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Hydrodesulfurization of diesel feeds by association of a catalytic process and a separation process using charge-transfer complexes

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While deep hydrodesulfurization of gas oil is more and more important, elimination of sulfur compounds such as 4,6-dialkyldibenzothiophenes still attracts considerable attention. A new process based on the association of a separation process by charge-transfer complex (CTC) formation and classical catalytic hydrotreating (HDT) was evaluated. The results indicated that a CTC pretreatment allows the rate of hydrodesulfurization (HDS) to increase and the final sulfur level to decrease. This process is even more efficient for feeds difficult to desulfurize.

KEY WORDS: hydrodesulfurization; gas oil; charge-transfer complexes; alkyldibenzothiophenes.

1. Introduction

In order to protect urban areas, environmental legislation has been adopted to limit the sulfur level in diesel fuel, and the need to produce extremely clean transportation fuel is continually increasing. For example, the sulfur content of light oils has been imposed to be 500 ppm in the EEC since 2000, and in Japan since 1997. More severe specifications with a sulfur content of 350 ppm are now currently practiced, and a sulfur content as low as 10 ppm is being proposed in Europe for the year 2005. Very deep conversion of sulfur compounds is therefore of vital importance.

Concerning such ultra deep HDS, it is now well established that among all the sulfur-containing compounds present in gas oil, alkyldibenzothiophenes with alkyl groups near the sulfur atom (fourth and six positions) are the most refractory [1–4], and numerous studies have been carried out in the last few years to better understand why such species are the most difficult to eliminate [5–10]. Most scientists now agree that after adsorption via an aromatic ring, the dibenzothiophene molecule is first hydrogenated to dihydrodibenzothiophene (as postulated by Singhal *et al.* [11]), which being intermediately transformed via two pathways on similar catalytic sites by hydrogenation into tetrahydro and hexahydrodibenzothiophene, or by desulfurization according to an elimination mechanism, results in biphenyl derivatives. In such a mechanism, the alkyl groups are not hindering the adsorption process on the catalytic surface but the elimination step by sterical effect. To eliminate this family of compounds in a gas oil, several techniques are considered at present. The easiest is to use more and more severe conditions: higher pressure of H_2 and/or higher temperature and lower LHSV. These are expensive solutions. Another possibility is to search to increase the activity of the catalyst, using new active phases [12–18], new supports [19–20 and reference therein] or a new way of preparing of classical $Co(Ni)Mo/Al_2O_3$ [21].

However, refractory sulfur molecules such as alkyldibenzothiophenes not only present a very low reactivity [10] but also a very low concentration in the real feed, conditions which lead naturally to a difficult catalytic process. An alternative to the classical hydrodesulfurization catalytic process has been proposed recently by some of us and is based on the formation of insoluble charge-transfer complexes (CTC). Considering the electron-rich structure of alkyldibenzothiophenes, these compounds could react with suitable π-acceptors [22–24]. By choosing the right complexing agent we can decrease the concentration of refractory molecules in the initial gas oil, and after filtration of the precipitate we recover a "new" charge which could be further desulfurized.

The aim of the study was to examine the association of a catalytic process and a separation process using charge-transfer complexes in order to quantify the gain in HDS obtained. This was done by comparison of untreated and CTC-treated gas oils under the same conditions of catalytic hydrotreating, on an $NiMo/Al_2O_3$ industrial catalyst and in a batch reactor.

2. Experimental

2.1. Materials

The first gas oil (G1) examined was a Straight Run Oil, with 13 200 ppm of sulfur, 3200 ppm (24%) included

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in benzothiophenes (BTs) and 10 000 ppm (76%) in dibenzothiophenes (DBTs). The second, a Light Cycle Oil (G2), contained 12 700 ppm of sulfur, 4000 ppm (31%) coming from BTs and 8700 (69%) coming from DBTs. These two gas oils seemed to be good model samples, because their sulfur concentrations are in the range of the industrial condition before HDS and their BT/DBT ratios are quite different.

The π-acceptor compound used for CTC formation was 2,4,5,7-tetranitrofluorenone (TENF) from Acros and was used as received.

For all the catalytic tests an NiMo/Al_2O_3 (Mo, 9 wt%; Ni, 2.4 wt%) commercial catalyst was used. The catalyst was first crushed, screened (80–125 μm) and presulfided for 4 h at 400 °C under atmospheric pressure with an H_2/H_2S gas mixture (molar ratio 15/85, total flow 4 l/h). The catalyst was cooled down to room temperature under the same atmosphere.

2.2. *Apparatus and reaction conditions*

The reactor used for catalytic tests was a 200 cm^3 stirred slurry tank reactor (STR) operating in the batch mode. The autoclave was equipped with a four-bladed mechanically driven turbine (900 rpm) with four tunnels inside. This kind of stirrer permits the obtention of a very good dispersion of the gas into the liquid phase. A baffle was also placed into the reactor to get a perfectly stirred system.

In every case 100 ml of the original or of the CTC-treated gas oil was introduced into the reactor. After that 250 mg of freshly presulfided catalyst was then added. N_2 was bubbled through the solution for 10 min to avoid any air contamination. Thereafter the reactor was heated under N_2 atmosphere and stirred up to the reaction temperature. N_2 was then replaced by H_2 by pressurizing the reactor to 5 MPa. This last step was taken as zero of the reaction time, and the pressure maintained constantly with a pressure controller. Samples were periodically removed during the reaction course and analyzed.

2.3. *Analysis*

Quantitative analysis of the total sulfur concentration was determined by energy X-ray fluorescence spectroscopy with an SLFA-1000 Series Horiba Ltd. sulfur analyzer, using 20 mm i.d. PTFE cells with 7 μm Mylar film windows. In order to eliminate the effect of the matrix on the gas oil the calibration of the apparatus was made with a series of different gas oils containing between 100 and 13 200 ppm of sulfur [25].

For the qualitative analysis of the sulfur-containing molecules, a gas chromatograph associated with a sulfur specific detector (Sievers MODEL 355 B SCD) was used. The operation is based on the chemiluminescence from the reaction of ozone, with sulfur monoxide (SO) produced from combustion of the analyte. The model provides high sensibility (<1 pg S/sec), linear and equimolar (per S atom) response, and high selectivity. For qualification of the components, the BT and DBT were commercially available and various alkyldibenzothiophenes have been synthesized as previously reported [10].

3. Results

3.1. *Preliminary study of the HDS of the original gas oils*

In order to check the best conditions for comparison of the various oils, initial velocities of HDS have been determined at several temperatures, with 250 mg of catalyst and 100 ml of feed. For gas oil G1, an apparent activation energy of 131 kJ/mol was calculated, which indicates that the experiments were performed in the absence of mass-transfer limitation. A temperature of 320 °C allowed one to determine the rate of desulfurization with good accuracy, and comparison of oils G1 and G2 is given in figure 1. The decrease of the rate of reaction with the conversion could be attributed to the inhibiting effect of H_2S produced by the desulfurization reaction, or as evidence of the presence of sulfur compounds that are more and more difficult to be transformed. Analyses of these feeds with the Sievers detector indicate that, after 160 and 90 h of reaction for gas oils G1 and G2, the unreacted sulfur compounds are mainly of dibenzothiophene types (figure 2).

3.2. *Elimination of sulfur compounds by CTC formation*

Experiments have been firstly performed in order to estimate the levels of desulfurization which could be reached for gas oils by charge-transfer complexes formation. 2,4,5,7-Tetranitrofluorenone (TENF) was added to 50 ml of gas oil, the mixture was stirred for 24 h, and the sulfur content of the residual feed was determined after filtration of the precipitate. Results collected in tables 1 and 2 indicate that for both feeds there is a limit of complexation under our experimental conditions. Such a limit was observed for about 42 mg and 39 mg of TENF per ml of gas oil G1 and G2 respectively. Such limits correspond to an elimination of about 14% of the total sulfur. Addition of more TENF did not allow one to get higher desulfurization.

Evolution of the sulfur compounds in oil during the process of complexation was controlled using the Sievers analyzer. Chromatographs reported in figure 3 for gas oil G1 indicate a progressive elimination of dibenzothiophenes. Moreover, estimation of the BT and DBT concentrations in the gas oil before and after CTC treatment indicates the BT concentration to be stable in the limit of the precision of the analysis, and the DBT disappearance to be in good agreement with the sulfur

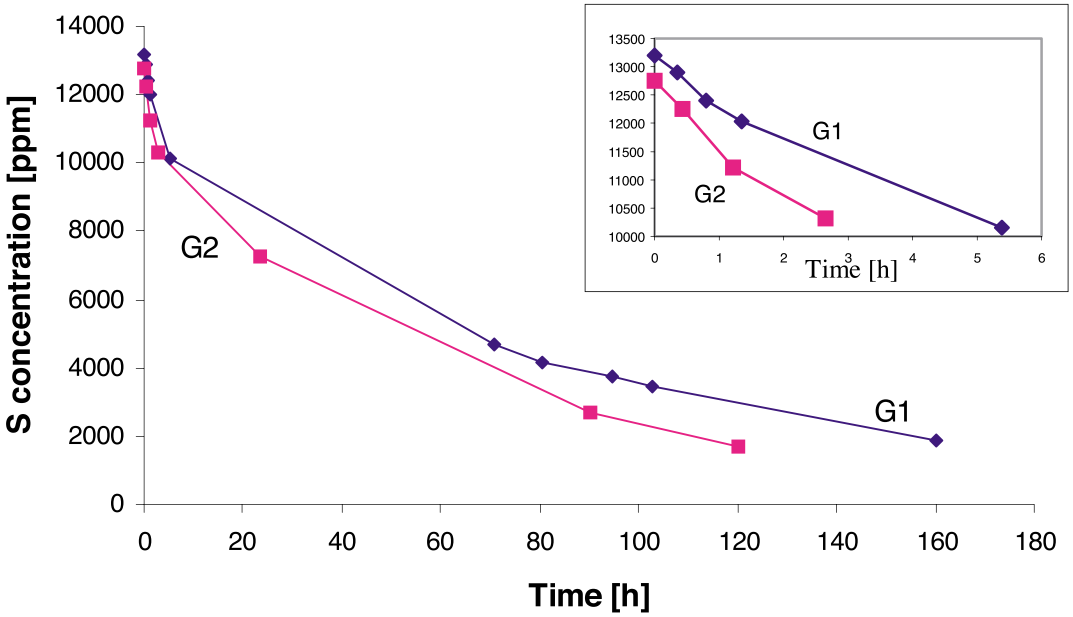

Figure 1. Evolution of the sulfur content in gas oils G1 and G2 during the course of the catalytic desulfurization process.

concentration decrease. The results show that the complexation in a suspension of sulfur compounds has a very good selectivity towards DBT-type molecules.

From the density of the oil, the concentration of sulfur could be estimated, and the variation of the sulfur content with the TENF addition allows one to calculate an efficiency factor of TENF relative to sulfur complexation, which was defined by

$$E_{\mathrm{S}}\left(\frac{\Delta S}{C_{\mathrm{TENF}}}\right)\cdot 100$$

where E_{S} is efficiency factor accessibility, ΔS is μmol/ml of sulfur compound eliminated by complexation and C_{TENF} is μmol/ml of TENF added.

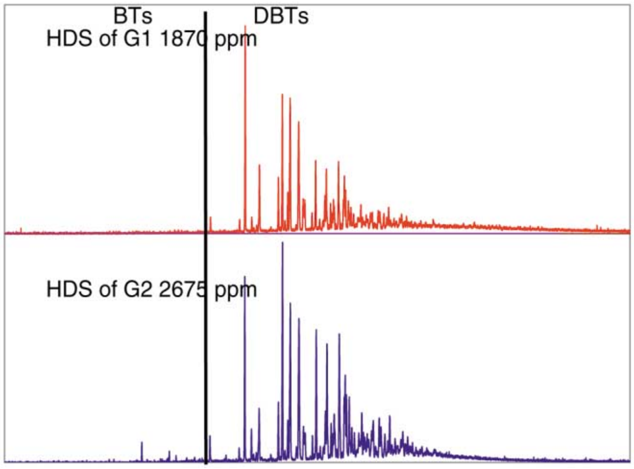

Figure 2. Sievers analyses of G1 and G2 gas oils after respectively 160 and 90 h of HDS reaction.

Values reported in tables 1 and 2 show that when the plateau of desulfurization is reached, only about 42% of the TENF was used for complexation of sulfur compounds, if we assume an equimolecular complexation between TENF and sulfur compounds. Such an observation suggests a possible association between TENF and some other donor molecules, or a partial insolubility of the TENF in the oil.

3.3. *Effect of the CTC treatment on the HDS of gas oils*

After treatment with 2,4,5,7-tetranitrofluorenone, gas oils G1 and G2 were submitted to a catalytic hydrotreating process under the same conditions as those used for the original oils: 320 °C and a pressure of 5 MPa. Results of initial rates of hydrodesulfurization reported in table 3 clearly show how the CTC treatment leads to oils that are more easy to desulfurize since the initial rate of sulfur-compound transformation is between 30 and 50% higher.

Other information could be deduced from the curves of figures 4(a) and (b), which report the evolution of the sulfur concentration *versus* the time of reaction. Indeed, the deeper the level of desulfurization required, the more interesting the association of a CTC pretreatment with the catalytic process appears.

4. Discussion

Gas oils G1 and G2 present about the same sulfur content, but different composition as regards the nature of the sulfur compounds. Comparisons in the

Table 1
Evolution of G1 gas oil sulfur content with TENF addition.

TENF added (ml of gas oil)		[S] ppm	Δ[S] ppm	Δ[S] (%)	[S] μmol/ml	Δ[S] μmol/ml	E_S (%)
mg	μmol						
0	0	13 200			343.6		
6	16.7	13 026	174	1.32	339.1	4.5	26.9
12	33.3	12 609	691	5.2	328.2	15.4	46.2
18	50.1	11 978	1222	9.3	317.8	25.8	51.0
24	66.8	11 780	1420	10.7	310.6	33.0	49.4
30	83.5	11 679	1521	11.5	304.0	39.6	47.4
36	100.2	11 560	1640	12.4	300.9	42.7	42.6
39	108.5	11 457	1743	13.2	298.2	45.4	41.8
42	116.9	11 320	1820	13.8	294.7	48.9	41.8
48	133.6	11 300	1900	14.4	294.1	49.5	
54	150.3	11 310	1890	14.3	294.4	49.2	
60	167.0	11 318	1882	14.2	294.6	49.0	

Table 2
Evolution of G2 gas oil with TENF addition.

TENF added (ml of gas oil)		[S] ppm	Δ[S] ppm	Δ[S] (%)	[S] μmol/ml	Δ[S] μmol/ml	E_S (%)
mg	μmol						
0	0	12 752			331.3		
6	16.7	12 541	211	1.65	325.8	5.5	32.9
12	33.3	12 002	750	5.9	311.8	19.5	58.5
18	50.1	11 526	1226	9.6	299.4	31.9	63.0
24	66.8	11 380	1372	10.8	296.6	34.7	51.9
30	83.5	11 240	1512	11.8	292.0	39.3	47.0
36	100.2	11 104	1648	12.9	288.4	42.9	42.8
39	108.5	11 000	1752	13.7	285.7	45.6	42.0
42	116.9	10 996	1756	13.8	285.6	45.7	

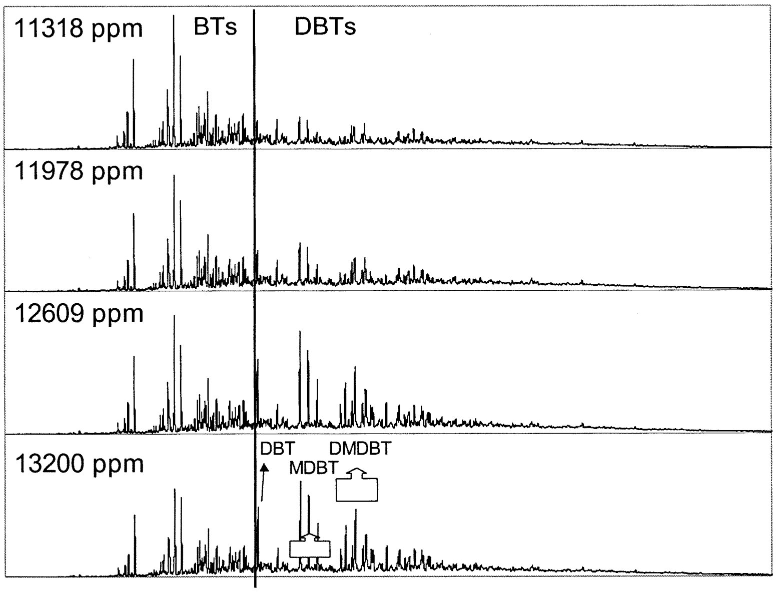

Figure 3. Evolution of the sulfur compounds during the course of the CTC process (Sievers analyses).

Table 3
Initial velocity of HDS for the treated and untreated samples.

	R_{HDS} [a]	$R_{\mathrm{CTC+HDS}}$	Changing [%]
G1	250	381	+50
G2	265	340	+30

[a] R is expressed in μmol S min^{-1} g^{-1}.

desulfurization rates at the beginning of the process and under conditions of deep HDS could therefore be made in relation to such variations. The initial rates of reaction of 250 and 265 μmol S min^{-1} g^{-1} could be attributed to the transformation of benzothiophenes, and the results of figure 2 confirm the transformation of these compounds to proceed first. Moreover, though the slight variations of initial HDS rates could be considered inside the experimental reproducibility, the difference is in favor of gas oil G2, which has the higher proportion of benzothiophenes (31% *versus* 24% for G1). On the contrary, G1 appears to reach less rapidly the level of deep conversion, which could be explained by the higher proportion of dibenzothiophenes, well known as highly refractory sulfur compounds.

As regards the formation of charge-transfer complexes for both gas oils, the high selectivity of TENF with dibenzothiophenes as compared to benzothiophenes is clearly illustrated by the results of figure 3. However, this process does not allow for desulfurization higher than 14%, and if we assume the stoichiometry of

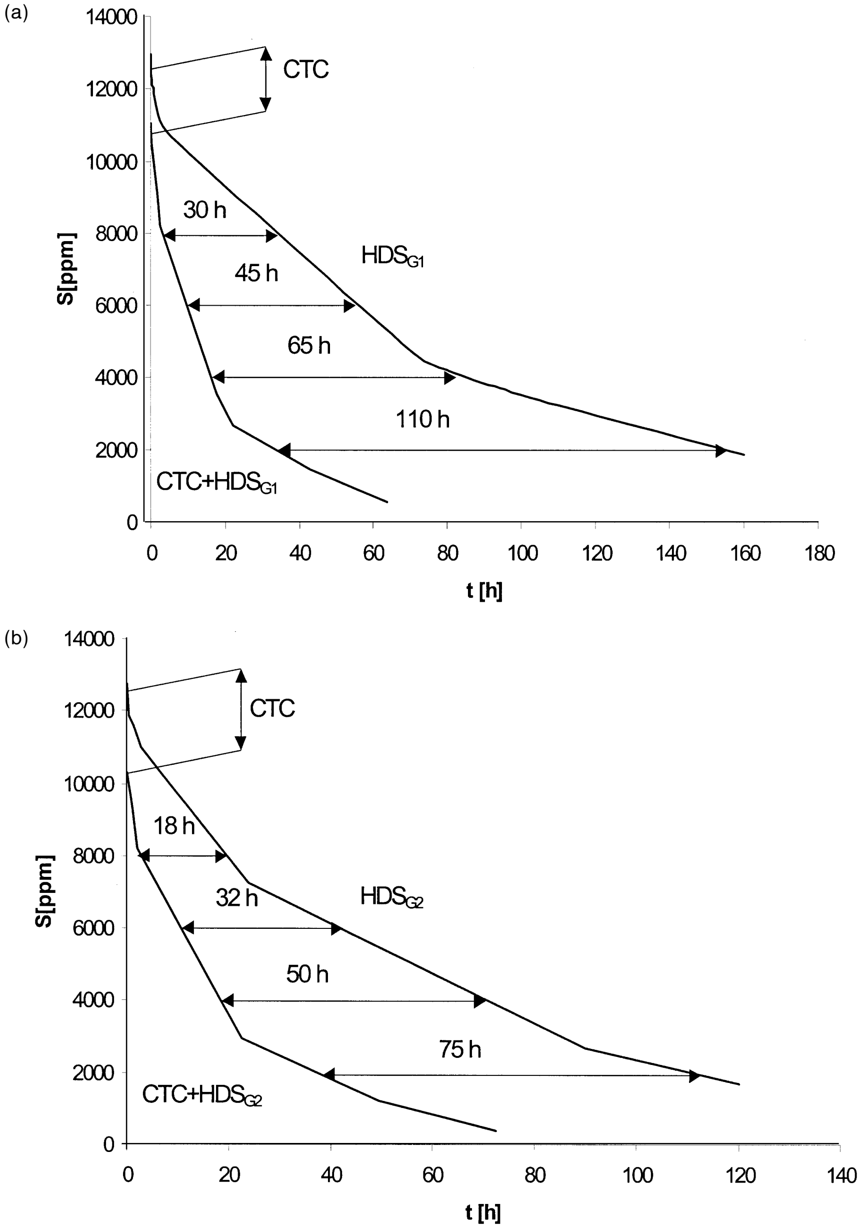

Figure 4. Comparison of the sulfur evolution for CTC treated and untreated gas oils (figure4(a) for G1, figure 4(b) for G2).

the complexation to be one molecule of TENF per molecule of sulfur compound, the efficiency of the TENF is only about 40% in both cases.

Nevertheless, and even with an efficiency of the complexation of sulfur compounds of only 40%, a strong effect of the CTC pretreatment over the hydrodesulfurization was observed. A positive effect is first evidenced by the initial rate of transformation of the oils, which means the transformation of benzothiophenes. This could appear surprising since no benzothiophenes have been eliminated by the CTC pretreatment, but it is probably proof of an inhibiting effect of dibenzothiophenes on the desulfurization of these benzothiophenes. Moreover, values of initial rates reported in table 3 indicated the CTC pretreatment to be more interesting on G1 than G2, in agreement with the higher concentration of dibenzothiophenes in the former.

Figures 4(a) and (b) also allow one to analyze the variations between both gas oils at different levels of HDS. For the same level of desulfurization required, the gain in reaction time obtained by the CTC pretreatment is more important on G1 (figure 4(a)) than G2 (figure 4(b)), in agreement with the higher proportion of dibenzothiophenes in the former.

5. Conclusion

New and more restrictive legislation has given vital importance to deep hydrodesulfurization. For deep hydrodesulfurization, a new process based on the successive elimination of sulfur by charge-transfer complexation and a classical catalytic HDT has been proposed and evaluated in batch experiments on real feeds.

The results indicated that:

- pretreatment with 2,4,5,7-tetranitrofluorenone as a π-acceptor leads to elimination of alkyldibenzothiophenes;
- the pretreatment changes the initial HDS velocity for the two gas oils studied, and the effect is more pronounced for the oil more difficult to desulfurize;
- the positive effect of CTC pretreatment is higher when we are nearer to the "deep" HDS conditions.

Work is in progress to evaluate these CTC pretreated feeds in continuous flow microreactors.

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