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Oxidative desulfurization of synthetic diesel using supported catalysts Part I. Study of the operation conditions with a vanadium oxide based catalyst

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Abstract

In this work, an experimental study was carried out to obtain the reactivity of different organic sulfur compounds and to examine the effect of various parameters, such as temperature, solvent and the amount of oxidant reagent in oxidative desulfurization (ODS) reaction. The oxidation was performed through a vanadium based catalyst in the presence of hydrogen peroxide under mild reaction conditions, atmospheric pressure and temperature range of 303–343 K. The sulfur compounds studied were: 2-methylthiophene (2-MT), 2,5-dimethylthiophene (2,5-DMT), benzothiophene (BT), dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT). All of them are typical thiophenic sulfur compounds present in diesel fuels. A synthetic diesel was prepared with these compounds in hexadecane. The experimental results showed that oxidation reactivities decreased according to the following order: DBT > BT > 4-MDBT > 2-MT > 2,5-DMT > 4,6-DMDBT. A fraction of the S compounds removed from the diesel phase, was not transformed to its corresponding sulfone, under these experimental conditions. It is only removed as sulfur compound by extraction, without ODS reaction. The surplus amount of oxidant promoted the equilibrium reaction, but the thermal decomposition of oxidant and oxidation reactions produces water, which inhibits the ODS reactions. Therefore, the controlled addition of H_2O_2 improves ODS reactivity of sulfur compounds.

Keywords: Diesel; Kinetic parameters; Oxidant reagent; Oxidative desulfurization; Refractory sulfur compounds; Solvent effect; Ultra-low sulfur diesel

1. Introduction

In order to effectively control air pollution due to diesel fuel combustion, the US Environmental Protection Agency (EPA) has released a new regulation requiring the use of ultra low-sulfur diesel fuel (ULSD). This rule requires that the sulfur content of the on-road diesel fuel limited to 15 ppm, and it has to be effective by 2006 [1,2]. In Mexico similar regulation is to be issued. At present, the current specification is 500 ppm of S. Due to this specification; increasing technical and operational challenges are imposed to traditional hydrodesulfurization (HDS), which is an integral part of refining operations. To produce diesel fuels with an ultra-low level of sulfur, deep HDS techniques must be adopted. These techniques require HDS to be operated under more severe conditions, including the use of higher temperatures, higher hydrogen pressures, more active catalysts and longer residence time. However, it is expected that deep HDS produces negative effects, such as reduced catalyst life, higher hydrogen consumption and higher yield loss, thereby resulting in higher operating costs [3]. The HDS process is not cheap because of several reasons. One of them is the high hydrogen pressure needed for kinetic and catalyst stability purposes. Another reason is related to dibenzothiophene derivate compounds that constitute very refractory molecules to the process, such as 4,6-DMDBT, resulting in significant difficulty to achieve the very low sulfur content required. To eliminate undesirable sulfur compounds or to convert them into more innocuous forms, various alternative processes to HDS, have been employed. For instance, these processes include the physical extraction

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with a liquid, the selective adsorption over suitable materials, reductive and oxidative microbial processes, or the catalytic oxidation [4]. Thus, the most effective options for ultra deep desulfurization should be chosen, since removing all sulfur from the fuels might be too expansive or result in extremely high refinery CO_2 emissions [3]. In this sense, technologies that do not use hydrogen are considered to be attractive for attaining high levels of sulfur removal by shifting the boiling points of sulfur-containing compounds, separating by extraction and decomposition via selective oxidation.

Oxidative desulfurization (ODS) produces oxidized compounds that can be physically separated and could be easily processed downstream. Sulfur compounds are known to be slightly more polar than hydrocarbons of similar structure, i.e. oxidized sulfur compounds, such as sulfones or sulfoxides are substantially more polar than sulfides. This permits the selective removal of sulfur compounds from hydrocarbons, by a combined process of selective oxidation and solvent extraction or solid adsorption.

The oxidizing agents for ODS are hydrogen peroxide, peracids, hydroperoxides, chlorine, nitrogen oxides, oxygen or ozone [5–7]. The most common oxidant is hydrogen peroxide, generally in formic acid [8,9]. However, the reaction can be carried out in non-acidic media, in the presence of catalytic amounts of tungsten, molybdenum or vanadium [10,11], on silicates, zeolites, molecular sieves and mesoporous materials [12,13] or various supported catalysts [14], i.e. MoO_3, NiMo, CoMo, CrO_3 and WO_3 supported on alumina.

It is evident that the greatest advantages of the ODS process are the low reaction temperature and pressure, and that expensive hydrogen is not used in the process. Moreover, HDS refractory sulfur compounds are easily converted by oxidation [15]. Recently, UOP and EniTecnologie reported the economic benefits of implementing an ODS process to produce near-zero-sulfur diesel [16]. Therefore, ODS has a great potential to become a complementary process to traditional HDS in the production of deeply desulfurized diesel fuels.

Dibenzothiophene (DBT), 4-methyl dibenzothiophene (4-MDBT) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT) are typical refractory sulfur compounds in diesel and other gas oils. It is well known that the HDS reactivity of DBTs decreases dramatically with the increase of methyl substitutes at the sterically hindered positions (positions 4 and 6). Otsuki et al. [9] reported the following trend for the sulfur compound oxidation reactivity in a formic acid/H_2O_2 system: methyl phenyl sulfide > thiophenol > diphenylsulfide > 4,6-DMDBT > 4-MDBT > DBT > BT > thiophenes. This trend confirms that the refractory sulfur compounds in HDS are the most reactive in the oxidation reaction. However, other studies have shown important differences, for a series of polyoxometalate/H_2O_2 systems [8], the oxidation reactivities decreased in the following order: DBT > 4-MDBT > 4,6-DMDBT, it is the same reactivity trend that exists in HDS [3]. The fact that the polyoxometalate/H_2O_2 and formic acid/H_2O_2 systems showed completely different reactivity order for the same oxidation of dibenzothiophenes, suggests that the molecular size of the catalyst may be playing an important role. ODS reactivity decreases, in presence Mo/Al_2O_3 catalysts [14], from DBT > 4-MDBT > 4,6-DMDBT $\gg$ BT, which is very different from the results obtained without a solid catalyst.

Due to the differences on the results obtained from an ODS system, the purpose of this paper is to examine the effect of various parameters, such as temperature, solvent and the amount of oxidant reagent, on the synthetic diesel ODS kinetics by hydrogen peroxide over vanadium oxide based catalyst. Secondly, we sought to obtain information on the applicability of the oxidation method to the selective transformation of the organic sulfur compounds for the ultra deep desulfurization of diesel fuels.

2. Experimental

2.1. Materials

All the reagents employed in this study were commercially available (Sigma/Aldrich) and were used without further purification. 847 S ppmw of 2-methylthiophene (2-MT), 720 S ppmw of 2,5-dimethylthiophene (2,5-DMT), 612 S ppmw of benzothiophene (BT), 445 S ppmw of dibenzothiophene (DBT), 414 S ppmw of 4-dimethyldibenzothiophene (4-MDBT) and 387 S ppmw of 4,6-dimethyldibenzothiophene (4,6-DMDBT) dissolved in hexadecane were used as a synthetic diesel. These concentrations are typically found in straight run gas oils. Hydrogen peroxide (aqueous solution, 30 wt.%) was used as oxidizing agent and acetonitrile was used as solvent.

TiO_2 anatase supported V_2O_5 (10 wt.%) was used as catalyst. Ammonium metavanadate (Aldrich, 99.8%), as source of V_2O_5 and titania (Hombitec K, 120 m^2/g) were used. The catalyst was prepared by the wet-impregnation method. The required amount of ammonium metavanadate was dissolved in a 2 M oxalic acid solution and mixed with the support. The excess water was then slowly evaporated and continuously stirred. The residue thus obtained was dried at 100 °C for 12 h and calcined at 500 °C for 6 h in an open-air furnace.

2.2. Catalytic experiments

The catalytic oxidation of sulfur-containing organic compounds with hydrogen peroxide was carried out in a glass batch reactor, equipped with a magnetic stirrer, a thermometer and a condenser. In a typical run, the solid catalyst (100 mg) was suspended under stirring (750 rpm) in a mixture containing synthetic diesel (50 mL), the solvent (diesel/solvent ratios 1:10, v/v) and H_2O_2 (O/S ratios 2.13 to 21.3) at a constant temperature (between 303 and 343 K).

Solvent and diesel phases were recovered at various times. They were analyzed qualitatively by GC–MS (HP G1800B) and GC-PFPD (Varian CP-3800), after filtration and eventually decantation step. Reaction products were quantitatively analyzed by GC–FID using a PONA capillary column (Methyl silicone Gum, 50 m × 0.2 mm × 0.5 μm film thickness) in a HP5890 Series II chromatograph. The hydrogen peroxide, presented during the reaction, was measured by standard iodometric titration.

2.3. Conversion or removal of sulfur compounds from diesel phase

Removal or conversion (Xa) for a given organic sulfur compound was calculated using their initial concentration (C_0) and concentration after t minutes of reaction (C_t), as: $Xa = (C_0 - C_t)/C_0$, assuming that the volume and mass of the reaction mixtures were constant, since only small amounts of liquid samples were withdrawn during the reaction. The oxidative reaction of each sulfur compound follows a first-order kinetics, according to previous results, obtained with aromatic sulfur compounds on solid catalysts [6,12,14,17]. Due to a large excess of oxidant, we assumed that the hydrogen peroxide concentration is constant. Thus, the rate constant (k) and reaction time (t) can be described using the following equation: $\ln(C_t/C_0) = -kt$, where $k = A \exp(-E/RT)$, A is the pre-exponential factor, E the apparent activation energy, R and T are the gas constant and reaction temperature (K), respectively.

3. Results and discussion

It is well known that organic sulfides, thiophenes, benzothiophenes, dibenzothiophenes and their alkyl-substituted derivates are the major sulfur-containing compounds present in liquid hydrocarbon fuels. Thus, a series of experiments was carried out, in order to assess the kinetic parameters, and evaluate the effect of temperature, oxidant reagent and solvent in ODS reaction.

3.1. Reactivity of different sulfur compounds

Under the experimental conditions above described, the oxidation reaction of benzothiophene compounds led directly to the corresponding sulfone. Sulfoxides were not detected in the products. According to ODS results of model compounds and gas oils, with formic acid as catalyst [9], the oxidation of thiophene derivatives (2-MT and 2,5-DMT) did not take place.

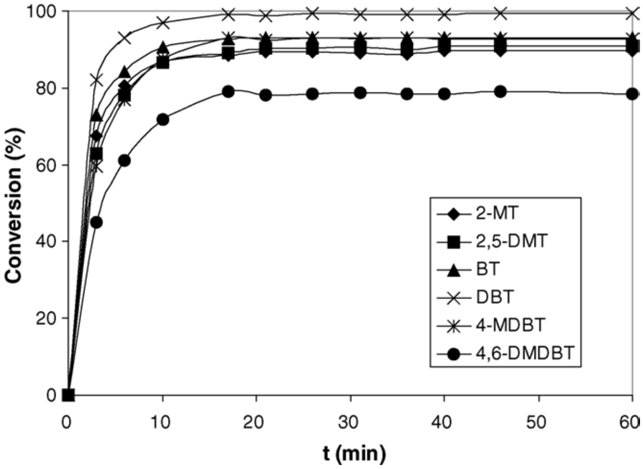

Fig. 1. Removal of organic sulfur compounds vs. reaction time at 325 K.

The removal of organic sulfur compounds as a function of reaction time at 325 K is showed in Fig. 1. The results plotted in this figure lead to the following comments: the equilibrium conversions are obtained in about 15 min for all sulfur compounds. The alkyl-thiophenes, BT and 4-MDBT are removed at similar rates. The condensed aromatic thiophene, DBT, is more reactive than other compounds, and 4,6-DMDBT is the most refractory compound under these conditions, as in HDS process. Similar behaviors were observed at 303 and 343 K, for all compounds, but the equilibrium conversions were reached in about 60 and 5 min, respectively, for the mentioned temperatures.

Since H_2O_2 was present in excess (O/S ratio was 21.3), the reaction data were fit into a first-order rate equation. A plot of $\ln(C_t/C_0)$ versus reaction time displayed a linear relationship that confirmed the pseudo-first-order reaction kinetics. Therefore, the reaction rate constants at various temperatures can be obtained from the slopes for the sulfur compounds. The rate constant at 343 K for DBT oxidation was 0.41 min^{-1} and 0.14 min^{-1} for 4,6-DMDBT. The apparent activation energies of all compounds were obtained from the slopes of the Arrhenius plots, and were 35.3–48.4 kJ/mol. These values indicated a decrease in the reactivity of DBT when was incorporated the methyl substitute group, suggesting that steric hindrance is important. ODS activation energies were lower than those of HDS, which may be explained as ODS reaction was conducted at a lower reaction temperature compared to HDS. Moreover, these results also suggested that mass transfer processes could be important.

The constants of apparent oxidation rate obtained from the kinetic coefficients of pseudo-first-order reaction are shown in Fig. 2, for the different temperatures. These results showed that the reactivity of sulfur compounds during the oxidation with H_2O_2 differs importantly to observed in the HDS process and obtained by other authors in ODS [3,8,14]. ODS reactivities, in this case, decreased according to the following order: DBT > BT > 4-MDBT > 2-MT > 2,5-DMT > 4,6-DMDBT. It seems that the sulfur compounds such as BT and DBTs, which are hard to treat by HDS, are readily oxidized with H_2O_2 under mild reaction conditions. However, the 4,6-DMDBT in ODS reaction is also the most refractory compound. According to the previous results

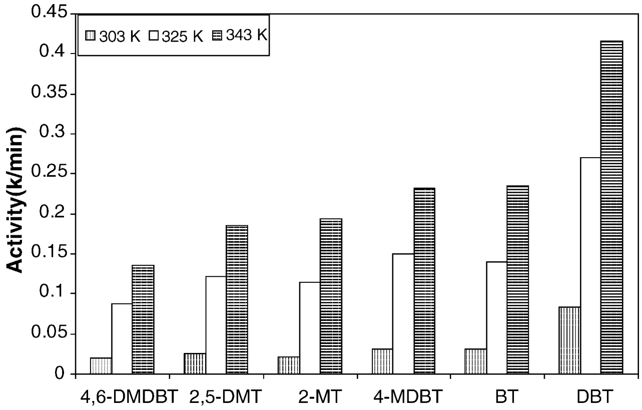

Fig. 2. ODS activities of organic sulfur compounds, evaluated as oxidation rate constants (*k*) at various temperatures.

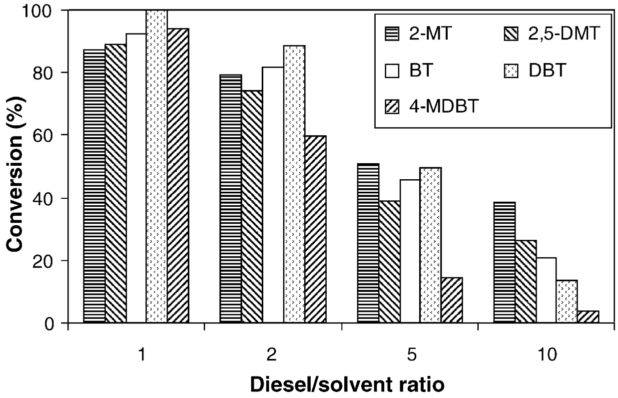

Fig. 4. Removal of S compounds after 1 h of reaction at 343 K.

obtained with other catalysts, these differences in activity trends can be explained by the steric hindrance of the methyl substitution [14]. The reactivity trend is different when sulfur compounds were tested without a solid catalyst [8,9].

3.2. Solvent effect

The solvent plays a very important role in the catalytic reactions carried out in the liquid phase, and the results obtained in the oxidation of sulfur compounds with H_2O_2 confirmed this assertion [12,13,18]. This effect is strongly dependent on the catalyst type and the nature of the substrate. In fact, during ODS process the sulfur compounds are transferred to the polar solvent, and the solvent can influence the mass transport and diffusional problems, especially with porous catalysts. We have studied the reaction system under different conditions, in order to study the solvent effect on the ODS of model diesel.

The extraction of sulfur compound took noticeably place with no catalyst (see Fig. 3). It is possible to remove about 20% of methyl substituted DBTs, close to 40% of DBT and 2,5-DMT and up to 50% of 2-MT and BT by means of the extraction process. In contrast, with catalyst and oxidant although without solvent, there was no oxidation reaction of these compounds and the conversion was practically zero. Nevertheless, another important factor is the minimum amount necessary for the reaction–extraction process. In this regard, the reaction was carried out with different diesel/solvent ratios. The results on solvent effect are reported in Fig. 4. They showed that the ODS activity decreased about 50% when the ratio is 5 and up to 90% for 4-MDBT for a ratio of 10. Therefore, the relative ODS activity of different sulfur compounds was affected by diesel/solvent ratio due to the differences in solubility, as the solvent amount was diminished. Moreover, as the H_2O_2/S ratio was kept constant, the water (as reaction product) to solvent ratio increased. Consequently, the water hindered the catalytic performance [12]. By the way, ODS activity tests at 333 K were carried out using mixtures of water–acetonitrile as solvent (diesel to solvent ratio = 1). The results are shown in Table 1. In this table we can observe that DBT sulfone production is strongly affected by the presence of water in the reaction system. This can be explained, by the fact that the oxidized organic sulfur compounds are fully soluble in acetonitrile and only partially soluble in water. Thus, the solvent performances depend considerably on the solubility of the sulfur oxidation products in the reaction mixture.

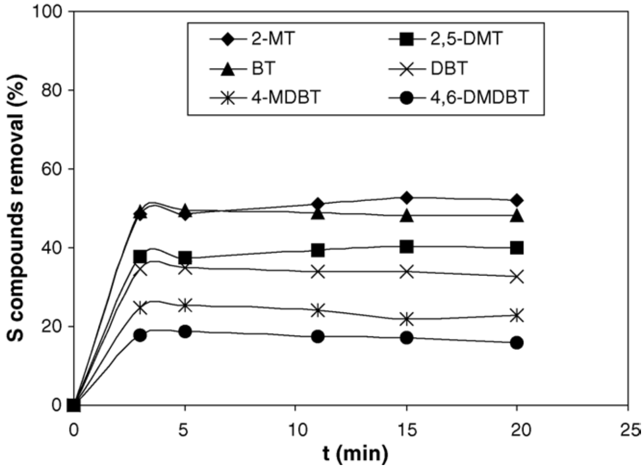

Fig. 3. Sulfur compounds removal vs. reaction time. The test was carried out without catalyst and oxidant reagent, at 333 K and diesel/solvent ratio = 1.

3.3. Influence of the oxidant reagent

As a preliminary test, hydrogen peroxide and tertbutyl hydroperoxide were assayed as oxidants. The results showed

Table 1
Water effect on ODS reactivity of DBT at 333 K

Test	Acetonitrilo in solvent (vol.%)	Water in solvent (vol.%)	DBT sulfone produced (ppm)
1	100	0	886
2	75	25	346
3	50	50	65
4	0	100	0

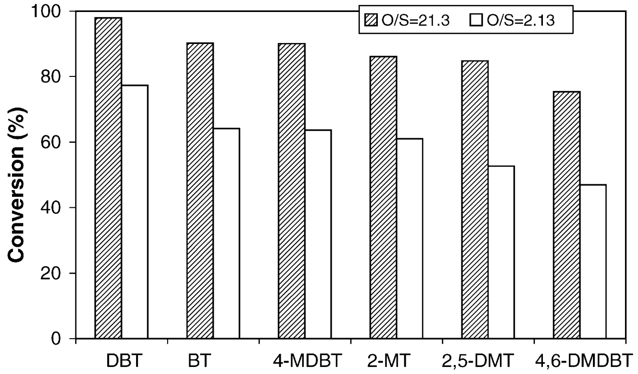

Fig. 5. S compounds removal at different H_2O_2/S ratios (O/S), after 30 min of reaction at 333 K.

that the total S removal and ODS reactivity to sulfones are significantly favored by H_2O_2, under similar conditions. This oxidant was selected for all activity tests.

The effect of the variation of H_2O_2 to substrate ratio has been studied by using synthetic diesel as organic reagent and acetonitrile as solvent (diesel/solvent ratio = 1.0), with a H_2O_2/S ratio of 21.3 or 2.13. The reaction was performed at 333 K. The results, obtained after 30 min of reaction, are shown in Fig. 5. The conversion of sulfur compounds increased with increasing H_2O_2 concentration. The BT conversion increased from 78 to 99% as the ratio of H_2O_2/S increased, whereas the conversion of 4,6-DMDBT increased from 45 to 78%. These results show the balance of two opposing factors, the excess of reactant (oxidant reagent) increases the activity and the water produced (from ODS reaction and thermal decomposition) hinders the ODS reaction. Therefore, in these conditions the former effect is more significant. Because of the maximum amount of water produced (O/S = 21.3), by total decomposition, represents only up to 20% of the reactive mixture volume. Hence, it is very important to control the oxidant reagent addition in these tests, because the thermal decomposition of hydrogen peroxide is well known.

The hydrogen peroxide present during the reaction was measured by standard iodometric titration. The results showed that the oxidant reagent is mainly in the solvent phase and its decomposition occurs in a few minutes, though, the reaction reaches the equilibrium because oxidant reactant was decomposed. We have suggested adding small amounts of hydrogen peroxide successively, in order to get rid of this problem.

Figs. 6–9 show the results of the test at 343 K with successive additions of H_2O_2, diesel to solvent ratio = 1 and initial O/S ratio = 4. Fig. 6 represents the removal of the reactants in the diesel phase, and Figs. 8 and 9 the percentage of reactants and sulfones in the solvent phase. Fig. 7 shows the profiles of the amount of H_2O_2 in the reactor. Initially, H_2O_2 was loaded in the reactor but after only 3 min it was completely consumed, therefore, the thermal decomposition was the main contribution. Afterwards, we added small amounts of H_2O_2 at 10, 20 and 30 min of reaction time, which were consumed in a few minutes.

In Fig. 6 we observe that the reactant conversions were appreciably increased at 10, 20 and 30 min, when hydrogen peroxide was added (see Fig. 7). Whereas, at the same reaction time, reactant and product contents in the solvent phase (Figs. 8 and 9, respectively) were modified. The extraction of the sulfur compounds decreased and the

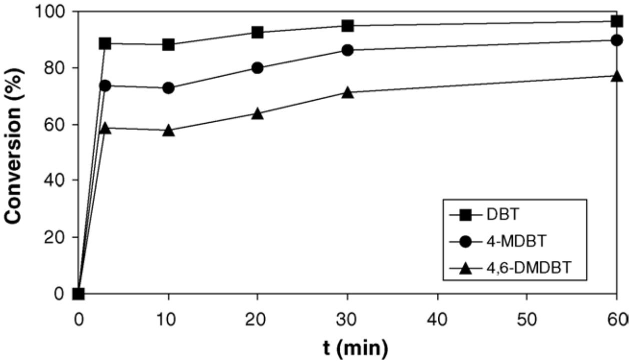

Fig. 6. Sulfur compounds conversion vs. reaction time at 343 K. Diesel/solvent ratio = 1 and initial H_2O_2/S ratio = 4.

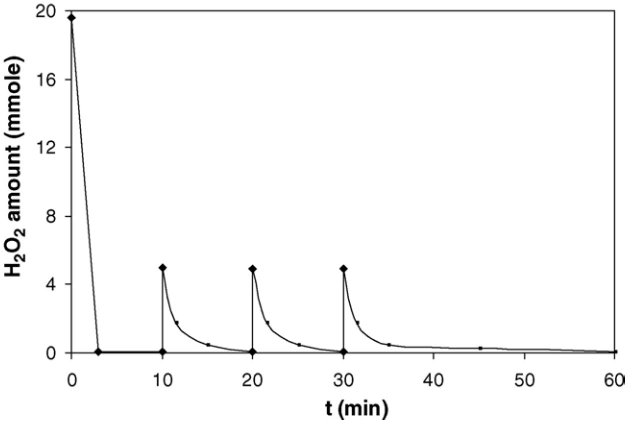

Fig. 7. H_2O_2 amount in the reactor, during ODS reaction at 343 K. Obtained by standard iodometric titration.

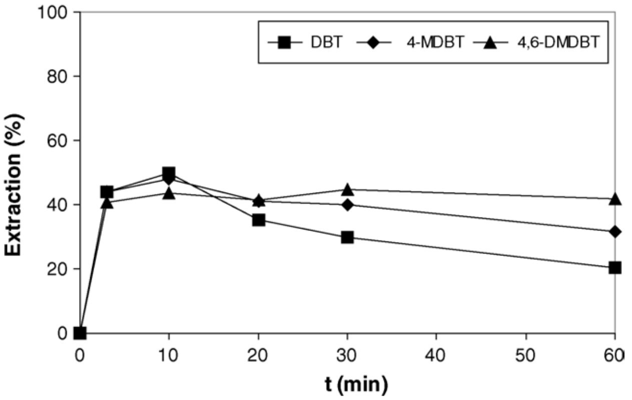

Fig. 8. S compounds extracted by the solvent, during ODS reaction at 343 K.

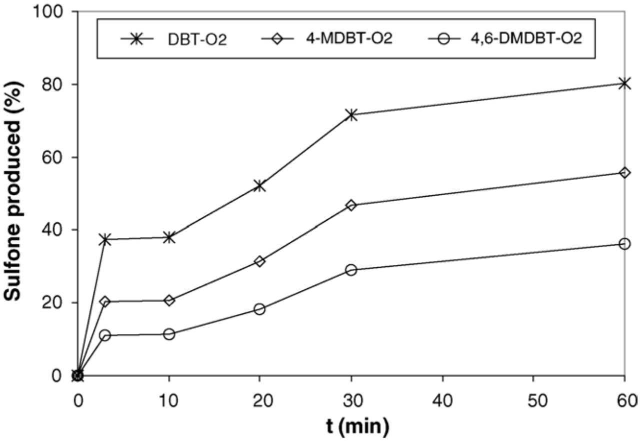

Fig. 9. Sulfones produced in solvent phase, during ODS reaction at 343 K.

conversions to sulfones increased noticeably. Consequently, the consumption of oxidant reagent is higher than the stoichiometric amount required for the ODS reactions (due to the thermal decomposition of H_2O_2), and the fact that the excess of H_2O_2 inhibits reactivity (due to a high amount of water in the reactor), shows the importance of a good dosage control so as to obtain the enough amount of oxidant reactant. This effect is not clear in Fig. 5, since it only shows the total S removal. For this reason, it is very important to evaluate the oxidized organic S compounds obtained during the ODS process.

4. Conclusions

Oxidative desulfurization of sulfur compounds in hexadecane was conducted in the presence of H_2O_2 at different temperatures, with a vanadium oxide based catalyst.

The following conclusions can be drawn from the above results: oxidation activities decreased according to the following order: DBT > BT > 4-MDBT > 2-MT > 2,5-DMT > 4,6-DMDBT. The oxidation of the sulfur compounds was achieved under mild reaction conditions and it was easy to increase the reaction temperature in order to achieve high oxidation conversions, even for the least reactive compound in HDS. The apparent activation energies of the sulfur compounds were 35.3–48.4 kJ/mol. These values indicated a decrease in the reactivity of DBT when the methyl substitute group was incorporated, thus suggesting that steric hindrance plays an important role during the oxidation reaction.

Whereas the oxidant amount in excess advances the equilibrium reaction, the water produced (due to the thermal decomposition and oxidation reactions) inhibits ODS reactions. Therefore, the controlled addition of H_2O_2 improves ODS reactivity of sulfur compounds.

Removal of sulfur compounds present in diesel can be carried out efficiently in the conditions studied here, with a yield higher than 80%, depending on the reactivity of each compound. A fraction of the eliminated compound in the diesel phase, is not totally transformed to its corresponding sulfone, it is only removed as a sulfur compound through extraction, without ODS reaction. For the extraction process, it is possible to remove about 20% of methyl substituted DBT, close to 40% of DBT and 2,5-DMT and up to 50% of 4-MT and BT, under these conditions.

Acknowledgements

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