

The Oxidation of Tetralin and Its Effect on the Stability of Fluidized Catalytic Cracked Diesel

Gaoyou Tian, Daohong Xia,* and Fengtao Zhan

College of Chemistry and Chemical Engineering, State Key Laboratory of Heavy Oil Processing, University of Petroleum, 257061 Dongying, People's Republic of China

Received March 20, 2003. Revised Manuscript Received September 23, 2003

The auto-oxidation of hydrocarbons in fluidized catalytic cracked (FCC) diesel fuel was studied, and the products were analyzed by ultraviolet spectroscopy, infrared spectroscopy, and gas chromatography–mass spectroscopy. The results show that the auto-oxidation of hydrocarbons varied with different molecular structures. The tetralin, which contains two active H atoms (α -H), was easily auto-oxidized to hydroperoxide, and the concentration of hydroperoxide (Wt- $_{OOH}$)% increased to 5.01%, after being heated under the following conditions: a temperature of 373 K for 30 h with an airflow rate of 90–100 mL/min. Cetene, cetane, and 1-methylnaphthalene were very stable and could not produce hydroperoxides under the same conditions. Great co-oxidation existed between tetralin and cetene. The extent of auto-oxidization increased as the initial concentration of tetralin and the rate of airflow each increased. The auto-oxidation reactions were strongly inhibited by antioxidants such as phenols and thiols. The products from the auto-oxidation of hydrocarbons were mainly carbonyl and hydroxyl compounds. The mechanism of auto-oxidation was free-radical chain reaction. Controlling the auto-oxidation of active hydrocarbons in the FCC diesel fuel is one of the effective ways to improve the stability of diesel fuel.

Introduction

During the entire lifetime of a fuel, from when it is first produced in the refinery until the moment when it is consumed by the engine, the problem of fuel instability always exists. Fuel degradation can cause engine failure and engine malfunction, as well as affect engine performance. The question of how to improve the stability is becoming an increasing concern in the refinery industry. Much research has been focused on the factors that affect the instability.^{1–4} The concentration of heteroatoms in the deposit formed during the storage conditions is much greater than that in the fuel, which has caused much attention to be focused on the study of the effects of non-hydrocarbons on the instability. The general conclusion was that non-hydrocarbons were detrimental to the stability of the fuel. Our previous research also showed that the non-hydrocarbons, particularly thiols and phenols, were harmful to the stability of the catalytic cracked diesel fuel.⁵ On the other hand, hydrocarbons, which are the main compo-

nents of the fuels, were known as the “stable and good” components. Consequently, their effects on fuel stability were rarely studied. Diesel fuel, particularly cracked diesel, contains a certain amount of active hydrocarbons, such as olefins and active aromatic compounds,⁶ that can easily be auto-oxidized to hydroperoxides. The hydroperoxide, which is one of the most reactive compounds, can initiate the reactions of other compounds such as alkyl-indole⁷ and thiols⁸ and do great harm to the stability. Therefore, it is very important to study the oxidation of hydrocarbons during the storage conditions and determine their effects on the stability. In this paper, one active aromatic compound (tetralin) in combination with other typical hydrocarbons were chosen as model compounds to study the effects on the stability of catalytic cracked diesel fuel. The concentration of hydroperoxides was measured during the accelerated auto-oxidation process, and the products were analyzed by several methods, including infrared (IR) spectroscopy, ultraviolet (UV) spectroscopy, and gas chromatography–mass spectroscopy (GS–MS). The effects on the stability were studied, and mechanisms were postulated.

Experimental Section

Analysis of Hydroperoxides by Iodometric Titration. Samples with masses of 0.5–1.0 g were weighed and dissolved

* Author to whom all correspondence should be addressed. E-mail address: xiadh@hpu.edu.cn.

(1) Beaver, B. Long-Term Storage Stability of Middle Distillate Fuels from a Chemical Mechanistic Point of View, Part 1. *Fuel Sci. Technol. Int.* **1991**, 9, (10), 1287–1335.

(2) Batts, B. D.; Zuhdan Fathoni, A. A Literature Review on Fuel Stability Studies with Particular Emphasis on Diesel Oil. *Energy Fuels* **1991**, 5, 2–21.

(3) Beaver, B. Long-Term Storage Stability of Middle Distillate Fuels from a Chemical Mechanistic Point of View, Part 2. *Fuel Sci. Technol. Int.* **1992**, 10, (1), 1–37.

(4) Zuhdan Fathoni, A.; Batts, B. D. A Literature Review of Fuel Stability Studies with a Particular Emphasis on Shale Oil. *Energy Fuels* **1992**, 6, 681–693.

(5) Tian, G.; Zhan, F.; Xia, D. An Approach to the Changes of Non-Hydrocarbons during the Deterioration of the Stability of Fluidized Catalytic Cracked Diesel. *Pet. Sci. Technol.* **2002**, 20, (9/10), 1093–1101.

(6) Marshman, S. J. Determination of Phenalenes in Distillate Diesel Fuels Using High-Performance Liquid Chromatography. *Fuel* **1991**, 70, (8), 967–970.

(7) Mushrush, G. W. Interactive Effects of 2,5-Methylindoles and tert-Butyl Hydroperoxide in a Shale Diesel Fuel. *Energy Fuels* **1990**, 4, 15–19.

(8) Morris, R. E.; Mushrush, G. W. Fuel Instability Model Studies: The Liquid-Phase Cooxidation of Thiols and Indene by Oxygen. *Energy Fuels* **1991**, 5, 744–748.

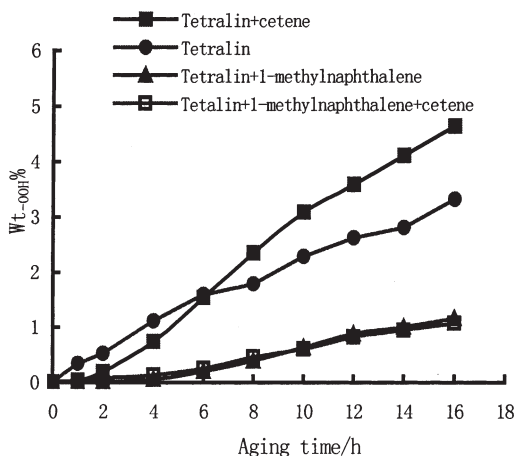


Figure 1. Concentration of hydroperoxide produced during the aging process of different hydrocarbons.

in 25 mL of acetic acid. Saturated potassium iodide (KI) solution (1 mL) then was added to the aforementioned solution and N_2 was allowed into the system, to exclude the oxygen (to eliminate oxygen interference with the analysis). After the sample solution was placed into a dark place and allowed to react for 10 min, the sample was diluted with 25 mL of H_2O and titrated by 0.1 mol/L $Na_2S_2O_3$. When the color of the solution had almost disappeared, 1 mL of 1% starch solution was added and the titration further continued until all the solution color disappeared. A blank experiment was also performed, via the same procedure, using a colorless solution. The concentration of hydroperoxides ($Wt_{-OOH}\%$) was calculated using the following equation:

$$Wt_{-OOH}\% = \frac{N(V - V_0)M}{2000W} \times 100\%$$

where N is the concentration of $Na_2S_2O_3$ (in units of mol/L), M the molecular weight of $-OOH$ (33), W the sample weight (in grams), V the volume of $Na_2S_2O_3$ used for sample analysis (in milliliters), and V_0 the volume of $Na_2S_2O_3$ used for blank analysis (also given in milliliters).

Fourier Transform Infrared (FTIR), GC-MS, and UV Analysis. Fourier transform infrared (FTIR) analysis was performed using an IR analysis system (model Magna750 IR). The detector was DTGS-KBr, and the solvent used was CCl_4 . GC-MS analysis was performed using model VG707E equipment. The silica capillary column had a length of 50 m and an inner diameter of 0.2 mm, and the column was coated with HP-5. UV analysis was performed (model Cary-50).

Accelerated Aging Process. The sample was aged at 373 K for 16 h, according to the standard method SH/T0238-92.

Samples. All the mixtures of hydrocarbons were mixed using equal proportions of every hydrocarbon. The FCC diesel fuel was sampled from the Shenghua Refinery in China.

Results and Discussion

The Oxidation of Hydrocarbons. Each purified hydrocarbon, or their mixture, was aged at 373 K and aerated with an airflow rate of 90–100 mL/min. The concentration of hydroperoxides formed at different times was measured by iodometric titration. The results are shown in Figure 1. The data demonstrate that the possibilities of hydrocarbons to be oxidized to hydroperoxides vary with their molecular structures. Tetralin, which contains two active H atoms (α -H), is easily converted to free radicals by heat or light. Consequently, it can easily be auto-oxidized to hydroperoxides. During the aging process, the concentration of hydroperoxides

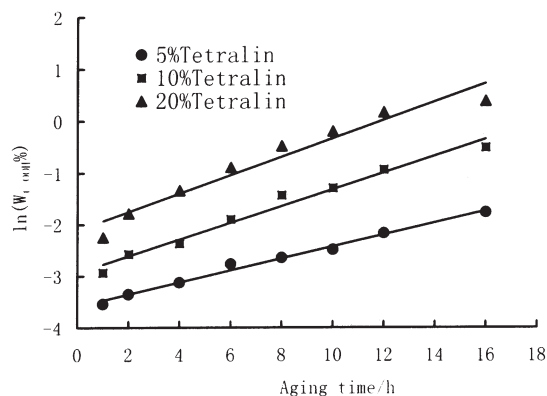


Figure 2. Plot of $\ln Wt_{-OOH}\%$ versus time at different low initial concentrations of tetralin aged at 373 K.

increases with time, finally attaining a value of $Wt_{-OOH}\% = 5.01\%$ after being heated at 373 K for 30 h. The conversion of cetene, cetane, and 1-methylnaphthalene, which do not have the active H atoms that tetralin does, cannot easily be initiated by heat or light. Thus, during the aging process, no hydroperoxides are produced. Cetene contains one double bond, and the addition reaction can occur with other free radicals. Consequently, when it was aged with tetralin, it could be reacted with radicals that are produced from the oxidation of tetralin to form hydroperoxides. Thus, the concentration of hydroperoxides ($Wt_{-OOH}\%$) is greater than that for the aging of tetralin alone. On the other hand, when cetene was aged together with 1-methylnaphthalene, no hydroperoxides were formed. This situation can be explained by the fact that 1-methylnaphthalene could not be oxidized to hydroperoxide; consequently, it cannot initiate the oxidation of cetene. Figure 1 also shows that 1-methylnaphthalene has remarkable inhibition to the oxidation of tetralin or the mixture of tetralin and cetene.

Influence of Initial Concentration on the Oxidation of Tetralin. Different concentrations of tetralin in petroleum ether (363–393 K) were heated at 373 K for 16 h and aerated with an airflow rate of 90–100 mL/min simultaneously. The concentration of hydroperoxides ($Wt_{-OOH}\%$) was measured at regular intervals. The concentration of hydroperoxide increased with time at any given initial concentration of tetralin during the auto-oxidation process. Further kinetic analysis revealed that, at a low initial concentration of tetralin, the hydroperoxide content in the reaction system increases exponentially with time and can be expressed as $Wt_{-OOH}\% = ae^{kt}$ (Figure 2). However, at high concentrations of tetralin, the hydroperoxide content increases linearly with time and can be calculated using the relation $Wt_{-OOH}\% = kt + a$ (Figure 3). If the reaction rate is expressed by the production rate of hydroperoxide as $r = dWt_{-OOH}\%/dt$, then the relationship of the initial reaction rate r_0 with different initial concentrations of tetralin at low concentration can be figured as shown in Figure 4.

These results show that hydroperoxide is one of the reactive compounds in diesel fuel, which can initiate other compounds to change and finally cause the deterioration of the stability of diesel fuel. Therefore, the contents of the reactive hydrocarbons such as tetralin, olefin, and aromatic olefin should be limited in FCC diesel fuel.

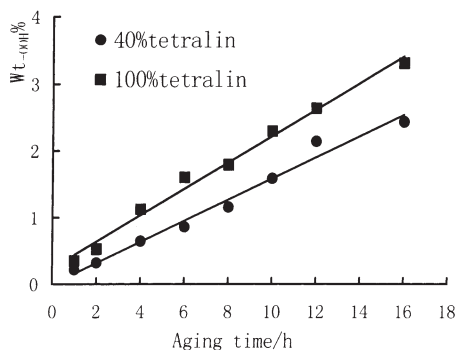


Figure 3. Plot of $Wt_{-OOH}\%$ versus time at different high initial concentrations of tetralin aged at 373 K.

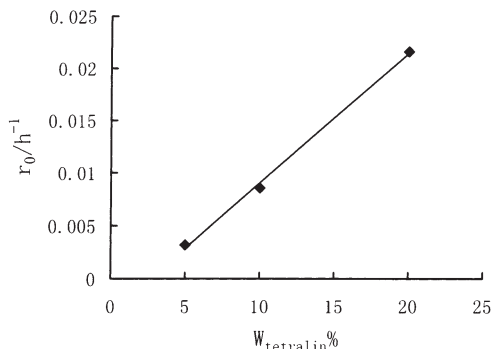


Figure 4. Initial reaction rate r_0 at different low initial concentrations of tetralin.

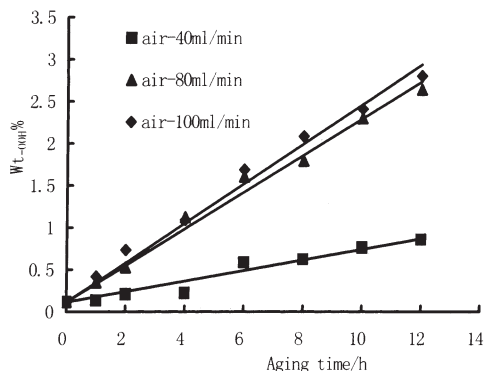


Figure 5. Plot of $Wt_{-OOH}\%$ versus time in the oxidation of tetralin with different airflows.

Influence of Air on the Oxidation of Tetralin. Tetralin was heated at 373 K for 16 h while being aerated with different flow rates of air. The hydroperoxide contents were measured at different times and are shown graphically in Figure 5. The relationship of the production rate of hydroperoxide and the flow rate of air is plotted in Figure 6. The results reveal that the auto-oxidation of tetralin is closely associated with O_2 and the hydroperoxide content and its production rate increase as the airflow increases. Based on these data, it can be concluded that, to avoid the oxidation of hydrocarbons, it is best to limit the exposure of FCC diesel fuel to air.

Influence of Non-hydrocarbons on the Oxidation of Tetralin. Many non-hydrocarbons are present in FCC diesel fuel; therefore, it is very important to study their effects on the auto-oxidation of hydrocarbons. In our experiments, a quantity (0.2 wt %) of some non-hydrocarbons was added to the tetralin and heated at 373 K for 16 h, while being aerated with air at a rate

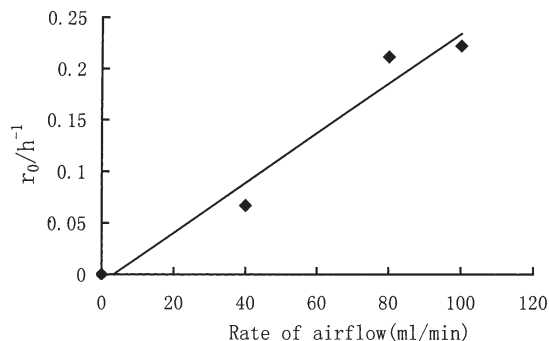


Figure 6. Production rate of hydroperoxide in the oxidation of tetralin at different rates of airflow.

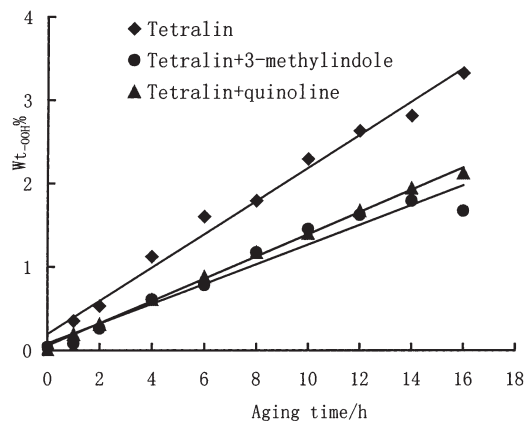


Figure 7. Plot of $Wt_{-OOH}\%$ versus time in the coexisting system of tetralin and other non-hydrocarbons aged at 373 K.

of 90–100 mL/min. The concentration of hydroperoxides, measured at different times, is shown in Figure 7. The compounds that were tested, such as 3-methylindole and quinoline, illustrated in Figure 7, show a slight ability to inhibit the auto-oxidation of tetralin, because smaller hydroperoxide contents were measured in the co-oxidation system. The other experimental non-hydrocarbons, such as antioxidant 264, 1-naphthanol, *p*-methylthiophenol, and cresol, exhibit complete inhibition to the auto-oxidation of tetralin. From these experimental results, it can be concluded that some non-hydrocarbons existing in the FCC diesel fuel are beneficial to improving the stability of diesel fuel.

Effect of the Oxidation of Tetralin on the Stability of FCC Diesel Fuel. To demonstrate the relationship between the stability of FCC diesel fuel with the oxidation of tetralin, 25% (v/v) tetralin was added to FCC diesel fuel that was produced in the Shenghua Refinery and aged at 373 K for 16 h. The color changes of the diesel fuel were recorded and compared with that of diesel fuel without the addition of tetralin. The data listed in Table 1 show the color indexes before and after aging of the FCC diesel fuel with and without tetralin. The data show that the addition of tetralin can darken the diesel fuel. Furthermore, the addition of tetralin with hydroperoxide or TBHP can cause the diesel fuel to become darker than that without hydroperoxide, which demonstrates that hydroperoxides have a more detrimental effect on the fuel; controlling the formation of hydroperoxides is one of the important ways to improve the stability of diesel fuel.

Analysis of Products during the Oxidation of Tetralin. As one of the products, the hydroperoxide

Cochise Technology Ex. 2017
W.R. Grace v. Cochise Technology - IPR 2023-01063

Table 1. Tetralin Effects on the Stability of FCC Diesel Fuel

sample	FCC diesel fuel without added tetralin	FCC diesel fuel with added tetralin*		
		Tetralin-0 ^a	Tetralin-1 ^b	Tetralin-2 ^c
color degree (ISO) before aged	2.0	2.0	2.0	2.0
color degree (ISO) after aged	3.5	6.5	8.0	8.0

^a In Tetralin-0, the initial hydroperoxide content is zero. ^b In Tetralin-1, the initial hydroperoxide content is 0.12%. ^c Tetralin-2 has 0.5% *tert*-butylhydroperoxide.

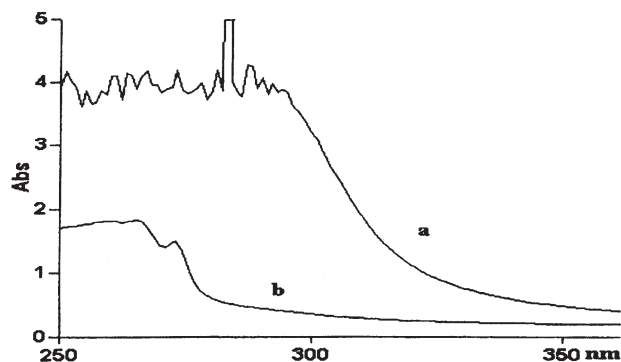


Figure 8. UV spectra of aged and unaged tetralin: (a) tetralin aged at 373 K for 16 h and (b) unaged tetralin.

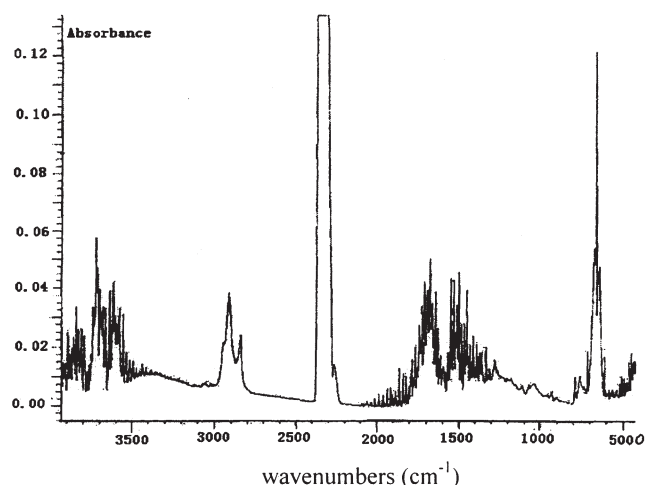


Figure 9. IR spectra of the colored compounds separated from aged tetralin.

content was definitely measured during the oxidation of tetralin. For further identification of the other products in the reaction system, modern analytical methods such as UV and FTIR spectroscopy, as well as GC/MS, were used to perform the product analyses.

1. UV Analysis. The aged and unaged tetralin samples were extracted using 0.02 mol/L NaOH solution, and the extracts were analyzed using UV spectroscopy. The results are shown in Figure 8, which shows that the absorption of aged tetralin is much greater than that for unaged tetralin. These results show that, during the aging process, tetralin is oxidized into polar compounds, which can be extracted using NaOH solution.

2. FTIR Analysis. During the accelerated aging progress, the color of the tetralin solution changed from transparent to yellow and finally red. The aged tetralin solution was separated by column layer chro-

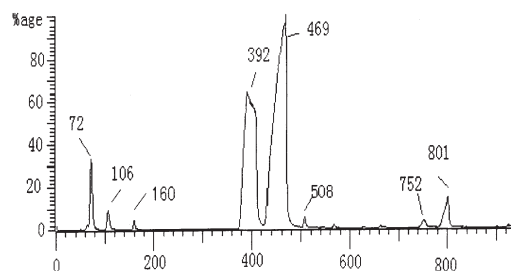
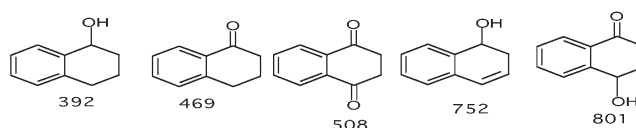


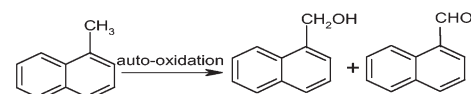
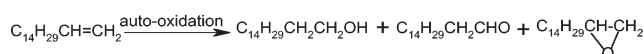
Figure 10. GC-MS spectra of the colored compounds separated from aged tetralin.

matography, using a column that was filled with silica gel, and the colored compounds were obtained and analyzed directly by FTIR spectroscopy. The results are shown in Figure 9. This figure shows that great absorption exists in the broad bands near 3600 cm⁻¹ in the hydrogen-bonded OH stretching region, which is evidence that some compounds that contain hydroxyl groups have been formed during the aging process.

3. GC-MS Analysis. The colored compounds separated from aged tetralin were analyzed using GC-MS, and the results are shown in Figure 10. The results reveal that tetralin can be oxidized to the compounds that contain hydroxyl or/and carbonyl groups, which further demonstrates the UV and FTIR analytical results. Several of the detected compounds are listed as follows:



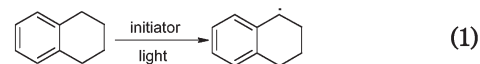
The products from the auto-oxidation of cetene and 1-methylnaphthalene were also analyzed by GC-MS; the analysis indicated that the following chemical reactions were occurring:



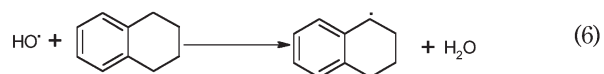
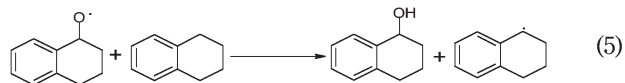
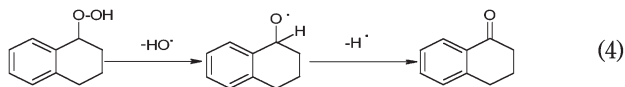
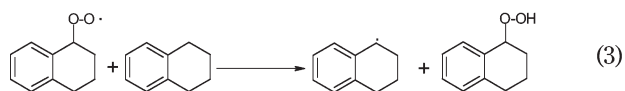
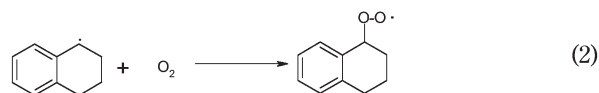
Mechanism of the Auto-oxidation of Tetralin.

The auto-oxidation of tetralin is strongly inhibited by free-radical antioxidant 264, which shows that the auto-oxidation mechanism is a free-radical reaction. According to the analysis of the products, and all the evidence from the reaction, the possible mechanism of the auto-oxidation of tetralin is postulated as follows:

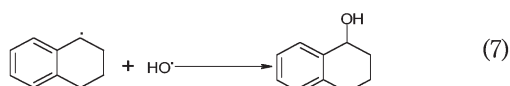
Initiation:



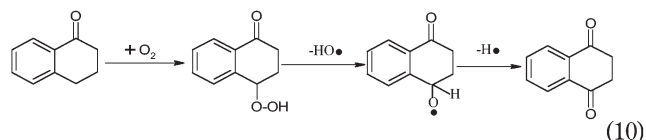
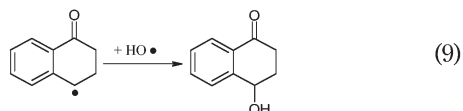
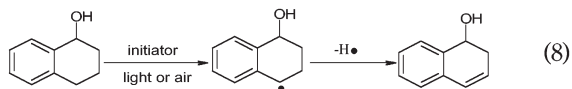
Propagation:



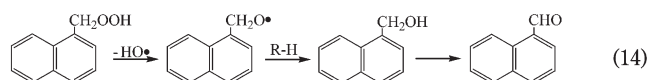
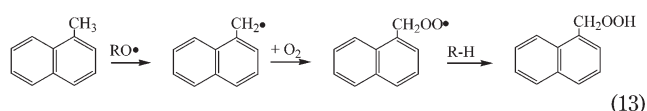
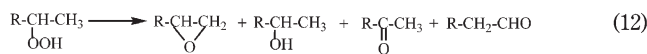
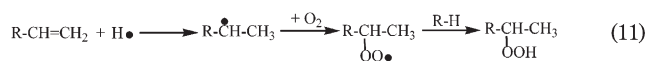
Termination:



1-hydroxyltetralin or 1-carboxyltetralin still has one active H atom (α -H) and could be oxidized to another hydroperoxide. Such a reaction produces more polar compounds, as shown in reactions 8–10:



Olefins and other hydrocarbons could be initiated by the radicals that are produced from the auto-oxidation of tetralin and oxidized to hydroperoxides and further decomposed to carbonyl or hydroxyl compounds, as shown in reactions 11–14:



Conclusion

The auto-oxidation of hydrocarbons varies with their molecular structures. Tetralin can be auto-oxidized to hydroperoxide easily; however, cetene, cetane, and 1-methylnaphthalene are very stable and cannot produce hydroperoxides under the same conditions. A great co-oxidation relationship exists between tetralin and cetene. However, 1-methylnaphthalene has remarkable inhibition to the oxidation of tetralin or the mixture of tetralin and cetene. The extent of auto-oxidation increases as the initial concentration of tetralin and the aerating rate of airflow each increase. Although all the tested non-hydrocarbons have the ability to inhibit the auto-oxidation of tetralin, the antioxidant 264, 1-naphthanol, *p*-methylthiophenol, and cresol exhibit complete inhibition action. The products from the auto-oxidation of hydrocarbons are mainly carbonyl and hydroxyl compounds. The mechanism of auto-oxidation is free-radical chain reaction. In regard to auto-oxidization to hydroperoxides, tetralin has a more detrimental effect on the stability of FCC diesel fuel.

EF030066Q