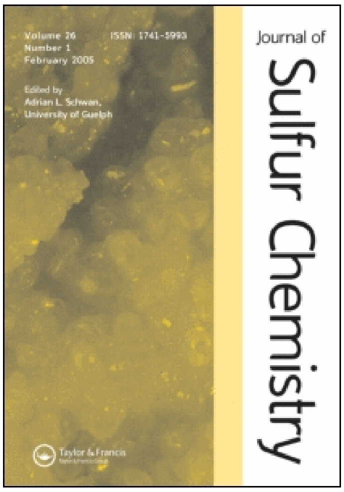

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Martin Bajus[a]
[a] Department of Chemistry and Technology of Petroleum, Slovak Technical University, Bratislava, Czechoslovakia

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SULFUR COMPOUNDS IN HYDROCARBON PYROLYSIS

MARTIN BAJUS
Department of Chemistry and Technology of Petroleum, Slovak Technical University, CS-812 37 Bratislava, Czechoslovakia

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The influence of sulfur compounds on the kinetics and mechanism of the thermal decomposition of hydrocarbons is described. The reactivity of some organic and inorganic sulfur compounds under the conditions of initiated pyrolysis from the viewpoint of acceleration of the radical decomposition of hydrocarbons, selectivity improvement towards the desired alkenes and decrease of secondary reactions, the consequence of which is coke formation, are discussed.

Key words: Disulfides, hydrogen sulfide, petroleum, sulfides, sulfur, thiophene, pyrolysis, hydrocarbon.

CONTENTS

0. INTRODUCTION

The purpose of this review, which covers the chemical literature up to 1987, is to discuss the reactivity of some sulfur compounds from the point of view of affecting radical transformations in hydrocarbon pyrolysis, selectivity improvement towards the desired alkenes and decrease of secondary reactions, the consequence of which is the formation of coke.

Olefins and aromatics are among the most important petrochemical products. Olefins are obtained mainly by thermal fission of hydrocarbons from crude oil and natural gas.

Single component feedstocks, such as ethane or propane, or multicomponent hydrocarbon feedstocks, such as natural gas liquids and naphthas and gas oils from crude oil, may be used for the production of olefins. Today, ethylene is produced almost exclusively via the pyrolysis of hydrocarbons in tubular reactor coils installed in externally fired heaters. The properties of the feedstocks and the conditions at which the reactor coils are operated determine reactor effluent product distribution. High selectivity toward the production of desired olefins and diolefins (i.e., ethylene, propylene, 1,3-butadiene, methylpropene, isoprene and 1,3-cyclopentadiene) with minimum methane and coking in the coils leading to longer heater runs are achieved by operating the pyrolysis heaters at high temperatures (750–900 °C), short residence time (0.1–0.6 s), and low hydrocarbon partial pressure. Steam is added to the feedstock to reduce the hydrocarbon partial pressure and the amount of carbon being deposited on the tube walls. The steam-to-hydrocarbon weight ratios usually vary from 0.3 for ethane to as high as 1.0 for gas oils[74b].

The advantages and disadvantages of pyrolysis are known. In the past few years, it seemed that the technology of pyrolysis in tube furnaces was in the final stages of development. However the rapid rise of crude oil prices in the last decade or so, and the growing demands of the chemical industry for olefins have pointed, to a greater extent, to the shortcomings in this area. The historical development of hydrocarbon pyrolysis is characterized by the continuously growing capacities of pyrolysis plants; an increase of space-time yields in the overall process; an increase of ethylene selectivity; an improvement in energetic efficiency, especially by a better utilization of the waste heat; the extension of running times; a wider range of feedstock flexibility; and the expansion of the feedstock basis toward high-boiling fractions. These advances and increases in performance are due, first of all, to constructional and technological improvements of the cracking furnace and its equipment[98a].

The pyrolysis of individual hydrocarbons and of petroleum fractions proceeds under conditions where the rate and the selectivity of conversion to alkenes are relatively low. Among the unwanted products are methane, pyrolysis oil, pitch, and coke. While methane is formed predominantly by primary reactions, heavy liquid pyrolysis fractions, pitch, coke, and carbon oxides are created through secondary reactions, proceeding in the multicomponent highly reactive system of alkenic-aromatic nature with an appreciable participation of the inner surface of the reacting system. The properties of the construction material of the reactor, the ratio of the inner surface of the reactor to its volume, and the chemical activation or passivation of the inner surface by various chemical substances have a bearing on the reaction rate and on the composition of the reaction products. The literature dealing with the surface phenomena contains essentially qualitative data, which are often contradictory and spurious.

One of the feasible ways of improving the production of lower alkenes is pyrolysis in the presence of substances that make it possible to lower the pyrolysis temperature, enhance the rate of the radical conversion, increase the flexibility of the pyrolysis process, improve the selectivity, and use feedstock with different properties. Such compounds (initiators, catalysts, activators, promotors), of homogeneous or heterogeneous nature that affect favorably the pyrolysis process, as well as other substances (inhibitors, retarders, deactivators, passivators) that suppress the formation of unwanted pyrolysis products, are at present being extensively sought. Among compounds capable of influencing the thermal decomposition process are some inorganic or inorganic nitrogen, oxygen, sulfur, and phosphorus compounds. Sulfur-based additives can in various ways affect the process favorably or unfavorably. A bonus of sulfur compounds is that they are added to the system in low concentrations, several times lower than other additives. Under the conditions of the pyrolysis, sulfur compounds decompose mainly to hydrogen sulfide, which is readily removed from the pyrolysis gas by alkali washing. The main drawback, on the other hand, is the corrosion of the exposed parts of the pyrolysis apparatus. Part of the sulfur concentrates in the liquid products, diminishes their quality, and gives rise to difficulties during their further treatment. Nevertheless, the application of sulfur compounds, which are comparatively inexpensive and available, is very attractive.

1. THERMAL DECOMPOSITION OF HYDROCARBONS AND SULFUR COMPOUNDS

1.1 General aspects

Thermolysis is defined as "decomposition or dissociation by heat"[39a]. From this definition are derived other commonly used terms, such as: thermal decomposition, thermal dissociation, thermal cracking, thermal splitting and thermal fission. Pyrolysis means dissociation "caused or produced by fire" and although its use may thus be somewhat inaccurate it does seem to convey the additional useful meaning of a process occurring well above ordinary laboratory temperature of a fire[70a]. In chemical technology thermal cracking is used for transformation of mazut to distillate and fuel oil (visbreaking) or coke[83a]. Paraffin waxes may be thermally cracked to produce C_2-C_{20} linear, primarily α-olefins[56a]. Steam cracking of hydrocarbon feedstocks is a principal source of ethylene and other olefins and diolefins[74a,b].

In the thermal cracking of hydrocarbons, molecules attain energy in the form of heat. To the reactions which predominate belongs primarily cracking into two hydrocarbons or a hydrocarbon and hydrogen. To others belong secondary reactions which can lead to macromolecular substances and after their dehydrogenation to carbenes and carboids which are the fundamental components of coke formation. These substances are highly condensed with a high C:H ratio.

From the change of the standard free enthalpy of formation it follows that the stability of hydrocarbons of all homologous series decreases with increasing temperature with the exception of acetylene[133]. Table 1 contains values of the standard free enthalpy of formation for some hydrocarbons. The tendency of hydrocarbons to decompose increases with increasing molecular mass, irrespective of the homologous series. In the transition from alkanes and cycloalkanes to alkenes and aromatics, the thermodynamic stability increases. Similarly increases the resistance of alkenes to decomposition in comparison with alkanes.

The stability of thiols, sulfides and disulfides is comparable to that of alkanes. Thiophene and its homologues are more resistant to decomposition, not only in comparison with aromatics, but also with alkenes. Carbon disulfide and hydrogen sulfide form an exception and in the region of higher temperatures the stability of hydrogen sulfide decreases (Table 1). The radicals are formed by preferential scission of C-C bonds

Table 1. ΔG_f^0 (kJ mol^{-1}), hydrocarbons and sulfur compounds[133]

Temperature, K	300	400	500	600
Heptane	9.2	76.8	147.0	218.9
Methylcyclohexane	28.4	91.4	156.9	224.0
Ethylcyclopentane	45.6	105.1	167.3	231.1
Toluene	122.5	147.7	174.5	202.2
Ethylene	68.2	74.0	80.5	87.5
Diethyl disulfide	22.9	60.3	93.9	140.8
1-Butanethiol	11.6	48.2	83.3	123.2
Thiophene	126.8	133.2	137.2	148.8
Carbon disulfide	66.6	50.1	35.2	21.1
Hydrogen sulfide	−33.1	−37.1	−40.0	−42.2
Temperature, K	**700**	**800**	**900**	**1000**
Heptane	292.0	365.8	440.1	514.7
Methylcyclohexane	292.0	360.4	429.2	498.0
Ethylcyclopentane	296.1	361.7	427.8	494.1
Toluene	230.6	259.3	288.4	317.6
Ethylene	94.9	102.5	110.2	118.2
Diethyl disulfide	172.6	222.3	264.0	309.2
1-Buthanethiol	161.3	204.1	245.1	288.8
Thiophene	151.3	164.8	172.8	181.7
Carbon disulfide	7.7	−16.1	−16.7	−17.4
Hydrogen sulfide	−43.9	−50.7	−45.6	−41.0

Table 2. Bond dissociation energies of hydrocarbons[90] and sulfur compounds[37]

C–C and C–H bonds	kJ mol^{-1}
CH_3–CH_3	360
C_4H_9–C_3H_7	314
CH_2=CH–CH_3	394
C–C in cyclopentane ring	293
C–C in cyclohexane ring	310
C_2H_5–H	410
$(CH_3)_3C$–H	373
CH_2=CH–CH_2–H	322
C_6H_5–H	427
C–H in cyclopentane ring	389
C–H in cyclohexane ring	389
C–S, S–S, and S–H bonds	**kJ mol^{-1}**
CH_3S–CH_3	323
C_6H_5S–CH_3	281
C_4H_9–SH	289
RS–C_2H_5	310
RSS–C_2H_5	226
RSS–C_6H_5	291
CH_3S–SCH_3	310
C_6H_5S–SC_6H_5	230
HS–H	379
RS–H	379
C_6H_5S–H	374

as a result of the larger dissociation energy of C-H bonds.[90]. For the selective generation of radicals by thermal heating are used thermal initiators with chemically different, more liable bonding, for example, C-O or C-N. Especially sensitive are some bonds like C-S, S-S and S-H[37] (Table 20).

Besides by selection of various types of precursor radicals, greater selectivity in thermal cracking of chemical bonds in organic compounds is reached by using unconventional thermal sources, which supply an intensive flow of infrared photons. In contrast to traditional methods, it is possible to generate reactants with specific populations of vibration levels by interaction with infrared laser radiation. The interaction of reactants with infrared CO_2 laser radiation which can be attuned to many characteristic vibrations can lead to many new and uncommon chemical reactions which cannot be carried out by other techniques and the course of which is made possible by primary activation of the reactants or the specific conditions of these reactions. Such is also laser pyrolysis, to be more exact, laser-induced homogeneous pyrolysis (LIHP) of hydrocarbons[99,100,128].

The thermal decomposition of hydrocarbons going through radicals is chain-like and does not involve chain branching. It is remarkable because its course is not unequivocal with the formation of a rich gamut of reaction products, small selectivity and complex kinetics.

Basic radical reactions are studied on simple molecular systems, often requiring complicated physical and spectroscopic methods in combination with electron paramagnetic resonance[44,86,98,106]. The lifetime of highly reactive radicals in pyrolysis is short and their concentration relatively low[72,119] (Table 3). Success can be achieved either by methods which indicate the level of free radicals directly in the stable state by the dynamic method, or methods where radicals from the hot zone are isolated by rapid freezing on a static or rotating cryostat[122].

ESR spectra of alkyl- and sulfur-containing radicals provide important information about the delocalization of the unpaired electron and the geometry of the species[36,40,58,59,86]. Alkyl radicals have a smaller g factor than oxyl or peroxyl radicals, or radicals with an unpaired electron on sulfur (Table 4). The greater the delocalization of an electron on substituents, the smaller is the absolute value of the splitting constant a ($a_{d\text{-}h}$).

An unpaired electron in a radical does not only show up in the electron resonance spectrum but also causes different vibrations between the atoms of the radical, so that infrared spectroscopy can also supply supplementary findings about the structure of a radical. The main primary process in the pyrolysis of l-hexene, 2,5-dimethyl-1,5-hexadiene and 1,5-hexadiene is fission leading to the formation of an allyl radical which can be characterized by means of infrared spectroscopy[63].

About the chemistry of radicals, the causes of their formation and the course of their reactions, that is in general, about the mechanisms of radical reactions, substantially less is known up to the present than about reactions taking place via carbon ions. These for a long time occupied one of the foremost places in investigations devoted to the clarification of reaction mechanisms. This is caused, before all, by the fact that radical reactions very often are equivocal with the formation of complex reaction mixtures and low selectivity.

Another hindrance is the fact that radical reactions have a chain character with

Table 3. Concentration of radicals in the pyrolysis of ethane and propane[119]

Starting hydrocarbon Radical concentration	Ethane mol · l^{-1}	Propane mol · l^{-1}
$H^\cdot$	$10^{-8.3}$	$10^{-9.3}$
$CH_3^\cdot$	$10^{-8.3}$	$10^{-7.7}$
$C_2H_3^\cdot$	$10^{-6.6}$	$10^{-7.0}$
$C_2H_5^\cdot$	$10^{-6.7}$	$10^{-7.7}$
$C_3H_5^\cdot$	$10^{-7.9}$	$10^{-6.4}$
$1\text{-}C_3H_7^\cdot$	–	$10^{-9.3}$
$2\text{-}C_3H_7^\cdot$	–	$10^{-8.0}$
$C_4H_7^\cdot$	$10^{-6.6}$	$10^{-7.4}$
$1\text{-}C_4H_9^\cdot$	$10^{-10.3}$	–
$2\text{-}C_4H_9^\cdot$	–	$10^{-10.6}$

Experimental conditions:
Ethane: 1123 K, 50 mol % steam
Propane: 1123 K, 40 mol % steam

Table 4. ESR spectra of radicals[53,36,40,48,59]

Radical	g-factor	$a_{\alpha-H}$ (mT)
$C_6H_5^\cdot$	2.0023	2.75
$CH_3^\cdot$	2.0025	2.29
$CH_3CH_2^\cdot$	2.0025	2.22
$C_6H_5CH_2^\cdot$	2.0026	1.63
$CH_3SCH_2^\cdot$	2.0049	1.65
$RS^\cdot$	2.0106	–
$CH_3SO^\cdot$	2.0100	1.15 (3 H)
$CH_3SO_2^\cdot$	2.0049	0.055

complicated kinetics, which considerably complicates direct measurements of the rates of individual processes. A breakthrough in the study of radical reactions was brought about only after the introduction of new analytical and kinetic methods. The application of modern analytical and before all, chromatographic methods, makes it possible to carry out a quick quantitative analysis of pyrolysis products. This allows the unequivocal identification of the primary and secondary or even further products of the consecutive steps of thermal decomposition. This contributes to the determination of the rates of many elementary reactions.

Methods based on the analysis of reaction products are among the indirect methods of investigating radical reactions taking place in the pyrolysis of hydrocarbons.

1.2. Composition of the reaction system

Hydrocarbon feedstocks for pyrolysis and pyrolysis products are, before all, characterized by their detailed composition: alkanes-alkenes (*n*-, *iso*-); alkylcycloalkanes-alkylcycloalkenes (with a five- or six-membered ring), mono-, di-, polycycloalkanes and polycycloalkenes; alkylaromatics (mono-, di-, polyaromatics); cycloalkenoaromaticscycloalkanoaromatics (indanes, indenes, acenaphthenes); total sulfur content and basic types of sulfur compounds (alkylthiophenes, benzothiophenes, alkyl sulfides and thiols). Among other characteristics are ASTM distillation, hydrogen content, density, molecular mass, viscosity, refraction index and origin of feedstock[6,7,8,9,91,94]. In analyzing a certain hydrocarbon fraction, it is important to have some idea about the boiling points of the components in question. The boiling points of the components and their mutual differences are, as a rule decisive for the choice of other separation methods. Details of a method for the determination of distillation characteristics of liquids have been specified by the American Society for Testing and Materials (ASTM).

1.2.1. Sulfur compounds Sulfur compounds almost invariably accompany petroleum feedstocks for pyrolysis such as primary naphtha, kerosenes, gas oils and vacuum distillates. The sulfur content in crude oils and crude oil fractions is dependent on their origin and distillation range. In general, its content increases with increasing boiling point of the crude oil fraction. The presence of sulfur compounds in hydrocarbon feedstocks is decisive before all for the quality of pyrolysis gasoline, fuel oil and for the production of hydrogen sulfide.

Sulfur in petroleum fractions is most frequently found in the form of thiols, sulfides, disulfides, polysulfides and cyclic sulfides-thiophenes. In the distillation range up to 100° C it is present virtually exclusively in the form of thiols which with increasing boiling temperature up to 250° C completely disappear[87]. The amount of sulfur in gas oils depends on their origin and for approximately the same distillation range it is 0.04 to 2 to 2.4% (by mass). Among the characteristic sulfur compounds in gas oils are: alkyl sulfides, disulfides, thiophenes, benzothiophenes, and aromatic sulfides. With increasing aromatization of hydrocarbons the concentration of sulfur also increases. Polyaromatic compounds which represent 18.9% (by mass) of the analyzed gas oil contain 61.4% (by mass) of the total quantity of sulfur. In monoaromatic fractions, sulfur compounds occur in the form of cyclic sulfides and benzothiophenes. Diaromatic fractions contain sulfur substances which consist mainly of naphtho-cyclic sulfides, benzothiophenes, diaryl disulfides. The composition of the aromatic fraction points to a complex mixture of sulfur compounds with approximately 4% molecules which contain more than one sulfur atom[132].

In the pyrolysis of vacuum distillates 25 to 30% sulfur from sulfur componds is liberated in the form of hydrogen sulfide. The remaining sulfur is concentrated in the pyrolysis oil which contains 2.5 to 3 times more than the starting feedstocks[62]. Pyrolysis gas contains about 10% (by volume) of hydrogen sulfide and a trace amount of thiols[120], before all, methane- and ethanethiol. Also a small amount of dimethyl sulfide is present. In liquid pyrolysis products no thiols are found. Thiophene and its homologues play a dominant role in pyrolysis oil[96].

In gas chromatographic analysis of liquid pyrolysis products with a flame photometric detector (FPD) the presence of sulfur compounds can be seen but their identification by means of GC-MS is not possible as a consequence of their low concentration and insufficient separation[14,3]. Their identification is easier when the end of the capillary column is placed into the ion source of a quadrupole mass spectrometer[42]. In a quadrupole mass spectrometer, the analysis time is shortened, the selectivity of separation of sulfur substances from hydrocarbons improved and the sensitivity is increased[127]. In pyrolysis products the following compounds have been analyzed in this way: thiophene, 2- and 3-methylthiophene, 2- and 3-ethylthiophene, 2- and 3-vinylthiophene and benzothiophene[14]. In chromatographic analysis for the identification of sulfur compounds, retention data are also of great help[3,118,60,66,65,93].

2. INITIATED PYROLYSIS

The pyrolysis of hydrocarbon feedstocks to alkenes runs under conditions when the rate and selectivity of the conversion, even under optimal conditions of running the process, are relatively low. While methane is formed in substantial amount in the primary reactions, heavy-liquid pyrolysis fractions, pitch, coke and oxides of carbon are formed as a result of secondary reactions, the course of which is made possible by a multicomponent, highly reactive, system of alkene-aromatic nature, with an appreciable participation of the inner surface of the reactor. One of the feasible ways of improving the production of lower alkenes is to carry out the pyrolysis process in the presence of substances which make it possible to lower the pyrolysis temperature, enhance the rate of the radical conversion, increase the flexibility of the pyrolysis process, improve the selectivity and use feeds of different properties. Presently there is going on an intensive search for such compounds (initiators, catalysts, activators, promotors) of a homogeneous and heterogeneous nature, which favorably influence the pyrolysis process and compounds (inhibitors, retarders, deactivators, passivators) that suppress the formation of unwanted pyrolysis products[47]. With this end in view have been studied several types of chemical substances; their broader application under running conditions is most often limited by their efficiency, availability or cost.

2.1. Sulfur and its compounds

Among the compounds which have the ability to influence the radical process of thermal decomposition of hydrocarbons are some inorganic and organic sulfur compounds. The effect of sulfur-containing additives on the pyrolysis process can be either favorable or unfavorable in various ways. One of the great advantages is that sulfur compounds are dosed into the system in small concentrations, several times smaller than in the use of other additives for the same end. In the conditions of the pyrolysis, sulfur compounds decompose mainly to hydrogen sulfide, which is readily removed from the pyrolysis gas by alkali washing. Several of the favorable effects of sulfur compounds can be seen irrespective of the conditions and type of feedstock. As far as negative effects are concerned they are, before all, corrosion of the exposed parts of pyrolysis equipment. Part of the sulfur which is concentrated in liquid products, deteriorates their quality and causes difficulties with their further processing. On the other hand, the use of sulfur compounds is very attractive, not only because of the low cost, but before all, for their ability to influence the radical process of thermal decomposition of hydrocarbons, especially the course of secondary reactions, which causes considerable difficulties.

Hydrogen sulfide accelerates or retards the pyrolysis of hydrocarbons and influences the selectivity of the conversion. Changes of rate and selectivity were observed in the pyrolysis of ethane[92,110], propane[101,121], methylpropane[97], butane[85], 2,2-dimethylpropane[109], decane[76], l-dodecene, butylbenzene, tetraline[103] and hexadecane[104]. In the pyrolysis of the above-mentioned hydrocarbons hydrogen sulfide is fulfilling the function of a catalyst in replacing the slow transfer of hydrogen by more rapid reactions[35,102,103]. A similar effect have also hydrogen chloride and hydrogen bromide. A change in selectivity occurs in the pyrolysis of 2-methyl-2-pentene[55] and piperylene[71] in the presence of hydrogen sulfide. While the mechanism of isoprene formation does not change, there occurs a change of mechanism in the formation of by-products, such as 2-methyl-1-pentene, methylpentadiene and 4-methyl-2-pentene. In the thermal decomposition of piperylenes, the dominant reaction is cyclization to cyclopentadiene and decomposition to butadiene. In the case of the thermal decomposition of 3-methyl-2-*cis*-pentene was observed a higher initial rate of decomposition and a retardation of isomerization to 2,3-dimethyl-1-butene[61].

The passivation of the stainless steel reactor surface under the action of hydrogen sulfide suppresses the course of secondary reactions as a consequence of which coke is formed in the pyrolysis of propane[43,123], ethane[46,108], and propene[52,57]. In the pyrolysis after sulfiding of the surface there is formed more ethylene from ethane, with less hydrogen and carbon monoxide, and from propane less hydrogen and methane. A decrease in the rate of coking in the pyrolysis of gaseous feeds in the presence of hydrogen sulfide is accompanied by a decrease of carbon monoxide and carbon dioxide among the gaseous products[49,88,108].

Reactions of elemental sulfur with hydrocarbons are well known[126]. Depending on the reaction conditions, sulfur reacts with alkanes with the formation of thiols, sulfides and polysulfides which subsequently decompose to alkenes and hydrogen sulfide. Also well-known is "S-dehydrogenation" of alkanes to alkenes, dienes, acetylene or benzene. Under very severe conditions of decomposition of alkanes with elemental sulfur are formed high-molecular compounds whose character is asphaltic. In the reaction of sulfur with alkanes there occurs cyclization with the formation of heterocyclic compounds such as thiophene and thiophane. Carbon disulphide is formed by "S-oxidation" of alkanes.

The dehydrogenating properties of sulfur are used in the pyrolysis of propane to propene[84]. Under specific conditions a dehydrogenating effect is also observed with sulfur dioxide[84], dimethyl disulfide and methanethiol[39]. Low-molecular thiols and ammonium sulfide are used as promotors of the cracking of methylpentenes to isoprene[54,74]. Diethyl sulfide and dimethyl sulfoxide inhibit coke formation and favor decomposition of nonane to alkenes[45]. Thanks to this, in the pyrolysis of hydrocarbons the yields of the desired alkenes improve. Sulfur added to the pyrolysis system directly or in the form of thermally decomposable compounds diminishes the carburization of the reactor wall and suppresses the formation of carbon monoxide. An inhibiting effect of sulfur compounds is also observed in the formation of coke in the gaseous and liquid phase and also on the inner surface of the reactor[1,38,50,56,78,112,113,114,115].

According to Starshov and Fakhriev this effect does not depend on the kind of sulfur compounds such as ammonium sulfide, thiols, sulfides or sulfoxides. What is decisive is that in their decomposition hydrogen sulfide is formed. They base their opinion on the key position of hydrogen sulfide on the fact that effective inhibitors of coking are also found among sulfur substances from gas condensates (LPG)[117] and crude oil fractions[116]. Hydrotreating desulfurization of gas condensates with a total volume of sulfur 1.092%

(by mass) (0.637% thiols; 0.271% sulfides; 0.011% disulfides) is seen in pyrolysis as judged by the formation of carbon monoxide (9% by mass) and carbon dioxide[95].

2.2. Kinetics and mechanism of the thermal decomposition of hydrocarbons in the presence of sulfur compounds

From the study of the pyrolysis of individual hydrocarbons it follows that the reaction conditions and the kind of hydrocarbon together with the properties of the inner surface of the reaction system are reflected in the kinetic parameters of the thermal decomposition of hydrocarbons and in the quantitative and qualitative composition of the reaction products. The aim of our research was to give an answer to the question of how sulfur additives affect the kinetics and mechanism of the pyrolysis of hydrocarbons and the yields not only of gaseous and liquid, but mainly also of solid pyrolytic products (coke). Bearing in mind past results, the influence of homogeneous additives on the kinetics and mechanism was studied in the conversion of heptane[9]. Coke formation was followed in the pyrolysis of heptane[18] and reformer raffinate[5,125], which represents a

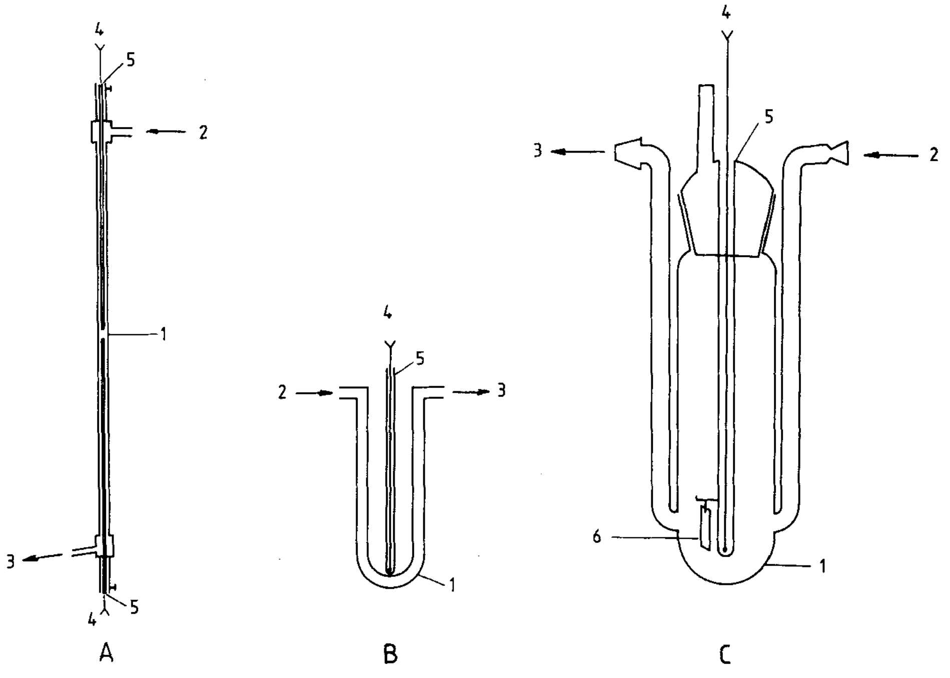


Figure 1. Pyrolysis flow reactors:
1. reactor; 2. reactor inlet; 3. reactor outlet; 4. thermocouple; 5. thermotube; 6. coupon. A: The flow reactor, made from stainless steel (Czechoslovak standard 17246, composition in % by mass: Cr 16.82; Ni 10.67; Mo 0.25; Mn 1.10; Si 0.40; C 0.085) was of the tubular type[6]. The outer tube (length 750 mm; i.d. 12 mm) was placed in an electrically heated furnace. The outside diameter of the inner tube was 6 mm. The inner reactor surface-to-volume ratio was 6.65 cm^{-1}. B: The U-shaped stainless steel reactor possessed the inner diameter 0.6 cm and inner surface-to-volume ratio 6.66 cm^{-1}. Chemical composition of the material of the pyrolysis reactor (% by mass): Cr 17.46; Ni 9.40; Mo 0.15; Mn 0.70; Si 0.76; C 0.18[10]. The reactor was used to study coke formation. C: The coupons were approximately 20 by 15 by 2 mm; they were inserted into 200 mm lengths of a 22 mm i.d. quartz tubular reactor[33].

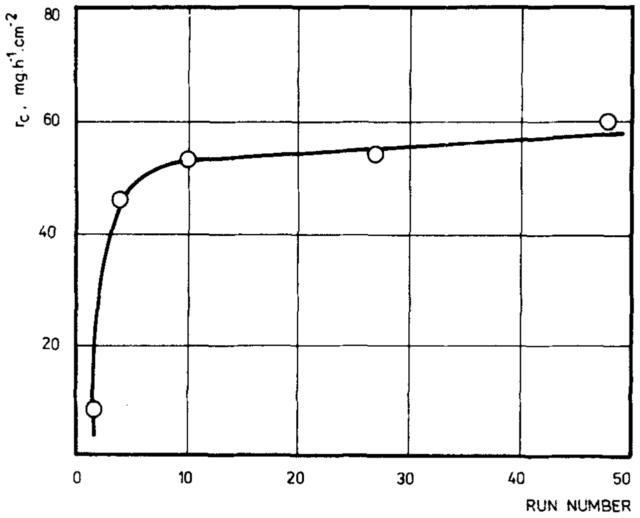


Figure 1a. Effect of the number of reactor activations with air on the coke formation rate during the pyrolysis of reformer raffinates[10]. Pyrolysis temperature 820° C; residence time: 0.25 s; duration of experiment: 1 h; experiment without inert diluent.

highly refined mixture of hydrocarbons (without O, S, N) after the extraction of aromatics from the catalytic reforming of naphthas. In studying the influence of kinetic parameters and sulfur additives on the conversion of individual hydrocarbons and hydrocarbon mixtures, we used tubular flow reactors[6] (Fig. 1, reactor A). The U-shaped tubular reactor is advantageous for studying the course of secondary reactions as a consequence of which coke is formed[10] (Fig. 1, reactor B). To eliminate as much as possible the reactor's "history", we proceeded in such a way that into the reactor made of inert material, for example quartz, we placed the materials which were studied[33] (Fig. 1, reactor C). This makes it easier to continuously follow the influence of the material on the kinetics and selectivity of hydrocarbons pyrolysis with the same sample.

The pyrolysis of hydrocarbons is regularly accompanied by the deposition of coke inside the reactor[67,68,69]. In laboratory through-flow type reactors, the amount of coke formed at a given temperature, pressure and surface is independent of the amount of the starting feeds or the residence time. The quality of hydrocarbon feedstocks and the internal surface are decisive. As the amount of coke being formed is not dependent on the concentration of reacting compounds, it is possible to suppose that the reaction is of zero order ($r_c = k_oC^o = k_o$).

While the size of the inner surface of the reactor during pyrolysis does not change, on the wall of the reactor or in its surroundings qualitative changes take place as a consequence of the deposition of pyrolytic carbon in the form of coke. The quality of the wall material of the reactor, especially one with a small diameter, does not, to any considerable measure, influence the formation of coke. The rate of coke formation on the stainless steel surface (steel 17246 of chemical composition: Cr 17.14; Ni 10.04; Mo 0.20; Mn 0.90% (by mass)) is an order of magnitude higher than the rate of coking on copper, titanium and non-metal surfaces (Table 5). A higher rate of coke formation on a metal surface is related to the catalytic activity of iron, chromium and nickel, which are components of steel. Carbonaceous sediments on copper, titanium and non-metal surfaces have their origin in reactions taking place in the gaseous phase without any catalytic effect on the surface[33]. A layer of silica or enamel has a marked inhibiting effect on coke formation. Silica was coated on the steel surface (steel 17246) from a solution of tetraethyl silicate and, after decomposition at 800 °C, a layer 6 to 9 μm thick had been deposited. The enamel was formed from a suspension of enamel coating by decomposition at 820 °C.

The silica layer not only abolishes the catalytic effect of the material of the reactor wall, but also forms a barrier preventing the transfer of carbon into the metal structure (carburization).

Coke from the reactor tube is repeatedly removed by air burning. The amount of coke being formed in the pyrolysis of hydrocarbons increases with every burn-out (activation by oxygen) of the reactor. The rate of coke formation does not stabilize in the stainless steel reactor even after forty experiments[10] (Fig. 1a).

The coking rate is highest in the initial stage of pyrolysis. It means that in the cyclic burning of coke by air there occurs activation of the inner surface by oxygen. The results obtained from the pyrolysis of reformer raffinate[10] (Fig. 3) are quantitatively in agreement with the results obtained in the pyrolysis of propane[43], heptane[18,80,81], methylcyclohexane[82], and octane[111].

The coke formation is influenced not only by the number of activations (burnings), but also by the mode of activation (treatment). In a completely new reactor without any activation, coke formation is low in comparison with the yields obtained after activation by steam or long-lasting activation by acids[5,10]. The mode, kind and number of activations of the inner surface of the reactor before pyrolysis has been set running, influences the coke formation in the course of the pyrolysis. A serious problem is the formation of a complex of metal oxides at a temperature over 700 °C in the burning out of coke by air or oxygen from the reactor. After every coke burning, the mass of the reactor decreased from 0.10 to 0.15% by mass[18]. The remaining product after the burning out of coke from the reactor is a fine powder of dark-brown color (containing 17.6% by mass of oxygen)[17]. It consists of oxides of iron and chromium or other metal components in the steel employed[124]. For the decomposition of the surface oxides an acid solution is suitable (3% HCl and 3% H_2SO_4). By the action of acids, probably all or most of the surface oxides are dissolved and a fresh steel surface is exposed.

Table 5. Rate of coke formation on different surfaces[33]

Reactor material	k_0, s^{-1}
Stainless steel	0.6923
Nickel	0.0396
Silica deposited on steel	0.0234
Quartz (SiO_2)	0.0207
Titanium	0.0179
Alundum (α-Al_2O_3)	0.0147
Enamel	0.0140
Copper	0.0056

Pyrolysis of reformer raffinate without inert diluent; temperature: 800 °C, residence time: 0.65–1.2 s.

For the decoking of the pyrolysis reactor the air-steam method is used. A certain part of the steam reacts with pyrolytic carbon with the formation of carbon monoxide and carbon dioxide. This reaction is slower than the burning out with air and requires higher temperatures to reach a marked increase in rate. It seems that burning with steam is catalyzed by iron and nickel which diffuse into the layer of deposited coke from the material of the reactor. Sulfur acts as a poison of these catalysts and retards the gasification of coke. Another part of the steam reacts with the inner surface of the reactor according to reaction (2.1):

$$(\mathrm{METAL})_{\mathrm{surface}} + H_2O \rightleftharpoons (\mathrm{METAL\ OXIDES})_{\mathrm{surface}} + H_2 \qquad (2.1)$$

Metal oxides = NiO, Fe_3O_4, Fe_2O_3

Metal oxides are also formed in reaction (2.2) by the action of air oxygen[124]:

$$(\mathrm{METAL})_{\mathrm{surface}} + O_2 \rightleftharpoons (\mathrm{METAL\ OXIDES})_{\mathrm{surface}} \qquad (2.2)$$

Metal oxides = Fe_2O_3, Fe_3O_4, Cr_2O_3

Metal oxides which are formed by reaction (2.1) and (2.2) in air-steam decoking, markedly favor the course of secondary reactions as a result of which coke is formed in the initial operational phase of the pyrolysis[10].

In the pyrolysis of hydrocarbons the presence of sulfur and its compounds in the reaction system makes itself felt in the course of specific reactions in the gaseous phase and also on the heterogeneous surface of the reactor in several ways[24,25,26]. What is most required is its positive influence on the rate of decomposition, improvement of the selectivity of conversion and the retardation of the course of secondary reactions leading to pyrolytic carbon which in the form of coke is deposited in the pyrolysis system. There also occur irreversible reactions between the wall reactor, hydrocarbons and sulfur compounds. In a short-lasting use of the reactor (an extent of a few months) there do not occur any substantial changes of the reactor steel. In long-lasting use (a few years) there occur interactions between the metal surface of the reactor and pyrolytic carbon when metal carbides are being formed (carburization). If in the reaction system sulfur compounds are present, metal sulfides are formed. After prolonged use of the reactor the quantity of carbon increased eight times and that of sulfur six times[17].

2.2.1. Hydrogen sulfide In the presence of hydrogen sulfide there takes place a reaction with the inner surface which results in an increase of the weight of the reactor (Fig. 2). Under the conditions of the pyrolysis, part of the hydrogen sulfide can undergo fission according to reaction (2.3):

$$H_2S \rightleftharpoons {}^{\cdot}SH + {}^{\cdot}H \qquad (2.3)$$

In the presence of hydrogen radicals the decomposition of hydrogen sulfide can take place with the formation of thiyl radicals according to reaction (2.4):

$$H_2S + H^{\cdot} \rightleftharpoons HS^{\cdot} + H_2 \qquad (2.4)$$

Under specific conditions[105] (at temperatures of 2700 to 3800 K and concentrations of hydrogen sulfide in the reaction zone of 25 to 200 ppm) a course of reactions is assumed

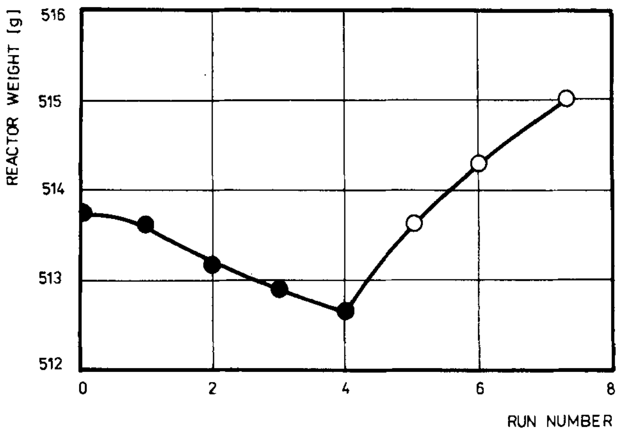


Figure 2. Effect of oxygen and of hydrogen sulfide on the weight of the reactor: ● oxygen; ○ sulfiding[18]. Pyrolysis of heptane without inert diluent; temperature: 820 °C; residence time: 0.25 s; duration of experiment: 1 h.

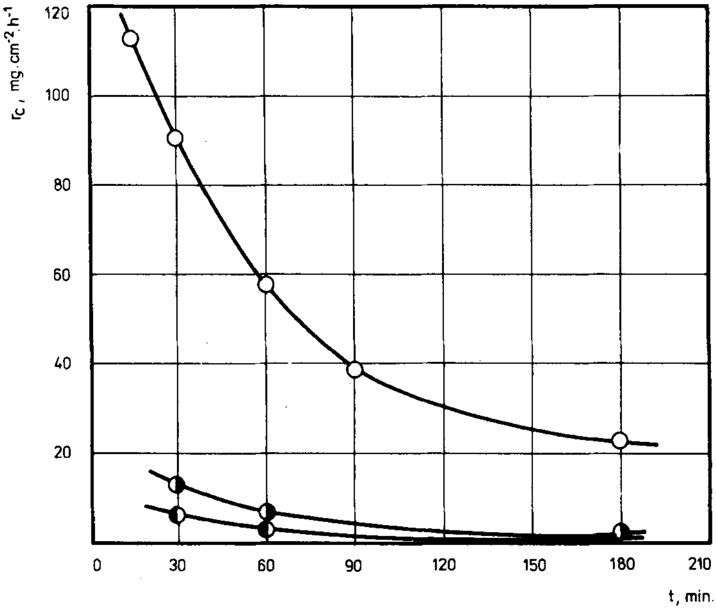


Figure 3. Formation of coke during the pyrolysis of reformer raffinates without inert diluent. Temperature 820 °C; residence time: 0.25 s; ○ feed without inhibitor; ◑ 0.05% by mass sulfur; ◐ feed with 0.1% by mass sulfur[5,10].

where there is a release of elemental sulfur in atomic form and of S_2 with paramagnetic properties. The $HS^{\cdot}$ radicals or S_1 and S_2 can take part in reactions in the gaseous phase or in reactions with a metal surface of the reactor where metal sulfides are formed according to reaction (2.5):

$$(\mathrm{METAL})_{\mathrm{surface}} + \mathrm{HS}^{\cdot}\ (\mathrm{S}_1, \mathrm{S}_2) \rightleftarrows (\mathrm{METAL\ SULFIDES})_{\mathrm{surface}} + \mathrm{H}^{\cdot} \tag{2.5}$$

With the formation of metal sulfides the quality of the reactor wall significantly changes which can be seen especially in the formation of carbonaceous sediments. In the pyrolysis of heptane there was such a strong inhibiting effect of the sulfide layer on the formation of coke that in comparison with pyrolysis without passivation by hydrogen sulfide coking was not observed at all or only slightly[18,35] (Table 6). As a result of many times increased intense passivation of the reactor by hydrogen sulfide and the subsequent pyrolysis of heptane there gradually accumulated a layer of sediments as a consequence of which the internal diameter of the reactor decreased, especially at the place of the highest temperature. We did not succeed in a thorough removal of the sediments, not even with chromosulfuric acid, nor with the oxidative action of oxygen and steam. The layer of sulfides which is deposited in several layers from 1 to 2 mm thick is characterized by great toughness, hardness and porosity.

From the analysis of the sediments which cover the inner surface of the reactor it follows that they consist mostly of graphite, carbides and sulfides[75]. The amount of carbides is about 90% by mass and that of the sulfides about 8% by mass. Chromium carbides are predominant, there is less iron and manganese[17]. In the passivation of the reactor by hydrogen sulfide before pyrolysis, followed by pyrolysis of hydrocarbon feedstock, the quantity of sulfides in the carbonaceous sediments increases from 17 to 36% by mass. These are, before all, chromium sulfides (36.4% by mass) and iron (22.5%

Table 6. Influence of the passivation of the reactor by hydrogen sulfide on coke formation in the pyrolysis of heptane[18]

Temperature, °C		820	
Flow H_2S, ml·min^{-1}	–	50	50
Duration of treatment H_2S, min	–	10	10
Weight of sediments, g	–	0.25	0.20
Duration of exp. in pyrolysis, min.	60	60	90
Flow of heptane, g·h^{-1}	31.0	30.6	30.6
Residence time, s	0.25	0.25	0.25
Amount of coke, g	1.00	0	0.18
Coke, % mass	3.22	0	0.60

Table 7. Analysis of sediments from the reactor after passivation by hydrogen sulfide and pyrolysis of heptane at 820 °C (sulfide analysis)[17]

Sample	Amount of sulfides % by mass	Content of sulfides Cr	Fe	S	Content of C
1.	36.4	–	–	25.0	41.6
2.	25.2	36.4	22.5	23.4	0.76
3.	17.0	31.5	23.5	36.6	–

by mass) (Table 7). In the pyrolysis of hydrocarbon feedstock in the presence of elemental sulfur mainly sulfides of iron and manganese are formed.

The possibility of suppressing the coke formation in pyrolysis reactors by modification of the inner surface can be explored most simply by conversion of the metal oxides formed after steam-air decoking to the corresponding sulfides by the action of hydrogen sulfide[29]. The safety of the pre-operation phase of the furnace is very important since there often occur considerable temperature fluctuations which substantially increase the rate of coke formation.

2.2.2. Elemental sulfur Similarly, as in the case of hydrogen sulfide, also in the presence of elemental sulfur in the hydrocarbon feed there is observed in the pyrolysis a substantial decrease of coke formation (Table 8). According to the coke coefficient, the rate of coking, after the addition of 0.05% by mass of elemental sulfur, decreases by one order of magnitude and by adding 0.1% by mass of sulfur two orders of magnitude. From the comparison of data without elemental sulfur and in its presence, there is an obvious difference in the course of the initial phase of coking (Fig. 3).

The dependence of the amount of coke on time (the duration of the pyrolysis experiment) has an asymptotic course. Coking, the sedimentation of coke at a constant temperature, pressure and flow of feedstock, is most pronounced in the initial phase of pyrolysis. An evaluation of the kinetic data, however, is not simple, because the mechanism of the course of the secondary reactions as a consequence of which coke in pyrolysis is formed is not known. The dependence of the coking rate on time can be expressed formally by the following empiric kinetic equation[33]:

$$\ln(100 - X_c) = k_c \cdot t$$

It is based on the fact that coke can be formed only from carbon. Hydrogen does not take part in coke formation, on the contrary, it retards it. In the evaluation of the material balance, only the amount of coke contained in the feedstock is considered (on the basis of the elemental analysis) which is formed in the reactor while the experiment lasts. The conversion of the starting feedstock to coke has also been determined from pure carbon. In such a case, conversion X_c expresses the quantity of coke (mol) formed in the course of pyrolysis in the flow reactor relative to the quantity of carbon (mol) supplied by the feedstock to the reactor in a given time interval. This makes the calculations somewhat easier, based on the assumption that coke contains only carbon. This assumption is admissible on the condition that coke is formed at medium temperature pyrolysis when the content of carbon in the coke is above 95% by mass. The

Table 8. Inhibitory effect of elemental sulfur on coking[10]

Amount of sulfur	k_c at 820 °C
Without sulfur	$2.948 \cdot 10^{-2}$
0.05 % by mass sulfur	$0.192 \cdot 10^{-2}$
0.1 % by mass sulfur	$0.0959 \cdot 10^{-2}$

Pyrolysis of reformer raffinate without inert diluent; residence time: 0.25 s.

determinations of k_c make it possible to evaluate the inhibitory effect of additives on the formation of coke and the disposition to coking of different hydrocarbon feedstocks.

Elemental sulfur considerably retards the rate of coking, especially at the beginning of the experiment, when the influence of the inner surface on coke formation is decisive. It leads one to think that sulfur reacts with active sites of the surface with the formation of a protective film. The qualitative analysis of this film[17] confirmed the presence of metal sulfides. The film is of a dark grey color and covers not only the interior of the reactor, but also its outlet closure and part of the cooler. In its burning, gases of a yellow-brown color are evolved. Complete removing of the metal sulfides and restoration of the original surface by air burning and by means of acids is very difficult. The nature of the protective film is dependent not only on the total sulfur content in the feed, but also on the type of the sulfur compound. Elemental sulfur affords a protective film which passivates the inner surface of the reactor still for a certain additional time, if feed without the inhibitor is subsequently supplied [5,10,17,18,19]. The preformed sulfide layer will suffice to lower the level of coking for approximately two hours. After this period the effect of the protective film disappears because it is disrupted by reaction products.

The equivalent reactor volume of a reactor is a quantity proportional to its equivalent surface because it is determined for a tubular reactor of a constant diameter. In other words: the influence of an equivalent reactor volume also represents a corresponding influence of an equivalent reactor surface. The temperature profile *I* is broader and for approximately this shape the equivalent reactor volume is in the range 5 to 7 cm^3. The temperature profile II is narrower and the corresponding calculated equivalent volume of the reactor is in the range 4 to 5 cm^3.

The rates of conversion of heptane in a relatively large equivalent volume in the presence and absence of sulfur are very close. On the other hand, when pyrolysis takes place in a smaller equivalent volume, elemental sulfur accelerates the thermal decomposition of heptane (Table 9). In comparison with pyrolysis without sulfur the average rate constant (Fig. 4, $k = 4.85\ s^{-1}$) is increased by 27.6%. The mean molecular weight of the gaseous products from the pyrolysis of heptane in the presence and in the absence of elemental sulfur lies in the range 25.3 to 28.6. The amount of the pyrolysis gas grows with increasing conversion. The differences recorded between yields at a given conversion with a different content of elemental sulfur in the feed in both temperature profiles are negligible.

The conversion of heptane and the yields of different products are decisively influenced by temperature, residence time, temperature profile of the longitudinal reactors and the presence of sulfur. The influence of temperature and residence time have been examined in detail for the pyrolysis of pure heptane in a relatively large equivalent

Table 9. The reactivity of elemental sulfur in the pyrolysis of heptane[10] at 700 °C. Mass ratio steam to heptane: 3.0

Additive	$k\ s^{-1}$	$k/k°$
0.02 % by mass sulfur	5.1	1.34
0.05 % by mass sulfur	4.7	1.24
0.1 % by mass sulfur	4.8	1.26

k° = rate constant of pure heptane conversion[6]

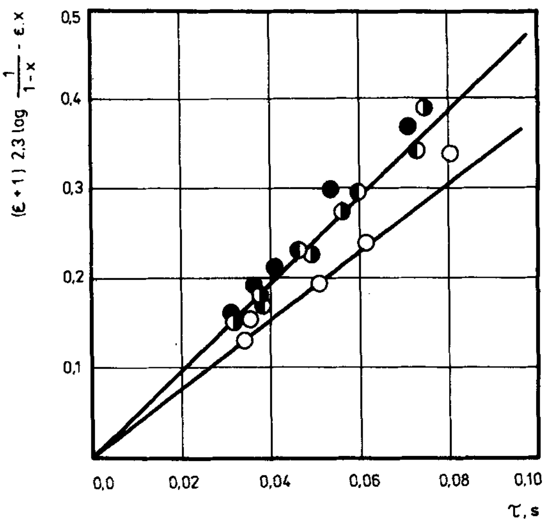


Figure 4. Graphic representation of the rate equation for the thermal decomposition of heptane in the presence of: ● 0.02% by mass S; ◐ 0.05% by mass S; ◑ 0.1% by mass S; ○ without sulfur[10]. Temperature: 700° C; mass ratio of steam to heptane: 3.

reactor volume (TP I)[6]. In the observed time interval, in a smaller equivalent reactor volume (TP II) there is formed more ethylene and less ethane and carbon monoxide than when the pyrolysis takes place in a large equivalent reactor volume (TP I). In the temperature profile II the yields of the mentioned products do not change upon prolongation of the residence time. On the other hand, in the same dependence, but under the conditions of temperature profile I, the yields of ethylene increase, those of carbon monoxide decrease and the yields of methane pass through a maximum. The differences in the yields of propene, 1-butene, 1-pentene and 1-hexene are negligible.

The influence of the residence time on the selectivity of heptane conversion in both temperature profiles in the presence of elemental sulfur is shown in Fig. 5. In the pyrolysis of heptane with an added 0.1% by mass of sulfur, very similar yields of ethylene, propene, 1-butene, 1-pentene, and 1-hexene were obtained, irrespective of the shape of the temperature profile. However, there are differences with respect to methane and carbon monoxide. The situation here is similar to that in the pyrolysis of heptane without elemental sulfur: in the temperature profile II the yields are lower.

The course of secondary reactions can successfully be retarded by doses of elemental sulfur into the reaction system. At a temperature over 200 °C (the boiling point of sulfur is 444.6 °C) an equilibrium between S_4, S_3, and S_2 is established and the higher the temperature, the more it moves to the right. Above 500 °C S_2 predominates. At higher temperatures (over 1000 °C) sulfur vapor even contains monatomic sulfur (S)[126]. The S_2 molecule possesses two unpaired electrons and therefore is paramagnetic. It is assumed that a reaction occurs between sulfur or sulfur compounds and the inner surface of the reactor according to reaction (2.6):

$$(\mathrm{METAL})_{\mathrm{surface}} + \mathrm{S}\ (\mathrm{S}_2) \rightarrow (\mathrm{METAL\ SULFIDES})_{\mathrm{surface}} \qquad (2.6)$$

The coke formation decreases, on a sulfur deactivated surface, to a fraction of the

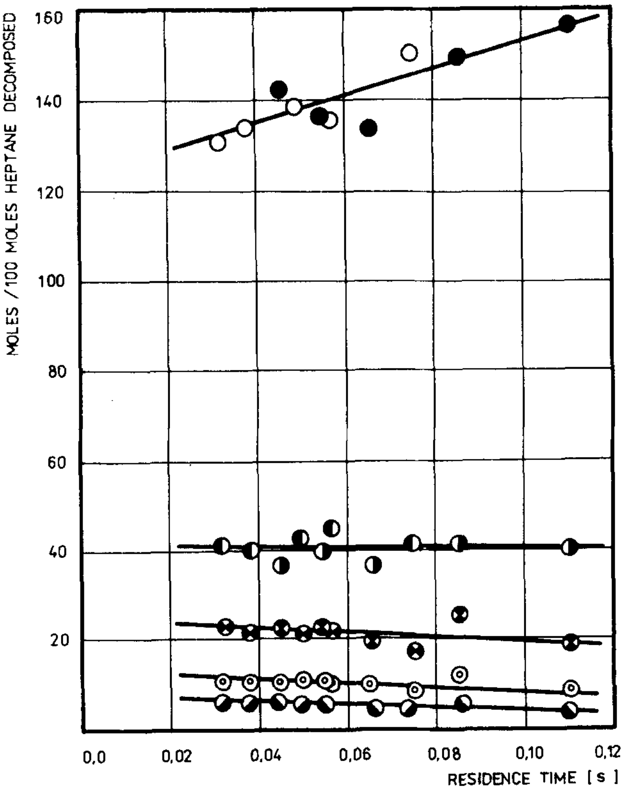


Figure 5. Product distribution dependence on heptane residence time at 700 °C in the presence of steam and 0.1% by mass sulfur[10]. Temperature profile I: ● ethylene; ◑ propene; ⊗ 1-butene; ⊙ 1-pentene; ◒ 1-hexene. Temperature profile II: ○ ethylene; ◐ propene; ⊖ 1-butene; ⊙ 1-pentene; ◔ 1-hexene.

original rate. The sulfide film on the inner surface of the reactor is created and maintained by the addition of elemental sulfur to the feedstock. The solubility of elemental sulfur in petroleum hydrocarbons under laboratory conditions reaches up to 1% by mass. The sulfide formation according to reaction (2.6) is strongly simplified because sulfur even before entering the reaction zone of the reactor can react with the starting hydrocarbons to form sulfur compounds. Alkanes react with sulfur at temperatures which decrease with their molecular weight and their numbers of tertiary carbon atoms[126]. For instance, sulfur reacts with octane at 160 °C and with light hydrocarbons up to C_6 at 210 °C. Of the original amount of sulfur in the feedstock, only a small fraction remains in the liquid pyrolysis product[10,107,108]. The major part of sulfur leaves the pyrolysis reactor in gaseous products among which, together with low-molecular thiols, sulfides, disulfides and thiophenes, hydrogen sulfide plays a dominant role. This means that dehydrogenated reaction products of sulfur predominate over condensed ones. These features are also reflected in Table 10, where the influence of the concentration of elemental sulfur on the yields of some heptane pyrolysis products is shown. With increasing sulfur concentration in the feedstock the yields of 1,3-butadiene, 1-pentene

Table 10. The influence of elemental sulfur on the yields of products of pyrolysis of heptane at 700 °C[10]

Conversion, %	12.14	14.57	13.53	13.31
Sulfur amount, % by mass	-	0.02	0.05	0.1
	mole/100 mole of heptane decomposed			
Methane	53.11	44.62	39.49	41.33
Ethylene	148.01	136.22	128.83	130.44
Ethane	13.44	13.42	10.92	9.33
Propene	38.66	38.81	42.76	40.62
1-Butene	10.69	22.45	21.41	22.73
1,3-Butadiene	1.70	2.29	2.35	2.65
1-Pentene	8.88	10.77	12.13	10.57
1-Hexene	3.85	5.34	5.67	5.86
Total hydrocarbon	293.5	283.0	272.5	273.2

Mass ratio steam to heptane: 3.0

and 1-hexene increase too. On the other side, the yield of methane, ethylene, and ethane decrease.

On the basis of this finding one can assume that in the reaction zone there is a higher concentration of $\cdot SH$ radicals, which are formed either by dehydrogenation reactions of sulfur with the starting hydrocarbons (reaction 2.7):

$$C_7H_{16} + S_2 \rightarrow C_7H_{15}^{\cdot} + {}^{\cdot}S_2H \qquad (2.7)$$

$$C_7H_{16} + {}^{\cdot}S_2H \rightarrow C_7H_{15}^{\cdot} + 2\,{}^{\cdot}SH$$

or of sulfur with higher radicals such as butyl, pentyl and hexyl, or by fission of the hydrogen sulfide formed (reaction 2.3).

Therefore it is very probable that in the reaction with a heterogeneous phase, on which a thin layer of metal sulfides is being formed, $\cdot SH$ radicals are involved. Also in the homogeneous phase sulfur can participate in the individual steps of radical decomposition in the form of $\cdot SH$ radicals, for instance in the propagation of a reactant according to equation (2.8). This is supported by the increased rate and improved selectivity of heptane decomposition.

$$C_7H_{16} + {}^{\cdot}SH \rightarrow C_7H_{15}^{\cdot} + H_2S \qquad (2.8)$$

A favorable effect of sulfur or $\cdot SH$ radicals on the rate of heptane decomposition is noticeable when the pyrolysis is taking place in the reactor with a smaller equivalent volume (Fig. 6). Evidently this is due to the radical reactions in the homogeneous phase where the contribution of $\cdot SH$ radicals in the initiation of the reactant predominates over the contribution of the inner surface of the reaction system. This effect of $\cdot SH$ radicals has a decreasing tendency with increasing equivalent volume of the reactor, which probably reflects the increasing proportion of secondary and terminating reactions at the reactor wall. Dehydrogenation reactions involving elemental sulfur in the final stage form hydrogen sulfide (reaction 2.8). It is known that hydrogen sulfide can act as a catalyst[103,35] of hydrogen transfer and accelerate or retard as well as influence the selectivity of the pyrolysis. Similar effects are also seen with inorganic hydrides. The effect of hydrogen sulfide is mainly due to the replacement of a slow hydrogen transfer step (2.9):

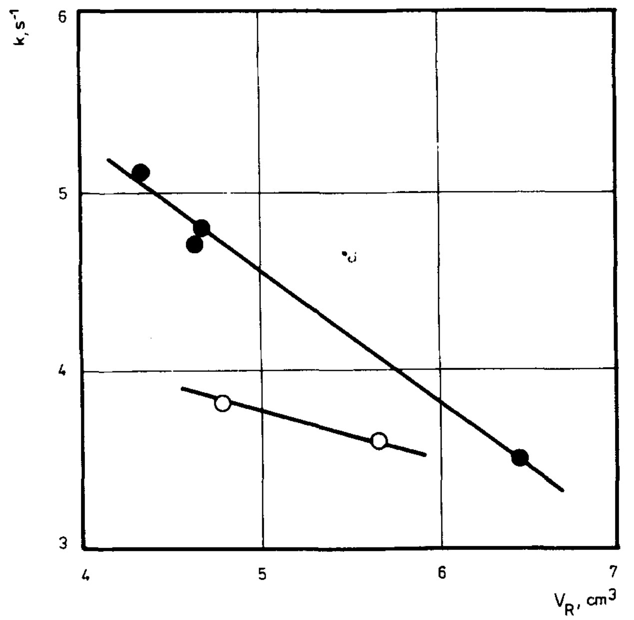


Figure 6. Effect of the equivalent reaction volume on the heptane conversion rate in the presence of sulfur (●); and in the absence of sulfur (○)[10]. Temperature: 700 °C, mass ratio of steam to heptane: 3.

$$R_1^{\cdot} + C_7H_{16} \rightarrow R_1H + C_7H_{15}^{\cdot} \quad (2.9)$$

by two faster ones (2.10 and 2.11):

$$R_1^{\cdot} + H_2S \rightarrow R_1H + HS^{\cdot} \quad (2.10)$$

$$HS^{\cdot} + C_7H_{16} \rightarrow H_2S + C_7H_{15}^{\cdot} \quad (2.11)$$

$$(R_1 = H^{\cdot}, CH_3^{\cdot}, C_2H_5^{\cdot})$$

In a smaller reactor equivalent volume the selectivity for ethylene during the whole residence time is greater than in the reactor with a larger equivalent volume. In the pyrolysis in the presence of sulfur these differences disappear, while the ethylene yields with shorter residence time are below the level and, with longer residence time, above the level reached in pyrolysis with a smaller reactor equivalent volume. A larger reactor equivalent volume has a favorable influence on the formation of methane and carbon monoxide. This suggests that with a larger inner surface methane is formed not only by primary, but also by secondary reactions as a result of which pyrolytic carbon is formed which reacts with steam to form carbon monoxide. Here it must be considered that carbon monoxide can be formed not only by gasification of solid pyrolysis products, but also from gaseous products, for instance from methane and ethane. The inner surface favors, and elemental sulfur inhibits the formation of carbon monoxide.

2.2.3. Thiophene Thiophene represents another type of sulfur compounds, other than elemental sulfur and hydrogen sulfide, which by decomposition give ˙SH radicals.

Thiophene is a sterically unhindered, unsubstituted heteroarene able either to inhibit pyrolysis like aromatics, e.g. benzene, in general or promote it as do some sulfur compounds. The presence of thiophene in the feed in the concentrations of 0.1 and 0.5% by mass is marked by a rate increase, in comparison with the conversion of heptane in the absence of sulfur compounds, of 13.9%. A further increase of the amount of thiophene in the reaction system has no favorable effect on the rate of decomposition[11,23]. The rate constant at 1% (by mass) concentration of thiophene is the same as that of the conversion of heptane itself (Table 11).

Table 11. The reactivity of thiophene in the pyrolysis of heptane[11] at 700 °C. Mass ratio steam to heptane: 3.0

Additive	k, s^{-1}	k/k°
0.1% by mass thiophene	4.1	1.14
0.5 % by mass thiophene	4.1	1.14
1.0 % by mass thiophene	3.6	1.00

k° = rate constant of pure heptane conversion[6]

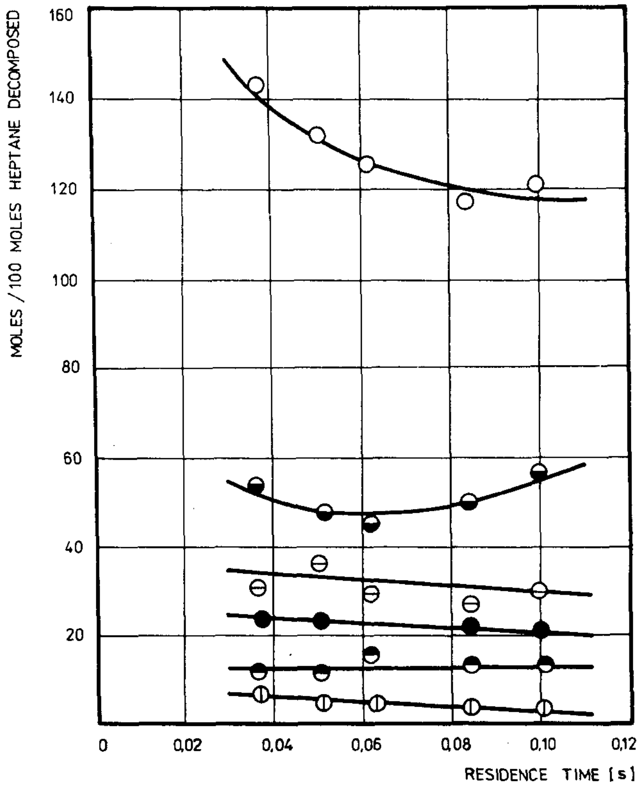


Figure 7. Product distribution vs. residence time for the conversion of heptane with 1.0% (by mass) of thiophene: ○ ethylene; ◒ methane; ⊖ propene, ● 1-butene; ◓ 1-pentene; ⏀ 1-hexene[11]. Temperature: 700 °C; mass ratio of steam to heptane: 3.

Thiophene only slightly influences the yields of propene, l-butene, l-pentene, and l-hexene. In the case of hydrogen, methane, and carbon monoxide the differences are greater, but their dependence on residence time is not unequivocal either. Most obvious is the influence of thiophene on the selectivity of the conversion of heptane to ethylene. Although in all the three thiophene concentrations, in the feed, about 140 moles of ethylene per 100 moles of consumed heptane were obtained it unequivocally follows from the results that at a given concentration residence time is decisive. Within the observed residence times, the most uniform yields of ethylene were obtained at 0.1% thiophene concentration. Selectivity toward ethylene formation increases rapidly with increasing residence time at 0.5% concentration of thiophene. On the other hand, at the highest concentration of thiophene, a slight decrease was observed (Fig. 7).

The presence of thiophene in a hydrocarbon feed leads to an unequivocal decrease of coking (Table 12). With increasing thiophene concentration the coking rate decreases. The course of coking indicates that at the beginning, the influence of the inner surface

Table 12. The inhibitory effect of thiophene on coking[11] of reformer raffinate at pyrolysis without inert diluent.

Additive	k_c at 820 °C
Without thiophene	$2.948 \cdot 10^{-2}$
0.05 % by mass thiophene	$1.451 \cdot 10^{-2}$
0.10 % by mass thiophene	$0.667 \cdot 10^{-2}$
0.50 % by mass thiophene	$0.290 \cdot 10^{-2}$

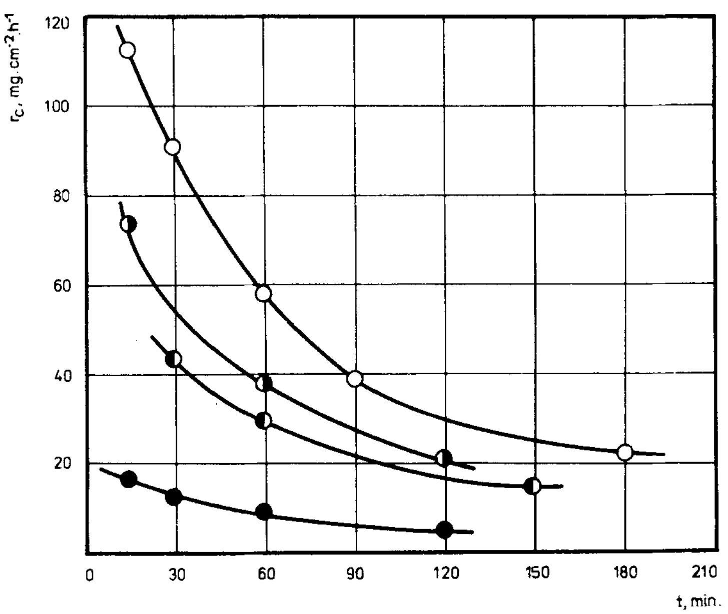
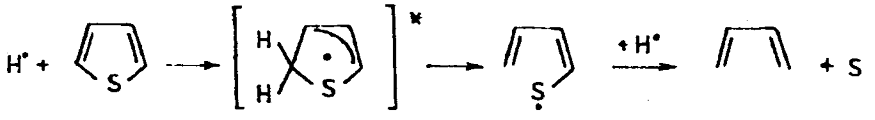


Figure 8. Rate of coke formation during the pyrolysis of reformer raffinate with varying thiophene contents: ○ without inhibitor; ◑ 0.05; ; ◐ 0.1; ● 0.5% by mass of thiophene[11]. Temperature 820 °C; residence time: 0.25 s; experiment without inert diluent.

is decisive for the formation of coke. The formation of coke is catalyzed by the metal surface. Only after a certain time, when the surface is covered by carbonaceous deposits, a steady state is reached (Fig. 8). Compared to the pyrolysis of a neat reformer raffinate under constant conditions, for example at 0.5% content of thiophene, an approximately tenfold decrease was observed.

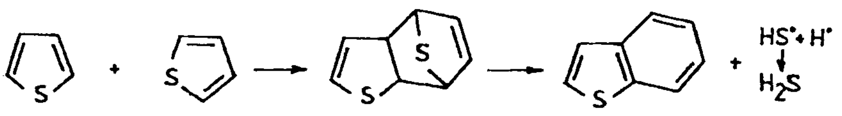
The activation energy of decomposition of hydrocarbons is mainly determined by the dissociation energy of C-C bonds (280 to 350 kJ mol^{-1}) which are cleaved preferentially. In the presence of aliphatic sulfur compounds the reaction can be initiated by the cleavage of C-S bonds, because the dissociation energy in most cases is less than 300 kJ mol^{-1}. However, this need not be so for thiophene which is very similar in its physical and chemical properties to benzene. The p-orbitals of the double bonds and of the sulfur atom overlap, giving rise to aromatic delocalized π orbitals. The resulting energy of stabilization by resonance is 129.8 kJ mol^{-1} for thiophene and 163.3 kJ mol^{-1} for benzene.

A comparison of the kinetics, the selectivity of heptane decomposition and of the coking rate of reformer raffinate leads to the finding that thiophene influences the radical conversion in the homogeneous phase and the surface reaction in the reactor. Under the conditions of pyrolysis a reaction can occur between the thiophene molecules themselves and between thiophene and the highly reactive radicals resulting from the decomposition of hydrocarbons, for example, $H^{\cdot}$ and $R^{\cdot}$. Decomposition of thiophene in the presence of hydrogen at 300–700 K under lower pressure is very selective[70]. Among the reaction products no sulfur compounds were found, except hydrogen sulfide. On this basis it is possible to postulate that the reaction (2.12) is initiated at the C-2 of thiophene, which is also the most reactive position for electrophilic substitution. This gives rise to a radical which, while opening the ring, decomposes to a thiobutadienyl radical, which further reacts with a hydrogen radical to butadiene and a sulfur atom.

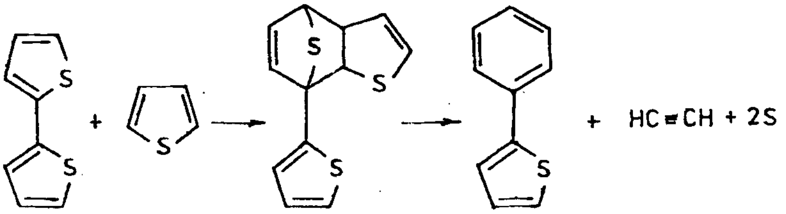


(2.12)

On the other hand, in the pyrolysis of thiophene at 800 to 850 °C besides bithienyl also benzothiophene and phenylthiophene are formed. The formation of these products was explained by Diels-Alder addition of thiophene to itself according to reactions (2.13) and (2.14)[129]:

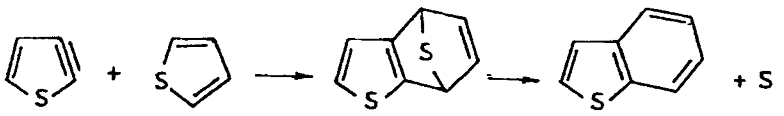


(2.13)



(2.14)

On the basis of results from the pyrolysis of thiophene at 690 °C, a very important role is ascribed to thiophyne[51], which can be formed as a reactive intermediate by intramolecular dehydrogenation of thiophene. Reaction with a thiophene molecule could give benzothiophene according to reaction (2.15).



(2.15)

In the proposed mechanisms for the thermal conversion of thiophene, the formation of atomic sulfur (reactions 2.12, 2.14, 2.15) and of hydrogen sulfide (reaction 2.13) are characteristic. Sulfur eliminated from thiophene can enter into reactions in the gaseous state. It can also react with the metal surface of the reactor, similar to the case of aliphatic sulfur compounds. Among the possible reactions sulfur can initiate propagation according to reaction (2.16) with the formation of heptyl and ˙SH radicals and the formation of hydrogen sulfide according to reactions (2.10 and 2.11).

$$C_7H_{16} + S \rightarrow C_7H_{15}^{\cdot} + {}^{\cdot}SH \qquad (2.16)$$

The observed increase in the rate of heptane decomposition shows that the reaction course according to reactions (2.16, 2.10, and 2.11) is preferred whenever the concentration of thiophene in the reaction system is low (less than 0.5% by mass per feed). Thus, at higher thiophene concentration, a state is reached where either thiophene or its decomposition products behave like unsaturated hydrocarbons or aromatics. These compounds act as scavengers of active radicals from hydrocarbon decomposition, and the rate of thermal decomposition decreases.

Radicals ˙SH from reactions (2.13) and (2.16) can also cause propagation according to reaction (2.8), termination according to the reverse reaction (2.3), or react with the stainless steel surface to metal sulfides according to reaction (2.5).

2.2.4. Dibenzyl sulfide and dibenzyl disulfide Among the sulfur compounds which could favorably influence the pyrolysis of hydrocarbons to alkenes the most important are sulfides and disulfides, before all aromatic ones, which decompose to highly stabilized radicals. Such compounds are dibenzyl sulfide and dibenzyl disulfide[14,21].

Dibenzyl sulfide and dibenzyl disulfide accelerate the thermal decomposition of heptane; in the case of dibenzyl sulfide by 16 to 26%, with dibenzyl disulfide by 8% (Table 13). From the kinetics of coking it is obvious (Fig. 9) that the catalytic effect of

Table 13. The reactivity of dibenzyl sulfide and dibenzyl disulfide in the pyrolysis of heptane[14] at 700 °C. Mass ratio steam to heptane: 3.0

Additive	k, s^{-1}	k/k°
0.1 % by mass dibenzyl sulfide	4.4	1.16
0.5 % by mass dibenzyl sulfide	4.8	1.26
1.0 % by mass dibenzyl sulfide	4.6	1.25
1.0 % by mass dibenzyl disulfide	3.9	1.08

k° = rate of pure heptane conversion[6]

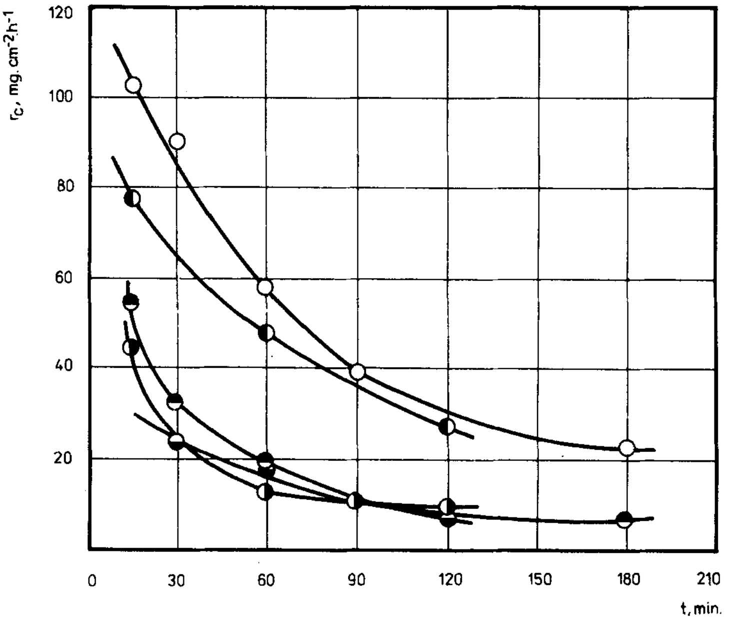


Figure 9. Rate of coke formation during the pyrolysis of reformer raffinate without inert diluent and with varying additive content (% by mass): ◐ 0.1% and ◑ 0.5% dibenzyl sulfide; ◓ 0.1% and ◒ 0.5% dibenzyl disulfide; ○ without inhibitor[14]. Temperature 820 °C; residence time 0.25 s.

the surface of the metal reactor on the coke formation can eliminate dibenzyl sulfide and dibenzyl disulfide, which can be seen in the substantial decrease of the coking coefficient (Table 14).

In the thermal decomposition of hydrocarbons the manner of initiation, propagation and termination of radicals plays a decisive role. From the comparison of the kinetics and the selectivity of the decomposition of heptane and the rate of coking of reformer raffinate it can be seen that dibenzyl sulfide and dibenzyl disulfide influence the fate of radicals in the homogeneous phase and on the reactor surface. Concerning aromatic sulfides and disulfides it is known that their decomposition takes place preferentially by cleavage of C-S bonds as a consequence of a relatively low dissociation energy:

		Ref.
$C_6H_5CH_2-SCH_3$	221.5 kJ·mol^{-1}	89
$C_6H_5CH_2SCH_3$	213.2 kJ·mol^{-1}	90
	248.3 kJ·mol^{-1}	41
$C_6H_5-SCH_3$	250.8 kJ·mol^{-1}	4
	282.1 kJ·mol^{-1}	41
$C_6H_5CH_2-SH$	221.5 kJ·mol^{-1}	90

Upon decomposition, phenylthiyl and benzyl radicals are formed with stabilization

Table 14. The inhibitory effect of dibenzyl sulfide and dibenzyl disulfide on coking[14] of reformer raffinate in pyrolysis without inert diluent.

Inhibitor	k_c at 820 °C
Without inhibitor	$2.9848 \cdot 10^{-2}$
0.1 % mass dibenzyl sulfide	$1.341 \cdot 10^{-2}$
0.5 % mass dibenzyl sulfide	$0.984 \cdot 10^{-2}$
0.1 % mass dibenzyl disulfide	$0.687 \cdot 10^{-2}$
0.5 % mass dibenzyl disulfide	$0.401 \cdot 10^{-2}$

energies of 40.1 and 57.2 kJ · mol^{-1}, respectively[41]. Benzyl radicals can be formed during the decomposition of dibenzyl sulfide according to reaction (2.17) and of dibenzyl disulfide, reaction (2.18). Nevertheless, cleavage of dibenzyl disulfide with the formation of two benzylthiyl radicals according to reaction (2.19) is likely to occur.

$$PhCH_2{=}S\text{-}CH_2Ph \rightarrow PhCH_2\cdot + PhCH_2S\cdot \qquad (2.17)$$

$$PhCH_2{=}S{-}S{-}CH_2Ph \rightarrow PhCH_2\cdot + PhCH_2{-}S{-}S\cdot \qquad (2.18)$$

$$PhCH_2{-}S{=}S{-}CH_2Ph \rightarrow 2\,PhCH_2S\cdot \qquad (2.19)$$

The dissociation energies of S—S and S—H bonds are substantially higher, for example 290–305 kJ · mol^{-1} for dialkyl disulfides[90,77] and 372 kJ · mol^{-1} for methanethiol[77]. A benzylthiyl radical can also be formed by reaction (2.17) and a benzyldithiyl radical according to reaction (2.18). The further fate of the primary products of the monomolecular decomposition of aromatic sulfides and disulfides depends on the reaction conditions. Under very low pressure pyrolysis (VLPP) the cleavage of aromatic sulfides is highly selective[41]. On the other hand, under the conditions of pyrolytic chromatography, the decomposition of dibenzyl disulfide at temperatures of 180 to 300 °C yields hydrogen sulfide, ethanethiol, dimethyl sulfide, methyl phenyl sulfide, ethyl phenyl sulfide, phenylmethanethiol and 2-phenylethanethiol[83]. At 600 °C sulfur compounds other than hydrogen sulfide are not formed. Among the reaction products only benzene and toluene are present. In the presence of radicals generated by thermal decomposition of hydrocarbons (Ri) reaction can occur with aromatic sulfides or disulfides, under formation of a range of thiyl radicals, for example according to reaction (2.20).

$$C_6H_5CH_2 - S{—}S{—}CH_2C_6H_5 + (R_i) \rightarrow (R_i)S\cdot + C_6H_5CH_2{—}S{—}CH_2C_6H_5 \qquad (2.20)$$

A characteristic property of benzyl, benzylthiyl and alkylthiyl radicals is that they enter reactions where they can cause abstraction of hydrogen. Under pyrolysis conditions, thiyl radicals can abstract hydrogen from a heptane molecule by reaction (2.21), thereby initiating the propagation of reactants in the homogeneous phase.

$$C_7H_{16} + R_2^{\cdot} \rightarrow C_7H_{15}^{\cdot} + R_2H \qquad (2.21)$$

$$R_2^{\cdot} = C_6H_5CH_2^{\cdot},\ C_6H_5CH_2\,S^{\cdot};\ R_1S^{\cdot};$$

This is apparent from the increase of the rate of heptane decomposition in the presence of dibenzyl sulfide and dibenzyl disulfide. Variation of the dibenzyl disulfide concentration does not affect the overall cracking rate of heptane significantly; however, a decrease in selectivity of the heptane decomposition into ethylene, ethane, and methane with increasing dibenzyl sulfide concentrations can be concluded from the data in Table 15. At the same time the content of l-alkenes C_4 to C_6 and of 1,3-butadiene increases. From a mechanistic point of view an increasing concentration of thiyl radicals has no influence on the course of hydrogen transfer, reaction (2.21), but it does influence the course of the decomposition reactions (2.22) and (2.23). In the presence of a greater number of thiyl radicals in the decomposition of hexyl, pentyl, butyl and butenyl radicals, the cleavage of C—H bonds according to reaction (2.22) is favored over the cleavage of C—C bonds according to reaction (2.23).

$$R_n^{\cdot} + R_2^{\cdot} \rightarrow \text{1-alkene} + R_2H \qquad (2.22)$$

$$R_n^{\cdot} = \text{1-hexyl-, 1-pentyl-, 1-butyl radical}$$

$$R_n^{\cdot} \rightarrow R_{n-2}^{\cdot} + C_2H_4 \qquad (2.23)$$

This is obviously connected with the energy required for abstracting a hydrogen atom from the hydrocarbon radical in reaction (2.22), which is about $167\,\text{kJ}\cdot\text{mol}^{-1}$ while the dissociation energy of the C—H bond in heptane decomposing according to reaction (2.21) is in the range $372\text{–}422\ \text{kJ}\cdot\text{mol}^{-1}$. The decrease in the decomposition of radicals according to reaction (2.23) in comparison with the decomposition reaction (2.22) is also seen in the decrease of the total number of moles of hydrocarbon products per mole of decomposed heptane (Table 15). An increase of the dibenzyl sulfide content causes a decrease in the number of the consecutive radical decomposition steps per molecule of decomposing reactant.

The same effect as dibenzyl disulfide on thermal decomposition has also elemental sulfur (Table 10): first, with increasing concentration decreases the selectivity with respect to methane, ethane, ethylene; second, the formation of l-alkenes C_4 to C_6 and 1,3-butadiene is favored and, third, the overall rate of decomposition increases and does not change with the concentration of elemental sulfur[10]. On the basis of similar dependences, it is possible also in the case of elemental sulfur to assume the course of reactions (2.21), (2.22), (2.23) in such a manner, that the role of $R_2^{\cdot}$ radicals also can be played by molecular sulfur S_2, atomic sulfur S and $^{\cdot}$SH radicals.

Table 15. The influence of dibenzyl sulfide on the product composition in the pyrolysis of heptane at 700 °C (mole/100 mole of heptane decomposed)[14]

Dibenzyl sulfide, % by mass	0	0.1	0.5	1.0
Conversion	17.5	16.5	16.1	16.7
M. B. % by mass	100.5	97.9	102.0	100.9
Methane	47.8	41.4	31.5	37.8
Ethane	13.0	10.8	10.9	8.5
Ethene	147.3	145.8	135.3	128.3
Propene	39.5	41.5	37.8	37.1
1-Butene	20.6	21.4	25.1	24.1
1,3-Butadiene	1.9	2.1	3.3	3.1
1-Pentene	10.3	12.8	13.7	13.8
1-Hexene	5.7	5.0	7.6	7.8
Total hydrocarbon	289.7	287.6	261.8	255.6

Mass ratio steam to heptane: 3.0

A decrease in selectivity of methane, ethane and ethylene formation was also observed by Rebick[104] in the pyrolysis of hexadecane in the presence of hydrogen sulfide. Unlike our results it was found that with increasing concentration of H_2S butane and higher alkanes are formed, and the overall rate of decomposition increases. The probable cause is the different influence of dibenzyl sulfide and elemental sulfur on one hand, and hydrogen sulfide on the other, on the course of hydrogen transfer reactions which predominate in the radical mechanisms both from the point of view of reaction rate and selectivity. It can be assumed that with increasing concentration of sulfur additives in the feed, an increase occurs in the formation of benzyl and thiyl radicals in the reaction zone, giving rise to further characteristic reactions with compounds possessing π-bonds according to reaction (2.24)

$$R_2^{\cdot} + \pi\text{-system} \rightleftharpoons R_2\text{-radical adduct} \qquad (2.24)$$

Because among the olefinic reaction products, ethylene is found to be the main product, it is very probable that the diminished yield is caused by a greater participation of dibenzyl sulfide in reaction (2.24). This would result in the formation of adduct radicals from ethylene and benzyl and benzylthiyl radicals, respectively. These adduct radicals can either decompose by the reverse reaction to the original components or, in consecutive reactions, react with organosulfur compounds, which is proven by the presence of thiophene and methyl-, ethyl-, vinyl-, and benzothiophenes.

Thermal decomposition of sulfur compounds is, as a rule, always accompanied by the formation of hydrogen sulfide. This has also been verified in the pyrolysis of aromatic sulfides[41] and disulfides[83]. On this basis it is legitimate to assume that in the reaction zone an increased concentration of radicals $^{\cdot}SH$ exists, either as intermediate products in the formation of hydrogen sulfide or from the decomposition reaction of hydrogen sulfide (2.3). Atomic sulfur is also formed. $^{\cdot}SH$ radicals or S atoms can react not only with heptane according to reaction (2.21), but also enter into reactions with the metal surface of the reactor under formation of metal sulfides according to reaction (2.5).

The metal sulfides which are formed according to reaction (2.5) inhibit the course of the secondary reactions on the inner surface of the reactor as a result of which coke is formed in the pyrolysis of hydrocarbons.

2.2.5. Other sulfur compounds Compared with the decomposition of pure heptane, some of the sulfur compounds examined favor, while others retard the thermal decomposition. Among sulfur compounds which have an accelerating effect in the range from 5 to 17% are: didecyl sulfide, *p,p'*-dichlorodiphenyl disulfide, 1-butanethiol, *O,O*-di-(1-butyl) dithiophosphate zinc and carbon disulfide. A decrease of the heptane decomposition rate by 3 to 14% was observed in the presence of diethyl disulfide and of *O,O*-diethyl dithiophosphoric acid[16-19,20] (Table 16).

With increasing residence time the formation of ethylene, propene, and methane increases whereas that of 1-butene, 1-pentene, and 1-hexene decreases in the presence of didecyl sulfide, 1-butanethiol, *O,O*-diethyldithiophosphoric acid and *p,p'*-dichlorodiphenyl disulfide. This also holds for the pyrolysis of heptane in the presence of *O,O*-di-(1-butyl) dithiophosphate zinc with the exception of ethylene, where the selectivity does not change with residence time. Diethyl disulfide and carbon disulfide also cause very interesting effects. In pyrolysis in the presence of diethyl disulfide (Fig. 10) the

Table 16. The reactivity of sulfur compounds in the pyrolysis of heptane[16] at 700 °C. Mass ratio of steam to heptane: 3.0

Additive	Amount, % by mass	k, s^{-1}	k/k°
1. *p,p*'-Dichlorodiphenyl disulfide	0.25	4.2	1.17
2. *O,O*-Di-(1-butyl) dithiophosphate zinc	1.0	4.0	1.11
3. Carbon disulfide	0.1	3.9	1.08
4. Di-(1-decyl) sulfide	1.0	3.8	1.06
5. 1-Butanethiol	1.0	3.8	1.06
6. Diethyl disulfide	1.0	3.5	0.97
7. *O,O*-Diethyl dithiophosphoric acid	1.0	3.1	0.86

k° = rate constant of pure heptane conversion[6]

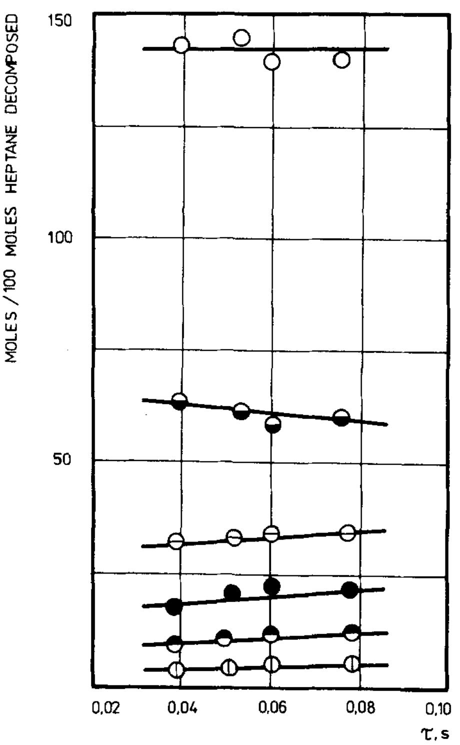


Figure 10. Effect of residence time on the formation of products during the pyrolysis of heptane at 700 °C in the presence of 1% by mass diethyl disulfide: ○ ethylene; ◒ methane; ⊖ propene; ● 1-butene; ◓ 1-pentene; ⦶ 1-hexene[16]; *mass ratio of steam to hexane: 3.*

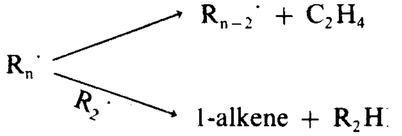
amount of ethylene does not change with residence time, the methane level decreases and the selectivity for 1-butene, 1-pentene and 1-hexene increases, which is a little surprising in view of the effects of sulfur[10], dibenzyl sulfide, dibenzyl disulfide, and thiophene[11]. In the case of carbon disulfide, in a linear dependence, the yield of ethylene increases markedly, while the yields of methane, propene and of the 1-alkanes C_4-C_6 decrease.

Compared to the pyrolysis of pure heptane, the decomposition to ethylene in the presence of diethyl disulfide, *p,p'*-dichlorodiphenyl sulfide is more selective in the whole range of residence times. At shorter residence times it is the same as in thermal decomposition in the presence of *O,O*-diethyl dithiophosphoric acid, *O,O*-di-(1-butyl) dithiophospate zinc and 1-butanethiol. With longer residence times the selectivity to ethylene is less pronounced than in their abscence.

The dissociation energy of C—S and S—S bonds is in most cases lower than that of hydrocarbon bonds[37] (Table 2). By thermal decomposition of sulfur compounds are formed thiyl radicals in which the sulfur atoms carry a substituent. Among the most common thiyl radicals are those in which carbon is bonded to sulfur.

In the same way as dibenzyl sulfide and dibenzyl disulfide[14] exert their initiation effects so does also *p,p'*-dichlorodiphenyl disulfide. This is so because *p*-chlorophenylthiyl radicals, thanks to the relatively low dissociation energy of S—S bonds ($230\,kJ \cdot mol^{-1}$) are easily generated. The rate constant increase of 19% is more than twice than that obtained with dibenzyl disulfide, the selectivity of the conversion to ethylene being the same.

In dialkyl sulfides the dissociation energy of the C—S bond is $226\,kJ \cdot mol^{-1}$. This could make diethyl disulfide an excellent initiator which, upon thermal decomposition, could give a substantial amount of ethyldithiyl radicals. Against this expectation diethyl disulfide is a disappointment. Not only does it not accelerate the thermal decomposition of heptane, but, on the contrary, it rather causes retardation. On the other hand, the selectivity to ethylene is high with a balanced dependence on the residence time. In contrast to other sulfur compounds with the same dependence, diethyl disulfide increases the yields of 1-butene, 1-pentene, and 1-hexene (Fig. 10). That means that with increasing severity of pyrolysis, the decomposition of C_4 to C_6 α-radicals to ethylene in the presence of ethylthiyl radicals takes place at a constant rate (2.25a), while the rate of decomposition and of the abstraction of a hydrogen radical according to reaction (2.25b) with the formation of l-alkenes increases.



$$R_n^{\cdot} \longrightarrow R_{n-2}^{\cdot} + C_2H_4 \qquad (2.25a)$$

$$R_n^{\cdot} \xrightarrow{R_2^{\cdot}} \text{1-alkene} + R_2H \qquad (2.25b)$$

$R_n^{\cdot}$ = 1-hexyl, 1-pentyl, 1-butyl radical

$R_2^{\cdot} = C_2H_5S{-}S^{\cdot};\ C_2H_5S^{\cdot}$

It is noteworthy that ethylthiyl and ethyldithiyl radicals exhibit marked fission and especially dehydrogenation properties only after the thermal initiation of the reactant to radical.

Although dialkyl sulfides have a higher dissociation energy of their C—S bonds

(309.3.3 kJ·mol^{-1}) than the corresponding disulfides, di-(l-decyl) sulfide has an initiating effect on the decomposition of heptane due to reaction (2.21). In comparison with the pyrolysis of pure heptane, the decomposition proceeds 5.6% faster than in its absence. Similar effects as di-(l-decyl) sulfide has also l-butanethiol in the decomposition of heptane. An increase of the pyrolysis rate by 5.6% is evidently due to the similarity of the dissociation energy of the C—S bonds (228.4 kJ·mol^{-1}) in thiols and that in dialkyl sulfides. While the heptane pyrolysis rates in the presence of di-(1-decyl) sulfide and 1-butanethiol are equal, the selectivity for ethylene is less in the latter case.

O,O-Diethyl dithiophosphoric acid and *O,O*-di-(1-butyl) dithiophosphate zinc are compounds containing both organic (alkoxy, RO) and inorganic (sulfur, phosphorus, zinc) components. In thermal decomposition at temperatures 200 °C and higher, are formed as typical decomposition products alkenes, thiols, sulfides, disulfides, and hydrogen sulfide, that is, compounds which are, under the conditions of the decomposition, in the gaseous phase. Liquid and solid products are also formed. The solid residue has rather the character of an inorganic compound, the liquid products contain mainly alkyl esters of mono- through tetrathiophosphoric acid[15,79].

On the basis of such a rich spectrum of decomposition products of dialkyl dithiophosphates an unequivocal effect on the pyrolysis of heptane cannot be expected. This applies to *O,O*-diethyl dithiophosphoric acid and *O,O*-di-(1-butyl) dithiophosphate zinc, the former possessing a retarding and the latter an initiating effect.The two dialkyl dithiophosphates which were studied are comparable as far as the selectivity to ethylene is concerned.

Carbon disulfide belongs to the simplest compounds in which sulfur is bonded to carbon by a double bond. The dissociation energy of the C=S bond, 432.2 kJ·mol^{-1}, exceeds that of the C—H bonds of hydrocarbons. In spite of this, the pyrolysis of heptane is 8.3% favored by carbon disulfide.

The reactivity of diethyl disulfide and diethyl dithiophosphoric acid can be seen in the retardation of heptane pyrolysis. In the thermal decomposition of these sulfur compounds a characteristic feature is the possibility of the formation of, besides thiyl radicals, also ethyl radicals. Ethyl radicals probably enter into termination reactions either directly with the most reactive radicals, such as hydrogen and methyl, with the formation of ethane and propane, or, more advantageously, indirectly through the reaction, where ethyl radicals form ethylene and atomic hydrogen which take part in the termination reactions[9]. Similar effects have also ethyl radicals which are formed in the thermal decomposition of diethyl ether[33]. In the conversion of radicals, ethyl radicals in this manner expel highly reactive hydrogen and methyl radicals which then are missing in the initiation of the reactant, which can be seen in the retardation of the hydrocarbon conversion.

An unequivocal influence of the investigated sulfur compounds was observed in the inhibition of coke formation[17]. 1-Butanethiol (Table 17), *O,O*-di-(1-butyl) dithiophosphate zinc, *O,O*-diethyl dithiophosphoric acid and carbon disulfide (Fig. 11) retard the formation of coke in the pyrolysis of reformer raffinate in a similar way as elemental sulfur[10], thiophene[11], dibenzyl sulfide and dibenzyl disulfide[14]. With increasing content of 1-butanethiol in the hydrocarbon feed the amount of the deposited coke decreases (Table 17). This can be explained in such a way that the same sulfur-containing decomposition or intermediate product is formed, and this product then suppresses the

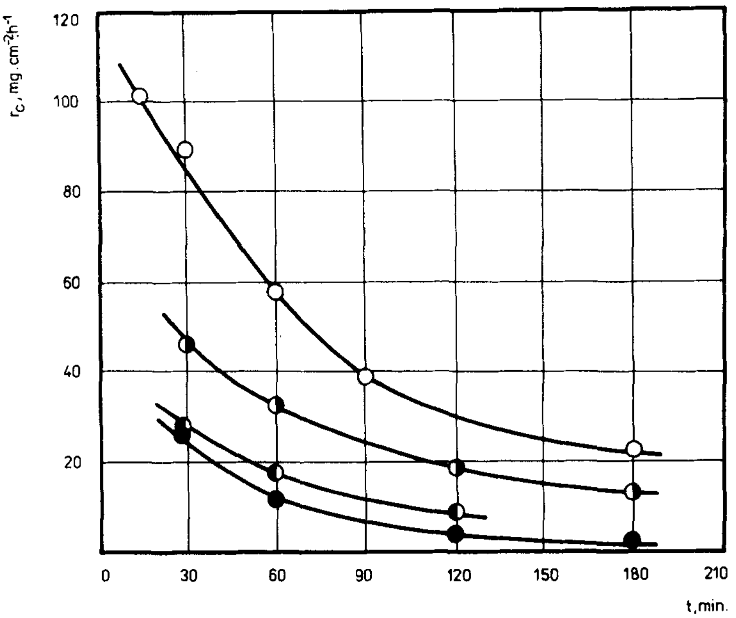


Figure 11. Coking rate dependence on the experiment duration for the pyrolysis of a reformer raffinate without inert diluent in the absence of sulfur compounds ○ and in the presence of ◑ 0.1% by mass 1-butanethiol; ◐ 0.5% by mass 1-butanethiol; ● 0.1% by mass carbon disulfide[17]. Temperature: 820 °C; residence time: 0.25 s.

Table 17. The inhibitory effect of 1-butanethiol on coking[20] of reformer raffinate at pyrolysis without inert diluent.

Additive	k_c at 820 °C
Without additive	$2.948 \cdot 10^{-2}$
0.1 % by mass of 1-butanethiol	$0.618 \cdot 10^{-2}$
0.5 % by mass of 1-butanethiol	$0.5735 \cdot 10^{-2}$

coke formation regardless of the properties of the initial sulfur compound added. This product, which is always formed during the thermal decomposition of sulfur compounds, could be hydrogen sulfide. Thiyl radicals $^{\cdot}SH$ as reaction intermediates play a decisive part in the formation of hydrogen sulfide. These radicals are most easily formed by fission of alkanethiols[2,131], according to reaction (2.26). The decomposition of 1-butanethiol at 697–762 °C is by this radical mechanism according to reaction (2.26)

$$1\text{-}C_4H_9\text{-}SH \rightarrow C_4H_9^{\cdot} + {}^{\cdot}SH \rightarrow C_2H_5CH{=}CH_2 + H_2S \qquad (2.26)$$

which is first-order[34]. The amount of eliminated hydrogen sulfide increases in the following order: 1-butanethiol < 2-butanethiol < 2-methyl-2-propanethiol[130]. Alkylthiols occur as the profiling reaction products even in the thermal decomposition of dialkyl dithiophosphates[48,73]. In a study of *O*,*O*-bis-(2-ethylhexyl) dithiophosphate zinc by means of pyrolysis gas chromatography, octanethiol isomers and octenes were the main fragmentation products[107], no dialkyl sulfides or disulfides were identified. Thiyl radicals can, under pyrolysis conditions also be formed by the decomposition of hydrogen sulfide in the presence of hydrogen radicals according to reaction (2.4). In the decomposition of hydrogen sulfide with elemental sulfur S or paramagnetic S_2 are formed especially at 2700–3800 K[105] and at low concentrations of hydrogen sulfide in the reaction mixture. The $HS^\cdot$ radicals, S and S_2 can enter either into gas phase reactions or into reactions with the metal surface of the reactor with the formation of metal sulfides. According to present-day knowledge, secondary reactions take place as a result of which pyrolytic carbon is formed, both in the gaseous phase and on the inner surface of the reactor. Thiyl radicals $RS^\cdot$ in the gaseous phase can capture active hydrocarbon radicals according to the combination reaction (2.27) and the addition reaction (2.24) as a consequence of which they prevent the formation of coke precursors. Such a course of events is supported by the fact that pyrolysis in the presence of sulfur compounds leads to stable sulfur compounds such as thiophene, 2- and 3-methylthiophene, 2- and 3-ethylthiophene, 2- and 3-vinylthiophene, and benzothiophene.

$$RS^\cdot + R'^\cdot \rightleftharpoons RSR' \qquad (2.27)$$

The main effect of thiyl radicals and elemental sulfur (S, S_2) is their reaction with the metal surface to form a layer of metal sulfides. Metal sulfides inhibit the course of secondary reactions as a consequence of which pyrolytic carbon, in the form of coke, deposits on the inner surface of the reactor. Because of the high efficiency of *O*,*O*-diethyl dithiophosphoric acid and *O*,*O*-di-(1-butyl) dithiophosphate zinc in suppressing coke formation in comparison with other sulfur compounds it can be inferred that the formation of thiophosphoryl intermediates can play a part in the reaction with the metal surface inasmuch as these intermediates can give phosphides which possess a passivating effect.

2.3. *Pyrolysis of petroleum factors in the presence of elemental sulfur*

An increase of the conversion of a kerosene fraction to gaseous pyrolysis products can be achieved by the addition of elemental sulfur or sulfur compounds (Table 18). Moreover, the conversion of hydrocarbons to pyrolytic carbon is largely prevented so that it does not deposit appreciably in the form of coke on the inner surface of the pyrolysis equipment[28].

In the reaction of steam with coke to carbon monoxide and hydrogen, or with precursors of coke (higher polyaromatics, polyalkenes) in the pyrolysis of a hydrogenated fraction 160–280 °C a decisive role is played by the nature of the inner surface of the metal reactor. From Table 19 it can be seen that the formation of carbon monoxide is favored by stainless steel or metal oxides, the formation of which in the presence of steam cannot be excluded. The passivation of the metal surface by hydrogen sulfide before pyrolysis prevents the formation of carbon monoxide. Hydrogen sulfide reacts with surface atoms to metal sulfides (reaction 2.5) which form a protective layer and thus prevent the formation of carbon monoxide. By passivating the inner surface of the reactor by hydrogen sulfide before the pyrolysis of the hydrogenated fraction 160–280 °C or by pyrolysis in the presence of elemental sulfur it is possible to effectively inhibit the formation of carbon monoxide (Tables 18 and 19). At the same time the gradually decreases. The course of coking points to the fact that at the beginning of the

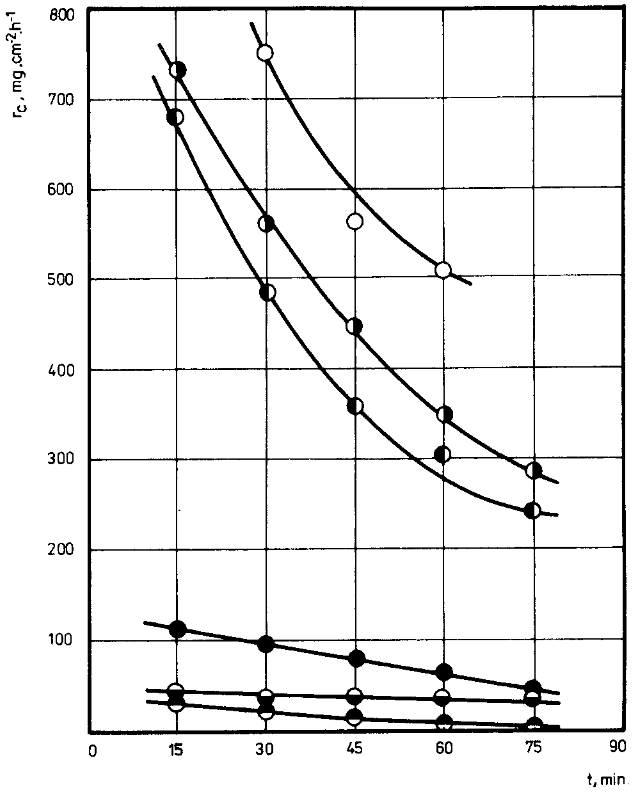


Figure 12. Rate of coke formation during the pyrolysis[13] of ● primary kerosine, temperature 800 °C, residence time: 0.25 s.; ◑ hydrogenated kerosine, temperature 800 °C, residence time 0.33 s.; ○ hydrotreated kerosene, temperature: 810 °C, residence time: 0.34 s.; ◐ hydrogenated fraction 160–280, temperature 810 °C, residence time: 0.41 s.; ◒ hydrogenated kerosine + 0.05% by mass sulphur, temperature 810 °C, residence time: 0.41 s; ◓ hydrogenated fraction 160–280 + 0.05% by mass sulfur, temperature: 810 °C,

formation of aromatics increases which can be deduced that not only coke, but also aromatic hydrocarbons can react with steam to carbon oxides.

The coke formation in the pyrolysis of hydrocarbon feedstocks is a serious problem which can, in many ways, be a limiting factor. This is especially valid for the pyrolysis of hydrotreated feedstocks[64,13,30,31,32]. The study of coking in the pyrolysis of hydrotreated feedstocks shows that the coke formation is enhanced as compared to primary feeds[13] (Table 20). From Fig. 12 it can be seen that the rate of coking is highest at the beginning of the experiment and that with the duration of the experiment it gradually decreases. The course of coking points to the fact that at the beginning of the experiment the influence of the inner surface is decisive on the course of the reaction as a consequence of which coke is formed in the pyrolysis of kerosenes.

Addition of elemental sulfur to hydrotreated feeds results in an unequivocal decrease of coking[64,13,30,31,32]. A retardation of the course of secondary reactions, as a result of which coke is formed, can be explained by the coating of the inner surface with a layer of metal sulfides which are formed by the reaction of elemental sulfur or ˙SH radicals with the stainless steel surface according to reaction (2.5) (Table 20).

Much research work is presently devoted to an increase in gas oil conversion, as well

Table 18. Pyrolysis of a kerosine fraction and of hydrotreated kerosines[13,28] at 800 °C. Mass ratio of steam to feedstock: 0.8

Characteristic	Feedstock Primary kerosine fraction		Hydrogenated kerosine	Dealkaned hydrogenated fraction	
Distillation range, °C	180–240		159–231	160–280	
Rel. mol. weight	170		153	179	
Content of aromatics, % by mass	19.1		2.9	3.8	
Additive to feedstock, % by mass					
Elemental sulfur	–	0.05	–	–	a
Yields (% by mass)					
Gases C_1–C_4	64.8	69.1	71.3	78.9	64.2
Methane	13.2	15.7	12.7	17.2	15.5
Ethylene	25.1	28.2	30.9	23.0	26.9
Propene	12.3	11.2	13.2	14.8	8.9
1,3-Butadiene	3.7	3.6	6.3	6.5	5.1
Benzene	2.3	2.7	2.0	0.9	4.8
Toluene	3.6	4.1	3.2	1.5	4.5
Styrene	2.1	2.0	1.5	0.5	2.5
Naphthalene	4.6	4.0	1.7	0.8	3.7
Carbon monoxide	–	–	0.4	10.4	0.3

[a] Passivation of reactor inner surface by hydrogen sulfide or by addition of elemental sulfur to feed.

Table 19. The formation of carbon monoxide and hydrogen in the pyrolysis of hydrogenated fraction 160–280 at 800 °C[13]. Mass ratio of steam to feedstock: 0.8

Without passivation Duration of exper. min.	Carbon monoxide, % by mass	Hydrogen, % by mass	Passivation with H_2S Duration of exper. min.	Carbon monoxide, % by mass	Hydrogen, % by mass
1	6.67	3.44	1	1.20	1.83
5	1.86	2.13	5	0.30	0.71
10	4.44	2.18	10	0.28	0.85
51	6.57	1.88	38	0.30	0.88
54	21.10	2.50	61	0.28	0.70
57	44.47	1.96			
62	19.14	2.41			

as to a decrease of pyrolysis oil and coke formation, because a marked increase in the formation of pyrolysis oil and coke in pyrolysis with simultaneously increased yields of the desired alkanes would result in a substantial improvement of the economic parameters. One of the possibilities of improving the selectivity of the radical process in the case of gas oil is pyrolysis in the presence of elemental sulfur[27]. A marked increase of conversion to gaseous pyrolysis products can be achieved in this way. Thus, for example, in the presence of 0.05% by mass of elemental sulfur, with the same selectivity, the yields of ethylene, propene, 1,3-butadiene, methane, and ethane are increased (Table 21). The monoxide is favored by stainless steel or metal oxides, the formation of which in the

Table 20. Coke formation in the pyrolysis of kerosines[13] without inert diluent.

Feedstock	k_c at 810 °C
Primary kerosene	$3.25\cdot10^{-2}$
Hydrofining kerosene	$35.58\cdot10^{-2}$
Hydrofining kerosene + 0.01% by mass sulfur	$12.45\cdot10^{-2}$
Hydrofining kerosene + 0.05% by mass sulfur	$8.56\cdot10^{-2}$

Table 21. Pyrolysis of primary gas oil[12] at 800 °C. Mass ratio of steam to feedstock: 0.8

Characteristic			
Distillation range (°C)		234–360	
Relative molecular weight		269	
Composition (% mass)			
Alkanes		54.3	
Cycloalkanes		21.2	
Aromatics		24.5	
Additive to feed (% by mass)			
Elemental sulfur	–		0.05
Yields (% by mass)			
Gases C_1–C_4	51.6		62.0
Methane	9.5		12.8
Ethylene	22.9		25.1
Propene	9.6		12.1
1,3-Butadiene	3.6		4.4
Benzene	6.8		5.0
Toluene	4.5		3.6
Styrene	1.9		1.5
Naphthalene	2.5		2.4

Table 22. Coke formation in the pyrolysis of gas oils[33] without inert diluent.

Feedstock	k_c at 770 °C
Primary gas oil (fraction 234–360 °C)	5.03
Primary gas oil + 0.05% by mass sulfur	4.66
Primary gas oil + 0.1% by mass sulfur	4.68
Hydrogenated gas oil (fraction 200–350 °C)	6.49
Hydrogenated gas oil + 0.05% by mass sulfur	3.16

presence of steam cannot be excluded. The passivation of the metal surface by hydrogen sulfide before pyrolysis prevents the formation of carbon monoxide. Hydrogen sulfide reacts with surface atoms to metal sulfides (reaction 2.5) which form a protective layer and thus prevent the formation of carbon monoxide. By passivating the inner surface of the reactor by hydrogen sulfide before the pyrolysis of the hydrogenated fraction 160–280° C or by pyrolysis in the presence of elemental sulfur it is possible to effectively inhibit the formation of carbon monoxide (Tables 18 and 19). At the same time the influence of elemental sulfur on the formation of low-molecular alkenes and alkanes is desired because it takes place at the expense of the liquid pyrolysis products[27]. At the same time there is a retardation of coke formation (Table 2.2).

Sulfur compounds which are present in primary crude oil fractions or added to the starting feeds undergo, under pyrolysis conditions, decomposition to gaseous, liquid and solid products. The quality and quantity of sulfur substances and the type of starting feedstock, together with the working conditions, in a decisive measure influence the distribution of sulfur in the products[33]. In the pyrolysis of primary crude oil fractions changing from naphtha (0.023% by mass S) through kerosenes (0.16% by mass S) to gas oils (0.70% by mass S) the content of sulfur gradually decreases in the gaseous products (naphtha 81.4% by mass, kerosene 55.5% by mass, gas oil 55.2% by mass S). The sulfur content in coke has a decreasing tendency (6.5%, 3.6% and 1.9% S by mass). On the other hand, going from light crude oil fractions to heavier ones, the sulfur content of the liquid pyrolysis products increases (32.5%, 34.4%, 55.2% S by mass)[33]. With increasing severity of pyrolysis, not only does the conversion to gaseous products increase, but also their sulfur contents increases. An addition of elemental sulfur of up to 0.1% by mass in principle does not influence the distribution of sulfur in the pyrolysis products.

In the pyrolysis of recycled oil from hydrocracking in the presence of 0.05% by mass of elemental sulfur there occurs an increase of conversion to gas pyrolysis products and at the same time an improvement of the selectivity for ethylene[32]. Elemental sulfur has the same effect in the pyrolysis of kerosenes and gas oils[27]. Also the formation of coke or carbon monoxide can be inhibited, either by passivation of the internal surface of the reactor by hydrogen sulfide or by dosing the starting feedstock with sulfur compounds. With respect to the dehydrogenation properties of elemental sulfur it is reasonable to assume the formation of $^{\cdot}SH$ radicals, and on the other hand, radicals arising from the hydrocarbon reactants. The fission of C—H bonds of the hydrocarbon molecules in kerosene, gas oil, or recycled oil from hydrocracking takes place by the action of paramagnetic S_2, most likely at the sites which are highly energy-consuming for the propagation of the hydrocarbon chain, with hydrocarbons and hydrogen radicals. The consecutive fragmentation of the radicals formed from feedstock molecules favors the decomposition to gas pyrolysis products.

3. TABLE OF SYMBOLS

S	inner surface of the reactor
V	reactor volume
V_R	equivalent reactor volume
X	conversion of reactant
k	first-order rate constant
ΔG_f^o	change of the standard free enthalpy of formation
ΔG_r^o	change of the standard free enthalpy of reaction
r_c	coking rate
k_o	rate constant of coke formation
c	reactant concentration
t	time of coking (time of experiment duration)
X_c	conversion of reactant to coke
k_c	coking coefficient
T.P.	temperature profile
M.B.	material balance
ASTM	American Society for Testing and Materials

ε relative volume change in the reactor
τ residence time
γ moles of product formed per mole of reactant decomposed

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