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FOULING FORMATION OF AN OLEFIN IN THE PRESENCE OF OXYGEN AND THIOPHENOL*

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ABSTRACT: A kinetic model was developed to predict the fouling rate for autoxidation of indene in the presence of thiophenol. The kinetic constants were determined by analyzing the fouling data obtained with and without thiophenol. An initial rapid formation of hydroperoxide was observed in the presence of thiophenol; however, the product(s) formed by thiophenol was found to inhibit further formation of hydroperoxide. The maximum concentration of hydroperoxide and gum were about the same for experiments with and without thiophenol; however, the maximum was reached faster for runs with thiophenol. The effects of bulk temperature, and concentration of thiophenol and oxygen on the fouling rate were analyzed using the fouling model developed previously.

INTRODUCTION

Fouling of petroleum derived fluids is commonly encountered in the process industries. The presence of a small fraction of reactive compounds produces fouling precursors, which will react further to form insoluble foulant. The role of olefins and sulfur compounds in the overall-fouling process has been the subject of several investigations, because they have been found to be the major sources of precursor formation in petroleum products. Sulfur content in petroleum products can range from trace quantities to several percent, and a large fraction of sulfur is usually found in fouling deposits. Common sulfur compounds identified in petroleum products are thiols, thiophenes, and sulfides [Taylor, 1976]. Although, disulfides and polysulfides have not been identified in crude oils, they can be formed from thiols during processing of petroleum products [Tarbell, 1961]. Olefins have been shown [Russell, 1954; Zhang et al., 1993] to form hydroperoxides in the presence of oxygen. The further reaction of hydroperoxide produces polyperoxides that become increasingly insoluble as the molecular weight increases with polymerization. The effects of trace quantities of sulfur compounds on deposit formation from deoxygenated hydrocarbons were studied by Taylor [1976]. The results indicated that, in general, polysulfides, sulfides, and thiols increase the rate of formation of deposits. Offenhauer et al. [1957] investigated sediment formation in catalytically-cracked middle distillate and

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showed that aromatic thiols accelerate sediment formation and reduce the fuel stability. On the other hand, Daniel and Heneman [1983] showed that sulfides and disulfides in the concentration range of 10 to 1000 ppm inhibited deposition while thiols and dibenzothiophene promoted deposit formation. Kennerly and Patterson [1956] reported that autoxidation of indene is retarded by reaction products of oxygen and disulfide. Denison [1944] indicated that sulfur compounds act as antioxidants in lubricating oils; however, sulfur compounds can be oxidized to products that promote deposit formation. Kharasch et al. [1938] indicated that the end products of thiols and α-olefins are 2-hydroxyethyl sulfides. They also suggested that generation of the end products can follow two routes depending upon formation of either peroxides or alkoxyl radicals. A report on co-oxidation of thiols and olefins by Oswald and Wallace [1961] pointed out that the end products were formed through the peroxide route. The investigation of Morris and Mushrush [1991] showed that thiophenol inhibited the autoxidation reaction by acting as a radical trap and breaking the chain reaction. They found that the major product formed by co-oxidation of indene and thiophenol is 2-phenylthiyindan. Some of the other products observed are 2-phynylthiyl-indanol, 2-phenylthiyl-indanone, and phenyl disulfides. Their observation was consistent with that of Rahman and Williams [1970] who used thiols, sulphoxides, disulfides and sulfides in n-dodecane. They showed that all of the sulfur compounds mentioned above reduced the rate of autoxidation of n-dodecane in the order of thiols=sulphoxides>disulfides>sulfides, and the rate of reaction increased with temperature for all cases except that for sulfides.

The literature contains some contradictory data; however, it is clear that sulfur compounds are very reactive with complex reaction mechanisms. It is necessary to develop a practical kinetic model to account for precursor generation leading to formation of insoluble foulant. The present investigation was carried out to understand the interactions of olefins and sulfur compounds in the presence of oxygen. The objective was to evaluate the applicability of the model developed for fouling formation due to autoxidation of olefins [Yap, 1994; Panchal and Watkinson, 1993] to fouling in the presence of sulfur compounds.

FOULING MODEL

The predictive capability of a fouling model depends upon two elements: (1) kinetics of foulant formation and (2) fluid dynamics that accounts for heat, mass and momentum transfer. Panchal and Watkinson [1993, 1994] developed a model on the basis of an assumption that the interactive effects of transport processes and chemical reactions produce three cases depending on whether fouling precursor is formed in the bulk of fluid, in the thermal-boundary layer or at the solid/fluid interface. The focus of the present investigation was to develop a kinetic model for co-oxidation of indene and thiophenol, and incorporate it in the fouling model.

Reaction Mechanism for Indene and Thiophenol

The kinetic model was developed with the focus that autoxidation of indene is the governing mechanism. It was observed in the present investigation that hydroperoxide concentration reached to a maximum value soon after injection of thiophenol and then decreased. This can be explained on the basis that thiophenol acts as a catalyst for rapid formation of peroxide. Subsequently, product(s) formed by thiophenol inhibits formation of hydroperoxide. The overall model is as follows:

$$RH + O_2 \xrightarrow{RSH} \text{Hydroperoxides} \rightarrow \text{Soluble Gum} \rightarrow \text{Foulant} \qquad (1)$$

$$RSH'$$

$$\text{Soluble Gum} \rightarrow \text{Foulant}$$

$$\text{Side Products}$$

Where RH, RSH, and RSH' represent indene, thiophenol, and thiophenol products, respectively. Detailed reaction steps are as follows:

$$RH + O_2 \xrightarrow{k2} ROOH \qquad (2)$$

$$RH + O_2 \xrightarrow[[ROOH]]{k3'} ROOH \qquad (3)$$

$$2ROOH \xrightarrow[[RSH']]{k4} \text{Soluble Gum} \qquad (4)$$

$$2RH + 2O_2 \xrightarrow{k5} \text{Soluble Gum} \qquad (5)$$

$$ROOH + RSH \xrightarrow[[O_2]]{k6} \text{Soluble Gum} \qquad (6)$$

$$\text{Soluble Gum} \xrightarrow{k7} \text{Foulant} \qquad (7)$$

The objective of the present approach was to utilize the kinetic model developed for indene [Yap, 1994] and add appropriate steps to account for reactions with thiophenol. Therefore, the reaction of indene and oxygen to form peroxide (reaction 2) and production of soluble gum (reactions 4 and 5) are assumed to be the same as the case without thiophenol. However, the autoxidation reaction of indene in the presence of peroxide radicals is inhibited by thiophenol product, which can act as a radical trap. This assumption is based on the investigation of Morris and Mushrush [1991], and Kennerly and Patterson [1956]. Therefore, the rate constant for reaction 3 is different from that for reaction with indene alone. In addition, thiophenol and/or its products react with hydroperoxide to form soluble gum. Little is known about the mechanism for reaction 7 and it is generally assumed that the foulant formation involves chemical reactions and physical processes leading to large molecule weight substances that would precipitate in the thermal-boundary layer or at the solid/fluid interface. It was assumed that the foulant-formation reaction 7 would not be affected by the presence of thiophenol and its derived products. It implied that only the formation of peroxides and gum is affected by the presence of sulfur compounds. Therefore, rate constant k7 [(5.16 10^3 exp(-76.4/RT) L/s] was kept the same as that determined for indene alone [Yap, 1994].

The rate of formation of hydroperoxide is as follows:

$$d[ROOH]/dt = k2[RH]^{3/2}[O_2]^{1/2} + k3'[RH][ROOH]^{1/2} - k4[ROOH] - k6[RSH]^n[ROOH] \qquad (8)$$

The reaction orders in the above equation were derived from the literature data. However, reaction order for RSH could not be found and a first-order reaction was assumed.

The rate of soluble gum formation is as follows:

$$d[Gum]/dt = 1/2\ k4[ROOH] + k5[RH]^{3/2} + k6[RSH]^{n}[ROOH] - k7[Gum] \qquad (9)$$

The rate of consumption of thiophenol is expressed as follows:

$$d[RSH]/dt = -k6[RSH]^{n}[ROOH] \qquad (10)$$

Here, it is assumed that all of thiophenol reacted goes to formation of soluble gum and there are no other side reactions in which it is consumed. This assumption needs to be validated with chemical analysis of fluid and deposits.

Fluid-Dynamic Model

The model developed earlier [Panchal and Watkinson, 1993 and 1994] was used to predict the fouling rate. The model was developed on the basis of assumptions that the fouling process can be represented by one of the three cases depending upon the region where precursor (i.e., soluble gum) is formed. Depending upon the interactive effects of chemical reactions and heat/mass transfer, precursor can form in the bulk, in the thermal-boundary layer or at the wall surface. It was shown that the model based on the assumption of precursor and foulant formation in the thermal-boundary layer predicted the fouling rate more accurately than the other two cases.

EXPERIMENTAL PROCEDURE

A detailed description of the experimental apparatus is given by Panchal and Watkinson [1994]. Experiments were conducted in a closed-flow loop used for conducting fouling tests. Commercial odorless kerosene obtained from Aldrich was used as the test fluid. An appropriate amount of indene was mixed with about 4 liters of kerosene and the fluid was transferred to an aeration column. The fluid was aerated for about 4 hours and then transferred to the reservoir. The system pressure was held constant all the time to maintain a proper saturation level. Separately, a measured amount of thiophenol was mixed in about 100 ml of kerosene and stored in a sample bottle attached to the system. The test fluid was circulated by a gear pump and temperature was raised to the test condition by the heater. After steady state operation was reached in about 1 to 2 hours, thiophenol was injected at the system pressure. The previous experiments with indene showed that the hydroperoxide formation was insignificant during the heating cycle.

Fluid samples (100 ml) were taken at predetermined intervals. Samples were immediately cooled to ice temperature and refrigerated overnight at about -4 °C for chemical analysis the next day to determine the concentration of hydroperoxide and soluble gum. It was observed that the amount of gum that could be precipitated at -4 °C was not affected by adding n-hexane. The sample together with bottle was weighed (0.001g accuracy). The sample was then filtered and rinsed with cold hexane, and the bottle, filter paper, and filtering funnel were vacuum dried. The gum weight was calculated as difference in weight of filter paper with gum and the original paper weight.

The filtrate was used to determine readily reducible hydroperoxide concentration by using ASTM Standard E298. Sodium iodide was added to the sample and iodine was liberated by peroxide. Iodine is then titrated with standardized 0.1N sodium thiosulfate solution with starch solution as an indicator. The sample and all reagents were deaerated prior to analysis by purging with carbon dioxide to stop further reaction with oxygen. Peroxide number was calculated from the following equation:

$$\text{Peroxide number} = \frac{1000 \times 0.1 \times (Na_2S_2O_3 \text{ volume})}{\text{sample volume}} \quad \text{meq/L} \qquad (11)$$

ANALYSIS OF RESULTS

The analysis of the data was based on measurements of (1) indene consumption, (2) hydroperoxide formation, (3) soluble gum formation, and (4) the rate of fouling deposition. The first task was to determine kinetic constants for reactions described by Equation 2 through 7. Table 1 shows a summary of the test conditions, which included three thiophenol concentrations, three pressures, and two bulk temperatures. Indene concentration, fluid velocity, and wall temperature were maintained at 10%, 1 m/s, and about 190 °C , respectively.

TABLE 1
Summary of Test Conditions.

Test Number	Bulk Temperature °C	Wall Temperature °C	Pressure kPa	[RSH] ppm S	[Indene] mol/L	$[O_2]$ mol/L
1	83	190	320	300	0.71	0.0056
2	83	188	406	300	0.71	0.0
3	83	189	816	300	0.71	0.015
4	85	191	420	300	0.71	0.0075
5	83	188	420	1,000	0.71	0.0075
6	100	191	420	300	0.71	0.0073
7	83	194	420	100	0.71	0.0075
8	82	186	420	0	0.71	0.0056

Indene Consumption

Kinetic constant k1 for indene consumption was assumed to be the same as that without thiophenol. This assumption can be justified on the basis that indene concentration was significantly greater than thiophenol. The data from tests at the University of British Columbia (Zhang et al., 1993) were used to calculate the kinetic constants. The resulting equation is as follows:

$$k1 = 0.1959 \exp(-22.8/RT) \qquad (12)$$

where

T = fluid temperature, K
R = Gas constant, kJ/mol

Peroxide Formation

Kinetic constants k2, k3, and k4 were determined using the fluid analysis data for indene. Figure 1 shows typical concentration profiles for hydroperoxide with and without thiophenol. A detailed analysis to determine the kinetic constants is given by Yap [1994]. The resulting equations are as follows:

$$k2 = 8.4\ 10^{11} \exp(-119/RT) \quad (13)$$

$$k3 = 0.112 \exp(-26.7/RT) \quad (14)$$

$$k4 = 1.0\ 10^{7} \exp(-76.4/RT) \quad (15)$$

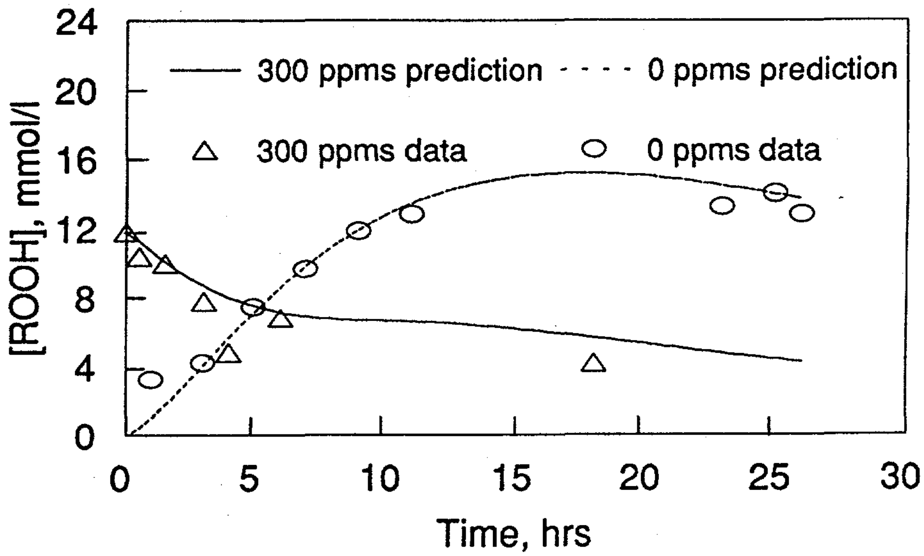


Figure 1. Hydroperoxide concentration profile with and without thiophenol for tests.

For all experiments with thiophenol, the hydroperoxide concentration was observed to be the highest for the first sample taken 15 minutes to 30 minutes after injecting thiophenol. The initial sample taken before injecting thiophenol showed negligibly small (< 1 mmol/L) hydroperoxide concentration. In a similar investigation at the University of British Columbia (Asomaning and Watkinson, 1994), the system was momentarily depressurized during injection of indene and thiophenol. As a result, hydroperoxide formation was rapid but was not instantaneous as observed at Argonne. This can be explained on the basis of dissolved oxygen being the rate limiting component. In developing the kinetic model, it was assumed that thiophenol acts as a catalyst for formation of hydroperoxides. This assumption is justified by the stoichiometry. For low concentration of thiophenol of 2.53 mmol/L, the hydroperoxide level reached 7.2 mmol/L, which was significantly greater than thiophenol concentration. As shown in Figure 2, the initial instantaneous concentration of hydroperoxide seemed to follow an asymptotic behavior with thiophenol concentration. The data in Figure 2 were empirically fitted to the following equation:

$$[ROOH]_i = [ROOH]_o + 2.61\ [Thiophenol]^{0.243} \quad (18)$$

where

$[ROOH]_i$ = initial peroxide concentration

$[ROOH]_o$ = initial concentration without thiophenol

= 0.6 mmol/l at Tb = 82 C and P = 420 kPa (air)

Rate constant, k6, was determined by adjusting its value to match the experimental and predicted slope of peroxide concentration vs time for the initial period of about 2 hours. The approach was based on an assumption that reaction 6 would be a governing step. Test data for runs 3, 6 and 7 were used to determine k6, which was found to be proportional to square root of concentrations of oxygen and thiophenol. Therefore, the rate of consumption of peroxide was expressed as follows:

$$-d[ROOH]/dt = k6[O2]^{0.5}[RSH]^{0.5}[ROOH] \quad (17)$$

where

$$k6 = 7.13\ 10^{5}\exp(-54.6/RT) \quad (18)$$

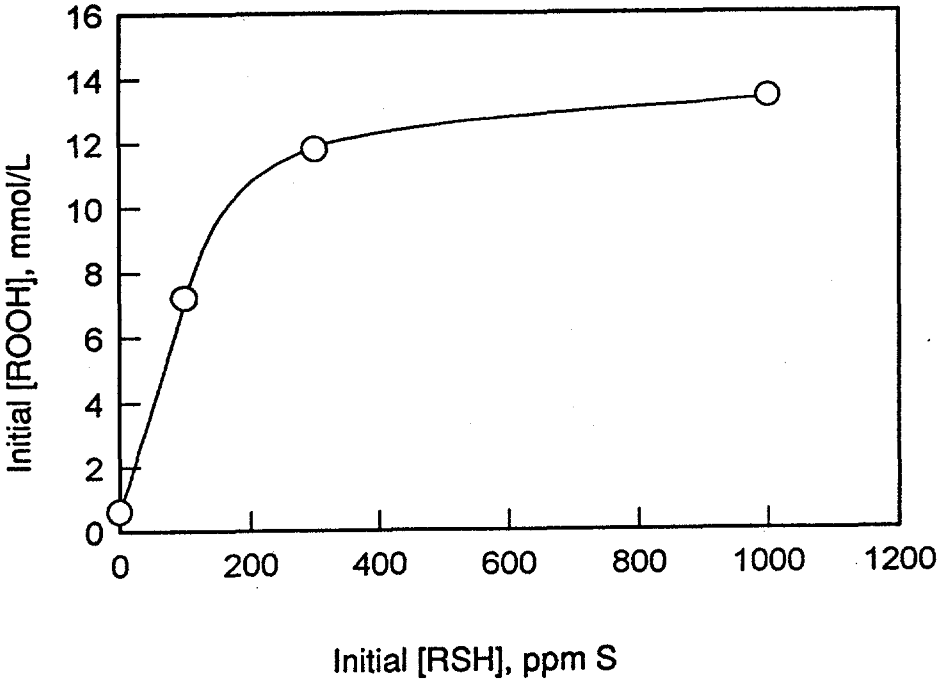


Figure 2. Initial hydroperoxide concentration as a function of thiophenol concentration.

The experimental data for consumption of hydroperoxide could not be explained by reaction 6 alone, and the following inhibition reaction was added to the kinetic model:

$$\text{Rate of autoxidation} = \frac{k4\,[RH]\,[ROOH]^{n+0.5}}{([ROOH] + k8'[Prod])^{n}} \quad (19)$$

where

$k8' = 8.4\ 10^{12}\exp(-77.4/RT)$, and $n = 0.25$

Here, [Prod] represents inhibitor concentration and was assumed to be proportional to products formed from thiophenol (i.e. $[Prod] = \alpha\,[RSH]$).

Gum Formation

Figure 3 shows comparison of gum concentration as a function of time for test runs 4 and 8 with and without thiophenol, respectively; other conditions being comparable. The initial rate of gum formation was higher in the presence of thiophenol than without. This can be explained on the basis of reaction shown by Equation 6. However, the gum concentration seemed to be comparable with and without thiophenol towards the end of test run.

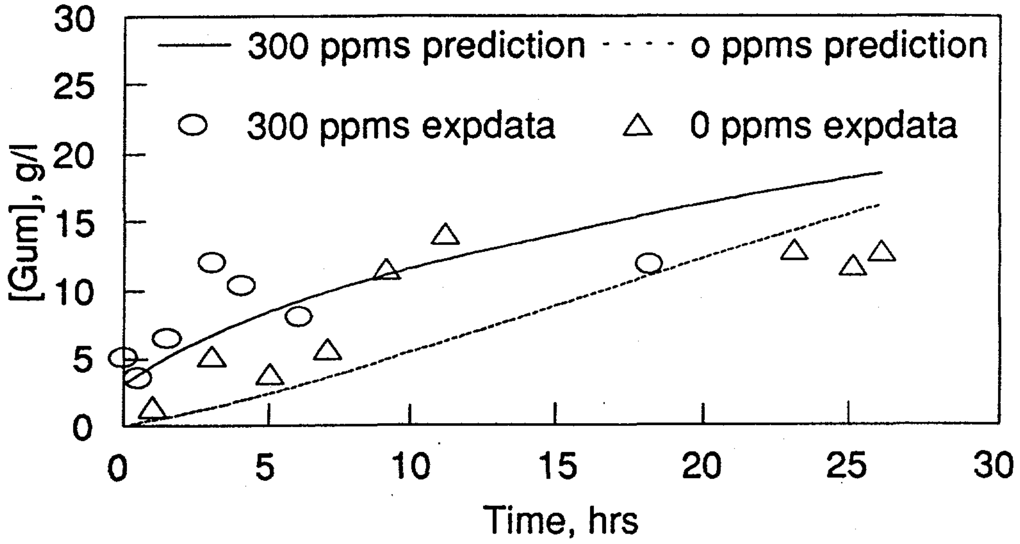
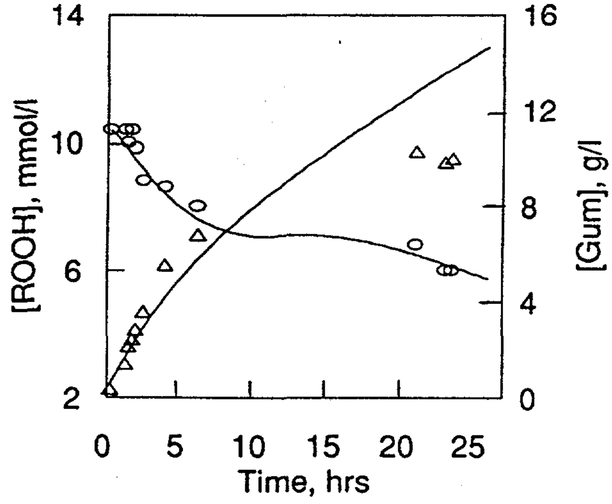


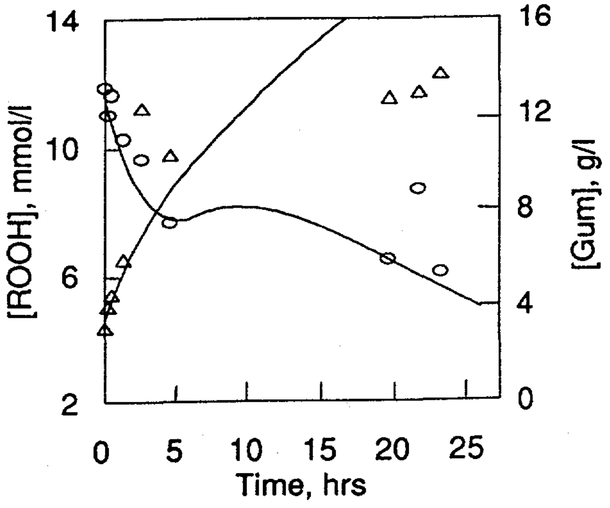
Figure 3. Gum concentration profiles with and without thiophenol.

Comparison of Prediction with Data

The kinetic constants were determined using the data during the initial period of about 5 hours and the model was expected to predict concentration profiles for the rest of the test period. The predicted and experimental hydroperoxide and gum concentrations are shown in Figures 4 through 9, for each of the 6 test runs. Symbols for Figures 4 through 9 are as follows: O [ROOH] experimental; Δ [Gum] experimental; predictions are shown by solid lines. The hydroperoxide concentration predicted by the model was in a reasonable agreement for both temperatures and at two thiophenol concentrations of 100 and 300 ppms. Predicted peroxide concentration was generally lower than the experimental value towards the end of test runs. Comparison of the results for 300 and 1000 ppms showed that the inhibition effect on peroxide formation might have a weaker dependency than 0.25 assumed in the present model. Taylor [1976] indicated that deposit formation increased by a factor of two when disulfide concentration was increased from 300 to 3000 ppms. The present model assumes power of 1/2 to thiophenol concentration, which is qualitatively in agreement with the Taylor's results. The predictions at three different air pressures (oxygen concentrations) are fairly good; Figures 4, 5 and 6. For low concentration of thiophenol, a point of inflection was observed in the range of 5 to 9 hours, which may be due to consumption of the product that inhibited the hydroperoxide formation.



Fiqure 4. Data for test 1.



Fiqure 5. Data for test 3.

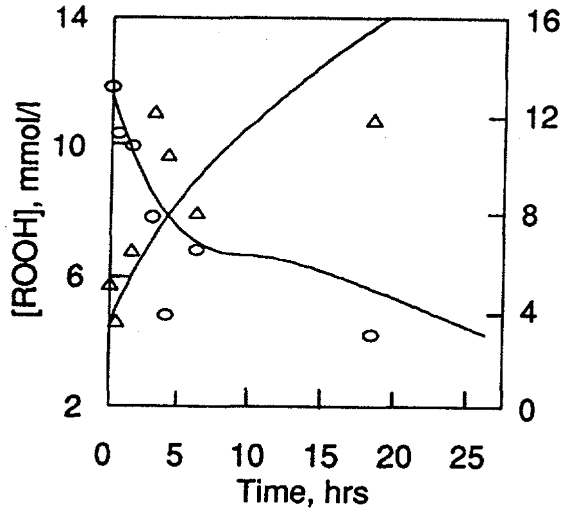


Figure 6. Data for test 4.

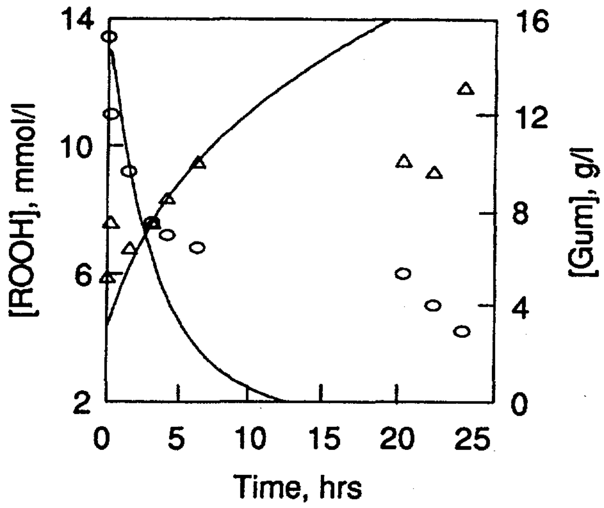


Figure 7. Data for test 5.

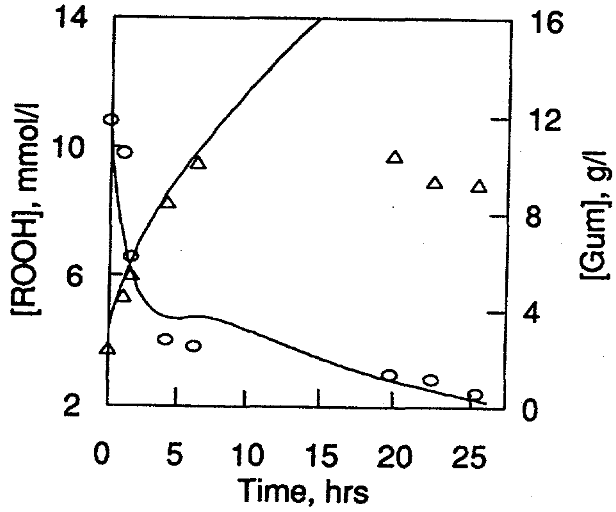


Figure 8. Data for test 6.

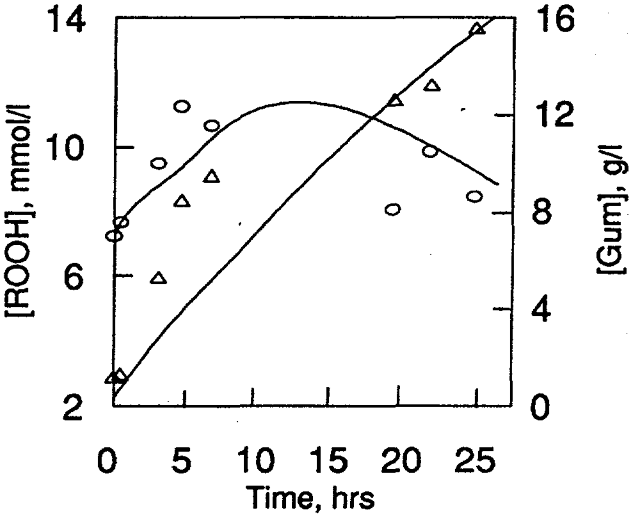


Figure 9. Data for test 7.

The predicted gum concentration in general followed the experimental data for the first five hours of the test period. However, the predictions were generally higher than the experimental values towards the end of test run. This observation suggests there might be an additional reaction not considered in the present analysis.

Foulant Formation

Figure 10 shows comparison of the measured and predicted fouling resistance as a function of time for test 1. The predicted fouling resistance at a given time was lower than the experimental value. However, it is important to compare the fouling rate at a given time or during a given time period. The experimental and predicted rates of fouling (slope of the linear part of the fouling curve between 5 and 15 hours) for this test run were 0.04 and 0.032 (m^2 K/kW)/hr, respectively. The fouling rates for all test runs shown in Table 1 are presented in Table 2. In general, the predicted rate of fouling was greater than the experimental values for test runs for which the predicted gum concentration was higher than the experimental data. Therefore, if the model can be improved to predict the gum concentration for the later part of the test period, prediction of the fouling rate will also improve.

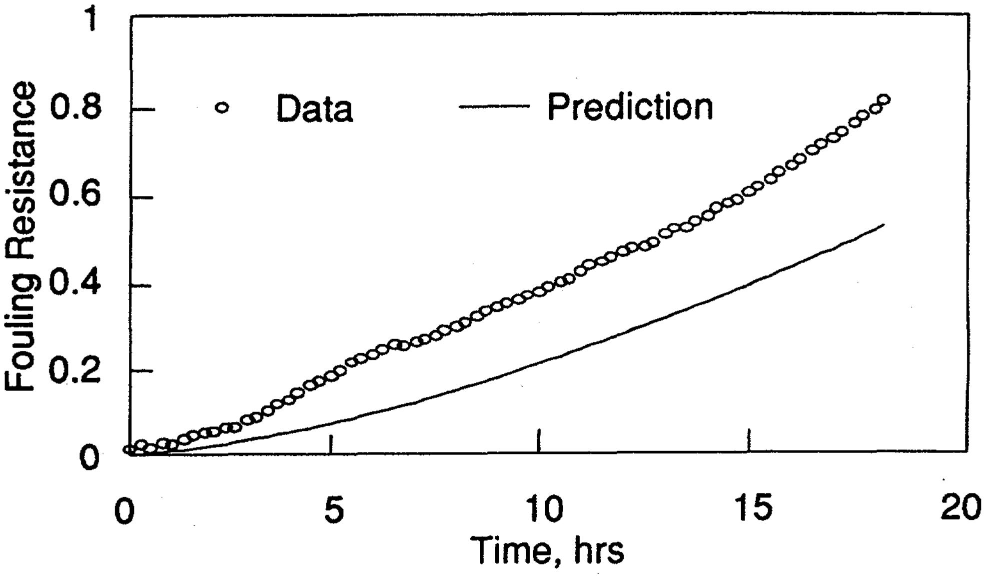


Figure 10. Comparison of predicted and experimental fouling resistance.

TABLE 2
Comparison of experimental and predicted fouling rate.

Test No.	Fouling rate, (m^2 K/kW)/hr	
	Experimental	Predicted
1	0.040	0.032
3	0.020	0.045
4	0.061	0.039
5	0.045	0.046
6	0.011	0.060
7	0.016	0.034
8	0.044	0.035

CONCLUSIONS

A kinetic model is developed for fouling due to co-oxidation of indene and thiophenol. The analysis is based on three measured parameters; hydroperoxide, soluble gum, and the fouling resistance. A possible reaction mechanism is developed to explain the experimental data. Although, the kinetic constants were determined by a somewhat complex method with a limited number of data points, the analysis provided a technical basis to explain the fouling process. The major conclusions are as follows:

1. There is a finite relationship between hydroperoxide, soluble gum and fouling deposition.
2. Hydroperoxide is formed by a rapid reaction in the presence of thiophenol. The instantaneous hydroperoxide concentration is limited by oxygen and thiophenol. The subsequent formation of hydroperoxide is inhibited by product(s) formed by thiophenol.
3. The kinetic models developed for autoxidation of olefins can be extended to analyze the overall fouling process in the presence of thiophenols. It leads to believe that the effects of other sulfur compounds can be analyzed with a similar approach.

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