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Deep hydrodesulfurization of diesel fuel: Design of reaction process and catalysts

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Abstract

Deep hydrodesulfurization (HDS) of diesel fuel oil was designed based on the recognition that alkyl dibenzothiophenes such as 4-methyl- and 4,6-dimethyldibenzothiophenes were the main target for deep HDS. Multi-stage and fractional HDS were very effective to achieve satisfactory HDS in terms of both sulfur level and fluorescent color of desulfurized oil. Catalysts with the selective hydrogenation of refractory sulfur species in major aromatic partners and isomerization–disproportionation of their alkyl groups prior to HDS were also designed to promote the desulfurization of such sulfur species.

Keywords: Dehydrosulfurization; Diesel fuel

1. Introduction

Hydrodesulfurization (HDS) process is required to produce the low-sulfur diesel fuel below 0.05 wt.-% according to the recent increasing demands for the environmentally-accepted clean fuel with the least cost increase.

In our previous study [1–4], alkyl-dibenzothiophenes with alkyl groups at the 4- and/or 6-positions, such as 4,6-dimethyl-dibenzothiophene (4,6-DMDBT), showed much lower reactivities in HDS than dibenzothiophene. In general, the lighter fractions containing more reactive sulfur compounds, for example alkyl benzothiophenes, can be more easily desulfurized within a first few minutes of reaction, while the heavier fractions containing unreactive sulfur compounds as described above are hardly desulfurized in the conventional HDS process [5].

On the basis of the above understanding, the present authors proposed three approaches to achieve the deep desulfurization, multi-stage or fractional desulfurization and catalyst design for the selective hydrogenation of the refractory sulfur species in major aromatic matrix and isomerization of alkyl dibenzothiophenes prior to their HDS.

2. Experimental

The catalytic reaction was studied using a conventional batch-autoclave, for details we refer to a previous paper [2]. The total reaction pressure was controlled at the designed pressure throughout the reaction by adding gaseous hydrogen into the autoclave to compensate for its consumption. The catalysts used were commer-

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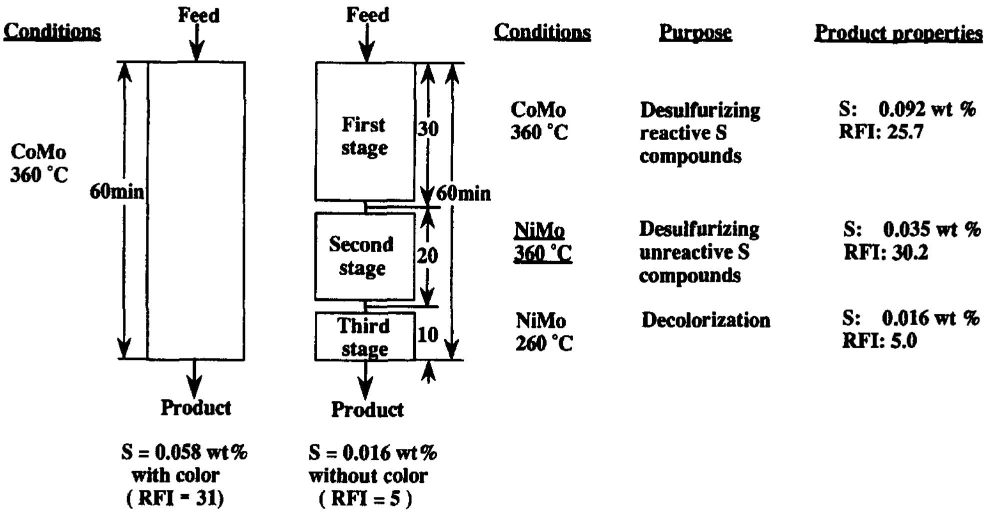


Fig. 1. Comparison of single and three-stage desulfurization of diesel fuel. Sulfur content in feed: 0.706 wt.-%.

cial Ni–Mo/Al_2O_3, Co–Mo/Al_2O_3 provided from Nippon Ketjen Co., and Co–Mo/Al_2O_3 + Zeolite provided from a petroleum company. Ru/Al_2O_3 catalyst was prepared by impregnating $RuCl_3$ on Al_2O_3 extrudate. The catalysts were presulfided before used.

A diesel fuel and its fractions (F1–F5) were supplied from a petroleum refinery. 4,6-dimethyldibenzothiophene (4,6-DMDBT) was prepared according to the literature [6]. The feeds and their hydrotreated products were analyzed by GC and GC–MS. Fluorescent color of oils was observed using fluorescence spectrometer by describing its relative fluorescent intensity (RFI), referring to a previous paper [3].

3. Results

3.1. Multi-stage desulfurization

Fig. 1 illustrates the results of three-stage hydrodesulfurization of diesel fuel under a total pressure of 2.9 MPa. The first stage achieved the sulfur level of 0.092 wt.-% over the Co–Mo at 360°C for 30 min, exhibiting strong fluorescent color of RFI 25.7. The second stage over the NiMo at 360°C for 20 min reduced further the S level to 0.035 wt.-%, desulfurizing refractory sulfur compounds as shown in Fig. 2, although it emphasized the fluorescent color to RFI 30.2. In order to remove the fluorescent

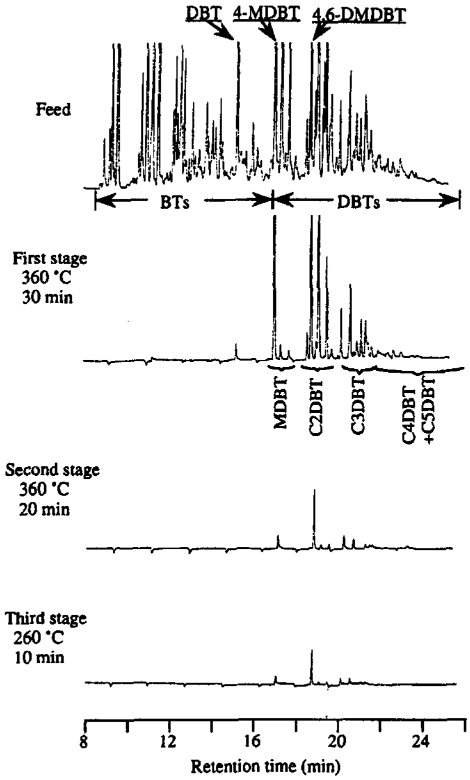


Fig. 2. GC–FPD chromatograms of feed and product oils in different stages.

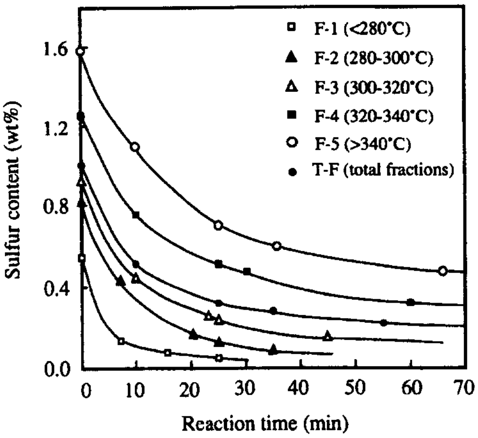


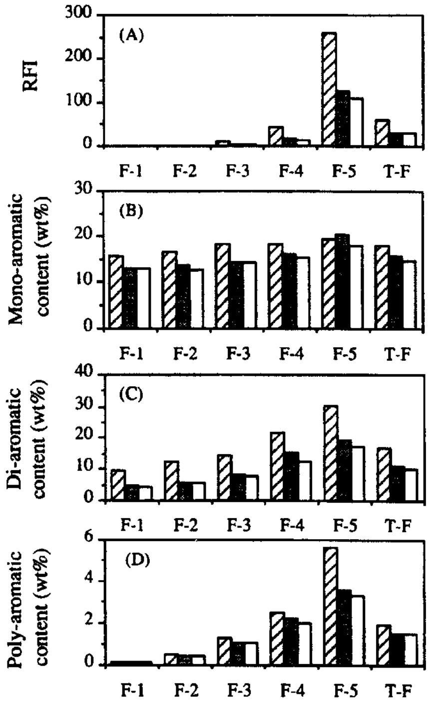
Fig. 3. Sulfur content of each fraction as a function of reaction time.

color in deeply desulfurized oil, the third stage was performed over the same Ni–Mo catalyst at a lower temperature of 260°C, where the RFI was reduced to 5.0 and the sulfur content was also further reduced to 0.016 wt.-%. Thus, such a three-stage hydro-desulfurization satisfied both sulfur level and color of the product oil by an acceptable reaction time (60 min). In this multi-stage desulfurization, pure hydrogen was used in the second stage to reduce the retardation by produced H_2S, which was found to be one of the major inhibitors for the HDS of refractory sulfur compounds [2,7]. In contrast, the single stage HDS at 360°C for 60 min over CoMo provided 0.058 wt.-% of S and RFI 31.

3.2. *Fractional desulfurization*

The heavier fractions of F4 (320–340°C) and F5 (> 340°C) carried a major portion of refractory sulfur species such as 4-methyl- and 4,6-dimethyldibenzothiophene. Fig. 3 illustrates the desulfurization reactivities of respective fractions at 360°C, 2.9 MPa over Ni–Mo. The heavier fraction exhibited the least reactivity. While the desulfurization of lighter fraction was almost completed at 20 min, its high reactivity being noted. Fig. 4 illustrates color and aromatic components in the fractions before and after the desulfurization. The color appeared to be strong in both heavier fractions and their desulfurized oils, which required the color removal by the hydrogenation. The heavier fraction carried polyaromatic species and more sulfur compounds, which retarded the desulfurization of the refractory sulfur species.

On the basis of the difference in the fractional reactivity and the color, the fractional desulfurization appears to be more economical for deep HDS. Fig. 5 illustrates a new proposal of the desulfurization scheme, where the lighter and heavier fractions are desulfurized respectively at upper and lower parts of a reactor, which is different from the SynSat process [8]. By such a reactor, the lighter fractions are desulfurized very rapidly for shorter reaction time of 20 min over the CoMo catalyst, where the inhibition of H_2S can be overlooked due to



Reaction conditions: 360 °C, 2.9 MPa, 25 min
▨ Feed
■ Product by CoMo
□ Product by NiMo

Fig. 4. Change in fluorescent color and aromatic contents of the fractions in respective HDS.

the high reactivities of the sulfur species in them. No color development occurs ruling out the stage of post-hydrotreatment. In contrast, longer reaction time and staged reaction zones for the deep desulfurization and color removal of the heavier fractions can be designed with optimum catalysts at optimum temperatures. A countercurrent liquid–gas flow is suggested in such a reactor to reduce the inhibition of produced H_2S and to decrease the temperature of the reactor bottom for the color removal. Detailed design of reactor and catalysts are necessary to allow the conventional gas/oil ratio.

3.3. Catalyst design

The catalysts for the desulfurization of refractory sulfur species are designed by two approaches. The first approach is to find a catalyst of selective hydrogenation to the refractory sulfur species among the major presence of polyaromatic hydrocarbons. Ru is a noble metal which has been reputed to be active in the presence of H_2S [9]. Thus, a hybrid of Co-Mo/Al_2O_3 and Ru/Al_2O_3 enhanced the desulfurization of 4,6-DMDBT through its selective hydrogenation in the presence of naphthalene.

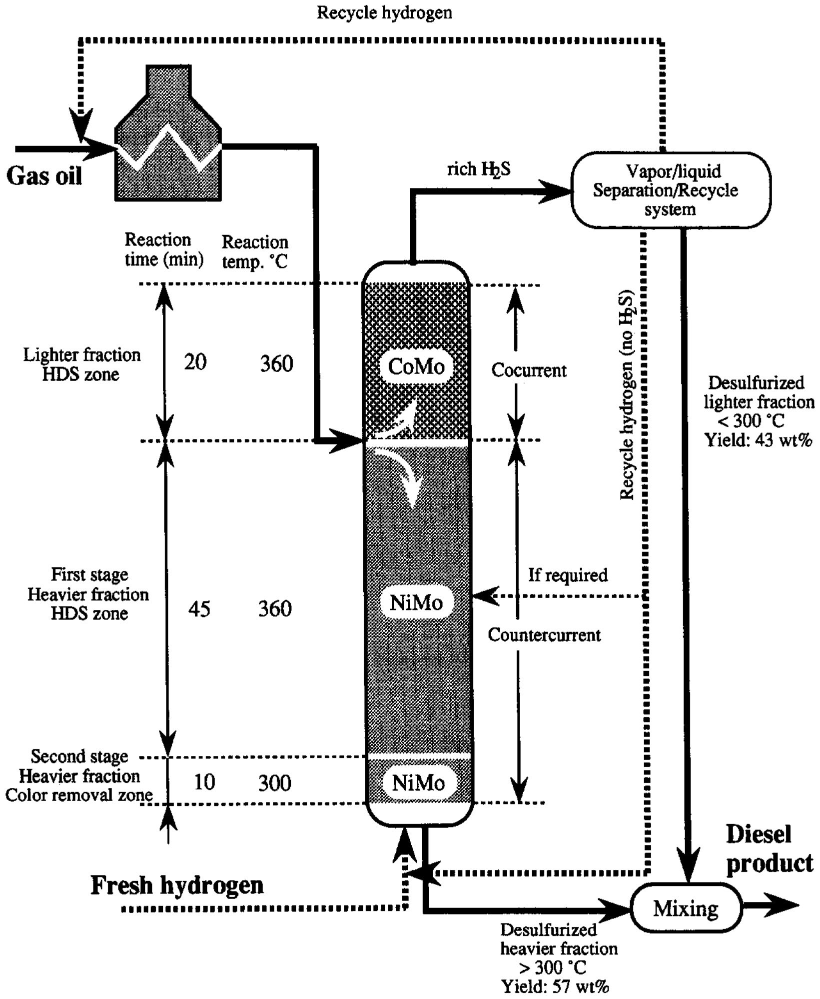


Fig. 5. Deep HDS reactor design with cocurrent and countercurrent liquid–gas contact in separate catalyst beds.

Higher selectivity for 4,6-DMDBT was obtained than that for naphthalene [10,11].

The quantum chemical calculation indicated that hydrogenation of the benzene ring neighboring the S atom not only increases the electron density at the S atom, but also liberates the steric hindrance through the molecular puckering of the refractory sulfur compounds [4]. Such a selective hydrogenation can be possible by a multi-point planar adsorption of aromatic species to form π-coordination. The MO calculation shows that the HOMO of 4,6-DMDBT is a π orbital concentrated on the S atom vertical to the molecular plane, which can act as an anchor for the selective multi-point adsorption.

The second approach is the isomerization of methyl groups on the DBT skeleton to remove their steric hindrance to the desulfurization. A zeolite-containing Co–Mo/Al_2O_3 catalyst showed a slightly higher activity than conventional Ni–Mo/Al_2O_3 and Co–Mo/Al_2O_3 because of higher conversion of 4,6-DMDBT. The product analysis indicated the isomerization and disproportionation of its methyl groups.

4. Discussion

The present study discussed the reactivity of sulfur species, inhibitor of H_2S and aromatic partners, selectivity of the catalysts for the hydrogenation of refractory sulfur species among dominant aromatic hydrocarbons and isomerization of methyl groups on DBT skeleton.

The desulfurization reactivity is basically governed by the electron density of sulfur when steric hindrance is absent. Hydrogenation of benzene ring of 4,6-DMDBT is effective to remove the steric hindrance by breaking the coplanarity of DBT skeleton [4]. The produced H_2S and coexistent aromatic hydrocarbons hinder the sulfur removal and hydrogenation of refractory sulfur species.

On the basis of the above mechanistic understanding, multi-stage, fractional desulfurization and their combination are very effective for the deep desulfurization with color removal.

Finally, the catalysts for selective hydrogenation and methyl migration are designed to enhance the desulfurization of refractory sulfur species. Selection of metallic species and control of acidity appear very effective to develop new type of HDS catalysts.

References

[1] K. Sakanishi, X. Ma. and I. Mochida, J. Petrol. Inst. Jpn., 36 (1993) 145.

[2] X. Ma, K. Sakanishi and I. Mochida, Ind. Eng. Chem. Res., 33 (1994) 218.

[3] X. Ma, K. Sakanishi and I. Mochida, Fuel, 73 (1994) 1667.

[4] X. Ma, K. Sakanishi, T. Isoda and I. Mochida, Energy Fuel, 9 (1995) 33.

[5] X. Ma, K. Sakanishi, T. Isoda and I. Mochida, Ind. Eng. Res. Chem., 34 (1995) 748.

[6] R. Gerdil and E. Lucken, J. Am. Chem. Soc., 87 (1965) 213.

[7] M.J. Girgis and B.C. Gates, Ind. Eng. Chem. Res., 30 (1991) 2021.

[8] A. Suchanek and G. Hamilton, 1992 NPRA Annu. Meet., (1992) AM-92-19.

[9] A.S. Hirschon, R.B. Wilson Jr. and R.M. Laine, Appl. Catal., 34 (1987) 311.

[10] T. Isoda, S. Nagao, X. Ma, Y. Korai and I. Mochida, Prepr., Am. Chem. Soc., Div. Fuel Chem., 40 (1995) 982.

[11] T. Isoda, S. Nagao, X. Ma, Y. Korai and I. Mochida, Prepr., Am. Chem. Soc., Div. Fuel Chem., 40 (1995) 989.