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The Photo-desulfurization of Crude Naphtha by UV Irradiation

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The photolysis of crude naphtha in the presence of an oxidizing reagent was studied with a view to accomplishing the desulfurization of crude naphtha. The irradiation of crude naphtha consisting of 0.15% sulfur by means of a 200-W high-pressure mercury-vapor lamp, with the aeration of air or oxygen at the flow rates of 5—15 ml/min at 0 °C, resulted in an 80—90% photolysis of the principal mercaptans and sulfides in the crude naphtha within 20 min. The major photo-oxidation products were water-soluble oxygenated sulfur compounds; thus, this process resulted in 67.8% desulfurization when the irradiated naphtha was washed with water. The effects on the photolysis of the molecular weights and the structures of sulfur compounds were also examined with 11 mercaptans and 3 sulfides.

An alkali-sweetening process, *e. g.*, doctor sweetening, Merox process, the Unisol process, is a low-cost process to remove corrosive and malodorous mercaptans and to increase the lead susceptibility of gasoline, but it has several disadvantages: the susceptibility to the oxidation of the mercaptans by alkali solution is markedly influenced by the structural features of mercaptan, and thus the process is not effective for removing *tert*-mercaptans; desulfurization is usually low because sulfides in crude naphtha cannot be removed by this method, and this process produces a malodorous waste liquor.

In this paper a photo-desulfurization of light straight naphtha was studied on the basis of the fact that mercaptans and sulfides can be photolyzed by UV irradiation.

Although many reports on the photolysis of mercaptans and sulfides have been published, most of them have been focused on the reaction mechanism of the photolysis of these sulfur compounds,[1-10)] and few works have been undertaken for the purpose of a practical application.[11-12)] In related works, Murray[11)] studied the photo-oxidation method as a possible means of controlling malodorous waste gases containing mercaptans and sulfides from a kraft pulp mill. In his study of the effects of UV light on the oxidation of methyl mercaptan (MM), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS), Murray was able to demonstrate the photo-oxidation of these compounds at both 2537 and 3600 Å. By monitoring the disappearance of the starting materials, he showed that DMDS undergoes photo-oxidation most rapidly, while DMS was found to be the least reactive. In addition MM exposed to solar radiation was found to disappear with a half-life of approximately 7 days during a period with an average noon temperature of 10 °C.

Bentley[12)] has reported that about a 7-hr irradiation of dimethyl sulfide in air with a 200-W high-pressure mercury-vapor lamp caused a more than 91% decomposition of the sulfide.

In this study 11 mercaptans, *i. e.*, ethyl-, *n*-propyl-, isopropyl-, *n*-butyl-, *sec*-butyl-, isobutyl-, *tert*-butyl-, *n*-amyl-, *sec*-isoamyl-, *tert*-amyl-, and *n*-hexyl-mercaptans and 3 sulfides, *i.e.*, diethyl-, di-*n*-butyl-, and diallyl-sulfides, were irradiated with a 100-W low-pressure mercury-vapor lamp at 0 °C to determine the effects of the molecular weights and structures of these sulfur compounds on the photolysis; further experiments were also performed in order to determine the rates of the photo-decomposition and photo-oxidation of important mercaptans and sulfides in crude naphtha by the irradiation of light straight naphtha with a bp 27—95 °C from Iranian heavy by means of a 200-W high-pressure mercury-vapor lamp at the temperatures of 0, 30, 50 °C, and by irradiation in the presence of oxidizing reagents, air, and oxygen at 0 °C.

The results showed that the irradiation of the crude naphtha consisting of 0.15% sulfur by means of a 200-W high-pressure mercury vapor lamp, with the aeration of air or oxygen at the flow rate of 5—15 ml/min and at 0 °C, resulted in an 80—90% photolysis of the major mercaptans and sulfides in the crude naphtha within 20 min; unlike the alkali-sweetening process, no difference in the reactivity of mercaptan due to its structural features has been observed. The principal photo-oxidation products were SO_2, SO_3, and sulfonic acids; the reaction afforded a 67.8% reduction of the total sulfur content in the photo-desulfurized naphtha.

Experimental

1. Materials and Apparatus. The mercaptans and sulfides used to determine the effects of thier molecular weights and structures on the photolysis, and used as the internal standards for the gas chromatography, were analytical-standard reagents (Poly Science Corp.).

The crude naphtha used for the photo-desulfurization study was a light straight naptha (bp 27—95 °C) from Iranian heavy.

The photolysis was conducted in a 200-ml round-bottom, Pyrex flask fitted with a water-cooled lamp housing, a thermometer, and a reflux condenser cooled with ice water.

The light sources were a 100-W low-pressure mercury-vapor lamp, which emits predominantly 2357 Å light, in the runs for determining the effects of the molecular weights and structures on the photolysis of mercaptans and sulfides, and a 200-W high-pressure mercury-vapor lamp with a predominant light of 3650 Å in the runs for the photo-desulfurization of crude naphtha.

Gas chromatography was done by means of Micro Tek Instruments Corp. Model 160 gas chromatograph equipped with a flame photometric detector and a 3 m × 3 mm i.d. Teflon analytical column packed with 1,2,3-tris(cyanoethoxy)-propane on Shimalite 25%, 80/100 mesh.

2. Procedure. Each 100-ml portion of *n*-hexane solutions (100 ppm) of mercaptans and sulfides or the crude naphtha was placed in the flask, and the reaction solution was irradiated with a mercury-vapor lamp at a constant temperature. One ml portions of the sample solution were taken off at discrete periods of irradiation time and mixed with the *n*-propyl sulfide standard solution (prepared by dissolving 10 μl of the sulfide in 5 ml of *n*-hexane and stored in a cooled dark place) to serve as internal standards for the gas chromatography.

The rates of the reaction of mercaptans and sulfides on the photolysis were determined by comparing the peak area of each sulfur compounds to be analyzed with that of the internal standard, calculated by means of a digital integrator; the relative amounts of sulfur compounds in the sample solutions were compared with those in the original solutions.

In the runs to study the effects of the molecular weights and structures of mercaptans and sulfides on the photolysis, the reactions were carried out at 0 °C; in the runs of the photo-desulfurization of the crude naphtha, the reaction temperatures of 0 °C, 30 °C, and 50 °C were used.

The experiments of the photo-oxidation of the crude naphtha were performed at 0 °C; with the aeration of air or oxygen at the flow rates of 5—30 ml/min. In these experiments, corresponding dark reactions under the same reaction conditions except for irradiation were done in order to check the amount of possible mechanical losses or chemical reactions.

The total sulfur contents in the crude and the photo-desulfurized naphtha were determined by the UOP oxygen-hydrogen combustion method (UOP 586—66); the reaction product was washed with distilled water, and a measured aliquot of the water solution was used for determining SO_2 and SO_3 by gravimetric $BaSO_4$ analysis.

The reaction product formed by UV irradiation was identified as higher-molecular-weight sulfides by gas chromatography utilizing a mercaptan-substracting column ($Hg(CN)_2$ 1% on Chromosorb).

Results and Discussion

The studies of the photolysis of organic sulfur compounds indicate that the photolysis of disulfide is initiated through –S–S– fission[1] rather than C–S fission,[2] while in the cases of monosulfides and mercaptans, the reactions are believed to occur through an initial cleavage of the C–S and S–H bonds respectively.[4,12]

In any case, however, the initial photo-decomposed reaction products are thinyl and alkyl radicals; these radicals are considered to produce hydrocarbons, mercaptans, and various sulfides by the following series of recombination reactions:

$$CH_3\cdot + \cdot CH_3 \rightarrow C_2H_6 \quad (1)$$

$$CH_3S\cdot + \cdot CH_3 \rightarrow CH_4 + CH_2{=}S \quad (2)$$

$$CH_3S\cdot + CH_3SCH_2R \rightarrow CH_3SH + CH_2{=}SCH_2R \quad (3)$$

$$CH_3S\cdot + CH_3S\cdot \rightarrow CH_3SSCH_3 \quad (4)$$

$$CH_3S\cdot + CH_2{=}S \rightarrow CH_3SCH_2S \xrightarrow{\cdot CH_3} CH_3SCH_2SCH_3 \quad (5)$$

The reaction becomes complex and produces oxygenated sulfur compounds (*i.e.*, sulfoxides, sulfones, sulfonic acids, SO_2 and SO_3) and oxygenated compounds (*i.e.*, alcohols, carboxylic acids, aldehydes, and esters) when an oxidizing reagent, such as air or oxygen is present in the reaction system.

A possible reaction mechanism for the formation of the oxygenated sulfur compounds, proposed by Bentley,[12] can be briefly described as follows:

$$CH_3S\cdot + O_2 \rightarrow CH_3SOO\cdot \xrightarrow{RH\ (e.g.,H_2O)} CH_3SOOH + R\cdot \quad (6)$$

$$CH_3SOO\cdot \rightarrow SO_2 + \cdot CH_3 \quad (7)$$

$$CH_3SOOH \xrightarrow{h\nu} CH_3SO\cdot + \cdot OH \quad (8)$$

$$CH_3SO\cdot + RH \longrightarrow CH_3SOH + R\cdot \quad (9)$$

$$3\,CH_3SOOH \longrightarrow CH_3SOOSCH_3 + CH_3SO_3H \quad (10)$$

(1) Effect of the Molecular Weight on the Photolysis of Mercaptans. When the photochemical labilities of five mercaptans with a straight carbon chain (*i.e.*, ethyl-, *n*-propyl-, *n*-butyl-, *n*-amyl-, and *n*-hexyl-mercaptans) are compared, photochemical stability is found to increase with an increase in the carbon number of mercaptans.

As is shown in Fig. 1, with ethyl- and *n*-propyl-mercaptans a 3-hr irradiation of *n*-hexane solutions of these mercaptans at 0 °C with a low-pressure mercury-vapor lamp gave a more than 50% conversion, while with C_4–C_6 straight chain mercaptans the photolysis afforded only a 15—30% conversion under the same reaction conditions. Although a 6-hr irradiation caused an 85% decomposition with C_2 and C_3 mercaptans, C_4–C_6 mercaptans afforded only a 30—40% decomposition.

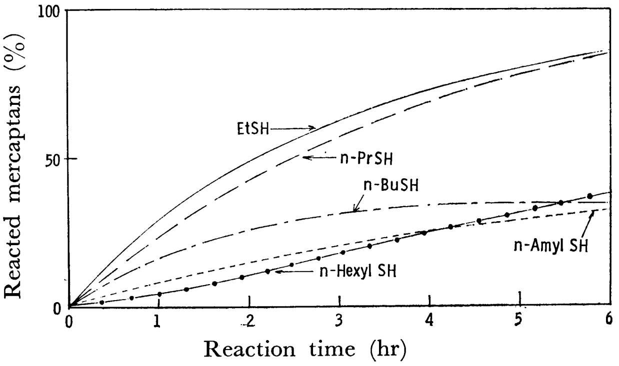

Fig. 1. Effect of molecular weight on photo-decomposition of mercaptans.

(2) Effect of the Molecular Structure on the Photolysis of Mercaptans and Sulfides. As the photolysis of mercaptans and sulfides is considered to be initiated through –S–S–, C–S, or S–H fission, the photochemical labilities were compared with *n*-propyl, isopropyl-, *n*-butyl-, *tert*-butyl-, *sec*-butyl, isobutyl, *n*-amyl-, *sec*-isoamyl-, and *tert*-amyl-mercaptane in order to examine the difference in photochemical stability with the structural features of the carbon atom attached to the –S– or –SH group.

In the cases of mercaptans with lower molecular weights, as is shown in Figs. 2 and 3, no difference in photochemical stability due to the change in the molecular structure was observed. With butyl mercaptan isomers, only a slight difference in the photochemical

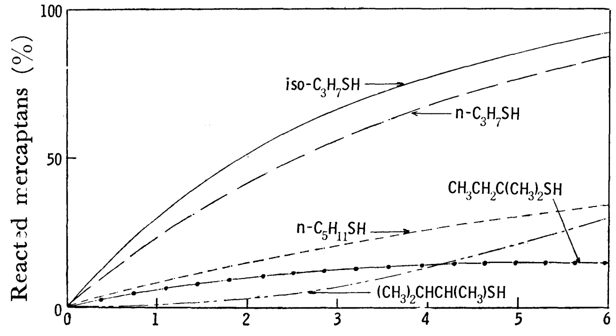

Fig. 2. Effect of molecular structure on photo-decomposition of mercaptans.
(Propyl mercaptans and amyl mercaptans)

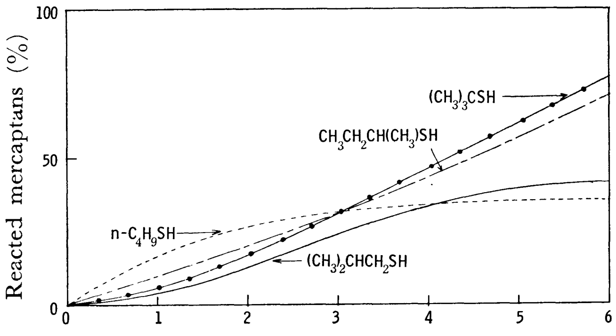

Fig. 3. Effect of molecular structure on photo-decomposition of mercaptans.
(Butyl mercaptans)

stability was observed at the beginning of the irradiation, but after a 6-hr irradiation *n*-butyl- and isobutylmercaptans, which have primary carbon atoms, were decomposed by 35—40%, while the irradiation of mercaptans containing secondary or tertiary carbon atoms (*i.e.*, *sec*-butyl- and *tert*-butyl-mercaptans) resulted in a 70—75% conversion.

It is, however, apparent from a comparison of the amyl mercaptan isomers with mercaptans of higher molecular weights, that the structural features of the carbon atoms attached to the –SH group slightly influence the photochemical stability.

Sulfides are more stable upon photolysis than the mercaptans, and Milligan[8] reported that, on the photolysis of dialkyl polysulfides, no simple correlation of the stability of dialkyl polysulfides with the nature of the alkyl substituents was observed.

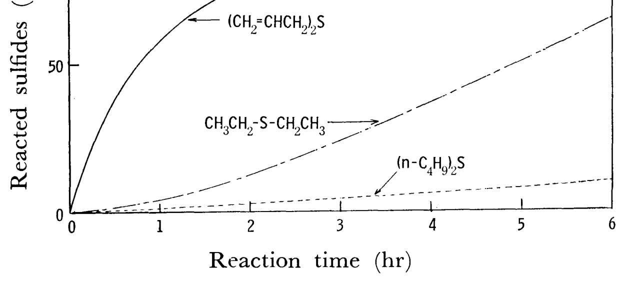

Fig. 4. Effect of molecular structure on photo-decomposition of sulfides.

However, the presence of an unsaturated linkage in the carbon chain of the sulfide markedly reduces the photochemical stability of the sulfide. This fact can be demonstrated by comparing the rates of the photodecomposition of three sulfides. As is shown in Fig. 4, a 2-hr irradiation of diethyl sulfide and di-*n*-butyl sulfide resulted in a 5—15% conversion, while diallyl sulfide, a typical unsaturated sulfide, afforded a 75% conversion, which corresponds to that of the photochemical labile mercaptans with lower molecular weights.

(3) Effect of the Reaction Temperature on the Photolysis of Mercaptans and Sulfides in Crude Naphtha. Inaba[4] reported that no temperature effect had been observed on the photolysis of methyl mercaptan in a gaseous phase because of the heat stability of the thinyl radical, formed as an initial photo-decomposition product of mercaptan.

In this study, UV irradiations of the crude naphtha were carried out at 0, 30, and 50 °C in order to examine the effect of the reaction temperature on the photolysis of the principal mercaptans and sulfide (*i.e.*, ethyl-,

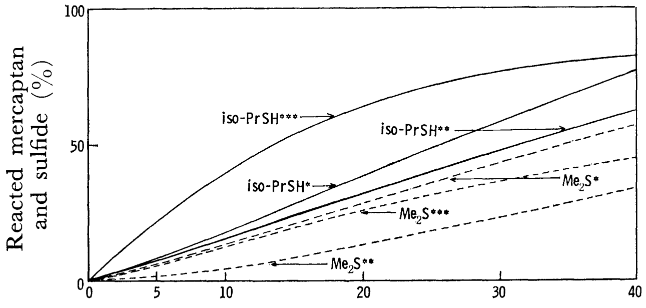

Fig. 5. Effect of reaction temperature on photo-decomposition of mercaptan and sulfide in crude naphtha. (*iso*-PrSH and Me_2S)
* irradiated at 0°C
** irradiated at 30°C
*** irradiated at 50°C

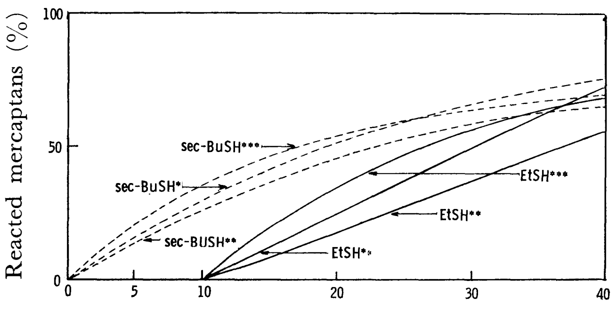

Fig. 6. Effect of reaction temperatures on photo-decomposition of mercaptans in crude naphtha. (EtSH and *sec*-BuSH).
* irradiated at 0°C
** irradiated at 30°C
*** irradiated at 50°C

Table 1. Percentages of reacted mercaptans and sulfides in the crude naphtha by UV irradiation under various reaction conditions

Mercaptans and sulfides	Reaction conditions																			
	Irradiated at 0 °C					Irradiated at 30 °C					Irradiated at 50 °C					Irradiated at 0 °C with aeration (5 ml air/min)				
	Reaction time (min)					Reaction time (min)					Reaction time (min)					Reaction time (min)				
	5	10	20	30	40	5	10	20	30	40	5	10	20	30	40	5	10	20	30	40
Ethyl mercaptan	0	3	32	55	76	0	7	27	53	67	0	1	38	57	71	23	47	80	92	98
Isopropyl mercaptan	10	20	43	58	75	18	27	43	60	70	31	35	59	69	77	40	57	81	91	96
Dimethyl sulfide	3	12	33	42	58	8	8	19	36	44	10	14	26	34	43	31	43	66	77	87
Methyl ethyl sulfide	15	33	68	83	91	19	39	61	78	87	41	56	72	82	90	51	69	90	97	100
sec-Butyl mercaptan	17	30	51	65	73	23	38	47	61	69	33	41	51	59	68	42	55	76	86	93
Isobutyl mercaptan	11	31	53	80	82	37	44	60	69	85	31	48	45	52	71	38	56	74	87	92
Diethyl sulfide	8	33	52	62	69	24	29	50	52	55	14	30	27	53	36	37	52	68	77	82

Mercaptans and sulfides	Reaction conditions																			
	Irradiated at 0 °C with aeration (15 ml air/min)					Irradiated at 0°C with aeration (5 ml O_2/min)					Irradiated at 0 °C with aeration (15 ml O_2/min)					Irradiated at 0 °C with aeration (30 ml O_2/min)				
	Reaction time (min)					Reaction time (min)					Reaction time (min)					Reaction time (min)				
	5	10	20	30	40	5	10	20	30	40	5	10	20	30	40	5	10	20	30	40
Ethyl mercaptan	25	55	90	99	100	24	59	95	100	100	22	60	94	99	100	9	35	81	97	100
Isopropyl mercaptan	33	53	83	97	100	37	57	88	99	100	26	51	84	93	99	17	34	66	88	98
Dimethyl sulfide	27	50	81	96	100	34	56	90	100	100	33	62	94	100	100	18	43	81	98	100
Methyl ethyl sulfide	54	73	100	100	100	48	81	100	100	100	52	72	96	100	100	22	51	88	100	100
sec-Butyl mercaptan	47	62	88	97	100	37	66	89	99	100	41	59	89	98	99	20	44	75	90	98
Isobutyl mercaptan	54	69	100	100	100	44	100	100	100	100	46	64	100	100	100	16	45	65	100	100
Diethyl sulfide	43	64	87	100	100	43	74	95	100	100	51	74	95	100	100	20	52	84	100	100

isopropyl-, and *sec*-butyl-mercaptans and dimethyl sulfide) in the crude naphtha.

As is shown in Figs. 5 and 6, no influence of the reaction temperature was observed with any mercaptan or sulfide.

(4) Effect of an Oxidizing Reagent on the Photo-oxidation of Mercaptans and Sulfides in Crude Naphtha. Bentley[12] obtained CH_3SO_3H (21%) and SO_2+SO_3 (30 %) as the principal photo-oxidation products on the photolysis of dimethyl sulfide in air, and he concluded that the presence of air had altered the mode of the photolysis of the sulfide.

In this study, photolysis in the presence of oxidizing reagent, air, and oxygen was undertaken with a view to accomplishing the desulfurization of the crude naphtha rather than to oxidize the mercaptans to the sulfides. As the irradiation was conducted with aeration, the reaction temperature was kept at 0 °C to prevent any possible mechanical losses or chemical reactions.

Figures 7 and 8 compare the rates of the photo-oxidation of several principal mercaptans and sulfides in crude naphtha. The presence of an oxidizing reagent markedly increases the rate of the photo-decomposition of mercaptans and sulfides, but the difference in either the nature or the flow rate of the oxidizing reagents resulted in no practical influence on the rate of the photo-oxidation (cf. Table 1). This suggests that the irradiation of crude naphtha by means of a high-pressure mercury-vapor lamp initiates the S–H and C–S fission of mercaptans and sulfides; thus, the formation of thinyl and alkyl radicals and the subsequent recombination reactions of free radicals (1—5), or the oxidation of these free radicals (6—10), takes place. In the presence of the oxidizing reagents, the oxidation of free radicals might occur in preference to the recombination reactions, but the former would not be accelerated by the presence of an excess of the oxidizing reagent.

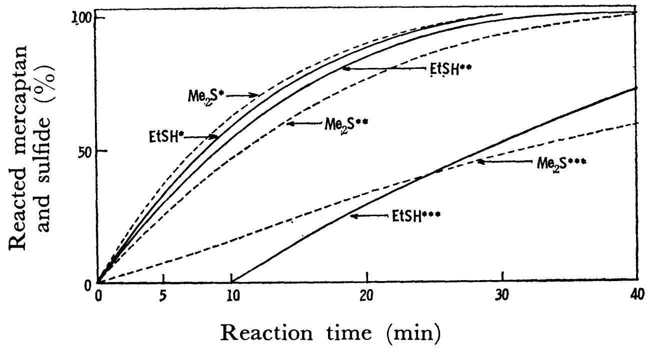

Fig. 7. Effect of oxidizing reagent on photo-decomposition of mercaptans and sulfides in crude naphtha.
* irradiated at 0°C with aeration (15 ml O_2/min)
** irradiated at 0°C with aeration (15 ml air/min)
*** irradiated at 0°C without aeration.

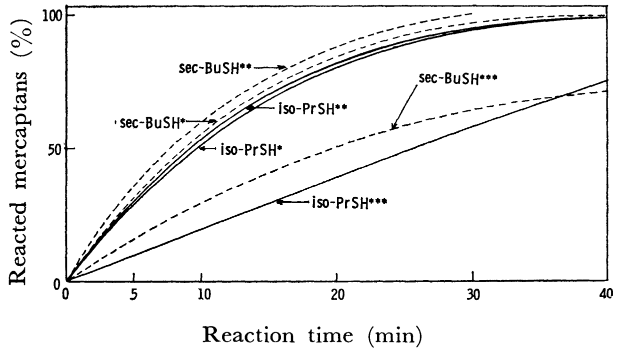

Fig. 8. Effect of oxidizing reagent on photo-decomposition of mercaptans. (*iso*-PrSH and *sec*-BuSH)
* irradiated at 0°C with aeration (15 ml O_2/min)
** irradiated at 0°C with aeration (15 ml air/min)
*** irradiated at 0°C without aeration.

The total sulfur content of the photo-desulfurized naphtha, obtained by washing the irradiated naphtha with water after a 40-min irradiation with aeration, decreased by 32.2%, and the sulfur compounds in the oil layer consisted mainly of higher-molecular-weight sulfides produced by the recombination reactions; 67.8% of the original sulfur compounds in the crude naphtha was converted into water-soluble oxygen-containing sulfur compounds, such as SO_2, SO_3, and sulfonic acids.

Unlike the results of the gas-phase photolysis of methyl mercaptan, dimethyl sulfide, and dimethyl disulfide, as reported by Rayner[11] and Haines,[7] or Milligans study[8] of the photolysis of several alkyl polysulfides, in this study no difference was observed in the rates of the photolysis of mrecaptans and sulfides in crude naphtha in either the presence or the absence of an oxidizing reagent.

Conclusion

Although a certain difference was observed in the rates of the photolysis of mercaptans due to their molecular weights and structural features, the UV irradiation of crude naphtha caused a rapid photolysis of the sulfur compounds in it. This fact indicates the possibility of the practical application of this method for the desulfurization of the crude naphtha.

Thus, the irradiation of crude naphtha consisting of 0.15% sulfur by means of a 200-W high-pressure mercury-vapor lamp, with the aeration of air or oxygen at the flow rate of 5—15 ml/min and at 0 °C, resulted in an 80—90% photolysis of the principal mercaptans and sulfides in the crude naphtha within 20 min.

As the major photo-oxidation products were water-soluble oxygenated sulfur compounds, this process resulted in 67.8% desulfurization of the crude naphtha when the resultant UV irradiated naphtha was washed with water.

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