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Removal of Dibenzothiophene from the Simulated Petroleum by γ-Irradiation Induced Reaction

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A novel method for the removal of sulfur compounds in petroleum was put forward and investigated on the basis of the radiochemical reaction induced by γ irradiation. Dibenzothiophene (DBT) dissolved in dodecane was employed as the simulated petroleum. The results showed that the removal efficiency of DBT was about 33% when the radiation dose was 185 kGy. The apparent reactions for the removal of DBT were presumed, and the corresponding kinetics equation was deduced and proven experimentally. Meanwhile, some methods were preliminarily used to improve the removal of DBT in the presence of γ irradiation at room temperature. Among which, the mixture of hydrogen peroxide (H_2O_2) and acetic acid (HAC) appeared to be synergic to the radiation removal of DBT. Also, Cobalt-oxide showed significant promotion to the removal of DBT under the irradiated situation, and the removal efficiency increased by over 40% compared with radiation only.

1. Introduction

It is well-known that petroleum is derived from organic matter in nature and contains a certain amount of organic sulfur compounds, ranging from 0.05 to 6%.[1] As the worldwide regulation on sulfur levels of liquid fuel is getting stricter, the demand for the cleaner and lighter oil fractions is increasing.[2] The US-EPA Tier II regulations have required the reduction of sulfur in highway diesel from the current average of 500 to 15 ppmw by June 2006 and that in gasoline from 350 to 30 ppmw by January 2005. In 2009, the maximum S content will be limited to 10 ppmw.[3−5] Because of the gradual reduction of the statutory sulfur content in most western countries, the studies on deep desulfurization of diesel fuel have attracted more and more attention.[6,7]

Radiation technology has been applied to the fuel process during these years. The early studies were focused on the effect of γ-rays radiation on coal chemistry.[8,9] It was also introduced to the desulfurization and demineralization from high-sulfur coals.[10] At the same time, the electron beam radiation method was preliminarily applied to assist with thermal cracking of heavy oil and desulfurization.[11,12] In our previous study, γ radiation was used to remove mercaptan compounds from the simulated petroleum, and it appeared to be a potential approach. Meanwhile, acetone and carbon tetrachloride was found to display a high promotion to the radiation removal of mercaptans by γ-rays.[13]

In addition to mercaptans, dibenzothiophene (DBT) and its derivative are also the main organic sulfur compounds existing in petroleum. Because these heterocyclic compounds are relatively stable with respect to their molecular structure, the traditional processes, such as acid−alkali treatment, are inefficient to remove them from petroleum. Hydrogenation has been widely used for petroleum desulfurization. Because of the rigorous operating conditions (higher pressure and temperature in the presence of the catalyst) and the consumption of hydrogen, this technique appeared to be expensive both in its capital investment and in the operating cost. In addition, DBT and its derivatives are relatively difficult to be converted by hydrogenation among the organic-sulfur compounds. Therefore, the sulfur compounds that remain in the transportation fuel are mostly in the form of dibenzothiophene and its alkylated derivatives.[14,15] In this paper, the method based on γ-rays radiation was employed to remove DBT in the simulated petroleum. Besides, some methods were experimentally attempted to improve the removal of DBT.

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[1] Speight, J. G. *The Chemistry and Technology of Petroleum*, 2nd ed.; Marcel Dekker: New York, 1991.

[2] Jung, H.; Shin, J. S.; Yoon, W. L.; Park, J. S.; Lee, H.; Lee, D. K. *Energy Fuels* **2004**, *18*, 924−929.

[3] Avidan, A.; Klein, B.; Ragsdale, T. *Hydrocarbon Process* **2001**, *80*, 47−52.

[4] Regulatory Impact Analysis: Heavy-Duty Engine and Vehicle Standards and Highway Diesel Fuel Sulfur Control Requirements; United States Environmental Protection Agency, December 2000, I-4, EPA420-R-00−026.

[5] Mathieu, M.; Marc, S.; Alain, F.; Marc, L. *Ind. Eng. Chem. Res.* **2004**, *43*, 7843−7849.

[6] Marroquín, G.; Ancheyta, J.; Farfán, E.; Ram’rez, A. *Energy Fuels* **2001**, *15*, 1213−1219.

[7] Liu, Y. O.; Liu, C. G.; Que, G. H. *Energy Fuels* **2002**, *16*, 531−535.

[8] Henely, E. J.; Karasyk, L. *Fuel* **1961**, *40*, 155−161.

[9] Ram, L. C.; Tripathi, P. S. M.; Jha, S. K.; Sharma, K. P.; Mishra, S. P. *Fuel Process. Technol.* **1997**, *53*, 1−14.

[10] Tripathi, P. S. M.; Mishra, K. K.; Roy, R. R. P.; Tewari, D. N. *Fuel Process. Technol.* **2001**, *70*, 77−96.

[11] Zaykina, R. F.; Zaykin, Y. A.; Mirkin, G.; Nadirov, N. K. *Radiat. Phys. Chem.* **2002**, *63*, 617−620.

[12] Zaykina, R. F.; Zaykin, Y. A.; Mamonova, T. B.; Nadirov, N. K. *Radiat. Phys. Chem.* **2002**, *63*, 621−624.

[13] Yan, N. Q.; Zhao, Y. F.; Wu, WD.; Jia, J. P.; Yao, S. D.; Wang, W. F. *Fuel Process. Technol.* **2004**, *85*, 1393−1420.

[14] Nakayama, N.; Matsubara, T.; Ohshiro, T.; Moroto, Y.; Kawata, Y. *Biochim. Biophys. Acta* **2002**, *1598*, 122−130.

[15] Hernández-Maldonado, A. J.; Yang, R. T.; Cannella, W. *Ind. Eng. Chem. Res.* **2004**, *43*, 6142−6149.

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2. Experimental Procedures

2.1. Apparatus. The experimental setup in this study has been described previously.[13] The radiation source of γ-rays is ^{60}Co, with the intensity of about 10^5 Ci. The radiation dose rate (R, kGy/h) is dependent upon the radial distance between the sample and the center of the source, which is calibrated regularly by the Fricke Dosimetry method (GB193-89). The range from 2.21 to 9.40 kGy/h of the radiation dose rate was used in this paper. The radiation dose (D, kGy) was calculated as follows:

$$D = Rt \tag{1}$$

where, R and t are the radiation dose rate and the accumulating radiation time, kGy/h and h, respectively.

2.2. Reagents. The chemicals of DBT and dodecane were of chromatographic purities, which were purchased from Sigma−Aldrich. The other chemicals were of analytical purities and obtained from Shanghai Chemical Reagent Corporation. The aeration gases were air or nitrogen (high purity, filled in steel cylinders). To simplify the reaction system in this study, only dodecane was used as the simulated petroleum and the concentration of DBT in it ranged from 0.5 to 30.0 g/L.

2.3. Catalyst Preparation. Catalysts in this study were prepared on the basis of the impregnation method with metal nitrate. The detailed procedures were as follows: (1) using metal nitrate to prepare the solution, the concentration was dependent upon the demanded laden amount of catalyst on the carrier; (2) active γ-Al_2O_3 powder (100 mesh, Shanghai Chemical Reagent Corporation) was used as the carrier of the catalyst, and it was washed and dried before being employed; (3) certain amounts of solution was taken, and γ-Al_2O_3 powder was immersed into it, while leaching the redundant solution, heating to dry the powder at about 100 °C, and then, immersing the dried powder into the redundant solution again. After 2−3 runs of soaking and drying, all of the metal nitrate in the solution was uniformly deposited on the surface of γ-Al_2O_3 powder; and (4) the γ-Al_2O_3 powder impregnated with the nitrate was gradually heated to 400 °C in air, and the remaining powder was heated to the temperature at about 400 °C for 2 h to convert the metal nitrate to metal oxide. The content of metal oxide on γ-Al_2O_3 was about 5%.

2.4 Analysis. All of the samples from the experiments were analyzed with a GC-14B (Shimadzu, Japan), which was equipped with a flame photometric detector and capillary column (ϕ, 0.54 mm × 30 m). For quantitative analysis, a standard solution consisting of DBT was diluted to various demanded concentrations and then the calibration curve was obtained with these solutions. The removal efficiency of DBT, η, was calculated as follows:

$$\eta = (C_i - C)/C_i \times 100\% \tag{2}$$

in which, C_i and C represent the initial and remaining concentration of DBT in the dodecane solution before and after irradiation, respectively.

The products derived from the removal of DBT and dodecane in the irradiated samples were identified with GC/MS (Shimadzu, P2010) and LC/MS techniques (HP1100), respectively.

The total sulfur in the samples was analyzed by a microcoulometer (Jiangsu Electronic Analytic Instrument Factory, China). The calculation method of removal efficiency of total sulfur was the same as that of DBT.

3. Results and Discussion

3.1. Dependence of the Removal Efficiency on the Initial DBT Concentration. The removal efficiency of DBT with various initial concentrations was investigated in a static reactor (without the aeration of air or nitrogen) with the radiation dose rate of 3.95 kGy/h, and the results are shown in Figure 1.

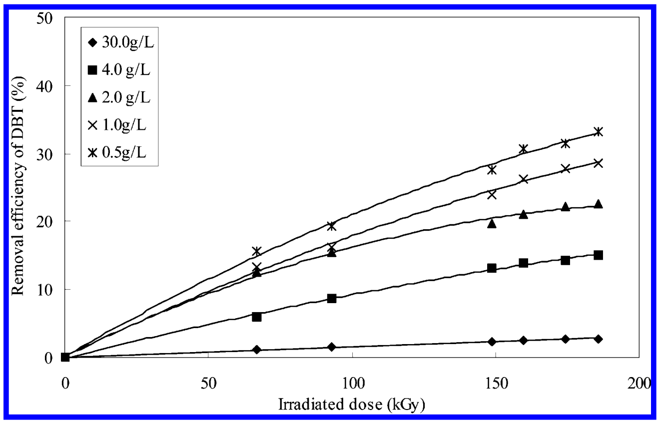

Figure 1. Removal efficiency of DBT with a different initial DBT concentration at various radiation doses. Dibenzothiophene was dissolved in dodecane and irradiated at 298 ± 2 K at a static condition. The radiation dose rate was 3.95 kGy/h.

It was found that the removal efficiency of DBT increased with the rise of the radiation dose, and η decreased with the increase of the initial concentration. With the radiated dose of 185 kGy, η was about 33% for DBT when the concentration was 0.5 g/L. However, it dropped to about 15% as the concentration increased to 4 g/L. When the initial concentration further increased to 30 g/L, η was only about 2.5% for DBT with the above-mentioned dose. This indicated that γ radiation was more effective for the removal of DBT at lower concentrations; therefore, the initial DBT concentration was set at 0.5 g/L in the following study if it was not stated clearly.

3.2. Kinetics of DBT Conversion by Radiation. It was observed from Figure 1 that the depletion rate of DBT approximately appeared to be the first-order mode with respect to DBT when its concentration was low. However, the depletion rate was close to zero-order kinetics when the concentration of DBT was up to 30 g/L.

Although the exact mechanism for DBT removal by γ radiation was not accessible with the setup in this study, the apparent reaction paths for DBT removal can be speculated as follows. First, the activated species, A*, were produced through reaction 3 in the irradiated system, in which M represented solvent molecules. It should be noted that A* can be regarded as the equivalent of all active species that can react with DBT and remove it. Therefore, k_1 merely represented an apparent rate constant of all of the reactions that produced A*. Similarly, reaction 4 was also an overall reaction, and k_2 was also the integrative rate constant for all reactions that can deplete DBT. Meanwhile, because the active species A* were not stable, they would decay through the interaction with the bulk molecules (solvent molecules), and the overall reaction was expressed as reaction 5 with the apparent rate constant of k_3

$$\mathrm{M} + \gamma\text{-}h\nu \xrightarrow{k_1} \mathrm{A}^* \tag{3}$$

$$\mathrm{A}^* + \mathrm{DBT} \xrightarrow{k_2} \text{products} \tag{4}$$

$$\mathrm{M} + \mathrm{A}^* \xrightarrow{k_3} \text{decay} \tag{5}$$

where M is the bulk molecule (ground state) in the irradiated solution. Because dodecane is the preponderant component in the solution (~99.95%), M can be regarded as only the dodecane molecule here. γ-$h\nu$ denotes the γ photon. If the above reactions were tenable, the reaction rate for DBT removal can be expressed as

$$\frac{dC}{dt} = -k_2[A^*]C \tag{6}$$

in which [A*] represents the equivalent concentration of all of the active species and C represents the concentration of DBT during the reaction.

Also, the reaction for DBT was a slow reaction, and it lasted for several tens hours in this study. Therefore, the [A*] can be approximately regarded as a constant during the radiation process. Equation 7 was obtained for this case

$$\frac{d[A^*]}{dt} = k_1[M]R^n - k_2[A^*]C - k_3[A^*][M] = 0 \tag{7}$$

where [M] represents the concentration of dodecane, R still denotes the radiation dose rate, and n is the exponent respect to R. Further, eq 6 can be rewritten as

$$\frac{dC}{dt} = k_2[A^*]C = k_1[M]R^n\frac{C}{\frac{k_3}{k_2}[M] + C} = N_{max}\frac{C}{C_s + C} \tag{6'}$$

Here, N_{max} is the potential maximum removal rate of DBT under the given condition, g/(L h), which was relevant to both the reaction system and the radiation dose rate. In addition, C_s represents a specific concentration constant, which was dependent upon the rate constant ratio of k_3/k_2. A larger C_s meant the lower selectivity for the DBT removal reaction, and most active species were annihilated through the apparent reaction 5. The two parameters in eq 6′ are defined as

$$N_{max} = k_1[M]R^n \tag{8}$$

$$C_s = \frac{k_3}{k_2}[M] \tag{9}$$

In addition, eq 10, which was obtained from eqs 1 and 6′ and based on the different method, was approximately used to verify whether the above consideration was suitable on the ground of the experimental data

$$\frac{(C_i - C)}{\Delta D} \approx \frac{N_{max}}{R}\frac{C_i}{C_s + C_i} \tag{10}$$

$$\frac{\Delta D C_i}{R(C_i - C)} \approx \frac{C_i}{N_{max}} + \frac{C_s}{N_{max}} \tag{10'}$$

where, C_i is the initial concentration of DBT and C is the concentration of DBT after irradiated with the radiation dose amount of ΔD.

The results between $\Delta DC_i/R(C_i - C)$ and C_i for DBT are shown in Figure 2. It can be seen that the two appeared with a good linearity ($R^2 > 0.99$) at various radiation doses, which indicated that eq 10 or 6 was suitable to describe the kinetics properly. Therefore, the predicted apparent reactions 3−5 were reasonable for the static radiation reaction in the DBT/dodecane system. Further, N_{max} and C_s for 3.95 kGy/h of the radiation dose rate were determined by the slope and intercept of the line in Figure 2, which were 0.021 (±0.002) g/(L h) and 2.2 (±0.2) g/L, respectively.

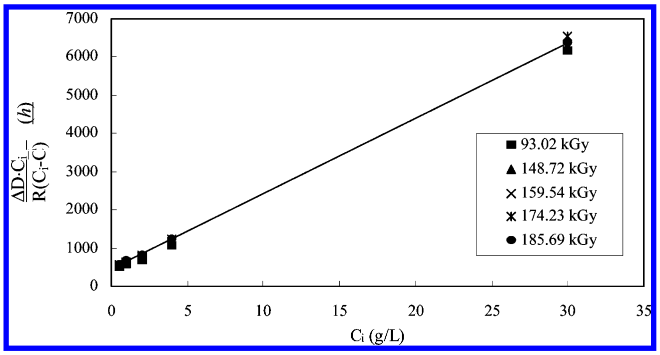

Figure 2. Relationship between $\Delta DC_i/R(C_i - C)$ and the initial DBT concentration C_i at various radiation doses. Dibenzothiophene was dissolved in dodecane and irradiated at 298 ± 2 K at a static condition. The radiation dose rate was 3.95 kGy/h.

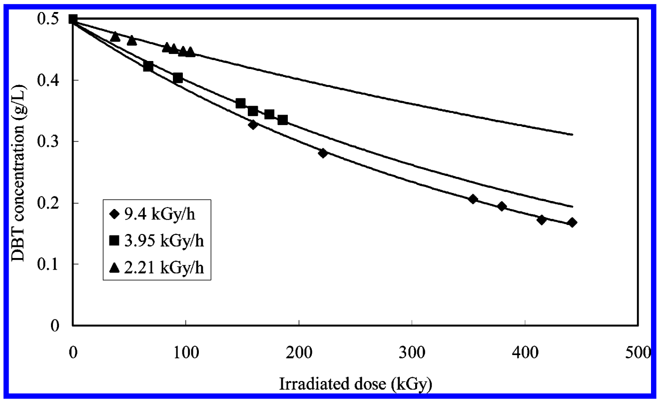

Figure 3. DBT concentration in the simulated oil versus the irradiated dose at various radiation dose rates. Dibenzothiophene was dissolved in dodecane and irradiated at 298 ± 2 K at a static condition.

3.3. Influence of the Radiation Dose Rate. The depletion of DBT, under the static radiation condition (without aeration), was investigated at the different radiation dose and dose rates, which were illustrated in Figure 3. It was obvious that the higher radiation dose rate corresponded to the higher removal efficiency at the same radiation dose. When the radiation dose was about 160 kGy, the removal efficiency was 16, 30, and 35% for the radiation dose rate of 2.21, 3.95, and 9.4 kGy/h, respectively.

This kind of tendency was different from that for the radiation depletion of dodecanethiol or dibutyl sulfide, and the removal efficiency of the latter two was higher at the lower radiation dose rate.[13] This phenomenon can be explained from the molecular structure of DBT. DBT is made up of conjugate π bond, in which the π electrons are nonlocalized. When it is irradiated by γ photo, the energy absorbed by these molecules will be distributed in the whole molecule quickly. Therefore, the probability of energy focusing in one definite bond is low, which invert the π electron from the high excitation state to the low excitation state, and the probability of the reaction will decrease. When the radiation dose rate is higher, the possibility of the reaction is higher.

Moreover, eq 6 was still available to describe the kinetics of the DBT conversion reaction when the radiation dose rate was 9.4 and 2.2 kGy/h, and C_s also ranged around 2.1 (±0.2) g/L. However, N_{max} varied greatly with the dose rate; it was about 0.054 (±0.005) and 0.0085 (±0.001) g/(L h) for the above two radiation dose rates, respectively. Therefore, n in eq 7 or 8 was about 1.2 ± 0.1, according to the dependence of N_{max} on R for the static radiation.

3.4. Influence of the Aeration with Nitrogen and Air. The influence of aeration with nitrogen and air (with about 21% of oxygen) on the radiation removal of DBT is illustrated in Figure 4. The removal efficiency for the aeration with nitrogen was nearly the same as that without aeration, which suggested that the agitation effect of aeration had less promotion on the removal of DBT by radiation. However, the aeration of air displayed inhibition on the removal of DBT. When the radiation dose was 185 kGy, the removal efficiency was about 33% for the static radiation or with the aeration of nitrogen, but it decreased to below 15% when air was continuously introduced to the solution. This indicated that oxygen was not helpful to the depletion of DBT in the reaction system with dodecane and DBT only.

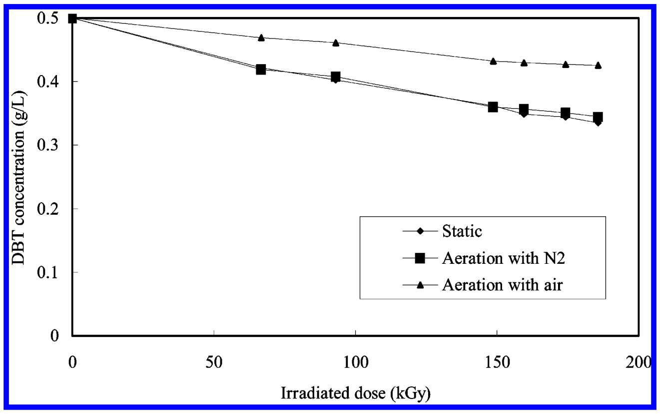

Figure 4. DBT concentration in the simulated oil versus the irradiated dose under different aeration conditions. Dibenzothiophene was dissolved in dodecane and irradiated at 298 ± 2 K. The radiation dose rate was 3.95 kGy/h. The flow rate of nitrogen or air was about 30 mL/min when aeration was stated.

Also, the removal characteristics of DBT seemed to be unique compared to dodecanethiol and dibutyl sulfide, and the latter two were more effectively removed in the presence of oxygen.[13] The reason can be attributed to the different demanded radicals or active species for the removal of these compounds by γ radiation. The active species, A* in eq 5, which were necessary for removal of DBT, maybe were inclined to be scavenged by oxygen.

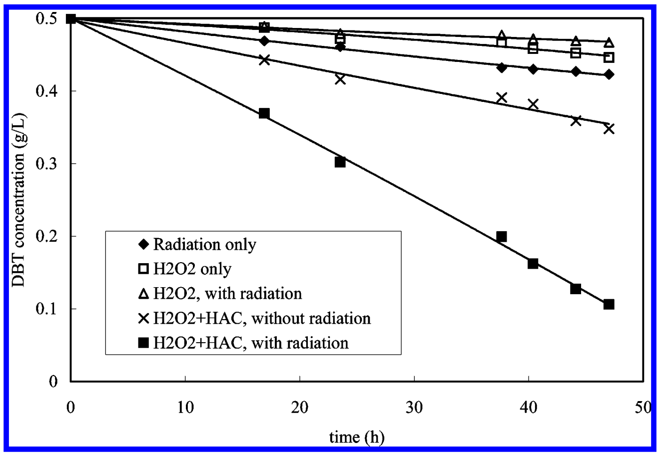

Figure 5. DBT concentration in the simulated oil versus the reaction time in the presence of H_2O_2 and acetic acid. The content of H_2O_2 in the aqueous solution was about 30% (wt). The volume ratio of the simulated oil, H_2O_2 solution, and acetic acid (if involving) was 5:1:1. The oil and aqueous phases were blended by bubbling with air (30 mL/min). The radiation dose rate was 3.95 kGy/h at 298 ± 2 K.

3.5. Preliminary Study on the Methods To Promote the Removal of DBT by γ Radiation. As indicated above, the removal efficiency of DBT only by γ radiation was not high enough to meet the practical demand. Thus, some methods were tentatively attempted to improve the removal of DBT in the presence of γ radiation. The liquid chemical additives and the solid catalysts were employed in the investigation.

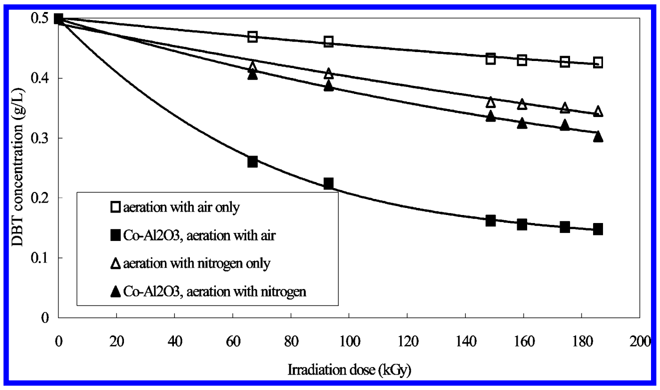

Figure 6. DBT concentration in the simulated oil versus the irradiated dose in the presence of the catalyst $Co-Al_2O_3$. Dibenzothiophene was dissolved in dodecane and irradiated at 298 ± 2 K. The radiation dose rate was 3.95 kGy/h. The flow rate of nitrogen or air was about 30 mL/min. The content of the catalyst ($Co-Al_2O_3$, 60−80 mesh to 100 mesh) in the simulated oil was about 0.1 g/mL.

3.5.1. Assistance with Chemical Additives. To improve the removal of DBT by radiation, some chemicals such as acetone, acetic acid, and hydrogen peroxide (H_2O_2) were used in the radiation reaction. Although acetone can greatly accelerate the radiation conversion of dodecanethiol, no obvious effect of acetone was observed upon the removal of DBT. Also, acetic acid displayed an insignificant effect on it.

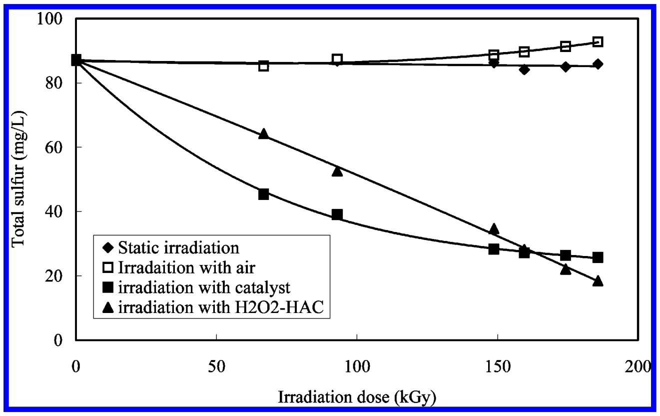

Figure 7. Total sulfur in the simulated oil versus the irradiated dose at various conditions. The radiation dose rate was 3.95 kGy/h at 298 ± 2 K. The initial concentration of DBT was 0.5 g/L. The flow rate of nitrogen or air was about 30 mL/min. The content of the catalyst ($Co-Al_2O_3$, 100 mesh) in the simulated oil was about 0.1 g/mL.

The effect of H_2O_2 was investigated as follows. The aqueous solution of H_2O_2 (about 30 wt %) was mixed with the simulated oil phase by bubbling with air, and the volume ratio of oil phase/aqueous solution phase was 5:1. The results are shown in Figure 5, and it was seen that H_2O_2 itself could slightly improve the removal of DBT under γ radiation. However, when H_2O_2 worked with acetic acid (HAC), a significant improvement was observed upon the removal of DBT under radiation at room temperature. As shown in Figure 5, when the volume ratio of oil/H_2O_2/HAC was 5:1:1 and the initial concentration of DBT was 0.5 g/L, about 80% of DBT was removed from oil with a radiation dose of 185 kGy. Similarly, about 70% of DBT was removed from oil when the initial concentration was 20 g/L

Table 1. Removal Efficiency of DBT with Various Catalysts under Different Conditions[a]

condition/catalyst	Al_2O_3 (%)	Zeolite (%)	Al_2O_3-Fe (%)	Al_2O_3-Cu (%)	Al_2O_3-Ni (%)	Al_2O_3-Co (%)
catayst without radiation	11.2	9.3	6.1	4.4	5.2	3.8
catayst with radiation	22.4	16.3	27.1	16.6	14.7	70.4
radiation without a catalyst	15.2					

[a] The radiation dose was 185 kGy (with a radiation dose rate of 3.95 kGy/h) if γ radiation was involved. All of the test were performed with aeration of air at 298 ± 2 K, and the duration was 47 h.

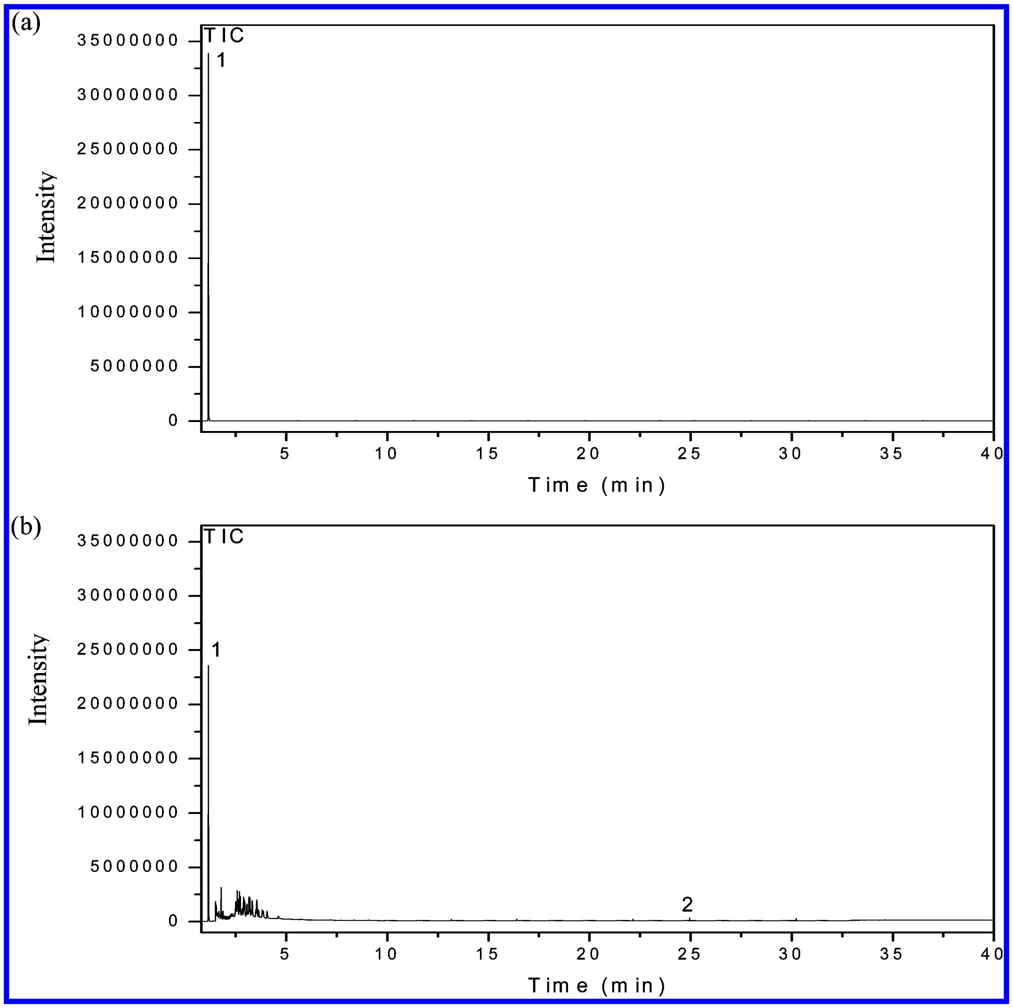

Figure 8. GC/MS spectrum of DBT before irradiation (a) and after irradiation (b) in a static reactor, respectively. The peak 1 and 2 represented DBT and disulfide ($C_{24}H_{50}S_2$), respectively. The radiation dose rate was 3.95 kGy/h, and radiation dose was 185 kGy.

with about 500 kGy of radiation dose. Further, when the volume ratio of oil/H_2O_2 solution/HAC was 3:1:1, almost 100% of DBT was converted with the above-mentioned dose. The results indicated that the combination of H_2O_2−HAC and γ radiation could remove DBT efficiently. However, the consumption of chemicals (H_2O_2 and HAC) seemed to be excessive, which would result in a higher cost.

3.5.2. Radiation Removal of DBT in the Presence of Catalysts. To accelerate the removal of DBT and reduce the required radiation dose, some catalysts consisting of metal oxides were investigated experimentally for this purpose. The catalysts were prepared with the foregoing method. Aeration of air or nitrogen was still necessary during the radiation processes to suspend the solid catalyst powders (100 mesh) evenly in the simulated oil phase. Table 1 shows the results in the presence of various catalysts under different conditions, among which the adsorption of these catalysts was investigated without radiation. It can be seen that γ-Al_2O_3 and Zeolite showed slight adsorption to DBT; only about 10% of DBT in the oil was adsorbed without irradiation. Also, the adsorption capacity decreased when γ-Al_2O_3 was impregnated with some metal oxides.

When the catalysts worked with γ irradiation, a different effect on the removal of DBT was observed. Fe−Al_2O_3 (Iron oxide impregnated on γ-Al_2O_3) displayed a minor promotion to the removal of DBT. However, Co−Al_2O_3 showed significant catalysis to the removal of DBT in the presence of radiation; the removal efficiency of DBT increased from 15.2 to 70.4% with the aeration of air. The other catalysts all showed insignificant effect upon the removal of DBT if adsorption was considered.

Figure 6 showed the effect of the aeration of a different gas upon the radiation removal of DBT in the presence of Co−Al_2O_3. When nitrogen was aerated, the removal efficiency with Co−Al_2O_3 was only slightly higher than that without the catalyst and catalysis was not significant upon addition to the adsorption. Although oxygen appeared to be negative to the removal of DBT by only radiation, it was necessary for catalytic removal of DBT with Co−Al_2O_3. The oxygen molecule was supposed to be activated by irradiation in the presence of suitable catalysts, and the activated oxygen species can react with DBT. The selection of the catalysts with a better performance and the mechanism of the catalysis under γ irradiation will be further studied elsewhere.

3.6. Total Sulfur Removal under Various Conditions. The total sulfur, which included all of the sulfur compounds in the sample that can be oxidized to sulfur dioxide when burnt, was measured under various conditions, and the results are shown in Figure 7. For the static radiation of DBT, the total sulfur almost remained constant during the radiation process despite that the concentration of DBT decreased with the rise of the radiation dose. This indicated that the sulfur-containing products from DBT conversion still existed in the simulated petroleum and that the desulfurization of DBT only by γ radiation was not completed. When the simulated oil was irradiated with the aeration of air or nitrogen, the total sulfur even increased slightly because of the slight evaporation of dodecane when the gas stream passed through the simulated petroleum (DBT was less volatile than dodecane).

When H_2O_2−HAC was introduced into the reaction, the total sulfur in the oil phase decreased synchronously with DBT removal in the oil phase during the radiation, which meant that almost all of the converted DBT was transferred from the oil phase to the water phase. This combination of radiation and H_2O_2−HAC seemed to be a relatively completed method for DBT removal.

Additionally, the total sulfur in the simulated petroleum decreased with the depletion of DBT in the presence of a Co−Al_2O_3 catalyst. As stated above, because oxygen was indispensable to catalytically convert DBT, the oxygen-containing derivatives were assumed to be the main products, which were easily adsorbed by the catalyst surface. Therefore, this was also a complete method for the desulfurization of DBT.

3.7. Identification of the Conversion Products of DBT under Various Conditions. The conversion products of DBT under different conditions were identified by means of GC/MS and LC/MS techniques. Figure 8 is the result of GC/MS spectra of the samples after the static irradiation. The main products from DBT conversion were dodecane disulfide ($C_{24}H_{48}S_2$). This indicated that the sulfur atom can be detached from DBT, and it would further combine with the dodecane molecule. Because disulfide was more easily removed from oil than DBT by conventional technology, the treatment with static radiation was still helpful for the predesulfurization of DBT and its derivatives.

When H_2O_2−HAC was introduced, the main sulfur-containing compound from the conversion of DBT was dibenzothiophone according to LC/MS analysis.

To evaluate the side effect of γ irradiation on hydrocarbon in petroleum, the degradation products of dodecane were also identified. Some oxidation derivative species of dodecane were ascertained in the samples irradiated with oxygen. The main products were dodecanol, dodecyl ketone, and dodecyl aldehyde. The result of semiquantitative analysis by GC showed that the degradation of dodecane was very slow and the total concentration of the oxidation species was about 1.2% even though oxygen was abundant, which meant that the radiation had a less destructive effect on the main components of petroleum.[13]

4. Conclusions

A novel method for the removal of sulfur compounds in petroleum was investigated on the basis of the radiochemical reaction induced by γ irradiation. The results showed that DBT was difficult to be decomposed only by γ irradiation, and the removal efficiency was about 33% when the radiation dose was 185 kGy. The apparent reactions for the removal of DBT were presumed, and the corresponding kinetics equation was deduced and proven experimentally.

Some methods were preliminarily used to improve the removal of DBT in the presence of γ irradiation at room temperature. Among which, the mixture of H_2O_2 and acetic acid (HAC) appeared to be synergic to the radiation removal of DBT. Also, co-oxide impregnated on γ-Al_2O_3 showed a significant promotion to the removal of DBT under the irradiated situation, and the removal efficiency increased by over 40% compared to radiation only. It would be a potential alternative to remove DBT in petroleum by means of γ irradiation combined with a catalyst.

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