

PYROLYSIS OF PRIMARY AND HYDROGENATED KEROSENES

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Dedicated to the Academician J. Mostecký on the occasion of his 60th birthday.

Pyrolysis of primary, hydrotreated and hydrogenated kerosene and hydrogenated fraction 160–280 after separation of alkanes was studied in a stainless steel tubular reactor at 800°C in the presence of steam. Pyrolysis of hydrogenated feedstocks leads to an increased conversion into low molecular olefins and alkanes. The presence of 0.05% of elemental sulphur increases the conversion of primary kerosene into gaseous pyrolysis products. The formation of carbon monoxide is inhibited by the passivation of the reactor wall with hydrogen sulphide. The effect of elemental sulphur on the formation of coke was investigated in the pyrolysis of kerosene in a stainless steel tubular reactor at 800 and 810°C without steam. In comparison with the pyrolysis of primary kerosene, hydrogenated materials are more inclined to form coke. In the presence of 0.05% sulphur coking decreases.

A lack of traditional feedstocks for pyrolysis is forcing processors in a greater measure to orient themselves to middle petroleum fractions (kerosenes, gas oils) and that in spite of the fact that the pyrolysis is more difficult. Most of the problems have to do with the composition of middle petroleum fractions where with rising boiling point the content of hydrogen or alkanes, which provide most olefins, decreases, and the content of aromatic hydrocarbons increases, which decompose to olefins only when they contain alkyls on aromatic nuclei. The condensed aromatics which, to a great extent, do not undergo decomposition, allow the formation of high molecular substances, pitch and coke by the condensation of high boiling fractions from pyrolysis in the effluent heat exchangers (TLE) and in the quench system.

The suitability of middle petroleum fractions as feedstocks for pyrolysis can be improved by removing aromatic hydrocarbons either by solvent extraction or by their transformation in a hydrogenation process in which polyaromatic compounds and cycloalkanes get saturated and cracked^{1–5}. The opposite process may also come into consideration, that is, the pyrolysis of alkanes isolated by separation on zeolitic adsorbents with refinery use of cycloalkanic and aromatic portions. In the pyrolysis of n-alkanes C₁₀–C₁₇ (with profiling representation C₁₂–C₁₆) at 820°C, 87% gaseous pyrolysis products were formed, which contained 42.3% ethylene and 15% propylene⁶. Besides the treatment of feedstocks where significant qualitative changes take place, optimal composition is also very important, for instance by specification of the distillation range of a petroleum fraction. Very attractive is also the treatment of starting materials by homogeneous additives which favorably influence the radical process of thermal

decomposition of hydrocarbons and, at the same time, decrease the formation of unwanted products. Among the compounds which have the ability to influence the radical process of thermal decomposition, some inorganic and organic derivatives of nitrogen, oxygen, sulphur and phosphorus are most effective. In our laboratory we have investigated the influence of sulphur compounds: elemental sulphur^{7,8,11}, thiophene⁹, dibenzyl sulphide and dibenzyl disulphide¹⁰ increase the rate of thermal decomposition of hydrocarbons and at the same time inhibit the formation of coke.

In this work we present the results from the pyrolysis of primary and hydrotreated middle petroleum fractions where, together with kinetic parameters, the influence of elemental sulphur and hydrogen sulphide on the formation of gaseous, liquid and solid pyrolysis products has been investigated.

EXPERIMENTAL

All experiments were performed in two flow apparatuses with stainless steel tubular reactors.

Kinetics and selectivity of the conversion of primary and hydrotreated feedstocks were studied in equipment described in detail earlier¹². The reactor is of the "tube-in-tube" type with a surface to volume (S/V) ratio of 6.65 cm^{-1} . The stainless steel used had the following composition (%): Cr 16.8; Ni 10.7; Mn 1.1; C 0.08. Pyrolysis of primary kerosene and hydrotreated materials was carried out in the presence of steam. The mass ratio of steam to feedstock was 0.75 and 0.8, the amount of the hydrocarbon material changed from 0.11 to 0.21 mol h^{-1} and the amount of water from 0.78 to 1.43 mol h^{-1} .

The formation of coke was studied in the flow equipment described previously⁷. The tubular reactor was of the U type, with $S/V = 6.66 \text{ cm}^{-1}$. The construction material was stainless steel (%): Cr 17.5; Ni 9.4; Mn 0.7; C 0.18. The pyrolysis was carried out without steam. The amount of coke formed was determined by weighing the reactor before and after the experiment. The yields of coke were determined with standard deviation of 5–12%.

The equivalent volume of the reactors was calculated from the temperature profile of the non-isothermal reactor. The residence times were determined as described previously¹².

The composition of the gaseous and liquid products was determined by gas chromatography as described previously^{7,12}. The yields of characteristic products were determined with standard deviation smaller than 1 per cent.

Feedstocks. Investigation was undertaken of the pyrolysis of primary and hydrotreated fractions within distillation range of kerosene. The characteristic properties of feedstocks employed are given in Table I. Kerosene and hydrotreated kerosene were obtained from Slovnaft Refinery. Hydrogenated kerosene was obtained by hydrogenation of primary kerosene in the presence of a bifunctional catalyst, palladium deposited on amorphous aluminosilicate. The hydrogenated fraction 160–280 was obtained by hydrogenation of the product from which alkanes had previously been separated by adsorption; for hydrogenation a catalyst was used in which palladium was deposited on amorphous aluminosilicate.

Comparison of primary and hydrotreated feedstock shows that under typical conditions of the hydrotreating process there occurs mainly desulphurization where the content of aromatics virtually unchanged. In the case of the hydrogenated kerosene and the fraction 160–280 not only the content of sulphur compounds but also of aromatic significantly decreases. The distillation range remains approximately the same.

TABLE I
Description and characteristic of investigated hydrocarbon fractions

No	Fraction	Origin	Distillation range, °C	Content		Relative molecular mass
				aromatics w. %	sulphur	
1	Kerosene	distillation of petroleum	154—235	17.1	0.15 w. %	145
2	Hydrotreated kerosene	hydrotreated on Co-Mo catalyst	154—235	16.6	48 ppm	148
3	Hydrogenated kerosene	hydrogenation on Pd/Al-Si catalyst	159—231	2.9	6.5 ppm	153
4	Hydrogenated fraction 160—280	after separation of alkanes by adsorption, the product was hydrogenated on Pf/Al-Si catalyst	160—280	3.8	2.0 ppm	179

RESULTS AND DISCUSSION

The pyrolysis of primary kerosene and hydrotreated materials took place under comparable reaction conditions: temperatures 800 and 810°C; weight ratio of steam to feedstock 0.75, 0.8 and residence time from 0.10 to 0.23 seconds. Coke formation was examined without the presence of steam.

The thermal decomposition under these conditions leads to gaseous and liquid products whose composition for primary kerosene pyrolyzed alone or in the presence of elemental sulphur is given in Table II. From primary kerosene, about 55% gaseous products are obtained, where the ethylene yield is around 22%. The influence of residence time on the formation of ethylene and butadiene for kerosenes is given in Fig. 1. In the pyrolysis of primary kerosene in the presence of 0.05% of elemental sulphur, there occurs an increase of conversion into gaseous pyrolysis products of about 13%. This effect of elemental sulphur reflects favourably also in the yields of ethylene (an increase of 16%) and propylene. A marked increase of conversion into gaseous pyrolysis products could be obtained even in the pyrolysis of gas oil in the presence of 0.05% of elemental sulphur¹¹. With preserved selectivity the yields of ethylene, propylene, 1,3-butadiene, methane and ethane have increased. The enhanced formation of low molecular olefins and alkanes takes place on account of liquid pyrolysis products.

On the basis of dehydrogenation properties of elemental sulphur, it is possible to assume in the reaction system the $\cdot\text{SH}$ radicals and the radicals arising from hydrocarbon reactant. The splitting of C—H bonds in a hydrocarbon molecule takes place by the action of S_2 molecules, or S atoms with paramagnetic properties, mo-

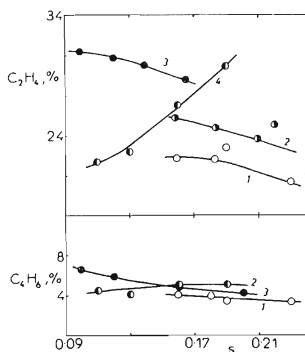


FIG. 1

Effect of residence time on yields of ethylene and butadiene at 800°C in pyrolysis of 1 primary kerosene, 2 primary kerosene 0.05% sulphur, 3 hydrogenated kerosene and 4 hydrogenated fraction 160–280

TABLE II
Product distribution from steam cracking of primary kerosene at 800°C

S addition to the feed, w.%	—	—	0.05	0.05
Residence time, s	0.16	0.19	0.17	0.18
Steam/hydrocarbon mass ratio	0.75	0.75	0.75	0.75
Yields of gaseous products, w.%	54.4	56.6	62.8	62.1
Hydrogen	1.05	0.65	0.79	0.79
Methane	9.82	13.18	11.97	12.40
Ethane	2.63	3.35	3.36	2.07
Ethene	21.55	22.69	25.68	24.72
Propane	0.32	0.31	0.33	0.33
Propene	8.54	8.51	9.33	11.33
Methylpropane	0.02	0.01	0.02	0.01
Butane	0.04	0.02	0.03	0.03
2-Methylpropene + 1-butene	2.62	1.95	2.16	2.38
<i>trans</i> -2-Butene	0.29	0.23	0.29	0.29
<i>cis</i> -2-Butene	0.75	0.49	0.55	0.62
1,3-Butadiene	3.90	3.33	5.53	4.10
1-Pentene	0.11	0.08	0.07	0.07
2-Methyl-1-butene	0.11	0.07	0.07	0.07
<i>trans</i> -2-Pentene	0.06	0.01	0.04	0.03
<i>cis</i> -2-Pentene	0.06	0.01	0.03	0.04
2-Methyl-2-butene	0.03	0.01	0.03	0.02
2; 3-Methylpentane	0.03	0.01	0.03	0.04
Isoprene	0.31	0.25	0.41	0.43
Benzene	6.26	7.95	6.12	6.95
Toluene	4.41	4.08	4.69	4.54
C ₈ aromatic hydrocarbons	3.85	3.45	3.27	3.67
Styrene	1.76	2.52	2.04	2.16
Indane	1.03	0.97	0.83	0.91
Indene	1.24	1.48	1.04	1.09
1-Methylindene	0.72	0.62	0.64	0.72
2-Methylindene	0.70	0.76	0.61	0.64
Naphthalene	3.23	3.54	2.57	2.87
2-Methylnaphthalene	1.35	1.58	1.23	1.44
1-Methylnaphthalene	1.30	1.40	1.11	1.30
Biphenyl	0.51	0.53	0.43	0.45
2-Ethyl-naphthalene	0.43	0.45	0.33	0.39
Fluorene	0.51	0.33	0.27	0.33
Phenanthrene + anthracene	0.73	0.36	0.30	0.46
Other hydrocarbons	19.73	14.79	13.80	12.28

likely on reaction centres which otherwise require high energy for propagation of the radical reaction chain by the action of hydrocarbon and hydrogen radicals. The consecutive splitting of radicals obtained from molecules of primary kerosene favours the decomposition into gaseous products.

The composition of products from the pyrolysis of hydrogenated fraction 160 to 280 is given in Table III. In comparison with the pyrolysis of primary kerosene, in the pyrolysis of hydrogenated kerosene an increase in the conversion to gaseous pyrolysis products is observed, manifesting itself in increased formation of profiling hydrocarbons, such as methane, ethylene, propene, C₄ hydrocarbon. As a counterbalance, there are formed fewer aromatic hydrocarbons: benzene, toluene, C₈ aromatics, naphthalene and its homologues and other polyaromatics. A still higher conversion to gaseous products was found in the pyrolysis of hydrogenated fraction 160–280. The liquid pyrolysis fraction represents only about 10%. Here it is necessary to remark that the selectivity of decomposition to ethylene is smaller in comparison with hydrogenated kerosene. The main cause is the formation of carbon monoxide, which in many cases surpasses 20%, and of methane, which reaches as much as 17%. The formation of ethylene is very sensitive to residence time (Fig. 1). The yields of ethylene are in the range of 21 to 29%. There was a marked decrease in the formation of aromatics which are present in the liquid pyrolysis products.

A characteristic feature of the pyrolysis of hydrogenated kerosene and hydrogenated fraction 160–280 in comparison with primary kerosene (Fig. 1) is an increased formation of dienes, especially 1,3-butadiene and isoprene. This points to a considerable hydrogenation activity of the bifunctional catalyst in the conversion of aromatic molecules to their alicyclic analogues. A characteristic feature of the thermal decomposition of cycloalkanes is the formation of butadiene and isoprene.

In the reaction of steam with coke to carbon monoxide and hydrogen or with precursors of pyrocarbon (higher polyaromatics, polyolefins) in the pyrolysis of hydrogenated fraction 160–280, a decisive role is played by the quality of the inner surface of the metal reactor. From Table IV, it is evident that the formation of carbon monoxide is favoured by stainless steel or metal oxides, whose formation cannot be excluded in the presence of steam. The passivation of the metal surface by hydrogen sulphide before pyrolysis prevents the formation of carbon monoxide. Hydrogen sulphide reacts with surface atoms to metal sulphides which form a protective layer and thus prevent the formation of carbon monoxide. The presence of metal sulphides was confirmed by the analysis of carbonaceous sediments from the reactor. After passivation with hydrogen sulphide, they contained 25.5% of metal sulphides, out of which there was 36.4% of chromium sulphides and 22.5% of iron sulphides. By the passivation of the inner surface of the reactor with hydrogen sulphide before pyrolysis or by pyrolysis of hydrogenated fraction 160–280 in the presence of elemental sulphur it was possible to inhibit effectively the formation of carbon monoxide (Table III). At the same time the formation of aromatics increased, which sug-

TABLE III

Product distribution from steam cracking of hydrogenated kerosene and fraction 160–280 at 800°C

Feedstock	Hydrogenated kerosene		Hydrogenated fraction 160–280				
	0·10	0·14	0·10	0·20	0·11 ^a	0·16 ^a	0·22 ^b
Residence time, s	0·10	0·14	0·10	0·20	0·11 ^a	0·16 ^a	0·22 ^b
Steam/hydrocarbon mass ratio	0·8	0·8	0·8	0·8	0·8	0·8	0·8
Yields of gaseous products, w. %	82·6	77·5	89·2	91·1	62·1	69·2	58·5
Hydrogen	0·65	0·59	1·06	0·59	0·71	0·74	0·45
Methane	13·37	12·67	17·25	17·30	12·12	15·47	11·74
Ethane	3·16	2·97	2·82	5·42	3·09	3·60	4·93
Ethene	32·34	30·98	23·92	26·24	21·32	26·96	22·29
Propane	0·47	0·34	0·55	0·43	0·31	0·31	0·25
Propene	13·40	13·22	14·82	10·56	10·64	8·93	10·24
Methylpropane	0·07	0·05	0·09	0·08	0·05	0·06	0·01
Butane	0·05	0·08	0·05	0·04	0·03	0·02	0·50
2-Methylpropene + 1-butene	4·46	3·92	4·49	3·60	3·52	2·59	2·15
<i>trans</i> -2-Butene	0·63	0·38	0·49	0·38	0·32	0·32	0·27
<i>cis</i> -2-Butene	0·91	0·92	0·78	0·48	0·70	0·90	0·53
1,3-Butadiene	7·56	6·30	6·55	4·18	4·37	5·09	2·99
1-Pentene	0·15	0·12	0·39	0·14	0·15	0·42	0·10
2-Methyl-1-butene	0·22	0·13	0·40	0·20	0·29	0·05	0·11
<i>trans</i> -2-Pentene	0·16	0·10	0·29	0·13	0·28	0·05	0·11
<i>cis</i> -2-Pentene	0·16	0·11	0·26	0·11	0·05	0·05	0·06
2-Methyl-2-butene	0·05	0·05	0·13	0·10	0·04	0·04	0·02
2-, 3-Methylpentane	0·12	0·12	0·13	0·07	0·09	0·12	0·03
Isoprene	1·02	0·77	1·23	0·70	0·82	0·64	0·31
Benzene	4·72	1·96	0·86	0·63	5·81	4·81	7·10
Toluene	2·43	3·20	1·46	0·53	5·35	4·47	8·01
C ₈ aromatic hydrocarbons	1·24	1·98	1·09	0·80	3·04	2·21	2·89
Styrene	0·81	1·48	0·46	0·81	1·97	2·15	4·05
Indane	0·09	0·36	0·34	0·14	0·47	0·17	0·32
Indene	0·46	0·95	0·55	0·67	1·82	1·53	1·96
1- 2-Methylidene	0·45	0·93	0·60	0·53	1·56	1·05	0·96
Naphthalene	0·92	1·71	0·81	1·61	2·41	3·72	4·75
2-Methylnaphthalene	0·25	0·61	0·19	0·44	0·65	1·06	1·57
1-Methylnaphthalene	0·20	0·51	0·17	0·30	0·45	0·84	0·90
Biphenyl	0·07	0·11	0·04	0·07	0·17	0·23	0·22
2-Ethyl-naphthalene	0·07	0·17	0·03	0·09	0·19	0·28	0·40
Fluorene	0·21	0·44	0·12	0·31	0·60	0·80	0·87
Phenanthrene + anthracene	0·17	0·48	0·10	0·28	0·52	0·72	1·00
Other hydrocarbons	8·54	10·88	7·04	4·64	16·03	8·92	7·97
Carbon monoxide	0·41	0·41	10·42	17·04	0·25	0·32	0·39

^a Reactor surface passivated by hydrogen sulphide. ^b 0·05% w. of sulphur added to the feed.

gests that not only coke but also aromatic hydrocarbons can react with steam to carbon oxides.

The formation of coke in the pyrolysis of hydrocarbons is a serious problem which in many respects can be a limiting factor. This is especially valid for the pyrolysis of hydrotreated materials. The study of coking in the pyrolysis of hydrotreated

TABLE IV
Formation of carbon monoxide and hydrogen in the pyrolysis of hydrogenated fraction 160–280^a

Without passivation			H ₂ S passivation		
Experiment duration min	carbon monoxide %	hydrogen %	Experiment duration min	carbon monoxide %	hydrogen %
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			

^a Temperature: 800°C, residence time: 0.16 s, mass ratio of water to feed 0.8 : 1, passivation by H₂S: 14 l/h during 15 min before experiment.

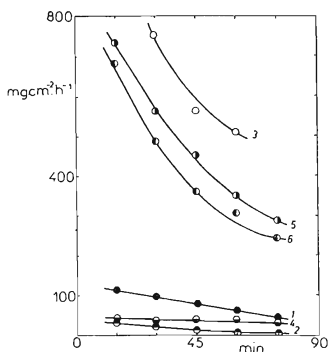


FIG. 2.
Rate of coke formation during the pyrolysis of 1 primary kerosene, 6 hydrogenated kerosene, 3 hydrotreated kerosene, 5 hydrogenated fraction 160–280, 2 hydrogenated kerosene 0.05% sulphur, 4 hydrogenated fraction 0.05% sulphur

TABLE V
Formation of coke in the pyrolysis

Experiment duration min	Residence time s	Flow of feed g h ⁻¹	Coke deposited g	Gaseous product g
Primary kerosene, 800°C				
15	0.23	25.4	0.1	4.5
30	0.24	25.8	0.3	8.6
45	0.24	26.3	0.4	12.5
60	0.23	26.7	0.4	16.4
75	0.26	25.7	0.4	20.1
Hydrotreated kerosene, 800°C				
15	0.34	25.4	2.38	4.5
30	0.33	25.5	3.44	8.45
45	0.33	25.4	3.90	11.05
60	0.33	25.4	4.70	12.46
Hydrogenated kerosene, 810°C				
15	0.34	25.4	1.7	4.03
30	0.34	25.3	2.6	6.86
45	0.34	25.5	3.1	10.02
60	0.33	25.7	3.2	12.45
75	0.34	25.4	3.3	16.28
Hydrogenated fraction 160—280, 810°C				
15	0.41	24.87	1.6	4.63
30	0.42	24.79	2.3	7.96
45	0.41	24.75	2.5	11.39
60	0.41	24.75	2.8	14.76
75	0.41	24.83	2.8	18.10
Hydrogenated kerosene 0.05% S, 810°C				
15	0.40	25.14	0.1	4.59
30	0.40	25.02	0.2	8.55
45	0.41	25.06	0.3	12.77
60	0.41	26.02	0.4	16.82
75	0.40	25.10	0.4	20.93
Hydrogenated fraction 160—280 0.05% S, 810°C				
15	0.48	24.71	0.06	3.54
30	0.49	24.79	0.10	7.53
45	0.48	24.76	0.10	11.35
60	0.48	24.72	0.10	15.12
75	0.49	26.67	0.10	18.75

feedstocks shows that the formation of coke is enhanced in comparison to primary feeds (Table V). From Fig. 2, it can be seen that the rate of coking is higher at the beginning of the experiment and that with the duration of the experiment it gradually decreases. The course of coke formation points to the fact that at the beginning of the experiment the influence of the inner surface is decisive.

The addition of elemental sulphur to hydrotreated feeds results in a decrease of coke formation. A retardation of secondary reactions, the consequence of which is the formation of coke, can be explained by the coverage of the inner surface by a layer of metal sulphides which are formed by the reaction of elemental sulphur or 'SH radicals with the surface of stainless steel.

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