PYROLYSIS OF HYDROCARBONS IN THE PRESENCE OF ELEMENTAL SULFUR

Martin BAJUS and Václav VESELÝ

Department of Petroleum Chemistry and Technology,
Slovak Institute of Technology, 880 37 Bratislava

Received February 6th, 1979

The effect of elemental sulfur on the kinetics and selectivity of conversion of heptane was studied with regard to the inhibition of the coke formation during pyrolysis of raffinates from naphtha reforming. The experiments were conducted in stainless steel tubular through-flow reactors at atmospheric pressure. The heptane decomposition rate in the absence of sulfur was compared with that in the presence of 0·01, 0·02, and 0·1 wt.% sulfur at 700°C and with the steam-to-feed ratio 3 : 1. The influence of the inner surface of the reactor was investigated by using reactors with different equivalent volumes. The effect of sulfur on the coke formation during the pyrolysis of the reformer raffinate was examined at 820°C without any inert diluent.

The pyrolysis of individual hydrocarbons and of petroleum fractions proceeds in conditions where the rate and the selectivity of conversion to olefins are relatively low. Among the unwanted products are methane, pyrolytic oil, pitch, and coke. While methane is formed predominantly by primary reactions, heavy liquid pyrolytic fractions, pitch, coke, and carbon oxides are created through secondary reactions, proceeding in the multicomponent highly reactive system of olefinic-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 anomalous; one of the reasons of this are the different reactor surface-to-volume ratios.

One of the feasible ways to improve the production of lower olefins 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 feeds of different properties. Such compounds (initiators, catalysts, activators, promotors) of homogeneous or heterogeneous nature that affect favourably 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 organic nitrogen, oxygen, sulfur, and phosphorus derivatives. Sulfur-based additions can in various ways affect the process favourably or unfavourably. A bonus of sulfur compounds is that they are added to the system in low concentrations, several times lower than other additions. In 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, depreciates 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. Sulfur added to the system, either directly or bonded in thermally unstable compounds, inhibits or retards the formation of carbon monoxide and metal carbides[1]. The inhibiting effect of sulfur compounds shows up also during the formation of the carbon created in the bulk phases as well as on the wall of the reactor[2,3]. Some sulfur compounds exhibit dehydrogenation activity, resulting in better yields of the desired olefins[4]. Low-molecular mercaptans are employed also as promotors of the cracking of methylpentenes to isoprene[5].

In the present work, we give the results obtained in conditions of medium temperature pyrolysis of hydrocarbons predominantly to ethylene in the presence of elemental sulfur in reactors with increased inner surface, for a study of the kinetics of the process, the composition of the reaction products, and formation of coke.

EXPERIMENTAL

The pyrolysis equipment was of the through-flow type. The reactor used was made of stainless steel and was the "tube-in-tube" type. The inner surface-to-volume ratio was 6·65 cm^{-1}. The chemical composition of the construction material denoted Reactor 1 is given in Table I. The experimental pyrolysis apparatus and the working procedure have been described in detail in our previous papers[6,7]. The pyrolysis products were analyzed by gas chromatography[6].

TABLE I

Chemical Composition of the Construction Material of the Pyrolysis Reactors (wt.%)

Element	Reactor 1	Reactor 2
	Chemical analysis	
Cr	16·82	17·46
Ni	10·67	9·40
Mo	0·25	0·15
Mn	1·10	0·70
Si	0·40	0·76
C	0·085	0·18
	Spectral analysis	
Ti	0·5	0·5
V	0·1	0·1
Al	0·2	0·2
Cu	0·2	0·2
W	present	present

The apparatus for the study of the coke formation was represented by the pyrolysis equipment shown schematically in Fig. 1. The **U**-shaped stainless steel reactor possessed the inner diameter 0·6 cm and inner surface-to-volume ratio 6·66 cm^{-1}. The chemical analysis of the material is given in Table I under the heading Reactor 2. The starting material reservoir was represented by a glass burette fitted at the bottom with a three-way cock. A thinner calibrated burette served for the dosing of the material into the reactor. Continuous dosing was provided by a micropump MC-706 (Mikrotechna Prague). The starting material was evaporated in a preheater at 400°C. The reaction products were fed through a cooler into a separator, and after further cooling were frozen out at —18°C. The reaction tube was placed in a furnace allowing it to be heated up to 1 200°C; the temperature was monitored by means of a Pt–Rh/Pt thermocouple with the accuracy of ± 2°C. The temperature in the preheater and in the pyrolysis furnace was controlled by using a regulator TRS-12 (Závody průmyslové automatizace, Jinonice). All experiments were conducted at atmospheric pressure. The valve V and the junction points 12 (Fig. 1) served for the isolation and dismantling of the reactor out of the through-flow system after the finishing of the experiment so that neither the reactants nor air could enter the reactor during the cooling period.

Working procedure. The pyrolysis apparatus was employed for measuring the amount of the coke that had deposited inside the reactor during the experiment. The reaction tube was weighed and mounted into the through-flow system. The apparatus was flushed with nitrogen and checked for leaks. During the 40 min heating, nitrogen was passed through the system to ensure that air was removed and the atmosphere was inert. After the temperature became steady inside the reactor and the preheater, the starting material was supplied. Simultaneously, a stop watch was started up to measure the experiment duration. The supply of the first batches of the starting material resulted in an approximately 10°C decrease of the temperature; this had been taken into account during the heating of the reactor. After a preselected period, the material supply and the heating were stopped, and the valve for the nitrogen inlet into the pyrolysis system was opened. Under constant nitrogen feed, the reactor was disconnected from the preheater and the cooler, and was rapidly closed with sealing screws to prevent air inlet into the reaction space. After cooling, the reactor was carefully taken out of the pyrolysis furnace and weighed. The weight increment was taken as the amount of coke formed during the experiment in question.

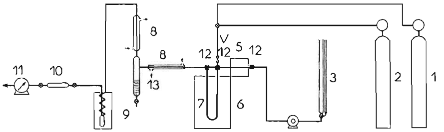

FIG. 1

Experimental Equipment

1 Nitrogen pressure bottle, 2 air pressure bottle, 3 raw material reservoir, 4 proportioning pump, 5 preheater, 6 pyrolysis furnace, 7 reactor, 8 water cooler, 9 freezing trap, 10 gas sample container, 11 gas flow meter, 12 junction points, 13 separator, V valve.

For the results to be reproducible, in was not only necessary to conduct the experiments in identical conditions, such as the temperature, material supply, and pressure; of prime importance was the procedure for the regeneration of the reactor whose inner surface was covered with coke. The carbonaceous sediments were removed from the reactor by burning using air of the temperature 800—850°C; this procedure lasted 15 to 60 min, occasionally longer. The problem is that the combustion is accompanied by oxidation of the inner surface of the reactor, which results in a poorer measurement reproducibility; this topic will be the subject of our forthcoming publication.

Starting materials. Heptane (Loba-Chemie, Wien), purity 99·69% was used for the study of the kinetics of conversion.

The coke formation was examined during the pyrolysis of the raffinates obtained from the catalytic reforming of naphtha after the extraction of aromatics from Slovnaft, Bratislava, with the following characteristics: density 699 kg m^{-3}, distillation limits 27 to 156°C, composition (wt.%): n-alkanes 18·8, isoalkanes 60·4, cycloalkanes 10·3, aromatics 6·0, unidentified products 4·5.

RESULTS AND DISCUSSION

The reaction conditions and kind of the starting material along with the character of the inner surface of the reaction system have a bearing on the kinetic parameters of the thermal decomposition of hydrocarbons and on the quantitative as well as qualitative composition of the reaction products. The aim of this work was to seek how elemental sulfur affects the kinetics of the hydrocarbon pyrolysis and the yields of not only the gaseous and liquid pyrolysis products, but particularly of the solid products (coke). To make the properties of the inner surface show up, reactors with enhanced inner surface – small diameter ones in the "tube-in-tube" arrangement – were used for the experiments. Taking into account our previous results[6], we studied the effect of elemental sulfur on the conversion of heptane. The formation of coke was studied during the pyrolysis of the reformer raffinates.

Coke Formation

The inner surface area does not alter during the experiment, but on the wall of the reactor and in its neighbourhood qualitative changes occur as the pyrolytic carbon deposits there in the form of coke. After each experiment, this coke was removed from the reaction tube by burning with air. The amount of coke created during the pyrolysis of the reformer raffinates increased after each burning (by activation) of the reactor with air or oxygen. Fig. 2 shows that the coke formation rate did not attain a steady state value in the stainless steel reactor even after forty experiments. The coking rate was highest in the initial stage of the experiment; this implies that during the cyclic burning of the coke with air, the inner surface is activated with oxygen. This is in accordance with the results obtained for the pyrolysis of propane[8] and octane[9].

The coke formation is influenced not only by the number of activations (burnings), but also by the way of activation (treatment). In a new reactor without any activation the coke formation is low as compared with the yields obtained on activation with steam or long-term activation with acids (Table II). Thus the way, kind, and number of activations of the reactor inner surface prior to the experiment have a bearing on the coke formation during the pyrolysis. If reproducible results are to be obtained during the investigation of the effects of temperature, experiment duration, and residence time on the coke formation, identical, stabilized surface of the reactor must be available. A serious problem is here the formation of metal oxides at temperatures above 700°C during the burning of the coke. Shah and coworkers[9] suggest the application of an acid solution -3% HCl $+ 3\%$ H_2SO_4 – for the decomposition of the surface oxides. The surface treatment with the acids results in the dissolution of most if not all of the surface oxides; a fresh steel surface is thus obtained and the

TABLE II

Formation of Coke on the Activation with Steam and Long-Term Activation with Acids (HCl + + H_2SO_4)

Reactor surface	nonactivated		activated		
			with water	with acids	
Experiment duration, min	15	30	15	15	30
Residence time, s	1·03	0·98	0·95	0·95	0·95
Proportion of the liquid, wt.%	0·89	1·70	—	—	—
Proportion of coke, wt.%	0·14	0·31	2·71	1·61	2·70

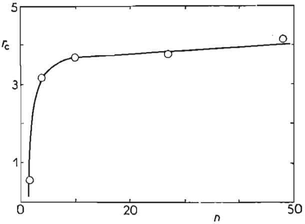

FIG. 2

Effect of the Number of Reactor Activations with Air on the Coke Formation Rate during the Pyrolysis of the Reformer Raffinates

Pyrolysis temperature 820°C, residence time 1 s, duration of the experiment 1 h.

measurement reproducibility improves considerably. This is evidenced by Fig. 3 presenting the results for two reactors of identical shape and material, obtained after a "stabilization" period. The maximum deviation in the coke amount for the two reactors is 10%, the maximum deviation for one reactor is below this value.

After the reactor stabilization, the experiments were carried out at the temperature 820°C and the residence time 1 s, the experiment duration being 15 to 180 min. The suppression of the coke formation was investigated by adding 0·1 or 0·05 wt. % elemental sulfur into the reformer raffinate. The results from the pyrolysis of both the pure reformer raffinate and the sulfur-containing raffinate are shown in Fig. 4. In the initial stage of the experiment without inhibitor, the coking proceeds with an enhanced rate. After a time period, a steady state is attained. The higher coking rate at the beginning is due to the effect of the reactor wall, which diminishes as the wall covers with coke. The elemental sulfur present in the hydrocarbon feed brings about a considerable decrease of the coke yield – after 180 min ten and twenty times for the concentrations of elemental sulfur 0·05 and 0·1%, respectively, as compared with the pure raffinate. A substantial difference is apparent between the data for the presence and absence of sulfur notably during the initial stage of coking; elemental sulfur depresses the coking rate particularly at the beginning of the experiment, when the effect of the inner surface on the coke formation is decisive. This suggests that sulfur reacts with the active surface sites with the formation of a protective film. Qualitative analysis[3] of the film created revealed the presence of metal sulfides. The coating was dark grey and covered not only the interior of the

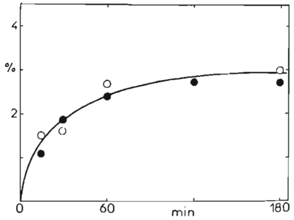

FIG. 3

Formation of Coke (wt.% of the raw material) during the Pyrolysis of the Reformer Raffinates

Temperature 820°C, residence time 1 s, in two stainless steel reactors of the same shape and made from the same material; ● reactor 1, ○ reactor 2.

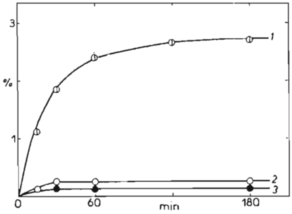

FIG. 4

Formation of Coke (wt.% of the raw material) during the Pyrolysis of the Reformer Raffinates

Temperature 820°C, residence time 1 s, *1* feed without the inhibitor, *3* feed with 0·1 wt.% sulfur, *2* feed with 0·05 wt.% sulfur.

reactor, but also the outlet closure and part of the cooler. During its burning, yellow-brown gases evolved. Perfect removing of the metal sulfides and restoration of the original surface by air burning and by means of acids is very difficult. The quality of the protective film depends 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 that passivates the inner reactor surface for some longer time even if feed without the inhibitor is subsequently supplied. Fig. 5 shows the results achieved during the pyrolysis of the reformer raffinate on a surface conventionally treated and on one coated with the sulfide layer created during the pyrolysis of the same feed containing 0·1 wt.% elemental sulfur. It follows from a comparison that the prior formed sulfide layer is capable of depressing the coking level within 120 min; after this period the effect of the protective film does not appear, because the protective layer is disturbed by the reaction products.

Kinetics of Decomposition

Our preceding paper[6] dealt with the study of the kinetics of heptane pyrolysis. The effect of elemental sulfur on the conversion of heptane was examined in the following reaction conditions: temperature 700°C, residence time 0·02 – 0·12 s, steam-to-hydrocarbon weight ratio 3 : 1. The temperature was monitored along the reactor. From the longitudinal temperature profile measured, the equivalent volume of the reactor V_R was calculated according to Hougen and Watson[10].

Fig. 6 shows two temperature profiles: the temperature profile I is broader and for

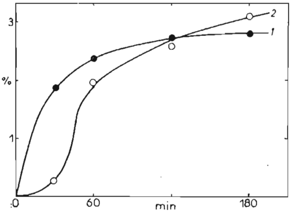

FIG. 5

Formation of Coke (wt.% of the raw material) during the Pyrolysis of the Reformer Raffinates

1 On pure reactor surface; 2 on a prior formed sulfide film, temperature 820° C, residence time 1 s.

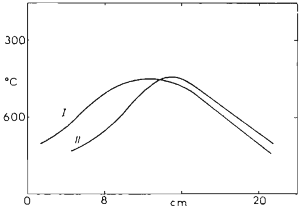

FIG. 6

Longitudinal Temperature Profiles of the Pyrolysis Reactor

Calculated V_R for the temperature profiles I and II 5—7 and 4—5 cm^3, respectively (Table III).

approximately this shape the equivalent volume of the reactor is 5 – 7 cm^3; the temperature profile II is narrower and the equivalent volume calculated from it lies in the range 4 – 5 cm^3. The equivalent volumes of the reactor in the experiments performed are given in Tables III and IV. The equivalent volume of a reactor is a quantity proportional to the equivalent surface of the reactor, as it is determined

TABLE III

Rate Constants of the Heptane Conversion at 700°C

Sulfur content wt.%	V_R cm^3	k_{anal} s^{-1}	Standard deviation %	k_{graph} s^{-1}
—	5·63	3·68	13·58	3·6
0·1	6·45	3·42	4·97	3·5
—	4·80	3·99	8·52	3·8
0·1	4·68	4·73	9·93	4·8
0·05	4·64	4·69	5·97	4·7
0·02	4·34	5·23	4·39	5·1

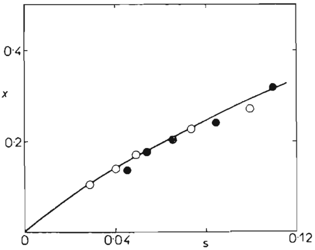

FIG. 7

Degree of Heptane Conversion (x) in Dependence on the Residence Time (τ) for the Temperature Profile I

○ In the absence of elemental sulfur, ● in the presence of 0·1 wt.% elemental sulfur.

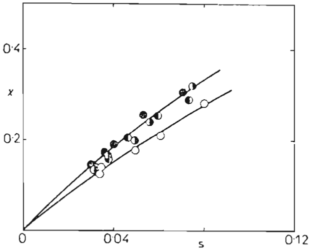

FIG. 8

Degree of Heptane Conversion (x) in Dependence on the Residence Time (τ) for the Temperature Profile *II*

Sulfur content (wt.%): ○ 0, ● 0·02, ◐ 0·05, ◑ 0·1.

for a tubular reactor of constant diameter. In other words, the effect of the equivalent volume represents that of the equivalent surface as well.

The dependence of the conversion of heptane on the residence time for different temperature profiles (Table III) for the cases of absence and presence of elemental sulfur is portrayed in Figs 7 and 8. An addition of 0·1 wt.% elemental sulfur to the starting hydrocarbon in the conditions of the temperature profile I virtually does not affect the conversion, in the range of lower equivalent reaction volumes (temperature profile II) elemental sulfur has a favourable effect on the heptane conversion (Fig. 8).

TABLE IV

Composition of the Products from the Pyrolysis of Heptane at 700°C (mol per 100 mol of decomposed heptane)

V_R, cm^3	6·38	6·38	4·25	4·92	4·60	4·63	4·66	4·51	4·42	4·46
Conversion, %	17·86	31·97	14·16	28·13	16·36	31·69	15·61	28·53	17·08	30·35
Sulfur content %	0·1	0·1	—	—	0·1	0·1	0·05	0·05	0·02	0·02
Hydrogen	57·84	25·16	33·44	42·13	31·93	34·25	42·52	31·47	37·51	39·52
Methane	61·52	58·48	53·31	51·56	41·47	47·56	48·46	41·55	40·79	41·75
Ethane	11·08	11·97	11·82	12·86	12·37	14·61	10·82	13·90	12·52	13·72
Ethene	136·53	155·94	145·74	147·49	134·46	150·63	129·98	142·72	139·85	152·36
Propane	1·11	1·12	1·26	1·18	1·12	1·08	1·13	1·18	1·35	1·32
Propene	39·47	39·51	37·92	41·05	39·79	41·77	42·55	43·87	43·50	44·88
Butane	0·40	0·39	0·70	0·56	0·31	0·33	0·22	0·33	0·27	0·19
1-Butene	22·24	18·86	19·92	15·76	21·60	17·33	21·85	19·40	20·66	19·00
trans-2-Butene	0·31	0·40	0·33	0·41	1·03	0·45	0·61	0·57	0·37	0·65
cis-1-Butene	0·21	0·32	0·31	0·33	0·83	0·52	0·11	0·52	0·44	0·65
1,3-Butadiene	2·06	2·88	2·12	2·38	2·66	3·38	2·46	3·44	2·13	2·97
3-Methyl-1-butene	0·22	0·24	0·26	0·18	0·49	0·30	0·42	0·26	0·44	0·22
1-Pentene	10·36	8·25	9·55	8·56	10·54	8·10	10·51	9·44	9·52	8·55
2-Methyl-1-butene	0·29	0·24	0·12	0·18	0·49	0·30	0·27	0·26	0·43	0·24
trans-2-Pentene	0·28	0·32	0·27	0·39	0·54	0·44	0·35	0·46	0·54	0·36
cis-2-Pentene	0·17	0·21	0·34	0·27	0·67	0·45	0·67	0·38	0·54	0·35
1-Hexene	5·48	3·71	5·28	4·84	5·87	4·52	5·75	4·88	6·32	4·23
1-Heptene	0·59	0·34	0·27	0·13	0·21	0·17	0·19	0·17	0·36	0·25
Carbon monoxide	9·84	18·73	14·77	22·03	9·54	10·62	8·55	9·07	4·15	4·62

The conversion of heptane is a first order reaction both in the presence and in the absence of elemental sulfur. The equation

$$k\tau = -(1 + \varepsilon)\ln(1 - x) - \varepsilon x \qquad (1)$$

was employed for the calculation of the rate constant. In Figs 9 and 10 the right side of this equation is plotted as a function of the residence time. The rate constants determined graphically and those calculated numerically are given in Table III. The maximum deviation of the numerically calculated values is 13·6%. Within this range of errors, the rate constants do not exhibit a decreasing trend with the proceeding conversion; thus the rate of the heptane pyrolysis is not retarded by the thermal decomposition products.

In a larger equivalent volume, the heptane conversion rates in the absence and in the presence of sulfur approach each other closely (Fig. 9), whereas if the pyrolysis is conducted in a smaller equivalent volume, elemental sufur promotes the thermal decomposition of heptane. In the concentration range 0·02–0·1 wt.% sulfur, the differences in the rates are negligible (Table III). In comparison with the pyrolysis without sulfur, the average rate constant determined from Fig. 10 ($k = 4{\cdot}85\ \mathrm{s}^{-1}$) is 27·6% higher.

Composition of the Reaction Products

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 25·3–28·6.

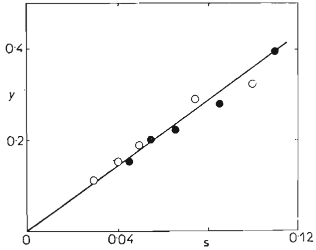

FIG. 9

Plot of the Rate Equation of the First Order for the Temperature Profile I

○ In the absence of sulfur, ● in the presence of 0·05 wt.% sulfur; y denotes the right side of Eq. (*1*).

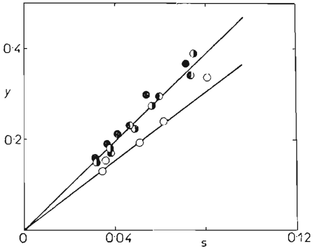

FIG. 10

Plot of the Rate Equation of the First Order

Sulfur content (wt.%): ○ 0, ● 0·02, ◐ 0·05, ◐ 0·1; y denotes the right side of Eq. (*1*).

The amount of the pyrolysis gas grows with increasing conversion. The differences between the yields for a conversion with different sulfur contents in the feed are negligible for both temperature profiles (Fig. 11). The qualitative and quantitative analysis of the gaseous and liquid products of the heptane pyrolysis is given in Table IV; the qualitative composition of the products is affected neither by elemental sulfur nor by the shape of the temperature profile. The dominant decomposition product is ethylene. Among other significant components are methane, propylene, 1-butene, 1-pentene, 1-hexene, hydrogen, and carbon monoxide. The conversion of heptane and the yields of the products are substantially affected by the temperature, residence time, temperature profile of the longitudinal reactor, and presence of sulfur. The effect of temperature and residence time has been examined in detail[6] for the pyrolysis of pure heptane in conditions of the temperature profile I. The effect of the temperature profiles I and II on the yields of ethylene, methane, and carbon monoxide is depicted in Fig. 12.

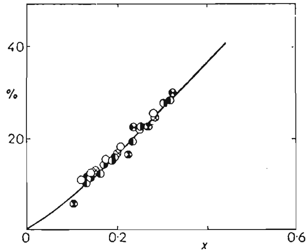

FIG. 11

Formation of Gas (wt.% of the starting material) as a Function of the Heptane Conversion (x) for Various Contents of Elemental Sulfur

Temperature profile I, the point with full × vertical without sulfur, dtto — horizontal 0·1% sulfur; temperature profile II, sulfur content (wt.%): ○ 0, ◑ 0·02, ⊗ 0·05, ◐ 0·1.

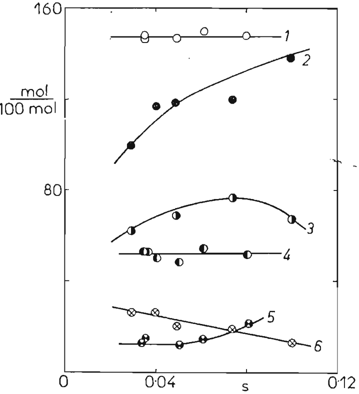

FIG. 12

Contents of the Products (mol per 100 mol of the reacted heptane) in Dependence on the Heptane Residence Time at 700°C

Temperature profile I: *1* ethylene, *3* methane, *6* carbon monoxide; temperature profile II: *2* ethylene, *4* methane, *5* carbon monoxide.

Within the time interval examined, more ethylene and less ethane and carbon monoxide are formed in the smaller reaction equivalent volume (temperature profile II) than in the larger equivalent volume (temperature profile I). In the temperature profile II the yields of these products do not change if the residence time is prolonged, whereas in the conditions of the temperature profile I the yields of ethylene increase, of carbon monoxide decrease, and those of methane pass through a maximum. The differences in the yields of propene, 1-butene, 1-pentene, and 1-hexene are negligible.

The effect of the residence time on the selectivity of the heptane conversion for the two temperature profiles in the presence of elemental sulfur is shown in Figs 13 and 14. During the pyrolysis of heptane to which 0·1 wt.% sulfur had been added, very similar yields were obtained of ethene, propene, 1-butene, 1-pentene, and 1-hexene,

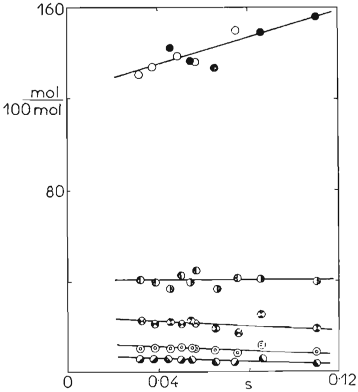

FIG. 13

Contents of the Products (mol per 100 mol of the reacted heptane) in Dependence on the Heptane Residence Time at 700°C in the Presence of 0·1 wt.% Sulfur

Temperature profile I: ● ethylene, ◑ propylene, the point with full × vertical 1-butene, ⊙ 1-pentene, ◒ 1-hexene; temperature profile II: ○ ethylene, ◐ propylene, the point with full × horizontal 1-butene, the point with double ring 1-pentene, ◔ 1-hexene.

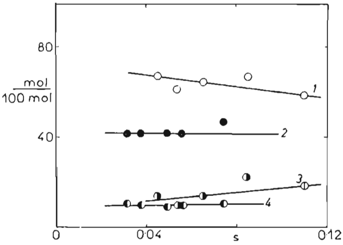

FIG. 14

Contents of the Products (mol per 100 mol of the reacted heptane) in Dependence on the Heptane Residence Time at 700°C in the Presence of 0·1 wt.% Elemental Sulfur

Temperature profile I: *1* methane, *3* carbon monoxide; temperature profile II: *2* methane, *4* carbon monoxide.

irrespective of the temperature profile shape. This is not the case with methane and carbon monoxide; here the situation is analogous to that with elemental sulfur being absent from heptane – in the temperature profile II the yields are lower (Fig. 14).

Reaction Mechanism

The thermal decomposition of hydrocarbons proceeds *via* a series of primary and secondary reactions, the latter being appreciably promoted by the inner surface of the reactor, contributing particularly to the formation of carbon, its oxides, hydrogen, and metal oxides and sulfides. The principal function of steam is to depress the partial pressure of the reacting components and thus to prevent the formation of high-molecular fractions resulting from condensation and polymerization reactions; however, the steam reacts partly with the carbon, with a participation of the reactor wall:

$$C + H_2O \rightarrow CO \quad (\text{or } CO_2) + H_2 . \tag{A}$$

Another part of the steam reacts with the inner surface of the reactor:

$$\text{metal} + H_2O \rightarrow \text{metal oxides} + H_2 . \tag{B}$$

During the burning with air of the carbon that is present as coke, metal oxides are formed similarly as with steam:

$$\text{metal} + O_2 \rightarrow \text{metal oxides} . \tag{C}$$

These metal oxides formed favour the secondary reactions, notably those leading to the formation of coke. Thus oxidants can on the one hand participate in the removing of coke, and on the other hand, create favourable conditions for its formation.

The secondary reactions can be well suppressed by adding elemental sulfur to the reacting system. A reaction is assumed to proceed between sulfur or its derivatives and the inner surface of the reactor:

$$\text{metal} + S \rightarrow \text{metal sulfides} . \tag{D}$$

The coke formation is several times diminished on the sulfur-deactivated surface. The sulfide film on the inner surface was formed and sustained by adding elemental sulfur to the feed. In fact, the sulfide formation according to the reaction (*D*) is considerably simplified, as sulfur can react with the starting hydrocarbons with the formation of hydrogen sulfide or sulfur derivatives even before entering the reaction zone of the reactor. Alkanes react with sulfur at temperatures that are the lower, the higher their molecular weight is and the more tertiary carbons they involve[11]. For example, the sulfur reaction with octane proceeds at 160°C and with light hydrocarbons up to C_6 at 210°C. Only a negligible fraction of the initial amount in the feed remains in the liquid product on the pyrolysis of heptane (Fig. 15), most of it leaves the pyrolysis reactor in the gaseous form, where hydrogen sulfide dominates alongside low-molecular mercaptans, sulfides, and disulfides. Hence, dehydrogenation reactions of sulfur prevail over the condensation ones. This is corroborated by the results given in Table V, showing the effect of concentration of elemental sulfur

TABLE V

Composition of the Heptane Pyrolysis Products at 700°C (mol per 100 mol of the reacted heptane)

Conversion, %	12·14	14·57	13·53	13·31	13·88	13·64
V_R, cm^3	4·80	4·34	4·64	4·68	5·63	6·45
Sulfur content, wt.%	—	0·02	0·05	0·1	—	0·1
Hydrogen	32·62	35·68	34·98	35·29	51·06	50·27
Methane	53·11	44·62	39·49	41·33	49·52	67·02
Ethene	148·01	136·22	128·83	130·44	116·65	142·42
Ethane	13·44	13·42	10·92	9·33	6·18	10·88
Propene	38·66	38·81	42·76	40·62	31·90	36·64
1-Butene	19·69	22·45	21·41	22·73	21·30	22·20
1,3-Butadiene	1·77	2·29	2·35	2·65	2·63	1·76
1-Pentene	8·88	10·77	12·13	10·57	13·03	9·92
1-Hexene	3·85	5·34	5·67	5·86	6·00	5·27
Carbon monoxide	12·89	4·04	9·29	10·84	26·10	13·50

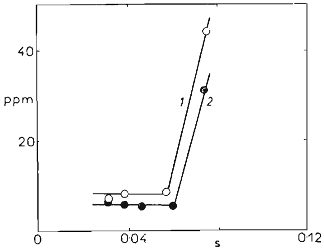

FIG. 15

Sulfur Content in the Liquid Products from the Pyrolysis of Heptane +0·1% wt.% Sulfur *1* and of Heptane +0·05 wt.% Sulfur *2*.

on the yields of some heptane pyrolysis products. The yields of 1,3-butadiene, 1-pentene, and 1-hexene grow with increasing concentration of sulfur in the feed.

From this it can be inferred that in the reaction zone, •SH radicals occur in an enhanced concentration, being formed either through dehydrogenation reactions of sulfur with the starting hydrocarbons:

$$C_7H_{16} + S \rightarrow C_7H_{15}\cdot + \cdot SH \tag{E}$$

or of sulfur with higher radicals such as butyl, pentyl, and hexyl, or by cleavage of the hydrogen sulfide formed:

$$H_2S \rightarrow \cdot SH + \cdot H \tag{F}$$

or by decomposition of low-molecular mercaptans.

The •SH radicals are therefore likely to enter reaction with the heterogeneous phase on which is formed a thin layer of metal sulfides. In the •SH radical form can sulfur be involved in the various steps of the radical decomposition also in the homogeneous phase, *e.g.*, during the initiation of the reactant according to the reaction (*G*). This is indicated by the increase of the rate and improvement of the selectivity of the heptane decomposition.

$$C_7H_{16} + \cdot SH \rightarrow C_7H_{15}\cdot + H_2S\,. \tag{G}$$

The favourable effect of sulfur — or the •SH radicals — on the heptane decomposition rate appears appreciably if the pyrolysis is accomplished in a reactor with a lower equivalent volume (Fig. 16). This is obviously associated with the radical conversion in the homogeneous phase, where the contribution of the •SH radicals

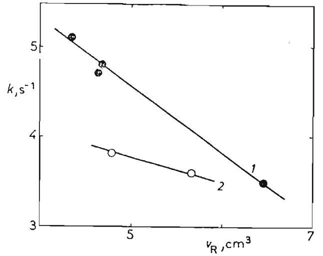

FIG. 16

Effect of the Equivalent Reaction Volume on the Heptane Conversion Rate in the Presence of Sulfur *1* and in the Absence of Sulfur 2 during the reactant initiation prevails over that of the reacting system's inner surface. This effect of the $\cdot$SH radicals has a decreasing tendency with the increasing equivalent volume of the reactor, which probably reflects the growing participation of secondary and termination reactions occurring on the reactor wall. In the conditions of smaller equivalent volume the selectivity to ethene is in the entire residence time interval examined higher than in a reactor with a larger equivalent volume. If, however, sulfur is present, these differences diminish, the ethene yields for a shorter residence time being below and for a longer residence time above the ethene level attained in the reactor with smaller equivalent volume. A larger equivalent volume of the reactor has a favourable effect on the formation of methane and carbon monoxide. This points to the fact that with a larger inner surface, methane is created not only through primary reactions, but also through secondary reactions leading to carbon, which in turn reacts with steam to give carbon monoxide. It should be borne in mind that carbon monoxide can form not only on the gasification of the solid pyrolysis products, but also from the gaseous pyrolysis products, such as methane and ethane[6]. Table V demonstrates that the formation of carbon monoxide is favoured by the inner surface and inhibited by elemental sulfur. The results obtained indicate that there exists a limiting concentration of sulfur in the feed, below which the formation of carbon monoxide is suppressed, and above which, on the other hand, the sulfur favours the creation of carbon monoxide, its level, however, being still lower than in the case that sulfur is absent from the system.

LIST OF SYMBOLS

k	rate constant, s^{-1}
n	number of experiments
r_c	coking rate, $\mu g\ s^{-1}\ cm^{-2}$
S	inner surface of the reactor, cm^2
t	experiment duration, min
T_R	reference temperature, K
V	volume of the reactor, cm^3
V_R	equivalent volume of the reactor calculated from the temperature profile according to Hougen and Watson[10], cm^3
x	degree of heptane conversion
ε	relative volume change in the reaction
τ	residence time, s

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Translated by P. Adámek.