Investigation of Coke Deposition & Coke Inhibition by Organosulfur Compounds in the Pyrolysis of Naphtha in the Jet Stirred Reactor System

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Abstract

A study on coke deposition and coking inhibitors during naphtha pyrolysis was made in a jet stirred reactor system. This system is noted for its simple structure, easy alteration of operating parameters, small volumes of feedstock used for pyrolysis, high accuracy of coke formation measurements, and short operating cycle. It is also particularly suitable for identifying coking inhibitors over a wide range of conditions. The effect of the addition of CS2, DMS, DMDS and Disulfideoil in the naphtha feed was investigated. It was found that for a given concentration of sulfur in the feed, the asymptotic coking rate decreases in the order: Dimethyl disulfide > Disulfideoil > Dimethyl sulfide > Carbon disulfide.

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 small amounts of Ni, Cr, and Fe elements. Based on our results, this paper aims to provide a closer insight into the coking problem in industrial steam crackers.

Keywords: *Thermal cracking, coke deposition, coke inhibition, organosulfur compounds*

Introduction

Ethylene is one of the most important building blocks of synthetic organic chemistry. It is used in the manufacture of polyethylene and other products. The majority of the ethylene produced today is based on the steam cracking or pyrolysis of alkanes, such as ethane, propane, and butane, as well as heavier feedstocks such as naphtha and gas oil [1]. The steam cracking operation involves heating the hydrocarbon in radiant coils in the presence of steam in a furnace. The heat is transferred to the coils by radiation period. The coils themselves are made of high alloy materials capable of withstanding a high temperature of above 800°C in the bulk fluid. To avoid undesired side reactions, which would lower the selectivity of ethylene in the process, the reactants must be cooled down as quickly as possible. This step is carried out in a transfer line exchanger (TLEs) immediately after the

radiant cracking zone [2]. A minor but technologically important byproduct of steam cracking is coke. Its formation not only affects heat transfer, but also increases the pressure drop, shortens the operating cycle, decreases the capacity of the plant and the yield of the objective products. Collectively, these problems make it necessary to periodically shut down the plant, resulting in great economic loss. Therefore, further study of the coke formation process and to develop of a corresponding technique for inhibiting coke formation is an urgent problem [3].

This paper reports the concentration effect of a variety of organosulfur inhibitors such as Carbon Disulfide, Dimethyl Sulfide, Dimethyl Disulfide and Disulfideoil on coke formation and coke morphology in the steam cracking of naphtha.

Mechanisms of Coke Formation

The three mechanisms by which coke is produced in the coil and transfer line exchanger (TLE) of a cracking furnace are reviewed as follows:

Catalytic Coking Mechanism

Industrial cracking coils frequently contain different wt% of chromium, nickel and iron. As shown in Fig. 1, during the startup of a furnace, the reacting gas mixture is in contact with the bare reactor walls. Hydrocarbon molecules, initially, are chemisorbed on a metal crystallite at the surface and converted to coke by a surface reaction. Carbon atoms thus dissolve in and diffuse through the metal particle. The carbon accumulation in the particle causes a pressure buildup at the dislocations and the grain boundaries, which may exceed the tensile strength of the metal. The metal particle is then lifted from the surface and the carbon crystallizes at the rear of the particle. A growing carbon stem thus develops, carrying the crystallite at its top. The precipitation of carbon can give rise to structural deficiencies in the carbon lattice, thereby creating reactive carbon centers along the filament skin.
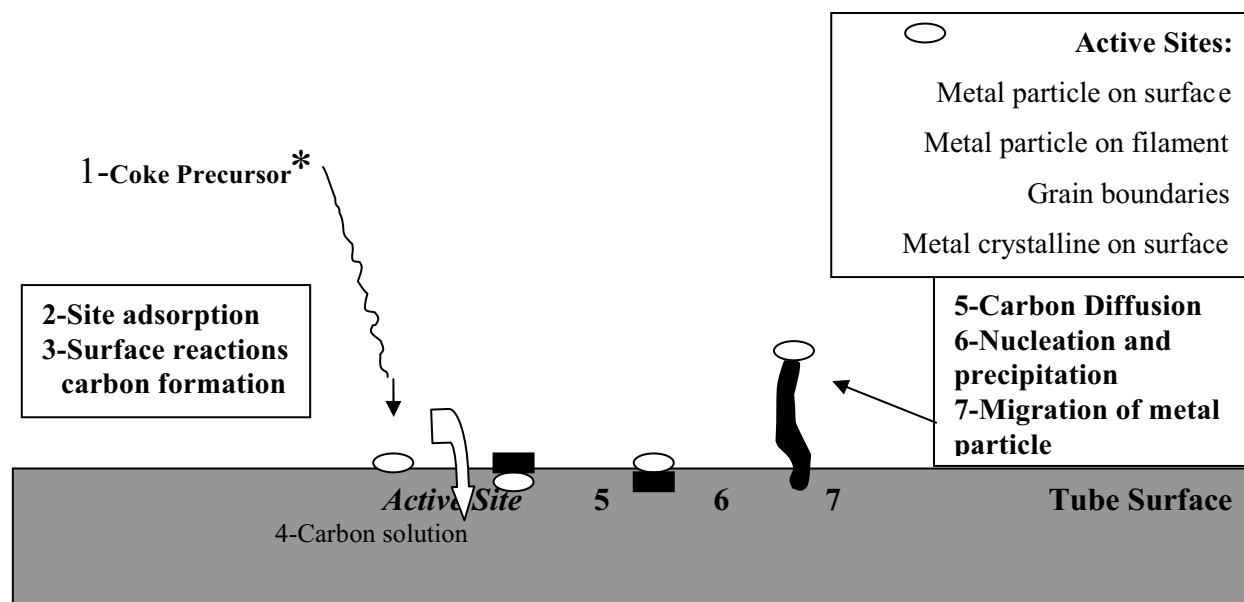

Figure 1. Formation of filamentous coke with catalytic mechanism

Hydrocarbon radicals and molecules from the gas phase are incorporated at these reactive sites, whereby lateral growth of the filaments occurs. In this way a porous layer of interwoven filaments is formed. Carbon migrating over the metal surface precipitates on the metal surface surrounding the carbon steam. Surface carbon may thus be formed, encapsulating the metal and preventing further growth. The properties of the metal are very important in this mechanism. Encapsulation of the metal particles reduces the rate of dehydrogenation of the chemisorbed hydrocarbon atoms. At this stage, the catalytic activity of the metal particle decreases both carbon formation and CO production [4-9].

Radical Coking Mechanism

At the gas /coke interface layer, the polyaromatics are not completely dehydrogenated. At this surface, hydrogen abstraction reactions by free radicals from the gas phase can occur. Hydrogen, methyl, and ethyl radicals are the most active species. As a consequence, the concentration of the active sites at the coke surface becomes a function of the gas phase composition. This shows that the feedstocks generating more active radicals also yield more coke.

As shown in Fig.2, at the free radical positions on the coke surface, certain gas phase molecules or radicals react via an addition mechanism. All unsaturated molecules from the gas phase are potential precursors. The long aliphatic side chain of these molecules is subjected to decomposition. The remaining part of the molecule converts, in a few steps, to a ring structure, in which the dehydrogenation reactions proceed very rapidly. In this way, the aromatic structure continues to grow further and the free radical site at the coke surface is regenerated by further hydrogen abstraction. This mechanism explains the formation of coke layers containing carbon atoms in sp^2 hybridization. The hydrogen content of such a deposit is very low, in agreement with industrial observations. The cross-linking of aromatic layers explains why samples of coke layers from industrial coils are extremely hard and can hardly be drilled. This mechanism is the most important one in the coke formation [10-12].
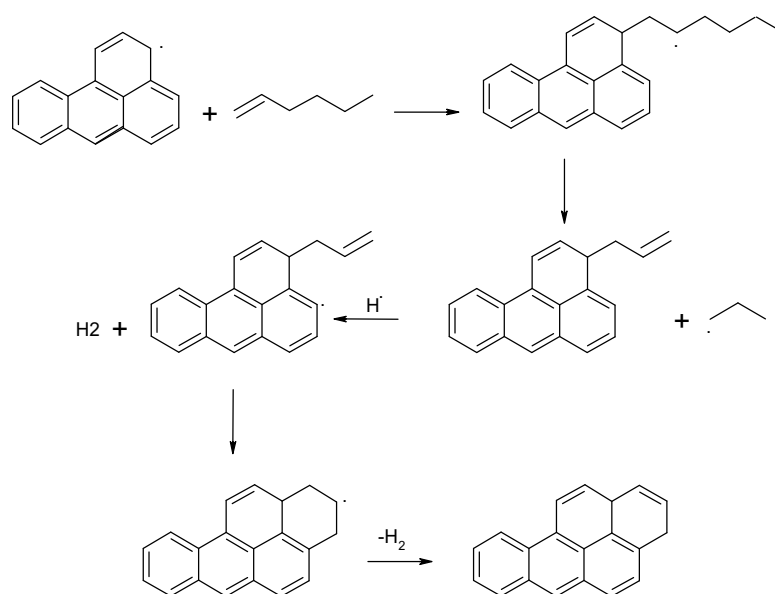

Figure 2. Growth of coke by radical coking mechanism

Polyaromatic Condensation

This third mechanism implies the formation of polynuclear aromatics in the gas phase via free radical reactions. As shown in Fig.3, aromatics are the most important intermediates; some aromatics are produced by trimerization and other reactions involve acetylene. Starting with simple aromatics, condensation and dehydrogenation reactions occur to produce tar droplets or soot particles that can be liquid or even solid at the conditions prevailing in a thermal cracking reactor. Part of the droplets impinges on the tube wall. Some rebound into the gas phase, but it is more likely that they adhere to the surface and are incorporated in the coke layer, since the outer surface of the droplets is not completely dehydrogenated. Hence, hydrogen abstraction reactions by gas phase radicals becomes possible and the coke layer can grow further. This mechanism is considered to be important in the cracking of liquid feedstocks, such as heavy naphtha and atmospheric or vacuum gas oil. The condensation mechanism is generally relatively unimportant at temperatures of 700°C or less. The exact temperatures depend, to some extent, on the hydrocarbons being pyrolyzed [7,13].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 of the materials of the construction of the reactor, alteration of the surface chemistry of the reactor, or the addition of coke inhibitors to the feedstock [14-15]. 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 alkaliearth metals at parts per million (ppm) quantities, which are believed to promote coke gasification by steam. Phos-phorus and chromium were reported to have a beneficial effect in suppressing coke formation [14]. There are some reports in literature for inhibiting the effect of sulfur compounds. Most studies on the influence of sulfur on coke formation reported in the literature pertain to the cracking coil and TLE section [16-20]. In this paper, we report the concentration effect of a variety of organo-sulfur inhibitors such as Carbon Disulfide, Dimethyl Sulfide, Dimethyl Disulfide or Disulfideoil on coke formation and coke morphology in the steam cracking of naphtha in a bench scale reactor.

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.4.

The system is noted for its simple structure, easy alteration of operating 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 distillated water for preparing dilute steam, which enters preheaters from individual containers using two regulated syringe pumps. Preheaters made of cupper 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 8x8 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 [21].

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.
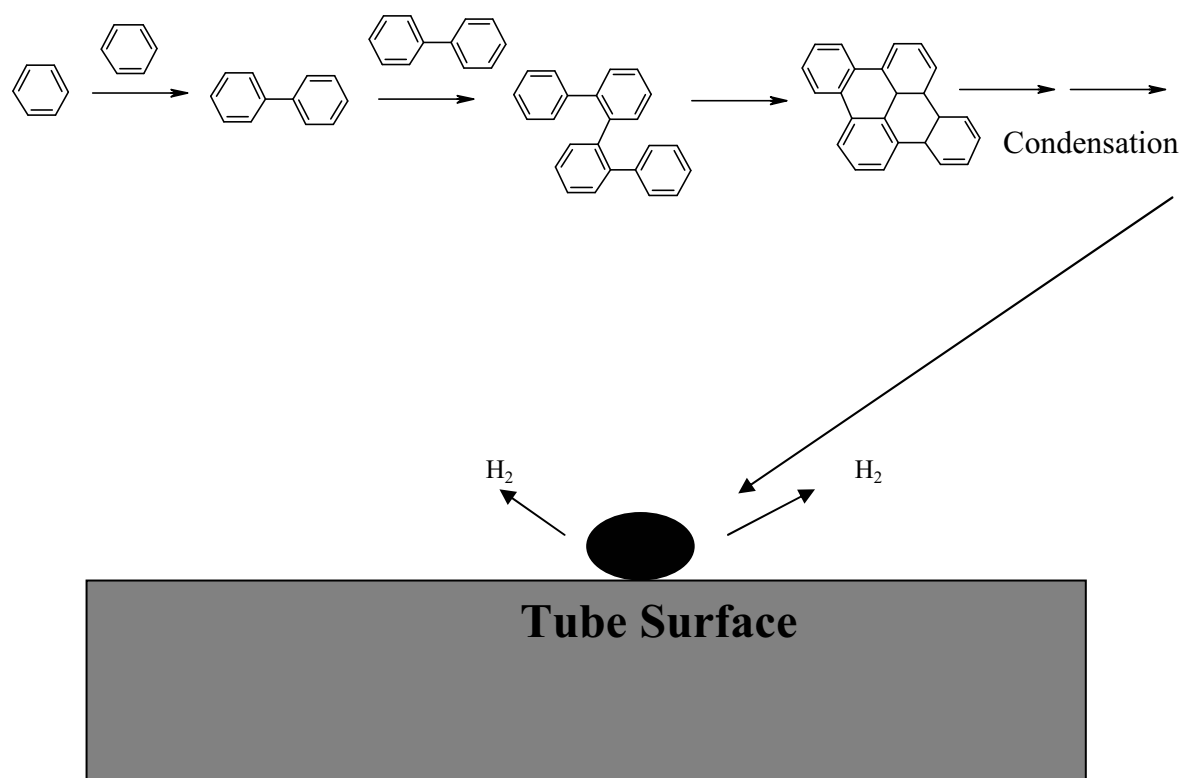

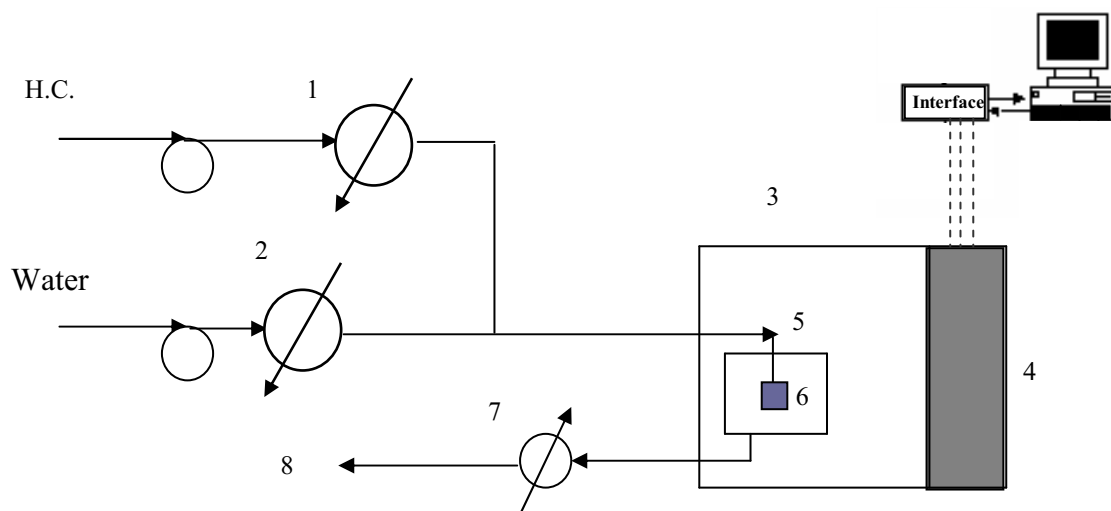**Figure 3.** Growth of coke by condensation mechanism

Figure 4. Schematic diagram of laboratory system for 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. Gaseous output

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 taken 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 crackers. 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:

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

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; ρ_{HC} the density of hydrocarbon;

$Mw_{(HC)}$, the molecular mass of hydrocarbon; $Mw_{(W)}$, the molecular mass 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.

Results 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 860ºC. Naphtha compositions are listed in Table 1. All pyrolysis runs conducted under specific conditions are shown in Table 2.

Effect of Sulfur Content of Feed

To study the effectiveness of organosulfur compounds as coke inhibitors on coking rate, pyrolysis runs were carried out in the presence of different carbon disulfide (CS_2), dimethyl sulfide (DMS), dimethyl disulfide (DMDS) or disulfudeoil (Figure 5). Disul-

fideoil, used in our experiments, is a complex mixture of organosulfurous compounds obtainnned from the Kanghan' Gas Refinery as a by product of the gas sweetening process. Disulfideoil contain the dimethyl disulfide, diethyl disulfide, methyl ethyl disulfide and other organosulfurous compounds, with a total sulfur content of about 51.2%. As shown in Fig.5, the coke formation is decreased with increasing sulfur concentrations.

Table 1. Naphtha composition

Component	wt'/.
Paraffine	41.78
Isoparaffine	36.91
Naphthene	14.67
Olefine	1.8
Aromatics	3.09
Other hydrocarbon	Balance

Table 2. Operating conditions of naphtha cracking

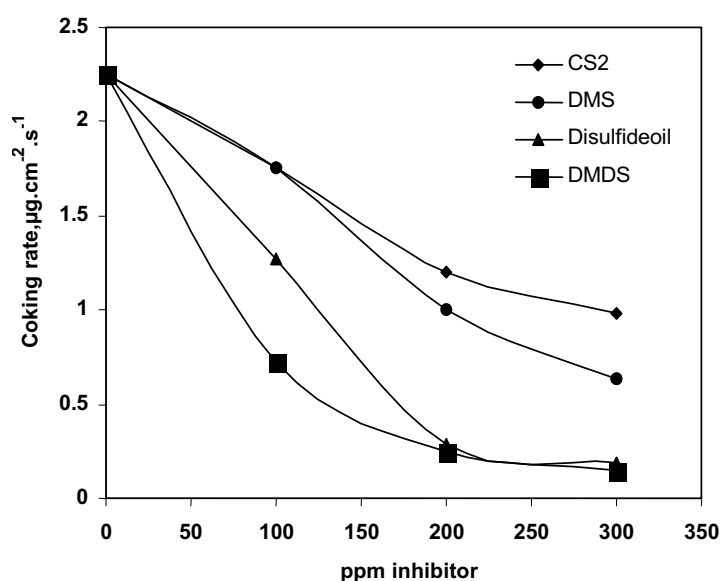|	
Temperature (°C)	860
Residence time (sec)	0.4
Pressure (mmHg)	640
Duration Time (hr)	1.5
Naphtha flow rate (cc/hr)	8.42
Steam flow rate (cc/hr)	3.88
Dilution (kg/kg)	0.7

Figure 5. The inhibiting effect of various organosulfur compounds to coke deposition products for sampling and analyzing

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 organosulfur compounds 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. In the case of dimethyl disulfide, the α effect enhances the reactivity of the sulfur as compared with carbon disulfide. As a consequence, for the same concentration of sulfur in the feed, the amount of sulfur actually adsorbed on the surface is the highest for dimethyldisulfide. 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. The amount of sulfur adsorbed on the surface depends on the temperature, pressure, nature and concentration of sulfur compounds.

Diffusion of carbon through the metal is a crucial step in catalytic carbon formation. The influence of S on these steps is difficult to evaluate, but the solubility and diffusion of carbon through the alloy surface will probably be affected by the presence of S⋅ Investigations of sulfur uptake [17] by iron and steel in hydrogen sulfide-containing atmosphere at 1000-1100°C, showed that with increasing carbon content, the rate of diffusion of sulfur decreases, while with increasing sulfur content the rate of carbon diffusion decreases. Therefore, continuous addition of sulfur can be expected to have a complex influence on all steps involved in catalytic coke formation.

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.

Fig.6 illustrates the relationship between temperature and decomposition of some common sulfur compounds. Dimethyl disulfide (DMDS) is completely decomposed at 400-500 $^{\circ}$C, even before entering the cracking coil, since the temperature in the preheated section reaches 600 $^{\circ}$C. Some other sulfur compounds are more stable and require a higher energy level to decompose. Dimethyl sulfide remains unchanged until 650 $^{\circ}$C. Carbon disulfide is a more stable molecule and decomposes above 800 $^{\circ}$C. For a given concentration of sulfur in the feed, the asymptotic coking rate decreases in the order:

Dimethyl disulfide > Disulfideoil > Dimethyl sulfide > Carbon disulfide

For a given sulfur concentration in the feed, the amount of sulfur fed per surface unit differs considerably for the various units. For ethane, propane and butane cracking conditions typically used in industrial practice, the addition of 100-200 ppm S as DMDS corresponds to 480-968 mgS/m^2, while for the pilot unit this value amounts to 47.85 mg S/m^2. When spiking naphtha feed, its sulfur content is used as a guide.

Microstructure and Analysis of Deposited Coke
To study the microstructure of coke depo-

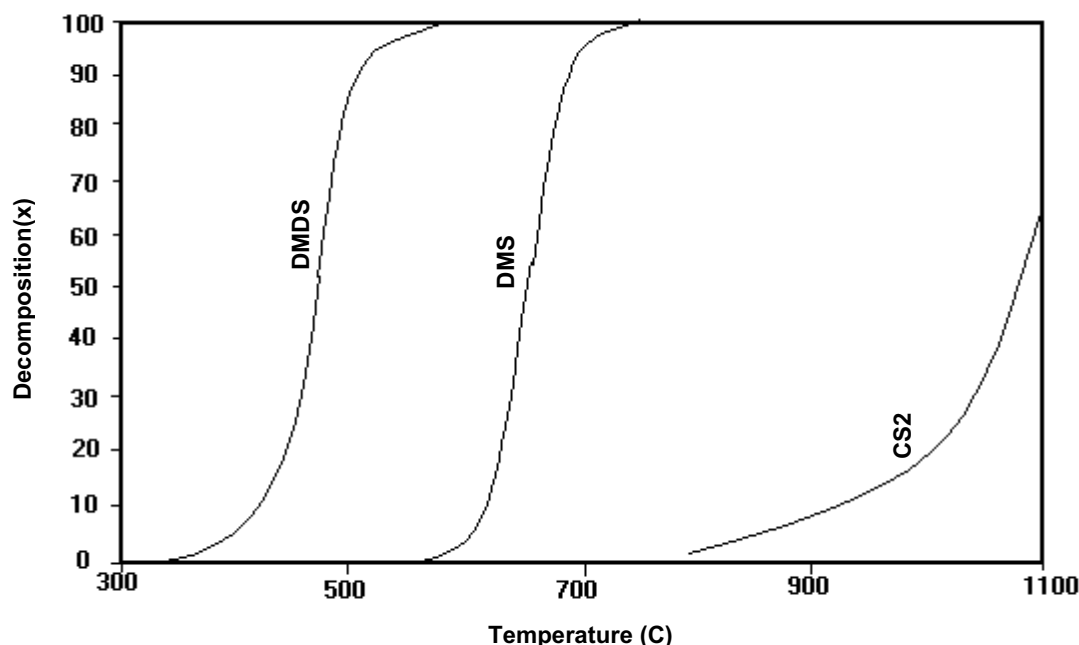**Figure 6.** Percentage of Decomposition of Thiochemical Compounds

sits, a number of runs were taken at the same operating conditions (T=1133K, τ = 0.5s, run time = 1.5h) in the presence of CS_2, DMS, DMDS and Disulfideoil as inhibitors. The deposited coke was analyzed using a scanning electron microscope (LEO 440 i) equipped with an energy-dispersive X-ray analyzer (EDAX). Fig.6 shows the photo-micrographs of coke deposited during the pyrolysis of naphtha without an inhibitor but with CS_2, DMS, DMDS or Disulfideoil as inhibitors. All the photographs are of coke surfaces, which were in contact with the gas.

Fig.7a shows that the majority of morpho-logies in the absence of inhibitor are of spiral filament. This type of coke has a structure with a high density. The morphology of coke in the presence of CS_2 (Fig.7b) as a coking inhibitor, has a uniform structure with fluffy particles and a low amount of filament coke. The morphology of coke in the presence of DMS (Fig.7c) is of constant diameter fila-ments and needle coke. The morphology of coke in the presence of DMDS (Fig.7d) contained small pieces with irregular shapes. The morphology of coke in the presence of Disulfideoil (Fig.7e) containing spherical, needle, and long filament coke.

Comparing morphology of deposited cokes in the presence of organosulforous 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 fin coke, and in this case, decoking time period. The required air and steam also reduces.
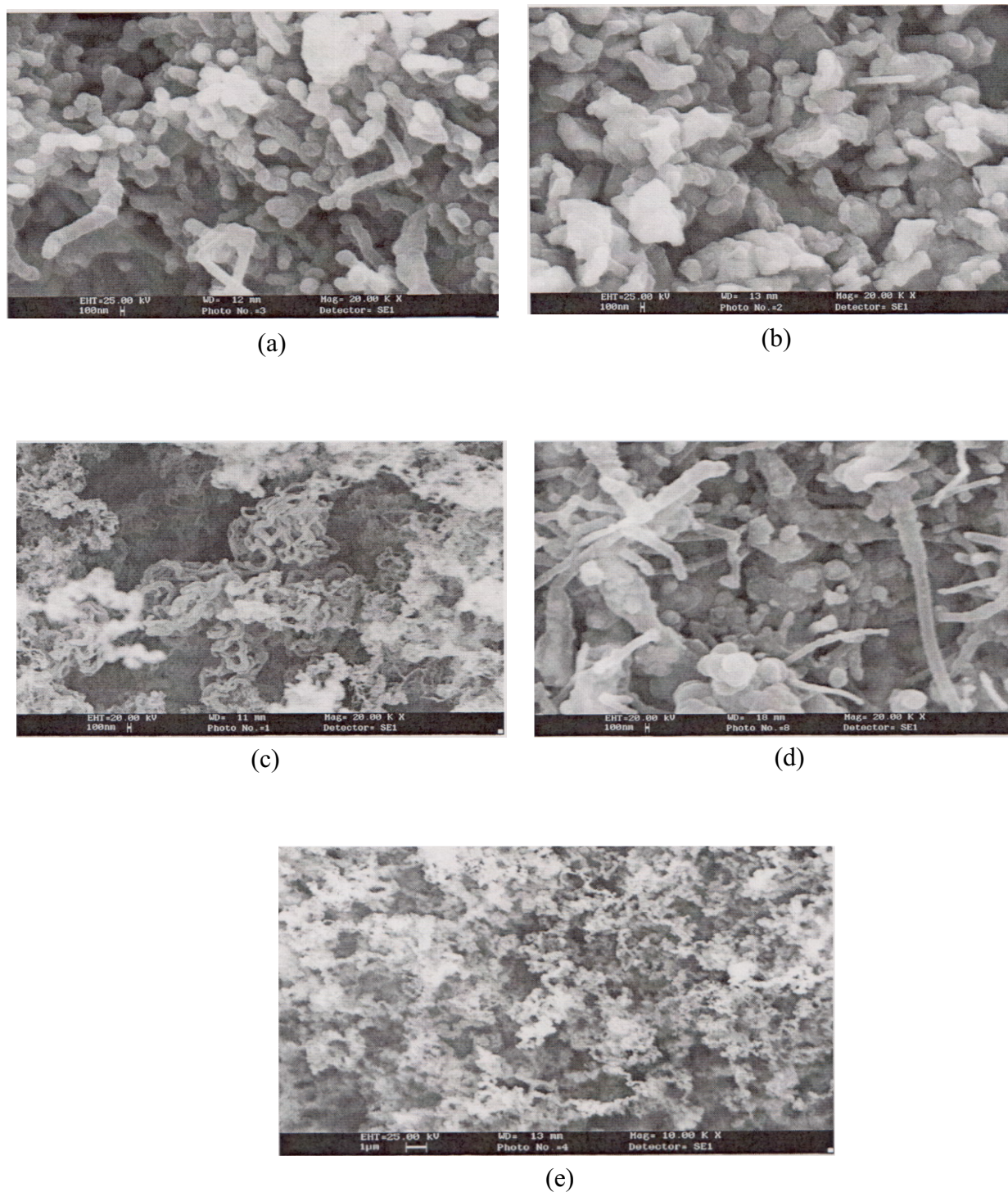
EDAX results of these coke samples show

(a)

(b)

(c)

(d)

(e)

Figure 7. Photomicrographs of coke deposited during pyrolysis of naphtha without inhibitor (a) and with CS$_2$, (b) DMS (c) and (d) Disulfideoil as inhibitor.

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.

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 demonstrates that CS_2, DMS,

DMDS and Disulfideoil, introduced into the reaction system together with the starting naphtha, influence the formation of coke in the pyrolysis of naphtha. Alternatively, SH· Radicals and S atoms can be formed, reacting with the inner surface of the reactor to produce metal sulfides. By the formation of a protective layer of metal sulfides, the inner surface is passivated, and the formation of coke is inhibited in the pyrolysis of naphtha. The presence of sulphur containing additives in the feed causes evident decreases in coking. SEM analysis was used to study the morphologies of coke formed on the surface.
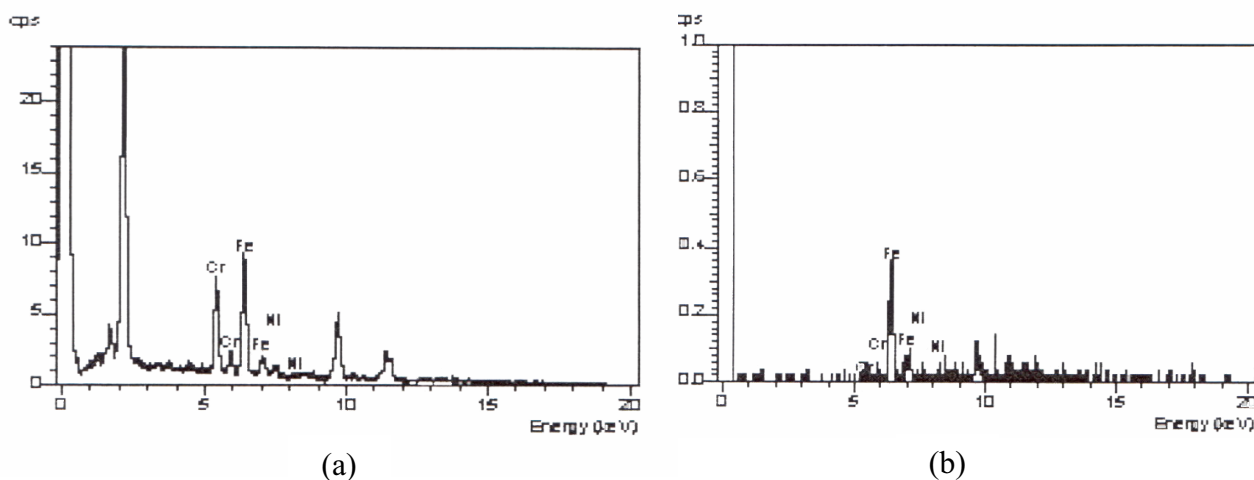
(a)   (b)

Figure 8. EDAX analsis of coke deposits during pyrolysis of naphtha in both without inhibitor (a) and with DMDS (b) as inhibitor

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