PYROLYSIS OF UNSUBSTITUTED BICYCLIC HYDROCARBONS AND GAS OIL

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Dedicated to Professor V. Veselý on the occasion of his 70th birthday.

Pyrolysis of tetraline, decaline, 1,1'-bicyclohexane, cyclohexylbenzene and gas oil was studied in stainless steel and quartz flow tubular reactors at 780 and 800°C, residence time 0·08 to 0·5 s and at the mass ratio of steam to the raw material changing from 0·5 to 1·5. The effect of reaction temperature, the mass ratio of steam to the raw material, reactor material and of the added elemental sulphur on the yields of individual reaction products is reported. Of bicyclic hydrocarbons, condensed hydrocarbons are more stable than those with noncondensed rings, cyclanoaromates being more stable than bicyclanes. Pyrolysis of gas oil in the stainless steel reactor yields greater amounts of ethylene, propylene, butadiene and smaller amounts of methane and ethane, compared to the pyrolysis carried out under identical conditions in the quartz reactor. Elemental sulphur increases the conversion of gas oil into gaseous pyrolysis products.

From middle petroleum fractions, gas oil has been widely used as the starting material for industrial pyrolyses because of the lack of natural gases and straight-run naphthas. As the middle distillation fractions contain in addition to higher alkanes and cyclanes also greater amounts of aromatic hydrocarbons, the desired olefins are formed to a lesser extent, coke formation is more extensive and some problems arise concerning the further treatment of a considerable amount of liquid products, especially of pyrolysis oil[1,2].

To overcome the above problems, one needs data relating to the mechanism of thermal decomposition of middle and higher petroleum fractions, on the basis of which the optimal model of pyrolysis process can be postulated[3]. The study of radical and intermolecular conversions of hydrocarbons with higher molecular mass is based on the investigation of the effect of multiple factors on the formation of olefins, light alkanes and aromatic hydrocarbons. At the same time, the coking should be minimal. Besides reaction conditions, the main parameters are the type of reactor, the properties of its internal surface and the chemical nature of hydrocarbons.

From these aspects the pyrolyses of the following hydrocarbons were studied: pentadecane[4], tetradecenes, docosene[5], tetraline[6-8], decaline[8-11], indene[12], methylindene, dihydronaphthalene[7], hydroanthracenes[8], adamantane[13] and hydrophenanthrene[8,9]. Hydrophenanthrene contains 95·7 (% mass) of perhydrophenanthrene and 4·3% (by mass) of octahydrophenanthrene. It is assumed that perhydrophenanthrene occurs in the form of *cis-syn-cis* stereoisomer and octahydrophenanthrene in the form of symmetrical isomer. The properties of reactor material, the ratio of internal surface to the volume of reactor and the chemical activation or passivation by different chemical substances leads frequently to changes in the rate and selectivity of a given reaction. The same holds also for the pyrolysis of hydrocarbons in laboratory tubular reactors which have smaller diameters compared to industrial oven tubes and work frequently also at lower pressures.

The present work reports the results of the study of tetraline, decaline, 1,1'-bicyclohexane, cyclohexylbenzene and gas oil conversions. The relationship between the composition of the starting material and the formation of reaction products in the pyrolysis of these hydrocarbons in stainless steel and quartz reactors is investigated in relation to reaction temperature, residence time, the mass ratio of steam to starting material, the reactor wall and the effect of the addition of elemental sulphur.

EXPERIMENTAL

The flow pyrolysis apparatus used was described in detail earlier[14]. The tubular reactors were made from stainless steel and from quartz. The metal reactor was of the type "tube-in-tube", the ratio of the internal surface to the reactor volume (S/V) being 6·65 cm^{-1}. The stainless steel used had the following composition (% mass): Cr 16·8; Ni 10·7; Mn 1·1; C 0·08. The quartz reactor had $S/V = 5{\cdot}02\ cm^{-1}$. Pyrolysis of individual bicyclic hydrocarbons and of gas oil was carried out in the presence of steam. The mass ratio of steam to individual bicyclic hydrocarbons was 0·5, whereas the amount of hydrocarbons was changed from 0·117 to 0·65 mol h^{-1}. In the pyrolysis of gas oil, the mass ratio of steam to the material was 0·5, 0·75, 1·0 and 1·5, the amount of the hydrocarbon material changed from 0·062 to 0·169 mol h^{-1} and the amount of water from 0·833 to 1·555 mol h^{-1}. In the course of measurement, temperature profile along the reactor was recorded and used to calculate the equivalent reactor volume[15]. The value thus obtained was used to calculate residence time[14]. Experiments were carried out at atmospheric pressure.

Composition of gaseous and liquid pyrolysis products was determined by gas chromatography. The procedure, separation conditions and treatment of data were the same as in our previous papers[14,16].

Starting compounds. Decaline, 99·6% and tetraline, 99·4%, were supplied by Lachema, Brno and used without further purification. 1,1'-Bicyclohexane (98·7% purity) was obtained[17] by hydrogenation of biphenyl. Cyclohexylbenzene (99·98% purity) was prepared[18] from benzene and cyclohexanol in the presence of sulphuric acid. Gas oil from pipeline petroleum (Slovnaft, Bratislava) had the following properties: density 855·7 kg m^{-3}, mean molecular mass 242, distillation range 230 to 360°C, content of aromatic hydrocarbons 25·8% (by mass) (determined by elution chromatography), sulphur content 0·91% (by mass).

RESULTS AND DISCUSSION

Individual Hydrocarbons

Tetraline, decaline, 1,1'-bicyclohexane and cyclohexylbenzene were pyrolysed in a quartz tubular reactor at 780°C. The composition and yields of pyrolysis products are presented in Table I.

Under reaction conditions used, the conversion of hydrocarbons exceeded 80 per cent. The presence of methane, ethylene, 1,3-butadiene, benzene, toluene, styrene,

TABLE I

Composition of products of the pyrolysis of individual bicyclic hydrocarbons at 780°C, residence time 0·3 s and the steam/starting material mass ratio 0·5

Starting hydrocarbon	Tetraline	Decaline	Cyclohexylbenzene	1,1′-Bicyclohexane
Yield of gases, % mass	17·95	46·20	27·24	60·47
Products				
Hydrogen	0·24	1·33	0·28	0·62
Methane	5·62	11·88	7·23	9·93
Ethane	2·77	4·41	2·33	6·69
Ethene	7·88	18·15	12·36	21·07
Propane	0·08	0·31	0·10	0·67
Propene	0·75	4·81	2·58	9·31
Butane	0·13	0·14	0·12	0·17
1-Butene + 2-methylpropene	0·06	0·58	0·17	1·73
trans-2-Butene	0·03	0·21	0·10	0·92
cis-2-Butene	0·03	0·19	0·12	0·83
1,3-Butadiene	0·21	2·27	1·19	7·68
3-Methyl-1-butene	—	0·03	—	0·08
Pentane	—	—	—	0·01
1-Pentene	0·01	0·02	0·01	0·08
2-Methyl-1-butene	—	0·01	0·01	0·02
trans-2-Pentene	—	—	0·01	0·10
cis-2-Pentene	—	0·01	0·02	0·10
2-Methyl-2-butene	—	—	0·01	0·02
2-Methylpentane	0·03	—	0·01	—
Isoprene	0·02	0·15	0·04	0·20
Hexane	—	0·01	—	0·05
C_5 and C_6 olefins	0·09	1·70	0·55	1·34
Benzene	1·66	3·23	4·51	3·77
Toluene	3·40	4·64	3·16	3·36
C_8 aromatic hydrocarbons	3·43	2·02	0·30	1·25
Styrene	6·38	10·65	4·45	1·70
Indane	—	—	1·46	0·50
Indene	2·95	1·44	4·04	1·60
Naphthalene	28·55	6·05	10·21	3·10
2-Methylnaphthalene	0·47	1·03	1·04	0·69
1-Methylnaphthalene	0·50	0·87	1·39	0·53
Biphenyl	1·26	0·69	1·95	0·25
Ethylnaphthalene	—	0·40	—	0·11
3-Methylbiphenyl	0·63	0·71	1·55	0·40
Fluorene	—	0·18	2·33	0·49
Phenanthrene	—	0·10	0·69	0·23
1,2-Dihydronaphthalene	10·42	—	—	—

TABLE I
(*Continued*)

Starting hydrocarbon	Tetraline	Decaline	Cyclohexyl-benzene	1,1′-Bicyclo-hexane
Yield of gases, % mass	17·95	46·20	27·24	60·37
Products				
Tetraline	17·36	—	—	—
Decaline	—	17·02	—	—
Cyclohexylbenzene	—	—	21·14	—
1,1′-Bicyclohexane	—	—	—	13·23
Liquid residue	5·00	4·77	14·54	8·33

indene and naphthalene is characteristic of reaction products. In the case of tetraline and cyclohexylbenzene, even at such a high conversion, the yield of gaseouss products are relatively low. In this case, the dehydrogenation to naphthalene and for tetraline also its dehydrogenation to 1,2-dihydronaphthalene prevails over the decomposition to gaseous products. The decomposition to gaseous olefins and alkanes is more distinct in pyrolysis of decaline and 1,1′-bicyclohexane. In pyrolysis of the latter compound the highest conversion speaks for easy initiation and the high proportion of ethylene, 1,3-butadiene and benzene indicates that we deal here most likely with the splitting of C—C bonds in the 1,1′ position to give two cyclohexyl radicals which are further split with ring opening to yield ethylene and butadiene or they undergo dehydrogenation *via* formation of cycloolefins to yield benzene. As far as the splitting of bicyclic hydrocarbons to gaseous olefins and alkanes is concerned, one can state that the hydrocarbons with condensed rings are more stable than the hydrocarbons with noncondensed rings, cyclanoaromates being more stable than bicyclanes.

Gas Oil

Quartz reactor. Pyrolysis of gas oil was carried out at 780 and 800°C and the effect of residence time (0·08 – 0·5 s) and the mass ratio of steam to gas oil (0·5 – 1·5) was studied. The yields of pyrolysis products under selected reaction conditions are presented in Table II. The effect of residence time and mass ratio of steam to gas oil on formation of ethylene, propylene, butadiene and methane in dependence on reaction conditions is illustrated in Figs 1 and 2. The yields of characteristic products were determined with standard deviation smaller than 1 per cent. Thus, for example, in the pyrolysis of gas oil at 780°C and at the mass ratio of water to feed equal to 1, the standard deviation is 0·82% for methane, 0·61% for ethylene, 0·91% for propylene and 0·30% for butadiene. At a temperature of 780°C, the content of ethylene changes from 17·8 to 23·3% (by mass), nearly 70 per cent of experimental yield of ethylene being in the range 20–22% (mass). However, one should take into account

TABLE II

Composition of products of the pyrolysis of gas oil in a quartz reactor

Temperature, °C	780	780	780	800	800
Residence time, s	0·46	0·17	0·15	0·24	0·17
H_2O/starting material	0·75	1·0	1·5	0·75	1·0
Yield of gases, % mass	59·16	55·27	53·99	51·21	59·46
Products					
Hydrogen	0·68	0·41	0·37	0·57	0·56
Methane	16·54	13·28	13·50	13·82	15·03
Ethane	5·52	5·94	5·39	4·74	3·23
Ethene	21·38	21·06	20·71	19·60	24·00
Propane	0·41	0·59	0·46	0·36	0·47
Propene	7·40	8·37	8·74	7·38	10·10
Methylpropane	0·11	0·07	0·07	0·08	0·17
2-Methylpropene + 1-butene	1·07	1·41	1·25	0·85	1·29
trans-2-Butene	0·87	0·17	0·06	0·10	0·16
cis-2-Butene	0·18	0·23	0·05	0·17	0·15
1,3-Butadiene	1·95	2·18	2·15	1·55	2·48
1-Pentene	0·03	0·07	0·07	0·04	0·06
2-Methyl-1-butene	0·01	0·03	0·02	0·02	0·03
cis-2-Pentene	0·01	0·03	0·02	—	0·02
2-Methyl-2-butene	0·03	0·04	0·06	0·02	0·02
2-; 3-Methylpentane	0·04	0·01	0·02	0·01	0·02
Isoprene	0·18	0·17	0·23	0·11	0·24
Benzene	5·23	6·40	3·56	7·56	6·21
Toluene	2·69	3·02	3·56	4·29	4·15
C_8 aromatic hydrocarbons	1·14	1·42	2·05	1·18	1·22
Styrene	1·18	0·84	1·35	0·92	1·01
Indane	0·39	0·49	0·69	0·27	0·45
Indene	0·51	0·66	1·35	0·77	0·95
Naphthalene	2·33	2·13	2·15	2·62	2·72
2-Methylnaphthalene	1·34	1·57	1·70	1·63	1·73
1-Methylnaphthalene	1·32	1·80	1·69	1·65	1·57
Biphenyl	0·99	0·60	0·66	0·62	0·74
2-Ethylnaphthalene	1·16	1·15	0·93	0·91	1·15
3-Methylbiphenyl	1·36	1·19	0·97	1·19	1·07
Fluorene	1·26	1·00	1·04	1·01	1·16
Phenanthrene	0·30	0·30	0·30	0·68	0·47
Other hydrocarbons	22·39	23·41	24·83	25·38	17·25

that in the residence time region investigated, the yield of ethylene, propylene and and methane (Fig. 1) show considerable scatter with change in the partial pressure of reactants. This is understandable, since the effect of residence time and of the ratio of diluent to the starting material is opposite. The increasing portion of steam in the given feed leads to the decrease in the residence time of reacting hydrocarbons in the reaction system. Regardless of these facts, in general the yields of ethylene, propylene and methane increase with residence time, whereas the yields of butadiene do not change. Detailed comparison of yields obtained for the steam to gas oil mass ratio 1·0 and 1·5 in the narrow region of residence times (0·10–0·25 s) reveals (Fig. 2) that the above findings are valid also here, except for propylene. It is further evident that the different partial pressure of reactants under conditions where the mass ratio of steam to the starting material is 1·0 and 1·5 exerts the effect on the formation of methane, propylene, and butadiene. At lower partial pressure, the formation of 1,3-butadiene and propylene is decreased and the formation of methane is favoured, the yields of ethylene being essentially unaffected. This can be caused by the decrease in polymerization reactions and by the increase in splitting reactions of thermal decomposition of hydrocarbons from gas oil.

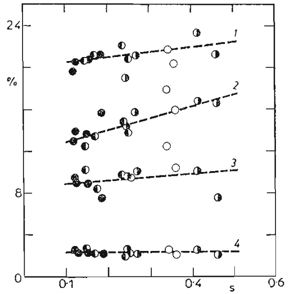

FIG. 1

Effect of residence time (s) on yields (% mass) of ethene *1*, methane *2*, propene *3* and butadiene *4* in pyrolysis of gas oil at 780°C and steam/gas oil mass ratio ○ 0·50, ◑ 0·75, ◐ 1·00, ● 1·50

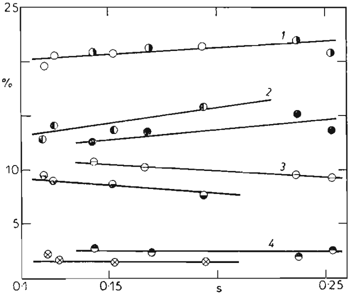

FIG. 2

Effect of residence time (s) on yields (% mass) of ethene *1*, methane *2*, propene *3* and butadiene *4* in pyrolysis of gas oil at 780°C and steam/gas oil mass ratio 1·0 (◑ ethene, ● methane, ⊖ propene, ◓ butadiene) and 1·5 (○ ethene, ◐ methane, ◒ propene, ⊗ butadiene)

Metal reactor. Pyrolysis of gas oil was carried out at 800°C, residence time 0·10 – 0·25 s and mass ratio of steam to starting material 0·8. The composition of reaction products under above reaction conditions is summarized in Table III. From comparison of these data with the results obtained in quartz reactor it follows that there are no qualitative differences in reaction products, in contrast to the yields obtained. Fig. 3 shows the effect of residence time on the formation of ethylene, propylene and butadiene in pyrolysis of gas oil in both the quartz and stainles steel reactor While in the stainless steel reactor the formation of alkenes is more preferred compared to the quartz reactor, the opposite situation in encountered in the case of light alkanes. The yields of methane (Fig. 4) and ethane (Fig. 5) are lower. The difference in the amount of mono- and polyaromatic hydrocarbons are not so distinct as are in the case of main gaseous pyrolysis products.

On the basis of the above results one can state that the improvement of the selectivity of pyrolysis of gas oil in the stainless steel reactor is due to the decrease in the yields of methane and ethane with simultaneous increase in the yields of ethylene, propylene and butadiene. The smaller amount of light alkanes formed in the metal reactor is likely caused by secondary reactions which take place on catalytically activated surface on which highly reactive methyl and ethyl radicals do not react to split-off hydrogen from other compounds present in the reaction system (especially

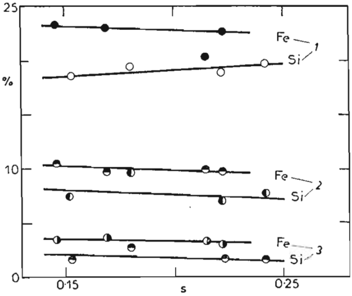

FIG. 3

Effect of residence time (s) on yields (% mass) of ethene *1*, propene *2* and butadiene *3* in pyrolysis of gas oil carried out at 800°C in a stainless steel reactor (Fe) and in a quartz reactor (Si)

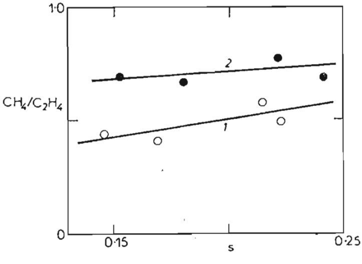

FIG. 4

Effect of residence time (s) on the yield of methane in pyrolysis of gas oil. The CH_4/C_2H_4 mass ratio at 800°C obtained in a stainless steel reactor *1* and in a quartz reactor 2

TABLE III

Composition of products of the pyrolysis of gas oil in a stainless steel reactor

Temperature, °C	800	800	800	800
Residence time, s	0·17	0·22	0·16	0·24
H_2O/starting material	0·8	0·8	0·8	0·8
S addition in the feed, % mass	—	—	0·05	0·05
Yield of gases, % mass	54·84	54·65	66·12	65·66
Products				
Hydrogen	0·65	0·86	0·81	0·41
Methane	9·48	11·25	12·82	12·67
Ethane	2·76	2·68	3·38	3·47
Ethene	22·98	22·64	25·11	29·54
Propane	0·33	0·32	0·44	0·87
Propene	9·61	9·67	12·07	10·62
Methylpropane	0·05	0·07	0·10	—
2-Methylpropene + 1-butene	2·11	1·63	2·80	1·96
trans-2-Butene	0·27	0·24	0·36	0·21
cis-2-Butene	0·44	0·38	0·54	0·39
1,3-Butadiene	3·62	2·87	4·42	3·39
3-Methyl-1-butene	0·07	0·07	0·09	0·06
1-Pentene	0·17	0·14	0·13	0·11
2-Methyl-1-butene	0·10	0·07	0·11	0·07
trans-2-Pentene	0·08	0·06	0·12	0·05
cis-2-Pentene	0·07	0·14	0·11	0·05
2-Methyl-2-butene	0·03	0·08	0·07	0·02
2-; 3-Methylpentane	0·06	0·15	0·07	0·05
Isoprene	0·36	0·26	0·48	0·28
Benzene	6·80	9·34	4·98	6·90
Toluene	4·50	5·69	3·60	4·34
C_8 aromatic hydrocarbons	2·04	2·00	1·78	1·55
Styrene	1·92	2·18	1·51	1·54
Indane	0·26	0·12	0·11	0·15
Indene	0·72	1·89	1·16	0·98
1-; 2-Methylindene	1·06	0·80	0·56	0·42
Naphthalene	2·46	2·71	2·41	2·67
2-Methylnaphthalene	1·98	2·13	1·35	1·19
1-Methylnaphthalene	2·03	1·91	1·32	1·25
Biphenyl	0·50	0·61	0·12	0·47
2-Ethylnaphthalene	0·58	0·87	0·72	0·70
3-Methylbiphenyl	0·20	0·16	0·10	0·12
Fluorene	0·57	0·81	0·50	0·41
Phenanthrene	0·30	0·20	0·15	0·09
Other hydrocarbons	20·89	15·18	15·60	12·88

of reactants) to give methane and ethane. It seems likely that these radicals, with contribution of stainless steel surface, yield intermediate reaction products which lead to the formation of *e.g.* olefins (ethylene, propylene, 1,3-butadiene). The quality and size of internal surface is a determining factor in the case of further secondary reactions which yield condensed aromatic hydrocarbons and coke. The existence of these secondary reactions is made possible by multicomponent highly reactive olefin–aromatic system, with considerable contribution of internal surface of the reactor.

The increase in gas oil conversion as well as formation of pyrolysis oil and coke is now under extensive investigation, since the important decrease in the formation of pyrolysis oil and coke in pyrolysis, with simultaneous increase in the yields of desired olefins would result in substantial improvement of economic parameters. One of the possibilities how to increase the selectivity of radical process in the case of gas oil is the pyrolysis in the presence of elemental sulphur, since this allows to increase markedly the conversion into gaseous pyrolysis products. Thus, for example, in the presence of 0·05 mass% of elemental sulphur, at the same selectivity the yields of ethylene, propylene, 1,3-butadiene, methane and ethane are increased (Table III).

With respect to the dehydrogenation properties of elemental sulphur, it is reasonable to assume that the reaction system involves both radicals ·SH and the radicals arising from hydrocarbon reactant. The splitting of C—H bonds in the molecule of gas oil under the action of sulphur takes place most likely on the sites which are highly energy-consuming for the propagation of hydrocarbon chain by the action of hydrocarbon and hydrogen radicals. The consecutive splitting of the so formed radicals from molecules of gas oil favours the decomposition into gaseous products. It becomes clear that further study of the pyrolysis of petroleum fractions and individual hydrocarbons boiling within the range of gas oil is needed to verify the above mentioned presumptions and to extent our knowledge about the effect of elemental sulphur[19]. These problems will be the subject of our further investigation.

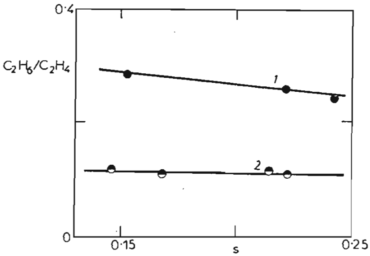

FIG. 5

Effect of residence time (s) on the yield of ethane in pyrolysis of gas oil. $C_2H_6/$ $/C_2H_4$ mass ratio at 800°C obtained in a stainless steel reactor *2* and in a quartz reactor *1*

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