromatogram [50–52].

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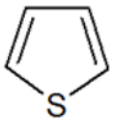
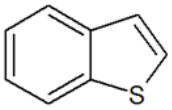
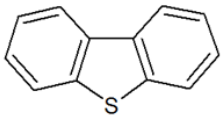
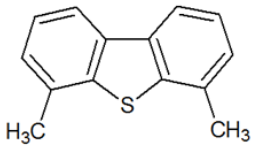
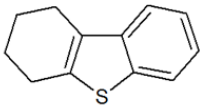
Using gas chromatography (GC) technique with a PFPD detector, Chica et al. [53] studied the ODS of a partially hydrotreated commercial diesel (330 ppmS) containing mono-, di-, and tri-methyl DBT in a continuous fixed bed reactor and calculated oxidation conversion of the sulfur compounds from GC-PFPD chromatograms. Recently in 2018 Estephane et al. [3] have also determined sulfide conversion into sulfones in a prehydrotreated LGO (light gas oil) 50 ppmS containing only alkyldibenzothiophenes (the most refractory compounds to HDS) using the GC technique with a specific sulfur detector. Their work was extended to a diluted straight run diesel (2000 ppmS) feed containing an important number of substituted BT and DBT sulfur species. Due to the overlap of alkyl-benzothiophenes (Cx-BTs) sulfones retention times with those of alkyl-dibenzothiophene (Cx-DBT) sulfides, the conversion calculations for each molecule could not be done in this case and was thus restricted to Cx-BTs sulfides and to DBT.

For high sulfur content fuels (> 0.5 wt.%S) without previous prehydrotreatment, this GC method has not yet been reported in the literature. Thus, until now, there is no analytical method evaluating sulfide conversion to sulfones for high sulfur content real feeds. Desulfurization rates are generally obtained after separation, keeping in mind that a part of sulfides molecules can also be extracted through the sulfones separation process.

2.3. Sulfur Molecules Reactivity

Table 3. Representative structures and electron densities on the sulfur atom for various sulfur-containing compounds.

Sulfur Compound	Structure	Electron Density
Thiophene		5.696
Benzothiophene		5.739
Dibenzothiophene		5.758
4,6-dimethyldibenzothiophene		5.76
Tetrahydrodibenzothiophene		5.923

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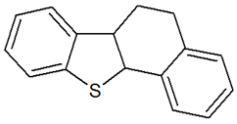
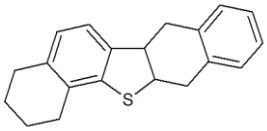
Tetrahydrobenzonaphthothiophene		5.921
Octahydrodinaphthothiophene		5.926

To go further in the understanding of ODS, few studies have reported on sulfur molecules reactivity when using heavy feedstocks. With model fuels containing a mixture of well-defined and well-known sulfide molecules, it was shown that one of the advantages of ODS process compared to HDS was that reactivity was observed in the reversed order, with the following order for ODS: 4,6-DMDBT > DBT > BT [10,54]. This behavior was related to the higher electron density found on the sulfur atom with attached electron rich aromatic rings, favorable to the electrophilic addition mechanism for the oxidation of sulfur. It was also reported that alkyls groups attached to aromatic groups were able to further increase sulfur atom electron density to explain better reactivity for 4,6-DMBDT compared to that of DBT [2]**.** Nevertheless, sulfur density values for these two molecules are very similar (Table 3). Others studies with model mixtures [50,55] showed these alkyl groups also induce a sulfur atom steric hindrance leading to ODS reactivity decrease [3].

Using GC equipped with a specific sulfur detector (GC-PFPD or GC-SCD) Estephane et al. (2018) [3] and Safa et al. (2017) [49] were able to recently report on the reactivities of different sulfur molecules remaining after hydrotreatment of a gas oil (LGO 50ppmS) and a middle distillate (339 ppmS), respectively. Both studies confirmed the negative effect of the steric hindrance of alkyl substituents around the sulfur atom (positions 4 and 6) as well as the size of the alkyl groups. Unexpectedly, works with diluted SRGO (2000 ppmS) only treated by ODS demonstrated that the global reactivities of BT and DBTs were found to be similar in this real feed contrary to results generally obtained using mixture of model molecules.

Reactivity studies have also been reported when performing ODS on high loaded sulfur fractions. Shiraishi et al. 2004 [24] studied the reactivities of sulfur compounds during the oxidative desulfurization of vacuum gas oil using acetic acid and hydrogen peroxide. The works were carried out on polyaromatic thiophenic sulfur compounds in VGO that do not exist in light feeds. The authors found that polyaromatic compounds having naphthenic rings adjacent to the thiophenic rings (dinaphthothiophene, tetrahydrodibenzothiophene, and octahydrodinaphtothiophene) have higher electron density on the sulfur atom (Table 3) thus better reactivity in comparison to thiophenic compounds, and this makes VGO oxidation easier than for light oils.

Moreover, in 2014 Krivstov and Golovko [14] introduced another factor affecting thiophenic molecules reactivities (substituted benzo and dibenzo thiophene) during the oxidative desulfurization of VGO using hydrogen peroxide and formic acid. They found that in addition to the increased electron density on the sulfur atom and steric hindrance due to the alkyl substituents, the inductive effect has a positive influence ameliorating reactivity rate. It extends over the C–C bond chain and leads to an increase of the electron density in the conjugated aromatic system facilitating reaction. They obtained desulfurization rates decreasing in the following order: 2-ethylDBT > DBT > 4-ethylDBT. The steric effect of the ethyl groups dominates in the 4th ethyl position, thus 4-ethyldibenzothiphene was less reactive than DBT. Nonetheless, the positive inductive effect was dominating in the case of 2-ethyldibenzothiophene enabling better reactivity in comparison to dibenzothiophene. Besides the nature of the sulfur molecule on reactivity, for heavy fractions and typically residual cuts, the presence of heavy molecules like asphaltenes (whose typical molecular structures are presented in Figure 4) is

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considered an extensively significant factor influencing desulfurization rate. Bukowski et al. (1983) [56] considered these stable compounds as inhibitors terminating free radical reactions through recombination and disproportionation. For Herrington (2004) [57], asphaltenes can also suppress radical chain formation and the catalytic decomposition of organic sulfur compounds by peroxides and hydroperoxides.

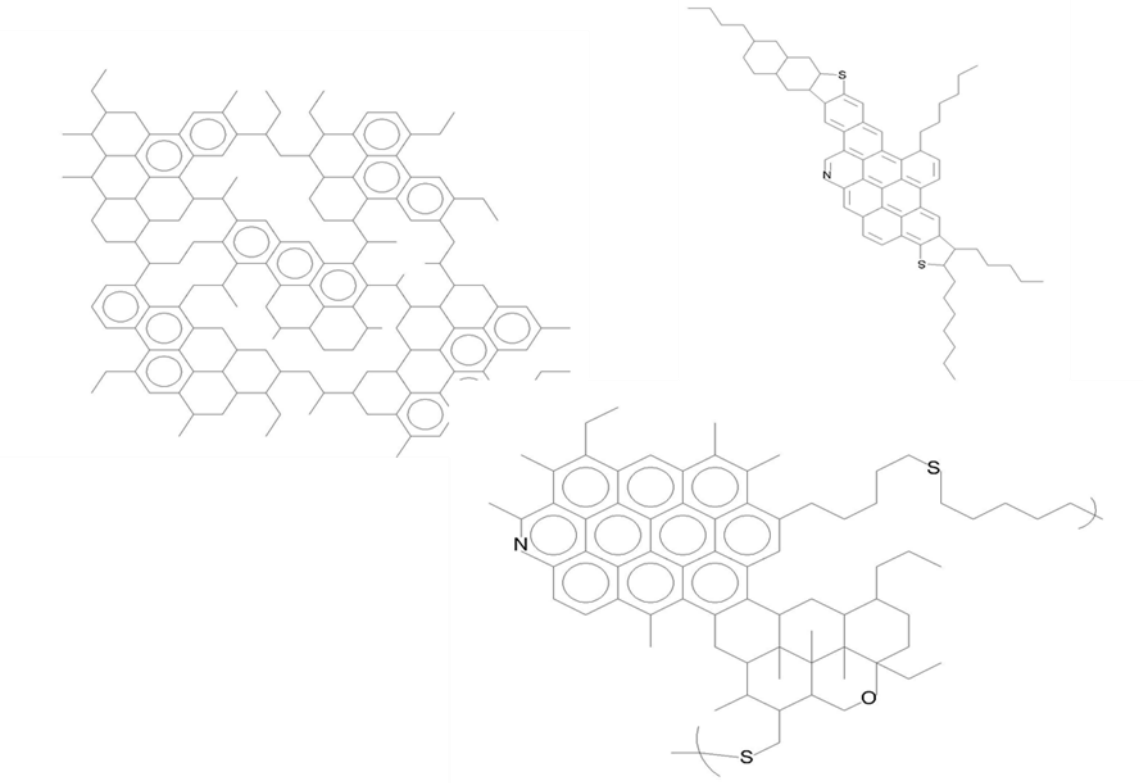

Figure 4. Presentation of typical asphaltenes molecular structures.

2.4. Noncatalytic Process

The use of a noncatalytic process based on the direct chemical oxidation of sulfur molecules has been scarcely explored and was dedicated to heavy feedstocks treatment.

Nitrogen oxides were proposed as chemical oxidants at the beginning of the 1970s by Guth et al. (1975) [58] who patented a continuous oxidative desulfurization process using them, and obtained a desulfurization rate of 86% after 4 minutes oxidation at 155 °C on a residual oil initially containing 2.2 wt.% S. Autoxidation using air was later studied in 2012 by Javadli et De Klerk [5] with a reaction carried out with a tar sand bitumen containing 5.2% of sulfur. Using air, sulfur is removed as sulfones as well as sulfur dioxide. Several conditions were tested to optimize the reaction. When increasing reaction temperature up to 175 °C the viscosity increased and bitumen hardening was noticed; this was explained by the authors through free radical reaction and side reactions caused by the complex nature of bitumen showing that attention must be paid to the optimization of reaction conditions in order to limit hazardous effects. At optimized conditions corresponding to a temperature of 145 °C for 3 hours, a 46% desulfurization rate was obtained after oxidation followed by solvent extraction using water. In 2016 Kazakov et al. [29] reported the use of ozone for the noncatalytic oxidative desulfurization of residual fuel. The sulfur content was reduced from 2.5 wt.%S to 0.46 wt.%S within 3 minutes at only 50 °C under 0.1 MPa pressure of ozone. These different studies showed that desulfurization using noncatalytic methods performed using selective oxidizing agents as air, ozone, or nitrogen oxides presents a main drawback: the emission of the reaction product SO_2 is detrimental to environmental

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protection since it is that product we are trying to avoid by removing the sulfur from the fuel before combustion.

The use of liquid oxidants such as nitric acid, potassium permanganate, and sodium hypochlorite without the use of catalysts has also been reported in two studies on low grade coal desulfurization. Coal contains sulfur as both combustible (sulfides, thiophene, thiols, etc.) and noncombustible (mainly in sulfate form) components which respectively are oxidized to SO_2, and remain in the ash during combustion [59]. The use of liquid oxidants enabled the transformation of combustible sulfur compounds into sulfate phases captured in the ash, avoiding SO_2 release after combustion; however, a high volume of oxidant (100 mL) is required to treat 20 g of coal. Guru et al. (2007) [59] successfully used nitric acid for the ODS of coal at ambient temperature with a desulfurization rate up to 35%. Using potassium permanganate and ferric sulfate as oxidants, Irum et al.2017 [60] obtained desulfurization levels up to 94% and 71% respectively, starting from a coal containing 5 wt.% of sulfur after a 1 hour reaction at 80 °C. Similarly, sulfur was transformed to sulfate and captured in the ash during the combustion.

Beside the simple oxidation process, the catalytic oxidation is considered as the most promising nonconventional method for upgrading different petroleum fractions. The main advantages relate to the high economic benefit obtained due to the mild operating conditions: low temperature and atmospheric pressure; and to better efficiency enabled by the use of a catalyst following the green principle chemistry nine. The ODS catalytic systems used are categorized into homogenous or heterogeneous catalysts; enzymatic catalysts have never been reported in the literature until now.

3. Homogeneous Catalytic Systems

The high efficiency due to the one phase catalysis system promoted the extensive use of homogeneous catalyst in the oxidative desulfurization process for heavy and high sulfur feedstock. Previous reviews have established a systematic comparison between homogeneous and heterogeneous catalysis [61], but model sulfur compounds were mostly considered as well as mechanism and reactivity parameters, without providing information about the efficiency of these systems with high sulfur feedstock such as diesels, vacuum gas oil, heavy fuel oil, or crude oil. This part of the review therefore focuses on results obtained using homogeneous catalysis for treating these different heavy fractions. Several parameters are discussed such as the nature and quantity of oxidant used, reaction temperature, reaction time, and mixing conditions.

3.1. Homogeneous Catalysts

The main type of homogeneous catalysts reported in the literature are carboxylic acids as well as homogeneous metallic systems such as polyoxometalates.

Formic and acetic acids are considered the most used catalysts in ODS among the carboxylic acids. With their use, the reaction is carried out according to the following steps: peracids (RCOOOH) are produced by the reaction of hydrogen peroxide and the carboxylic acid, then the formed peracid reacts with the sulfur compound to give the corresponding sulfone (Figure 5). Water is formed as byproduct.

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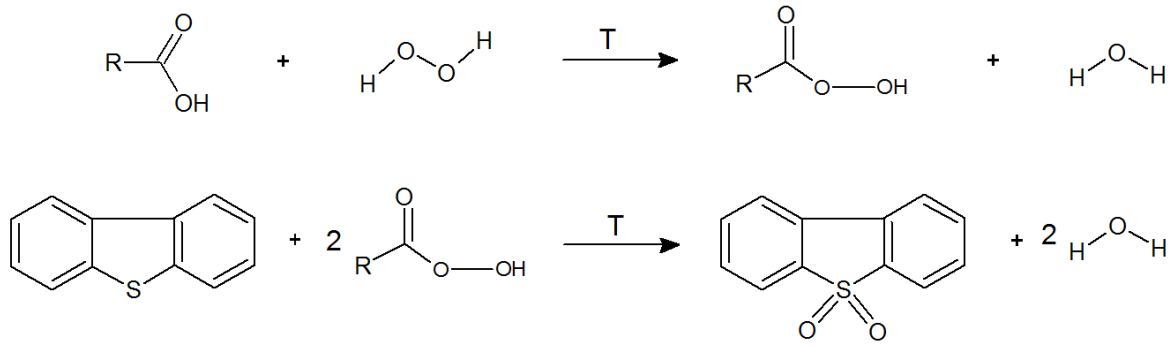

Figure 5. Mechanism of oxidative desulfurization reaction of dibenzothiophene (DBT) using carboxylic acid.

Different types of hydrocarbon fractions were targeted and used with this system. The use of formic acid has been studied by Aida in 1993 [62] who established a patent for oxidative desulfurization of heavy fuel oil using formic acid and hydrogen peroxide. The sulfur content in heavy fuel oil after oxidation and extraction decreased from 1.87 wt.%S to 0.21 wt.%S with this catalytic system.

Along with formic acid, acetic acid was widely used in ODS. In 1995 Zannikos et al. [16] applied oxidative desulfurization for a 2.87 wt.%S gas oil using hydrogen peroxide with a molar ratio of oxidant to sulfur equal 3 and acetic acid at T = 90 °C. After a one-hour reaction and extraction with methanol they achieved desulfurization down to 0.11 wt.%S in the gas oil.

Some articles compared the efficacies of formic acid and acetic acid. In 2015, Farshi & Shiralizadeh [26] and Otaibi et al. [34] concluded that better ODS results were obtained using acetic acid. Farshi et al. [24] found that the use of formic acid for oxidizing heavy fuel oil led to formation of byproducts such as sticky polymer materials. In the same way, for Otaibi et al. [32], the desulfurization rate for crude oil decreased using formic acid compared to acetic acid due to the higher acidity of formic acid, leading to an incomplete oxidation along with change in quality of the resulting oil.

With most of the systems mentioned previously, a huge amount of oxidant is being used with oxidant/sulfur ratio reaching up to 100. A major development in homogeneous catalysis was the application of peroxometallates as catalysts. These catalysts used in ODS process are salts of transition metals which form peroxycomplexes, improving catalytic performances.

Anisimov et al. (2003) and Fedorova et al. (2002) [12,63] oxidized a diesel fuel fraction using hydrogen peroxide as oxidant and vanadium peroxocomplexes as catalyst. Starting from 0.86 wt.%S, the sulfur reduction reached 0.2 wt.%S in the fuel after 3 hours of the reaction. A catalytic system of polyoxometalates and hydrogen peroxide-acetic acid system was also investigated by Trakarnpruk and Rujiraworawut in 2009 [15]. At 70 °C, a significant removal of sulfur was obtained with tungsten based heteropolyanions. Comparing the efficiency of heteropolyanions in the catalytic system, tungsten-based heteropolyanions were more active than those based on molybdenum. They enabled desulfurization of diesel fuels from 0.57 wt.%S to 0.01 wt.%S. Lately, in 2015, it was interesting to find a patent by Koseoglu and Bourane [64] about ODS of bunker fuel oil using homogeneous catalysis. Bunker fuel was mixed with hydrogen peroxide, acetic acid, and tungsten based polyoxoanions., the oxidant to sulfur molar ratio was fixed to 5, desulfurization with sulfur content from 3.5 wt.%S to 3 wt.%S was noticed after an hour and a half with a loss of 53% of the oil fraction giving low fuel recovery (47 %); which makes the process unacceptable.

3.2. Effect of Reaction Temperature

Reaction temperature is a critical parameter evolving with the feedstock used, it was further investigated. A range of temperatures was tested across the literature. Oxidation reactions are generally carried out at temperatures between 35 and 90 °C. Oxidation of petroleum feed at 35 °C was investigated by Krivstov and Golovko (2013) [14]. The oxidation of high sulfur diesel SRGO by hydrogen peroxide and formic acid with an oxidant to acid molar ratio H_2O_2:HCOOH of 3:4 followed by adsorption of

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oxidized products with silica gel reduced the total sulfur from 1.19 wt.%S to 0.05 wt.%S within eight hours. In these works, the composition of the fuel before and after adsorption was further analyzed. The authors found a change in the composition of diesel fuel. The relative amount of saturated HCs increased due to the removal of oxidized aromatic hydrocarbons and sulfur compounds after ODS reaction and adsorption. Otsuki et al. [10] carried out ODS of SRGO with 1.35 wt.%S and VGO containing 2.17 wt.%S using formic acid and hydrogen peroxide with the same quantity of oxidant for both fractions. They mixed 800 mL of fuel with 105 mL of formic acid and 480mL of hydrogen peroxide. Their works gave us the opportunity to compare ODS efficiency for two different petroleum fractions: the oxidation of SRGO was carried at 50 °C but a higher temperature (70 °C) was used for oxidizing VGO, taking into consideration the complexity and the higher viscosity of the gas oil mixture. The removal of sulfur by ODS reaction and extraction with DMF was very effective with a resulting sulfur content of 0.01 wt.%S and 0.1 wt.%S, respectively, starting from 2.17 wt.%S for VGO and 1.35 wt.%S for SRGO. Beside the expected direct effects improving kinetics and reaction rate, the use of higher temperatures was also investigated because of its expected effect to decrease the viscosity of highly viscous petroleum fractions, therefore permitting better diffusion of sulfur molecules and thus improving oxidation conversion. Mohammed et al. [31] performed oxidation of crude oil containing 1.494 wt.%S at 90 °C. After 15 minutes of reaction using a mixture of acetic acid and hydrogen peroxide with a oxidant/catalyst volume ratio of 1 and a catalyst/sulfur mass ratio of 8, followed by solvent extraction using n-heptane, the total sulfur content was reduced to 0.318 wt.%S. Several publications (Farshi & Shiralizadeh, 2015; Tetrisyanda et al., 2017; Toteva et al., 2009) [13,26,30] focused on the effect of temperature on ODS reaction. In most studies, increasing temperature from 35 °C to 90 °C enhanced sulfur reduction but above 90 °C, the increase in temperature had a reverse effect mainly due to the degradation of oxidant used and the formation of resins and asphaltenes [13].

3.3. Reaction Time

Reaction time is also a major parameter because it influences the possibility of scaling up the ODS process to an industrial scale. In ODS, it is quite rare to find an efficient oxidant–catalyst system allowing desulfurization in a few minutes. Oxidation time varies mostly between 1 and 10 hours [13,14,16,23,36]. However, Mohammed et al. [31] have demonstrated desulfurization of crude oil in 15 minutes (results mentioned above), while Otsuki et al. (2010) [10] reported the oxidation of SRGO and VGO using H_2O_2/HCOOH in 36 hours. This long reaction time was mainly related to the multiple steps used for the addition of oxidant and acid in small fractions. Krivtsov et Golovko (2014) [14] reported that increasing the reaction time enabled more sulfur reduction and highest desulfurization so that a sulfur content down to 0.046 wt.% S in the product was observed after 8 hours compared to 0.194 wt.% S after 1 hour. However, Toteva et al. (2009) [13] noticed that reaction time higher than 2 hours decreased sulfones concentration due to their oxidation into sulfates when treating 0.6 wt.% S light cycle oil (LCO) with hydrogen peroxide and acetic acid.

3.4. Oxidant

The quantity of oxidant used could also be one of the major factors affecting desulfurization efficiency. The stoichiometric oxidant/sulfur molar ratio (Ox/S) for ODS reaction forming a sulfone molecule is 2:1. The effect of this ratio was extensively studied [13,23,26,30,32]. In many cases, oxidation reaction of petroleum mixture was performed using a molar ratio of oxidant: sulfur of 2. In Abu Bakar 's study (2016) [32] starting from a crude oil with 1.13 wt.%S, the increase in oxidant to sulfur ratio from 1:1 to 5:1 enabled an increase in desulfurization activity such that the final sulfur content could be improved from 0.74 wt.%S (at Ox/S = 1) to 0.43 wt.%S (at Ox/S = 5). For economic reasons, the best ratio of oxidant: sulfur to use was reported as 2 because sulfur content was down to 0.58 wt.%S, showing no significance change with ratios higher than 2. Similarly, Farshi and Shiralizadeh (2015) [26] demonstrated that the increase of the ratio favored sulfur removal for the oxidative desulfurization of

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a 2.75 wt.%S heavy fuel oil. From Ox/S = 5 to Ox/S = 10, sulfur content reached 1.43 wt.%S instead of 2.15 wt.%S. Without further study of optimal Ox/S ratio, Ox/S ratio higher than the stoichiometry are sometimes preferred, as reported by Otaibi et al. (2015) [34] using a ratio of 8 when performing an ODS reaction of a crude oil fraction containing 2.5 wt.%S. This high ratio could be explained, not only by the initial sulfur content, but also by the heavy nature of the petroleum fraction used requiring high oxidant amount due to side reactions that can proceed, such as oxidation of aromatic hydrocarbons. This ratio was remarkably increased in the study of Shiraishi and Hirai (2004) [24] who reported the ODS of a 1.98 wt.%S vacuum gas oil diluted with decane using a huge oxidant to sulfur ratio of 100. The mixture was reacted with hydrogen peroxide and acetic acid with a molar ratio acid/sulfur of 50. After 3 hours, using this massive excess of oxidant and acid and after solvent extraction, sulfur content was decreased from 1.98 wt.%S to 0.032 wt.%S.

The use of a mixed homogeneous oxidant system containing together hydrogen peroxide and potassium permanganate was reported by Haruna et al. (2018) [36] for crude oil ODS. Hydrogen peroxide, potassium permanganate, and formic acid were mixed in equal quantity (5 mL each) to 15 mL of crude oil with sulfur content of 1.19 wt.%S at 60 °C for 2 hours. Reaction was followed by solvent extraction using dimethyl sulfoxide (DMSO). The authors demonstrated better results using this combined oxidant system compared to the use of potassium permanganate oxidant, with sulfur contents after reaction evaluated at 0.32 and 0.60 wt.%S, respectively.

Indeed, for environmental and economic reasons, minimizing the quantity of oxidant is a target in the development of ODS.

3.5. Reactivity of Different Fractions of a Heavy Fuel

Captivating work was realized by Otaibi et al. (2015) [34] and by Abu Bakar et al. (2016) [32]. The authors compared oxidative desulfurization rates for various petroleum fractions from the same crude oil, initially containing 1.12 wt.%S for Abu Bakar et al. and 2.5 wt.%S for Otaibi et al. Oxidation was carried out using hydrogen peroxide and acetic acid followed by extraction with DMF. After oxidation, the crude oil was further distilled into fractions and total sulfur content was determined for each cut. Results of desulfurization efficiency were distinctive. According to Abu Bakar et al [32], the maximum sulfur reduction was attained for the residuum cut with 75% desulfurization after 20 minutes. The reductions of sulfur content were 32% in gasoline, 45% in kerosene, and 69% in diesel. The sharper decrease for diesel was attributed to the presence in diesel feed of high amount of thiophenic compounds like dimethylbenzothiophene known as refractory in hydrodesulfurization process but considered as easily oxidized. For Otaibi et al., from a global desulfurization rate of 38% of the crude oil obtained after 60 minutes, desulfurization rates were then calculated for different fractions and observed to decrease in the following order: gasoline–diesel (59%) > VGO fraction (38%) > VR (13%) residue. In this case, the lowest desulfurization achieved with the residue was explained by its complex nature.

3.6. Stirring Conditions

Another factor that highly affects reaction efficacy is mixing conditions. In ODS, researchers aim to have a perfectly mixed medium in which intimate contact between the phases occurs. To achieve this, uniform contact is mostly desired. In the case of mixing highly viscous petroleum feeds, achieving uniformity is often a difficult challenge, but not impossible. To decrease the viscosity of petroleum fractions, some researchers tended to dilute the sample with an organic solvent, thus facilitating mixing conditions. Shiraishi and Hirai (2004) [24] used decane as solvent to increase the fluidity of vacuum gas oil. Other studies proposed to substitute the magnetic stirrer applied to lighter feeds with electrical stirring for perfect mixing conditions in the case of ODS of viscous crude oil [34] and heavy fuel oil [26]. In this latter work, Farshi & Shiralizadeh (2015) [26] reported oxidative desulfurization of heavy fuel oil using hydrogen peroxide and acetic acid. The reaction was followed by solvent extraction using

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acetonitrile. The resulting sulfur content was 1.14 wt.%S, reduced from 2.75 wt.%S. In the 1990s, Tam et al. (1990) [65] demonstrated oxidative desulfurization of an atmospheric gas oil using a continuous electric stirred reactor. Oxidation reaction was performed at 25 °C with nitric acid as the oxidant and acetic acid as the catalyst with the acid to oil ratio 0.03. The use of such a system allowed the sulfur content of the atmospheric gas oil to be reduced from 1.12 wt.%S to 0.38 wt.%S.

3.7. Additional Reagents

Additional chemical reagents were also introduced to the system containing fuel, oxidant, and catalyst with the purpose of accelerating reaction. Rakhamanov et al. (2016) [23] mentioned the use of phase transfer agents (PTA) reinforcing reaction, for the desulfurization process of a mixture of light gas oil with vacuum gas oil having 0.68 wt.%S, using the formic acid/hydrogen peroxide system with an oxidant to sulfur ratio of 4 and an acid to oxidant ratio of 1. Phase transfer catalyst was then added. The results showed that after 6 hours of reaction and after 3 extractions with DMF the desulfurization rate obtained was 90%. For the same purpose of facilitating reaction, sulfuric acid was introduced to the hydrogen peroxide/acetic acid system to 0.63 wt.% S gas oil (Yazu et al., 2001 [66]). It was reported that more acid was added to the medium to increase acidity and thus the catalytic activity. Desulfurization up to 90% was obtained. Similarly, sulfuric acid was used in the oxidative desulfurization of 0.63 wt.% S light cycle oil carried out by Toteva et al. in 2009 [13]. LCO was mixed with hydrogen peroxide, acetic acid, and sulfuric acid in the molar ratios: acid/sulfur = 2:1 and H_2SO_4/S = 1:1. Interestingly, the analysis of products before and after oxidation was further done using Fourier transform infrared (FTIR) spectroscopy. The FTIR served as analytical qualitative tool only comparing the intensity of sulfide peaks before and after oxidation as well as detecting sulfones peaks and comparing their intensities when changing reaction temperature without further study of overall desulfurization. Analyses were carried out after solvent extraction. The effect of reaction time was studied for reaction at 50 °C in the presence of oxidant with a molar ratio to sulfur equal to 3. Results indicated that increasing reaction time above 120 minutes had a negative effect reducing the quantity of sulfones formed due to the oxidation into sulfates detected using the FTIR. After extraction using DMF, the desulfurization rate was 90%.

In their works, Imtiaz et al. (2013) [8] proposed a phase transfer catalyst as phase transfer agent: an amphiphilic quaternary ammonium heteropolyoxometalate salt together with formic acid with a combination of two oxidants (hydrogen peroxide coupled to bubbled air) for performing oxidative desulfurization of several liquid fuels. For the same volume of fuel (20 mL) and oxidant (5 mL of hydrogen peroxide) different Ox/S ratios could be calculated and evaluated to 10, 20, 6, and 5, respectively, for naphtha (2 wt.%S), light gas oil (1.2 wt.%S), heavy gas oil (4 wt.%S), and bitumen (5 wt.%S). Reactions were carried at 80 °C for 30 minutes using ratio of oxidant/acetic acid = 2:1. It was shown by the authors that in the presence of the PTA, desulfurization efficiency was improved and reaction time was minimized. Desulfurization rates for the different fractions were evaluated after a two-step solvent extraction by acetonitrile–water (80:20) followed by methanol–water (80:20). Desulfurization yields were 83%, 85%, 69%, and 64% for naphtha, light gas oil, heavy gas oil, and bitumen, respectively. Comparable to Otaibi et al. [34] desulfurization rates decreased with heavier fractions. The result is always attributable to the heavier and more complex nature of compounds existing in the heavier feeds.

Feedstock complexity led researchers to apply homogeneous catalysis facilitating the contact between oxidant and sulfur molecules together with catalysts to obtain efficient sulfur removal. However, the use of homogeneous ODS industrial processes is still limited because homogeneous catalysts are molecularly dispersed with the reactant, making the recovery of products and solvents difficult.

4.Heterogeneous Catalysts

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Accordingly, attention has turned to heterogeneous catalytic systems for oxidation reactions. One of the advantages of heterogeneous systems is related to the easy product and catalyst separation. As previously observed for homogeneous ODS systems, heterogeneous catalysts have also been mostly used to model feedstock as well as hydrotreated middle distillate fractions with low amounts of sulfur, the ODS reaction being used as a finishing process.

In articles focusing on the ODS of high sulfur content fractions (> 0.5 wt.%S), heterogeneous catalysts are mainly composed of one active phase (often based on transition metals) dispersed on a support with large specific area. Among transition metals, the use of molybdenum [67–71], vanadium [72,73], and tungsten [74–76] as active phases has been reported. Comparative studies of the various active phases have been conducted [50,51] and various supports have been considered, including alumina [39,45,50,51,77], silica [38,78], and zeolites [79,80]. Interest is also growing in molecular sieves such as mesoporous silicates as well as activated carbon [48,81,82]. The various catalytic systems were mainly tested on model feedstocks and low sulfur light oils.

For heterogeneous systems, the use of tert-butylhydroperoxide (tBHP) has been patented for ODS of low sulfur feedstock (Kocal, 2001; Karas et al., 2008 [83,84]) and is often reported for oxidative desulfurization of diesel and heavy fuel oil fractions. Its main advantage is the one phase reaction medium enhancing mass transfer and allowing reactions in continuous fixed bed reactor.

Another type of catalyst, based on the presence of functional polymer, was studied by Ogunlaja et al. (2017) [25] and applied to the oxidative desulfurization of aromatic fraction of heavy fuel oil using tert-butyl hydroperoxide. Authors used nanofibers for adsorption of corresponding sulfones. The sulfur level decreased from 1.8% to 0.89%. The quantity of oxidant used was 10 times higher than that required by the stoichiometry of the reaction (oxidant to sulfur ratio equal to 20), which was justified by the authors by the nature of the fuel.

Hydrogen peroxide use was also noted for oxidation of crude oil and diesel oil. With this oxidant, the presence of two phases is reported, an aqueous polar phase containing the oxidant and an oil nonpolar phase. As a result, mass transfer problems can occur making the oxidation reaction more difficult by the separation of reactants. A study by Rafiee et al. (2016) [33] reported the ODS of crude oil in the presence of hydrogen peroxide oxidant with an Ox/S = 10 and 12% tungstophosphoric acid supported on montmorillonite as catalyst. After solvent extraction using acetonitrile sulfur content dropped from 0.1 wt.%S to 0.04 wt.%S.

Despite the complex nature of real feeds and the stringent conditions to apply, there are some efficient oxidant–catalyst systems that do not require high Ox/S ratios, with reported ratios close to stoichiometry. Prasad et al. (2008) [11] carried out ODS on light cycle oil having 0.8 wt.% sulfur using tert-butyl hydroperoxide as oxidant and 15% $MoO3/Al_2O_3$-SiO_2 with promoted with 3% bismuth. Desulfurization to 0.02 wt.%S was obtained after solvent extraction using N-Methyl-2-pyrrolidone NMP. Despite the high sulfur amount and the presence of substituted benzothiophene and dibenzothiophene low oxidant to sulfur ratio (Ox/S = 2.5) was used. The authors claimed that the deactivation of the catalyst caused by the adsorption of the sulfones during the ODS reaction was inhibited by the presence of bismuth acting as a promotor. The use of promoted catalyst was also investigated by Mokhtar et al. (2016) [18]. In this study complete desulfurization of 0.8wt.%S crude diesel was achieved after oxidation with tert-butyl hydroperoxide with a molar ratio oxidant to sulfur equal 3, in the presence of 16% molybdenum on alumina promoted by 4% tungsten and 2% vanadium, followed by 5 times solvent extraction using DMF. It has been reported that the catalyst was recyclable and 5 times usage of the catalyst was possible at laboratory scale.

The preparation method of the catalyst can also have a role in evaluating catalyst efficacy. A recent work was published by Palomeque-Santiago et al. (2018) [85] testing a tungsten zirconia supported catalyst. It was prepared using two different methods: traditional incipient wetness impregnation using ammonium metatungstate precursor and anionic exchange at low pH using peroxotungustic acid. In DBT oxidation the catalysts prepared using anion exchange had better activity in comparison to those prepared by the impregnation method and were thus tested in the ODS of SRGO 1.63% of sulfur. This diesel fraction was obtained from heavy crude oil. The reaction was carried out in the presence of tBHP

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with a high molar ratio of oxidant to sulfur equal to 20. After reaction and further extraction with butyrolactone, sulfur content decreased to 0.48 wt.%S, achieving 70% desulfurization. From the authors' point of view, the absence of WO_3 octahedral crystallites with the presence of tetrahedral species explained the enhanced catalytic activity.

One can notice the very limited application of heterogeneous catalysts for heavy fractions even though its use has always been convenient for model feedstock and light oils. However, growing opportunities are favoring the use of advanced heterogeneous catalytic systems due to the easy products and catalyst separation, high productivity, and also ecocompatibility.

Promising advances in lighter fuel ODS have included the use of titanium-containing catalyst in particular for treating diesel or kerosene [48,83,86–89]. As early as the 2000s, patents have been published regarding desulfurization without solvent use by Corma et al. [87–89] and using flow-type reactors by Kocal et al. for UOP LLC [83,86]; this opens the doors to the use of solid catalysts for ODS processes. Important factors need to be taken into consideration when it comes to residue feeds. At first, as mentioned before, heavy fuel oil as well as heavier cuts have high viscosity, therefore, mixing conditions are very important to ensure a perfectly mixed system. Catalyst optimization and adaptation to the heavy nature of the feedstock is a must to facilitate the diffusion of large complex molecules and to avoid deposition of large molecules of asphaltenes and metal chelates on the catalysts surface.

5.1. Ultrasound Technology

Interesting progress and noticeable results have been obtained using ODS technology for fuels with high sulfur content, nevertheless a main drawback making the industrial application of such a process difficult appeared to be the long reaction times due to low oxidizing rates. Reviewing heterogeneous catalytic systems for heavy fuels ODS, mass transfer problems have been previously identified as limiting the overall sulfur removal rate despite the use of active catalysts. To increase the reaction rate, strong stirring is required. Ultrasonic technology can be used in a broad range of industrial applications. Whilst they are not widely used yet, they could easily be implemented, for example in food processing. Energy produced from ultrasound can provide an extremely fine emulsion of immiscible liquids or assist mass transfer and surface activation (in a solid–liquid system). Cavitation created from ultrasound creates microbubbles that further grow and reach a critical size causing their collapse. Shock waves are formed producing very high temperatures and pressures thus increasing chemical reactivity [90]. Moreover, ultrasonication is also used as an upgrading method lowering feed viscosity and preventing asphaltene flocculation [91] thus facilitating oxidative desulfurization of heavy crudes.

For all these reasons, ultrasound assisted ODS process appears promising for sulfur removal.

Nevertheless, the application of ultrasound assisted oxidative desulfurization (UAOD) has been lately (after 2011) reported in the literature for low sulfur light gas oil (<0.22 wt.%S) [92–95] as well as model feedstock (S < 1000 ppm) [69,96,97].

In comparison with conventional ODS, the use of ultrasound waves enhanced considerably the results obtained in the same operating conditions. A paper by Hosseini & Hamidi (2014) [35] concerned the oxidative desulfurization of a crude oil using ultrasounds. Experiment was performed using acetic acid and hydrogen peroxide. Sulfur content was reduced from 5.2 wt.%S to 0.36 wt.%S after 20 minutes. Without ultrasound desulfurization efficiency was only 62% which indicates its important beneficial effect. Similar to conventional ODS, conditions such as temperature and feedstock type were considered and determined in ultrasound setup. Reaction temperature varied from 25 to 100 °C. Increasing temperature from 25 to 80 °C favored sulfur removal rate improvement from 10.26 to 34.84% in the case of UAOD of bunker fuel containing 3.5 wt.%S and using tert-butyl hydroperoxides as oxidant. Preferentially, reaction temperature was 75–80 °C. As for conventional ODS, temperature above 100 °C led to oxidant degradation decreasing desulfurization rate [28]. Moreover, authors took into consideration the complexity of the feed tested and the resulting consequence of handling difficulty due to the high viscosity; hence, to ensure the fluidity of Bunker-C oil, it was diluted with n-heptane solvent at volume ratio of 1/5 leading to a solution lighter in sulfur at 0.7 wt.%S.

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Using ultrasounds, in addition to conventional operating conditions, other parameters such as ultrasound reactor type, ultrasound frequency, and power should be considered. Reactor technology could influence kinetics of the reaction. Gaudino et al. (2014) [96] investigated the effect of reactor type on UAOD of model molecule DBT. Figure 6 presents three types of reactors used for desulfurization: (a) cup-horn like emitting plate (called also ultrasonic bath in which transducers are located at the bottom of the reactor and ultrasound irradiations transmit into the system indirectly), (b) a single horn system mostly used at the laboratory scale (a cylindrical probe immerged in the liquid transmits the waves into the medium directly), and (c) a sonitube (cylindrical tube at a position of 90°). The authors also used a multihorns system with horizontal flow reactor (continuous system). From the authors' point of view, considering energy consumption and efficiency, sonitube reactor offered the best compromise. In comparison to the other systems (probe type and cup-horn), this sonitube reactor was also considered by Gogate et al. (2011) more effective due to the uniform acoustic field, higher surface area of the sonicator as well as the geometry of the reactor [98].

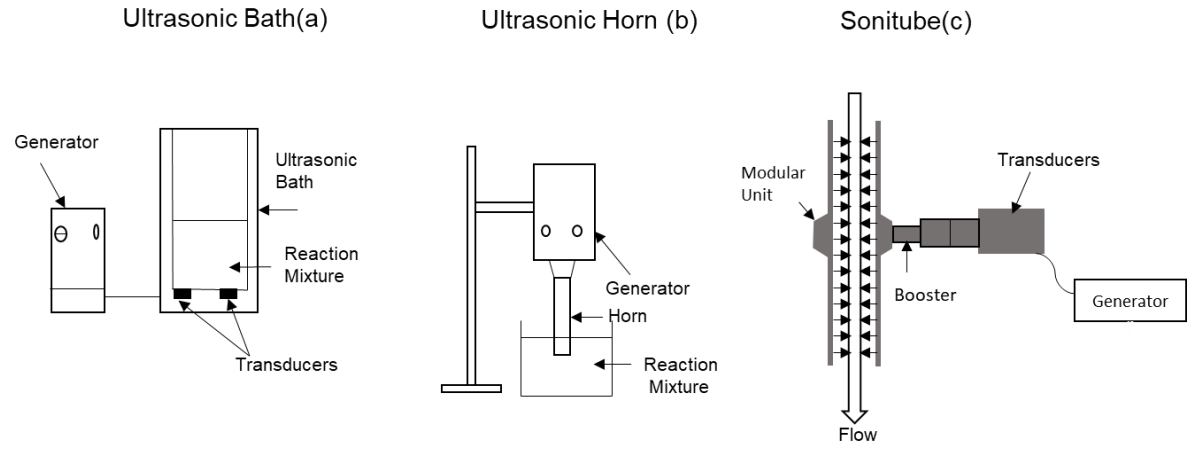

Figure 6. Schematics of different sonochemical reactors: (**a**) Ultrasonic Bath. (**b**) Ultrasonic Horn. (**c**) Sonitube adapted from [98].

With high sulfur feed, Wan et Yen (2008) [99] studied the UAOD for marine gas oil using two types of reactor: tubular reactor (vertical probe type reactor with several transducers) and probe type reactor (ultrasonic horn). Under similar conditions, they compared oxidative desulfurization using the two ultrasonic devices at different frequencies. Better desulfurization rates were obtained using the probe type reactor at a frequency f = 20 kHz (98.8% sulfur removal) in comparison with tubular reactor operating at f = 40 kHz (95.3% sulfur removal). However, in the attempt to scale up the UAOD process, continuous reaction was tried [99] and both ultrasound generators were compared (probe type and tubular sonoreactor). In the large scale continuous reaction, the sonoreactor gave better results: 90% desulfurization was obtained in 30 minutes using 200 W power output. In addition to the desulfurization results, economic aspects have been considered, the capacity of the sonoreactor was 25 times larger than that of the probe type offering a larger irradiation area which can be more efficient in scaled up system. This result points out the significant importance of reactor design on desulfurization rate. An optimized reactor enables better sulfur removal and lower energy consumption. In addition, ultrasound frequency is a crucial parameter affecting desulfurization efficiency. In the literature, with low sulfur feeds the frequencies used varied from 20 to 200 kHz. Indeed, at low frequencies, it was reported that less cavitation bubbles were produced, with more violent collapse giving a better sonophysical effect. The evaluation of frequency for low sulfur feed indicated that the optimal rate was between 20 and 40 kHz which was applied on high sulfur feeds.

The ultrasonication power was further investigated in the range between 100 to 800 W. Najafi et al. (2011), Tang et al. (2013), and Hosseini & Hamidi (2014) [19,28,35] studied the role of wave power

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amplitude by a set of experiments with different radiation conditions on high sulfur feeds diesel fuel (0.72 wt.%S), Bunker-C oil (3.6 wt.%S), and crude oil (5.2 wt.%S). As a result, they found that increasing wave power from 100 to 800 W enhanced sulfur removal; a higher intensity of ultrasound is introduced to the reaction which can accelerate oxidation reaction. However, notable attention must be paid to hazardous effect of high levels of wave powers. Tang et al. [28] reported that for UAOD of Bunker-C oil, increasing wave power can produce high volatile hydrocarbons due to the cracking of fuel oil. Thus, for side reaction and energy consumption considerations, it is not recommended to work with the highest power possible.

The use of phase-transfer catalysts (PTC) promoting reactions between reagents and facilitating the transport of reactants between phases is often associated with ultrasound technology. Tetraoctyl ammonium bromide is one of the most used PTC. Najafi et al. (2011) [19] studied the effect of phase-transfer catalyst for UAOD of diesel fuel, with phosphoric acid as PTC. Up to 10 g of phosphoric acid was added to 750 mL of diesel. They found that increasing its quantity from 3 to 10 g enhanced the sulfur conversion from 51% to 63%. However, with more than 10 g, its presence lowered the number of oxygen radicals and thus led to reduction of the conversion rate. Wan et Yen (2007) [20] studied the type of PTA to use for UAOD of marine diesel oil. They started with a comparison between two types of quaternary salts (tetraoctyl ammonium bromide TOAB and fluoride TOAF) on model feedstock. Results indicated that tetraoctyl ammonium fluoride gave better sulfur conversion in comparison with TOAB due the smaller molecular size of its anion. Thus, TOAF was further used for UAOD of marine gas oil with sulfur content 0.17%. After 10 minutes at 70 °C and 20 kHz frequency using PTA as catalyst, the desulfurization rate was 98%. The recovery of spent catalyst was evaluated and the desulfurization performance with the used catalyst was the same as the new catalyst which is promising for lowering capital cost and waste in the ultrasound process.

Without ultrasound, time needed to oxidize sulfur compounds for heavy high sulfur feeds can go up to several hours. With an ultrasound system, the reaction time decreased to minutes and sonication times reported in the different publications for model and real fuels ranged from 5 to 60 minutes. Different works also showed that slightly increasing sonication time increases desulfurization. Chen et al. (2010) [46] carried out ODS for pyrolysis oil containing 0.88 wt.%S. The increase of sonication time from 5 to 25 minutes increased desulfurization rate of pyrolysis oil from 21.2% to 43.6%. However, in 2004 Flores et al. study [27], the reaction time increased from 7.5 to 20 minutes in the UAOD of heavy fuel oil containing 3.8 wt.%S led to a decrease in sulfur reduction. The authors accounted this different result to the nature of the heavy fuel oil, where higher reaction time can favor secondary reactions such as recombination of heavy molecules.

Ultrasound technology was firstly and mainly applied using hydrogen peroxide as an oxidant because its major role was to improve mass transfer limited by the presence of aqueous and oil phases. Most researches were carried out using 30% hydrogen peroxide as oxidant.

With hydrogen peroxide, for economic reasons and for safety, it is recommended to work using low concentrations, and the effect of the percentage of hydrogen peroxide was studied by Kamal et al. (2017) [100] on a bitumen fraction with initial sulfur content of 5.2 wt.%S. Twenty milliliters of hydrogen peroxide with concentration varying from 0 to 30% were therefore added to 1 g of bitumen. Higher desulfurization yields were obtained when increasing concentration of hydrogen peroxide but above 5% H_2O_2, no significant difference in desulfurization was reported demonstrating that low concentrations of hydrogen peroxide are applicable in UAOD. Likewise, Flores et al. (2004) and Wan et Yen (2007) [20,27] studied the effects of concentration of H_2O_2 on UAOD of heavy fuel oil and marine gas oil. Similar results were found indicating the possibility of using a highly diluted hydrogen peroxide solution for a safer process.

For the high sulfur feedstock, UAOD was applied almost exclusively using homogeneous catalysts such as phosphotungustic acid [20,21,46,99], acetic acid [22,35], phosphoric acid [19], and Fenton-like catalysts [27]. Only one work of Tang et al. (2013) [28] was devoted to UAOD with a heterogeneous system using a molybdenum oxide powder.

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For better desulfurization efficiency, some researchers used more than one ultrasound unit. Chen et al. (2010) [46] combined two units connected in series for continuous UAOD (20 kHz, 500 W) followed by solid adsorption using alumina for pyrolysis waste oil containing 0.88 wt.%S. With two unit's better desulfurization results were observed giving 0.08 wt.% residual sulfur instead of 0.22 wt.%S with one unit. In addition, Wan et Yen (2008) [99] connected two parallel sonoreactors to reach higher sulfur reduction (92% instead of 90%).

To summarize, ultrasound assisted oxidative desulfurization was notably investigated using homogeneous catalytic systems. Its capacity of accelerating oxidation reaction was demonstrated at mild conditions with high efficiencies. UAOD was effective and has potential usage in the petroleum industry on different feedstocks.

However, since no industrial scale production was reported, a transition from laboratory scale to an industrial one is an important step to achieve. Developments should therefore focus on scale-up optimization to ensure uniform cavitational activity. In addition, more heterogeneous systems should be evaluated in ultrasound oxidation before reaching a commercial stage process.

5.2. Ionic Liquids

Amongst the nonconventional routes for oxidative desulfurization process, ionic liquids (ILs) have emerged and demonstrated their potential use. Ionic liquids were first known as molten salts. They are defined as liquids composed entirely of ions that are liquid at or below 100 °C. Ionic liquids are composed of organic cations and inorganic anions with side chains of alkyl or different functional groups such as alkylsulfates, alkylphosphates, or halogen containing anions. The most presented cations are imidazolium, ammonium, pyridinium, phosphonium, and sulfonium.

Properties distinguishing some ILs can include nonvolatility, solubility, high thermal and chemical stability, good catalytic activity, and recyclability. These properties induced their usage in various chemical processes in the fields of catalysis, bio catalysis, synthetic chemistry, and electrochemistry [101–103]. Their application has been widely extended in recent years mainly due to the need to have green chemicals less harmful for the environment. The distinctive properties of ionic liquids allow them to not only to have multiple applications in different chemical reactions, but also versatile utilizations for desulfurization. Many reviews [9,104–110] have reported in details the various applications of ILs for desulfurization as catalysts or as co-catalysts in oxidative desulfurization, as well as solvents for extraction. Together with these applications, the reviews included the study of several ILs parameters such as the quantity used, the temperature effect and their recovery.

Ionic liquids have been used as room temperature solvents for extraction of sulfur compounds [111–115] or as extractant of oxidized sulfur compounds after oxidative desulfurization reaction [40,116,117]. Extractive desulfurization studies have been performed using neutral ILs such as imidazolium- or pyridium-based ILs or acidic ILs for which it has been proposed that their Lewis acidity helped for better extraction of aromatic model sulfur compounds. It was also found that the IL extraction efficiency was improved when the sulfur compounds were first oxidized. The desulfurization of model feed containing DBT was about 12–22% while a better desulfurization was obtained up to 33–60% when achieving ODS using H_2O_2 (Ox/S = 11) and the same IL [117]. As a drawback, the extraction of sulfur compounds using ILs for extractive desulfurization could be limited by the co-extraction of aromatic compounds of the feed.

The main disadvantage of the system oxidant/ILs is the high amount of oxidant required with oxidant to sulfur ratio reported above 10 for model feedstocks. In the attempt of lowering the amount of oxidant required, researchers tended to use ILs as a co-catalyst, meaning that it is acting as a phase transfer agent added to the reaction medium containing the catalyst and oxidant, for activating the reaction. ILs were added to ODS reactions performed with different types of catalysts, mainly polyoxometalates [115,118,119]. Zhu et al. [117] compared the ODS efficiency using a homogeneous tungsten based catalyst [$WO(O_2)_2$.Phen.H_2O] with H_2O_2 as the oxidizing agent, and the same system

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with the addition of the $Bmim^+BF_4$ ionic liquid. After 3 hours at 70 °C they obtained 50% desulfurization of the model molecule, DBT; while in the presence of IL, the desulfurization reached up to 99%. These studies highlight the remarkable advantage of introducing ILs to catalytic reactions, the combination of ILs/catalysts offering a compatible system enhancing reaction efficiency.

Lately, the use of supported ILs aim to overcome shortcomings of one phase processes in which ILs are dissolved in the reaction media making their recovery difficult. Supported ILs catalysts were developed and tested [120], combining the advantages of ILs along with an easy separable system. The supported ionic liquid [Bmim]$FeCl_4$/Am TiO_2 system used by Xun et al. (2015) [121] led to complete desulfurization of DBT at 60 °C after 1 hour using H_2O_2 with Ox/S = 4. Desulfurization efficiency remained at 100% with recyclability up to 25 uses of the same catalyst. However, in this case attention must be paid to the ionic liquid loading on support to avoid the problem of leaching of the ionic liquid into the reaction medium. In these experiments, ionic liquids with tetrafluoroborate or hexafluorophosphate anions are used for extraction; however Freire et al. have demonstrated they are sensitive to hydrolysis, even at low temperature, which describe their instability [122].

In all of the systems mentioned, the work was carried out on model feedstock. One example in 2010 was achieved on real diesel feedstock containing 0.8% of sulfur. Kulkarni et Afonso [9] investigated real gasoline ODS in the presence of 30% hydrogen peroxide and $BMIM\text{-}PF_6^-$. After 10 hours, sulfur content was reduced from 0.8 wt.%S to 0.13 wt.%S.

Ionic liquids show a great potential for future application as a novel approach for ODS but consideration must be taken in the selection of ionic liquids with regards to Green Chemistry principle. However, researchers must focus on the application of these systems to high sulfur feedstock in order to evaluate their performance in the presence of real feeds and the consequent problems related to their regeneration.

5.3. Ultrasound and Ionic Liquid

One study has been conducted by Chan et al. (2008) [123] for oxidative desulfurization of diesel and heavy fuel oil samples combining ultrasound and ionic liquids together with superoxide oxidant. The main idea of this work was to find alternative highly efficient oxidant, cheaper, and easier to produce and to store in comparison with hydrogen peroxide and they proposed solid super oxides. These solids, like hydrogen peroxide, are known as reactive oxygen species and can generate other reactive oxygen species including hydrogen peroxide, hydroxyl radical, and perhydroxyl radical by a series of free radical reactions (Foote, 1995) [124]. Despite their limited application in ODS process, Chan et al. (2008) [123] attempted the UAOD (20 kHz) of diesel and heavy fuel oil using potassium superoxide KO_2. All experiments were carried out at 70 °C using an oxidant (KO_2 or H_2O_2), acetic acid, tetraoctylammonium bromide as phase transfer catalyst, and 1-n-butyl-3-methylimidazolium-hexafluorophosphate. It was interesting to notice that ionic liquid was used as a co-catalyst. Tested samples were sour diesel with 0.8 wt%S and heavy fuel oil with 2.6 wt.%S. Ninety-five percent desulfurization was achieved after 6 hours for diesel using KO_2 with molar Ox/S = 2.8. The same results were obtained for desulfurization of the same diesel but using H_2O_2 with Ox/S = 18. The results highlight the advantageous effect of using KO_2 because even though similar sulfur removal was obtained, a lower quantity of KO_2 was needed, which will limit oxidant consumption and storage capacity in the overall process. The same experiment using KO_2 was carried out for heavy fuel oil with a 65% sulfur decrease after 6 hours of reaction, demonstrating the feasibility of the reaction for heavy and residual fractions.

6. Conclusions

The development of ODS process has been ongoing for over 30 years, mainly to respond to the growing demand for ULSD. Oxidative desulfurization reaction can serve as a finishing step after hydrodesulfurization to remove from diesel the last few hundreds ppm of sulfur compounds like dialkyl dibenzothiophenes which are more refractory to HDS due to the steric hindrance caused by the

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alkyl derivatives. These compounds are easily oxidized to their corresponding sulfones in the presence of oxidant and catalyst at atmospheric pressure and relatively low temperature.

Advances in oxidative desulfurization systems mainly focus on simple model feedstock, or low sulfur and light petroleum fractions. However, upgrading the residue fractions is of immediate interest nowadays. At the same time, specifications for heavy petroleum products, such as bunker fuels, are more and more stringent to respond to sanitary and environmental concerns. These requirements highlight the need to purify heavier streams to obtain more valuable clean fuels. As a consequence, ODS process is further studied as an alternative or complementary process to HDS to avoid or reduce the economic deficiency related to operating conditions of HDS with high temperature, high pressure, and high hydrogen consumption.

Therefore, in this review, we intended to present and discuss the works carried out on oxidative desulfurization of high sulfur fractions of petroleum to better understand the viability of this method applied to high sulfur content, high viscosity, high boiling point feeds, and to point out the state of art on ODS of heavy oil with a highlight of the major breakthroughs.

To date, few studies report oxidative desulfurization of heavy fuels. In most papers, desulfurization rates are reported after a purification step through extraction or adsorption with no calculation of the actual conversion rate of sulfides to sulfones. Despite major developments in heterogeneous catalysis and its advantageous catalyst recovery, most of the reactions reported were carried out using homogeneous catalysis, mainly to overcome the problem of reaction in the presence of two phases. Heterogeneous catalysts deactivation and reuse also remain to be improved before scale-up of the process.

To increase exchanges between phases, and as an alternative to thermal energy to drive the oxidation reaction, ultrasound assisted oxidative desulfurization was reported for heavy sulfur feeds and despite its success in reaching low sulfur concentration, it was also mainly used with homogeneous catalysis. Recent applications to heavy crude oil suggest possibilities for heavy fuel oil as well.

Along with ultrasounds, ionic liquids have emerged and demonstrated their potential use for low sulfur diesel and model feedstock with no demonstration to high sulfur feeds.

Overall, the pragmatic analysis of papers reported indicates significant difficulties to perform ODS on heavy feeds, in which most of the sulfur is contained in polyaromatic structures, with high metal and asphaltene contents. Whilst ODS is not reported to reduce sulfur concentration in initially high sulfur heavy feeds to ppm level yet, preliminary results down to moderate to low concentration demonstrate its feasibility and encourage further developments. Application of ultrasound as well as ionic liquids will flourish with more efforts in residue heterogeneous catalytic systems development for increasing efficiency.

List of Abbreviations

DBT	Dibenzothiophene
DMDBT	Dimethyldibenzothiophene
DMF	N,N-Dimethylformamide
GC	Gas chromatography
HFO	Heavy Fuel Oil
IL	Ionic Liquid
LCO	Light Cycle Oil
ODS	Oxidative desulfurization
PTA	Phase Transfer Agents
PTC	Phase Transfer Catalysts

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SR-LGO	Straight Run Light Gas Oil
SRGO	Straight Run Gas Oil
TAOF	Tetraoctyl ammonium fluoride
tBHP	tert-butylhydroperoxide
TOAB	Tetraoctyl ammonium bromide
UAOD	Ultrasound Assisted Oxidative Desulfurization
ULSD	Ultra-Low Sulfur Diesel
VGO	Vaccum Gas Oil

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catalysts

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I.4. Conclusion and objectives of this thesis

Marine fuels are constituted by the heaviest fractions of oil. They are composed of a complex mixture that contains many molecules with high molecular weights and high boiling temperatures. First part of this chapter was dedicated to properties and composition of marine fuels, or more generally of heavy fuels, reported in the literature. Only one publication reports the composition of different marine fuels, showing various properties without specifying sulfur and other heteroatom distribution in these fuels.

The second part of this literature analysis focused on publications related to oxidative desulfurization (ODS) which can be a relevant process to achieve the desulfurization of marine fuels to meet IMO regulations. An increase in the number of publications dedicated to ODS has been observed since 2005 that accompanied the introduction of ultra-low sulfur diesel ULSD. Nevertheless, most of these publications focus on model feeds, or light feeds such as light gas oil and diesel fraction, with limited publications on heavy feeds. An extensive review of ODS on heavy fuels has been proposed in this chapter. However, the majority of the articles propose a desulfurization measurement by a global analysis of sulfur after separation of the sulfones. The sulfur content is measured before ODS reaction, then after reaction and extraction of the sulfones to obtain a global sulfur removal, without identification of the species present, sulfides and sulfones, in the complex charges and extracted phases, which does not provide an indication of the actual efficiency of the oxidation reaction.

Concerning the oxidizing agent, tBHP has the advantage of being miscible with fuel oil forming only one reaction phase, but it is expensive and can generate secondary products. Air as an oxidizing agent is the most economical but cannot be used due to the emission of SOx pollutants. Hydrogen peroxide, despite the formation of a two-phase system, has the advantage of a low price and of green secondary product. In the literature, the Ox/S ratio varies between 2 and 30, but work should be done to minimize this ratio.

Many catalysts have been tested in ODS in homogeneous and heterogeneous phase. In homogeneous catalysis, oxidant/organic acid systems are effective and have often been used for heavy cuts, but the problem of catalyst recovery and their high price make the use of heterogeneous catalysts more economical and environmentally friendly. These catalysts are often based on transition metal oxides or dispersed HPAs, numerous types of supports have been explored, such as alumina, silica, titania, carbon nanotubes. However, Mo and W based catalysts and TiO_2 based catalysts remain largely used among others. ODS test conditions can be very variable, making it difficult to compare catalytic performance. However, the assessment carried

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out on all catalysts used in ODS shows that molybdenum supported on alumina catalysts are more efficient that tungsten based ones. Promotion by other compounds is possible and beneficent. The use of heteropolyanions (HPA) as precursors for introducing active metals such as molybdenum on mesoporous supports can be considered by combining the textural properties of the support with the efficiency of HPAs as an active phase.

Owing to the huge number of publications dealing with ODS, however mainly devoted to model or light fuels, it was possible to screen the different operating conditions, oxidant and catalytic systems used, which can serve as a starting point for the study of marine fuel oil ODS. Furthermore, progress not only in the operating conditions but also in overall reaction made it possible to point out and highlight new technologies coupled to ODS like ultrasounds or ionic liquids to increase the performance without the need to have more severe operating conditions.

The analysis of the literature has shown few information on marine fuels properties, and the first goal of our work will be the development of a methodology for the analysis of sulfur molecules, comparing Sulf-UV and CHNS for elemental content, and using gas chromatography coupled with a specific sulfur detector in order to qualify and quantify the transformations of the sulfur molecules present. Indeed, the problems associated with the physical characteristics of the fuel (viscosity, possible presence of solids) need to be accounted for. Moreover, the study and analysis of nitrogen compounds in marine fuels will also be an important step to be completed for a better understanding of their behavior in oxidation.

Based on our literature review, reaction conditions have been selected as a starting point and will need to be optimized in the case of the ODS of marine fuels, especially regarding reaction time, oxidant and extracting solvent used. In the case of oxidant, since tBHP and H_2O_2 are mostly used nowadays, we will compare the performance of these oxidants. Ultrasound assisted oxidative desulfurization was reported, however mainly with homogeneous catalysis. We will thus study cavitation effects when applied to heterogeneous catalytic system in the case of marine fuel feedstock.

Finally, succeeding in developing a high-performance catalyst in oxidative desulfurization will also be essential. Since literature background emphasized the use of molybdenum as active phase in ODS, the catalyst initially chosen will be based on molybdenum oxide supported on alumina. To reach improved performance, research on both supported phase and supports will be carried out. Heteropolyacids and molybdenum peroxo species will be considered as alternative precursors with supporting study of promotor effect in case of molybdenum based catalysts. Different type of supports with distinctive properties will be tested (acid-base, oxygen mobility,

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high surface area and porosity…) to explore factors inducing improved ODS marine fuels catalytic performances.

I.5. References

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Experimental Section

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Chapter II Experimental Section

This chapter is devoted to the description of all the materials and equipments involved in the experiments carried during the thesis. First catalysts preparation method will be described followed by the characterization techniques applied, presented from a theoretical point of view together with a detailed presentation of the conditions adapted to the studied solids. A description of analytical methods used for the characterization of marine fuels will be then considered. Protocol of catalytic tests performed to evaluate catalysts efficiency in oxidative desulfurization reaction of marine fuels is fully described. Methods of sulfur evaluation for the determination of ODS performance is detailed as well as extraction protocol realized to calculate the sulfur removal rate.

II.1. Catalysts preparation

This part presents the supported molybdenum based catalysts investigated in this study and prepared by incipient wetness impregnation of commercial or synthetized supports. Different precursors of molybdenum were also used, as well as some additives, like phosphorus or vanadium.

II.1.1. Catalysts supports

We have considered the effect of several supports on the catalysts performance in the ODS of marine fuels: commercial supports such as alumina Al_2O_3, titanium oxide TiO_2, zirconium oxide ZrO_2, silica alumina SiO_2-Al_2O_3, and prepared ones like COK-12, TiO_2-COK-12 and CeO_2.

II.1.1.1. Commercial supports

Commercial supports alumina Al_2O_3, several titanium oxides TiO_2 (Alfa Aesar), zirconium oxide ZrO_2, silica alumina SiO_2-Al_2O_3 (ASA) were used in our work. In the case of titanium based supports, surface area and composition was given by the supplier and indicated in Table II.1.

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Table II.1: Surface area and composition of different titanium based supports given by supplier.

	BET surface area (m^2/g)	Composition (wt.%)
DT-51	90	-
MC-500	90	5 % Si
DT-W5	90	5 % W
DT-52	90	10 % W
TiO_2	120	-
HPX-100	250	-
G5-GRVS	400	-

II.1.1.2. Preparation protocol for synthetized supports

II.1.1.2.1. COK-12 support

COK-12 ordered mesoporous support with high surface area was synthetized, according to the protocol reported by Jammaer *et al.* [1].

The ordered mesoporous COK-12 was prepared with self-assembly method using long chain surfactant. 4.0 g of triblock copolymer P123 (Sigma Aldrich) was dissolved in 107.5 g H_2O. The buffer is prepared by adding 3.68 g citric acid monohydrate (Sigma Aldrich) and 2.54 g tri sodium citrate (Fisher Scientific). The solution is stirred overnight.

10.4 g sodium silicate solution (10 wt.% NaOH, 27 wt.% Honeywell Fluka) is further diluted with 30.0 g of water. This solution is added to the surfactant solution under stirring at 150 rpm with a mechanical mixer. Stirring is stopped after 5 min. The resultant mixture is kept at 90°C for 24 h.

The product is recovered by vacuum filtration and washed with 300 ml distilled water. The material is dried at 80°C and calcined at 300°C for 8 h and at 550°C for another 8 h with heating ramps of 1°C/min.

II.1.1.2.2. TiO_2-COK-12 support

The COK-12 support prepared according to the procedure described in section II.1.1.2.1 was then coated with TiO_2, the protocol being inspired of that described on SBA-15 by Bonne *et al.* [8]. TiO_2-COK-12 with a TiO_2 loading of 30 wt.% was prepared by impregnation in excess of solvent. It consists of the slow impregnation of a diluted solution of titanium isopropoxide (Fluka) $Ti(OiPr)_4$ in dry ethanol (ratio 0.2). A known volume of solution is slowly added to the silica

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support and the solvent is evaporated at room temperature for 24 hours. The solid is then aged one day under ambient conditions and dried at 80°C overnight before being calcined at 400°C using air for 3 hours with a heating ramp of 1°C/min.

II.1.1.2.3. CeO_2 support

CeO_2 was synthetized according to the co-precipitation method [2]. 3.7 g of cerium nitrate

Ce $(NO_3)_3$-$6H_2O$ (CN-Sigma Aldrich) is added to a 25% ammonia solution in a beaker so that the total volume of the reaction mixture is 580 ml. The CN solution was added at a uniform rate under vigorous mechanical agitation. The reaction was performed at room temperature for 3 hours. The yellow formed precipitate was then recovered by filtration and the excess ammonia was washed with distilled water until the pH became inferior to 8. The filtrate was then dried in an oven overnight at 65°C.

II.1.2. Preparation method

Incipient wetness impregnation is a commonly used technique for the synthesis of heterogeneous catalysts [3–5]. ODS catalysts were obtained by impregnation of the supports presented above, by a solution containing molybdenum precursors as well as eventual additives. Concentration of the precursor is calculated to ensure intended Mo loading in the final catalyst.

II.1.2.1. Impregnating solutions

Several Mo precursors were used for the preparation of the impregnating solutions, alone or with additives like phosphorus and vanadium.

II.1.2.1.1. Ammonium heptamolybdate based solutions, with or without P

In a volumetric flask containing water, the molybdenum precursor, ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24}$ (Sigma Aldrich) is added very slowly while stirring to allow proper dissolution.

For solutions doped with phosphorus, phosphoric acid 85% H_3PO_4 (Sigma Aldrich) is mixed with water before adding the molybdenum precursor. This dissolution reaction is endothermic. Once the temperature was back to room temperature, the solution was poured into a vial and water is added to adjust to the required volume and Mo concentration.

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II.1.2.1.2. Peroxomolybdate solution

Impregnation solutions containing peroxomolybdates seemed to be an interesting pathway to explore. The reaction between hydrogen peroxide and molybdenum oxide MoO_3 (Sigma Aldrich) leads to the formation of different peroxomolybdenum intermediates.

The preparation is made from 30 wt.% hydrogen peroxide (contains stabilizers, Sigma Aldrich) and MoO_3 with a ratio $H_2O_2/Mo = 6$.

- 30% weight solution of hydrogen peroxide:
  - Density = 1.11 $g.mL^{-1}$
  - $M(H_2O_2)$ = 34 $g.mol^{-1}$
  - $[H_2O_2] = (30 \times 1.11) / (34 \times 100 \times 10^{-3}) = 9.8\ mol.L^{-1}$
- Since $H_2O_2/Mo = 6$, then $[MoO_3] = 1.6\ mol.L^{-1}$
  - thus, $m(MoO_3) = (1.6 \times 10 \times 10^{-3} \times 144) = 2.35$ g

2.35 g MoO_3 is added to 10 mL of 30 wt.% hydrogen peroxide (H_2O_2, Sigma Aldrich). The solution is stirred overnight and the resulting color is yellow, characteristic of Mo peroxo species. Concentration was set to obtain 20 wt.% MoO_3 on Al_2O_3 on the final catalyst.

II.1.2.1.3. Silicomolybdate solution $H_4SiMo_{12}O_{40}$

The synthesis of silicomolybdic acid was carried out according to one of the methods described in the literature [6]. The overall balance of the reaction is:

$$12\ MoO_4^{2-} + SiO_3^{2-} + 22\ H_3O^+ \rightarrow SiMo_{12}O_{40}^{4-} + 33\ H_2O$$

A sodium molybdate solution Na_2MoO_4 is acidified with concentrated HNO_3. Then a solution of sodium metasilicate Na_2SiO_3 (0.2 M) is added drop by drop. The solution that has turned yellow is heated to 80°C for 40 min to promote the isomerization of the beta form to the α form.

After cooling at room temperature, silicomolybdic acid is obtained by adding 100 ml of concentrated hydrochloric acid at 12 M followed by extraction using ether. The principle of this extraction according to the Dreschel method is also described by Souchay [7].

After adding a volume of distilled water, the ether is evaporated and the acid crystallized at 4°C in the refrigerator. Yellow crystals appear after a few days. After filtration, we recovered the acid in the form of $H_4SiMo_{12}O_{40}$, 13 H_20.

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II.1.2.1.4. Phosphomolybdate solution $H_3PMo_{12}O_{40}$

This synthesis is described in the literature [8,9]. The overall reaction of the formation of 12-molybdophosphate ion is as follows:

$$12\ MoO_4^{2-} + HPO_4^{2-} + 23\ H_3O^+ \rightarrow PMo_{12}O_{40}^{3-} + 35\ H_2O$$

First, the sodium salt of heteropolyacid $Na_2HPMo_{12}O_{40}$ is formed (yellow precipitate) by adding a solution of $HClO_4$ perchloric acid (60%) to a solution containing sodium molybdate Na_2MoO_4 and phosphoric acid. The salt obtained in solution is recovered by filtration and then dissolved in a H_2O-HCl (2.9 M) mixture. Heteropolyacid is then isolated in the form of of etherate by ether extraction. After evaporation of the ether, the aqueous solution saturated with heteropolyacid is crystallized at 4°C and yellow crystals of the hydrate at 29 H_2O appear. After filtration, the hydrate is recovered with 13 water molecules: $H_3PMo_{12}O_{40}$, $13H_2O$. It is important to maintain a concentration in the order of 5.10^{-2} M heteropolyacid in solution to avoid partial degradation of the compound to isopolymolybdates.

II.1.2.1.5. Impregnation solutions with molybdenum and vanadium oxides.

The impregnation solutions were prepared using V_2O_5 (Sigma Aldrich) and MoO_3 using atomic ratio V/Mo=1/11. The ratio of H_2O_2/Mo is fixed to 6. 2.4 g MoO_3 is added to 10 mL of 30% hydrogen peroxide and stirred overnight. V_2O_5 was added to the resulting solution. Due to the high exothermicity of the reaction, it is carried out in an ice bath. The color of the solution obtained is reddish [10].

II.1.2.2. Incipient wetness impregnation method

The above presented solutions were used for impregnation of the supports, with a volume of solution equal to that of the water pore volume of the support and a Mo content corresponding to the Mo loading required on the final catalyst. Capillary action draws the solution into the pores. The next maturing step is carried out at room temperature, in a humid atmosphere for 3 hours to allow the solution to penetrate into the pores of the substrate.

The catalyst is then dried in an oven at 90 °C overnight to remove the water and calcined at 480 °C for 3 hours under air flow (0.3 $L.min^{-1}$), with a temperature of ramp 1 $°C.min^{-1}$. The purpose of this calcination step is to remove foreign counter ions not involved in the formation of the active phase and to structure the oxomolybdate phase in order to obtain the oxide precursor.

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The calcination step was not carried out in the case of catalysts prepared with peroxo compounds to avoid transformation of peroxo species.

The catalysts nomenclature and content are listed in Table II.2:

Table II.2 : Composition and nomenclature of synthetized catalysts.

Support	Catalyst (wt.%)	Promotor : Mo mol /mol	Symbol
Al_2O_3	10 MoO_3	0	10Mo/Al
	15 MoO_3	0	15 Mo/Al
	20 MoO_3	0	20 Mo/Al
	25 MoO_3	0	25 Mo/Al
	7% P 20% MoO_3	7:10	PMo/Al
	peroxo molybdenum= 20% MoO_3	0	peroxo/Al
	2% V_2O_5 18% MoO_3	1:11	VMo/Al
	20 PMo_{12}	0:00	20 PMo_{12}/Al
	20 $SiMo_{12}$	0	20 $SiMo_{12}$/Al
TiO_2	10 MoO_3	0	10 Mo/Ti
	15 MoO_3	0	15 Mo/Ti
DT-51	5 MoO_3	0	5 Mo/DT-51
	10 MoO_3	0	10 Mo/DT-51
	15 MoO_3	0	15 Mo/DT-51
MC-500	-	0	MC-500
DT-W5	-	0	DT-W5
DT-52	-	0	DT-52
HPX-100	15 MoO_3	0	15 Mo/HPX-100
G5-GRVS	15 MoO_3	0	15 Mo/G5-GRVS
ZrO_2	10 MoO_3	0	10 Mo/Zr
CeO_2	8 MoO_3	0	8 Mo/Ce
ASA	15 MoO_3	0	15 Mo/ASA
COK-12	20 MoO_3	0	20 Mo/COK-12
	25 MoO_3	0	25 Mo/COK-12
TiO_2-COK-12	20 MoO_3	0	20 Mo/Ti-COK-12

II.2. Characterization Methods

All prepared catalysts were characterized to provide qualitative as well as quantitative information about both their physical and chemical properties.

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II.1.1. Textural properties

Most catalysts are highly porous and possess large specific surface areas. Although the catalytic activity may be only indirectly related to the total available surface, evaluation of the surface area is generally considered to be an important requirement in catalyst characterization. Pore size is another important factor, in particular in relation to mass transfer of products and reactants. According to the IUPAC classification [11], materials can be divided into three groups depending on their pore size: with micropores (diameter < 2 nm), mesopores (diameter 2-50 nm) and macropores (diameter > 50 nm).

These properties were studied via N_2 adsorption-desorption measurements at liquid nitrogen temperature.

The principle consists in adsorbing a monolayer of nitrogen on the surface of the solid. The adsorption temperature is the temperature of liquid nitrogen -196 °C (77k).

The software coupled to the analyzer ASAP 2010 allows access to the specific surface area by a calculation based on the theory of "BET" at a relative pressure 0.05-0.3 from the following equation:

$$S = V_m . N . A_m . 10^{-20}$$

Where V_m is quantity of adsorbed gas, N=6.023.10^{23} Avogadro constant, A_m cross sectional area for one adsorbate molecule.

Based on the work of Langmuir, Brunauer, Emmett and Teller [12] demonstrated the validity of the equation called "BET transformed equation" which, once linearized, allows to calculate the volume of the monolayer from the physisorption data of nitrogen at 196°C. The equation is only valid at a relative pressure 0.05-0.3:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0}$$

With P, P_0 the equilibrium and the saturation pressure of adsorbates, V the volume adsorbed in one complete monomolecular layer at P and C a BET constant.

Mesoporous pore volume and pore size distribution are calculated using the BJH [13] (Barrett, Joyner and Halenda) method. This method implies that a capillary condensation phenomenon occurs in the mesopores. It consists of a step-by-step analysis of the adsorption-desorption of N_2 at -196°C, with a characteristic saturation level a mesoporous adsorbent, having a hysteresis loop of type H1 or H2.

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All analysis were carried out using a Micromeritics Tristar II apparatus. Before the experiment, the sample was pretreated under vacuum at 473 K during 5 h.

II.1.2. X-Ray Diffraction XRD

The ex-situ X-Ray Diffraction (XRD) patterns allow to identify the crystalline phases on catalysts and to eventually calculate the size of the crystallites. An XRD apparatus mainly consists of three parts: an X-ray tube, a sample holder and an X-ray detector. The principle of X-ray diffraction is based on the irradiation of a sample with a monochromatic wavelength beam (Figure II.1). When interacting with the material, a part of the beam is scattered in directions different to the incident beam but with the same wavelength.

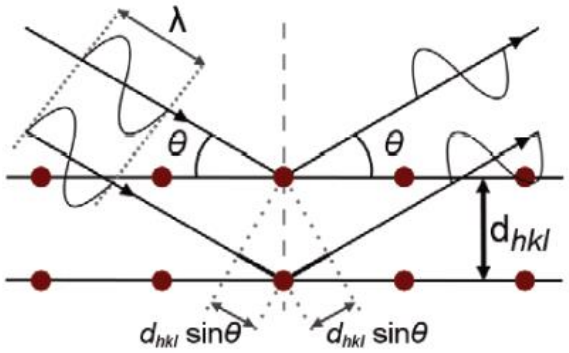

Figure II.1: Principle of Bragg diffraction.

The X-ray diffraction (wide angle) patterns were recorded by a Siemens D5000 diffractometer using Cu Kα radiation and a fast linear detector of the type Lynxeye and a copper anticathode, in Bragg Brentano geometry at room temperature from 10° to 90° with a scanning rate of 0.02° step size and 2 s step time.

Small angle X-ray scattering diffraction patterns (low angles) were recorded using a Rigaku device with a measuring step of 0.02°, an acquisition time of 15 seconds, in a range of 2θ from 0 to 6°. This is achieved by analyzing the elastic scattering behavior of X-rays when travelling through the material, recording their scattering at small angles (typically 0.1 - 10°, hence the "Small-angle" in its name).

Crystallite phases were determined by comparing the diffraction patterns with those in the standard powder XRD files published by the International Center for Diffraction Data. The half-width of the intense peak of the diffraction pattern and the Scherrer equation (equation 1) were used for calculation of average crystallite sizes of the catalysts.

$$\boldsymbol{d = \frac{k\lambda}{\beta \cos \theta}} \quad \text{(equation 1)}$$

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Where d is the average crystallite diameter, λ is the X-ray wavelength, β: the line broadening at half the maximum intensity (FWHM), θ is the Bragg angle.

II.1.3. Raman Spectroscopy

Raman spectroscopy is a vibrational spectroscopy, like IR spectroscopy [14]. It provides information about molecular vibrations that can be used for species identification.

The principle of this technique consists in focusing a laser type monochromatic light beam on the sample to be studied. The sample emits radiation that is collected and analyzed by a spectrometer, the intensities being measured with a specific detector (single channel photomultiplier type or multichannel type CCD). This detection includes two types of signals. The main part of the light is elastically scattered with the same frequency (Rayleigh diffusion). Weakly intense scattered light quanta, with frequencies different from those of the incident light quantum, are also observed, producing Stokes (or anti-Stokes) radiation [15], corresponding to the characteristic vibrational frequency of sample components.

The Laser Raman spectra of Mo-based catalysts were run on a Dilor XY800 spectrometer with a Krypton ion laser. Spectra Physics model A laser wavelength of 532 nm and a filter with diameter of 0.6 were used.

The dispersed radiation is received by the CCD (Charge Coupled Device) detector cooled with liquid nitrogen. Lab Spec software allows data acquisition and processing.

II.3. Analytical tools for characterization of fuel samples

II.1.1. Sulfur analysis by UV fluorescence (Sulf-UV)

The device used to determine total sulfur content is an ANTEK 9000S analyzer. The assay method is based on pyrofluorescence™, a patented method for fast and accurate quantification.

The first step of the quantification consists in burning the sample at high temperature in the presence of oxygen. This combustion takes place in a quartz tube filled with quartz beads to increase the contact surface between the sample and the oxidizing atmosphere at high temperature (1000°C).

The sulfur compounds are converted to sulfur dioxide SO_2 during combustion. The other products resulting from this combustion are carbon dioxide, water and other possible oxides. This gas mixture passes through the dryer tube which removes water and the gases are then introduced into the sulfur detector. The SO_2 produced is quantified by UV fluorescence. The range

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used to measure the residual sulfur content of samples can be chosen between 0 to 100 ppm or 50 to 300 ppm.

The reactions involved can be described as follows:

Combustion:

$$R\text{-}S + O_2 \rightarrow SO_2 + H_2O + CO_2 + \text{other oxides}$$

Detection:

$$SO_2 + h\upsilon \rightarrow SO_2^* \rightarrow SO_2 + h\upsilon'$$

The fluorescence radiation is then measured by a photomultiplier tube. In order to measure the correct total sulfur content it was important to prepare the samples according to the following protocol: dilution with dodecane, to comply with the concentration range analyzed by the apparatus, and heating with stirring to 80°C for 1 hour before injection for sample homogenization. The total sulfur content indicated in all chapters corresponds to total sulfur inside marine fuels corrected by the dilution factor.

All the technical characteristics of the analysis are presented in the following Table II.3:

Table II.3: Technical characteristics of Sulf-UV analysis

Sample	**Injected Volume**	5 µL
	Solvent	Dodecane
Conditions	**Furnace temperature**	1000°C
	O_2 inlet flow	25 mL.min^{-1}
	O_2 pyrolysis flow	450 mL.min^{-1}
	He flow	140 mL.min^{-1}

II.1.2. Elemental analysis using CHNS

CHNS analysis makes it possible to quickly quantify the elemental contents of carbon, hydrogen, nitrogen and sulfur present in the sample. It was carried out with an EA1110 thermo Fisher Flash type instrument, at the Oceanology and Geoscience laboratory UMR 8187 in Lille University.

The experimental protocol is as follows: a precise mass of sample between 1 and 2 mg is weighed and introduced into a cylindrical container which is then placed in the automatic passer. When the samples are introduced, the helium stream is temporarily enriched with pure oxygen and flash combustion occurs at 1000°C. Then the combustion gases are oxidized. The gases formed (N_2, CO_2, H_2O and SO_2) are carried by helium to a layer filled with copper, then onto the GC

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column (2 meters) that separates the combustion gases before detection by a Thermal Conductivity Detector (TCD). The setup is described in Figure II.2. In both cases calibration is ensured by the use of standard sulfur solution or solids.

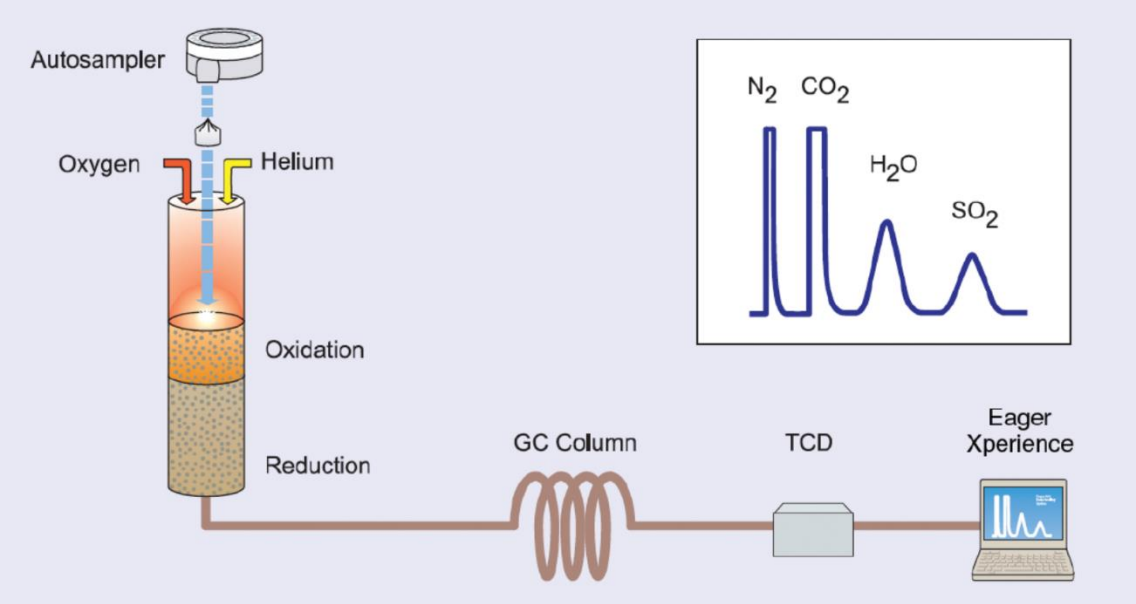

Figure II.2: CHNS configuration with TCD.

II.1.3. Analysis of sulfur species using Gas chromatography coupled to specific sulfur detector (GC-SCD)

The nature of the sulfur species is obtained by gas chromatography (GC, Agilent Technologies, 7890B) coupled with a specific sulfur detector SCD (Agilent Technologies, 8355) (Sulfur Chemiluminescence Detector). It enables separation as well as quantitative analysis of complex mixtures of sulfur containing molecules.

The sample to be analyzed is volatilized and swept by a stream of carrier gas through a heated column containing an absorbent support impregnated with a non-volatile liquid, which acts as the stationary phase. Capillary column GC, in which the stationary phase is bonded to the walls of a long capillary tube, permits far greater selectivity. The most widely used method of placing samples onto the column is a split/splitless injection.

The operation of the SCD is based on chemiluminescence (the production of light following a chemical reaction) from the reaction of ozone with sulfur oxide (SO) produced by combustion of sulfur compounds. A vacuum pump pulls the combustion products to a low-pressure reaction cell where excess ozone is added. The light produced as a result of the reaction is optically filtered and detected with a photomultiplier where the signal is amplified.

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The reactions involved are as follows:

$$R\text{-}S + O \rightarrow SO + H_2O + \text{other products}$$

$$SO + O_3 \rightarrow SO_2 + O_2 + h\upsilon\ (<300\text{-}400\ nm)$$

II.1.3.1. Choice of capillary column

The chromatographic column usually used for the analysis of conventional diesel fuels has been replaced by different types of column to find the most suitable for the analysis of marine fuels. The selected columns listed below have shorter lengths (30 m instead of 50 m) and a film thickness about half of that used with diesel samples. The expected benefits are a minimization of the passage time of the heaviest compounds in the column as well as a facilitation of the elution of these high molecular weight compounds.

- Agilent DB-1 without guard column (length: 30m, diameter: 0.25 mm, film thickness: 0.25 µm) which can withstand rising temperatures up to 300°C.
- Agilent column which has a longer length and a greater thickness, without co-guard, the "DB-Sulfur SCD" column, with the following characteristics: 40m long, 0.35mm diameter and 0.75µm film thickness. It can withstand rising temperatures up to 290°C.
- Phenomenex ZB-5HT high temperature range column consisting of a non-metallic 5%-phenyl/ 95%-dimethylpolysiloxane phase, stable at 430°C, MS certified for separation at boiling point.

With DB-1 and DB-Sulfur SCD columns, the chromatograms obtained for successive injections of fuel oil showed a very significant decrease in peak intensity of the injected samples after two days. Phenomenex ZB-5HT column gave repetitive results on a longer period, nevertheless, despite its better performance in comparison with other columns, after a period of 4 to 5 months, condensation of heavy molecules in the fuel oil during the analysis is observed and clogged the first part of the column. To avoid this problem without the need to cut the beginning of the column each period, which would result in changing sulfur compounds retention times, the chosen solution was to insert a 5 m long pre-column before the column. This pre-column is deactivated silica fused at high temperature with a diameter slightly thicker than the column (0.32 mm). In this case, when the problem occurs, a simple replacement of the pre-column is required each 4/5 months.

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II.1.3.2. Analytical conditions

The analytical conditions used for this work were optimized, in order to obtain adequate peaks separation, and correspond to an initial temperature of 50°C, a final temperature of 260°C with rate of temperature rise equal to 5°C/min. All samples were diluted with a factor of 20 with dodecane to correct total sulfur content of sample to the GC-SCD range of analysis (50-300 ppm).

All the technical characteristics and final settings of the GC-SCD are presented in the following Table II.4:

Table II.4 : Properties and settings of GC-SCD.

Automatic injector	**Plates**	16
	Injected Volume	1 µL
	Solvent	Toluene
	T	300 °C
	Split ratio	5:1
	Carrier gas	He
Samples	**Dilution**	1/20
	Solvent	Dodecane
Oven	**T_0**	50 °C
	T_{Final}	260 °C
	Ramp	5 °C.min^{-1}
	Final level	30 min
Column	**Type**	ZB-5HT
	Dimensions	30 m x 0.25 mm x 0.25 µm
	Pressure	0.1 psi
Detector	**T_{Plasma}**	800 °C

Final temperature is an important parameter that can affect the quantity of analyzed species, since marine fuels contain high boiling products that need high temperatures in order to be eluted. After checking that we obtained the same chromatogram at 400°C and at 260°C we decided to work at final temperature equal to 260°C to avoid bleeding of the stationary phase of the column at high temperature.

II.1.4. Speciation of nitrogen compounds using gas chromatography coupled to a nitrogen detector (GC-NCD)

The device used is a CPG Agilent 7890 with a 255 NCD detector. The Nitrogen Chemiluminescence Detector (NCD) is a nitrogen-specific detector. The overall operating principles for NCD and SCD are very similar and both follow the same general detection scheme. Similarly to GC-SCD, GC-NCD limits of detection vary between 50 and 300 ppm, therefore, all

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samples are diluted with a factor of 20 with dodecane to comply with the detection range of the apparatus. The detection step involves the characteristic NO + O_3 chemiluminescent reaction. This reaction generates a distinctive broadband near-infrared chemiluminescence emission centered around 1200 nm. The reaction mechanism has been established as the following:

$$R\text{-}N + O \rightarrow NO + H_2O + \text{other products}$$

$$NO + O_3 \rightarrow NO_2^* + h\upsilon$$

The same capillary column (ZB-5HT) with an integrated guard column as for sulfur compounds is selected for the detection of nitrogen compounds and the method used for the analysis of nitrogen species is the same as for sulfur species, taking into account the optimization steps achieved to guarantee the adaptability of analysis to the heavy nature of marine fuels. Table II.5 summarizes the overall conditions and the technical characteristics and settings of the GC-NCD.

Table II.5: Analysis conditions using GC-NCD.

Conditions CPG-NCD	
Injected Volume	1 µL
T injector	290°C
Flow of Helium	19.5 mL.min^{-1}
T plasma	800°C
T oven	From 50 to 260°C (at 5°C.min^{-1})

II.1.5. Analysis of aromatic hydrocarbons using liquid chromatography HPLC

The quantification of the different aromatic species is carried out by HPLC analysis using an LC Agilent 1200 series. Before each analytical campaign, the column is regenerated at 35°C under dodecane flow (0.5 mL.min^{-1}) for 4 hours. The dodecane flow rate is set at 0.5 mL.min^{-1} and the duration of each analysis is about 25 min. All the technical characteristics and settings of the device are presented in Table II.6. The apparatus is calibrated with a mixture of known non-aromatic and aromatic compounds (mono ring, di ring and tri ring) to determine the response factors and to verify the correct peak resolution and repeatability of injections. Each standard represents a family of aromatic compounds and are presented below:

- O-xylene: mono aromatic

- 1-methylnaphthalene: di aromatic

- phenanthrene: tri aromatic

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Table II.6: Properties and settings of HPLC

APPARATUS	**Injected Volume**	20 µL
	Pump	Q : several mL.min^{-1} P_{max} = 400 bar
	Detector	(RID) Refractometer-35°C 2 diodes and 1 cell 2 µL
CONSUMABLES	**Eluent**	Dodecane HPLC grade 99%$^{+}$ (Alfa Aeser)
	Column	K5NH2* Interchim (250 mm x 4 mm x 5 µm)
	Pre-column	K5NH2*Interchim (33 mm x 4.6 mm x 5 µm)
	Syringe injection	100 µL
SAMPLE	**Solvent**	Dodecane 99%$^{+}$ HPLC grade (Alfa Aeser)
	Dilution	20x
HPLC PARAMETERS	**T_{column}**	35°C
	$Q_{solvent}$	1 mL.min^{-1}
	Analysis Time	25 min

The composition of the solutions prepared for the calibration of the HPLC method is shown in Table II.7. The negative peak in the case of cyclohexane is caused by the difference in polarity with the eluent solvent (dodecane) but remains a peak that can be integrated. Linear calibration relationships could be established from the area of the peaks obtained and the compositions of the injected solutions (Figure II.3). Correlation of response factors obtained for each compound is higher than 0.99 which validate the calibration curves.

Table II.7: Compositions of calibration solutions used for the analysis of aromatic compounds.

Standard solution	cyclohexane (g/100mL)	o-xylene (g/100mL)	1-methylnaphtalene (g/100mL)	phenanthrene (g/100mL)
1	5.107	1.008	1.012	0.387
2	1.964	0.310	0.266	0.205
3	0.570	0.068	0.046	0.050
4	0.094	0.026	0.033	0.015

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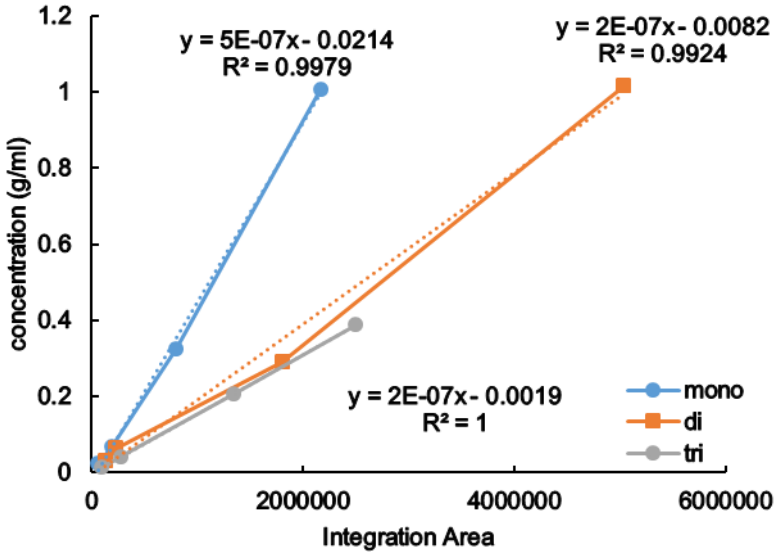

Figure II.3: Calibration curves for the analysis of aromatic standards.

II.4. Catalytic test

The ODS tests were carried out on different marine fuel oil samples in a 100 mL glass batch reactor at atmospheric pressure. 6 g of raw marine fuel or 30 g of diluted or liquid phase introduced into the reactor together with certain mass of catalyst. The system was heated to 80°C under reflux. The oxidant (hydrogen peroxide H_2O_2 or ter-butyl hydroperoxide TBHP) was then incorporated with the chosen oxidant/sulfur ratio.

It was necessary to optimize the mixing conditions for a good homogeneity of the reaction medium under the established conditions. Different types of agitation were used for the ODS test: agitation with a cylindrical magnetic rod in a tubular reactor, agitation in an autoclave reactor equipped with a mechanical blade and counter blades that break the vortex created during the reaction. However, under these conditions, no conversion was observed for all charges, pointing out the paramount importance of mixing issues when working with marine fuels. The optimal system leading to effective oxidation was a spherical balloon with an ovoid magnetic stirrer.

For 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, after optimization. Two cases were considered: ultra-sonication replacing mechanical stirring during reaction (the mixture (marine fuel, catalyst, H_2O_2 with Ox/S=3) was first heated to 80°C and then irradiated by probe type ultrasound reactor for 10 min) or ultrasonication of the reaction mixture followed by 15 min conventional stirring.

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At the end of the ODS reaction, the catalyst was recovered by filtration. The reactor walls and catalyst were washed with 50 mL of pentane to remove DBT and dodecane, and then with 50 mL of butyrolactone that due to its polar properties 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). Catalytic test experiments and post ODS reaction treatment are illustrated in Figure II.4.

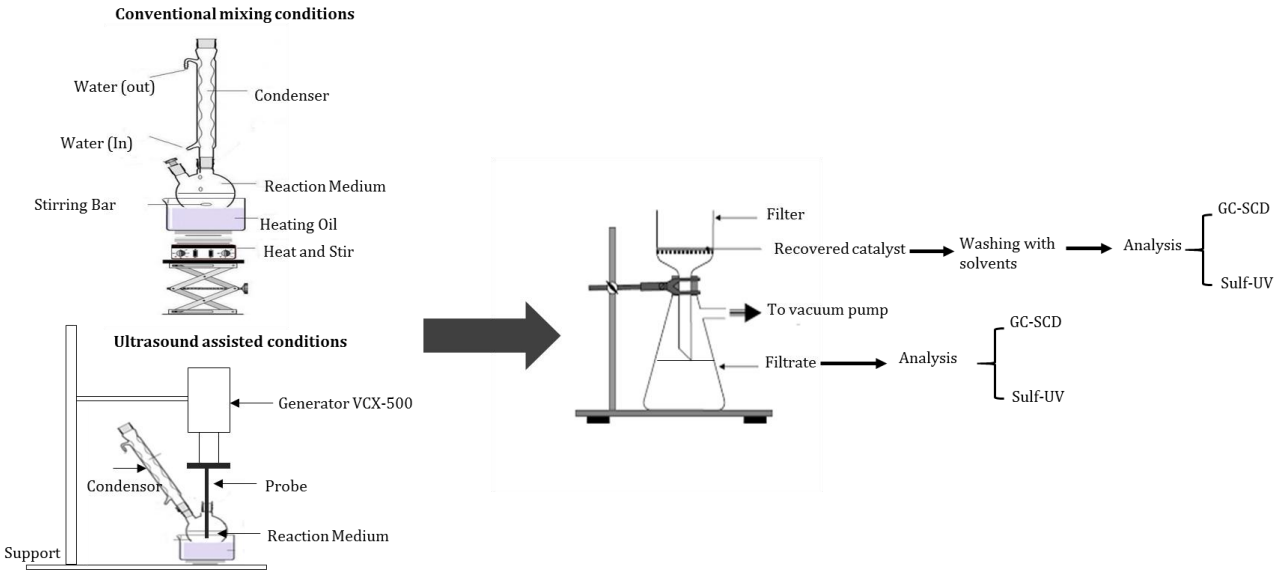

Figure II.4: Reactor schematics and treatment of the reaction medium after catalytic test.

II.5. Post ODS analysis: monitoring of sulfur species and sulfur content

The filtrate and washing solutions were weighed and analyzed by Fluorescence UV (Sulf-UV) to determine the overall sulfur content (sulfides and sulfones). In addition, in order to monitor the evolution of the reaction, GC-SCD gas chromatographic analysis is performed. A sulfur balance can thus be achieved and the retention rate of sulfur can be further calculated.

II.1.1. Mass balance and retention rate of sulfur species

The following example is for the ODS of 28 g of IFO380 fuel sample diluted 5x with dodecane. Total sulfur content before ODS was 7000 ppm and after ODS it was reduced to 6000 ppm and the mass of fuel recovered after filtration was 27.5 g.

The sulfur balance shall be carried out to ensure that the filtration and the washing are sufficient to recover the initial amount of sulfur in the charge.

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$$\mathbf{S_0 = S_{fil} + S_{sol}}$$

- Mass of sulfur before ODS in **IFO380-1 S_0**:

$$S_0 = \frac{Total\ S\ (ppm)\ x\ m\ (fuel\ used)(g)\ x\ 10^{-6}\ (correction\ ppm\ to\ g)}{dilution\ factor} = \frac{7000\ x\ 28\ x\ 10^{-6}}{5} = 0.0392\ g$$

- Mass of sulfur in filtrate solution **S_{fil}**:

$$S_{fil} = \frac{Total\ S\ (ppm)\ x\ m\ (fuel\ used)(g)\ x\ 10^{-6}\ (correction\ ppm\ to\ g)}{dilution\ factor} = \frac{6000\ x\ 27.5\ x\ 10^{-6}}{5} = 0.033\ g$$

- S_{sol} = Mass of sulfur in washing solutions

  = mass of sulfur in butyrolactone + mass of sulfur in pentane

  - Washing solution with pentane

    -Total sulfur: 6 ppm

    -Mass of sulfur in solution = total sulfur (ppm) x density (n-C5) ($g.mL^{-1}$) x volume used (mL) = $6 \times 0.63 \times 50 \times 10^{-6} = 0.000189$ g

  - Washing solution with butyrolactone

    - Total sulfur: 10 ppm

    - Mass of sulfur in solution= total sulfur (ppm) x density (BuL) ($g.mL^{-1}$) x volume used (mL) = $10 \times 1.13 \times 50 \times 10^{-6} = 5.65 \times 10^{-4}$ g

  $S_{sol} = 1.89 \times 10^{-4} + 5.65 \times 10^{-4} = 7.54 \times 10^{-4}$ g

- The retention rate is calculated as the difference of the sulfur content in the initial solution and in the reaction solution after filtration and corresponds to sulfones precipitated and/or retained on the catalyst.
  - Retention rate = $\left(\frac{S_{sol}}{S_0}\right) \times 100 = \left(\frac{7.54\ x\ 10^{-4}}{0.038}\right) \times 100 = 1.98\%$

- Mass balance of sulfur
  - M. B. = $\left(\frac{S_{fil} + S_{sol}}{S_0}\right) \times 100 = \left(\frac{0.033 + (7.54\ x\ 10^{-4})}{0.0392}\right) \times 100 = 84\%$

All sulfur balance results for the different marine fuels tested were found to be higher than 80% range, with a small percentage of retained sulfur on the catalyst that did not exceed 2%. Indeed, the high aromatic content in the real feed may facilitate the solubility of sulfones rather

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than their precipitation. Therefore, we considered neglecting the quantity of sulfur retained on catalyst in calculating conversion rates.

II.1.2. Evaluation of sulfur compounds using GC-SCD

After ODS, a decrease in the intensity of the peaks of sulfide species is observed together with the appearance of new peaks attributed to the sulfones formed. A quantitative study of these chromatograms is complicated due to the overlap of sulfide and sulfone peaks in the same retention times ranges.

To evaluate the overall conversion and monitor the sulfur species present, it was necessary to choose areas where the peaks of the sulfide species do not overlap with those of the sulfones: based on the chromatograms shown in Figure II.5 we have therefore chosen to follow the benzothiophenes family (Cx-BTs) present in the retention time range between 16 and 26 min and the DBT molecule, which, although in the sulfone area of the chromatogram, has a distinctive peak with no interaction with a sulfone peak, at a retention time of 28 min.

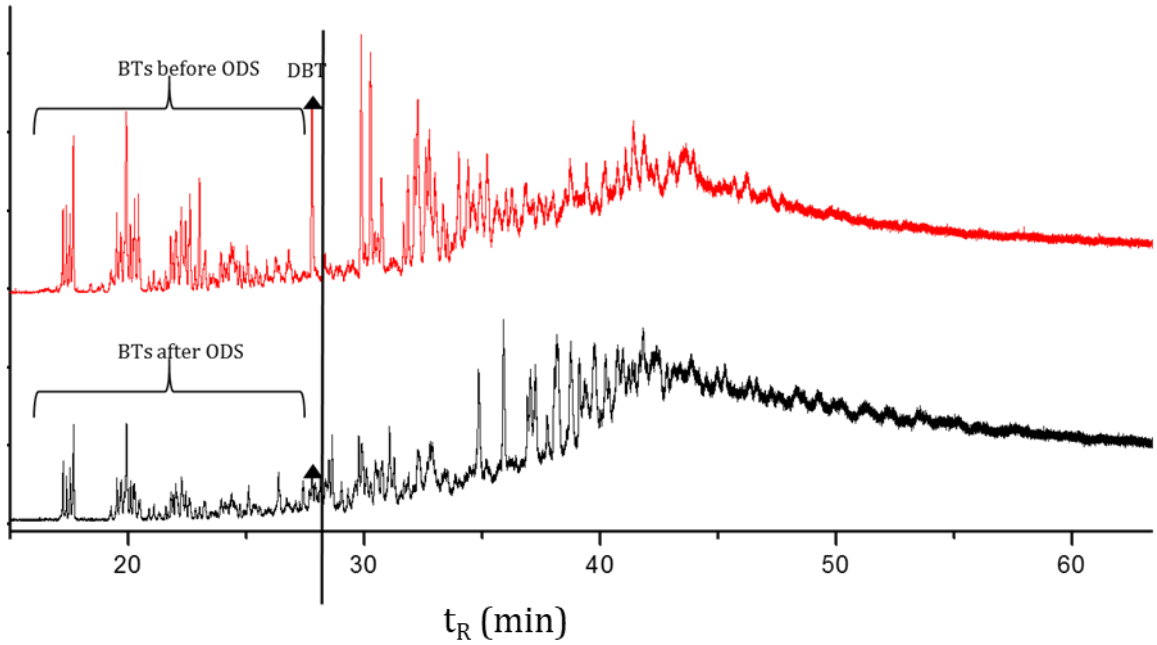

Figure II.5: Chromatograms of IFO500-LP before (red, top) and after oxidation (black, bottom) with the quantitative analysis of the catalysts efficiency by following the oxidation of the BTs and the DBT.

The conversion of sulfide species is obtained by comparing the surfaces of the peaks of the Cx-BTs or DBT in fuel oil before and after oxidation. Integration was performed between 15 and 60 min for the area corresponding to sulfides in the initial fuel. For Cx-BTs and DBT, integration

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method takes into account the area between the baseline and the chromatogram as illustrated in Figure II.6.

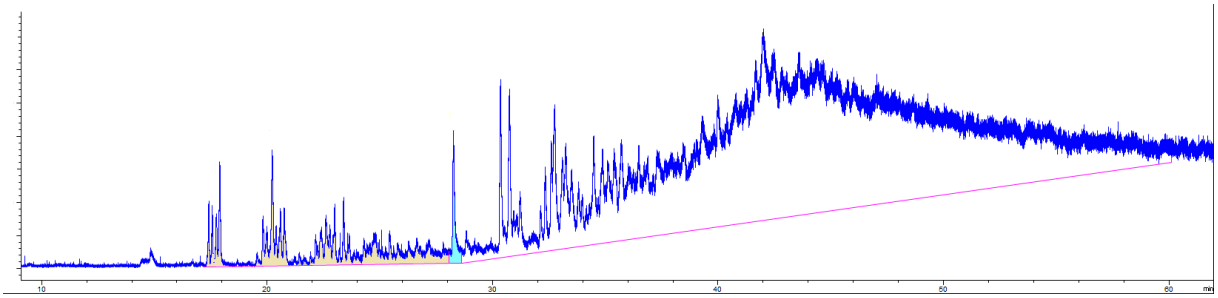

Figure II.6 : Example of integration taking into account the area between the baseline and the chromatogram.

Many experiments have been performed in order to evaluate the response factors of sulfide compounds. However, no reliable data could be obtained, making it compulsory to measure the sulfur content by CHNS or Sulf-UV.

II.6. Extraction experiments: Procedure

The extraction of sulfur compounds from the oxidized fuel was conducted using different solvents. A literature review made it possible to limit the list of solvents that may be of interest in our case: acetonitrile (ACN), N-Dimethylformamide (DMF), N-methylpyrrolidone (NMP) and butyrolactone. Properties of each solvent are presented in Table II.8. Solvents were used with different solvent/oil ratios. The extraction was carried out by mixing volumes of oxidized fuel and polar solvent at 50°C for one hour. The phases were allowed to settle and then separated in a separating funnel, and left until two separate layers of fuel and solvent formed. The extraction protocol is illustrated in Figure II.7.

Table II.8 : Dipole moment and dielectric constant of different extracting solvents.

Extraction Solvent	Dipole Moment (Debye)	Dielectric Constant
N, N-dimethylformamide (DMF)	3.24	36.71
Acetonitrile	3.53	35.94
N-methylpyrrolidone (NMP)	4.1	33
Butyrolactone	4.27	28

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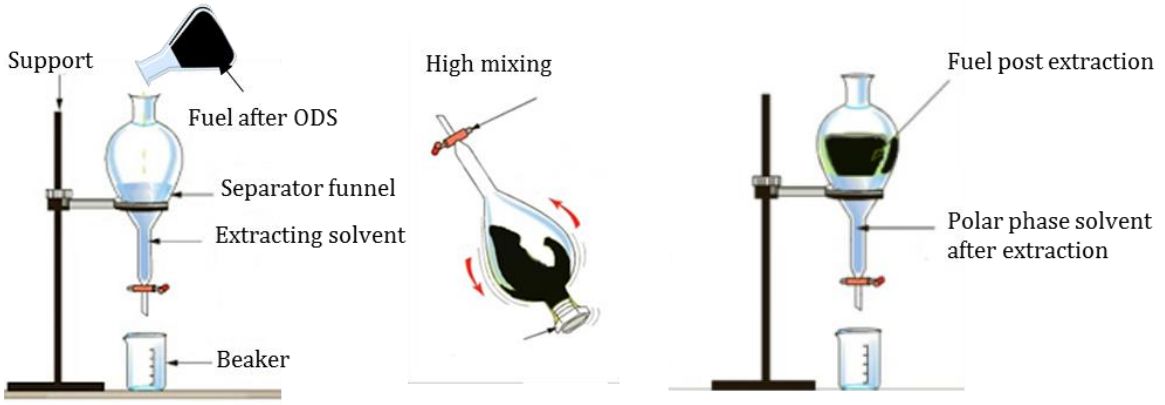

Figure II.7: Extraction protocol for oxidized marine fuels.

The reaction progress was monitored by measuring sulfur concentration using Sulf-UV and GC-SCD.

The sulfur compounds removal percentage (or desulfurization rate D.R.) after extraction is calculated as follows:

$$\text{D.R. (\%)} = \left(\frac{S_0 - S_t}{S_0}\right) * 100$$

where $\mathbf{S_0}$: initial concentration of sulfur in marine fuel oil and $\mathbf{S_t}$: sulfur concentration in oxidized marine fuel after extraction.

Marine fuel yield after extraction is calculated on the basis of marine fuel volume change before and after extraction:

$$\text{Marine fuel yield (\%)} = \left(\frac{V_{fuel\ before\ extraction}}{V_{fuel\ after\ extraction}}\right) \text{x } 100$$

Total aromatics removal after extraction is calculated on the basis of the difference in the percentage of aromatics compounds in the fuel phase before and after extraction:

$$\text{Total aromatic reduction (\%)} = \left(\frac{A_0 - A_t}{A_0}\right) \text{x } 100$$

where $\mathbf{A_0}$: percentage of aromatics in marine fuel oil and $\mathbf{A_t}$: percentage of aromatics in oxidized marine fuel after extraction.

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Marine Fuels Characterization

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Chapter III Marine fuels characterization

Marine fuel is a very complex matrix to analyze unlike lighter petroleum cuts for which a complete detailed composition is available in the literature. Developments in analytical techniques in order to respond to the need for more efficient hydrotreatment processes made it possible to improve identification of sulfur compounds present in diesel samples [1–8].

Regarding heavier feeds, few publications report the composition of marine fuels [9–12] or residuals [5,13–16]. As illustrated in schematic of Figure III.1, marine fuels are the waste of different refining processes consisting of heavy hydrocarbons with high sulfur accumulation. Complete analysis becomes problematic and sophisticated due to the huge number of isomers present with increasing boiling points and carbon number. Co-elution problems and difficulty in separating very similar components can occur [17,18]. Considering these limitations, only average structural information is obtained.

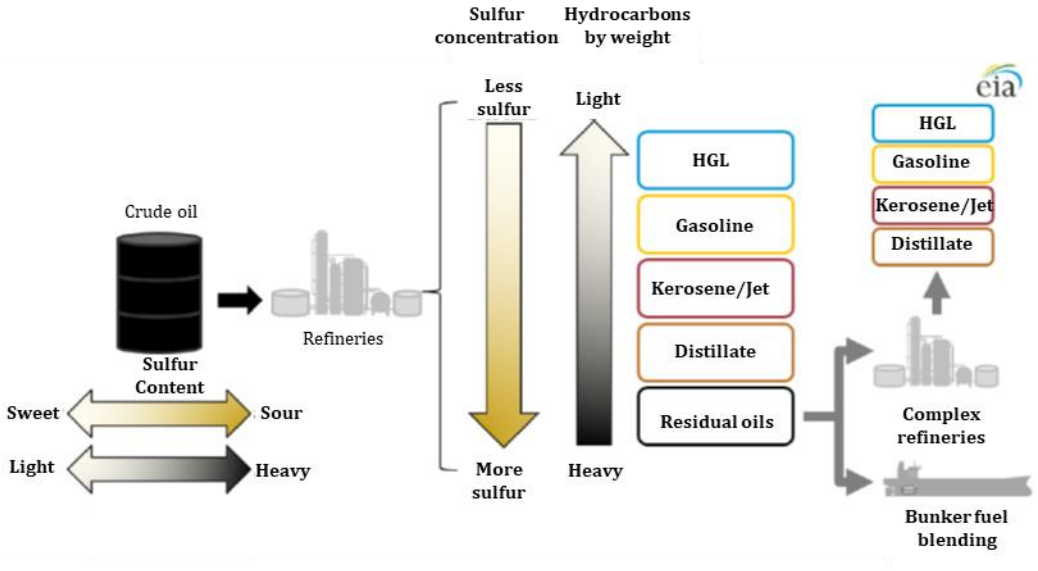

Figure III.1 : Schematic view of crude oil distillation and downstream products.

Nonetheless, heavy fuels characterization is becoming a major research subject to better understand the reactivity of molecules associated to different conversion processes. Several chemical analysis methods exist to determine different properties in heavy crudes like residual oil, crude oil and heavy fuel oil. Principal functional groups are determined using high performance liquid chromatography (HPLC) [19–21] and infrared spectroscopy (IR) [22,23], aromatic and aliphatic carbons using ^{13}C NMR nuclear magnetic resonance [24,25], molecular composition with Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS)

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[26,27], chemical functionalities and metals associated using liquid chromatography-inductively coupled plasma mass spectrometry (LC-ICP MS)[28]. In addition, advances in high temperature two dimensional gas chromatography made it possible to quantify sulfur containing compounds in crude oil fractions as well as identification of tetra, penta and hexa aromatic species [29].

Since individual hydrocarbon molecules characterization is delicate, researchers thought to simplify the matrix preventing interferences between molecules. They applied chemical fractionation methods, among which SARA separation is widely used [19,26,30–33]. Saturate, Aromatic, Resin and Asphaltene (SARA) is an analysis method that divides residual oil components according to their polarizability and polarity. The saturate fraction consists of non-polar material including linear, branched and cyclic saturated hydrocarbons (paraffins). Aromatics which contain one or more aromatic rings, are slightly more polarizable. The remaining two fractions, resins and asphaltenes, have polar substituents. The distinction between the two is that asphaltenes are insoluble in an excess of paraffinic solvent whereas resins are miscible with dodecane, heptane (or pentane). With sulfur containing compounds (SCC), distribution is more arduous. For instance, aromatic SCC can accumulate in aromatics, resin or asphaltene parts. None of these fractions purely contains one class of SCC, thus individual identification remains critical.

Ten marine fuels have been supplied by SEGULA, from various origins and different characteristics: 3 LSFO with viscosities of 380 cSt at 50°C, 4 IFO with viscosities of 380 and 500 cSt, 2 RMK with viscosities of 500 and 700 cSt and 1 HSFO with a viscosity of 700 cSt. Taking into account that a precise structural characterization and identification of marine fuel sample is unconceivable at the level of that of distillate fractions, but can be attempted, the present chapter outlines the characterization of these fuels particularly concerning sulfur containing species, but also regarding nitrogen containing compounds and aromatics (see analytical techniques developed in chapter II: CHNS, Sulf-UV and GC-SCD and -NCD). Analysis of samples will be performed in raw state, after dilution and after dilution and centrifugation.

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III.1. Methodology of analysis

Figure III.2 summarizes our methodology of analysis, with the different samples that will be considered in this study: raw (R), diluted (D) and diluted centrifuged samples (CD). Indeed, only CHNS analysis was performed on the raw fuels, because of their viscosity and presence of heavy molecules preventing injection in GC apparatus.

To simplify manipulations and mixing conditions of fuels, their dilution by organic solvents was performed. These samples will be referred to as D for diluted. Two types of solvents were used: paraffinic alkanes, n-heptane (C7) and n-dodecane (C12), leading to asphaltenes precipitation, and a mixture of dodecane and xylene (C12-X), a polar solvent suitable for asphaltenes solubilization. These diluted samples will be analyzed by Sulf-UV, CHNS and by GC-SCD. In the case of GC-SCD, injection will be realized using a syringe with a filter, thus avoiding injection of solid particles in the apparatus. The diluted filtered sample corresponding to part of the fuel analyzed by GC-SCD will be named DF.

After dilution, the samples were centrifuged, and the recovered liquid phase, named DC for diluted centrifuged, was analyzed by the above mentioned techniques in addition to GC-NCD and HPLC. The composition of the diluted samples obtained after centrifugation (DC) will be compared to that of the samples obtained after filtration (DF).

Since we expect that composition will not be same, ODS will be perform on raw (R), diluted (D) and diluted centrifuged (DC) samples to obtain more information about the effect of matrix composition on molecules reactivity in ODS.

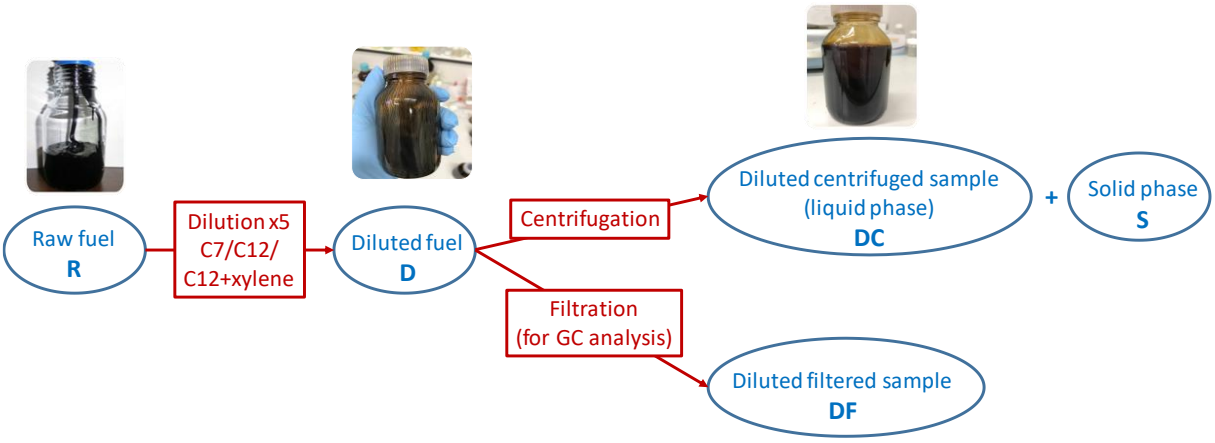

Figure III.2 : Scheme of the different fractions obtained from raw marine fuels (R), avec dilution (D), centrifugation (DC) or filtration (DF).

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III.2. Characterization of raw marine fuels

A specific nomenclature has been defined for the designation of fuel oils in this thesis, **Ay-z**, A indicating the category (**LSFO, IFO, HSFO** or **RMK**), y the viscosity (from 380 to 700 cSt, indicated by the supplier), and finally z the sample number when two samples of the same category presented the same viscosity.

The elemental composition in C, H, N and S obtained for raw marine fuel samples is presented in Table III.1:

Table III.1 : CHNS elemental analysis of raw marine fuels.

Marine fuel	Carbon/ (wt.%)	Hydrogen/ (wt.%)	Ratio H:C	Nitrogen/ (wt.%)	Sulfur/ CHNS (wt.%)
LSFO380-1	87.03	10.75	1.48	0.53	0.59
LSFO380-2	87.51	10.25	1.41	0.61	0.54
LSFO380-3	87.38	10.85	1.49	0.4	0.55
IFO380-1	87.14	11.04	1.52	0.49	0.76
IFO380-2	87.33	10.68	1.47	0.51	0.60
IFO500-1	85.79	10.37	1.45	0.37	3.27
IFO500-2	85.79	10.37	1.45	0.37	3.27
RMK500	84.89	10.55	1.49	0.40	2.76
RMK700	84.04	10.18	1.45	0.51	2.57
HSFO700	85.79	10.53	1.47	0.39	2.95

Similar H:C ratios were obtained in the different raw marine fuels, with values varying between 1.41 and 1.52. Such low H/C ratios are commonly reported for heavy fuels, in accordance with their high aromaticity. Rana *et al.* [34] and Garaniya *et al.* [15] have noticed similar H:C ratio of 1.4 for residue obtained after vacuum distillation .

Total sulfur content usually increases with increasing boiling point of the fraction. However, in some cases, depending on process temperature and if distillation occurs at temperature higher than 500°C, the high molecular weight sulfur compounds will break. In this case, middle fractions can contain more sulfur than higher boiling point fractions [35].Based on CHNS, we noticed that total sulfur content in LSFO380 was between 0.54 and 0.59 wt.%, while for IFO samples having also a viscosity of 380 cSt, total sulfur content ranged between 0.60 and 0.76 wt.%. Additionally, marine fuels with a viscosity of 500 cSt and higher had a sulfur content varying between 2.57 and 3.27 wt.%, in agreement with the heavy character of these feeds. The sulfur content in IFO depends on the respective quantity of intermediate and heavy refining

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fractions that have been mixed to obtain the fuel, thus explaining the large range of S content in these IFO samples.

The variation in the nitrogen content (0.37-0.61 wt.%) is much smaller than that measured for sulfur (0.54-3.27 wt.%). Nitrogen content is lower than the sulfur content except for LSFO380 samples for which both contents are almost similar. Such high N contents have been reported in HFO, with a value of 0.36% for a heavy fuel oil with a sulfur content of 2.63%, by Radovic *et al.* [12]. This amount is significantly higher than in lighter fractions like diesel and SRGO, where total nitrogen does not exceed several hundreds of ppm [36,37].

All the marine fuels samples supplied contain more than 0.5wt.% S, even the LSFO, they are therefore not suitable to operate in SECA nor any other zones by 2020 and thus require sulfur removal.

III.3. Centrifugation of fuels and characterization of diluted centrifuged samples DC (dilution with dodecane)

In ships, prior to combustion in the engines, the marine fuel passes through a treatment system where it is heated, decanted and centrifuged to allow the separation of water and the removal of solid particles present in the fuels. This process is a prerequisite to guarantee a fuel adapted to the combustion in the engine. In this study we considered centrifugation of the diluted fuels, prior to ODS reaction. In our case, centrifugation of the marine fuels diluted in dodecane also allows to separate the precipitated asphaltenes known as 'bad actors' in refineries as they promote sludge formation and cause catalyst deactivation during the processes [34]. It will also allow to see the effect on the ODS reaction of the presence or not of asphaltenes.

III.3.1. Optimization of the centrifugation step.

The first step focused on optimizing centrifugation conditions on one selected fuel IFO380-1, diluted 5 times with n-dodecane. The centrifugation was performed in a laboratory scale centrifuge equipped with tubes with maximum capacity of 15 mL. The maximum speed that can be achieved is 8000 rpm. The speed of centrifugation on board varies from 1000 to 3000 rpm.

Centrifugation was carried out for 20 min at various speed rates: 3000, 5000 and 8000 rpm. Two phases were obtained: **the diluted centrifuged** phase **DC** and a **solid** phase **SP**. These two phases were weighed and the sulfur content remaining in the DC was determined by Sulf-UV analysis, and calculated taking into account the 5 times dilution to be compared with the sulfur content of the diluted sample. Results are summarized in Table III.2, together with the mass

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fraction of solid phase compared to the initial mass of fuel, as well as the percentage of sulfur of the diluted fuel that is present in the diluted centrifuged sample.

Table III.2: Total sulfur content in diluted centrifuged phase DC, mass fraction of solid phase SP and percentage of sulfur in DC of IFO380-1 obtained with different centrifugation conditions.

Fuel	Centrifugation speed /rpm	[S] in DC /ppm	Mass fraction in SP/wt.%	% S in DC
IFO380-1 (7600 total S ppm)	3000	5750	23	59
	5000	6050	16	68
	8000	6000	12	70

When increasing the centrifugation speed from 3000 to 8000 rpm, the quantity of solid phase recovered decreases from 23 to 12 wt.% in relation with the better separation of solid particles and liquid. The amount of recovered solid decreases due to the higher centrifugation force that separated residual liquid from precipitated solid. At 3000 rpm the speed is not high enough to perfectly separate solid particles from liquids, the more the speed increases the more liquid is recovered with higher sulfur content. In ships, the quantity of solid phase recovered is 1 wt.%. Indeed, the type of equipment as well as the operating conditions are very different and are not comparable with our work. Moreover, in our case the fuel is diluted with dodecane with subsequent precipitation of asphalthenes, which are removed by centrifugation. The amount of sulfur present in the liquid phase increases from 5750 to 6000 ppm, which corresponds to a proportion of sulfur present in the liquid phase varying from 59 to 70%. So for further experiments the speed of centrifugation will be set at 8000 rpm, as it allows recovering the highest amount of sulfur in the liquid phase.

III.3.2. Characterization of the diluted centrifuged samples DC.

Table III.3 gathers the sulfur content of the marine fuels diluted with dodecane D, compared to that obtained in the liquid phase after centrifugation DC, determined using Sulf-UV and CHNS. The wt.% of solid phase (SP) recovered and the percentage of sulfur in the DC are also reported.

First, we have confirmed that the sulfur contents in raw R and diluted fuels D as determined by CHNS are the same (results of total sulfur content in raw fuels determined using CHNS presented in Table III.1), indicating that all sulfur is correctly analyzed by this technique even in the precipitated part of the diluted samples. By comparing the methods for determining total sulfur content and their applicability to marine fuels samples, we noticed that results obtained with Sulf-UV were not in agreement with the elemental analysis method when analyzing

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diluted sample of fuels. If similar values are measured for LSFO380 and IFO380, around half of the amount obtained with CHNS is measured by Sulf-UV for more viscous fuels with viscosities of 500 cSt and above. For instance, total sulfur content of IFO500 was 1.6 wt.% using Sulf-UV instead of 3.27 wt.% determined using CHNS.

Table III.3: Sulfur content in diluted marine fuels before (D) and after centrifugation (DC) determined by CHNS and Sulf-UV, mass percentage of recovered solid phase and percentage of S in the liquid phase DC.

Marine fuel	[S] in D /ppm CHNS	[S] in D /ppm Sulf-UV	[S] in DC /ppm CHNS	[S] in DC /ppm Sulf-UV	mass fraction SP /wt.%	% S in DC /% CHNS
LSFO380-1	5900	5000	5032	5500	14	80
LSFO380-2	5400	5200	4750	5000	17	77
LSFO380-3	5500	5000	5000	5000	7	85
IFO380-1	7600	6000	6500	6000	12	70
IFO380-2	6000	7000	6000	6000	5	95
IFO500-1	32700	16000	16000	16500	14	43
IFO500-2	32700	16000	16000	16500	17	42
RMK 500	27600	14000	13500	12500	14	39
RMK 700	25700	14000	15000	15000	16	49
HSFO 700	29500	12900	12000	12500	16	36

Sulf-UV could therefore not be advisable for the analysis of diluted marine fuel samples containing non-volatile high viscous and difficult to solubilize particles. Fluorescence Sulf-UV is based on standardized method of ASTM D5453 [38] which covers the determination of total sulfur in liquid hydrocarbons, boiling in the range from approximately 25 to 400°C, with viscosities between approximately 0.2 and 20 cSt (mm^2/S) at room temperature. It is believed that with residual fractions, part of the sulfur components, or other types of compounds, could be blocked in the ceramic during combustion, disabling the correct determination of total sulfur content. Thus, it will be more applicable to naphthas, distillates, engine oil, ethanol, Fatty Acid Methyl Ester (FAME), and engine fuel such as gasoline, oxygen enriched gasoline (ethanol blends, E-85, M-85, RFG), diesel, biodiesel, diesel/biodiesel blends, and jet fuel. Whereas CHNS, based on ASTM D5291 [38], is applicable to samples such as crude oils, fuel oils, additives and residues. Contrariwise, when analyzing the liquid phases obtained after centrifugation DC, sulfur content measured by Sulf-UV is comparable to that obtained by CHNS, indicating that with diluted centrifuged samples, all the high molecular weight solid particles have been removed eliminating analysis problems.

The quantity of material separated by centrifugation fluctuates between 12 and 17 wt.% of the total mass. For only LSFO380-3 and IFO380-2, the solid fraction after separation was around 5 wt.%. The quantity of sulfur in the liquid phase corresponds to values above 70% and up to 95% of that contained in the fuels with low sulfur content and low viscosity (LSFO and IFO380). For

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these samples, the liquid phase is almost equivalent to the diluted fuel. Precipitation of compounds with less sulfur content has thus occurred during dilution, the weight percentage of asphaltenes precipitated being almost the same for all samples. Indeed, asphaltenes are complex molecules which sulfur content may vary depending on the feed. Contrariwise, for fuels with higher viscosity and higher sulfur content, only 36-49 % of the sulfur is present in the liquid phase. A large amount of sulfur has thus precipitated in asphaltenes fraction and the recovered liquid phase is not completely representative of the sulfur species contained in those heavier fuels.

III.4. Characterization of diluted centrifuged samples DC (dilution with heptane and xylene)

Solubilization of asphaltenes is known to depend on the length of the paraffinic chain of the solvent. We thus used heptane (C7) to compare with dodecane (C12), and a mixture of dodecane with xylene (C12+X), an efficient solvent that would solubilize all asphaltenes. Xylene alone could not be considered, as its good efficiency as solvent did not allow an effective extraction of sulfones after ODS reaction. Xylene was then mixed with dodecane in a volume ratio 1:3, in order to minimize precipitation while maintaining effective extraction step. Table III.4 shows the sulfur content in the diluted fuels D and in the corresponding liquid phases obtained after centrifugation DC depending on the solvent, as well as the mass of solid phase recovered and the percentage of sulfur remaining after centrifugation in the liquid phase DC.

The effect of solvents on the precipitation of asphaltenes has been discussed in the literature. Usually for fuels, mass percentage of solid phase recovered after centrifugation decreases when paraffinic chain increases [39–43]. The use of higher carbon-number alkane solvents results in lower asphaltene yields and increased levels of maltenes materials. In our case, for IFO380-1 and HSFO700-1 no clear tendency is observed between the wt % of SP and the solvent used for dilution (n-C7 versus n-C12). But besides the importance of the solvent in obtaining consistent asphaltene fractions, separation method adopted in the literature is completely different to ours. Solvent to fuel ratio is 40, solvent is mixed with fuel at temperatures that change between 60-80°C and with different contact time. However, in our case separation is via centrifugation with a solvent to fuel ratio that is only 5 without heating. A more complete study should be necessary to understand this result.

For IFO380-1 with low sulfur content and low viscosity, the sulfur content in the liquid phase did not vary much with the diluting solvent, with %S in DC between 66 and 70%. Indeed, for this fuel, composition of the raw fuel is close to that of the liquid phase. In the case of HSFO700-1 for which we assume that not all asphaltenes have precipitated, using C7 instead of

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C12 led to a decrease in the percentage of sulfur in the liquid phase from 36 to 21% (41%), less sulfur containing species being thus solubilized in this case. As total sulfur analyzed in the liquid phase obtained via C12 is higher than C7, C12 was used as diluting solvent for further experiments.

Dodecane-xylene mixture enables more solubilization of asphaltenes (wt % of SP lower with C12-X) and of sulfur species compared to dodecane alone, with an increase of sulfur content in the liquid phase DC from 42 to 52% for IFO500-1 (24%) and from 36 to 59% for HSFO700-1 (67%). Therefore, it will be interesting to explore reactivity of fuels when diluted with this mixture, even if after ODS, extraction process remained difficult for these fuels (interface between the two phases difficult to see) leading to uncertainty on the evaluation of global sulfur removal.

Table III.4: Total sulfur content of diluted fuel (D) and diluted centrifuged fuel (DC), mass fraction of solid phase SP and percentage of sulfur in DC for IFO380-1, IFO500-1 and HSFO700-1 obtained after dilution with C7, C12 or C12-Xylene.

Marine fuel &solvent	[S] in D /ppm CHNS	[S] in DC /ppm Sulf-UV	Mass fraction in SP /wt.%	% S in DC /%
IFO380-1 C12	7600	6000	12	70
IFO380-1 C7	7600	5600	10	66
IFO380-1 C12-X	7600	5600	10	66
IFO500-1 C12	32700	16000	17	42
IFO500-1 C12-X	32000	19000	12	52
HSFO 700-1 C12	29500	12500	16	36
HSFO 700-1 C7	29500	7300	14	21
HSFO700-1 C12-X	29700	20000	13	59

III.5. Analysis of sulfur compounds using gas phase chromatography

For further study, three fuel oil samples were selected, with properties representative of the various marine fuels categories in terms of sulfur contents and viscosities: **IFO380-1, IFO500-1** and **HSFO700-1** (further referred to as IFO380, IFO500 and HSFO700)**.**

Despite the difficulties encountered during the analysis using gas chromatography due to the high molecular weight and complexity of the samples, it was possible to characterize sulfur containing compounds in the diluted marine fuel samples (D) and in the corresponding liquid phase obtained after centrifugation (DC), after optimization of the analytical injection procedure described in chapter III. In the case of diluted samples, the presence of undesired compounds (solid particles…) can damage the injector, column and detector. Consequently, a 0.2µm PTFE filter syringe was used for sample injection. This filter will retain some compounds, and thus the

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diluted filtered sample DF may have different properties, especially regarding sulfur content, than the diluted sample D. Analysis of DF will then be performed.

III.5.1. Sulfur content of the diluted filtered sample DF

The sulfur content after filtration with the syringe, corresponding to the compounds analyzed by GC, was measured by Sulf-UV in DF samples, and compared to that present in the liquid phase obtained after centrifugation DC (Table III.5). Percentage of sulfur analyzed in DF and DC corresponds to total S in DF and DC fuel divided by total S in raw marine fuels (without taking into account the mass of solid phase, as it could not be evaluated in the case of filtration by the syringe filter).

Table III.5: Total sulfur content determined using elemental analysis for diluted fuels D, for diluted filtered fuels DF and for diluted centrifuged fuels DC, with the percentage of sulfur in DF and in DC compared to D.

	S in D / ppm (CHNS)	S in DF /ppm (Sulf-UV)	S in DC /ppm (Sulf-UV)	% S in DF	% S in DC
IFO380	7600	7000	6500	90	85
IFO500	32000	16000	16000	50	50
HSFO700	29000	12500	12000	44	41

In the case of IFO380-DF, the overall sulfur content after filtration is very close to that of the diluted marine fuel D, which shows that almost all the sulfur species present in this sample are analyzed by GC-SCD. Indeed, diluted fuel D and liquid phase DC were already very close in composition for this sample. On the contrary, in the case of IFO500 and HSFO700 only 50 and 44% respectively of total sulfur containing compounds are analyzed by GC-SCD. For all samples, after filtration, the total sulfur content in the sample DF is comparable to that measured in the liquid phase DC obtained after centrifugation, indicating that filtration and centrifugation probably eliminate the same S compounds. These molecules belong to asphaltenes fractions which cannot be injected in the GC system due to their high degree of polarity as well as their size and their high boiling points [15]. Gas chromatographic analysis of 71 residual fuels using GC-FID was reported by Uhler *et al.* [11]. This study revealed the percentage of hydrocarbons analyzed upon quantitative GC/FID analysis and gravimetric analysis. These data were determined from the GC-FID analysis and integrations of individual peak areas and specific carbon ranges. Non detected range was deduced by difference of 100% with detectable hydrocarbons ($<C_{45}$). Some IFO380 samples contained very high percentage of chromatographable hydrocarbons (up to 100%) while with other types of IFO, the percentage decreased down to 40%. In addition, in the work of Garaniya *et al.* on HFO sample [15], even after the fractionation and separation of asphaltenes fraction, GC analysis indicated that only 42.8 wt.% of saturate fraction and 10.5 wt.% of aromatic

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fraction was able to be analyzed by GC. This result was obtained by comparing GC analysis with sequential elution solvent chromatography (SESC).

III.5.2. GC analysis of diluted fuels after filtration DF

Chromatograms (after injection in the GC-SCD with a syringe with filter) of the sulfur species present in the three diluted marine fuels DF and in a straight run gas oil (for comparison) are illustrated in Figure III.3.

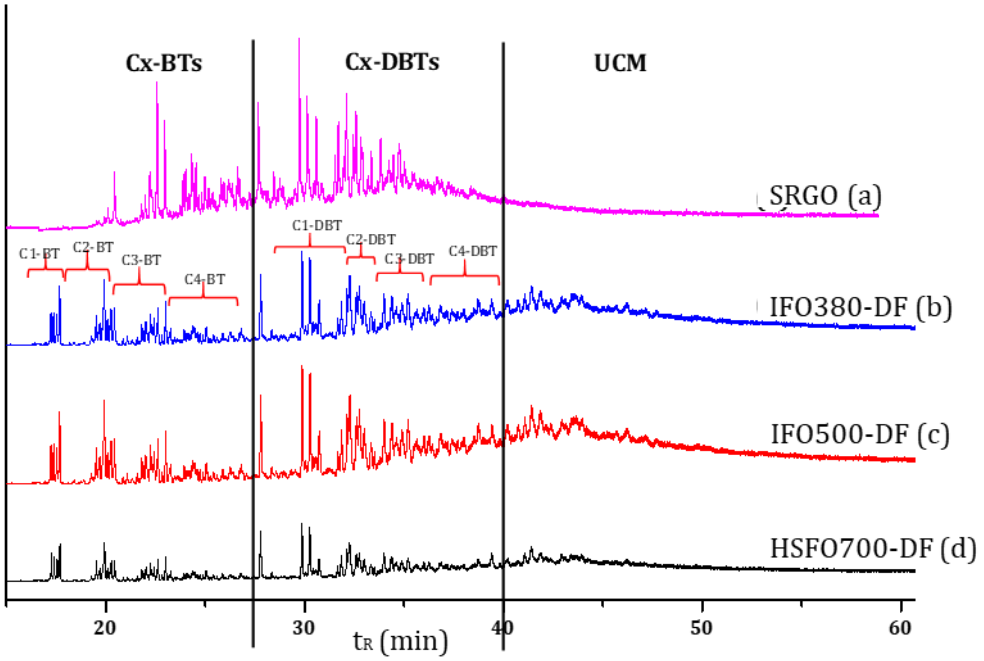

Figure III.3 : Chromatograms of diluted filtered samples DF of marine fuels IFO380-DF (blue) IFO500-DF (red), HSFO700-DF (black) and SRGO (pink).

Each well resolved peak corresponds to a sulfur compound the area of which varies according to its concentration. The presence of co-eluting products interfered peaks was difficult to avoid due to the large number of alkylated isomers of sulfur compounds. Some researchers tried to solve this problem using two dimensional system having higher selectivity, better mass spectral purity and more organized peak distribution allowing better separation and thus, easier identification of some sulfur molecules which peaks are superposed in one dimensional GC [2]. Nevertheless, analysis remains difficult with overlapping of different molecules.

Analysis of sulfur species indicates the presence of the same classes of organic sulfur compounds for the three DF fuels which are mainly thiophenic compounds attached to aromatic rings consisting of two families: the alkyl-benzothiophenes (BTs) family with a retention times range from 15 min to 28 min and the alkyl-dibenzothiophenes (DBTs) family with a range from

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28 to 40 min. Retention time ranges of mono, di, tri and poly alkylated BT and DBT are indicated in Figure III.3. Most of these compounds have been identified in the literature [5,7,44] in the analysis of straight run gas oil and other fractions of diesel. Surprisingly we can observe C1-BTs around 15 min that are not present in SRGO fraction. Above 40 min larger molecules are eluted in resolved peaks. By analogy with some studies [5,13,29] in which analysis of various fuel oils by GC 2D coupled with SCD detector was reported, we assume that these peaks correspond to the elution of benzonaphtothiophene type molecules such as illustrated in Figure III.4.

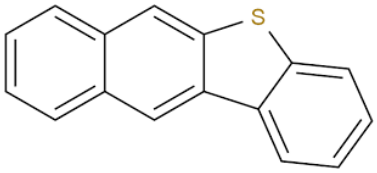

Figure III.4 : Benzonaphtothiophene molecule presentation.

In this range of retention times (>40 min, more precisely from 35 to 60 min), an important raise of the baseline due to coeluting compounds is observed in the chromatograms of the marine fuels and designated as Unresolved Complex Mixture (UCM). Such an UCM is also present on the chromatogram of the SRGO, however in a range of lower retention times (from 25 to 40 min), in agreement with the lower molecular weight of the SRGO components. As demonstrated by 2D GC of analyzed diesel fractions, this UCM seems to correspond to sulfides and thiols of high molecular weight, that coelute with dibenzothiophenes and naphtobenzothiophenes present in small quantities [1,45]. To explain this type of UCM another phenomenon has been proposed by Carbognani *et al.* [46]. They reported that secondary cracking phenomena can also occur during gas chromatography analysis, leading to fragmented species that could contribute to the UCM hump present on chromatograms. When analyzing an Athabasca bitumen using simulative temperature distillation gas chromatography, the authors found the occurrence of cracking peaks starting at 320°C despite that C-C bond tend to break at higher temperatures. They suggested that large residence time favored easier and increased formation of cracked products that were further eluted. However, in our case, the final temperature of the GC column is only 260°C. It is therefore difficult in our case to conclude whether this cracking phenomenon occurs in the chromatograph column and can therefore be involved in the development of the UCM.

The distribution of sulfur content between the 3 different classes of identified families was determined for the 3 DF samples of marine fuels and shown in Table III.6. The calculation of the percentage for each family was estimated by dividing the family integration area (15-28 min for Cx-BTs, 28-40 min for Cx-DBTs and 40-60 min for UCM) by the total area (between 15 to 60 min). It can be seen that similar distribution of sulfur families is observed for the three fuels. The composition evolves as follows: alkyl-BTs around 10%, alkyl-DBTs around 35% and UCM with a

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percentage around 55%. In all cases, the family of complex sulfur species to be analyzed is the most abundant, which is in accordance with the complex nature of heavy fuels.

Table III.6: Sulfur molar percentage of Cx-BTs, Cx-DBTs and UCM families in DF IFO380, IFO500 and HSFO700.

Fuel	% Cx-BTs	% Cx-DBTs	%UCM
IFO380	12	35	53
IFO500	10	36	54
HSFO700	10	37	53

If in our case we found similar compositions of our fuels samples, the distribution of sulfur compounds can differ appreciably as reported in the literature. Choudhary *et al.* [47] estimated the sulfur distribution of two heavy fuel oils with total sulfur content of 1.2 wt.% S and 3.2 wt.% S. Their analysis revealed a dominance of benzo- and di- benzothiophene families with total percentages of 29% and 27% respectively in a heavy oil containing 3.2 wt.% S whereas with the second fuel, the percentage of benzothiophenes is 19% and 36% for dibenzothiophenes. This difference in distribution is attributed to the different matrices with which each oil is blended. The different isomers of sulfur compounds will make it harder to identify all peaks corresponding to sulfur species. However, the identification of some sulfur species has been carried out. To identify specific chosen sulfide molecules, a comparison with known gas oil chromatograms was carried out. Two types of diesel fuel were used: a hydrotreated Light Gas Oil (LGO) with 50 ppm total sulfur, and a Straight Run Gas Oil (SRGO) containing 10000 ppm. Table III.7 summarizes the retention times of the identified species in marine fuels. Molecules identified are substituted alkylated dibenzothiophenes, susceptible to be the most resistant to hydrodesulfurization process and expected to be more reactive in oxidative desulfurization reaction [48]. Benzonaphtothiophene was also identified injecting the model commercial molecule.

Table III.7: Retention times of the identified sulfur species in marine fuels using GC-SCD.

Sulfur compound	Retention time (min)
DBT	26.5
4-EDBT	30.7
4,6-DMDBT	31.0
4,6-DEDBT	34.4
BNT	40.5

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III.5.3. Diluted centrifuged (DC) vs diluted filtered (DF) fuels

Comparison of the diluted filtered (DF) marine fuels analyzed by GC-SCD with the corresponding liquid phase obtained after centrifugation (DC) was carried out. The chromatograms of the sulfur species distribution for filtered fuel DF and liquid phases DC are illustrated in Figure III.5, Figure III.6 and Figure III.7. It should be noted that comparing the sulfur composition of the filtered fraction DF with that of the liquid phase DC unveils the presence of the same sulfur compounds, with a close sulfur content. Accordingly, the filter separation and the centrifugation technique seem to eliminate similarly the solid particles.

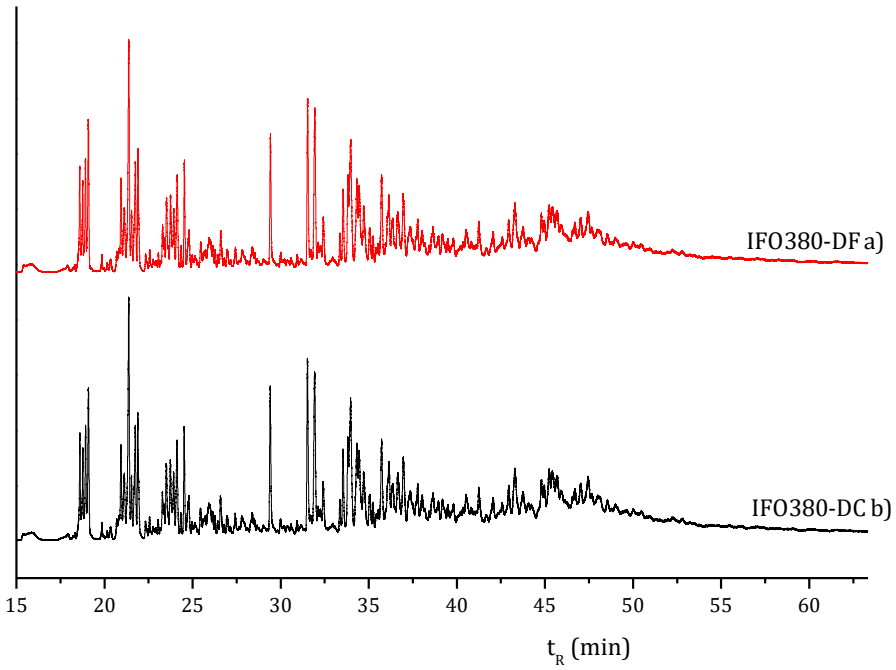

Figure III.5 : Chromatograms of diluted filtered marine fuel IFO380 DF (a) and its liquid phase obtained after centrifugation DC (b).

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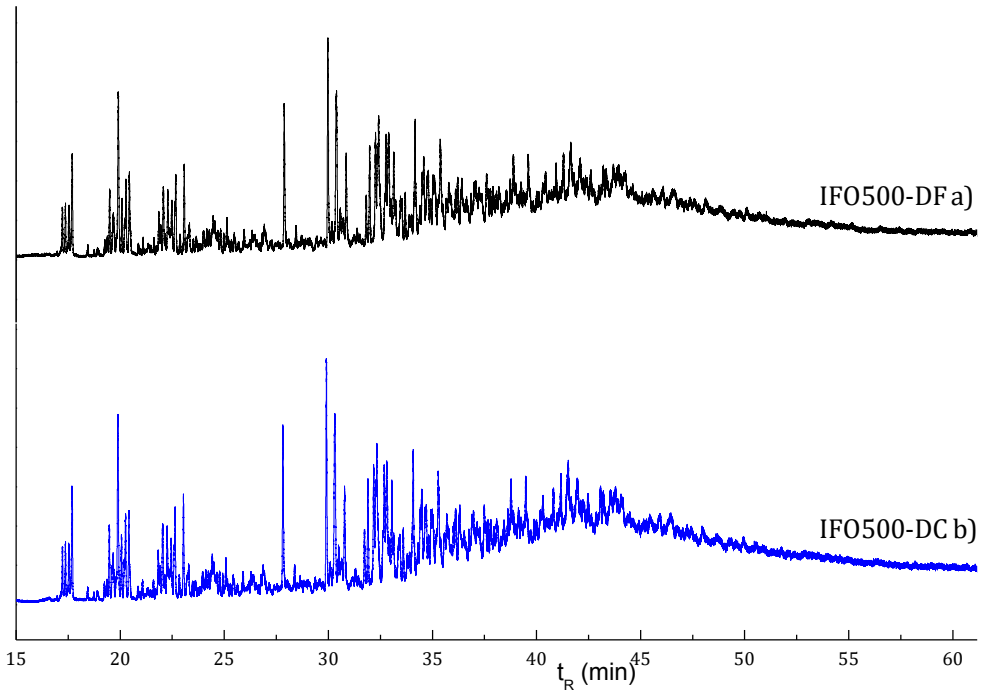

Figure III.6 : Chromatograms of diluted filtered marine fuel IFO500 DF (a) and its liquid phase obtained after centrifugation DC (b).

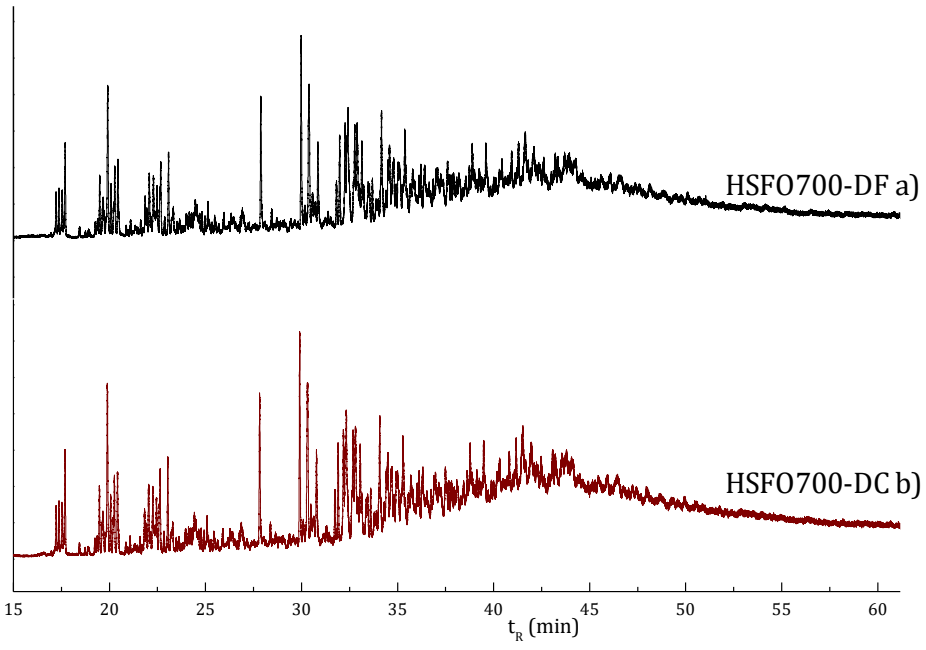

Figure III.7: Chromatograms of diluted filtered marine fuel HSFO700 DF (a) and its liquid phase obtained after centrifugation DC (b).

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III.6. Polyaromatic hydrocarbons using HPLC of diluted centrifuged samples DC

High-performance liquid chromatography (HPLC) was used for the analysis of aromatic hydrocarbon compounds present in diluted centrifuged samples DC. Characteristics of HPLC apparatus, mobile phase, calibration standard solutions preparation and all materials used were summarized and explained in chapter III. Figure III.8 presents HPLC analysis of SRGO gas oil used as reference to choose the integration zone for each family of IFO500-DC diluted 20x with dodecane.

Thanks to the chromatogram of the SRGO, whose composition was previously known, it was possible to define integration zones for each family of hydrocarbons (cf. experimental section). We can see that the same families than in SRGO are observed for fuel oil: linear alkane molecules (between 5 and 6 min), mono-aromatics (between 6 and 8 min), di-aromatics (between 8 and 10 min), tri-aromatics (between 10 and 13 min). However, the CPL of fuel oil has a 4th zone (13 to 18 min) that is attributed to polyaromatics with four and more rings.

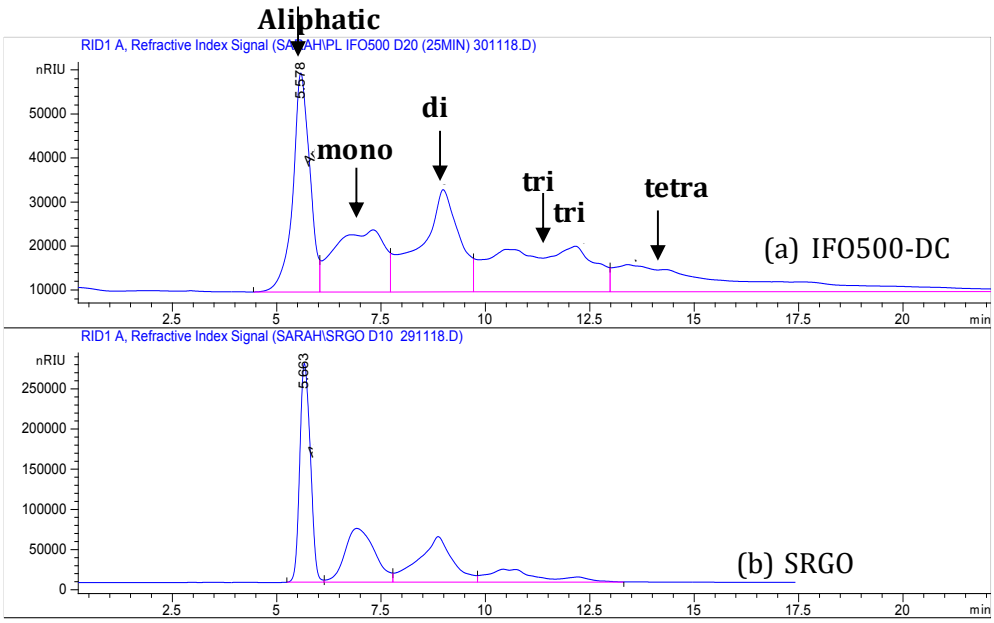

Figure III.8: HPLC analysis of IFO500-DC (a) and of SRGO (b).

Figure III.9 shows the HPLC analysis of the 3 diluted centrifuged samples. The same 4 zones are highlighted for these 3 fuels (very close spectras).

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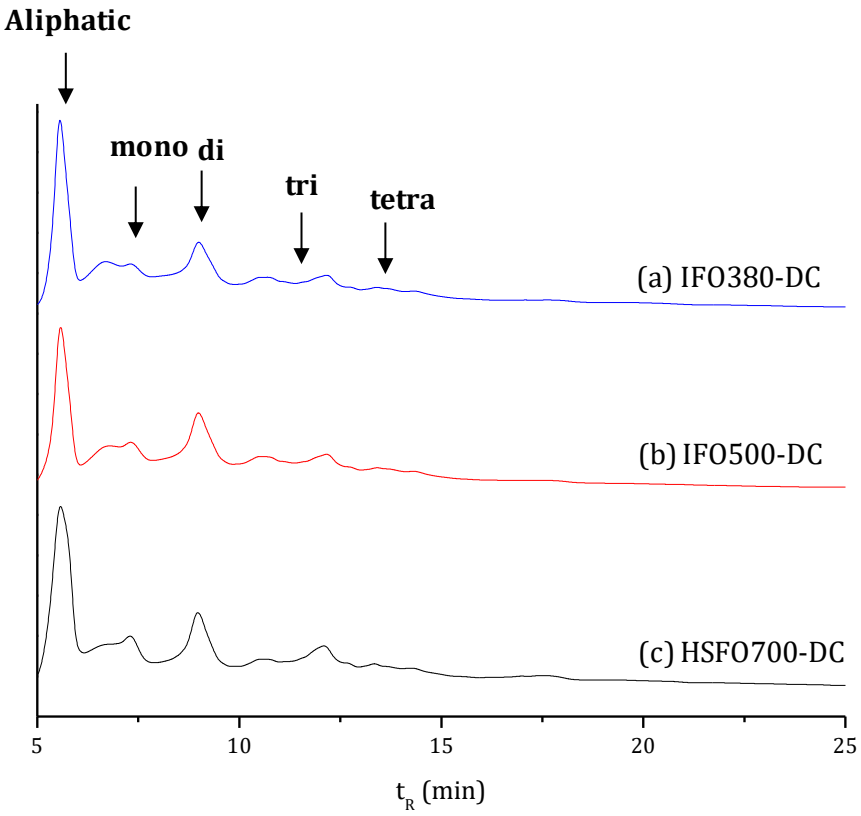

Figure III.9: HPLC analysis of IFO380-DC (a), IFO500-DC (b), HSFO700-DC (c).

Table III.8 presents the weight percentage for each aromatic family in the three DC samples and the SRGO gas oil used as reference. The weight percentage of each aromatic family was calculated on the basis of correlation factors identified in experimental section. According to the results, it can be seen that for all fuels, no significant variation in the aromatic concentration is observed. The polyaromatic hydrocarbon PAH distribution is dominated by lower molecular weight PAHs. The composition evolves as follows: Mono (16.7-18.9%) >Tri (8.4-10.4%) >Di (7.3-9.8) >Tetra+ (7.2-7.6%). The most abundant family corresponds to mono aromatics called BTEX (Benzene, toluene, ethylbenzene and Xylene) with an average percentage of 18 wt.% and then the other three families with comparable percentages, around 7-10%. In the literature, the most abundant aromatic family in some marine fuels diluted with dichlomethane DCM was found to be different compared to our work. Uhler *et al.* [11] analyzed concentration and distribution of some polyaromatics molecules in IFO and HSFO samples. In some samples, they found a prominence of the two and three rings PAHs while in some others they detected 4, 5 and 6 rings PAHs which are not present in distillate fuels. The authors assumed that these molecules are only present in HFOs derived from residuum.

Marine fuels contain a higher percentage of aromatics compared to diesel with 40-46 wt.% of aromatics instead of 30 wt.% in the case of diesel.

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Table III.8 : Weight percentage of aromatic families for diesel (SRGO) and diluted centrifuged phase of marine fuels (IFO380-DC, IFO500-DC and HSFO700-DC).

	Monoaromatics (wt.%)	Diaromatics (wt.%)	Triaromatics (wt.%)	Tetra+ (wt.%)	Total (wt.%)
SRGO 1%	20.3	7.9	3.6	0	31.8
IFO380-DC	16.7	7.3	8.4	7.2	39.6
IFO500-DC	18.8	9.8	10.4	7.6	46.6
HSFO700-DC	18.9	8.8	9.3	7.2	44.2

Since marine fuels can be residuals blended with lighter fractions, their composition is diversified, therefore, significant variation in the aromatic concentration can be observed. The percentage of aromatic fraction derived from SARA fractionation revealed a total percentage of 23.4 wt.% for an HFO fraction with Alvarez *et al.* [49], whereas from Radovic *et al.* [12] results the aromatic fraction of HFO was 38.2 wt.%, similar to the aromatic fraction obtained with our fuels even though the percentage was not calculated with the same method. Garaniya *et al.* [15] indicated a total aromatic fraction of 55 wt.% for another HFO fraction. Data of different marine fuels after SARA separation showed total aromatic fraction variation between 30 and 55 wt.% [31,32,49].

III.7. Speciation of nitrogen compounds in diluted centrifuged samples using GC-NCD

Even though nitrogen species are present in small quantities in light petroleum and diesel fractions, researchers are interested in nitrogen identification and quantification as in refinery industrial processes, N-compounds can reduce the efficiency of hydrotreating processes due to catalyst poisoning. In addition, studies in oxidative desulfurization show that N-compounds are in competition with sulfur containing species and can also be oxidized [36,37,50]. Elemental analysis of our marine fuels showed that nitrogen content varies between 0.37 and 0.61 wt.% which is an important amount and comparable with sulfur content in some fuels. The diluted centrifuged samples were analyzed using gas chromatography equipped with nitrogen chemiluminescence detector (GC-NCD). Main parameters and characteristics as well as analytical method used for analysis were summarized and detailed in chapter III. Figure III.10 displays the chromatograms of nitrogen species in the three DC samples of IFO380, IFO500 and HSFO700 and in a mixture LCO/SRGO fraction that contains 298 ppm of N.

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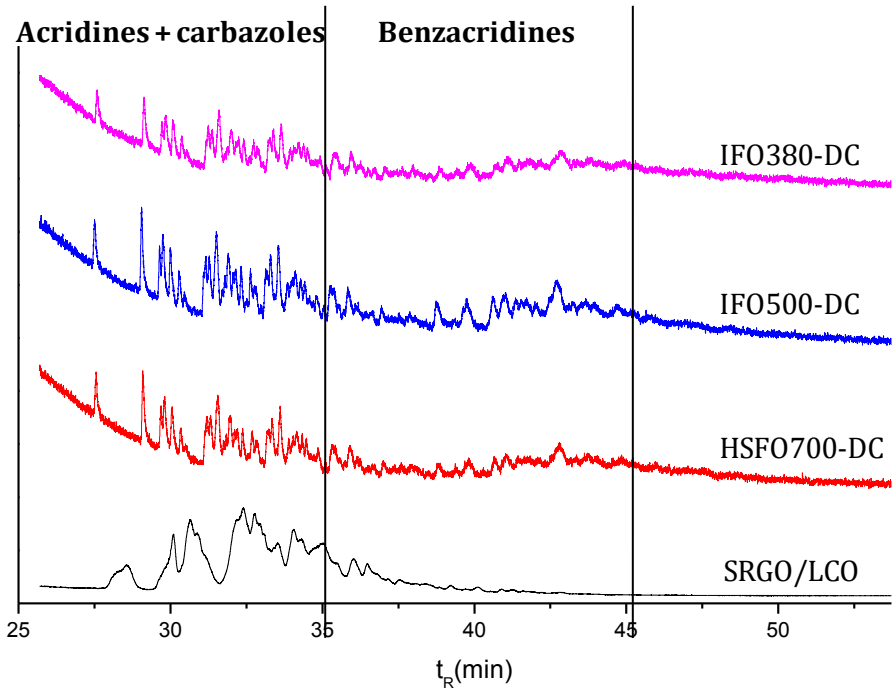

Figure III.10: Chromatograms of nitrogen species in diluted centrifuged samples using GC-NCD of IFO380-DC (a), IFO500-DC (b) and HSFO700-DC (c).

In the case of the 3 fuels, nitrogen peaks are observed from 27 min to 45 min. Same chromatograms were observed for the three fuels, indicating the presence of the same nitrogen compounds. Nevertheless, small variations in peaks intensity are related to the slightly different nitrogen contents. Chromatograms present N species at higher retention times than in the case of LCO/SRGO, in agreement with the heavier nature of these fuels.

The identification of some nitrogen species detected in marine fuels was performed by comparison with the diesel sample which families distribution is already known. It includes the substituted acridines and carbazoles family, for which retention times range from 27 min to 35 min, and the benzacridines family with three or four aromatic rings, with retention times from 35 to 45 min. Types of compounds are illustrated in Table III.9. In addition to nitrogen compounds identified via gas oil mixture analysis, after t_R>37 min, new peaks not observed in the chromatogram of LCO mixture can be observed. However, we do not have enough data to attribute these peaks.

Nitrogen containing species in petroleum may be classified as basic and non-basic compounds. Among identified families, basic compounds are composed mainly of acridines and benzacridines derivatives. The non-basic nitrogen compounds detected are carbazole types. Both types detected are classified as heavy nitrogen compounds normally concentrated in higher

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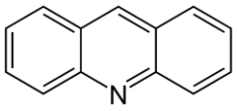
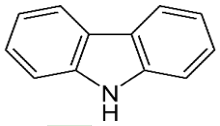
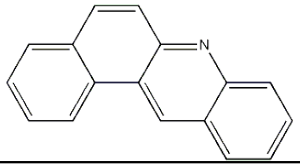
boiling fractions and residuals. The presence of pyrrole and indole was not identified in our marine fuel samples in agreement with the study of Dorbon *et al.* [51].

Table III.9 : Types of organic nitrogen compounds in marine fuels.

Nitrogen Compounds	Structure
Acridine	
Carbazole	
Benzacridine	

III.8. Conclusion on marine fuels properties

The characterization of different marine fuels has been performed in this chapter using various analytical techniques. The extended study included gas chromatography, high performance liquid chromatography and elemental analysis to provide further chemical characterization of marine fuels, focusing on sulfur compounds identification and quantification, but also considering nitrogen compounds and aromatics.

Since composition of marine fuels can be very diverse, it was essential to get these informations in order to understand conversion processes that we will be further applied. Moreover, few publications have addressed this issue and despite the high level of technology development and innovation in molecular characterization methods, it is currently impossible to characterize marine fuels as extensively as lighter fractions, in relation with the complexity of their composition.

For this study, marine fuels from different origins have been supplied by SEGULA, LSFO, IFO, RMK and HSFO, with viscosities varying from 380 to 700 cSt at 50°C. By CHNS, high sulfur content around 3 wt.% were measured on the samples with high viscosities (500 and 700 cSt), to be compared with values between 0.54 and 0.76 wt.% for LSFO and IFO fuels with lower viscosities of 380 cSt.

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Dilution with dodecane of the fuels was carried out in order to decrease samples viscosity and facilitate manipulation. It also leads to part of asphaltenes precipitation, which were separated by further centrifugation, together with solid particles already present in the fuel. More than 70% of the initial sulfur content is recovered in the diluted centrifuged samples (DC) in the case of LSFO and IFO fuels with low viscosity (380 cSt), while less than half of the sulfur content of the raw and diluted samples was measured in the liquid phase DC of IFO, RMK and HSFO samples with viscosity of 500 and 700 St. As similar mass of solid phase was recovered after centrifugation for all samples, it seems that asphaltenes with lower sulfur content are present in the lighter fuels than in samples of high viscosity and sulfur content.

It is to be noted that if similar sulfur contents were measured by CHNS and Sulf-UV for the all the diluted centrifuged samples and for diluted samples with low sulfur content and viscosity, only half of the sulfur content measured by CHNS could be detected by Sulf-UV in the case of the diluted samples with high sulfur content. Sulf-UV does not seem to be an adequate technique for sulfur content determination when solid particles are present.

Dilution with heptane was also performed and led to more precipitated species and less sulfur in the corresponding diluted centrifuged samples. A mixture of xylene and dodecane was also considered, as xylene is a good solvent for asphaltenes solubilization. As a consequence, more sulfur was recovered in the diluted centrifuged sample.

Diluted D and diluted and centrifuged DC phases of IFO380, IFO500 and HSFO700 were analyzed by GC-SCD analysis. A syringe with a filter was used for injection of the samples, solid particles needing to be removed not to damage the apparatus, in the case of D samples where solid particles have not been separated. Measure of sulfur content as well as examination of the obtained chromatograms showed that the part of the diluted samples that was analyzed by GC-SCD after filtration (diluted filtered sample DF) is similar to the liquid phase recovered after centrifugation (DC), and is thus not representative of all the sulfur species present in the fuels with high sulfur content and high viscosity. Despite the variety in sulfur content and viscosity, chromatograms recorded for diluted filtered DF samples show for all fuels a similar distribution of the sulfur species, with around 10% of Cx-BTs, 35% of Cx-DBTs and 55% of heavier compounds together with unresolved complex mixture. These analyses will allow to monitor the evolution of sulfur species during ODS.

Significantly higher N content than in diesel were measured, between 0.37 wt.% to 0.61 wt.% and as high as the sulfur content in the case of LSFO samples. This is indeed to be taken into account in the context of ODS as competitive oxidation may occur between these compounds and sulfur containing ones. For IFO380, IFO500 and HSFO700, same families of nitrogen

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compounds in the diluted centrifuged samples were observed by GC-NCD, attributed to substituted basic and non-basic acridine and carbazole derivatives. Aromatics compounds present in the diluted centrifuged samples analyzed by HPLC showed similar species distributions for the three marine fuels. IFO500and HSFO700 contained slightly higher percentage of aromatic fraction (45%) in comparison to IFO380 (39%) but with similar composition that evolves as follows: Mono>Tri>Di>Tetra.

Even though we are interested in sulfur containing compounds characterization, overall properties identified will be key factors in understanding the performance of oxidative desulfurization applied to marine fuels. Indeed, considering the high content of heterocycles in marine fuels, oxidation of sulfur compounds can be inhibited by competitive reactions of polyaromatics and nitrogen compounds. ODS of the different phases, raw, diluted and diluted and centrifuged, will be performed, and will give insight of the effect of the matrix composition on the reactivity of the molecules. GC-SCD analysis will allow to follow the conversion of sulfur molecules, which is scarcely done in the literature, where only overall sulfur removal results are provided.

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ODS using 20 Mo/Al: Optimization of reaction conditions and study of reactivity of different fuels

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Chapter IV ODS using 20 Mo/Al: Optimization of reaction conditions and study of reactivity of different fuels.

Compared to the studied realized on model molecules or hydrotreated diesel, only few works have reported the feasibility of ODS reaction on heavy feeds, such as residual fuel oil [1], crude oil [2,3] and aromatic fractions of crude oil [4], using different homogeneous or heterogeneous catalytic systems. The literature review detailed in chapter II provides an overview of the different operating conditions, which can serve as a starting point for the study of marine fuel oil ODS.

Since the performance of molybdenum based catalysts in the oxidation of sulfur compounds has been reported in various studies [5–8], the first part of this chapter is devoted to the preliminary study of oxidation of diluted centrifuged IFO500-DC using 20% MoO_3/Al_2O_3 (20 Mo/Al). The effect of parameters such as time, catalyst amount, extraction solvent, oxidizing agent nature and quantity, use of ultra-sounds, were further studied and optimized to operate with the best ODS conditions suitable for marine fuels. Competitive reactions will be considered, as nitrogen compounds contained in marine fuels can also be oxidized in ODS conditions.

Subsequently, using the optimum conditions, ODS reaction was tested on raw (R), diluted (D) and diluted centrifuged (DC) phases of IFO380, IFO500 and HSFO700 samples. Fuel reactivity was evaluated by measuring the conversions of Cx-BTs and of DBT molecule using GC-SCD together with total sulfur removal evaluated after extraction of oxidized fuels. In the case of diluted fuels, two solvents were used. The first study was achieved on fractions diluted 5 times with dodecane (C12). Then to improve solubilization of all compounds in fuel that include polar compounds in addition to apolar aliphatic long chain alkanes, a mixture of xylene-dodecane (C12-X) (volume ratio 1:4) was considered.

Since the provided marine fuels do not have the same sulfur content and viscosity, comparison of their reactivity will help us to determine factors influencing the conversion of sulfide molecules Cx-BTs and DBT in these different feeds. Moreover, we can compare the reactivity of the sulfide families depending on the matrix, in raw (R), diluted (D) and diluted centrifuged (DC) phases of marine fuels of different origins.

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IV.1. ODS of diluted centrifuged IFO500 (IFO500-DC)

To study the influence of reaction parameters as well as competitive reactions, IFO500 has been selected, as this fuel presents an intermediate viscosity and high sulfur content. The liquid phase obtained after dilution and centrifugation (IFO500-DC) was used for establishing optimum conditions, thus avoiding the presence of asphaltenes present in raw or diluted samples. A molybdenum based catalyst supported on alumina has been chosen, as its efficiency in ODS has been reported in the literature on model and real feedstocks [5,8–12].

IV.1.1. Study of the operating conditions

Reaction temperature was set at 80°C, as frequently used temperatures in ODS for real diesel fractions are between 60 and 90°C [11–15]. This temperature also allows to avoid problems that may arise from the high viscosity of the marine fuels by decreasing the viscosity of fuels. Regarding the oxidizing agent, H_2O_2 has been selected for the continuous onboard system, despite the formation of a two-phase system, because of its low price and for environmental reasons as the secondary product is only water while formation of alcohols or ketons could be observed using tBHP. Comparison with tBHP (tert-butyl hydroperoxide $(CH_3)_3$-OOH) will however be performed. Parameters to be optimized are reaction time, quantity of H_2O_2 and of catalyst, nature and quantity of solvent used for extraction with fuel yield obtained after ODS. Optimization of ultra-sound assisted ODS will also be considered.

IV.1.1.1. Influence of reaction time

Reaction time is a major parameter because it influences the possibility of scaling up the ODS process to an industrial scale. Moreover, ensuring that we have the optimum contact time is essential to guarantee the best catalytic activity. Accordingly, the effect of this parameter to know its optimum value has been investigated in the ODS of IFO500-DC using H_2O_2 with Ox/S=3.

Chromatograms of the reaction mixture were registered at 15, 30, 45, 60 and 120 min (Figure IV.1). After 15 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 24 min. Evolutions of Cx-BTs and of DBT molecule conversions are presented in Figure IV.2. The conversion of the DBT molecule appears to be higher than that of the Cx-BTs

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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) [8,16]. As shown in Figure IV.2, ODS reaction evolved quickly in the first minutes, with Cx-BTs conversion of 21.0% and DBT conversion of 46.0% at 15 min, increasing to 33% and 54% respectively at 30 min. Slight increase was noted afterwards, conversions remaining almost constant after 60 min of reaction for both Cx-BTs (35%) and DBT (60%). In further experiments, conversions will thus be given after 1 hour of reaction.

In ODS of model molecules it is possible to find an efficient oxidant–catalyst system allowing desulfurization in a few minutes [9,17]. However, with real feeds, higher reaction time is needed. The effect of reaction time was not studied for heavy fuels, but it was possible to find studies for diesel fractions. Garcia-Guitterez *et al.* studied the time required to oxidize 322 ppm S diesel using MoO_3/Al_2O_3, H_2O_2 system [18]. Sulfur elimination after 25 min attained 50% and reached 100% after 85 min. Similarly, Abdullah *et al.* [19] studied reaction time in ODS of 414 ppm diesel, desulfurization rate increased from 71% to 77% when reaction time increased from 10 to 20 min. Mokhtar *et al.* [15] achieved 80% desulfurization of 0.8 wt.%S diesel sample in 30 min.

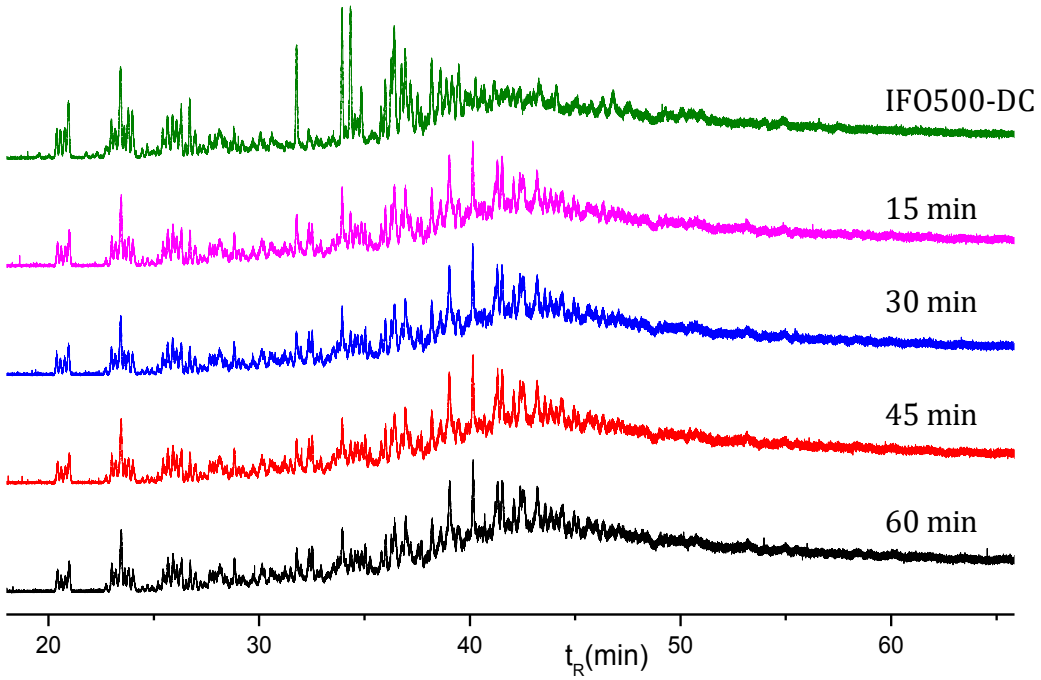

Figure IV.1 : Chromatograms of IFO500-DC before ODS and after ODS registered at 15, 30, 45 and 60 min (20 Mo/Al catalyst, H_2O_2/S=3, T=80°C).

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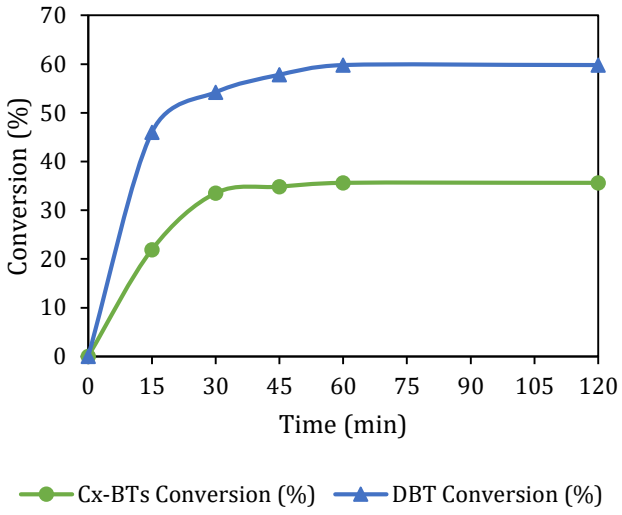

Figure IV.2 : Conversion of Cx-BTs and DBT in the ODS of IFO500-DC (20 Mo/Al catalyst, H_2O_2/S=3, T=80°C).

IV.1.1.2. Influence of Ox/S ratio and oxidant nature

IV.1.1.2.1. H_2O_2 as oxidizing agent

Even if a low Ox/S ratio was preferred in the framework of this project, it was interesting to explore the effect of oxidant amount in the ODS of IFO500-DC up to an Ox/S ratio of 25 (Ox/S=3, 10, 15 ,20, 25). The chromatograms obtained after ODS in the presence of H_2O_2 with Ox/S=3 and Ox/S=25 are shown in Figure IV.3. The conversions of Cx-BTs and DBT have been calculated and the graphs showing the variation of the conversions as a function of Ox/S ratio are presented in Figure IV.4. According to Figure IV.4, for both Cx-BTs and DBT, we notice that the conversion of sulfur compounds increases slightly from 30 to 42% for Cx-BTs and from 58 to 72% for DBT with the increase of Ox/S ratio, in a linear evolution. This result indicates that the large increase in the Ox/S ratio does not have a significant beneficial effect in the ODS reaction even though the quantity of oxidant was more than10 times exceeding the stoichiometric ratio. The effect of the oxidant to sulfur ratio has been investigated in the literature [7,8,11,18,20]. Garcia-Gutiérrez *et al.* [12] studied the hydrogen peroxide concentration in the ODS of diesel fuel using Mo/Al_2O_3 catalyst. In agreement with our results, they did not observe a marked effect on sulfur removal with the increase of H_2O_2/S ratio from 4 to 25. Higher quantity of H_2O_2 is not beneficial, which was attributed to the biphasic reaction medium, creating mass transfer problems that become more detrimental when the volume of oxidant increases.

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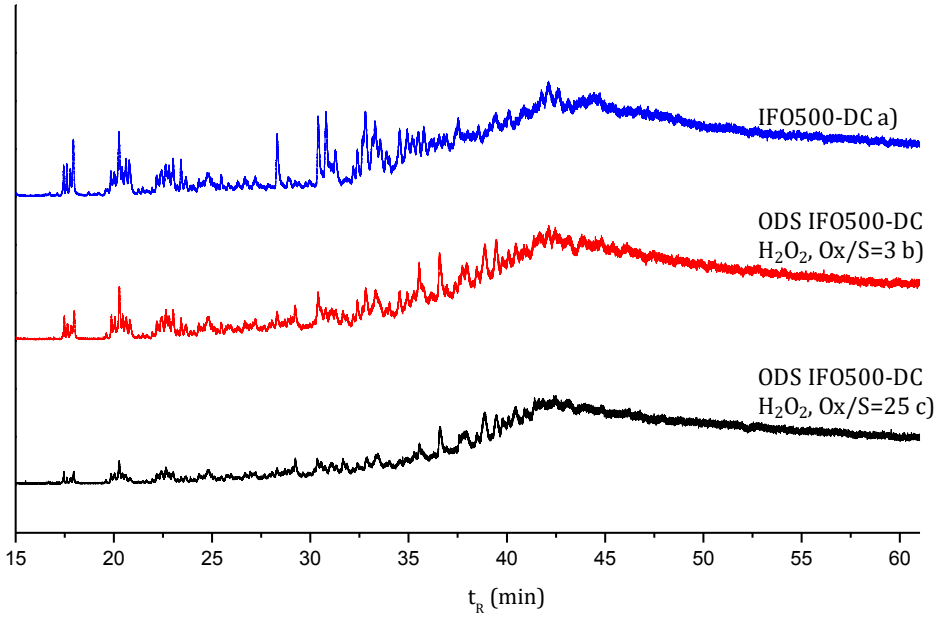

Figure IV.3: Chromatograms of IFO500-DC before (a) and after oxidation with H_2O_2 using Ox/S=3 (b) Ox/S=25 (c) (20 Mo/Al catalyst, T=80°C, t=60 min).

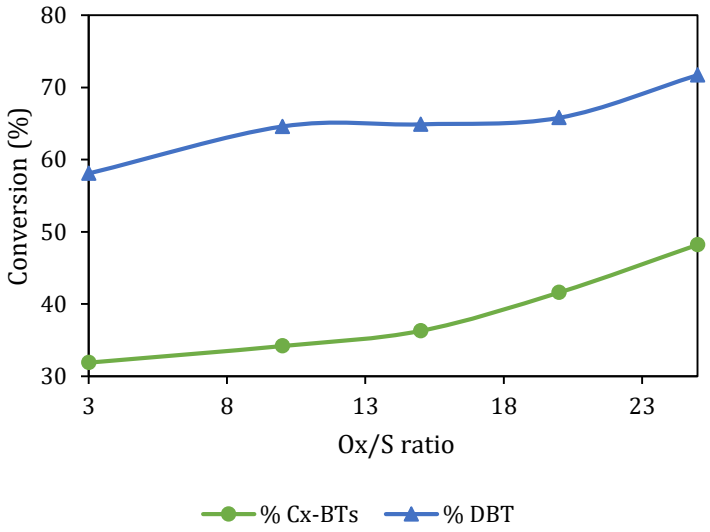

Figure IV.4 : Conversions of Cx-BTs family and DBT molecule using different Ox/S ratio in the ODS of IFO500-DC (20 Mo/Al catalyst, T=80°C, t=60 min).

IV.1.1.2.2. TBHP as oxidizing agent

As the use of hydrogen peroxide leads to a two-phase reaction medium that can create limited transfer issue in particular with high Ox/S ratio, another type of oxidant tBHP, miscible with fuel oil, has been considered for comparison. Its use has been reported in several ODS of real

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fractions [7,15,19,21–23]. The chromatograms obtained after ODS in the presence of tBHP with Ox/S=3 and 25 are shown in Figure IV.5 and the conversion results are summarized in Figure IV.6. With tBHP, slightly higher conversion of Cx-BTs (47% instead of 32%) and similar conversion of DBT (59 and 58%) than with H_2O_2 were observed for the ox/S ratio of 3, while complete conversion of Cx-BTs and DBT was reached for the ratio of 25. Previous works of Tang *et al.* [7] reporting ODS of marine fuel oil using tBHP as oxidant with showed that sulfur elimination increased with increasing tBHP/ S ratio from 2 to 6 and declined afterward. They attribute this result to the complex nature of heavy oil tested as well as to the stability of oxidant (tBHP) under the operating temperature of 80 °C. Furthermore, they indicated that excess of oxidant can inhibit chain reactions that decrease production of peroxide needed for ODS reaction. Some researchers compared the efficiency of the oxidizing agent. Cedeno *et al.* [24] studied the oxidation-extraction of a mixture of synthetic diesel-acetonitrile using tBHP or H_2O_2 as oxidant with same Ox/S ratio. They found that the total sulfur removal was more significant using H_2O_2 rather than tBHP. 90-100 % of dibenzothiophenic compounds were removed with H_2O_2 whereas only 30-50 % with tBHP. However, in their case, synthetic diesel is directly mixed with extraction solvent with very different conditions compared to our work.

In our case, at a low Ox/S ratio of 3, the similar results obtained with H_2O_2 and tBHP show that the biphasic medium obtained when using H_2O_2 is not detrimental to the ODS activity. Indeed, when increasing the quantity of oxidizing agent, contact with the fuel may become an issue in the biphasic medium with H_2O_2, while the good miscibility with tBHP guarantees increased performances. This confirmed our choice to work with H_2O_2 at low Ox/S ratio, for economic and environmental reasons, as it does not impact in this case the performance compared to tBHP with optimum miscibility.

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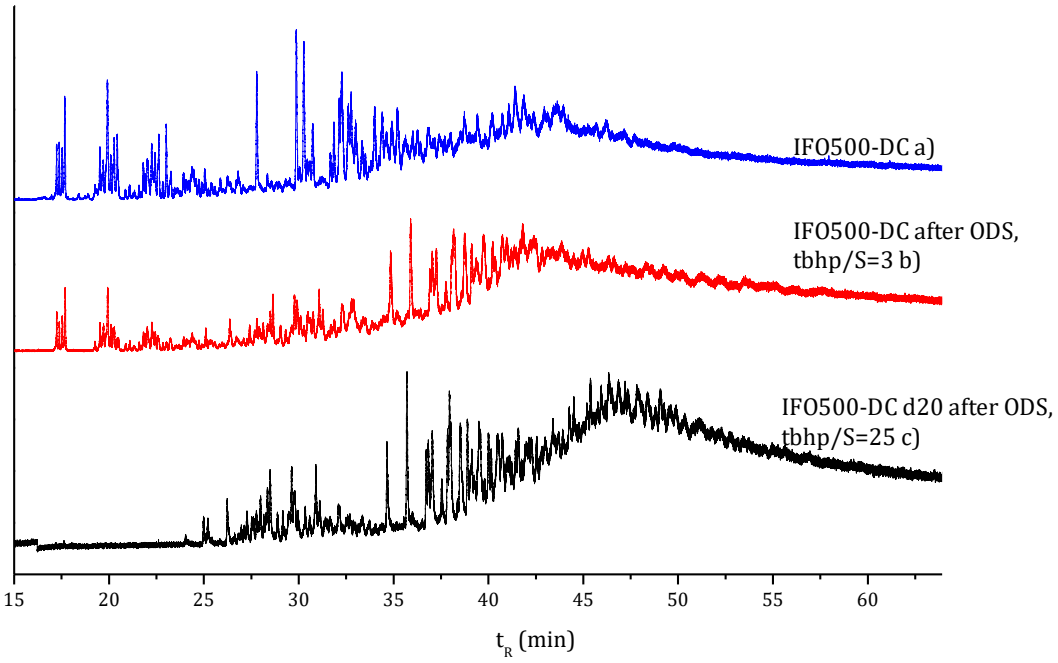

Figure IV.5 : Chromatograms of IFO500-DC a) before b) and after oxidation using tBHP with Ox/S=3 and c) Ox/S=25 (20 Mo/Al catalyst, T=80°C, t=60 min).

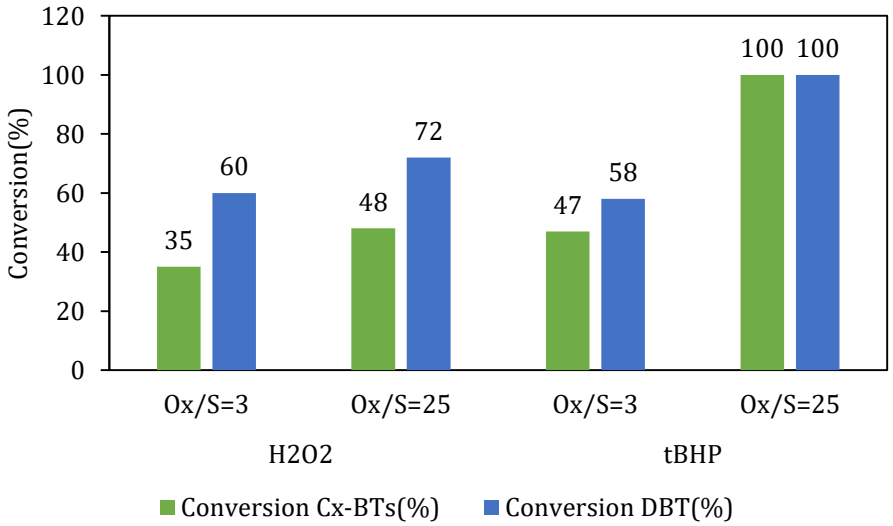

Figure IV.6 : Conversion of Cx-BTs family and DBT molecule using H_2O_2 and tBHP with Ox/S=3 and 25 in the ODS of IFO500-DC (20 Mo/Al catalyst, T=80°C, t=60 min).

IV.1.1.3. Effect of catalyst amount

A proper selection of catalyst amount is crucial to operate with the maximum efficiency and the minimum energy consumption. The effect of catalyst weight concentration (10, 20 and 30 g of catalyst per L of fuel) was further studied (Figure IV.7). Conversion of Cx-BTs and DBT molecule

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increased from from 12% to 27% and from 31% to 59% respectively with the increase of catalyst amount from 10 $g.L^{-1}$ to 20 $g.L^{-1}$, and decreased to 5% (Cx-BTs) and 51% (DBT) when further increasing the quantity to 30 $g.L^{-1}$. Oxidation was first enhanced with the increase of catalyst quantity, by providing larger number of active species, however, after a certain value, catalyst agglomeration (decrease the contact area between DBT and the catalyst as a result of the reunion of catalyst) could explain the decrease in activity.

Similar results were reported by Tang *et al.* [7] in the ultrasound assisted oxidative desulfurization of marine fuel diluted with n-heptane using H_2O_2. Total desulfurization of marine fuel entitled in their study MFO-380 increased with increasing molybdenum oxide catalyst mass up to about 20 $g.L^{-1}$ and declined beyond this value. They explained this result with the low dispersion of the powder in the reaction medium creating mass transfer limitation problems. During the ODS of real diesel fraction reported Mokhtar *et al.* [15] using H_2O_2 as oxidant and as catalyst 2.13%V/4.08%W/16.07%Mo/Al_2O_3, the best catalytic performance was observed for 10 g/L of catalyst for 500 ppm diesel, after this value, the same desulfurization results were noted. Teimouri *et al.* [10] studied the influence of catalyst quantity (MoO_3-V_2O_5/SBA-15) in the oxidative desulfurization of DBT molecule (500 ppm S), using H_2O_2 with Ox/S=4. By varying the quantity from 9.5 up to 20 $g.L^{-1}$, they found the optimum quantity at 13 $g.L^{-1}$. The amount of catalyst dosage used in both reported works was lower than the quantity used in our study, which can be related to the nature of the feedstock oxidized as well as total sulfur content. Teimouri *et al.* used 0.13 g for the oxidation of model solution of 500 ppm DBT (easily oxidized) whereas in our work, the fuel contains 16000 ppm S which is 32 times higher and the oxidation of multiple sulfur compounds occurs, therefore, more catalyst will be needed to ensure a better desulfurization.

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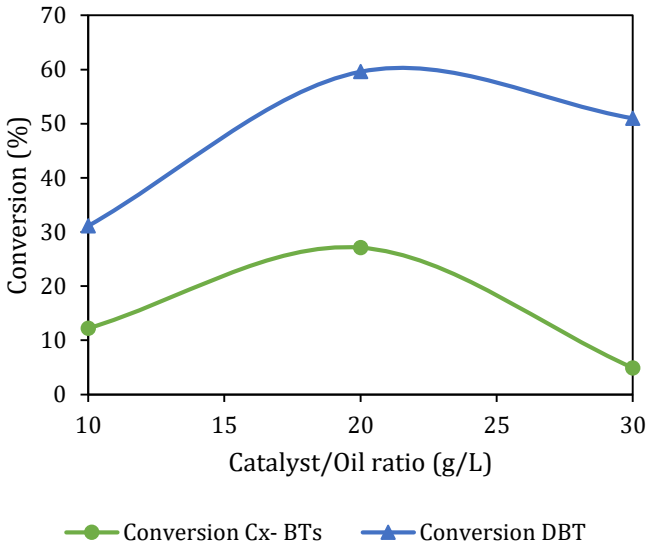

Figure IV.7 : Conversion of Cx-BTs and DBT as a function of catalyst dosage in the ODS of IFO500-DC (20 Mo/Al catalyst, H_2O_2/S=3, T=80°C, t=60 min).

IV.1.1.4. 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 with only low solubility to hydrocarbon mixture to avoid loss of fraction in the solvent.

Different types of solvents have been reported in the literature for sulfones extraction [3,24–33]. According to the mentioned publications, it was possible to limit the list of solvents that may be of interest in our case 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 extraction was not possible in our case.

Extraction was also performed on non-oxidized fuel IFO500-DC with both DMF and Bul, with a ratio solvent/fuel (solv/f) of 1. Sulfur reductions of non-oxidized fuel after extraction using DMF and Bul were the same, 30%, showing that sulfide compounds do migrate in the solvent phase and that extraction will not be selective to sulfones.

For extraction after ODS of IFO500-DC, DMF and butyrolactone were used with two solvent/fuel ratios, 0.5 and 1. After extraction the oil phase and solvent phase were analyzed using GC-SCD (Figure IV.8, Figure IV.9) and total sulfur content was determined using Sulf-UV.

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Chromatogram of oxidized fuel after extraction showed a decrease in the intensity of sulfide peaks and disappearance of sulfones peaks. Chromatograms of both solvents after extraction highlighted the presence of sulfone peaks in addition to some sulfide molecules that migrated to the solvent. In addition, it should be noted that color of oxidized marine fuel was black, but color of oxidized marine fuel after extraction turned to light brown.

The desulfurization results, fuel oil recovery rate or fuel yield and total aromatics reduction evaluated using HPLC for each extraction test are shown in Figure IV.10. Similar desulfurization rates were measured with both solvents, between 46 and 49% at a 0.5 ratio, and increased to 58 and 60 at a ratio of 1. This increase may be related to a better homogenization of the medium that promotes the migration of species to the polar phase when using a larger quantity of solvent. Using these two solvents has also been compared in the literature. Ramirez *et al.* [32] carried ODS of a diesel containing 320 ppm mixed with extracting solvent using solv/f=1 using WOx/ZrO_2. After reaction, the authors found higher desulfurization rate with DMF (56%) than with Bul (45%), with same ratio of solvent/fuel of 1. Since ODS reaction was carried out in the presence of aqueous solvent, desulfurization results were accounted to the synergism between the catalyst, the solvent and the oxidant. Aprotic solvents, like DMF enhance water and hydrogen peroxide dissociations to obtain OH^- and HO^{2-}, respectively. The perhydroxyl ion (HO_2^-) is quite stable in these solvents, and interacts with the hydroxyl groups formed during water dissociation to produce the superoxide radical O_2^-. This radical reacts with the WOx species present at the catalyst surface to generate a highly oxidant system. On the contrary, Garcia-Gutiérrez *et al.* [12] showed that the sulfur removal after reaction of diesel fuel containing 336 ppm S using solv/f=1.6 with solvent was higher using Bul (47%) than with DMF (34%). The highest sulfur elimination was obtained with the solvent with the higher dielectric constant (ε= 39 for bul and ε= 36.7 for DMF). In our case, we obtained similar desulfurization rates using both solvents, this different behavior could be attributed to the nature of the fuels, indeed compared to diesel, marine fuel oil represents a more complex matrix, as well as a large difference in total sulfur content.

If similar values were obtained for sulfur removal with DMF and Bul in our case (Figure IV.10), differences were observed concerning an important parameter, the fuel yield. An increase in the solvent/oil ratio led to an increase of the marine fuel yield, which reached 90% in the case of DMF with a ratio equal to 1, for only 80% with butyrolactone with the same ratio. In order to minimize fuel loss and for economic considerations for the overall ODS process, DMF with ratio solv/f =1 has thus been kept for all further experiments.

The total aromatic removal after extraction indicated in Table IV.1 was 20% for both solvents with solv/f =1 and solv/f =0.5, corresponding to total aromatic decrease from 46% to 37%. Apart from monoaromatics, other compounds (di, tri, tetra aromatics) see their percentage decrease

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after oxidation and extraction. It was expected to have a decrease in the total aromatic percentage since part of sulfur compounds are aromatics. Moreover, aromatic compounds are polar species that have potential to be transferred into the polar phase of solvent.

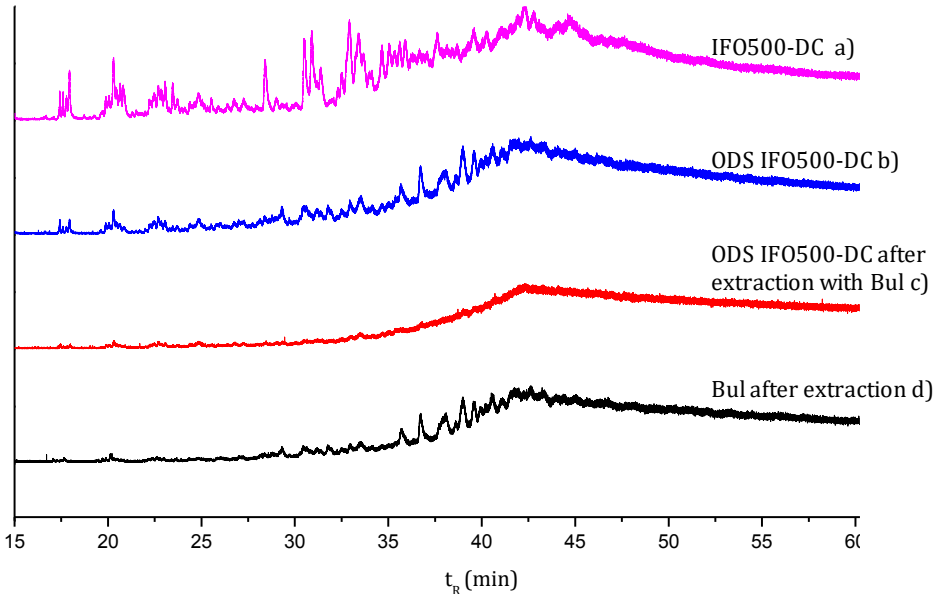

Figure IV.8 : Chromatograms of a) IFO500-DC before ODS b), after ODS c) after ODS and extraction using Bul, and d) of Bul after extraction (d) (20 Mo/Al, H_2O_2/S=3, T=80°C, t=60 min).

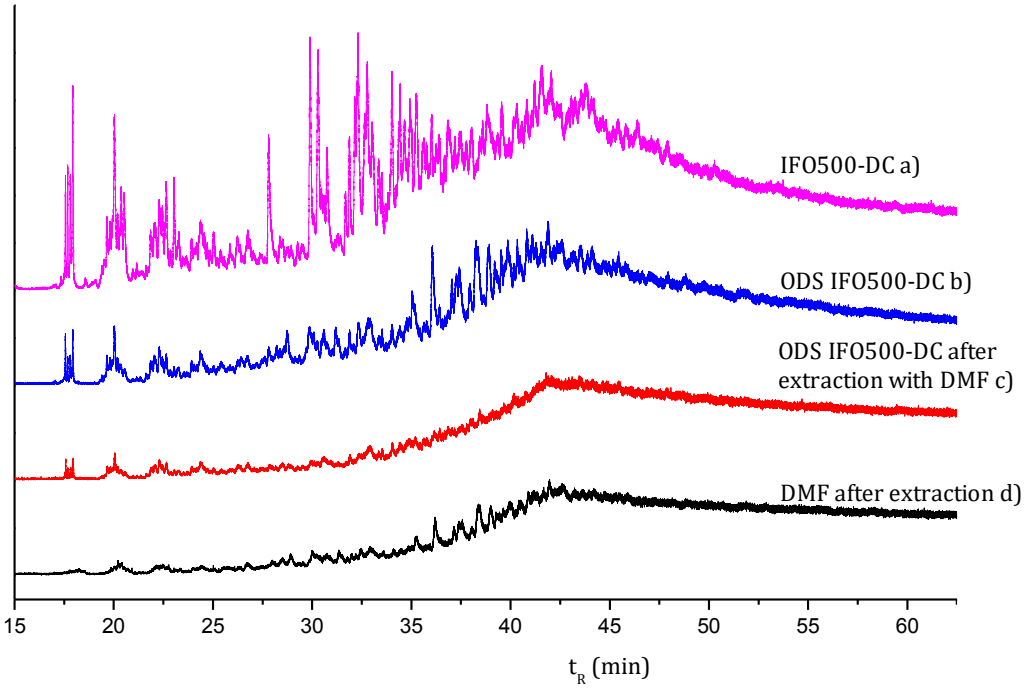

Figure IV.9 : Chromatograms of a) IFO500-DC before ODS b), after ODS c), after ODS and extraction using DMF and d) of DMF after extraction (20 Mo/Al, H_2O_2/S=3, T=80°C, t=60 min).

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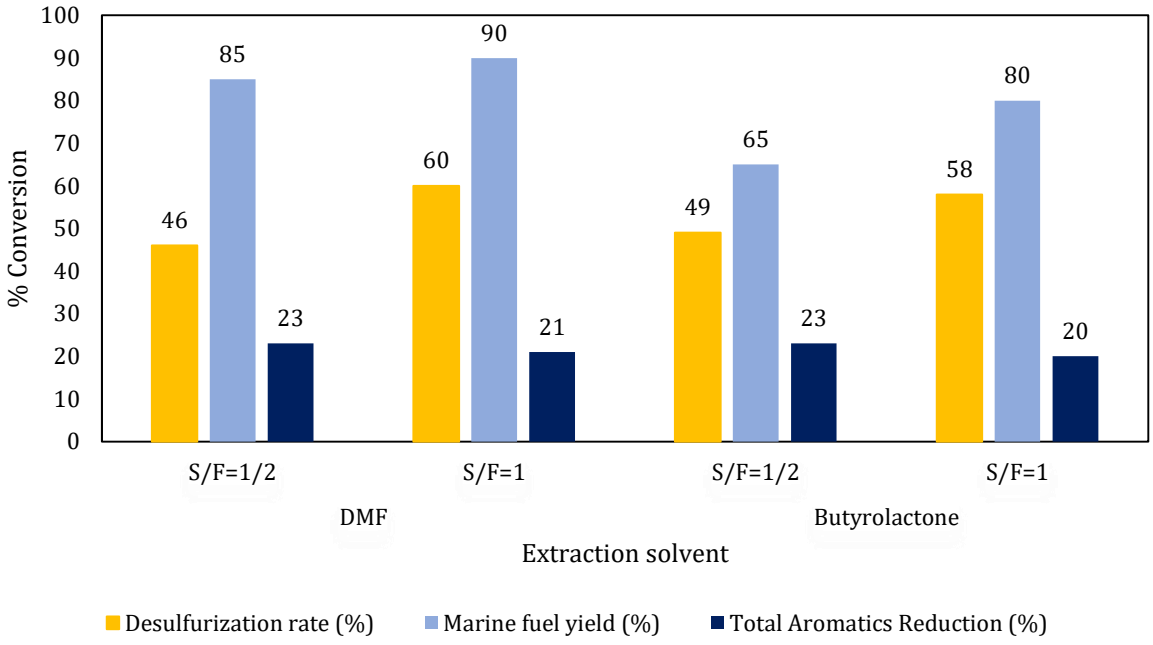

Figure IV.10: Desulfurization rate, marine fuel yield and total aromatics reduction after extraction of oxidized fuel using DMF and Bul (ODS of IFO500-DC, 20 Mo/Al, H_2O_2/S=3, T=80°C, t=60 min).

Table IV.1: Percentage of different aromatic families in IFO500-DC before oxidation, and after oxidation and extraction using DMF or Bul with solvent/fuel ratio of 0.5 or 1.

	IFO500-DC	**IFO500-DC after oxidation and extraction**			
		DMF solv/f =0.5	DMF solv/f =1	Bul solv/f =0.5	Bul solv/f =1
Mono aromatic (%)	18.8	20.9	19.6	20.3	21.7
Di (%)	9.8	6.3	7.6	7.7	7.9
Tri (%)	10.5	5.4	5.9	6.0	6.0
Tetra (%)	7.7	2.8	3.6	2.2	2.0
Total aromatics (%)	46.8	36.1	36.8	36.2	37.5

IV.1.1.5. Ultrasound assisted ODS of IFO500-DC

As we saw in the literature review in chapter I, application of ultra-sonication appears to be promising in ODS of heavy fuels. High energy ultrasounds can induce cavitation effect in marine fuels. Cavitation is defined as formation, growth and collapse of bubbles. Acoustic cavitation occurs in liquids under high intensity sound wave irradiation. As the sound wave passes, bubbles oscillate growing to an instable size resulting in implosions. In the ultrasound assisted oxidative desulfurization process, extreme conditions of temperature and pressure during acoustic

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cavitation create micro turbulence and can cause the formation of free radicals such as H· and OH· considered as strong oxidizing agents. Additionally, energy produced from ultrasound during oxidation can provide an extremely fine emulsion of immiscible liquids (in our case H_2O_2 and fuel) or assist mass transfer and surface activation (in a solid–liquid system) [34].

IV.1.1.5.1. Ultrasounds instead of mechanical stirring

Ultrasound assisted oxidative desulfurization (UAOD) of IFO500-DC was carried out, the ultra-sonication replacing mechanical stirring, and initial studies focused on optimization of ultra-sonication time. The evolution of Cx-BTs and DBT was monitored after 5, 10 and 20 min. Results indicate that conversion of both molecules increased from 20% to 35% for Cx-BTs and from 50% to 65% for DBT when time increased from 5 to 10 min. However, after 10 min, desulfurization rates remained the same. So as an optimum in terms of energy, we chose to work with 10 min of ultra-sonication. In the work of Akbari *et al.* [35] in the UAOD of model DBT in the presence of Mo/Al_2O_3 and hydrogen peroxide, the oxidation of DBT in high sulfur model diesel reached 75% within 15 min of the ultra-sonication, and 98% in 30 min, which appeared to be the optimum time. In the case of homogeneous work, using Fenton catalysts (ferric chloride and copper sulfate) in Flores *et al.* study [36] the reaction time increase from 7.5 to 20 min in the UAOD of heavy fuel oil containing 3.8 wt.% S led to a decrease in sulfur reduction from 25 to 17% at 20 min The authors accounted this result to the nature of the heavy fuel oil, where longer reaction time can favor secondary reactions such as recombination of heavy molecules.

After optimizing reaction time using ultrasound, comparison of performances under UAOD or mechanical stirring was performed. Conversion results of the Cx-BTs and DBT under both processes are indicated in Figure IV.11. The ODS reaction was effective in the case of ultrasound, with a slight improvement of the conversion of the Cx-BTs family from 35 to 38% and the DBT molecule from 60 to 65% with an Ox/S=3 ratio after 10 min. However, this difference is very small, therefore it could be more energy-effective to use conventional ODS. By increasing the amount of oxidant used, the beneficial effect of ultrasound is more visible with an Ox/S=25, for which we noticed that the conversion of Cx-BTs has increased from 48 to 71% and that of DBT in a less extent from 72 to 80%. This improvement, more pronounced in the case of the more refractory molecules, highlights the importance of using ultrasound in the presence of a large quantity of the aqueous phase, thus enhancing contact between organic and water phase.

Despite the wave shock energy that could be emitted using ultrasound, different results were reported in the literature. Type of catalyst used can have an impact on the efficiency of the system. Normally homogeneous catalysts proved very high performance due the one phase reaction between catalyst and reaction medium [37,38]. In all cases, better results were obtained

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with ultrasounds when compared to stirring. An increase in desulfurization rates between 30 to 47 % was reported when ultrasounds were applied to different fractions of VGO [37,38], diesel [38] or model molecules [37]. However, in the case of heterogeneous catalysts when using hydrogen peroxide oxidizing agent, we have a solid (catalyst)-liquid (H_2O_2) -liquid (fuel) system where mass transfer assist is needed for the two immiscible liquids as well as surface activation of catalyst-liquid system. This can further explain our results that are in agreement with the work of Choi *et al.* [39] applied to model feed BT and DBT using H_2O_2/sodium phosphotungstate heterogeneous system with stoichiometric Ox/S ratio. Ultrasound and mixing assisted ODS gave almost same desulfurization results. They accounted their results to the better mixing and emulsification at the start of conventional ODS reaction. However, with ultrasound, more time is needed to adequately emulsify the system. On the contrary, experiments of Tang *et al.* [7] that also applied an Ox/S=3 showed that ultrasonic irradiation favored desulfurization reaction of a MFO380 treated with tBHP/MoO_3 system. Instead of 18% desulfurization efficiency after 90 min of conventional stirring, a rate of 30% was obtained after 60 min irradiation. Despite the presence of solid catalyst, oxidant used was miscible with fuel therefore ultrasound energy was consumed to assist transfer between catalyst and liquid only.

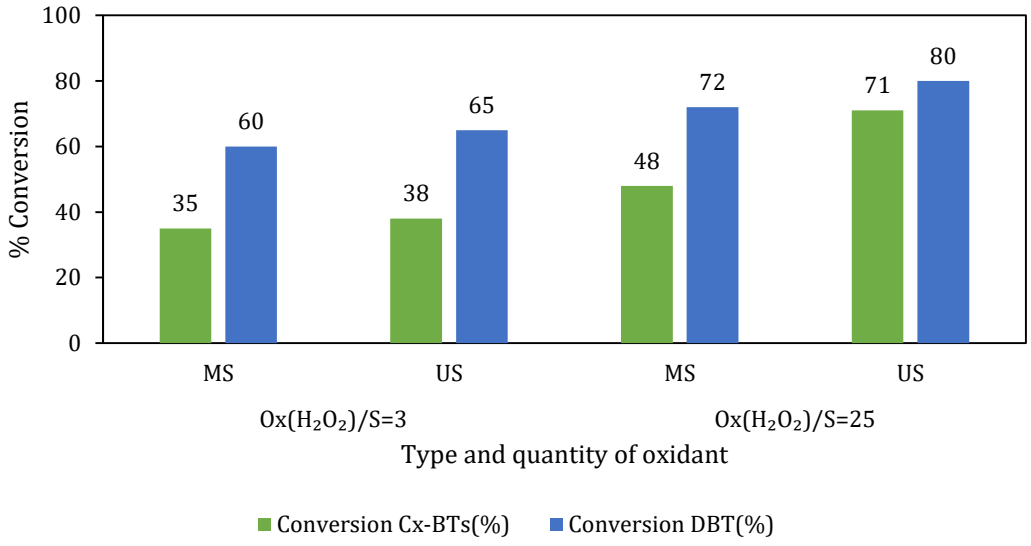

Figure IV.11 : Conversion of Cx-BTs and DBT in the ODS of IFO500-DC using mechanical stirring (MS) or ultrasounds (US) with different Ox/S ratios. (20 Mo/Al, H_2O_2/S=3, T=80°C).

IV.1.1.5.2. Combined system: ultrasounds followed by mechanical stirring

As ultrasound gave comparable results with mechanical stirring, optimized time of 10 min ultra-sonication followed by mechanical stirring (US+MS) was tested on the IFO500-DC feedstock. 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 (Figure

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IV.12). Hence, after extraction by DMF higher desulfurization rate of 76% was obtained, due to the presence of more polar sulfones easily extracted with the solvent.

Chan *et al.* [38] reported higher than 98% desulfurization of DBT when using first mixing (110 min) followed by 10 min ultrasound irradiation. However, similar results can be achieved with 180 min of mixing alone. The UAOD of IFO380 containing 1.6 wt.% S using KO_2 performed by the same authors demonstrated 50 % desulfurization, not enough to fulfil the 5000 ppm sulfur cap goal in 2020.

In our case, increase in reaction time does not increase desulfurization rates. Indeed, the combined system was beneficial, the shock waves created by ultra sounds favored contact between the two phases and introduced cavitation into the system, which improved the homogenization of the solution in conventional stirring applied afterwards.

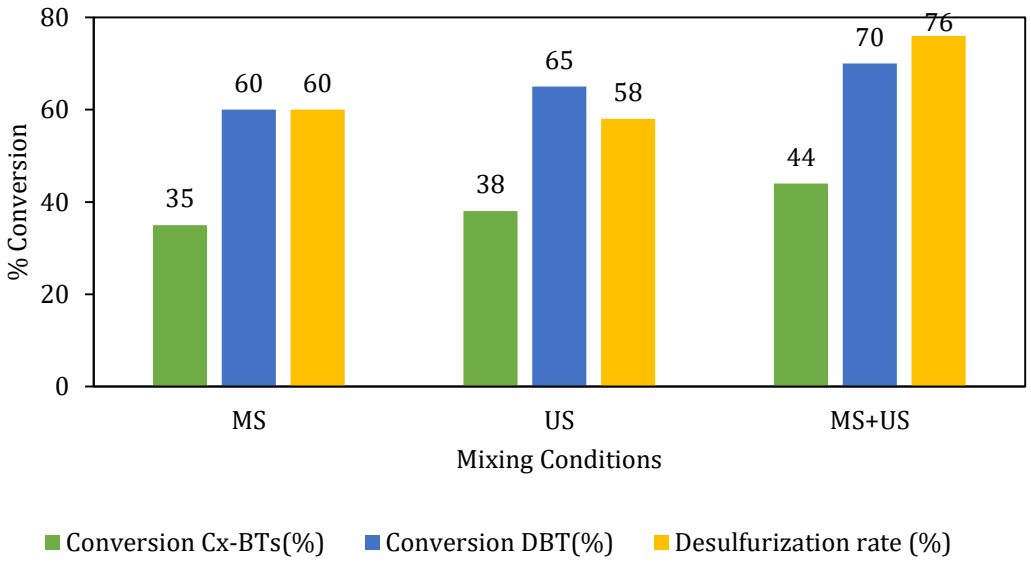

Figure IV.12 :Conversion of Cx-BTs and DBT and desulfurization rates of oxidized fuel IFO500-DC using mechanical stirring, ultrasounds, and ultrasounds followed by mechanical stirring (20 Mo/Al, H_2O_2/S=3, T=80°C).

IV.1.2. Study of the competitive reactions

IV.1.2.1. Hydrocarbon reactivity

The ODS selectivity toward sulfur species, while leaving hydrocarbon molecules intact, is an important parameter. In this regard, the relative percentage of different hydrocarbon families has been monitored after oxidation using HPLC method. The contents in IFO500-DC of mono, di,

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tri and tetra aromatics remained similar before and after oxidation, with no significant difference with both Ox/S ratios, as illustrated in Table IV.2. Adam *et al.* [40] studied the ODS selectivity of a VGO sample, they calculated the relative abundance of mono, di and tri aromatic families using two dimensional gas phase chromatography coupled to FID detector. They noticed no major changes in the relative abundance of hydrocarbon families after ODS.

Table IV.2 *:* Relative abundance of mono, di, tri and tetra aromatic families inside IFO500-DC before and after oxidation using Ox/S=3 or 25.

	IFO500-DC	**IFO500-DC after oxidation Ox/S=3**	**IFO500-DC after oxidation Ox/S=25**
Mono (%)	18.8	20.1	20.3
Di (%)	9.8	10.1	9.5
Tri (%)	10.5	10.3	9.6
Tetra (%)	7.6	5.1	5
Total aromatic (%)	46.8	45.6	44.5

IV.1.2.2. Nitrogen reactivity

To examine the effect of nitrogen compounds present in marine fuels and to find out if part of oxidant is consumed for nitrogen oxidation, GC-NCD analysis was performed on IFO500-DC before and after oxidation using H_2O_2 with Ox/S=3 and Ox/S=25. According to the chromatograms (Figure IV.13), there is a decrease in the intensity of the peaks corresponding to nitrogen compounds. In addition, this decrease is more intense when the amount of oxidant used increases. It was interesting that chromatograms of oxidized fuels using NCD detector do not show any new peak formed corresponding to oxidized nitrogen compounds which is not the case of oxidation of sulfur compounds where sulfone peaks appear using SCD detector.

The comparison of integration areas of fuel and oxidized fuel with Ox/S=3 and Ox/S=25 enables the calculation of total nitrogen content after oxidation. It was found to decrease from 3600 ppm to 1826 ppm using Ox/S=3, and from 3500 ppm to 476 ppm for Ox/S to 25.

This shows that nitrogen species are oxidized. Even with an amount of oxidant close to stoichiometry, part of the oxidant is consumed by nitrogen species.

There are few studies reporting oxidative denitrogenation reaction and in particular its competition with ODS. Ishihara *et al.* [11] oxidized a LGO using 16 % wt. MoO_3/Al_2O_3 and tBHP as oxidant with an Ox/S=15 ratio, and had a decrease in nitrogen content after adsorption from 13 ppm to 0.8 ppm, that they explained by the presence of easily oxidized nitrogen molecules in

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diesel fraction. The reactivity of nitrogen compounds lies in the following order: indole>quinoline>acridine>carbazole, carbazole being the most arduous to oxidize [41]. However, it was not possible to identify the oxidized products due to the multiple number of formed products consisting of different combinations of nitrogen and oxygen. None of literature work indicated or demonstrated the formation of NOx. Unlike the case with oxidation of sulfur compounds, where same type of sulfone will always form, it is believed that oxidation products of nitrogen compounds vary with the catalytic system. For instance, Shiraishi *et al.* [41] obtained nitrobenzene via the oxidation of aniline using Ti-HMS-H_2O_2 system, when V-HMS catalyst was used azoxybenzene was formed. As for the oxidation of carbazole over Ti-HMS carbazole-1,4-dione was formed but with V-HMS, no GC peak was detected prior to its oxidation, polymeric compounds were formed and they were only detected using infrared analysis IR. Some researchers demonstrated that their catalytic systems are adaptable and highly active for desulfurization and denitrogenation of diesel samples. Santiago *et al.* [13] studied the ODS of a SRGO (318 ppm of total nitrogen) using WOx/ZrO_2, H_2O_2 (Ox/S=25) system and obtained a 95% denitrogenation after reaction. Similarly, Shiraishi *et al.* [41] obtained 84% nitrogen removal using the acetic acid/H_2O_2 system and V-HMS catalyst for light oil (75 ppm nitrogen content). As for competition and how can nitrogen compounds inhibit oxidative desulfurization, some research work [24,42–45] studied the effect of addition of nitrogen compounds such as aniline, indole, quinoline and carbazole to model solutions consisting of DBT derivatives. They found that desulfurization rate decreases with the incorporation of such molecules, and the effect was more pronounced with aniline and indole rather than with carbazole. The result was attributed to the strong adsorption of nitride and their oxidized products on the active sites of the catalysts diminishing its activity. Accordingly, our process is adaptable and highly active for desulfurization and denitrogenation reactions overcoming SOx problems nowadays, and NOx problems when rules can be implemented in the near future.

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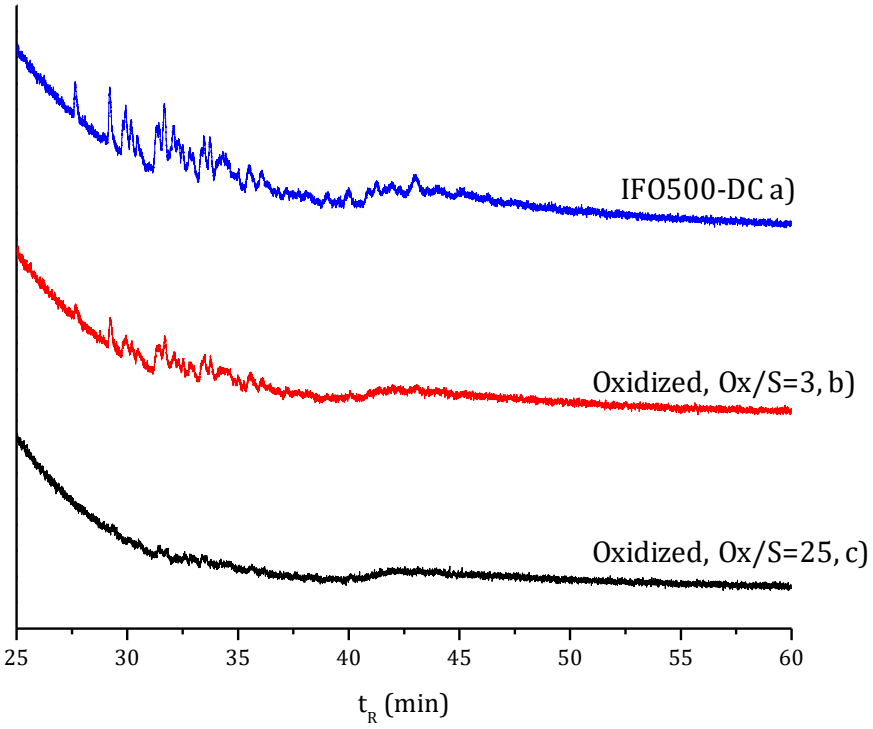

Figure IV.13: Chromatograms of a) IFO500-DC b) fuel after oxidation (Ox/S=3) c) fuel after oxidation (Ox/S=25) (20 Mo/Al, T=80°C, t=60 min)

IV.2. Influence of marine fuel type in ODS

A comparison study of marine fuel behavior was performed using IFO380, IFO500 and HSFO700. ODS experiments were applied to the three fuels, followed by extraction using DMF. Raw (R), diluted (D) and diluted and centrifuged (DC) samples were tested, in order to compare the reactivity of sulfur compounds depending on the complexity of the matrix.

IV.2.1. ODS of diluted centrifuged fuels (DC)

In Table IV.3, are collected for the diluted centrifuged phases of the three fuels their sulfur content before and after extraction by DMF. The sulfur content after ODS and extraction and the conversions of Cx-BTs and DBT are also mentioned, with mechanical stirring (MS) and with the combined system ultra-sounds followed by mechanical stirring (US+MS).

As mentioned in chapter III devoted to the characterization of the fuels, it is to be noted that liquid phase of IFO380-DC 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 contents around 3 wt.% S,

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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 after dilution with dodecane.

Table IV.3 : Sulfur content before ODS, after extraction with DMF, after ODS and extraction, corresponding desulfurization rates, and conversion of Cx-BTs and DBT for IFO380-DC, IFO500-DC and HSFO700-DC using mechanical stirring (MS) or combined system (MS+US) (20 Mo/Al, H_2O_2/S=3, T=80°C).

	IFO380-DC		IFO500-DC		HSFO700-DC	
	MS	US+MS	MS	US+MS	MS	US+MS
S before ODS (wt.%)	*0.7*		*1.6*		*1.5*	
S after extraction (wt.%)	*0.4*		*1.2*		*1.2*	
Desulfurization rates (%)	42		25		20	
S after ODS & extraction (wt.%)	0.28	0.13	0.64	0.37	0.90	0.54
Desulfurization rates (%)	60	81	60	77	40	64
Conversion Cx-BTs(%)	58	70	35	44	25	45
Conversion DBT (%)	76	80	60	70	60	75

Extraction was performed on the diluted centrifuged phase of fuels and it can be seen that part of the sulfide compounds migrated to the solvent (Table IV.3), with a desulfurization rate of 42% for IFO380-DC and around 20% for IFO500-DC and HSFO700-DC, leading to sulfur content in the extracted fuel of 0.4 wt.% for IFO380-DC and 1.2 wt.% for IFO500-DC and HSFO700-DC.

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 showing that whatever the marine fuel a beneficial effect on sulfur removal is obtained when performing ODS. This corresponds 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 of Cx-BTs and DBT were the highest for IFO380-DC (58 and 76% respectively) while close values were obtained for IFO500-DC (35 and 60%) and HSFO700-DC (25 and 60%), which presented the same initial content of sulfur (1.6 wt.%). When investigating parameters that can be relevant and influencing fuel performances, nitrogen content does not have an effect on desulfurization efficiency, the three fuels containing the same amount of nitrogen (0.35 wt.%). It seems that conversion of Cx-BTs and DBT is favored for the fuel with less sulfur content for the conditions and systems used. 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 being then available for oxidation [23]. Regarding the global sulfur removal, the desulfurization rate is higher for IFO500-DC than for

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HSFO700-DC, containing the same amount of sulfur and with close conversions of Cx-BTs and DBT. This indicates some other sulfur compounds in HSFO700-DC are more difficult to convert or do not migrate to the extracting solvent phase in comparison with IFO500-DC.

Ten minutes of ultra-sonication were applied prior to ODS, which was found to improve the reaction efficiency, the same trends being maintained when comparing the 3 samples. Conversions of Cx-BTs and DBT were increased to 70 and 80% respectively for IFO380-DC, and around 45 and 70% for IFO500-DC and HSFO700-DC, with again close values. This corresponds to an increase in DBT conversion between 5 and 15%, while improvement above 25% is measured for Cx-BTs. The effect of ultra-sounds is more pronounced on Cx-BTs, the more refractory compounds in ODS. 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 S contents of 0.13, 0.37 and 0.54 wt.%, which appear to be compatible with the intended stricter regulation.

IV.2.2. ODS of diluted fuels (D)

ODS reaction on the diluted fuels was performed using the optimized combined system ultrasounds followed by mechanical stirring (US+MS). These diluted marine fuels, obtained after dilution with dodecane or a xylene-dodecane mixture, contained in the diluted phase solid particles initially present in the fuel or precipitated during dilution, like asphaltenes.

Table IV.4 : Sulfur content before ODS, after ODS and extraction, corresponding desulfurization rates, fuel recovery and conversion of Cx-BTs and DBT for IFO380-D, IFO500-D and HSFO700-D using combined system US+MS (20 Mo/Al, H_2O_2/S=3, T=80°C).

	IFO380-D		**IFO500-D**		**HSFO700-D**	
	C12	C12-X	C12	C12-X	C12	C12-X
S before ODS (wt.%)	*0.79*		*3.27*		*2.95*	
S after ODS & extraction (wt.%)	*0.28*	*0.30*	*0.63*	*1.00*	*0.79*	*0.84*
Desulfurization rates (%)	65	62	82	69	73	71
Fuel Recovery (%)	70	50	70	50	65	45
Conversion Cx-BTs(%)	50	50	44	45	41	44
Conversion DBT (%)	70	71	81	70	73	66

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Extraction on non-oxidized diluted fuels using DMF was tried. However, it was not possible to obtain two separable phases. The presence of DMF induced immediate precipitation making impossible to evaluate sulfur removal. Extraction was possible after oxidation, even though it was hard to distinguish between the 2 phases, separation was carried on the basis of difference in density between polar phase and organic oxidized fuel that was further analyzed.

Results obtained on samples diluted (D) with C12 were compared to that of diluted centrifuged samples (DC) studied in the previous paragraph. 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.%. Solid phase removed by centrifugation contains little sulfur, the sulfur content varying from 0.79 wt.% in IFO380-D to only 0.70 wt.% in IFO380-DC. The compounds present in IFO380 that are removed by dilution and centrifugation may be detrimental to sulfur compounds oxidation.

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 82% for IFO500 and from 64 to 73% for HSFO700. In the diluted fuel IFO500 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 of liquid phase DC that varied between 80-90 % indicating 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 organosulfur compounds trapped inside asphaltene molecules extracted to the polar solvent phase or to oxidation of solid phase occurring when applying ODS on diluted phase.

Dodecane as dilution solvent alone leads to precipitation of asphaltenes particles inside the medium. To minimize quantity of solid particles precipitated due to the presence of dodecane (C12), xylene that is known as a good solvent for solubilization of asphaltenes was used. However, it cannot be used alone due to the problems of miscibility with DMF, leading to ineffective extraction. Therefore, dilution was achieved using a 3 volumes of dodecane per one volume of xylene (3/4) mixture (C12-X) rather than pure xylene allowing reduction of solvent polarity making extraction successful. Compared to dodecane, with the new mixture, percentage of solid phase in each fuel was reduced from 12 to 10 wt.% for IFO380, 16 to 12 wt.% for IFO500 and from 16 to 13 wt.% for HSFO700. Reactivity of Cx-BTs and DBT was comparable for diluted fuel with dodecane or dodecane-xylene. With IFO500-D and HSFO700-D, the quantity of solid phase is not the same when diluted with C12 or C12-X. Despite this difference, ODS efficiency was not

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influenced by the quantity of solid phase that can contains heavy compounds and conversions of Cx-BTs and DBT remained close whatever the nature of the fuel. Desulfurization rates with dodecane-xylene were slightly lower compared to those obtained with dodecane. Global sulfur content decreased from 0.79 to 0.3 wt.% (instead of 0.28 wt.% with C12) for IFO380, 3.27 to 1 wt.% (instead of 0.63 wt.% with C12) with IFO500 and from 2.95 wt.% to 0.65 wt.% (instead of 0.79 wt.% with C12) with HSFO700 with C12-X mixture. Beside evaluating total sulfur content after extraction, fuel recovery was further evaluated to see if the diluent solvent has an impact on the facility of migration of compounds. Total fuel recovery after extraction of oxidized fuels was between 45-50% when dodecane-xylene was used and around 70% when dodecane was only used. These values were lower than recovery of diluted phase that varied between 80-90%. This result can be associated to the presence of xylene. When diluting the fuel with part of xylene, polar asphaltene were dissolved which facilitated their migration to the polar phase of DMF. Tang *et al.* [7] evaluated recovery of bunker fuel MFO380 diluted 5x with n-heptane after oxidation followed by extraction using acetonitrile. They obtained 82.53% of recovered fuel. This loss was explained in the literature [16,21,26] by feedstock loss in the polar phase. Xylene favored better solubilization of particles and heavy compounds inside fuel, giving better vision regarding their reactivity in ODS. However, coupling oxidation with extraction was not efficient. With extraction we need to have a polar solvent that enhance only the migration of sulfones compounds leaving asphaltene fraction and other polar compounds intact inside the fuel avoiding high hydrocarbon loss. When carrying ODS with xylene, it would be recommended to use other separation technique like adsorption or thermal decomposition that are used in the literature.

IV.2.3. ODS of raw fuels (R)

One of the objectives was to be able to achieve ODS on raw fuels to reduce the number of steps and reagents incorporated in the process. ODS on raw IFO380, IFO500 and HSFO700 was achieved using same conditions of catalyst and oxidant but with Ox/S=10 since ODS of raw fuels with Ox/S=3 was not effective. Results of conversion and total sulfur content after oxidation and extraction with desulfurization rates for IFO380 and IFO500 are indicated in Table IV.5. No conversion could be measure for HSFO700. After oxidation on the raw fuels, we did not monitor numerically viscosity of fuel. Nonetheless, it was possible to detect visually an increase in viscosity of all fuels. Indeed, viscosity and physical properties change for HSFO700 was more pronounced turning the reaction mixture into a pasty formula. Therefore, conversions nor sulfur content after ODS and extraction could be evaluated for this fuel. The viscosity change could be attributed to condensation and aggregation of high molecular weight molecules or via their oxidation. When working with heavy feedstocks, Javadli et De Klerk [46] observed such a change in viscosity.

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Autoxidation using air was carried out with a tar sand bitumen containing 5.2 wt.% of sulfur. Using air, sulfur is removed as sulfones as well as sulfur dioxide. When increasing reaction temperature up to 175°C the viscosity increased and bitumen hardening was noticed; this was explained by the authors through free radical reaction and side reactions caused by the complex nature of bitumen.

Using the same optimized system ultrasound followed by mechanical stirring, conversion of Cx-BTs and of DBT were found similar in diluted and raw fuel for IFO380 and IFO500 (around 44-50% for Cx-BTs conversion and around 70-73% for DBT conversion). Conversions are thus not affected by the presence or not of asphaltenes in the liquid phase. Similarly, viscosity, different in raw and diluted samples, did not have a significant effect on desulfurization efficiency.

Total sulfur removal after extraction remained similar, equal to 65%, for raw and diluted IFO380, with final sulfur content of 0.27 wt.%. With IFO500, the sulfur removal increased from 80 for diluted to 90% for raw sample, decreasing the final sulfur content to 0.52 wt.% in the treated raw IFO500 fuel. For this fuel, more species could be extracted in the raw than in the diluted sample.

Table IV.5 : S content before and after ODS and extraction, desulfurization rates and conversion of Cx-BTs and DBT for diluted (D) and raw (R) IFO380, IFO500 and HSFO700. (20 Mo/Al, T=80°C).

	IFO380		**IFO500**		**HSFO700**	
	Diluted	Raw	Diluted	Raw	Diluted	Raw
S before ODS (wt.%)	*0.79*		*3.27*		*2.95*	
S after ODS & extraction (wt.%)	*0.28*	*0.27*	*0.63*	*0.52*	*0.79*	*x*
Desulfurization rate (%)	65	65	80	90	73	x
Conversion Cx-BTs(%)	50	43	44	50	45	x
Conversion DBT (%)	70	73	73	70	70	x

IV.3. Conclusion

Oxidation reaction of diluted centrifuged marine fuel IFO500-DC was conducted on MoO_3/Al_2O_3 catalyst using various conditions of time, oxidant nature and quantity, catalyst dosage, extraction solvent effect and stirring conditions. The following conclusions can be drawn from the results obtained:

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The oxidant imposed by the SOxLOW project is hydrogen peroxide H_2O_2 with an Ox/S as low as possible. Starting from a ratio of 3, we found that the increase in the Ox/S ratio up to 25 did not have a major effect on the conversion under test conditions, attributed to mixing issue in the biphasic reaction medium, more critical with a large amount of oxidant. Using tBHP, which leads to a single-phase reaction system, with an Ox/S=3 ratio, the conversions were only slightly higher than those obtained with H_2O_2, while with an Ox/S=25 ratio complete conversions of Cx-BTs and DBT were measured. This indicates that contact between the two phases is not critical with a low amount of H_2O_2, and a ratio of 3 was thus kept for further experiments.

Even though with real feeds, higher reaction time is needed due to their complex nature, ODS conversion of marine fuels remained the same after one hour. The optimum catalyst quantity to add to the reaction medium was found 20 $g.L^{-1}$. Concerning the extraction solvent, despite the fact that desulfurization rates of oxidized fuel using DMF and butyrolactone were the same, we preferred to use DMF due to the higher recovery rate of fuel after extraction.

Ultra-sound assisted ODS (UAOD) was tested as a way of optimizing stirring conditions. No improvement was noticed when replacing mechanical stirring by US, however applying ultrasounds before reaction under mechanical stirring provided significantly better desulfurization rates due to the synergetic effect provided by ultrasounds.

Once optimization of the reaction conditions was performed on diluted centrifuged IFO500-DC, ODS reaction was performed on the three fuels IFO380, IFO500 and HSFO700 on the raw (R), diluted (D) and diluted and centrifuged (DC) samples. ODS was effective on all samples, except on HSFO700-R, for which a very high viscosity mixture appeared during reaction. Also, an Ox/S ratio of 10 was required to oxidized the raw samples of IFO380 and IFO500. Results are gathered in Table IV.6.

Owing to SCD-GC analysis, conversion of Cx-BTs and DBT could be monitored during reaction. Similar values were obtained whatever the fuel and whatever the sample R, D or DC (around 45% for Cx-BTs and 70% for DBT), except for IFO380-DC for which higher values were measured (70% for Cx-BTs and 80% for DBT). Except for IFO380-DC, the results show that the sulfur content, varying from 0.79 to 3.27 wt.%, viscosity, presence or not of asphaltenes, has no impact on the conversion of Cx-BTs and DBT. In the case of IFO380-DC, the same quantity of solid phase has been removed by centrifugation as for the other fuels, however, containing very little sulfur. The sulfur content varying from 0.79 wt.% in IFO380-D to 0.70 wt.% in IFO380-DC, while half of the initial sulfur content is removed by centrifugation in the other fuels. The compounds present in IFO380 that are removed by dilution and centrifugation may be detrimental to sulfur compounds oxidation.

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After ODS and extraction, and thus taking into account the efficiency and selectivity towards sulfones of the extraction step, we see that the desulfurization rate increases in the order DC < D < R for IFO500 and HSFO700, indicating that, as Cx-BTs and DBT are similarly converted, some other sulfide compounds present in the raw and in a lesser extent in the D, further removed by centrifugation, are oxidized or extracted in the D and R samples. For IFO380, higher desulfurization rate is measured in DC sample, in agreement with higher conversion of Cx-BTs and DBT compared to R and D samples. In the case of diluted fuels with the mixture xylene-dodecane that leads to less asphaltenes precipitation, slightly lower sulfur removal was measured than with dodecane, but was accompanied by high hydrocarbon loss due to migration of polar high molecular weight and high boiling point asphaltenes type compounds.

These results, obtained for IFO380, IFO500 and HSFO700 in R, D and DC samples, on $20MoO_3/Al_2O_3$ catalyst, revealed the difficulty of the implementation of ODS on viscous samples and proved its efficiency on marine fuels, with final sulfur content close to the values imposed by the MARPOL regulations. Indeed, optimization of catalyst is still required, and will be further studied in the next chapter.

Table IV.6 : Total sulfur content before and after ODS and extraction, and desulfurization rate for raw, diluted fuel with dodecane, diluted centrifuged fuel DC of IFO380, IFO500 and HSFO700.

	IFO380			**IFO500**			**HSFO700**		
	R	D	DC	R	D	DC	R	D	DC
S before ODS (wt.%)	*0.79*	*0.79*	*0.7*	*3.27*	*3.27*	*1.60*	*2.95*	*2.95*	*1.50*
S after ODS & extraction (wt.%)	*0.27*	*0.28*	*0.13*	*0.52*	*0.63*	*0.37*	*x*	*0.79*	*0.54*
Desulfurization rate (%)	65	65	81	90	80	77	x	73	64
Conversion Cx-BTs(%)	43	50	70	50	44	44	x	45	45
Conversion DBT (%)	73	70	80	70	73	70	x	70	75

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Development of efficient catalytic system: Optimization of supported phase/support

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Chapter V Development of efficient catalytic system: Optimization of supported phase/support

In the previous chapter, optimization of reaction conditions (oxidant, mass of catalyst, temperature and mixing system) and comparison of the different fuels were performed using 20 wt.% MoO_3/Al_2O_3 conventional ODS catalyst.

However, it will be advantageous to have an efficient cost effective catalyst for the ODS of marine fuels. Therefore, in this chapter catalysts screening for ODS of marine fuels is explored. All ODS reactions will be carried on IFO500-DC using H_2O_2/S=3 at T=80 °C and for 1-hour reaction.

The first part of the chapter is devoted to study the effect of supported used in ODS reaction. First literature assessments carried out in ODS point out the effectiveness of molybdenum based catalysts for ODS reaction [1–4]. To explore more deeply, alumina supported catalysts with various Mo loadings are studied. Because phosphorous and vanadium metals proved to be good promotors in ODS reaction [5,6], the use of low loadings of phosphorous or vanadium on classical Mo/Al was examined. In addition, molybdenum based catalysts will be further explored by varying the Mo precursor for the synthesis. For instance, phosphomolybdic acid or silicomolybdic acid showed appealing results in ODS.[7–10] Finally, the synthesis of peroxomolybdates from H_2O_2 and MoO_3 supported on alumina was also investigated.

The second part is dedicated to support effect in ODS. As titanium based catalysts showed auspicious results in ODS [11,12], several titanium oxides with various textural properties and composition are tested. Other oxide supports with mesoporous properties or typical properties (acid-base, oxygen mobility) are explored because a number of studies revealed that the use of ordered mesoporous materials, typically SBA15, highly improves the oxidation ability and yielded better results in the removal of sulfur. We also report the use of the ordered mesoporous silica known as COK-12 as an alternative to SBA-15. COK-12 support has a 2D hexagonal structure in platelet form with short, straight pores supposed to allow easier diffusion of heavy molecules. Zirconium oxide and mixed Al_2O_3-SiO_2 acidic supports will be tested to see the effect of acid base properties on conversions. Moreover, cerium oxide support with particular redox capacity will be also examined.

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V.1. Mo based catalysts supported on alumina

V.1.1. Effect of molybdenum content

The effect of molybdenum content in Mo/Al catalyst was studied by varying its weight percentage from 10 to 25 wt.%. XRD patterns of the catalysts with different loadings of molybdenum were reported in Figure V.1. The peaks at 2θ = 37.0°, 46.0° and 66.7° in the XRD profile for γ-Al_2O_3 correspond to the planes of cubic Al_2O_3. The same diffraction pattern is observed for the 10 Mo/Al catalyst while with higher Mo loadings, other diffraction peaks are detected. At loading equal to 15 wt.%, only small diffraction peaks at 2θ= 23.7, 25.8, and 27.4° appear. They correspond to the most intense diffraction peaks of the MoO_3 crystallized phase. At 20 wt.% Mo loading and above, the small peaks at 2θ= 12.9, and 49.4°, also related to the MoO_3 crystallized phase, can be observed. The intensity of MoO_3 diffraction peaks becomes clearly much higher with molybdenum loading allowing to evaluate the increase of the crystallized MoO_3 particles size using the Scherrer equation. The average particle sizes of MoO_3 crystallites increased from 33 nm at 20 wt.% to 38 nm at 25 wt.% MoO_3.

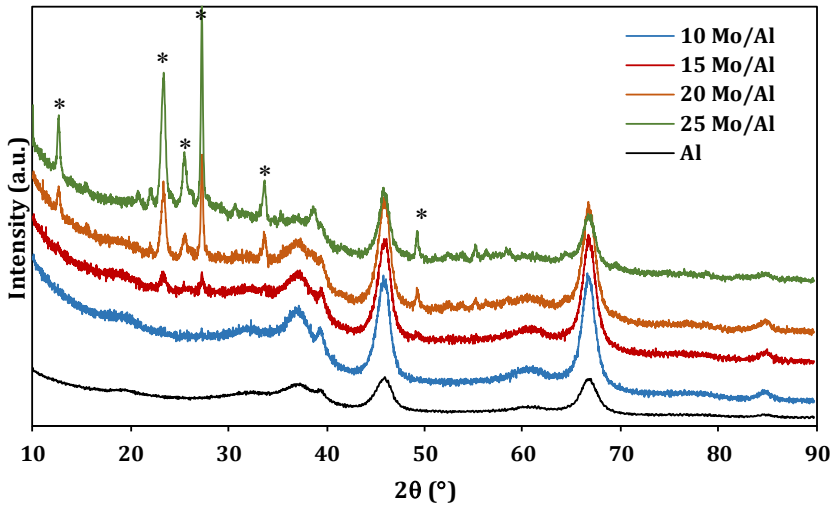

Figure V.1: XRD patterns of MoO_3 supported on alumina with different MoO_3 loadings. (*MoO_3)

XRD results were further confirmed with Raman spectra depicted in Figure V.2. In order to check the homogeneity of the oxide precursor, several grains were analyzed by Raman spectroscopy.

Raman spectra of the 10 and 15 Mo/Al shows unique large peak at 960 cm^{-1} assigned to polymolybdate species. These polymolybdates correspond to octahedral molybdenum species [13,14].

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With 20 Mo/Al, some grains (about 4 out of 17 grains) have spectra similar to the one obtained with 10 and 15 Mo/Al showing well dispersed polymolybdates with large band at 960 cm^{-1} assigned to polymolybdate species. In the other hand, some other spectra showed together with the large Raman band at 960 cm^{-1} new Raman bands at 243, 293, 343, 671, 820 and 995 cm^{-1} which are characteristic of MoO_3 crystallites. For 25 Mo/Al, whatever the grain analyzed, molybdenum is only detected as MoO_3 species. The 995 cm^{-1} band corresponds to the elongation mode of Mo=O and the band at 293 cm^{-1} corresponds to the deformation mode of Mo=O in MoO_3 [15]. At 20 wt.% MoO_3 and according to this preparation method, the presence of MoO_3 indicates that molybdenum species are poorly dispersed on the surface of the support. However, despite the presence of MoO_3 in 20 Mo/Al well-dispersed molybdenum species are also observed.

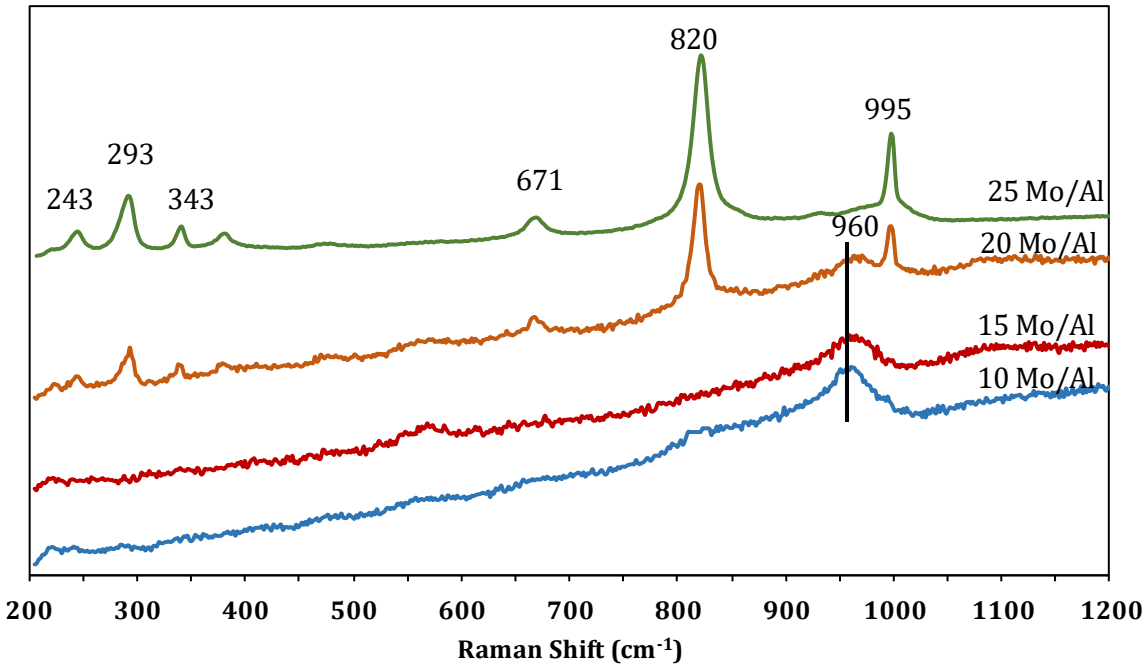

Figure V.2: Raman spectra for Mo/Al_2O_3 with different MoO_3 content.

Additionally, the analysis of textural properties reported in Table V.1 show only a slight decrease in BET surface area and pore volume of the catalyst when increasing molybdenum content.

The presence of MoO_3 does not alter significantly the textural properties: the surface variation is less than 10%, diameter less than 5% even at high Mo loading. Only the pore volume is more impacted with pore volume relative decrease of 20%, indicating some clogging of pores that is related to the formation of MoO_3 particles (with a size around 30 nm from XRD results) higher than some pore size of alumina support.

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Table V.1: Textural properties of Mo/Al_2O_3 with different MoO_3 content.

Catalyst	MoO_3 loading (wt.%)	S_{BET} ($m^2.g^{-1}$ catalyst)	S_{BET} ($m^2.g^{-1}$ support)	V_p ($cm^3.g^{-1}$)	Mean pore diameter (nm)
10 Mo/Al	10	174	193	0.68	12.5
15 Mo/Al	15	153	180	0.63	12.1
20 Mo/Al	20	148	185	0.58	11.3
25 Mo/Al	25	133	177	0.54	11.9

Figure V.3 shows the conversions of Cx-BTs and DBT as a function of MoO_3 loading after 1h of ODS using IFO500-DC.

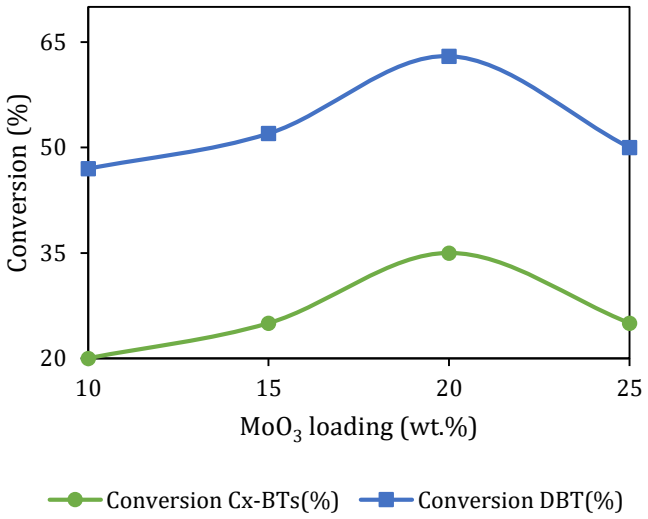

Figure V.3: Conversion of Cx-BTs and DBT in the ODS of IFO500-DC as a function of MoO_3 wt.% in MoO_3/Al_2O_3 (H_2O_2/S=3, T=80°C, t=60 min).

The Cx-BTs conversion and the DBT conversion follow the same trend with the increase of Mo loading on alumina. The results show that the conversion of the Cx-BTs family increased from 20 to 35 % and that of the DBT molecule from 45 to 65% when the molybdenum content increased from 10 to 20 wt.%. Above 20 wt.% of MoO_3, the conversion of sulfur compounds decreased, which shows that the optimal molybdenum content to be impregnated on the alumina support for ODS in marine fuels is 20 wt.%. At 25 wt.%, Mo is only present as MoO_3 while at 20 wt.% a polymolybdate phase is still observed by Raman analysis, it seems that the presence of MoO_3 in large amount is detrimental to the ODS activity. Before 20 wt.%, the increase in activity is explained by the increase of the polymolybdate phase content with Mo loading. Various studies reported the effect of molybdenum content in the ODS performance, when using model feeds of

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DBT an optimum loading of 10% was found [2,3], but with light gas oil fraction containing 50 ppm, 16 wt.% was the most efficient in ODS reaction [4]. Indeed, these values depend on the textural properties of the support used.

To sum up all, on the one hand high molybdenum content is needed to have better desulfurization results for ODS of IFO500-DC, but in the other hand, when increasing the Mo content, formation of MoO_3 molybdenum oxide appears with an increase of the particles size. This crystallized phase leading to a decrease of ODS activity for 25 Mo wt.% catalyst is then detrimental to ODS activity.

V.1.2. Impact of different promoters on the Mo/Al catalyst

To improve the activity of molybdenum-based catalysts, phosphorus and vanadium were used as additives.

V.1.2.1. Phosphorus

Abudallah *et al.* [16] and Garcia-Gutiérrez *et al.* [14] demonstrated very high performance of Mo-P/Al_2O_3 in the ODS of real diesel feed containing 300 or 400 ppmS. Additionally, Han *et al.* [5] showed that the addition of phosphate to Mo/SiO_2 enhanced almost 50 % desulfurization results of DBT in fixed bed reactor using P/Mo=1 ratio. They assigned these results to phosphate anions that withdraw the electron density of the Mo (VI) atoms, facilitating the formation of highly active peroxo molybdates in the oxidation reaction. P is also know to improve Mo dispersion [5,14,16]. We decided to prepare Mo/Al doped by phosphorus (as phosphate species) with a molar ratio P/Mo = 0.7 to obtain a better dispersion of molybdenum and to induce a better desulfurization result.

Figure V.4 compares the Raman spectra of the 20 MoP/Al catalyst with the 20 Mo/Al one. Even if the Raman spectrum of the P doped catalyst is a little bit noisy, a large increase of the peak located at 960 cm^{-1} and attributed to octahedrally coordinated polymeric molybdates is observed. Accordingly, the Raman peaks assigned to MoO_3 phase largely decrease. According to the literature, the new line located at 1095 cm^{-1} is assigned to P-O bond vibrations considering the oxygen atoms forming a bridge with the molybdenum atom, P-O-Mo [5,17]. No important textural modification is observed after phosphorus addition (Table V.2).

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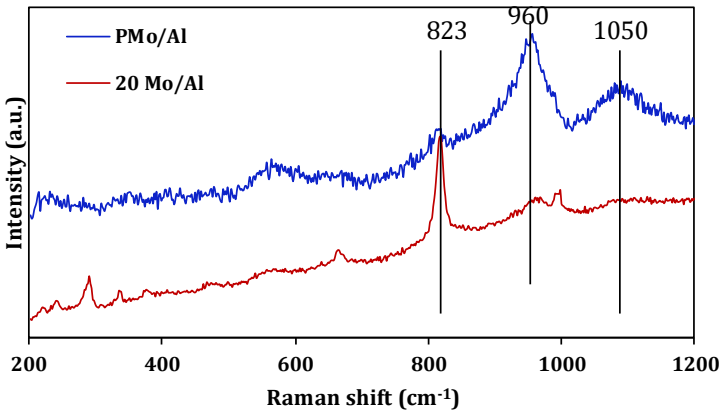

Figure V.4: Raman spectra for 20 MoP/Al and 20 Mo/Al.

Table V.2: Textural properties of 20 Mo/Al and MoP/Al.

Catalyst	Surface Area ($m^2.g^{-1}$ catalyst)	Surface Area ($m^2.g^{-1}$ support)	Pore volume ($cm^3.g^{-1}$)	Average pore diameter (nm)
20 Mo/Al	148	185	0.58	11.3
20 MoP/Al	122	171	0.51	12.7

ODS results on IFO500-DC with P doped catalyst showed a slight decrease in conversion rates of Cx-BTs from 35 to 30% and DBT molecule from 65 to 58% compared to 20 Mo/Al. Our results are not in agreement with literature data involving the addition of P as promotor and claiming a positive effect of P addition. In our case, conversions were almost comparable with negligible but negative effect of P. However, literature research work was applied on model DBT molecule and light gas oil or hydrotreated diesel. Thus, if the P addition can be efficient on light fractions, our results do not indicate such a beneficial effect with heavier fractions such as marine fuel.

V.1.2.2. Vanadium

Oxo vanadium complexes are known to be highly efficient oxidation homogeneous catalysts which are used to catalyze the transfer of an oxygen atom from a great variety of oxidizing agents into hydrocarbon molecules. To understand the role of vanadium in ODS reaction and to check if the introduction of V species could enhance reaction efficiency, mixed vanadium molybdenum oxides were prepared from V_2O_5 and MoO_3 with atomic ratio V/Mo=1/11. Mo loading was kept at 20 wt.%.

Raman spectrum after calcination of the Mo-V/Al catalyst is presented in Figure V.5. We still observe a main line corresponding to polymolybdates species even if we can notice a shift of this

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line (970 cm^{-1}) compared to that observed in 20 Mo/Al catalyst Raman spectrum (960 cm^{-1}). The very large line around 850 cm^{-1} by reference to the literature [18–20] is attributed to the presence of vanadate entities. Nevertheless, Raman spectrum does not exhibit any crystalline species of V_2O_5. Figure V.5 displayed the XRD pattern of V-Mo/Al catalyst. The presence of a small quantity of MoO_3 crystallized species is demonstrated by XRD analysis with a small reflexion centering at 2θ= 23.7°. The presence of vanadium does not alter Mo dispersion.

The introduction of vanadium in 20% Mo/Al led to a reduction of Cx-BTs conversion from 35 to 20% and DBT conversion from 65 to only 55%.

Indeed, V effect appears to be controversial in the literature. Some previous works have shown that vanadium based catalysts can be very active in ODS reaction with promising results when applied to model molecules, light gas oil and even heavy fuel oil [6,8,21,22]. Indeed, Teimouri *et al.* [21] recently showed that molybdenum/vanadium oxides supported on mesoporous silica MCM-41 showed high activity in the ODS of DBT using H_2O_2. Conversion to $DBTO_2$ increased from 80% to 100% when vanadium was added. They proposed that MoO_3 species acted as active phase in the presence of V_2O_5 inducing good desulfurization results.

On the contrary, Wang *et al.* [1] explained that vanadium can occupy octahedral sites which can decrease polarization of Mo-O band ascribed to V ions interacting strongly with the spinel type of Al_2O_3 lattice that contribute to the lower elimination of organosulfur compounds. Gonzalez et Caero. [23] showed that bimetallic V-Mo catalysts supported on alumina did not have any synergetic effect in comparison with V or Mo supported catalysts in the ODS of model molecules (DBT, 4-MDBT and 4,6-DMDBT) using H_2O_2 as oxidant (Ox/S=4). They suggest that activity was inhibited by microcrystals of Mo on V/Al catalyst considering V is the main active specie and Mo the promotor. Furthermore, they examined later the activity of reduced species of vanadium (V_2O_3, V_2O_4) as catalyst obtained via reduction in TPR apparatus at 10 °C/min up to 700 °C, in flow of H_2/air mixture. Reduced species of vanadium showed better activity when compared to corresponding oxide catalysts composed of V_2O_5. Later the same authors demonstrated [24] that reduced species of vanadium (V_2O_3 or V_2O_4) promote formation of active species like oxoperoxo complexes enhancing ODS performance.

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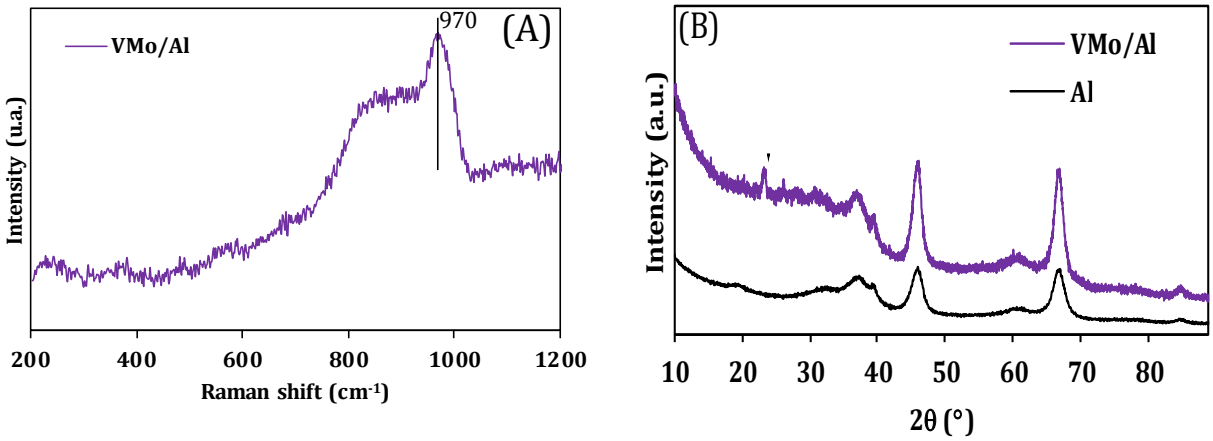

Figure V.5: (A) Raman spectrum of V-Mo/Al and (B) XRD patterns of V-Mo/Al and Alumina Al.

V.1.3. Mo based heteropolyacid catalysts

Current research efforts are mainly devoted to the development of improved preparation methods that ensure the stabilization of active Mo oxide species on the surface. In our work, the increase of the Mo loading proved to be profitable only to a limited extent. The performance of the catalysts went down due to the raise of bulk MoO_3 crystals. The appearance of such species can be correlated to the nature of the Mo precursor used. The heptamolybdate anions present in the impregnation solution proved to interact strongly with the external surface of the support, resulting in an uneven dispersion of the Mo phase. The use of heteropolyacids ($H_3PMo_{12}O_{40}$ or $H_4SiMo_{12}O_{40}$) as molybdenum precursor proved to enhance dispersion of Mo oxides [7,8,10]. In addition, they are multifunctional heterogeneous acid catalysts, which have been used to replace conventional liquid acid homogeneous catalysts known as very active and selective in ODS reaction. However, their separation and recovery are the main obstacles for using homogeneous HPA catalysts in industrial applications. Therefore, to improve the effectiveness of catalyst recovery and reuse, dispersion of HPAs on various solid supports has been reported in many researches. As an example, Choi *et al.* [9] explained that PMo_{12} are more active than $SiMo_{12}$ in the ODS of DBT mainly due to the formation of more stable peroxometal complex that favors oxidation reaction in sulfur compounds.

Garcia-Gutierrez *et al.* [14] compared the effect of PMo_{12} with ammonium metatungstate (AMT) precursor supported on alumina in the ODS of 400 ppm S diesel using tBHP as oxidant. Sulfur elimination was higher using phosphomolybdic acid supported on alumina compared to AMT, it was 84% instead of 50% in the case of AHM precursor.

In this perspective, molybdenum based HPA were synthetized. Two different types of molybdenum precursors with 20 wt.% MoO_3 were tried: the phosphomolybdic acid noted PMo_{12} and the silicomolybdic acid noted $SiMo_{12}$. Synthetized catalysts were characterized by Raman and

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XRD (Figure V.6). The lines observed in the Raman spectrum of PMo_{12}/Al at 950, 897, 566, and 220 cm^{-1} do not correspond to that of $H_3PMo_{12}O_{40}$ with a main peak expected around 990 cm^{-1} instead the observed one at 950 cm^{-1} but can be assigned to $AlMo_6O_{24}H_6^{3-}$ (noted $AlMo_6$) Anderson heteropolyanion species [25]. These species are formed during the drying step that was kept constant for all catalysts and that induces decomposition of PMo_{12} Keggin species. The same observation with formation of $AlMo_6$ can be done for the $SiMo_{12}$ based catalyst even if the corresponding Raman spectrum is less resolved. Nevertheless, both Raman spectra presenting large lines are in agreement with the presence of well dispersed $AlMo_6$ species and do not show MoO_3 formation. XRD patterns of $SiMo_{12}/Al$ and PMo_{12}/Al similar to that of alumina are in agreement with the presence of only well dispersed molybdenum with no molybdenum oxide cluster detected.

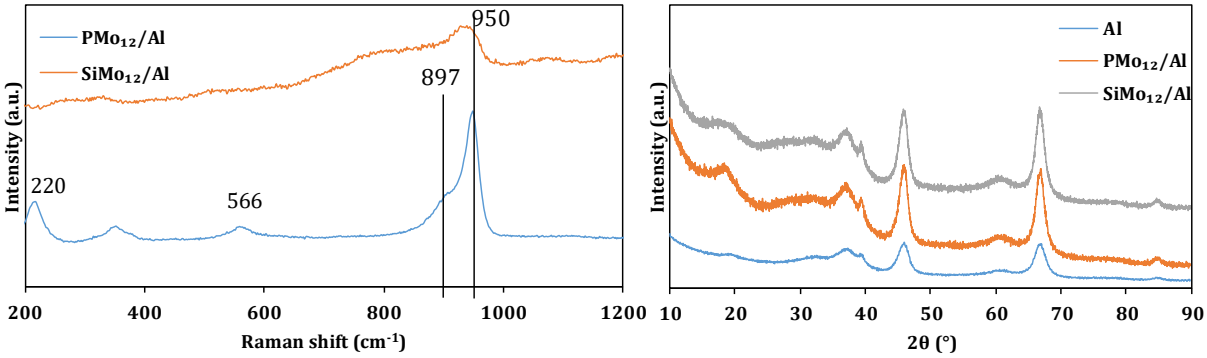

Figure V.6: Raman spectra (A) and XRD patterns (B) of $SiMo_{12}$ or PMo_{12}/Al.

The oxidation activity of the synthesized HPA based catalysts was evaluated in the ODS of IFO500-DC fuel and compared to that of 20Mo/Al. Table V.3 shows the results of the Cx-BTs and DBT conversions, as well as sulfur removal percentage.

Table V.3: Conversion of Cx-BTs, DBT molecule and desulfurization rates of oxidized IFO500-DC using 20 PMo_{12}, 20 $SiMo_{12}$ or 20 Mo/Al (H_2O_2/S=3, T=80°C, t=60 min).

Catalyst type	Conversion Cx-BTs(%)	Conversion DBT(%)	Desulfurization rate (%)
20 PMo_{12}/Al	30	62	50
20 $SiMo_{12}/Al$	25	54	56
20 Mo/Al	35	65	62

Results indicate that the catalysts prepared from HPA lead to slightly lower activities compared to that of 20 Mo/Al with total conversion of Cx-BTs decreasing from 35 to 30% with PMo_{12} and 25% with $SiMo_{12}$. DBT conversion declined from 65% to 62% (PMo_{12}) or 54% ($SiMo_{12}$). Total sulfur elimination after extraction was the highest with 20 Mo/Al with a total sulfur content

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reduced from 16000 to 6000 ppm, whereas for HPA based catalysts, sulfur elimination was reduced to 6900 ppm ($SiMo_{12}$) and 8000 ppm (PMo_{12}).

In our case, the addition of P as promotor or the use of Mo based HPA containing phosphorus did not enhance desulfurization results when compared to 20 Mo/Al.

V.1.4. Peroxocomplexes supported on alumina

The mechanism of oxidative desulfurization reaction using MoO_3/Al_2O_3 described in the work of Akbari *et al.*, García-Gutiérrez *et al.* and Abdullah *et al.* [2,14,16] indicates that the reaction pathway initially goes through the nucleophilic attack of H_2O_2 on Mo=O which was found on catalyst surface to form peroxo species. The oxidation process of DBT must proceed by nucleophilic attack of the sulfur by the positively charged peroxometallic complex to form first DBT sulfoxide and further regenerated polymolybdate species. Subsequently, the sulfoxide undergoes further oxidation to form corresponding sulfone. In all the mechanisms reported, formation of peroxomolybdate fragment on the catalyst surface is a key step that must be proceeded in order to generate corresponding sulfoxides and sulfones. To generate peroxo entities favoring ODS activity, the synthesis of peroxomolybdates supported on alumina was executed. The synthesis was carried out by reaction between hydrogen peroxide and molybdenum oxide MoO_3 leading to the formation of peroxomolybdenum intermediates. In the preparation protocol indicated in experimental section, the calcination step was not carried out with peroxo compounds to avoid transformation of peroxo species. Moreover, since these entities seem to be dependent on treatment temperature, to examine the effect of heating on catalyst stability, ODS reaction was carried out on maturated and dried catalyst. Catalyst characterization on maturated and dried catalyst as well as reaction results are detailed in the next section.

Raman analysis of the peroxo/Al_2O_3 catalyst maturated and dried was performed. The spectra are shown in Figure V.7. Raman spectrum of maturated catalyst shows a main line at 980 cm^{-1} with a line at 540 cm^{-1} both attributed to the formation of dimeric peroxomolybdate entities $Mo_2O_3(O_2)_4^{2-}$ [26]. The band at 883 cm^{-1} corresponds to the presence of free H_2O_2 in solution by reference to the literature [19]. The lines at 330 and 570 cm^{-1} are not attributed yet. In the dried sample the large Raman line 960 cm^{-1} suggests the formation of polymobdate species however the presence of the line at 570 cm^{-1} could indicate the formation of Anderson heteropolyanionic $AlMo_6$ species. The evolution of the peroxo entities is related to the drying of the sample suggesting that peroxo species are not stable at this temperature. As the use of HPA as molybdenum precursor, the use of peroxo species induces after drying the formation of well-dispersed Mo entities without MoO_3 formation.

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ODS test was performed on both catalysts. The results of the ODS tests performed with these catalysts are shown in Figure V.8. Dried Peroxo/Al gave comparable performance (35% Cx-BTs and 60% DBT) to 20 Mo/Al catalyst prepared from polymolybdates. The dried catalyst contains polymolybdates very similar to that present in the conventional Mo/Al catalyst without other element as Si or P, which could explain the catalytic activities very comparable, even if the conventional catalyst a part of molybdenum was forming MoO_3 particles as evidenced by Raman and XRD.

The maturated catalyst gave a 10% conversion of Cx-BTs instead of 35% and 50% instead of 60% for DBT when compared to the dry peroxo/Al. The presence of initial peroxo species does not allow to obtain better catalysis results and the less efficiency observed could be related to the presence of water in the pores unfavorable to the ODS catalytic activity.

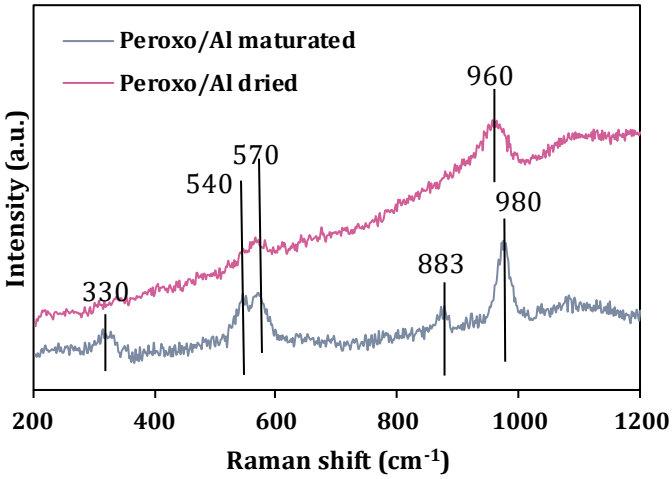

Figure V.7: Raman spectra for peroxo/Al after maturation and after drying.

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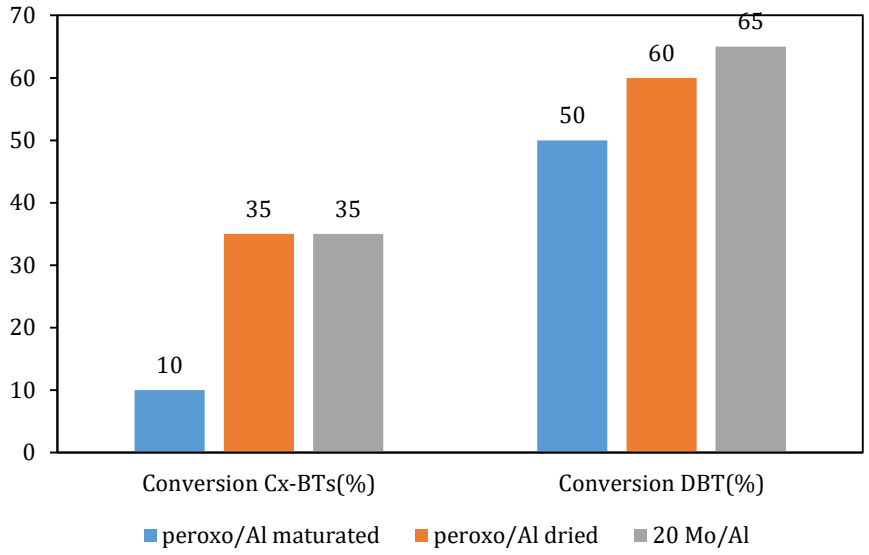

Figure V.8: Conversion of Cx-BTs and DBT in the ODS of IFO500-DC using peroxo/Al aged or dried and 20 Mo/Al (H_2O_2/S=3, T=80°C, t=60 min).

V.2. Titanium based catalysts for ODS reaction

Large amount of research was devoted to titanium based catalysts for ODS reaction [27–34] due to TiO_2 nanoparticles high activity for various oxidation reactions at low pressures and temperatures. Furthermore, TiO_2 was found to be a good metal oxide catalyst support due to the strong metal support interaction, chemical stability, and acid-base property. Titanium based catalysts in all its forms have attracted much attention. For instance, they proved high activity and stability of the molybdenum active phase on this support rather than on γ-Al_2O_3 in the ODS of model feed and light cycle oil [35].

However, TiO_2 supports usually have small specific surface area compared to alumina. This means that a higher amount of molybdenum oxide can be dispersed on alumina rather than on titania. Subsequently, the enhancement of activity brought by the use of titania is diminished by the poor textural properties of this support.

With progress made with mesostructuration procedures, mesoporous TiO_2 with higher surface areas than usual TiO_2 and open porosities can be nowadays commercially available. This opens new opportunities for the development of highly active catalysts in oxidative desulfurization. The objective of the present study is to examine the interest of titanium not only as a support for molybdenum oxide species in ODS but also as a catalyst in itself.

In order to examine the influence of the surface area, seven different samples of titanium oxide were studied as reported in Table V.4: four different commercial pure TiO_2 (named **DT-51,**

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TiO_2, HPX-100, G5-GRVS according the industrial supplier) and three composite titanium supports containing 5 wt.% silica **(MC-500)** and 5 or 10 wt.% tungsten (**DT-W5** and **DT-52** respectively). Textural properties determined for each support are presented in Table V.4. For supports containing only TiO_2, surface areas vary between 90 and 400 $m^2.g^{-1}$. TiO_2 based supports containing Si or W have a similar specific surface area of 90 $m^2.g^{-1}$. The pore size distribution range is high and fluctuates between 4.7 and 14.8 nm. The porous volume evaluated by N_2 adsorption varied between 0.33 and 0.49 $cm^3.g^{-1}$. Water porous volume that is an essential factor in the preparation by dry impregnation of aqueous solutions is more important from 0.5 to 1 $cm^3.g^{-1}$, indicating that the maximum active phase content which can be deposited in a single impregnation vary between 15 and 25 MoO_3 wt.%.

XRD patterns of supports presented in Figure V.9 clearly present diffraction peaks assigned to anatase phase with 2θ values equal to 25.4, 37.9, 48, 53.8 and 55.2°.

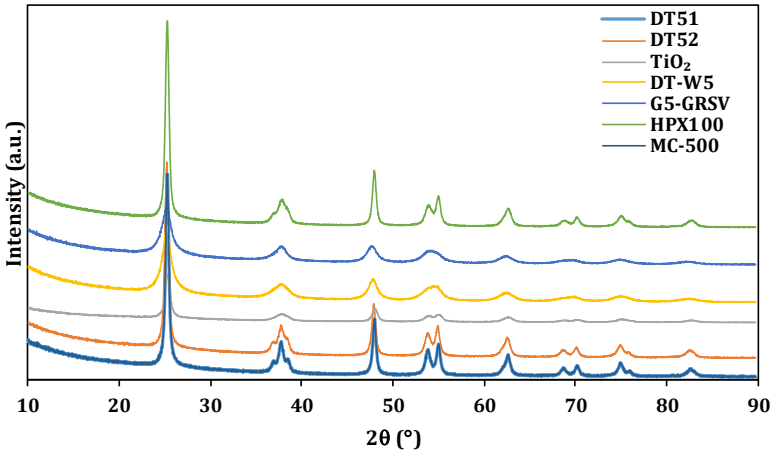

Figure V.9: XRD patterns of DT-51, DT-52, TiO_2, DT-W5, MC500, G5-GRSV and HPX-100.

Table V.4: BET surface area, composition, porous volume and mean pore diameter of different titanium supports.

	BET surface area ($m^2.g^{-1}$)	Composition (wt.%)	Porous volume ($cm^3.g^{-1}$)	Mean pore diameter (nm)	Water porous volume ($cm^3.g^{-1}$)
DT-51	90	TiO_2	0.37	13.0	0.8
MC-500	90	95% TiO_2, 5 % Si	0.33	11.5	1.0
DT-W5	90	95%TiO_2, 5 % W	0.35	13.0	0.6
DT-52	90	90% TiO_2, 10 % W	0.39	4.7	0.5
TiO_2	120	TiO_2	0.39	8.3	0.7
HPX-100	250	TiO_2	0.49	14.8	0.6
G5-GRVS	400	TiO_2	0.40	14.6	0.7

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V.2.1 ODS performance using titanium supports

ODS performance was evaluated for the different titanium based commercial supports using IFO380-DC with same reaction conditions as indicated previously. Conversion results of Cx-BTs and DBT are reported in Table V.5.

Table V.5: Different titanium based supports with conversion results of Cx-BTs and DBT in the ODS of IFO380-DC.

	Conversion Cx-BTs (%)	Conversion DBT (%)
20 Mo/Al	58	76
DT-51	35	68
MC-500	34	67
DT-W5	28	33
DT-52	12	16
TiO_2	35	68
HPX-100	22	30
G5-GRVS	32	55

Titanium based support alone without molybdenum showed effective performance in ODS reaction. For pure TiO_2 solids, conversion of Cx-BTs reached up to 35% and conversion of DBT attained 68% using DT-51 or TiO_2, showing a lower efficiency than that of 20 Mo/Al catalyst (58 % Cx-BTs and 76 % DBT). Unexpectedly, an increase of the surface area of the titania support has not a beneficial effect on ODS reaction because HPX-100 with a surface area of 250 gives a conversion of 30% DBT, 22% Cx-BTs, and G5-GRSV with 400 $m^2.g^{-1}$ gives 32% Cx-BTs and 55% DBT. A high surface area is not an advantage considering titania support. However, Cedeno-Caero *et al.* [36] compared the activity of two different titanium oxides, titanium oxide nanotube (TiNC) with 298 $m^2.g^{-1}$ surface area and TiH with 120 $m^2.g^{-1}$ surface area, in the ODS of DBT using H_2O_2 as oxidant. After 60 min reaction, DBT sulfone yield was 100% with TiNC versus 60% with TiH. The authors associated the result to the capability of the catalyst to decompose H_2O_2 and form the appropriate Ti-peroxo intermediate that renders the reactive oxygen species for the oxidation of the sulfur compound (DBTs) to the corresponding sulfone. In their case, the TiO_2 system with the highest surface area was the most active. Among mixed supports, MC-500 having 5 wt.% Si showed comparable performance as the best TiO_2 catalysts from our series. When the quantity of Si increased to 10 wt.%, conversions of Cx-BTs decreased slightly from 35 to 28% and sharply from 68% to 30% for DBT. Support DT-52 containing 10 wt.% WO_3 tungsten showed the worst conversion results, 12% Cx-BTs and 16% DBT, suggesting that when tungsten is added at 10%, its presence on the surface could decrease the available TiO_2 surface species, preventing ODS

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reaction. More importantly, this catalyst presents the smallest pore diameter (4.7 nm), which can be detrimental to transfer of heavy molecules present in marine fuels.

V.2.2 ODS performance using Mo impregnated on titanium supports

V.2.2.1 ODS results of IFO380-DC using 15 Mo supported on various titanium supports

Among titanium based supports with specific surface area of 90 $m^2.g^{-1}$ (DT-51, DT-52, MC500 and DT-W5) DT-51 had the highest activity, therefore it was chosen for Mo impregnation. To study the effect of the support surface area on Mo supported catalysts, TiO_2, HPX and G5-GRSV were also selected from the previous series, even if HPX and G5-GRSV had low conversion used as prepared. In fact, these supports with very high surface area could ensure a good dispersion of molybdenum, thus favoring oxidation results.

Since water pore volumes of the supports were different, we have chosen to impregnate 15 wt.% MoO_3 as a standard percentage. Raman spectra of the initial support and of its corresponding Mo impregnated one are presented in Figure V.10. Whatever the titania support, the main lines at 638, 517 and 396 cm^{-1} together with the small line around 800 cm^{-1} are assigned to the anatase structure in agreement with previous XRD analysis of the support. Both catalysts 15 Mo/DT-51 and 15 Mo/HPX100 show large peak at 966 cm^{-1} assigned to polymolybdate species that corresponds to octahedral molybdenum species. The Raman spectrum of the Mo catalyst prepared from G5-GRVS does not present typical peak of polymolybdate probably due to the large specific area (400 $m^2.g^{-1}$) inducing large dispersion of Mo. Results of conversion for the different supports in the ODS of IFO380-DC are indicated in Table V.6.

Table V.6: Conversion of Cx-BTs and DBT in the ODS of IFO380-DC using different Mo/Ti catalysts (H_2O_2/S=3, T=80°C, t=60 min).

Catalyst	Conversion Cx-BTs (%)	Conversion DBT (%)
15 Mo/DT-51	28	54
15 Mo/TiO_2	29	40
15 Mo/HPX-100	19	43
15 Mo/G5-GRVS	35	56

Titania supported molybdenum catalysts showed effective oxidation. The highest activity was obtained using 15 Mo/G5-GRVS where conversions of Cx-BTs and DBT were respectively 35 and 56% but similar to that of the support alone. ODS activity of 20 Mo/Al was still higher with 50% conversion of Cx-BTs and 70% conversion of DBT indicating that Mo is more active when

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alumina is used as support rather than titanium. DT-51 and TiO_2 exhibited better activity when they were used without molybdenum. Conversions decreased from 35 to 28% for Cx-BTs, 68 to 54 % for DBT with Mo/DT-51 and from 35 to 29% (Cx-BTs) and from 60 to 40% (DBT) with Mo/TiO_2. Despite that Mo is an active phase in ODS reaction, TiO_2 supports without Mo exhibited better oxidation results. No reported work in the literature compared ODS activity between supported and non-supported titanium with molybdenum. More often, comparison between several supports were performed for Mo based catalysts: it has been reported in the work of Wang *et al.* [1] dealing with ODS of DBT in kerosene at 110°C using oxygen as oxidant, that Mo catalysts supported on SiO_2–Al_2O_3 and TiO_2 show lower oxidation activity compared with that supported on Al_2O_3. Cedeno Caero *et al.* [37] examined the support effect in the ODS of model molecule DBT using H_2O_2 as oxidant and showed that titania support had very low activity, but when vanadia was dispersed on it, an important increase in ODS activity was noticed. Nevertheless, in the same work, authors compared the activity of vanadia on various supports. Total S-removal was close to 99% using vanadia as catalyst and decreased according to the support used in the next order: alumina > titania, they accounted the result to the difference in polarity of the V–O bond on different supports. Since there are fewer unsaturated sites in TiO_2 compared with Al_2O_3, it can be inferred that a lower polarity of V-O bond was obtained on TiO_2, leading to lower oxidation activity.

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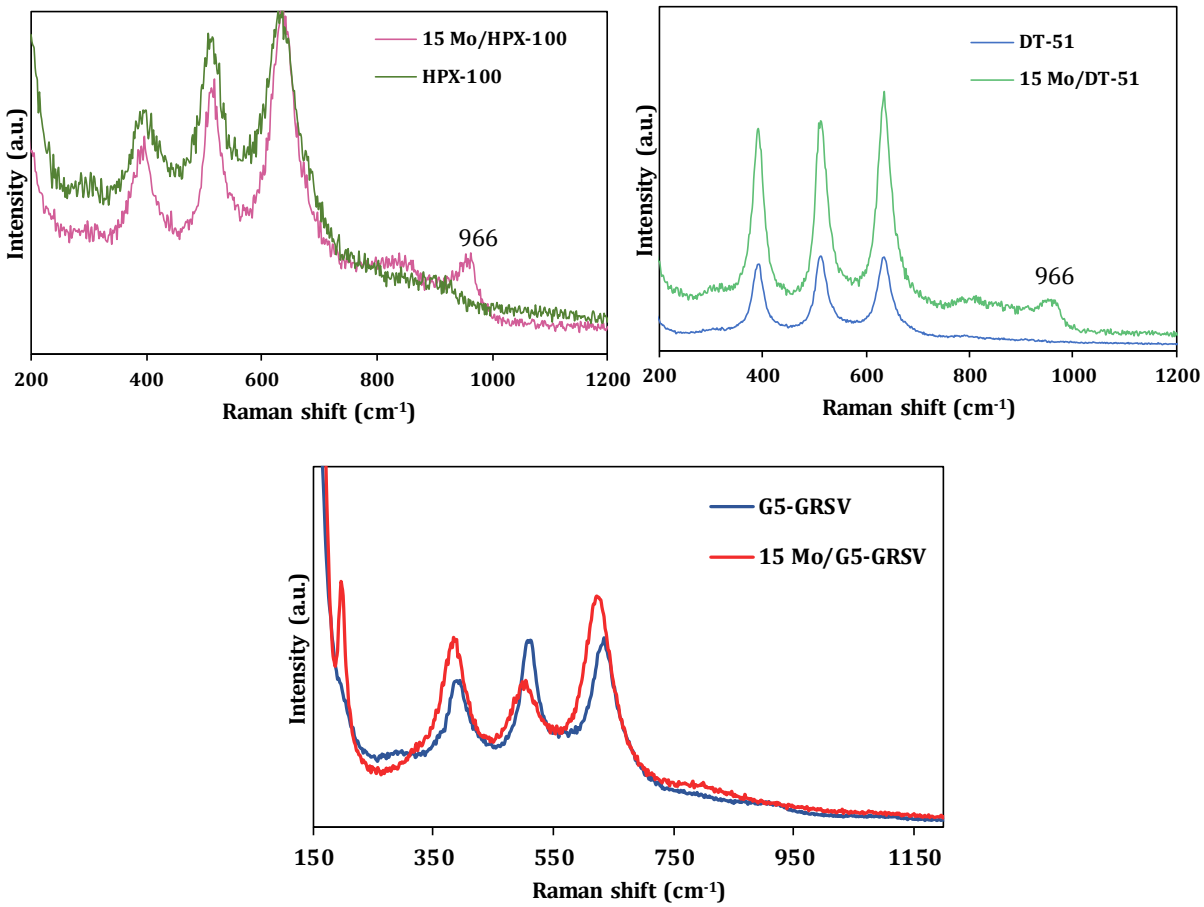

Figure V.10: Raman spectra of (A) HPX and 15 Mo/HPX-100 (B) DT-51 and 15 Mo/DT-51 (C) G5-GRSV and 15 Mo/G5-GRSV.

V.2.2.2 Influence of titania (DT-51) Mo loading on activity

DT-51 support exhibited high activity without any active phase. Since molybdenum is an active phase efficient in ODS, it was expected higher desulfurization rates when Mo was dispersed on titanium but improved catalytic performances were not observed for the 15 Mo wt.% supported corresponding catalyst. Considering the relative small surface area of this support (90 $m^2.g^{-1}$) compared to that of alumina, a loading of 15 Mo wt.% induces an important atomic density of molybdenum equal to 8.2 $at.g^{-1}$, higher than the density of Mo dispersed on alumina when using 20 wt.% (5.9 $at.g^{-1}$). Lower loading of Mo was thus tried on this support for comparison purpose. Mo was impregnated on DT-51 with two other percentages of MoO_3. Same atomic density on DT-51 than on Al_2O_3 was reached by synthesis of 10 wt.% Mo/DT-51. Furthermore, 5 wt.% Mo/DT-51 was also synthetized to complete the study of the effect of molybdenum loading. ODS results of IFO380-DC using these catalysts are reported in Table V.7. The variation of molybdenum content has a moderate effect on conversions of Cx-BTs and DBT

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molecule. When Mo loading decrease from 15 to 10 wt.%, conversion of Cx-BTs remains 28-29%, as for DBT, conversion changes from 54% to 60%. 5 Mo/DT-51 exhibited the same activity as 10 Mo/DT-51 with conversion of Cx-BTs (28%) and DBT (58%). Despite the increase in the conversions with decreasing Mo loading, DT-51 support as catalyst alone kept still the highest activity disabling us to combine TiO_2 support with molybdenum. Moreover, 10 Mo/DT-51 contains the same atomic density of molybdenum per nm^2 of support as 20 Mo/Al, allowing a direct comparison between the use of the two supports. Our results indicate that the efficiency of Mo evidenced on alumina support cannot be preserved on titania, this support acting itself as active phase.

Table V.7: Conversion of Cx-BTs and DBT in the ODS of IFO380-DC as a function of wt.% MoO_3/Al_2O_3.

Catalyst	Conversion Cx-BTs (%)	Conversion DBT (%)
15 Mo/DT-51	28	54
10 Mo/DT-51	29	60
5 Mo/DT-51	28	58

V.3. Exploration of other supports of Mo based catalysts

In order to improve the catalytic activity of supported molybdenum catalysts, several catalysts containing molybdenum were prepared by impregnation of ammonium heptamolybdate (AHM) solution on various supports. The dispersion of molybdenum oxide, its oxidation state and structure strongly depends on support. It was interesting to explore the performance of ordered mesoporous silica materials, as well as zirconia and mixed oxides reported in literature as efficient supports for ODS reaction [38,39].

V.3.1. 10 Mo/Zr

Zirconia received considerable attention as a support in catalysis due to its thermal stability, basic/acidic properties, reducing and oxidizing surface properties. All these properties make zirconia application appealing in different reactions [38,40–43]. Zirconia has been used as support in oxidation of alcohols [40], synthesis of methanol [41] and also in oxidative desulfurization reaction [44,45]. Unlike alumina, zirconium dioxide is not studied in depth in oxidation. In this work, molybdenum supported on zirconia was investigated using a commercial support shaped in cylindrical extrudates with a diameter of about 1.5 mm with monoclinic

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tetragonal structure. Water porous volume of the support was 0.6 $mL.g^{-1}$ and taking into account the AHM solubility, the synthesis of 10 wt.% Mo/Zr was applied.

The XRD patterns of zirconia support and synthetized 10 Mo/Zr presented in Figure V.11 confirm the supplier data concerning the crystallographic structure encountered for zirconia. XRD pattern of the support shows diffraction peaks characteristic of a mixture of monoclinic and tetragonal phases. A similar diffraction pattern is obtained for10 Mo/Zr catalyst, MoO_3 peaks are not observed, which indicates a good dispersion of molybdenum on the support.

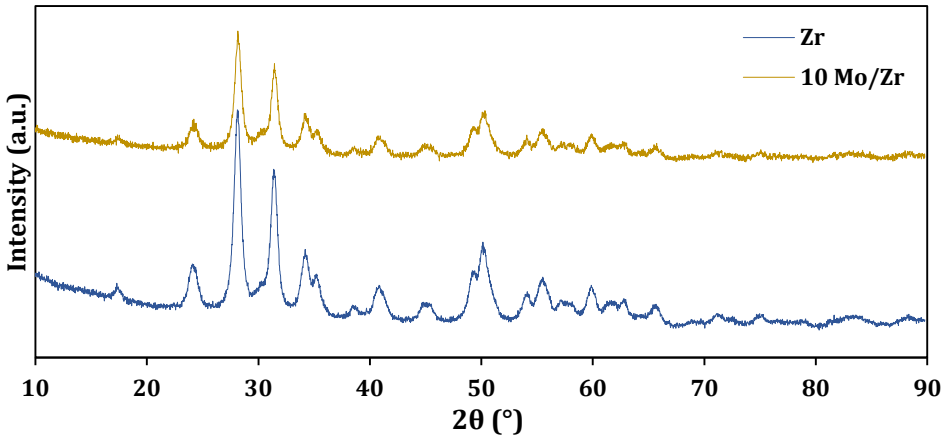

Figure V.11: XRD patterns of Zr and synthetized 10 Mo/Zr.

According to Table V.8, commercial zirconia has low specific surface area (<100 $m^2.g^{-1}$) and porosity. after impregnation of molybdenum, specific surface area of support remains almost the same, the pore volume and the average pore diameter as well, in agreement with a dispersion of molybdenum species on zirconia surface.

The distribution of pores for Zr and 10 Mo/Zr are presented in Figure V.12. Zr shows bimodal distribution with a small part of the pores centered around 4 nm and another ranging from 6 to 22 nm. Even if a part of the smallest pores (around 4 nm) is affected by Mo impregnation, the pore size distribution is preserved for the catalyst.

Table V.8: Textural properties of ZrO_2 and 10 Mo/Zr catalysts.

Catalyst	Surface Area ($m^2.g^{-1}$ catalyst)	Surface Area ($m^2.g^{-1}$ support)	Pore volume ($cm^3.g^{-1}$)	Average pore diameter (nm)
Zr (support)	96	96	0.3	9
10 Mo/Zr	88	96	0.27	7.9

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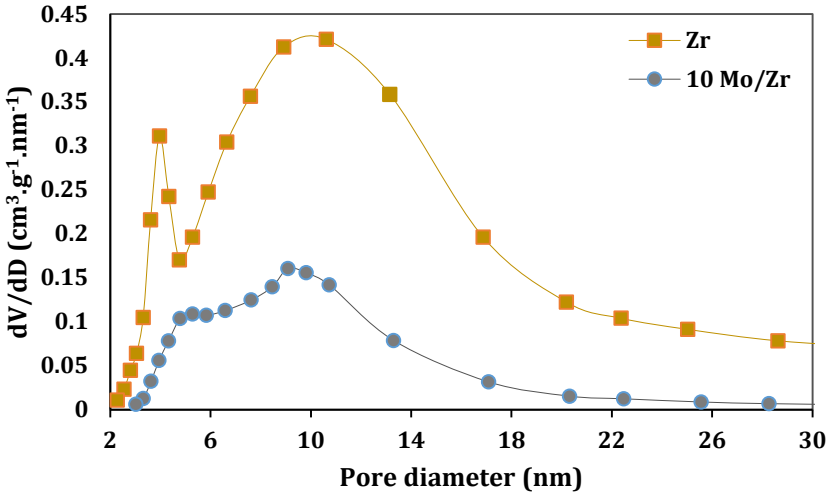

Figure V.12: BJH pores distribution of Zr and 10 Mo/Zr.

Figure V.13 shows the comparison between Raman spectra of zirconia and 10 Mo/Zr. For the Mo supported catalyst, together with the Raman lines assigned to zirconia, the large line at 960 cm^{-1} is ascribed to the dispersed polymolybdate phase, and more precisely to the (Mo = O) terminal vibration of the octahedrally coordinated polymeric molybdate. The large line at lower shift around 850 cm^{-1} is attributed to (Mo-O-Mo) vibration in polymeric molybdate [5,38,46]. Similar results are reported in the study of Chen *et al.* [46] on Mo supported on monoclinical zirconia Zr catalysts containing Mo contents of 11 wt.%.

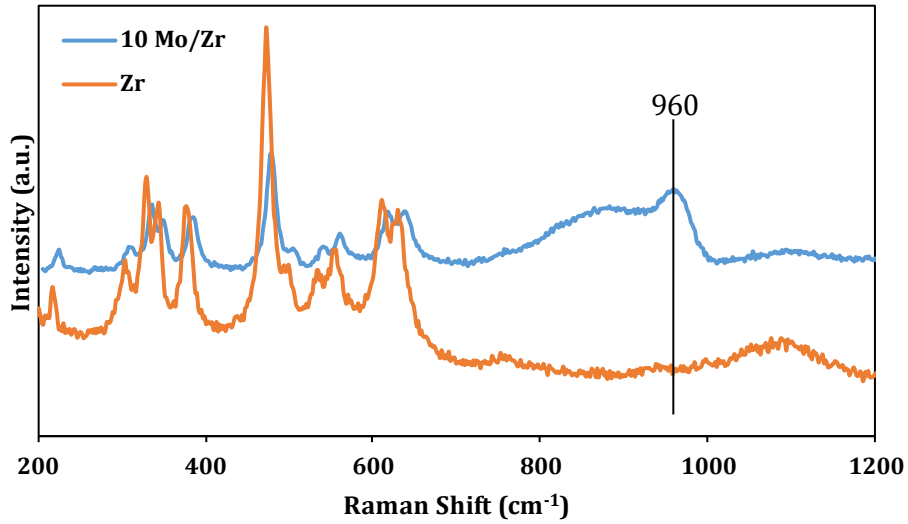

Figure V.13: Raman spectra for 10 Mo/Zr.

ODS reaction was performed on IFO500-DC. Conversion of Cx-BTs and DBT are monitored with no ODS activity obtained. Though we have already faced problems with diffusion of molecules and mixing conditions of fuels with oxidizing agents using 20 Mo/Al, it was impossible

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to obtain ODS reaction with 10 Mo/Zr, despite increasing rate of stirring speed as well as ensuring good position of magnetic stirrer inside the medium. To avoid possible diffusion limitation due to cylindrical extrudates with thick diameter, this catalyst was further crashed and used in powder form. However, still no ODS conversion was obtained.

V.3.2. 8 Mo/Ce

Cerium oxide has interesting redox properties and it is known for its capacity to store oxygen. This capacity is linked to the ability of the material to exchange oxygen reversibly with the medium. Thus, cerium oxide can capture oxygen in oxidizing medium and release it in reducing medium [47,48]. Cerium oxide was synthetized according to the protocol described in experimental section. Textural properties of the synthesized support are presented in Table V.9.

Table V.9: Textural properties of synthetized cerium oxide via ammonia precipitation.

Support	Specific Area ($m^2.g^{-1}$)	Porous Volume ($mL.g^{-1}$)	Mean pore diameter (nm)	Maximum quantity to be impregnated MoO_3 (wt.%)
CeO_2-PP	160	0.28	5.4	8.6

Due to the low water porous volume of the support (0.6 $mL.g^{-1}$), the synthesis of 8 wt.% MoO_3/Ce was applied. Diffraction patterns of CeO_2 and 8 Mo/Ce presented in Figure V.14.

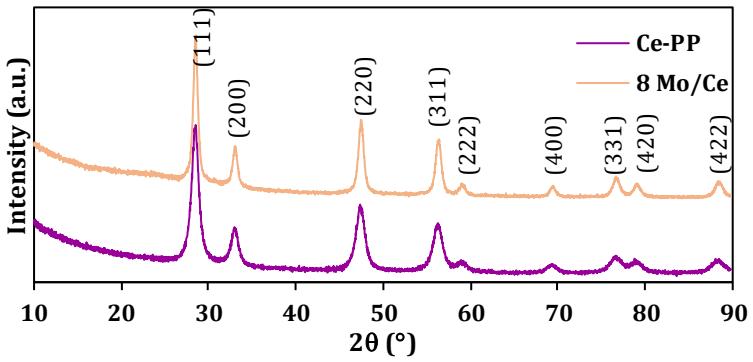

Figure V.14: High angle XRD patterns for Mo/Ce and Ce

The same diffraction pattern is obtained for both solids and the diffraction peaks can all be indexed to the CeO_2 phase. It is a face centered cubic fluorine (CaF_2) structure in which each metal cation is surrounded by eight oxygen atoms. No diffraction peaks of molybdenum are observed in Mo/CeO_2 catalyst indicating high dispersion of molybdenum species.

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Raman spectra of 8 Mo/Ce is displayed in Figure V.15. The typical band located at 461 cm^{-1} is assigned to the first order vibrational mode with F_2 symmetry in a cubic fluorite-type structure. This band essentially results from a symmetrical stretching vibration of the oxygen atoms enclosed cerium ions, and the second order band is present at 1190 cm^{-1} ascribed to the transverse acoustic 2TA mode and longitudinal optical (2LO) mode, respectively [49]. Raman spectra of 8 Mo/Ce does not show any band corresponding to MoO_3 indicating well dispersed Mo on the surface of cerium in agreement with XRD data

ODS reaction performed on IFO500-DC using 8 Mo/Ce was not effective, no sulfone appeared.

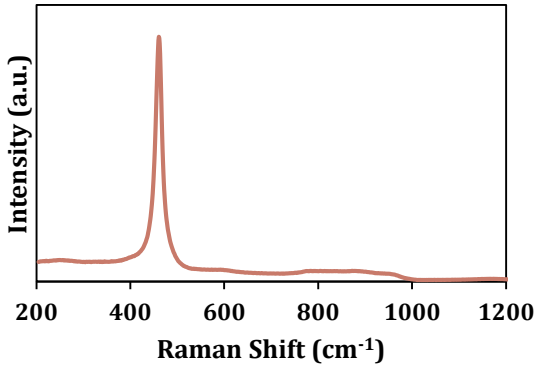

Figure V.15: Raman spectra of synthetized 8 Mo/Ce.

V.3.3. 15 Mo/ASA

Another type of composite supports has been explored in the ODS of marine fuels. In 2008 Prasad et al [39] observed that Mo/SiO_2-Al_2O_3 gives higher activity compared to Mo/Al_2O_3 in ODS of LCO containing 8000 ppmS. The authors proposed that it may be due to the change in acidic properties of the support. Siral SiO_2–Al_2O_3 being more acidic compared to Al_2O_3 alone, could have led to stronger Mo-support interactions in Siral supported catalysts. Taking into account this result, we used an industrial support prepared by "co gel" method containing 90 wt.% of SiO_2 and 10 wt.% Al_2O_3, known as Amorphous Alumina Silica (ASA) support. This support is in the form of ovoid grains with an average size of 4 mm. The textural characteristics of the ASA support are summarized in Table V.10. The pore diameter distribution is narrow with an average diameter of about 50 Å characteristic of mesopores as displayed in Figure V.16. Based on water pore volume of ASA support (0.67 $cm^3.g^{-1}$), 15 wt.% MoO_3/ASA (15 Mo/ASA) was synthetized.

Table V.10: Textural properties of silica-alumina support.

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Catalyst	Surface Area ($m^2.g^{-1}$)	Pore volume ($cm^3.g^{-1}$)	Average pore diameter (nm)
ASA	400	0.67	4.5

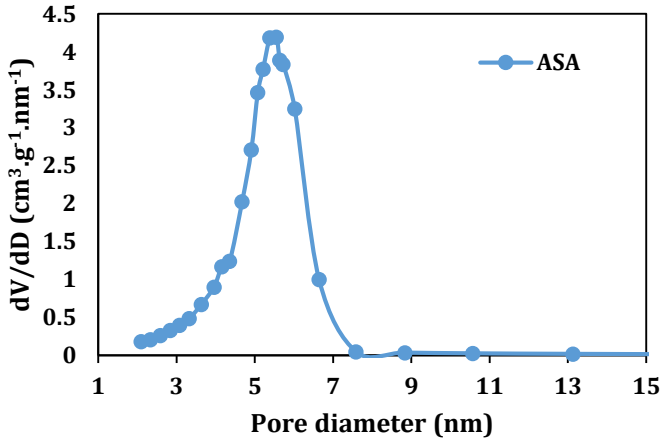

Figure V.16: BJH pores distribution of ASA.

Several grains were analyzed by Raman spectroscopy, presenting two different Raman spectra as reported in Figure V.17. Some Raman spectra are characteristic of MoO_3 crystallites with two intense peaks at 995 and 820 cm^{-1} while some grains (about 4 out of 10 grains) showed only well dispersed polymolybdates with a typical peak at 960 cm^{-1}. ODS reaction was performed on IFO500 however no desulfurization results using Mo/ASA were obtained whatever the use of the shaped catalyst or the powder form obtained after crushing.

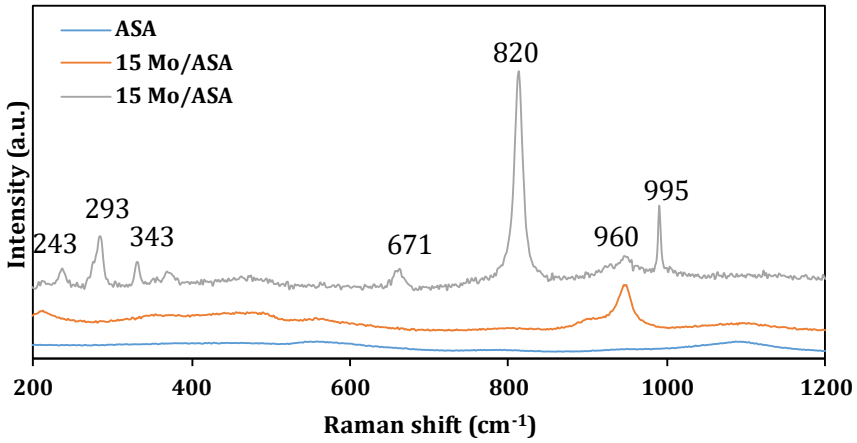

Figure V.17: Raman spectra of ASA support and synthetized 15 Mo/ASA.

V.3.4. ODS on straight run gas oil diesel SRGO

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Despite that 8 Mo/Ce, 10 Mo/Zr and 15 Mo/ASA characterization showed well dispersed molybdenum on the surface of supports, no desulfurization results were obtained using marine fuels. In the case of both shaped catalysts 10 Mo/Zr and 15 Mo/ASA, ODS reaction of crushed catalyst in powder form was assessed with no effective reaction. Literature review indicates good performance of these catalysts in the ODS of model molecules and real feeds such as hydrotreated diesel containing low sulfur amount <1000 ppm or SRGO fractions. However, no reports on the ODS on marine fuels was proposed.

Interpretation of characterization results makes it difficult to identify the problem behind the non-effectiveness of these catalysts. To make sure that synthetized catalysts are suitable for oxidation reactions but not particularly for marine fuels, the catalysts were tested in the ODS of straight run gas oil SRGO containing 1 wt.% S using same conditions applied on IFO500-DC (H_2O_2, Ox/S=3, 80°C). ODS reaction was effective. Conversions of Cx-BTs and DBT were further calculated and illustrated in Table V.11. In the case of SRGO, conversion of Cx-BTs is comparable with DBT. On the contrary to ODS of fuels, reactivity of both of families are almost the same. These results could be correlated to the difference in total nitrogen content where SRGO fraction contain less than 200 ppm of N compared to marine fuels that contain up to 3500 ppm of N. Highest conversions were found with 20 Mo/Al (60 % Cx-BTs and 57% DBT). Conversions decreased in the following order: 20 Mo/Al>10 Mo/Zr>8 Mo/Ce>15 Mo/ASA showing that even if these catalysts are efficient for diesel fractions, they show lower performance when compared to 20 Mo/Al. In agreement with our results, it has been reported that Mo catalysts supported on SiO_2-Al_2O_3 show lower oxidation activity compared to that supported on Al_2O_3 [1]. Similarly, our result can be explained by the difference of the polarity of Mo-O bond on different supports or the low Mo loading (8 wt.% MoO_3) in the case cerium based catalyst [1].

Table V.11: Conversion of Cx-BTs and DBT in ODS of SRGO using different Mo based catalysts.

Catalyst	Conversion Cx-BTs (%)	Conversion DBT (%)
20 Mo/Al	60	57
15 Mo/Asa	41	35
10 Mo/Zr	50	45
8 Mo/Ce	45	42

V.3.5. 20 Mo/COK-12

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The use of mesoporous silica supports such as SBA-15 and MCM-41 also has been indicated as beneficial because of their specific large surfaces, their high and controllable porosity and narrow pore size distribution. Different types of mesoporous silica have been explored with different pores organizations. For instance, a two-dimensional hexagonal phase (MCM-41), a cubic phase (MCM-48) and several lamellar phases, in particular the MCM-50 which are reported to be thermally stable. Since the first discovery of mesoporous materials FSM-16 and M41S, other phases such as SBA-n, HMS-n, KIT-n, FDU-n and AMS-n have been reported. Recently, Jammaer et al [50] have reported facile room temperature and quasi neutral pH synthesis of p6m ordered mesoporous silica COK-12.

Inspired by the submicron sized thin platelet morphology, COK-12 was chosen to be tested as support in the ODS of marine fuels. COK-12 support has a 2D hexagonal structure in platelet form with short, straight pores allowing easier diffusion of heavy molecules inside marine fuel. The diffraction patterns at low and high angles of synthetized COK-12 support and calcined 20 Mo/COK-12 catalysts are shown in Figure V.18. The COK-12 support calcined shows a very intense and well resolved diffraction peak at 0.82° indexed to reflection (100). The second peak, observed at values 1.43° is of low intensity and corresponds to the reflections (110). As reported in the literature, the observed peaks (100), (110) are indexed according to the hexagonal symmetry p6m [50].

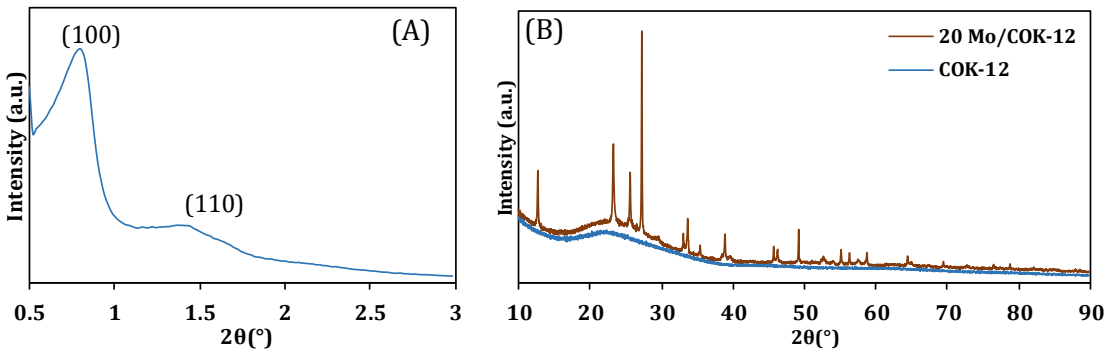

Figure V.18: (A) Low angle XRD pattern of COK-12. (B) High angle XRD patterns of COK-12 and 20 Mo/COK-12.

High angle XRD pattern of the Mo catalyst indicates the presence of MoO_3 crystallites peaks with reflexions centered at 2θ= 12.9, 23.7, 25.8, 27.4 and 49.4°. Textural properties of COK-12 and 20 Mo/COK-12 are presented in Table V.12. COK-12 possesses interesting textural properties with a high BET surface area around 500 $m^2.g^{-1}$ and average pore diameter of 6.6 nm with a pore volume close to 1 $cm^3.g^{-1}$.

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Table V.12: Textural properties of COK-12 and 20 Mo/COK-12.

Catalyst	Surface Area ($m^2.g^{-1}$)	Pore volume (cm^3/g)	Average pore diameter (nm)
COK-12 (support)	498	0.94	6.6
20 Mo/COK-12	455	0.9	6.1

We impregnated only 20 wt.% Mo. Textural analysis showed slight decreases in the specific surfaces of catalysts from 498 to 455 $m^2.g^{-1}$. Porous volumes vary little and pore diameters remained unchanged with the increase in the active phase content. In the study of Pochamoni *et al.* [51], the impregnation of 18% MoO_3 resulted in a 55% decrease in the BET surface of the COK-12 support.

Nitrogen adsorption-desorption loops and BJH distribution of COK-12 and 20 Mo/COK-12 are displayed in Figure V.19.

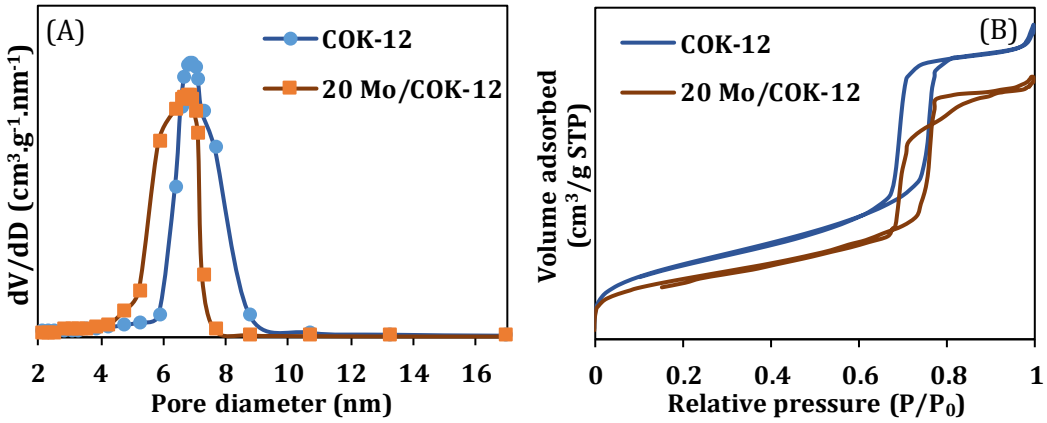

Figure V.19: (A) BJH distribution for COK-12 and 20 Mo/COK-12. (B) Nitrogen adsorption-desorption loops for of COK-12 and 20 Mo/COK-12

Nitrogen adsorption revealed type IV isotherms with type H1 hysteresis characteristic of materials with open cylindrical mesopores with a narrow pore size distribution. It presents bimodal pore size distribution structure with close pores sizes, one centered around 7 nm and another around 8 nm. Upon addition of Mo, the resulting catalyst maintained type IV isotherm with monomodal porosity with a narrow pore size distribution centered at 6 nm.

Figure V.20 presents Raman spectrum of 20 Mo/COK-12. Same Raman spectra were obtained in the analysis of different catalyst grains. Raman pics at 243, 293, 343, 671, 820 and 995 cm^{-1} were observed which are characteristic of MoO_3 crystallites.

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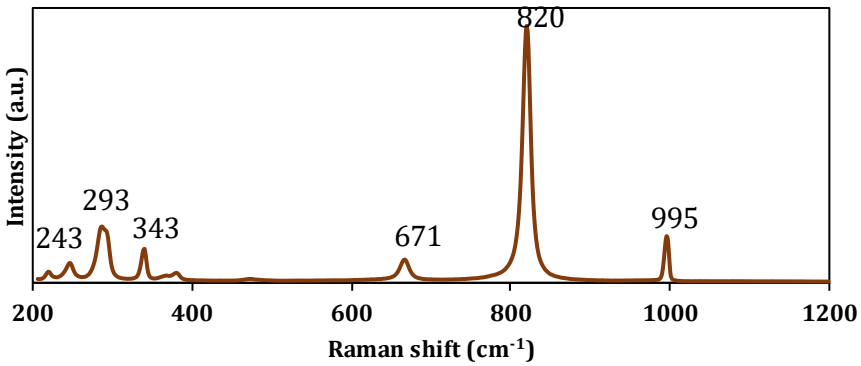

Figure V.20: Raman spectra of 20 Mo/COK-12.

Similarly, ODS reaction was evaluated on IFO500-DC. 20 Mo/COK-12 was compared to 20 Mo/SBA-15 a catalyst already prepared in our group and to 20 Mo/Al that gives the best results in our study until now. Among the mesoporous support, SBA-15 is largely used and possesses a 2D hexagonal distribution and uniform cylindrical mesopores while COK-12 has a 2D hexagonal platelet structure with short, straight pores. Conversion results of these three catalysts are displayed in Table V.13.

Table V.13: Conversion of Cx-BTs and DBT in ODS of IFO500-DC using 20 Mo supported on COK-12, SBA-15 and Al (H_2O_2/S=3, T=80°C, t=60 min).

Catalyst type	Conversion Cx-BTs(%)	Conversion DBT(%)
20 Mo/COK-12	58	75
20 Mo/SBA-15	56	70
20 Mo/Al	35	65

ODS reaction was clearly more effective when using mesoporous support compared to 20 Mo/Al. Conversion of Cx-BTs was ameliorated from 35 to 58% and of DBT from 60 to 75% using 20 Mo/COK-12. The conversion results for both catalysts supported on mesoporous silica are close, for Cx-BTs family conversion, 58%for Mo/COK-12 against 56% for Mo/SBA-15 and (75% compared to 70% for Mo/SBA-15). Even we can consider close catalytic results using 20 Mo/COK-12 or 20 M0/SBA-15, the easier COK-12 synthesis (compared to that of SBA-15) allows large scale production of COK-12 with continuous process which is an important parameter for the scale up of ODS process.

In the case of this efficient catalyst, extraction was subsequently performed after oxidation. Total sulfur content decreased from 1.6 wt.% to 0.23 wt.% instead of 0.6 wt.% in the case of 20 Mo/Al.

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COK-12 as a support exhibited the highest activity in ODS of marine fuels. The effect of the increase in molybdenum content on the supported catalyst on COK-12 was studied by varying the molybdenum content from 20 to 25 wt.%. However, a decrease in catalyst activity is observed by increasing the amount of molybdenum: Cx-BTs conversion decreased from 58 to 40% and that of DBT decreased from 75 to 70%. Indeed, desulfurization rates evaluated after extraction are more important with 20 Mo than 25 Mo/COK-12. Instead of a decrease of total sulfur content from 1.6 wt.% to 0.23 wt.%, total sulfur content decreased from 1.6 to 0.56 wt.% indicating that the optimal content of MoO_3 to be impregnated is not more than 20 wt.%.

V.3.6. Ti-COK-12

In our study, TiO_2 presented interesting ODS catalytic properties. Moreover, Mo supported mesoporous silica supports appeared also as efficient ODS catalysts. Composite titanium supports were already used in ODS reaction and different silica ordered mesoporous materials like MCM-41 [35], TS [52], SBA-15 [11,28,33,53], Beta [54], WMS (wrinkled mesoporous silica) and HMS (Sn-containing hexagonal mesoporous silica) [55] having high surface areas and uniform pore distribution have been prepared to ensure dispersion of TiO_2 particles. The creation of catalytic sites in these materials is attributed to the intimate interaction of TiO_2 and SiO_2 due to the formation of Ti–O–Si bonds [56]. In our work, we decided to combine COK-12 support together with titania. The catalyst was prepared by deposition of titania on high surface area silica via incipient wetness impregnation with 30 wt.% loading of TiO_2. Details of synthesis are given in the experimental section. Among the different classes of Ti-containing silica materials, nobody reported Ti-COK-12 catalyst for ODS reaction. Followed the synthesis, molybdenum was impregnated on the new support and both were further tested in ODS reaction.

V.3.6.1. Ti-COK-12 Support

It was essential to verify that textural properties of COK-12 were preserved after coating with TiO_2. COK-12 sample presents a type IV isotherm with H1 hysteresis loop typical characteristics of an ordered mesoporous material (Figure V.21-A). After impregnation of TiO_2, isotherm shape remains unchanged with a shift in P/P_0 desorption relative pressure, hysteresis type change to H2 which indicates a loss in cylindrical pore shape structure. Pore size distribution of COK-12 displayed in Figure V.21-B presents monomodal large pore size distribution structure, the diameters varying between 7 and 8 nm, but after impregnation of TiO_2 monomodal porosity with a narrow pore size distribution with maximum at 4.5 can be observed. The structural and textural properties of COK-12 before and after deposition of TiO_2 are summarized in Table V.14.

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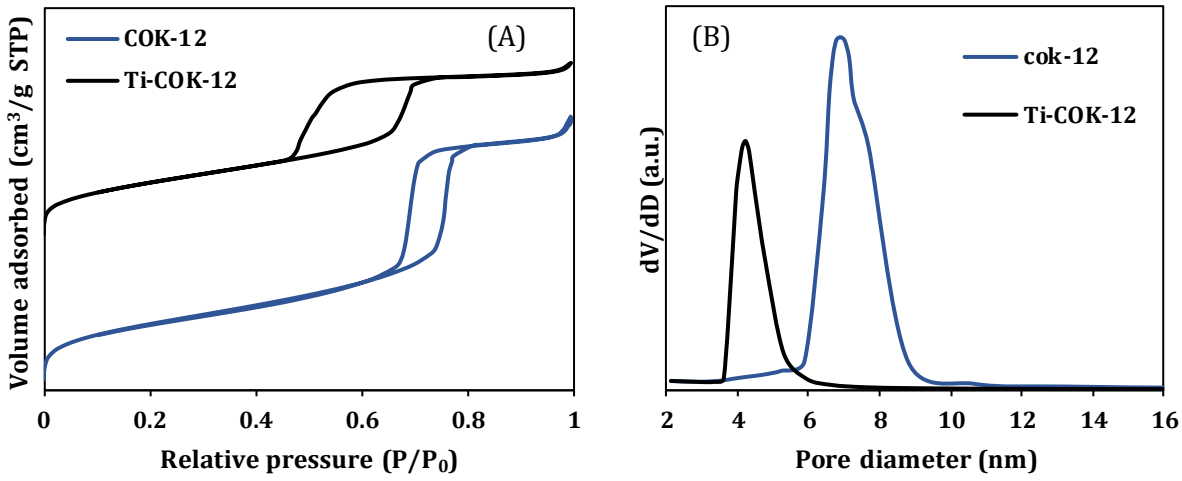

Figure V.21: (A) N_2 adsorption-desorption isotherms of calcined COK-12 and Ti-COK-12. (B) BJH pore size distribution of COK-12 and Ti-COK-12.

Table V.14: Textural properties of COK-12 and Ti-COK-12.

Catalyst	S_{BET} ($m^2.g^{-1}$)	V_p ($cm^3.g^{-1}$)	Mean pore diameter(nm)
COK-12	498	0.94	6.6
Ti-COK-12	480	0.67	4.3

For the composite, total surface area remains in the same range while a decrease in the mesoporous volume was observed from 0.98 to 0.67 cm^3 and in the mean pore diameters from 6.6 to 4.3 nm indicating slight pore blocking of TiO_2 nanoparticles on the surface of COK-12 and coating of the COK-12 channels. Low angle XRD for COK-12, Ti-COK-12 are presented in Figure V.22. The (100) silica peak is preserved even if its intensity decreased and the (110) peak almost disappeared after impregnation of TiO_2. The ordered and hexagonal pore structure of the mesoporous silica are maintained. High angle XRD diffraction patterns of the materials with 30 wt.% TiO_2 does not show any feature indicating the presence of anatase which suggest that titania species remains amorphous or with too small crystallites to be detected, and then titania species are well-dispersed on COK-12.

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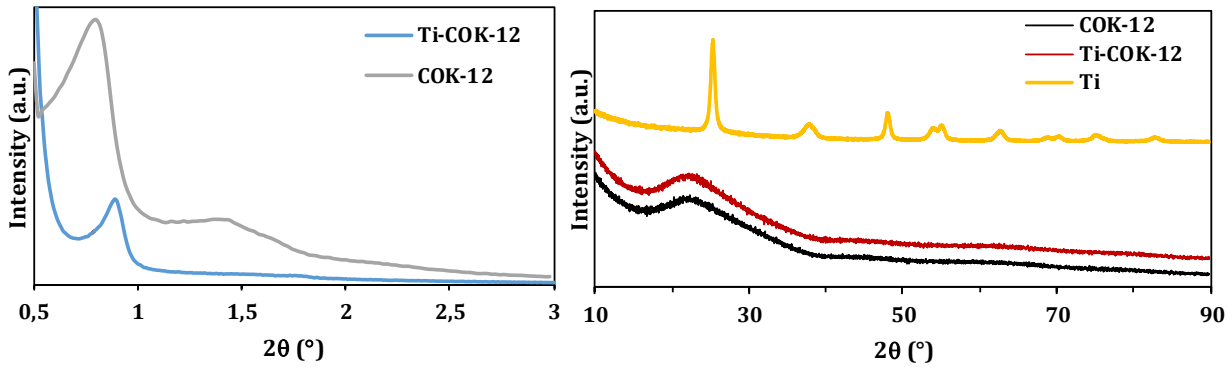

Figure V.22: Low angle XRD of COK-12, Ti-COK-12. (B) High angle XRD patterns of COK-12, Ti-COK-12 and TiO_2.

ODS test of IFO500-DC using Ti-COK-12 was effective. We can see from chromatogram displayed in Figure V.23 a decrease in the intensity of Cx-BTs and DBT peaks. Conversion results for DBT is almost the same (around 76%) with lower conversion of Cx-BTs (43% instead of 58%) using Ti-COK-12 when compared to 20 Mo/COK-12 catalyst. Moreover, we can see from chromatograms in Figure V.23 that DBT derivatives conversion is smaller though it was not evaluated quantitatively. Different Ti-SBA-15 catalyst have been assessed in ODS reaction in the literature, however, they differ by TiO_2 loading, the texture, the chemical composition and the oxidizing agent required for oxidation reactions as well as oxidized feed. For instance, Ti-SBA-15 with 2 wt.% Ti was evaluated in the ODS of thioanisole molecule using H_2O_2 as oxidant with Ox/S=1.1. Conversions reached only 43% within one hour. The reasons for the low catalytic activity of the Ti-SBA-15 samples are most likely a low titanium dispersion in the silicate matrix and its poor accessibility for the reactants due to the thick walls [33]. Only one work reported the use of such catalyst in the ODS of real feed. Cho et Lee [11] evaluated ODS of LCO containing 0.36 wt.% S in a continuous feed using tBHP and Ti-SBA-15 with high 19 wt.% Ti loading. 99.5% conversion of sulfur compounds inside LCO was detected after 6 hours. Recently, Andrei *et al.* [12] tested the oxidation with H_2O_2 of DBT using Ti-SBA-15, at temperatures lower than 70 °C using Ox/S=3, 65% conversion was reached.

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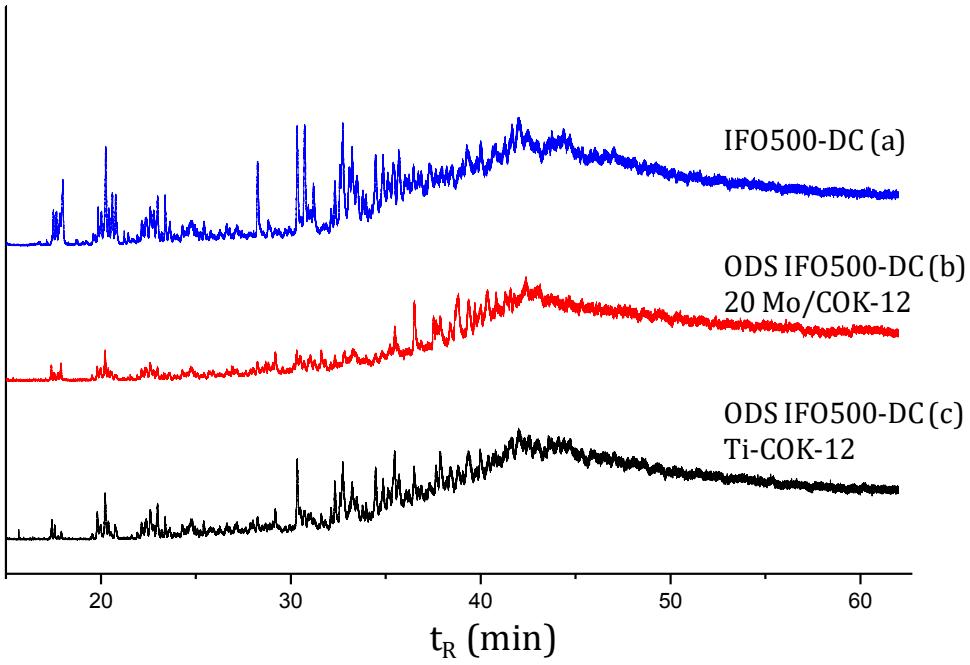

Figure V.23: Chromatograms of IFO500-DC (a), oxidized IFO500-DC using (b) 20 Mo/COK-12 or (c) Ti-COK-12.

V.3.6.2. 20 Mo/Ti-COK-12

20 wt.% MoO_3 supported on COK-12 was more efficient than the corresponding 25 wt.%MoO_3 catalyst. Despite the high surface area of COK-12, the lower loading is supposed to avoid large MoO_3 crystals inhibiting oxidation process even if with 20 Mo/COK-12, Raman spectra showed MoO_3 crystallites. Based on these data we decided to prepare the 20 Mo/Ti-COK-12 with the new composite support. Such composite was shown favorable to Mo dispersion as in the works of Dinh *et al.* [56,57] These authors proved for HDS catalysis that high loading of TiO_2 on CoMo/Ti-SBA-15 or 20 Mo/Ti-SBA-15 catalyst improved the dispersion of oxides on the support and reduced the appearance of crystallites at the surface of the catalyst.

XRD pattern of 20 Mo/Ti-COK-12 is displayed in Figure V.24 and shows peaks at 2θ= 23.7, 25.8, and 27.4° corresponding to MoO_3 crystallized phase. In comparison to XRD pattern of 20 Mo/COK-12, it is true that MoO_3 peaks are still observable but with less intense peaks. The presence of Ti in Ti-COK-12 composite reduced the crystallite size of MoO_3 particles from 94 to 80 nm for 20 wt.% MoO_3 loading. Consequently, better molybdenum dispersion, with smaller MoO_3 crystallites, is achieved over Ti-COK-12 composites which is in accordance with the dispersive character of titania. Despite the decrease in the size of MoO_3 particles, ODS reaction

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efficiency remained quite similar, conversion of Cx-BTs stayed 45% and for DBT conversion increased slightly from 76 to 80% but remains in same order of magnitude.

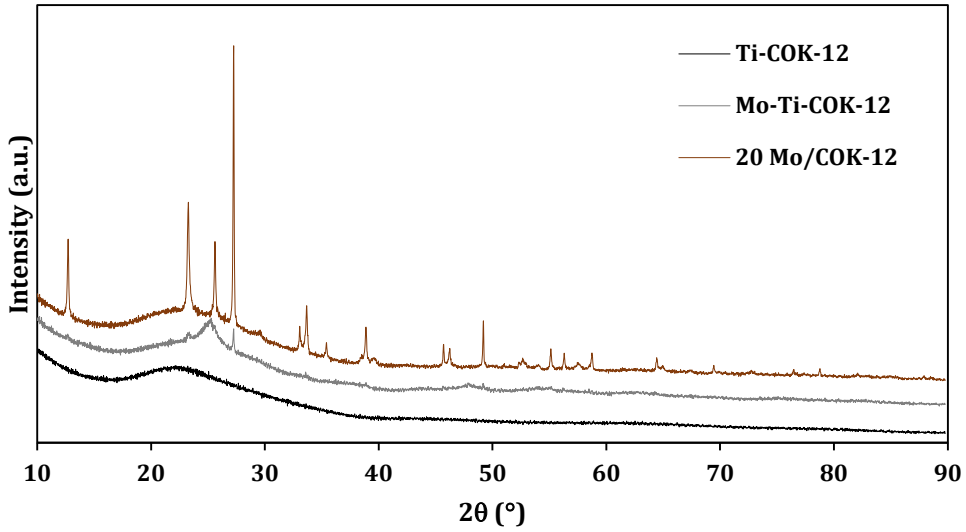

Figure V.24: XRD patterns of Ti-COK-12 and synthetized 20 Mo/Ti-COK-12

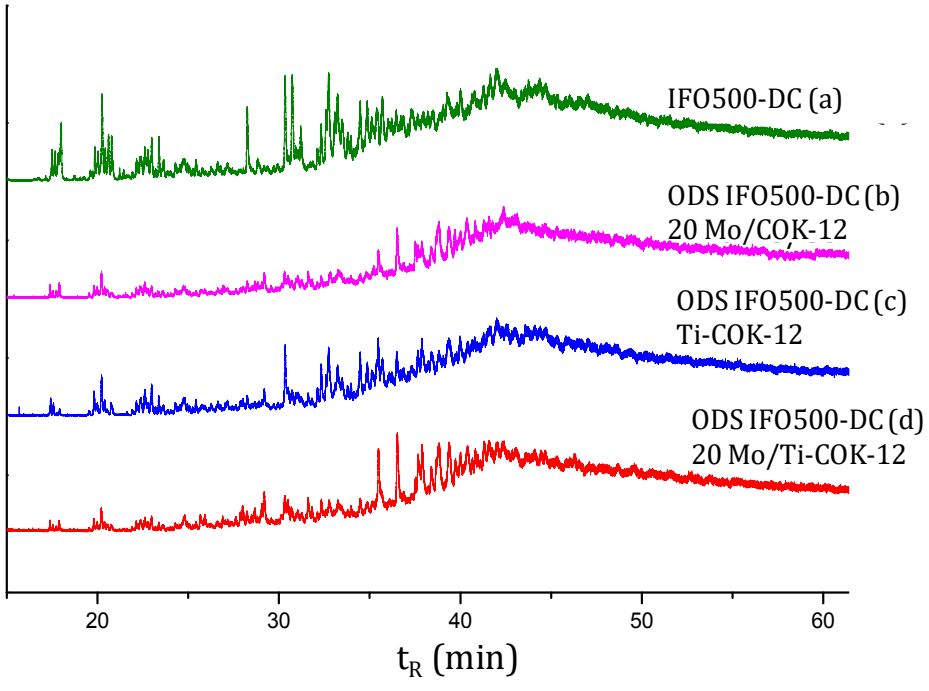

Figure V.25: Chromatograms of IFO500-DC (a), oxidized IFO500-DC using (b) 20 Mo/COK-12 or (c) Ti-COK-12 and (d) 20 Mo/Ti-COK-12.

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V.4. Conclusion

In summary, different types of catalysts were investigated in the ODS of IFO500-DC. A first optimization work started with the supported phase (Mo loading, promotor effect, Mo precursor) on alumina followed by optimization of support choice

The optimal molybdenum loading to be impregnated on alumina was found to be 20% MoO_3, from 20%, molybdenum oxide appears with an increase of particles size.

Catalyst prepared from HPA (PMo_{12} or $SiMo_{12}$) and molybdenum peroxo lead to lower activities compared to that of 20 Mo/Al. After drying of catalysts, the kegging structure was not preserved nor the peroxo entities both displaying $AlMo_6$ species. Despite that for all catalysts with 20% loading characterization pointed out dispersed $AlMo_6$ species with no MoO_3 detected, still desulfurization was lower when compared with 20 Mo/Al. Better dispersion of molybdenum species at the surface of catalyst was not beneficial to conversion. In the case of peroxo molybdenum based catalyst, efficiency was not as expected, but it was not possible to preserve dimerixcentities, therefore, in the future work it will be important to try to keep the dimeric entities while avoiding drying. This solution will be carried out by freeze-drying. ODS can be carried out using peroxo entites without the need to use Ox/S=3 (H_2O_2/S<3 or without H_2O_2). In this case, the advantage of such a system might be through the minimization oxidant consumption in the overall ODS process.

Despite the advantage indicated when adding vanadium or phosphorus to Mo/Al catalyst in the ODS of model compounds or light feeds, addition of such promoters decreased ODS performance in the ODS of marine fuel, when added to Mo/Al catalyst.

In summary, 20 wt. % MoO_3 molybdenum synthetized via AHM precursor was the best for ODS of fuels. Indeed, formation of hydroperoxomolybdate fragments on the catalyst surface with their subsequent interaction with sulfur molecules and oxidation of these sulfur compounds to sulfones are a key step in the ODS.

Among a series of titanium based catalysts with anatase structure and surface area ranging from 90 to 400 $m^2.g^{-1}$, DT-51 with the lowest surface area 90 $m^2.g^{-1}$ showed the highest activity in the ODS of IFO380-DC with conversion of Cx-BTs 38% and DBT 68% indicating that surface area does not have a major effect on enhancing conversions. Despite the good conversion, it was not highly performant as 20 Mo/Al gave better conversions of Cx-BTs (58%) and DBT (70%). DT-51 as catalyst alone exhibited better results compared to Mo/DT-51 disabling us to

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combine TiO_2 support properties with molybdenum. Mo was more active when alumina was used as support rather than titanium.

ZrO_2, ASA and CeO_2 supports have not been found effective in ODS of marine fuels despite that characterization results of Mo/Ce, Mo/Zr and Mo/ASA indicates the presence of polymolybdate species well dispersed on the surface of the supports. The same catalysts were tested in ODS of straight run gas oil SRGO using same conditions applied on IFO500-DC, ODS reaction was effective but desulfurization results were lower than with Mo/Al in terms of conversion rejecting the use of these supports in ODS of marine fuels.

An adequate preparation of mesoporous COK-12 type materials with relatively high TiO_2 (30 wt.%) loadings, maintaining the initial COK-12 structure with highly dispersed TiO_2 nano-clusters was possible. The Ti-COK-12 catalyst displayed high conversion of DBT (76%) and Cx-BTs (45%). The impregnation of molybdenum remained conversions of Cx-BTs and DBT the same when compared to Ti-COK-12.

Table V.15 Summarizes conversions of Cx-BTs and DBT in the ODS of IFO500-DC using molybdenum on various supports.

Table V.15: Conversion of Cx-BTs and DBT in ODS of IFO500-DC using different Mo based catalysts.

Catalyst type	Conversion Cx-BTs (%)	Conversion DBT (%)
20 Mo/Al	35	61
15 Mo/Ti	27	60
20 Mo/SBA-15	56	75
20 Mo/COK-12	58	75
25 Mo/ COK-12	40	70
Ti-COK-12	43	76
20 Mo/Ti-COK-12	45	80
14 Mo/CeO_2	0	0
10 Mo/ZrO_2	0	0
10 Mo/ASA	0	0

The study of the effect of the support on the molybdenum catalyst indicates that the ODS reaction was the most effective when using ordered mesoporous silica COK-12 known by its 2D hexagonal structure in platelet form with short, straight pores allowing easier diffusion of heavy molecules inside marine fuel. 20 Mo/COK-12 remains the most advantageous for the ODS of marine fuels. The highest conversion was obtained with conversions of 58% for Cx-BTs and 75% for DBT molecule. Total sulfur reduction after extraction was more than 80%, total sulfur content decreased from 1.6 wt.% S to 0.23 wt.% S instead of 0.6 wt.% in the case of Mo/Al. This catalyst needs to be further tested on other marine fuels and in the different states to make sure they become adaptable to IMO2020 regulations.

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Conclusion and Perspectives

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Conclusions and Perspectives

In the context of tightening of sulfur emission regulations for ships, SEGULA Technologies has developed a desulfurization project designated by SOxLOW, aiming at reducing the total sulfur content in the existing heaviest fractions of marine fuels in a continuous integrated process, with the objective that it could be adapted to existing vessels. Among the different steps of the process, this thesis is devoted to the development of oxidative desulfurization (ODS) of marine fuels of different origins and thus different viscosities and sulfur contents.

The first part of this work was devoted to a bibliographic overview of ODS reaction. The large majority of the papers concerned ODS of model feeds or of diesel fractions, however an extensive review was devoted to the ODS of heavy fuels, which enabled a screening of operating conditions as well as of catalysts, that was a starting point for our ODS investigations.

A crucial initial step was the characterization of the marine fuels provided by SEGULA, LSFO, IFO, HSFO, from various origins and with viscosities varying from 380 to 700 cSt at 50°C. Sulfur contents were measured between 0.5 and 3.3 wt.% by CHNS, with high nitrogen content varying from 0.3 to 0.5 wt.%. Dilution by dodecane of the raw samples allowed to decrease their viscosity and to separate different compounds of these complex matrices. Since this dilution led to asphaltenes precipitation, these were further separated by centrifugation. The asphaltenes appeared to be different depending on the type of fuels, their sulfur content being lower in low sulfur and low viscosity fuels.

Analytic techniques needed to be adapted and optimized regarding the complexity and high viscosity of the samples. Sulf-UV was not found relevant for the determination of sulfur content in the diluted samples, where precipitated asphaltenes were present: only half of the sulfur measured by CHNS could be accounted for by Sulf-UV for samples with high viscosity and high sulfur content. GC-SCD analysis could be performed on diluted centrifuged samples, after overcoming technical difficulties due to the presence of heavy molecules. Despite the variety in sulfur content and viscosity, chromatograms recorded for diluted centrifuged fuels showed a similar distribution of the sulfur species for all samples, with around 10% of alkyl-benzothiophenes Cx-BTs, 35% of alkyl-dibenzothiophenes Cx-DBTs and 55% of heavier compounds together with unresolved complex mixture. Similar distribution of nitrogen compounds and aromatic species were also recorded on all diluted centrifuged samples.

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In most papers, ODS efficiency is reported as a global sulfur removal rate from the initial feed, after oxidation and extraction of the formed sulfones. We have demonstrated that the commonly used solvents, like DMF and butyrolactone, are not completely selective to sulfones and that some sulfide compounds are also extracted. The global sulfur removal is thus not representative of oxidation effectiveness. To have an estimation of the reaction efficiency, we monitored the reaction mixture by GC-SCD, for diluted centrifuged or filtered samples. The species followed were the group of alkyl-BTs and the molecule of DBT, for which no overlapping with peaks of the formed sulfones occurred, allowing an accurate evaluation of these species evolution through integration of the peaks.

Before evaluating ODS performance of different marine fuels, a preliminary study of ODS reaction parameters was first conducted on diluted centrifuged fuel IFO500-DC, using MoO_3/Al_2O_3 catalyst under various conditions of time, oxidant nature and quantity, catalyst dosage, extraction solvent effect and stirring conditions, which resulted in a set of optimized parameters adapted to marine fuels. With H_2O_2, the oxidizing agent imposed by the SOxLOW project, an Ox/S ratio of 3, slightly above the stoichiometric one, appeared relevant, as similar conversions were obtained with tBHP; this later providing better homogeneity of the reaction medium due to its miscibility with fuels. Ultra-sound assisted ODS was also investigated, and the most efficient protocol consisted in a combined system of US prior to reaction under mechanical stirring. Significant improvement of ODS efficiency was noticed using this combined system, with an increase of more than 25% of Cx-BTs conversion and of global sulfur removal.

Nitrogen compounds reactivity was also monitored by GC-NCD and their oxidation in the reaction conditions was evidenced, confirming the competition between sulfur and nitrogen containing compounds in ODS. Contrariwise to sulfones identified after oxidation by GC-SCD, no oxidation products were detected by GC-NCD.

Using the conventional MoO_3/Al_2O_3 catalyst, ODS reaction was then applied to IFO380, IFO500 and HSFO700 presenting different viscosities and initial sulfur content from 0.79 to 3.27 wt.%, on the raw (R), diluted by dodecane (D) and diluted centrifuged (DC) samples. For the three DC samples, the same quantity of solid phase, around 20%, was removed by centrifugation allowing a first decrease of half sulfur content except for IFO380-DC where the sulfur content varied from 0.79 wt.% (IFO380-D) to only 0.70 wt.% (IFO380-DC).

ODS was found effective on all samples, except on HSFO700-R, for which a high increase in viscosity was observed during reaction. Also, instead a value of 3, an Ox/S ratio of 10 was required

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to oxidize the raw samples IFO380-R and IFO500-R. Similar conversions were obtained whatever the fuel and whatever the sample R, D or DC (around 45% for Cx-BTs and 70% for DBT), except for IFO380-DC for which higher values were reached (70% for Cx-BTs and 80% for DBT) letting us assume that compounds present in IFO380, removed by dilution and centrifugation, may be detrimental to sulfur compounds oxidation. This set of results shows that in these marine fuels, conversion of Cx-BTs and DBT is not directly related to sulfur content, viscosity and/or presence or not of asphaltenes.

An important final parameter is the desulfurization rate, calculated after ODS and extraction. It decreases in the order DC < D < R for IFO500 and HSFO700. Since Cx-BTs and DBT are similarly converted, we assume that some other sulfide compounds present in the raw and in a lesser extent in the D, further removed by centrifugation in DC, are oxidized or extracted in the D and R samples. For IFO380, higher desulfurization rate is measured in DC sample, in agreement with higher conversion of Cx-BTs and DBT compared to R and D samples. Moreover, to have less asphaltenes precipitation fuels were also diluted with a mixture xylene-dodecane. Nevertheless, even if only a slightly lower sulfur removal than that obtained using dodecane was noticed, a high hydrocarbon loss was observed in these diluted fuels; this was explained by extraction of polar high molecular weight and high boiling point asphaltene type compounds.

The study of the sulfur removal for IFO380, IFO500 and HSFO700 in R, D and DC samples, on 20 MoO_3/Al_2O_3 catalyst using ODS reaction proved its efficiency on marine fuels, with interesting final sulfur content close to the values imposed by the MARPOL regulations. Nevertheless, it also highlights the difficulty of the implementation of ODS on very viscous samples such as HSFO700.

To achieve higher desulfurization rates, optimization of catalyst was also required. Catalyst development focused on two aspects and was established via ODS of IFO500-DC. At first, optimization of the active phase content indicated that 20 wt.% MoO_3 synthetized via AHM precursor exhibited the highest activity. Use of different molybdenum based precursors such as $SiMo_{12}$, PMo_{12} and molybdenum peroxo with same MoO_3 loading (20 wt.%) did not enhance conversions. Moreover, the addition of P or V did not improve ODS conversion.

Titanium based support with anatase structure without molybdenum showed effective performance in ODS reaction of IFO380-DC. Among a series of titanium based catalysts with surface area from 90 to 400 $m^2.g^{-1}$, the titania catalyst having a 90 $m^2.g^{-1}$ surface area led to the best conversions of Cx-BTs and DBT in the ODS of IFO380-D. Whatever its Mo loading, titania alone was more active than the Mo supported disabling us to combine TiO_2 support with molybdenum.

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Different supports with variety of acidic properties (SiO_2-Al_2O_3; ZrO_2), with oxygen mobility (CeO_2) and ordered mesoporous with high surface area (SBA-15, COK-12) as well were studied. The highest activity was obtained when Mo was dispersed on COK-12, possessing a 2D hexagonal structure in platelet form. The highest conversions were then obtained with the solid 20% MoO_3/COK-12 with results around 57% for Cx-BTs and 80% for DBT molecule. Total sulfur reduction after extraction was more than 80%, total sulfur content decreased from 1.60 wt.% S to 0.23 wt.% S instead of 0.60 wt.% S in the case of Mo/Al.

Table 1 presents an overview of main desulfurization results obtained in this thesis. In this table are gathered total sulfur content for each state (R, D or DC) of each fuel (IFO380. IFO500 and HSFO700), before oxidation, and after oxidation extraction, using combined system ultrasound followed by mechanical stirring with 20 Mo/Al, and for IFO500-DC for reaction with 20 Mo/COK-12 without ultrasound.

Table 1: Total sulfur content before and after ODS and extraction for raw, diluted fuel with dodecane, diluted centrifuged fuel DC of IFO380, IFO500 and HSFO700 using US+MS system.

Fuel	State	S before ODS (wt.%)	S after ODS & extraction (wt.%)
IFO380	**R**	0.79	0.27
	D	0.79	0.28
	DC	0.7	0.13
IFO500	**R**	3.27	0.52
	D	3.27	0.63
	DC	1.6	0.37
	DC*	1.6	0.23
HSFO700	**R**	2.95	x
	D	2.95	0.79
	DC	1.50	0.54

DC*: ODS without US using 20 Mo/COK-12

Future work is indeed necessary to pursue the development of oxidative desulfurization process on marine fuels.

Better understanding of the fuels behavior in oxidation can be improved through more complete characterization of the fuels, in particular by more thorough identification and quantification of the sulfur compounds by 2D chromatography.

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A complementary assessment of sulfur evolution during ODS could be achieved by Infra-Red spectroscopy, that could allow evaluation and monitoring of sulfides and sulfones, which could be attempted even for the raw fuels after proper technical development.

Dilution of the fuels may be an inevitable step, as for instance HSFO700 ODS on the raw fuel was not feasible due to the high increase of viscosity during reaction. An extensive study of the solvents to be used, as well as optimization of their quantity, have to be carried out, as it is a crucial factor for scaling up the process.

Among the different solids developed, molybdenum supported on mesoporous COK-12 showed very good results when applied in the ODS of IFO500-DC using only mechanical stirring. Consequently, this catalyst must be further evaluated using the optimized combined system ultra-sounds followed by mechanical stirring, not only on the diluted centrifuged phases but more importantly on the diluted phases of all fuels and raw state of IFO380 and IFO500 for which optimization was needed to fulfil IMO2020 requirements. There is still room for improvement with optimization of the Mo content. Promising results can thus be expected for this solid.

To develop more efficient catalysts or further optimize the reactions conditions, a better understanding of the active species involved and of the reaction mechanism is necessary. The presence of peroxo species is required for effective oxidation reaction, we can thus consider monitoring their formation and evolution during reaction; in-situ Raman analysis could be a relevant technique for this goal.

All catalytic evaluations have been performed in batch reactor for the initial screening. Continuous reaction in fixed bed reactor is necessary to validate the performance of selected catalysts, and will also allow to assess their lifetime under reaction conditions. Recycling potential of the catalysts is also a crucial issue, that will have to be addressed in future work.

If considerable work remains for the development of ODS in the framework of the SOxLOW project, we have proven the feasibility of oxidative desulfurization when applied to fuels as complex as marine fuels. Moreover, screening of reaction conditions as well as catalytic systems has led to a set of parameters and to solids. Their combination led to residual sulfur content in the treated fuels in line with the sulfur content limits defined in future shipping environmental regulations, showing that the choice of ODS for sulfur removal of marine fuel can clearly enable to meet the new environmental regulations.

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