

## Coke Inhibition During Naphtha Pyrolysis

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### Abstract

*The effectiveness of binary mixtures of phosphorus and sulfur compounds as coke inhibitors for naphtha pyrolysis has been studied. As both phosphorus and sulfur compounds proved to be promising coke inhibitors, runs were made with mixtures of these compounds. The coke deposited was significantly lower when phosphorus was used together with sulfur. Also, the effect of the addition of Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> in the naphtha feed was investigated. It was found that the addition of Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> reduced the coke formation. Scanning electron microscope (SEM) was used for the microstructure of deposited coke and energy dispersive X-Ray spectroscopy (EDAX) for the surface elemental composition of coke formed on the surface of stainless steel coupons. It was found that in the presence of inhibitors, deposited coke has a porous structure and so small amounts of Ni, Cr, and Fe elements.*

**Keywords:** *Coke deposition, Coke inhibitor, Organosulfur compounds, Organophosphorus compounds*

### Introduction

Pyrolysis of naphtha and other hydrocarbons, which is of primary importance in the manufacture of light olefins, is always accompanied by formation of coke, which results in the fouling of the reactor and the transfer line heat exchanger. During the last few years, investigations have been made on coke formation during the pyrolysis of various hydrocarbons such as ethane, propane, n-hexane, n-octane and naphtha [1-7]. These studies have shown that coke deposition depends on several factors, such

as, the aromatic and sulfur content of the feedstock, hydrocarbon partial pressure, temperature, conversion and the material used in the construction of the reactor.

The coke deposits of a few millimeters to centimeters in thickness lead to poor heat transfer. In order to retain the same process temperature and hence the same conversion, plant operators have to raise the skin temperature continuously, which often leads to more rapid coke formation. The coke build-up also increase the pressure drop, which results in lower ethylene yield. With

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time, this accumulation of coke forces the operator to shut down the unit either on the skin temperature or on the pressure drop. The furnace is, therefore, taken offline for coke removal (decoking). Decoking is carried out by using a mixture of steam and air to burn out the coke. This process is very undesirable to the plant owner because of the following reasons: frequent decoking means lost ethylene production, high operating and maintenance costs and shortened life of the coil because of the constant thermal cycling. There is, therefore, an incentive for the operator to try to reduce coke formation or deposition to the minimum level [8].

Coke formation is mainly due to two mechanisms, catalytic coking and asymptotic coking. In the catalytic coking, base metal constituents (mainly Fe and Ni) catalyze the dehydrogenation of hydrocarbons at elevated temperatures. This dehydrogenation of hydrocarbons yields a product rich in carbon. This product deposits on the inner tube skin surface and finally degrades to filamentous deposits of coke. Catalytic coking rates are roughly proportional to the bare base metal area. As the metal area is covered progressively, the second mechanism takes over. The asymptotic coking is mainly due to gas-phase coking reactions [9]. The development of coke inhibitors has paralleled the various coke formation mechanisms described above. The techniques commonly used today to reduce coke formation include the pretreatment of feedstocks, a change in the materials used in the construction of the reactor, alteration of the surface chemistry of the reactor, or the addition of coke inhibitors to the feedstock [10-11]. The development and use of additives appears to be the most effective and practical method. Coke inhibitors reported in the literature include salts of alkali metals or alkali-earth metals at parts per million (ppm) quantities, which are believed to promote coke gasification by steam [10]. There are some reports in literature for inhibiting the effect of sulfur and phosphorus compounds. Phosphorus-

containing additives have been shown to be effective in inhibiting coking rates. The additive provided filming to passivate the metal surface to prevent it from catalyzing the coke formation. The increase in run length varied from 50% to 22.3%. Moreover, the steam-air decoking time decreased by 5-10% and cleaning exchangers was easier because of softer coke. In the above-mentioned studies on inhibition of coke formation using phosphorus additives, no information on the quantitative rates of coke formation has been revealed. Furthermore, very little information is available on the combined effect of phosphorus and sulfur on coking rates [12-17].

In this paper, we report the effectiveness of binary mixtures of phosphorus and sulfur compounds,  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ , as coke inhibitors on coking rate in the pyrolysis of naphtha.

## Experimental study of coke formation

### Experimental setup

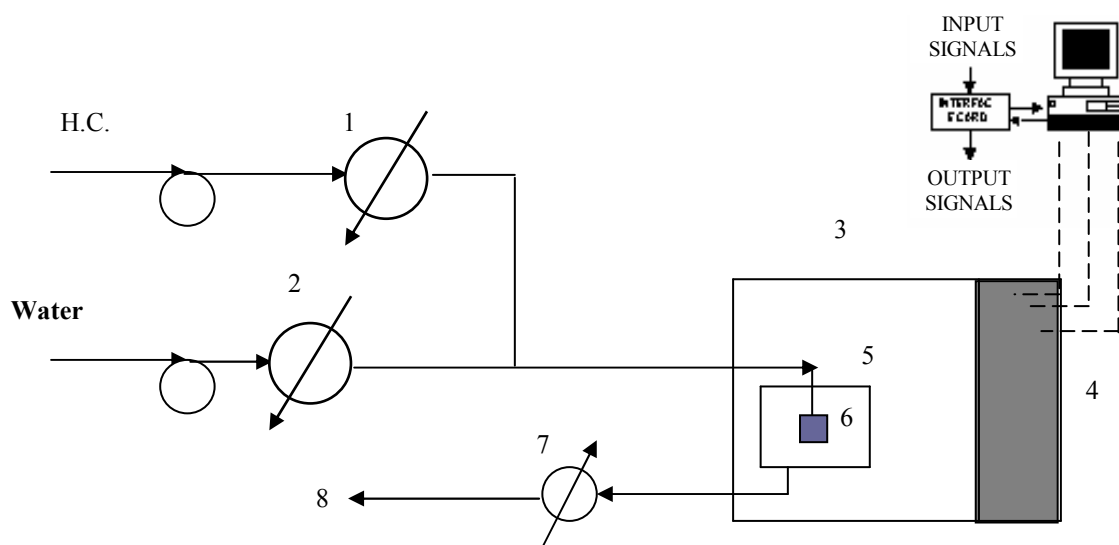
The setup used for the experiments of naphtha thermal cracking is a computer controlled bench scale system, which is shown schematically in Fig. 1.

The system is noted for its simple structure, easy alteration of operation parameters, small volumes of feedstock used for pyrolysis, high accuracy of coke formation measurement and short operating cycle. It is particularly suitable for identifying the coking rate and coke inhibitors over a wide range of conditions.

The feed consists of naphtha and distilled water for preparing dilute steam, which enters preheaters from individual containers using two regulated syringe pumps. Preheaters made of copper coils are heated electrically. The temperature of preheaters controlled by an electronic control system is in the range of 300-400°C. At this temperature range, both naphtha and water are in vapor form. They were mixed together completely and sent to the reactor. The

reactor, made of SS 321, is a cylinder having a volume of about 9cc, which is placed vertically in the electrical furnace. The analog signals of the thermocouples were connected to the process computer. The temperature of the reactor controlled by a PC was in the range of 800-950°C. The residence time in the reactor was regulated by the feed flow rate. Evaluation of the amount of precipitated coke was obtained by measuring the weight of a small coupon made of SS321, with dimensions of about 8×8 mm suspended in the reactor before and after each pyrolysis run. The reactor effluent passed through two condensers in a series to collect liquid products and water in receivers. The mixture of condensed liquid products and water was later separated, and their weights measured.

The gaseous products were analyzed by a gas chromatograph system. By using this system it became possible to obtain a variety of resident times via changing feedstock flows. The online computer control software was divided into monitoring and control sections. The PC process computer was connected online to the system which controlled the main part of the unit. It is connected to the system through analog to digital (A/D) and digital to analog (D/A) converters. An electronic kit, made in the petroleum research lab, is used for sending control signals to the final control element of the heaters. The power of the furnace and preheaters was controlled manually or by the process computer. Details of the system can be found in [18].



**Figure 1.** Schematic diagram of laboratory system naphtha steam cracking to study coke deposition. 1) Naphtha preheater. 2) Water preheater. 3) Electrical furnace. 4) Electrical furnace control system. 5) Steam cracking reactor. 6) Small coupon made of SS321 suspended in the reactor as coke deposition sampler. 7) Condenser for output gases. 8) Output gaseous.

In the monitoring section, the process gas, furnace and heater wall temperatures are monitored and displayed on a screen by means of a visual program in windows operating system. The set points for this temperature stabilizing control are included in the software. All measurements and control system information are saved in the text and graphical mode. The temperature reading is also visualized on a color digital thermometer display.

### Coke deposition procedure

Coke formation during the pyrolysis of naphtha was studied in the jet stirred reactor system. For a better estimation of coking parameters, the experiments were carried out at different operating conditions. The deposition of coke on the inner surface of the reactor is influenced by operating conditions such as temperature, partial pressure and residence time. Process gas temperature and tube skin temperature of the reactor are the most important factors affecting the rate of coke deposition.

The naphtha feed was introduced into the reactor and pyrolysed at a constant flow rate, pressure, steam ratio and constant temperature of the furnace. The furnace temperature and reacting gas temperature in the reactor were measured by thermocouples connected to a computer via an interface. The mass flow rate of naphtha and steam were controlled at certain time intervals.

The experiments were continued for about 2 hours under steady state conditions. The system was then prepared for the decoking procedure. At the completion of the run, the reactor was flushed with nitrogen, and then the coked steel coupons were removed. The amount of deposited coke on the surface of the coupon was quantified by measuring the weight of the coupon suspended in the reactor before and after each pyrolysis run. Scanning electron microscope (SEM) was used for the microstructure study of deposited coke and energy dispersive X-Ray

spectroscopy (EDAX) for surface elemental composition. Based on our results, this paper aims to provide a closer insight into the coking problem in industrial steam cracker. Analysis was used to study the morphology and structure of coke formed on the surface of stainless steel coupons.

### Residence time calculation

The residence time is calculated using the following relationship:

$$t = \frac{PV_r}{RT(V_{HC} \cdot \rho_{HC}) \left[ \frac{1}{Mw_{(HC)}} + \frac{S.R.}{Mw_{(w)}} \right]}$$

Where P is the atmospheric pressure;  $V_r$  the volume of the reactor; R the gas constant; T the temperature of the reaction;  $V_{HC}$  the flow of naphtha;  $\rho_{HC}$  the density of hydrocarbon;  $Mw_{(HC)}$  the molecular weight of hydrocarbon;  $Mw_{(w)}$  the molecular weight of water and S.R. the steam to naphtha ratio (kg steam / kg naphtha). In considering residence times for coke deposition, jet stirred mixed reactor volume was included. The coke deposition rate and gas composition were then compared at the same residence time [19].

### Result and discussion

In this work, to study the coking rate in the steam cracking of naphtha, pyrolysis runs, in which inert steam dilutions with a mass ratio of about 0.7 (kg steam / kg naphtha ) have been used, and were conducted at atmospheric pressure at a temperature of about 860°C. Naphtha compositions are listed in Table 1. All pyrolysis runs conducted under specific conditions are shown in Table 2.

#### Effect of $Na_2CO_3$ and $K_2CO_3$ on Coking Rate

To study of effectiveness of  $Na_2CO_3$  and  $K_2CO_3$  as coke inhibitors on coking rate, pyrolysis runs were carried out in the

presence of different  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ . (Fig. 2). As shown in Fig 2, the coke formation is decreased with increasing carbonate concentration.  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$

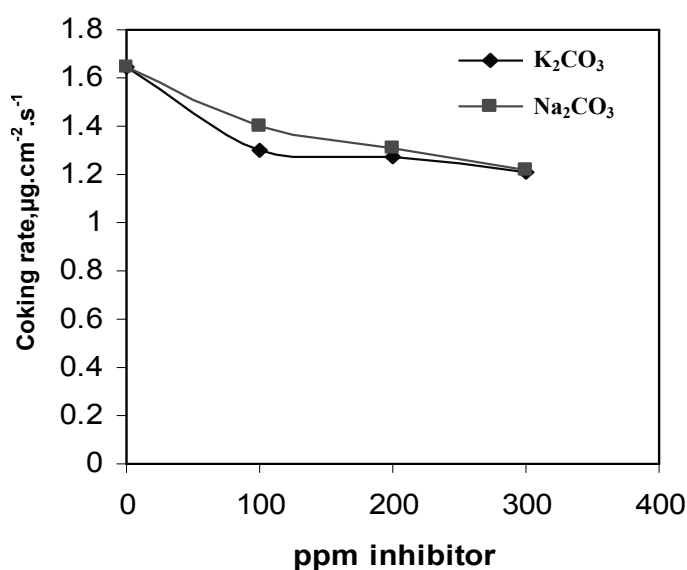
promote coke gasification by steam. This is the main reason for the decreased coke formation.

**Table 1.** Naphta composition

Component	Wt%
Paraffin	41.78
Isoparaffin	36.91
Naphthene	14.67
Olefine	1.8
Aromatics	3.09
Other hydrocarbon	Balance

**Table 2.** Operating conditions of naphta cracking

Temperature( $^{\circ}\text{C}$ )	860
Residence time(sec)	0.4
Pressure( mmHg)	640
Duration Time(hr)	1.5
Naphtha flow rate (cc/hr)	8.42
Steam flow rate (cc/hr)	3.88
Dilution (kg/kg)	0.7



**Figure 2.** The inhibiting effect of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  to coke deposition products

### Effect of DMDS

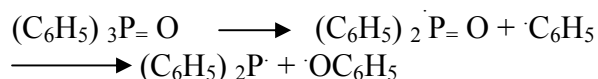
To study the effectiveness of dimethyl disulfide (DMDS) as a coke inhibitor on coking rate, pyrolysis runs were carried out in the presence of a variety of DMDS concentrations (Fig. 3). As shown in Fig 2, the coke formation is decreased with increasing DMDS concentration. As the first step in coil coking involves chemisorption of hydrocarbons, it is clear that the properties of the metal surface play an important role in the initial step of coke deposition. Under the conditions prevailing in the cracking coil, thermal decomposition of DMDS will occur, with the main decomposition products being dimethyl sulfide, methanethiol, carbon disulfide, carbonyl sulfide, thioformaldehyde, hydrogen sulfide, and SH radicals. Adsorption of sulfur components from the gas phase onto the metal particles proceeds more readily than the adsorption of either hydrocarbons or water. The presence of unshared electron pairs in sulfur compounds can lead to very strong chemisorption on the metal surface. This is the main reason for the much decreased coke formation. The sulfur present in the feed can react with the metal surface to form metal sulfides, thus passivating the reactor walls. Because sulfur adsorption can also influence dehydrogenation reactions, it can be expected that the characteristics of the coke layer, and in

particular its hydrogen content and its microstructure (density, porosity), can be altered by the addition of sulfur. Thereby, the kinetics of the hydrogen-abstraction reactions responsible for the creation of radical centers in the coke layer can be influenced.

The sulfur present in the feed can reduce the rate of coking in two ways. It can either react with the metal surface to form metal sulfides, thus passivating the reactor walls, or it can take part in the homogeneous gas phase free radical reaction.

### Effect of TPPO

Triphenyl phosphine oxide (TPPO) was found to be an effective coke inhibitor and the coke deposited decreased with the increasing concentration of TPPO in the feed (Fig. 4). At high temperature, TPPO can decompose in the following way:



The radicals  $(\text{C}_6\text{H}_5)_2\text{P}\cdot$  and  $\text{OC}_6\text{H}_5$  thus formed can combine with the metal surface to form a film. Initially, the metal surface is devoid of any coke so that the bare surface catalyzes the coke formation. With increasing run time, a film of the phosphorus-metal complex covers the surface and the metal activity is gradually reduced.

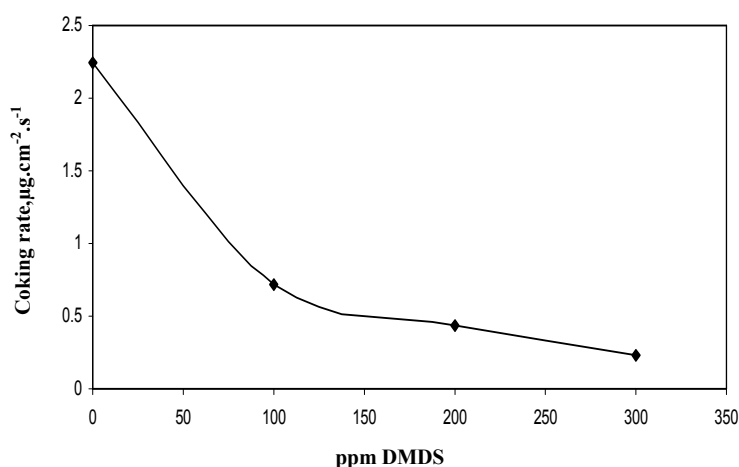
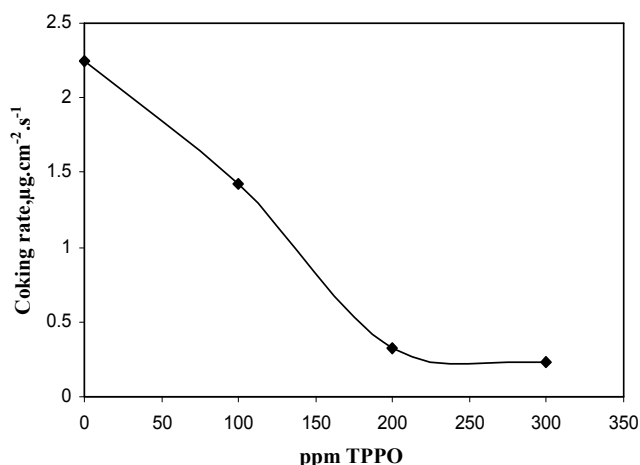


Figure 3. The inhibiting effect of DMDS to coke deposition products for sampling and analyzing



**Figure 4.** The inhibiting effect of TPPO to coke deposition products for sampling and analyzing

#### Effect of DMDS+TPPO mixtures

As both DMDS and TPPO proved to be promising coke inhibitors, runs were made with mixtures of these inhibitors. At a constant DMDS concentration (100 ppm), the coke deposited decreased with an increase in TPPO concentration (Fig. 5). According to chemical mechanisms for decomposition of sulfur and phosphorus compounds leading to produce respectively, sulfur and phosphorus free radicals, it can be concluded that the catalytic effects of the surface will be decreased due to the presence of these radicals that may attack the active catalytic sites of surface. Thus, in the presence of these radicals the deposition of coke is less than the conditions in which no sulfur or phosphorus radicals are produced.

#### Effect of temperature on the rate of coke formation.

To study temperature effectiveness on the rate of coke deposition, a series of tests were carried out at a temperature of about 800°C in the presence of TPPO. All pyrolysis runs were conducted in the same conditions, except for temperature. The results, shown in Fig. 6, indicated that as temperature is decreased the amount of coke deposition is

also decreased.

#### Microstructure and analysis of deposited coke

To study the microstructure of coke deposits, a number of runs were taken at the same operating conditions ( $T=1133\text{K}$ ,  $\tau = 0.5\text{s}$ , run time = 1.5h) in the presence of DMDS, TPPO and DMDS + TPPO. The deposited coke was analyzed using a scanning electron microscope (LEO 440 i) equipped with an energy-dispersive X-ray analyzer (EDAX). Fig. 7 shows the photomicrographs of coke deposited during pyrolysis of naphtha without an inhibitor and with  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ , DMDS, TPPO or DMDS+TPPO as inhibitors. All the photographs are of coke surfaces, which were in contact with the gas. Comparing the morphology of deposited cokes in the presence of inhibitors and deposited coke without any inhibitor show that the porosity observation in the deposited cokes in the presence of inhibitors is more than the porosity of coke without an inhibitor, and experiments show that this coke is softer. Note that the softer coke in industrial reactors is carried by gas flow, and therefore the amount of deposited coke in the internal walls of the reactor is reduced. In

this case, the thermal conductivity resistance is reduced, while the operating time for the reactor is increased. On the other hand, the

decoking process is easier for fine coke, and in this case, decoking time period, the required air and steam also reduces.

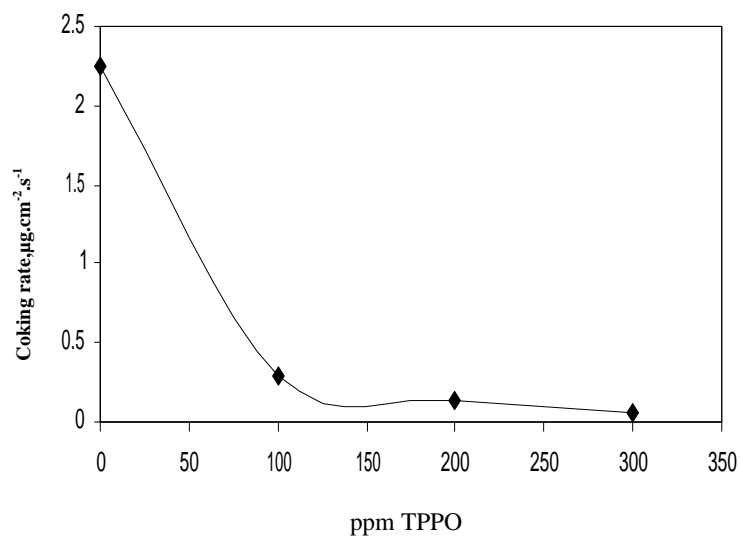


Figure 5. Effect of TPPO on to coke deposition in the presence constant DMDS concentration (100 ppm)

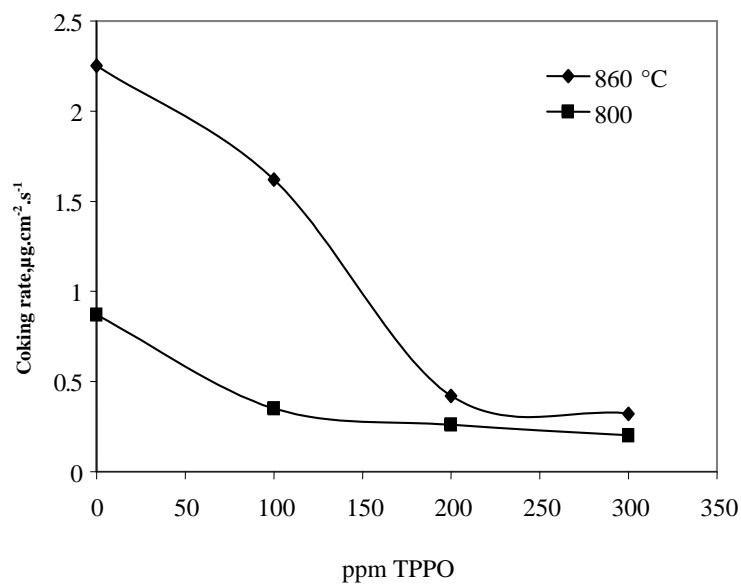
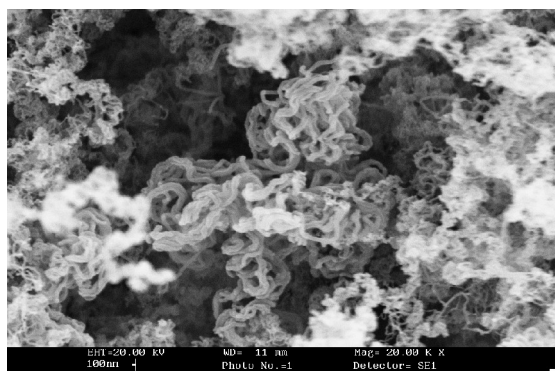
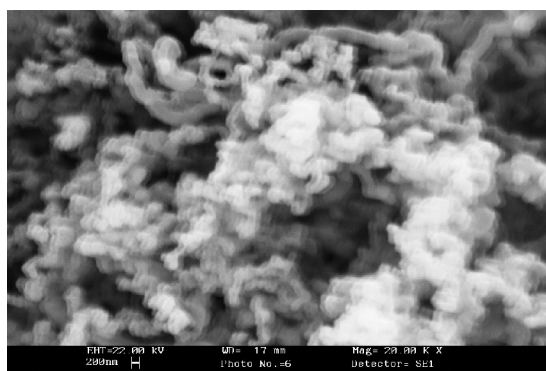


Figure 6. Effect of temperature on the rate of coke formation in the presence of TPPO

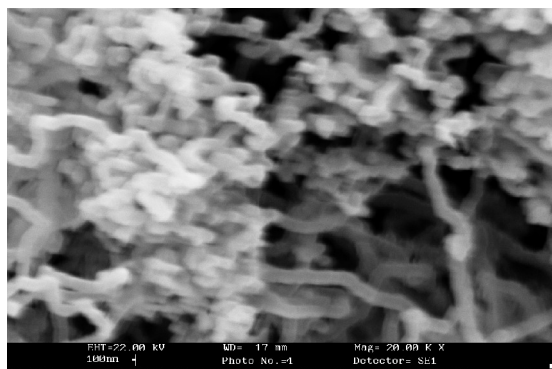




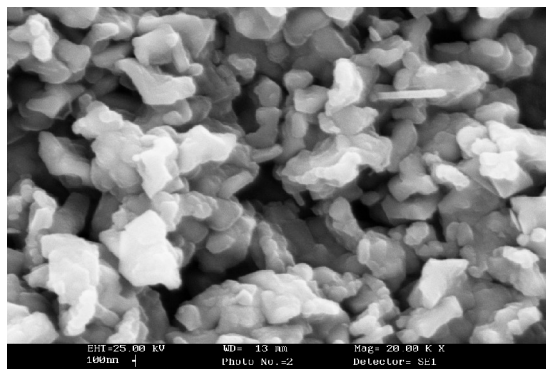
(a)



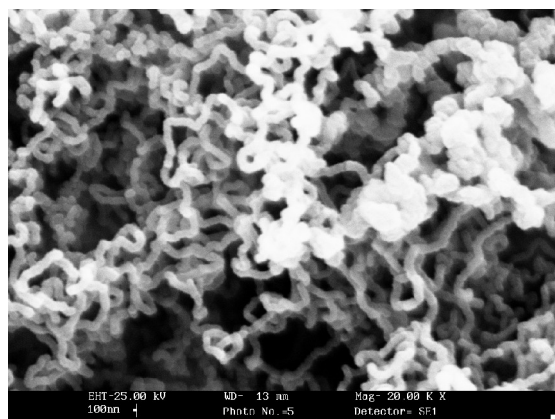
(b)



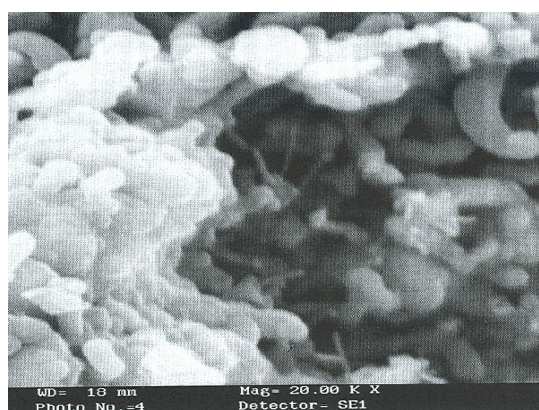
(c)



(d)



(e)

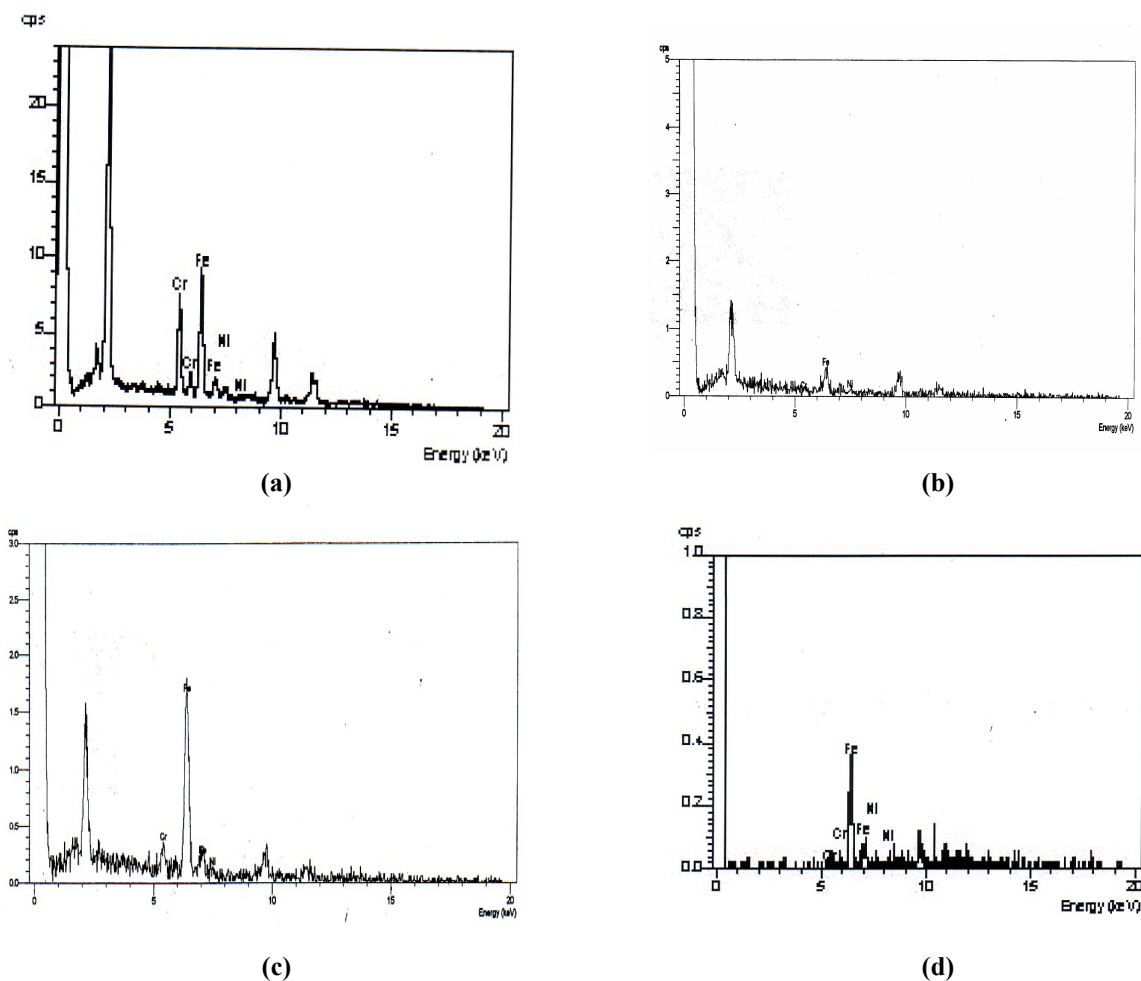


(f)

**Figure 7.** photomicrographs of coke deposited during pyrolysis of naphtha without inhibitor (a) and with  $\text{Na}_2\text{CO}_3$  (b),  $\text{K}_2\text{CO}_3$  (c), DMDS (d), TPPO (e) and (f) TPPO+DMDS as inhibitor

EDAX results of these coke samples show that the deposited coke in the process side was mainly carbon with detectable amounts of other elements present (Fig. 8). However, the process side of the deposited coke contain a relatively small amount of Cr and Fe. These observations could be related to metal dusting during the carbonization procedure. Furthermore, this observation indicates that during cracking, the internal surface of the radiant coil undergoes a slow carbonization

process and the traveling metal dusts to the coke surface. The concentration of iron, nickel, and chromium in the coke were significantly reduced when either DMDS, TPPO or DMDS+TPPO was added to the feed. These EDAX studies suggest that the organophosphorus and organosulfur compounds inhibit the coking rate by passivating the surface so that the concentration of metals incorporated in the coke is reduced.



**Figure 8.** EDAX analysis of coke deposits during pyrolysis of naphtha in both without inhibitor (a) and with DMDS (b), TPPO (c) and (d) TPPO+DMDS as inhibitor.

## Conclusions

We designed and assembled an experimental system for studying coke deposition in naphtha pyrolysis. The system is reliable and feasible for a wide range of research work.

This study shows that the rate of coke formation during naphtha pyrolysis can be significantly reduced by adding  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  or DMDS+TPPO mixtures to the naphtha. According to chemical mechanisms

for decomposition of sulfur and phosphorus compounds leading to produce respectively, sulfur and phosphorus free radicals, it can be concluded that the catalytic effects of the surface will be decreased due to the presence of these radicals that may attack the active catalytic sites of a surface. Thus, in the presence of these radicals the deposition of coke is less than the conditions in which no sulfur or phosphorus radicals are produced.

### **Acknowledgments**

We are most grateful for the continuing financial support of this research project by the University of Tabriz.

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