

# Oxidative desulfurization and denitrogenation of a light gas oil using an oxidation/adsorption continuous flow process

Atsushi Ishihara\*, Danhong Wang, Franck Dumeignil, Hiroshi Amano, Eika Weihua Qian, Toshiaki Kabe

Department of Chemical Engineering, Tokyo University of Agriculture and Technology,  
2-24-16 Nakacho, Koganei, Tokyo 184-8588, Japan

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## Abstract

The oxidation of undesirable sulfur compounds present in a desulfurized light gas oil (LGO; sulfur content: 39 ppm) was performed with *tert*-butyl hydroperoxide (*t*-BuOOH) as the oxidant in the presence of a 16 wt.% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. The oxidation activity of the sulfur compounds in the light gas oil increased when the O/S molar ratio increased up to 15; the activity slightly decreased for higher ratios. This optimal ratio was significantly higher than the stoichiometric one (=2) due to parallel oxidation reactions of olefins, etc., in the LGO. Further, we compared the oxidation reactivity of dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), and trimethyldibenzothiophene (C<sub>3</sub>-DBT), which are refractory compounds present in the light gas oil. The reactivity decreased in the order DBT ≫ 4,6-DMDBT > C<sub>3</sub>-DBT, irrespective of the WHSV and the temperature. Subsequent mathematical treatment revealed that the oxidative reaction of each sulfur compound follows a first-order kinetics. We found an activation energy of 32 ± 2 kJ mol<sup>-1</sup>, whatever the compound, suggesting that the oxidation mechanism was the same for these compounds. Then, according to the proposed global process, the previously oxidized molecules in the treated light gas oil were further removed by adsorption over a silica gel at ambient temperature. As a result, the total sulfur content could be decreased after oxidation/adsorption to less than 5 ppm. Further, N-containing model compounds were also treated according to the same procedure and the denitrogenation performance decreased in the order indole > quinoline > acridine > carbazole. Subsequently, the same process allowed decreasing the N content in the LGO from an initial value of 13.5 ppm to a value of 0.8 ppm, which is a remarkable result.

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## 1. Introduction

There is a stringent need for new methods of reducing the sulfur content in fuel oils in order to satisfy the upcoming pieces of legislation that will limit the sulfur content more and more drastically [1]. Indeed, the environmental regulations for on-road diesel fuels planned in Europe call for a sulfur content reduction from the current level of 350 to 50 ppm by 2005 [2] and to 10 ppm by 2009, while in the US the actual level of 500 ppm will have to be decreased down

to 15 ppm in 2006 [3]. Similarly, Japan will impose a decrease from 500 to 50 ppm by the end of 2004 and is planning to further lower this limit down to 15 ppm in the short/mid term. To achieve these new goals with the current hydrodesulfurization (HDS) technology, the use of higher temperature, higher pressure, larger reactor volume, and more active catalysts is indispensable but costly. Therefore, new solutions were alternatively proposed; among them, the oxidative desulfurization (ODS) appeared as particularly promising. Indeed, ODS can be conducted at room temperature and under atmospheric pressure, which allows a substantial cost reduction. In such a process, DBTs are oxidized into sulfones that can be subsequently easily

\* Corresponding author. Tel.: +81 42 388 7228; fax: +81 42 388 7228.  
E-mail address: [atsushii@cc.tuat.ac.jp](mailto:atsushii@cc.tuat.ac.jp) (A. Ishihara).

removed by conventional separation operations (e.g. distillation, solvent extraction, adsorption...) as their properties are significantly different from those of the hydrocarbons that constitute most of the fuel oils. We can find a certain number of studies on ODS methods in the literature [4–15]; Aida et al. reported that peroxyacids are particularly effective oxidants [4,5], while Collins et al. recently obtained a DBT conversion of 100% using a phosphotungstic acid/hydrogen peroxide system [6]. In addition, Zannikos et al. could remove 90% of the sulfur in a petroleum fraction under mild conditions by performing a solvent extraction after the oxidation step [7]. Similarly, Dolbear et al. could efficiently remove refractory sulfur compounds using peroxyacetic acid in the presence of catalysts at near-ambient temperature and atmospheric pressure [8–10]. Similarly, we showed that most of the DBTs contained in a LGO (light gas oil; 150 ppm of DBT and 145 ppm of 4,6-DMDBT) can be oxidized into sulfones in a batch reactor in the presence of ozone [16]. We also further successfully performed the oxidation of a SR-LGO and a VGO (vacuum gas oil) in the presence of hydrogen peroxide and formic acid [17]. However, this kind of process was limited to a batch reactor because, e.g., the oxidants are water-soluble, and it was further necessary to propose a flow-type ODS process allowing one to treat large amounts in order to develop commercially acceptable applications. Therefore, we first aimed at finding an adequate oil-soluble oxidant and proposed *tert*-butyl hypochlorite (*t*-BuOCl) in a recent study [18]. The DBT oxidation conversion reached 90% at 50 °C under atmospheric pressure in a batch system as well as in a flow-type system in the presence of a catalyst. Further, we found that *tert*-butyl hydroperoxide (*t*-BuOOH) is suitable to oxidize the sulfur compounds in kerosene [19]; optimal oxidation reaction conditions were determined as: a temperature of 80 °C, an O/S molar ratio of 3, a WHSV of 60 h<sup>-1</sup>, in the presence of a 16 wt.% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst.

In the present paper, we adapted the flow-type process described above in order to oxidize the refractory DBTs remaining in a pre-desulfurized LGO (sulfur content: 39 ppm). Further, the oxidation reactor was combined with an adsorption reactor disposed in line and a continuous oxidation/adsorption process was developed. In addition, the same experimental procedure was also successfully used to remove N-containing model compounds as well as the N-compounds in the LGO with a great efficiency.

## 2. Experimental

### 2.1. Catalyst

A  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with a surface area of 256 m<sup>2</sup> g<sup>-1</sup> supplied by Nippon Ketjen Co. was first crushed and screened to obtain

80–150 mesh granules. Then, a Mo/Al<sub>2</sub>O<sub>3</sub> catalyst containing 16 wt.% MoO<sub>3</sub>, which previously gave excellent performance in ODS [19], was prepared by incipient wetness impregnation of the Al<sub>2</sub>O<sub>3</sub> granules with an aqueous solution containing the desired amount of ammonium heptamolybdate. The catalyst was dried at 120 °C for 3 h and then calcined in air at 500 °C for 15 h before use.

### 2.2. Apparatus and procedure

The oxidation experiments were carried out in a combined system constituted by a fixed-bed flow reactor consisting of a stainless steel tube (i.d. 8 mm) packed with 1 ml of catalyst particles, followed by an adsorption flow reactor packed with 20 ml of adsorbent (a silica gel supplied by Wako). The light gas oil containing 39 ppm of sulfur was purchased from *Nippon Oil Corporation*. It was mixed with the oxidative agent *t*-BuOOH, purchased from Kishida, using the desired relative quantity. This feed was then introduced into the reactor pre-heated at the reaction temperature, using a liquid pump (Kyowa Seimitsu KHD-16). The concentrations of the various sulfur compounds present in the commercial LGO are given in Table 1. The main sulfur compounds are DBT, 4,6-DMDBT and C<sub>3</sub>-DBT. These compounds, which are known to be particularly difficult to desulfurize, accounted for about 50% of the total sulfur concentration. Accordingly, we focused the first part of the present study mainly on the monitoring of the desulfurization activity of DBT, 4,6-DMDBT and C<sub>3</sub>-DBT. Typical oxidative reaction conditions were as follows: atmospheric pressure; WHSV, 30 h<sup>-1</sup>; O/S molar ratio, 15; reaction temperature, 40–100 °C. The subsequent adsorption reaction was carried out at room temperature under atmospheric pressure. For each oxidation reaction, the liquid products were collected every 30 min after the steady state was reached (i.e. after 3 h of reaction). The composition of the reaction products were analyzed using a gas chromatograph (FID: agilent-6890) equipped with a Sulfur Chemiluminescence Detector (SCD: Sievers-355). In addition, the denitrogenation reactivity of N-containing model molecules (carbazole, acridine, indole and quinoline) was examined following the same experimental procedure. Furthermore, the LGO denitrogenation activity was also investigated in the same way. The total amount of sulfur and the total amount of nitrogen were measured using a Total Sulfur Analyzer (TS-100) and a Total Nitrogen Analyzer (TN-100), respectively.

Table 1  
Concentration of the sulfur compounds present in the LGO

	Concentration (ppm)	Sulfur (ppm)
Total sulfur		38.8
DBT	21.5	4.07
4,6-DMDBT	53.2	8.68
C <sub>3</sub> -DBT	28.7	4.38
Other alkyl-DBTs		21.67

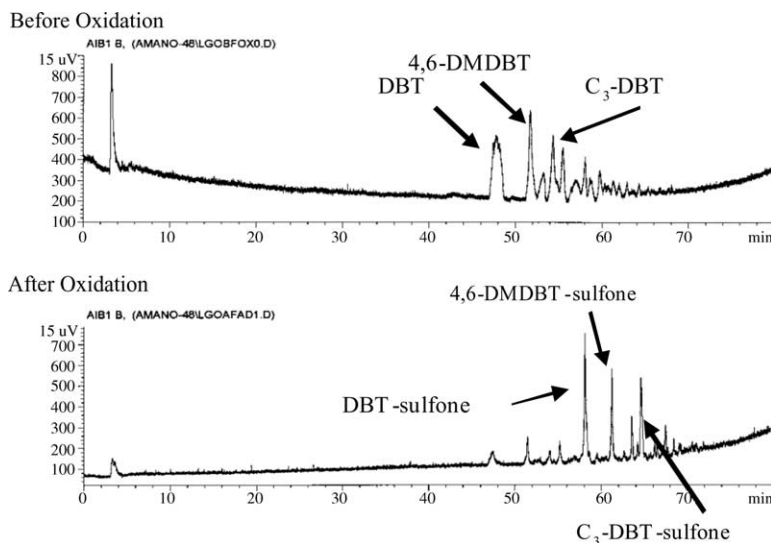


Fig. 1. SCD chromatograms of LGO and oxidized LGO.

### 3. Results

#### 3.1. Oxidation of the sulfur compounds present in the light gas oil with *t*-BuOOH over the Mo/Al<sub>2</sub>O<sub>3</sub> catalyst

The oxidation of the sulfur compounds in the light gas oil with *t*-BuOOH was first carried out over the Mo/Al<sub>2</sub>O<sub>3</sub> catalyst in a preliminary experiment aiming at identifying the reaction products. Fig. 1 shows the SCD chromatograms of the light gas oil obtained before and after this oxidation experiment performed with a O/S molar ratio fixed at 20. The peaks corresponding to DBT, 4,6-DMDBT and C<sub>3</sub>-DBT were identified by comparison of their retention times with reference compounds while the peaks of their corresponding sulfones were identified using a GC-MS (QP5050). After the LGO was oxidized with *t*-BuOOH, the peaks of the sulfur compounds shifted respectively to higher retention times, i.e. for heavier molecular masses. The peaks of the DBTs almost completely disappeared, while the peaks of the corresponding DBT sulfones appeared after oxidation, confirming that the oxidation of DBTs led to the formation of DBT sulfones.

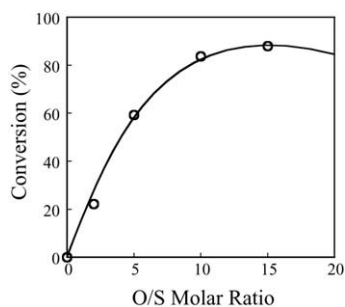


Fig. 2. Oxidation activity of sulfur compounds in light gas oil under various O/S ratios at 100 °C.

Then, we carried out the oxidation reaction of the sulfur compounds of the LGO under various O/S molar ratios at 100 °C using 2 ml of catalyst in order to investigate the effect of the amount of the oxidation agent on the oxidation activity. The O/S molar ratio was defined as the molar ratio of the amount of oxidation agent (*t*-BuOOH) to the total amount of sulfur analyzed by TS-100. A previous study [18] performed on model molecules suggested that, to fully oxidize DBTs to DBT sulfones, 2 moles of *t*-BuOOH are stoichiometrically required for the oxidation of 1 mole of DBTs. In contrast, as shown in Fig. 2, the oxidation activity of the sulfur compounds in the light gas oil increased with the O/S molar ratio up to O/S = 15 and then slightly decreased beyond this value. This value was much higher than the stoichiometric O/S molar ratio mentioned above. The difference was due to side reactions involving the oxidation of other major compounds of the LGO, such as olefins and nitrogen compounds, which consume *t*-BuOOH.

#### 3.2. Oxidation reactivity of the sulfur compounds of the light gas oil

In order to investigate the difference of reactivity between the different sulfur compounds, we carried out the oxidation of the sulfur compounds in question (DBT, 4,6-MDBT, and C<sub>3</sub>-DBT) in the LGO on the 16 wt.% Mo catalyst with a O/S molar ratio of 15 (optimal ratio) using various WHSV. The products were analyzed by SCD. Fig. 3 shows the oxidation activities of the sulfur compounds carried out under various WHSV at 80 °C using 1 ml of catalyst. The oxidation activity of all the sulfur compounds decreased with increasing the WHSV. Moreover, the results clearly showed that the oxidation reactivity decreased in the order of DBT ≫ 4,6-DMDBT > C<sub>3</sub>-DBT, indicating that DBT was

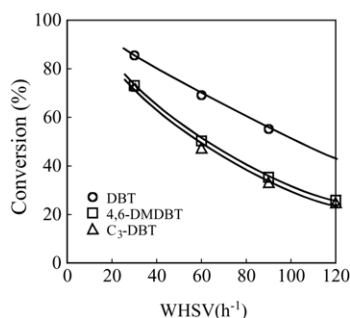


Fig. 3. Oxidation activities of sulfur compounds under various WHSV at 80 °C.

much more sensitive to the oxidation process than 4,6-DMDBT and C<sub>3</sub>-DBT for the present reaction conditions.

### 3.3. Determination of the kinetics of the oxidation reaction

The oxidation reaction of the sulfur compounds was examined under various WHSV conditions at 40, 60, 80, and 100 °C, in order to determine the reaction kinetics. The results are summarized in Table 2. In this table, ‘oxidation conversion’ indicates the oxidation activity of each examined sulfur compound; ‘sulfur concentration after adsorption’ indicates the total concentration of the sulfur compounds remaining in the LGO after a complete oxidation/adsorption procedure; ‘desulfurization conversion’ indicates the global desulfurization conversion after the complete process. We observed that the oxidation activity of each sulfur compound decreased with increasing WHSV and with increasing reaction temperature. Further, Fig. 4 shows the plots of  $\ln(C_A/C_0)$  versus  $1/\text{WHSV}$  for the oxidation reaction of the sulfur compounds conducted at 80 °C.  $C_A/C_0$  was defined as the ratio of the final sulfur

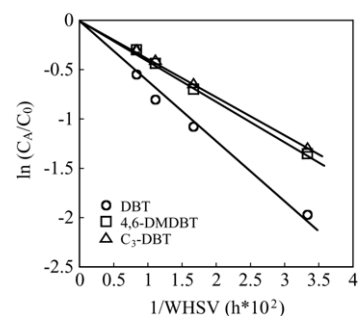


Fig. 4. First-order plots of  $\ln(C_A/C_0)$  and reaction time for the sulfur compounds at 80 °C.

concentration after reaction to the initial sulfur concentration; this could be easily calculated from the conversion of each sulfur compound. A linear relationship was obtained when plotting  $\ln(C_A/C_0)$  versus  $1/\text{WHSV}$  for each sulfur compound. Similarly, linear relationships were also obtained for the experiments carried out at 40, 60 and 100 °C for each sulfur compound (not represented here). These results suggested that the oxidative reaction of all the studied refractory sulfur compounds can be treated as a first-order reaction. Therefore, the reaction rate constant could be obtained at various temperatures from the slopes of the line obtained for each sulfur compound.

Fig. 5 shows the Arrhenius plots of the reaction rate constants for each sulfur compound. The apparent activation energies of the oxidation reaction of the sulfur compounds were obtained from the slopes of these plots. The calculated apparent activation energies were almost the same for the three examined compounds at  $32 \pm 2$  kJ/mol. This result suggested that there is essentially no difference in the mechanism of the oxidation reaction over the Mo/Al<sub>2</sub>O<sub>3</sub> catalyst for these sulfur compounds. On the other hand, this

Table 2  
Oxidation and desulfurization activities of sulfur compounds in light gas oil under various WHSV values

Oxidation temperature (°C)	WHSV (h <sup>-1</sup> )	Oxidation conversion (%)			Sulfur concentration after adsorption (ppm)	Desulfurization conversion (%)
		DBT	4,6-DMDBT	C <sub>3</sub> -DBT		
40	30	38.9	30.2	27.6	28.2	27.3
	60	22.6	15.6	12.1	32.2	17.0
	90	14.2	9.8	8.6	33.2	14.4
	120	9.8	6.2	5.8	34.4	11.3
60	30	62.1	50.7	48.9	18.6	52.1
	60	37.8	32.3	28.6	27.6	28.9
	90	24.2	21.6	19.7	30.2	22.2
	120	20.1	15.1	12.4	32.7	15.7
80	30	87.4	78.1	72.5	5.1	86.8
	60	69.2	52.3	47.3	13.8	64.4
	90	55.2	38.3	33.1	17.4	55.2
	120	41.3	28.8	24.8	23.6	39.2
100	30	92.3	84.6	82.3	4.1	89.5
	60	82.5	73.6	65.8	8.9	77.0
	90	65.8	58.1	56.6	15.9	59.0
	120	53.5	43.5	38.2	20.0	48.5

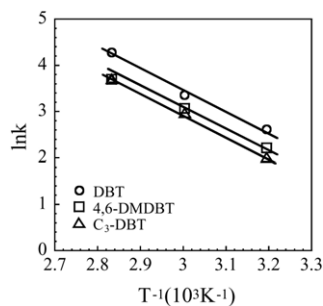


Fig. 5. The Arrhenius plots of the sulfur compounds.

value was much lower than that obtained for a conventional hydrodesulfurization reaction (in the order of  $\pm 100$  kJ/mol); this difference may be explained by the fact that the oxidation reaction is conducted at a very low temperature compared to the one needed by a classical hydrodesulfurization process.

#### 3.4. Adsorption of the oxidized sulfur compounds

As shown in Table 2, the desulfurization conversion observed after the oxidized sulfur compounds were adsorbed over silica gel at ambient temperature decreased with increasing WHSV. The best result was obtained when the adsorption (at ambient temperature) was performed after the oxidative reaction had been carried out at 100 °C with a WHSV of 30 h<sup>-1</sup> (desulfurization conversion of 90%). Further, a continuous experiment using these optimal parameters was performed to determine the breakdown point of the adsorbent for which the adsorbent is saturated and can adsorb no more oxidized molecules (i.e. determination of the maximal quantity of feed that can be efficiently treated with a given quantity of adsorbent). Fig. 6 shows the results; we can see that the total sulfur content in the light gas oil could be easily decreased to less than 5 ppm up to a ratio amount of feed to adsorbent less than 6. This value of 5 ppm is much less than the maximal sulfur content that will be imposed by USA legislation by 2006. In other words, even in the case of severe regulations an acceptable desulfuration level can be maintained, provided the adsorbent is regenerated after being used up to the limit ratio feed/adsorbent = 6.

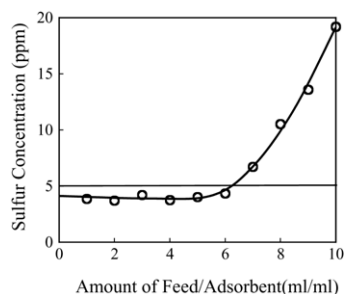


Fig. 6. Adsorption of oxidized LGO at ambient temperature.

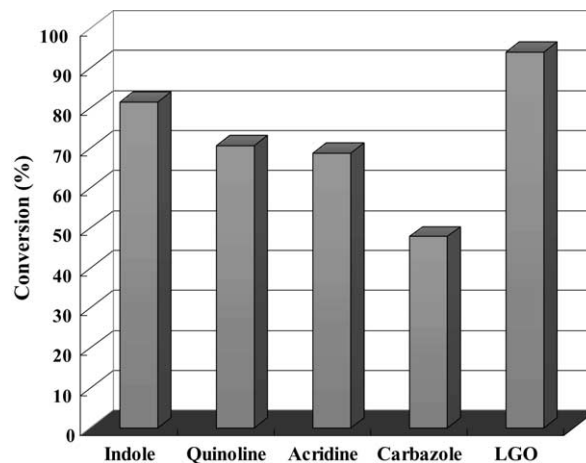


Fig. 7. Denitrogenation activities of nitrogen compounds and LGO.

#### 3.5. Denitrogenation of model nitrogen compounds and of denitrogenation of the LGO

The denitrogenation activity of the system was also examined using model nitrogen compounds (indole, quinoline, acridine and carbazole) dissolved in decalin as well as the light gas oil itself. Fig. 7 shows the results for the denitrogenation/adsorption process carried out at 80 °C. Here, the total amount of nitrogen dissolved in decalin was about 20 ppm for each nitrogen compound while it was about 13.5 ppm in the LGO (TN-100 results). As a result, the denitrogenation activity of the nitrogen compounds decreased in the order of indole > quinoline > acridine > carbazole, showing that the carbazole is the nitrogen compound that is most difficult to oxidize. Moreover, the nitrogen concentration in the light gas oil could be remarkably decreased from an initial value of 13.5 ppm to a final value of 0.8 ppm.

## 4. Discussion

#### 4.1. Oxidative reaction mechanism of DBTs with *tert*-butyl hydroperoxide

In the oxidation reaction of DBT, the mechanism of formation of the corresponding sulfone can be roughly described as follows: DBT first reacts with a *t*-BuOOH molecule to produce DBT sulfoxide, and then the DBT sulfoxide further reacts with another *t*-BuOOH molecule to form a sulfone [20]. In addition, Sheldon reported also that such a mechanism involves a metal peroxide intermediate formed consecutively with the reaction of an oxometal group with the alkyl hydroperoxide [20]. Further, Curci and Edwards proposed a review of the solvent effect [21]. All of their observations were explained by the oxidation mechanism proposed in earlier works of Overberger and Cummins [22], and of Bateman et al. [23]. These authors

postulated that the sulfur was oxidized by a nucleophilic attack on a peroxidic complex that contained peroxidic and protic structures. Further, Mashio et al. [24] proposed a model presenting the initial stage of the complex formation between the hydroperoxide and  $\text{MoO}_3$ . Moreover, according to a crystal structure analysis [25,26], the distance between the Mo atoms and the oxygen atom of  $\text{MoO}_3/\text{Al}_2\text{O}_3$  is 1.96 Å, while the distance between the oxygen atom directly attached to the tertibutyl group and the terminal hydrogen atom of *tert*-BuOOH is 1.93 Å. This result suggested that the coordination of the hydroperoxide to Mo–O is promoted by the polarization of  $\text{Mo}^{\delta+}\text{--O}^{\delta-}$  bond when  $\text{MoO}_3$  is dispersed on  $\text{Al}_2\text{O}_3$ , and therefore, the electrophilicity of the peroxy oxygen is promoted. On the basis of these results, we proposed previously a peroxidic oxidation mechanism of DBT on  $\text{MoO}_3$  catalysts with *tert*-BuOOH [19] (Fig. 8). According to this activation mechanism in which peroxy oxygen is involved in a pseudo-cyclic structure, the peroxide reacts with DBT to produce DBT sulfoxide, and further oxidation produces the corresponding sulfone according to the same mechanism.

Further, we found that the activation energy was almost the same for a series of molecules present in kerosene (BT, DBT, 4-MDBT, 4,6-DMDBT) at a value of about  $28 \pm 1 \text{ kJ mol}^{-1}$  [19]. It was deduced that all the reactions of the model molecules followed the same mechanism. Similarly, in the present study (LGO) we did not find any significant difference in the oxidation activation of DBT, 4,6-DMDBT and  $\text{C}_3$ -DBT with a value of about  $32 \pm 1 \text{ kJ mol}^{-1}$ , irrespective of the compound. That suggests that in this case as well the oxidation mechanism of these DBTs is similar, and is likely to be the one of Fig. 8. Further, this value of  $32 \pm 1 \text{ kJ mol}^{-1}$  is a little higher than the one previously obtained for the sulfur molecules present in kerosene [19] ( $28 \pm 1 \text{ kJ mol}^{-1}$ ). This might be due to a ‘solvent effect’ because the nature of the hydrocarbons present in a kerosene and the ones present in a light oil is different, and therefore the competitive adsorption extent is different for the two types of fuels. Moreover, in the case of the kerosene, the optimal O/S ratio was close to the stoichiometric ratio (2) with an actual value of about 3, while in the case of the light gas oil it was as high as 15.

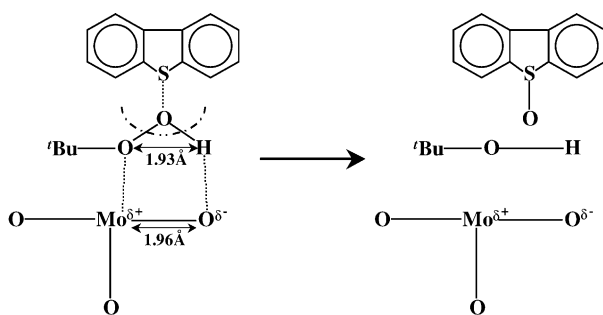


Fig. 8. Coordination of hydroperoxide to Mo–O on  $\text{MoO}_3$  catalyst and peroxidic oxidation mechanism of DBT with *t*-BuOOH (adapted from Ref. [19]).

This suggested the presence of side-reactions in the case of the light gas oil that consumes oxidant, which is in good agreement with the above remark. Therefore, it seems that there are competitive adsorptions/reactions that are responsible for an increase in the activation energy (and for oxidant consumption).

#### 4.2. Comparison of the oxidation reactivity of the sulfur compounds

DBT, 4-MDBT and 4,6-DMDBT are typical refractory sulfur compounds present in diesel fuel and gas oils. It is well known that the HDS reactivity of the DBTs decreases drastically with an increase in the number of the substituents or in the complexity of these substituents (i.e. their number of carbons) when they are present in a position that sterically hinders the HDS reaction (namely, position 4 or 6). Accordingly, the HDS reactivity of DBTs decreases in the order of  $\text{BT} > \text{DBT} > 4\text{-MDBT} > 4,6\text{-DMDBT}$ . In a previous study [17], we carried out the oxidation of model sulfur compounds (BT, DBT, 4-MDBT and 4,6-DMDBT) with hydrogen peroxide and formic acid in the absence of a catalyst. As a result, the oxidation reactivity of these model sulfur compounds increased in parallel with the increase in the electron density at the sulfur atom, which is modulated by the electron donation capacity of the respective methyl substituents. Indeed, the reactivity order was completely reversed when compared to the case of HDS, i.e.  $4,6\text{-DMDBT} > 4\text{-MDBT} > \text{DBT} > \text{BT}$ . This was in good agreement with the results of Aida et al. [27–29] who also performed the oxidation of DBT with hydrogen peroxide and formic acid. Thus, it suggests that the oxidation reactivity is enhanced for sulfur atoms with a high electron density. Similarly, Ford et al. [12] found that the oxidation rate of thiophenic compounds was lower than the one of sulfides. The trend observed for the reaction rate in relation to the structure was accounted for in terms of: (a) reduced availability of the lone pair of electrons; and (b) steric strain in the reaction products, sulfoxides and sulfones.

Further, we performed oxidation experiments in the presence of a catalyst [19]. The result was different as the reactivity of the sulfur compounds decreased in the order, i.e.  $\text{DBT} > 4\text{-MDBT} > 4,6\text{-DMDBT} \gg \text{BT}$  (kerosene; oxidation agent: *t*-BuOOH;  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst). The reactivity order of DBT, 4-MDBT and 4,6-DMDBT was reversed between the experiments performed in the presence of a catalyst and the experiments performed in the absence of a catalyst, suggesting that when a catalyst was used the main parameter governing the reactivity was no longer the electron density on the sulfur atoms. In contrast, BT exhibited the lowest reactivity in both cases (presence and absence of a catalyst). This was attributed to the significantly lower electron density on the sulfur atom of BT when compared to any of the other sulfur compounds. Indeed, for DBT, 4-MDBT and 4,6-DMDBT, the difference in the electron density on the sulfur is very small (5.739, 5.758

and 5.760, respectively) and this is the steric hindrance of the methyl groups that governs the reactivity: the methyl groups become an obstacle for the approach of the sulfur atom to the catalytic active phase (in an heterogeneous system). A similar result was obtained in the present study, i.e. the reactivity of the sulfur compounds decreased in the order of  $\text{DBT} \gg 4,6\text{-DMDBT} > \text{C}_3\text{-DBT}$ , meaning that the reaction rate of the model sulfur molecules in a LGO is also modulated by the steric hindrance induced by the DBTs substituents and not by the electron density on the sulfur atom.

#### 4.3. Comparison of the oxidation reactivity of the nitrogen compounds

The denitrogenations of model compounds (indole, acridine, quinoline and carbazole) and of the LGO were also investigated using the same experimental conditions. We will first examine the literature describing the products that can be obtained by oxidation of the above model compounds. The aniline oxidation will be also described, as it is a simple N-containing compound, of which the oxidation has been extensively studied, contrary to the other molecules studied in the present work.

##### 4.3.1. Description of the products that can be formed by mild oxidation of nitrogen compounds

**4.3.1.1. Aniline oxidation.** Studies have showed that the oxidation of aniline with  $\text{H}_2\text{O}_2$  gives selectively azoxybenzene in the presence of titanasilicate, and nitrobenzene in the presence of vanadosilicate [30,31]. Similarly, nitrobenzene was also the product observed for oxidation performed with *tert*-butylhydroperoxide over vanadosilicate [32]. Further, Sarasa et al. studied the oxidation of aniline by ozonation in aqueous solutions [33]. They found that the nature of the formed aromatic products depends on the pH. Indeed, while only nitrobenzene and azobenzene were observed at low pH, azoxybenzene and 2-pyridine-carboxylic acid were also formed under basic conditions (Fig. 9). Furthermore, Costas et al. showed that the use of  $\text{HOOH}$  as an oxidative agent in

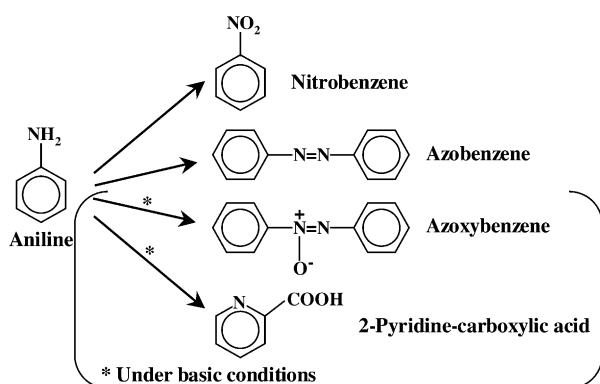


Fig. 9. Possible products of the aniline oxidation reaction.

the presence of  $\text{FeCl}_2\text{py}_4^+$  induces the formation of nitrobenzene as a main product [34]. Then, the formed nitrobenzene further reacted with aniline to give azobenzene and azoxybenzene. In contrast, the use of *t*-BuOOH led to the exclusive formation of nitrobenzene. Furthermore, it has also been shown that aniline can polymerize in an  $\text{H}_2\text{O}_2\text{-Fe}^{2+}$  system [35]. In brief, according to the reactions conditions (catalyst, oxidative agent, pH...) the selectivity of the aniline oxidation reaction can change drastically, illustrating the rich chemistry of the N-containing aromatic compounds.

**4.3.1.2. Indole oxidation.** Indole is catalytically converted into indoxyl under mild oxidation condition. Then, indoxyl further undergoes a spontaneous air oxidation to give isatin, indigo or indirubin [36], as represented in Fig. 10. In addition, the use of strong oxidation conditions can also lead to the cleavage of the pyrrole ring of indole [37]. Further, Shiraishi et al. showed recently that the oxidation of indole with  $\text{H}_2\text{O}_2$  in the presence of titanovanadate leads to the formation of a polymerized material that includes various types of N–H, C=O and OH groups in its structure [30]. The presence of a polymerized material is in good agreement with other works that showed that indole can polymerize electrochemically [38–40] or chemically in oxidizing solutions [41]. Further, the presence of C=O bonds is also in good agreement with the structure of the products presented in Fig. 10, while the presence of O–H bonds might be explained by the presence of tautomeric forms due to a cetone–enol equilibrium, which is for instance well described for the indigo molecule [42].

**4.3.1.3. Quinoline and acridine oxidation.** The literature concerning the partial oxidation of quinoline and acridine is rather scarce. Quinoline is a toxic pollutant and many studies focus on its degradation by wet oxidation at temperatures of more than  $200^\circ\text{C}$  [43–45] with the production of a great number of aromatics and aliphatic products. In fact, studies dealing with the acridine oxidation are quite rare, although the oxidative degradation of ‘acridine orange’, a dye polluting water, is the object of a few studies [46,47]. We could find one study specifically dealing with the electrochemical

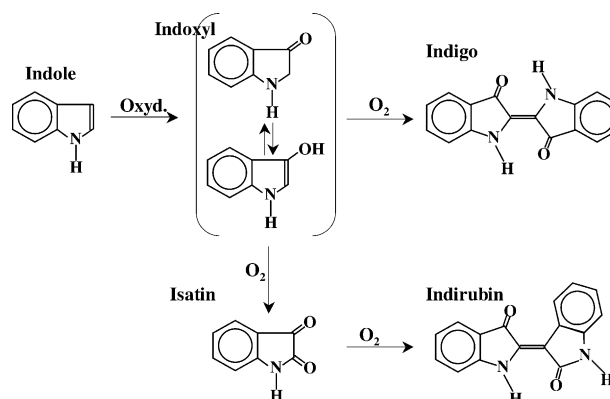


Fig. 10. Possible products of the indole oxidation reaction.

oxidation of acridine [48] and here acridine polymers were obtained.

Thus, as was observed for indole, we can suppose that under mild conditions a lot of compounds can be selectively obtained, according to the experimental conditions.

**4.3.1.4. Carbazole oxidation.** Shiraishi et al. obtained carbazole-1,4-dione by oxidation of carbazole with  $\text{H}_2\text{O}_2$  in the presence of a titanosilicate [30]. In addition, carbazole can also be converted for instance into 3-hydroxycarbazole [49] or 2'-aminobiphenyl-2,3-diol [50] under the action of specific enzymes. Further, as stated for aniline, indole and acridine, carbazole can give polymers by electrochemical oxidation [51]. Shiraishi et al. found recently that carbazole can be converted into a polymer containing C=O and OH groups when oxidized with  $\text{H}_2\text{O}_2$  over a vanadosilicate [52], which is in good agreement with the above-described case of indole.

In brief, the oxidation of these N-containing compounds gives a rich chemistry in which the product selectivity depends on the experimental conditions. Indeed, in addition to classical 'addition' reactions, cycle cleavage can occur, and even polymers can be obtained.

#### 4.3.2. Experimental results

In the present work, we compared the denitrogenation activity of indole, quinoline, acridine and carbazole. The activity order was indole > quinoline > acridine > carbazole (Fig. 7), which is in good agreement with the results of previous studies that suggested that carbazole is particularly refractory to the oxidation process. These experiments on model compounds showed that it is possible to use the process that we developed for the oxidative desulfurization for the oxidation/removal of N-containing compounds without any specific adaptation. Then, we subsequently checked the oxidative denitrogenation performances when using the LGO. As represented in Fig. 7, elimination of N-containing compounds in the LGO proceeded easily with a conversion as high as ca. 95%, indicating that the N-containing molecules present in the LGO are mainly compounds that can be easily treated. Consequently, the process developed for the ODS is particularly advantageous, as it can be also concomitantly used as is for ODN without any modification for treating the LGO.

Further, we tried to identify the N-products hydrogenation compounds using a GC-MS. For all the compounds, the chromatograms obtained after oxidation presented a great number of peaks of various intensities. Unfortunately, their identification was made quite difficult due to overlapping between not only the oxidized nitrogen compounds themselves but also with peaks attributed to oxidation products of the solvent as well as peaks attributed to various oxidation products of impurities present in the solvent, making the MS spectra quite difficult to interpret due to resolution problems. Nevertheless, careful examination of

the fragmentary ions confirmed that many products containing both oxygen atom(s) and nitrogen atom(s) were formed. Further, some *m/e* values were consistent with the presence of dimers or even trimers of the treated compounds. Especially, it seems like compounds like isatin or indirubin were formed and some fragmentary ions were in good agreement with the presence of indoxyl (as in Fig. 10). Further, we cannot exclude the possibility of a condensation between oxidized molecules derived from different nitrogen compounds for the experiments performed with a blend of model compounds.

In brief, while the identification of the products could not be satisfactorily achieved, the present results are in good agreement with the literature presented in Section 4.3.1 that showed that many compounds can be formed by mild oxidation of nitrogen compounds, and especially suggested that polymeric materials containing N and O were formed.

## 5. Conclusions

The oxidation of the sulfur compounds of a LGO was carried out over a 16 wt.% Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. The LGO oxidation activity increased with increasing the O/S molar ratio up to 15 and then slightly decreased above this value. This value was largely superior to the stoichiometric ratio (2), which indicated that oxidation side-reactions that consumes oxidation agent concomitantly occurred. Further, the oxidation reactivity of the sulfur compounds decreased in the order DBT  $\gg$  4,6-DMDBT > C<sub>3</sub>-DBT. This suggests that, unlike the cases for reactions performed without catalyst for which the rate is governed by the electron density on the sulfur atom, when the reaction is performed over a catalyst, the oxidation rate is limited proportionally to the substituents' complexity. In addition, the reaction kinetics for the above-mentioned sulfur compounds was also investigated. The results suggested that the oxidation reaction of each sulfur compound can be treated as a first-order reaction, which apparent activation energy was the same at  $32 \pm 2$  kJ/mol, irrespective of the sulfur compound.

The oxidized LGO was then treated in an experimental apparatus consisting of the oxidation reactor coupled with an adsorption reactor disposed in line. The adsorption of the oxidized light gas oil was performed on a silica gel at ambient temperature, and the total sulfur content could be decreased down to values less than 5 ppm (initial S content  $\sim$ 39 ppm), which is under the most drastic future restrictions that will soon be imposed by environmental laws.

In a second part of the study, we investigated the oxidation and adsorption of model nitrogen compounds dissolved in decalin using the same combined experimental apparatus. The denitrogenation activity of the nitrogen compounds decreased in the order of indole > quinoline > acridine > carbazole. Moreover, after the complete process, the nitrogen concentration in the light gas oil could be decreased from 13.5 ppm to a value as low



as 0.8 ppm. Further, while the oxidation products of the nitrogen compounds could not be fully identified, the results suggested the presence of polymeric compounds in good agreement with other recent studies.

In brief the experimental process proposed in the present study appears to be an excellent solution to face the future environmental challenges that will soon be imposed by the new regulations. Indeed, we could decrease the sulfur and the nitrogen sulfur contents of a commercial LGO down to values respectively better than 5 and 1 ppm, which is remarkable. In addition, we are now aiming at further improving the present process in order to achieve final S concentrations of less than 1 ppm, and the actual results are extremely encouraging.

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