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THE STUDY OF COKE FORMATION DURING COPYROLYSIS OF HEXADECANE, CYCLOHEXANE AND ISOOCTANE

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Abstract. *The aim of this work was to evaluate coke formation during pyrolysis of representants of linear, branched and cyclic alkanes and during their copyrolysis in mixture. The aim was to study coke formation during pyrolysis of hexadecane, 2,2,4-trimethylpentane (isooctane), cyclohexane and of mixtures hexadecane – isooctane (1:1 wt, mixture I), hexadecane – cyclohexane (1:1 wt, mixture II) and to determine product distribution in pyrolysis gases. The experiments were carried out in the steel tubular reactor at 710°C and 740°C at atmospheric pressure and feedstock flow rate 30gh*$^{-1}$.

It was found, that coking rate asymptotically declines at all feedstocks in dependence on experiment duration. The amount of formed coke during hexadecane pyrolysis at 740°C was approximately 1.5 - fold higher than the amount formed during pyrolysis of isooctane. The mass yields of coke at copyrolysis of hexadecane – isooctane are slightly lower during the whole experiment than the yields obtained at hexadecane pyrolysis. Isooctane accelerates decomposition of hexadecane.

The amount of coke formed from hexadecane at 710°C is approximately 1.3 - fold higher than the amount obtained from cyclohexane. Approximately equal quantity of coke was formed within the first 15 minutes of copyrolysis of hexadecane-cyclohexane in comparison with the yields from hexadecane. During the following experiments lower amount of coke was formed in comparison with pyrolysis of individual pure components. Thus hexadecane markedly influences decomposition of cyclohexane.

Key words: *coking, pyrolysis, copyrolysis, hexadecane, isooctane, cyclohexane*

Introduction

Coke formation on the inner surface of reactor and in the transfer line exchanger (TLE) is the most significant factor negatively influencing economy of steam cracking units [1,2]. Decrease in product yields, increase in energy consumption and decrease of operation life of pyrolysis tubes occur as a result of worsened heat transfer, pressure drop, and other factors. The deposited coke must be removed when limiting values of reactor skin temperature and pressure drop are achieved.

During the past twenty years large improvements in furnace modification and in optimisation of operation conditions were reached. Successful methods eliminating coke formation allow application of more severe working conditions. Chemical modification of surfaces and addition of coking inhibitors belong to commonly applied methods. Reducing the higher boiling portion of the feedstock that are prone to coke formation, e.g. by hydrocracking, fractionation and dearomatization is also effective [3]. Applying new alloys allows for working at higher temperatures, and at shortened residence times, as well as working at lowered pressure drop in the furnace coils [4]. The development progresses from the primarily utilised stainless steel with the content (% wt.) 18Cr/8Ni via cast-iron materials 25Cr/20Ni, to the recently applied high-alloy steels 25Cr/35Ni with addition of Si,Mo,Nb,W and other elements [5].

The coke formation during pyrolysis is influenced by several factors. The most important of them is the feedstock composition. Technical literature lists information on coking for different real hydrocarbon feeds, which are often multi-compound mixtures (naphtha, kerosene, etc.), or possibly for pure substances. Papers dealing with mutual influence between hydrocarbons with various structures forming coke during their copyrolysis are rare. The experiments carried out in this study are in context with our previous papers, which focused on hydrocarbons of various structures and how they mutually influence during copyrolysis in terms of changes in decomposition kinetics and product composition [6-9].

Experimental

The formation of coke, pyrolysis gases and pyrolysis liquid was estimated in a laboratory stainless steel U-shaped flow reactor. We chose severe conditions supporting the course of secondary reactions during the experiments, which is not typical for industrial pyrolysis. Therefore we worked without steam as an inert diluent.

We chose the following duration of individual experiments: 15 min, 15 min, 30 min, and 60 min, to be able to satisfactorily describe dependence of amount of formed coke on experimental time (experiment duration). After each experiment we cooled down the reactor in nitrogen atmosphere and we determined an increase in its mass. After finishing the series of four experiments we removed coke and we activated the reactor. Thus we were able to state the amount of coke on the clean surface in the first stage of coking and after formation of coke layer on the reactor walls.

Coking of the mixture composed of 2,2,4-timethylpentane (isooctane) with hexadecane (1:1 wt, mixture I) was realized at 740°C and the experiments with cyclohexane – hexadecane mixture (1:1 wt, mixture II) were carried out at 710°C and at feedstock flow rate 30 gh^{-1}. In order to establish mutual influence of components during copyrolysis we made experiments with individual pure hydrocarbons at corresponding temperatures and flow rates. The performed experiments were linked to the measurements of coke formation during copyrolysis of heptane-hexadecane [10].

The on-line connection of laboratory equipment to gas chromatograph HP 6890+ enabled a direct analysis of effluent gases after previous cooling of liquefiable fractions. We developed a new method for separation of pyrolysis gases. Three chromatographic columns were used for the analysis: HP PLOT Al_2O_3 „M", HP PLOT Q, HP PLOT Molsieve 5A and three switching valves. This system allows for a detailed separation of mixture of gaseous hydrocarbons, saturated and unsaturated, hydrogen, carbon oxides, and nitrogen in one sample.

Results and Discussions

At all feedstocks the amount of formed coke increases in a non-linear way with the time of experiment (Figures 1 – 2). On the other hand coking rate asymptotically declines with experiment prolongation at all feedstocks. High rates of coke formation at the beginning of experiment are caused by the catalytic effect of the metal surface in reactor during reactions leading to coke formation. The rates decline with longer time of experiment due to the catalytically active reactor surface being covered by a layer of coke.

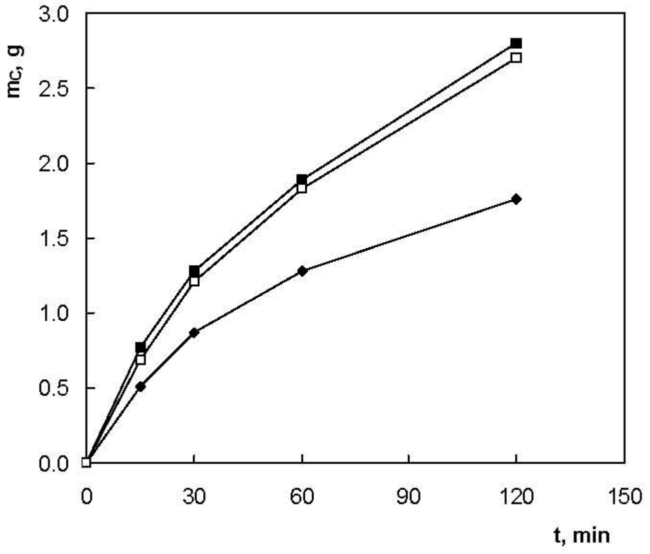

Figure 1. Mass of formed coke (m_C) in dependence on experiment time (t) at pyrolysis of ■ hexadecane, ◆ isooctane, and □ mixture I

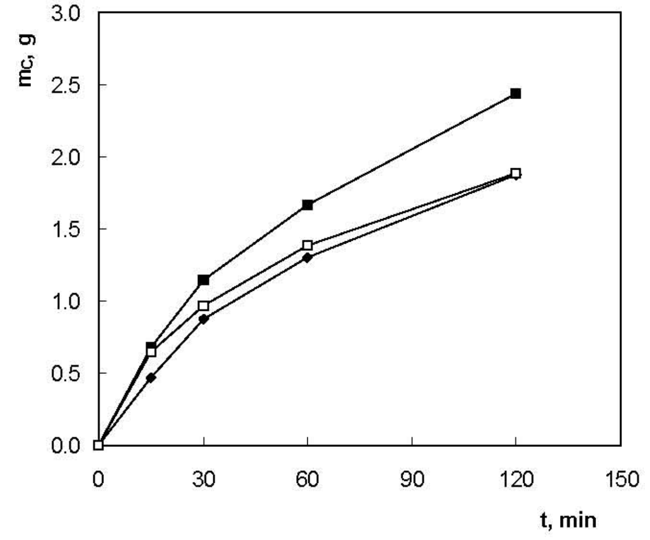

Figure 2. Mass of formed coke (m_C) in dependence on experiment time (t) at pyrolysis of ■ hexadecane, ◆ cyclohexane, and □ mixture II

Pyrolysis of Hexadecane at 740°C

We chose the pyrolysis temperature 740°C and the feedstock flow rate 30g.h^{-1} upon the results of previous experiments performed on the same laboratory equipment. The rate of coke formation at the beginning is rather high (285.2 mg.cm^{-2}.h^{-1}) and it sharply declines with experiment prolongation. The rate was more than 3.5-fold lower (79.1 mg.cm^{-2}.h^{-1}) at the end of the series of experiments in comparison with the beginning rate. These results confirm the previously found results about catalytic influence of reactor wall material on coke formation. A small amount of coke was deposited also in the bend, which connected the reactor with a cooler, especially during the first 15-minute experiments (0.04 g and 0.03 g, respectively).

During the experiment the formation of gas pyrolysis products (volume rate flow of pyrogas) was almost constant. The mass yield of pyrogas sharply increased, especially at the beginning of the series of experiments. The yields of some gaseous products are listed in Table 2. Ethylene and propene are prevailing components. Their mass yields increase with the experiment time (14.5 – 21.1 %wt, 9.1 – 14.1 %wt, respectively) as well as the yields of 1-butene (2.3 – 3.5 %wt) and 1,3-butadiene (1.5 – 3.0 %wt). The yield of hydrogen 1.8%wt during the first 15 minutes of the experiment is fairly high when we take into consideration its small molar mass. This yield of hydrogen indicates the catalytic influence of metal surface of a reactor on dehydrogenation reactions of hydrocarbons during coke formation.

Pyrolysis of Isooctane at 740°C

The pyrolysis temperature and the mass flow rate of the feed were equal to those for pyrolysis of hexadecane. The beginning rate of coke formation was 1.5-fold lower (193.8 mg.cm^{-2}.h^{-1}) than the one for during hexadecane pyrolysis and it sharply declined with duration of the experiment. At the end of experiment is more than 4.5 fold lower (43 mg.cm^{-2}.h^{-1}) than at the beginning of experiment. Coke was not deposited in the bend connecting the reactor with the cooler. The volume rate flow of pyrogas decreased during all four experiments. Yields of methane, propene, and methylpropene were rather high (11.5 – 12.6 %wt, 17.8 – 19.3 %wt, and 31.1 – 36.2 %wt respectively) (Tab.2).

Hydrogen, methane, propene, methylpropene, and isoheptenes are the primary products of isooctane decomposition. No ethylene was produced by primary decomposition. This fact explains why low yields of ethylene have been obtained (4.1 – 4.4 %wt). The product composition during experiments was practically constant.

Pyrolysis of Mixture I at 740°C

In order to estimate mutual influence of components in the mixture during copyrolysis, we performed experiments under the same conditions as those that were present during pyrolysis of pure components. The amount of formed coke increased in a non-linear way with the experiment duration. Absolute mass increments and mass yields of coke have been only slightly lower than those obtained from pyrolysis of pure hexadecane. The rate of coking shows similar behaviour than the rate for pyrolysis of pure hexadecane. The beginning rate was 268.5 mg.cm^{-2}.h^{-1} and it decreased at the end of the experiment 3.5-times to 76.6 mg.cm^{-2}.h^{-1} (Table.1).

Table 1. Component yields (M, %wt) in pyrolysis gases at pyrolysis of mixture I at 740°C and mass flow of feed 30 g/h

t (min)	15	30	60	120
τ (s)	0.082	0.088	0.101	0.104
V_F (l/h)	15.1	14.4	12.2	11.1
Y_G (%wt)	47.4	53.1	47.6	44.3
m_C (g)	0.65	0.97	1.39	1.89
R_C (mg/cm^2.h)	249.2	117.5	75.4	46.7
Component	M (%wt)			
Hydrogen	1.4	0.8	0.5	0.4
Methane	3.8	4.5	4.2	3.8
Ethane	4.6	5.2	4.6	4.3
Ethylene	14.8	17.2	15.7	14.2
Propane	0.7	0.7	0.6	0.6
Propene	9.7	11.4	10.3	9.4
Butane	0.2	0.2	0.1	0.1
2-Butenes	1.5	1.8	1.5	1.4
1-Butene	2.6	2.9	2.5	2.5
Methylpropene	0.1	0.1	0.1	0.1
1,3-Butadiene	4.2	5.1	4.5	4.5
2-Pentenes	0.2	0.2	0.1	0.1
1,3-Pentadiene	0.1	0.1	0.1	0.1
1-Pentene	0.8	0.7	0.7	0.7
Cyclohexane	1.9	1.4	1.1	1.1
1-Hexene	0.2	0.1	0.1	0.2
Benzene	0.2	0.1	0.1	0.1
C6+ unknown	0.6	0.7	0.7	0.7

The volume rate flow of pyrogas in the first two measurements of the series was approximately 10% higher than the rate in hexadecane pyrolysis. In the following measurements it reached roughly equal values. The mass yield of pyrolysis gases gradually increased. Ethylene, propene, and methylpropene reached the highest yields out of all gaseous products (12,8 – 15,4 %wt, 13,2 – 16,8 %wt, and 12,1 – 14,1 %wt, respectively). Yields of methane, ethane, 1-butene and 1,3-butadiene were also relatively high. The hydrogen yield in the first 15 minutes of the measurement was again high (Table.1).

The real yields were different from those calculated on the basis of additivity from the results obtained for pyrolysis of individual pure components. The real yields of ethane are on the average by 30% higher than the additive yields. The yields of ethylene, 1-butene, and 1,3-butadiene are higher approximately by 20%. The yields of methane are lower by 14 % and the yields of propene are lower by even 22%. From these results we can conclude, that hexadecane slows down decomposition of isooctane and vice versa.

Pyrolysis of Cyclohexane at 710°C

A large amount of coke was formed from cyclohexane at 740°C and at mass flow rate of the feed 30 g.h^{-1} that led to a complete choking of the reactor by coke already during the second 15-minute experiment. Therefore we reduced temperature to 720°C, but the reactor was full of coke that sedimented during the 30-minute experiment. Only at 710°C we were able to perform the whole series of four experiments. The beginning rate was 172.5 mg.cm^{-2}.h^{-1} and it decreased at the end of the experiment 3.5-times to 51 mg.cm^{-2}.h^{-1}.

Table 2. Component yields (M, %wt) in pyrolysis gases at pyrolysis of mixture II at 710°C and mass flow of feed 30 g/h

t (min)	15	30	60	120
τ (s)	0.082	0.088	0.101	0.104
V_F (l/h)	15.1	14.4	12.2	11.1
Y_G (%wt)	47.4	53.1	47.6	44.3
m_C (g)	0.65	0.97	1.39	1.89
R_C (mg/cm^2.h)	249.2	117.5	75.4	46.7
Component	M (%wt)			
Hydrogen	1.4	0.8	0.5	0.4
Methane	3.8	4.5	4.2	3.8
Ethane	4.6	5.2	4.6	4.3
Ethylene	14.8	17.2	15.7	14.2
Propane	0.7	0.7	0.6	0.6
Propene	9.7	11.4	10.3	9.4
Butane	0.2	0.2	0.1	0.1
2-Butenes	1.5	1.8	1.5	1.4
1-Butene	2.6	2.9	2.5	2.5
Methylpropene	0.1	0.1	0.1	0.1
1,3-Butadiene	4.2	5.1	4.5	4.5
2-Pentenes	0.2	0.2	0.1	0.1
1,3-Pentadiene	0.1	0.1	0.1	0.1
1-Pentene	0.8	0.7	0.7	0.7
Cyclohexane	1.9	1.4	1.1	1.1
1-Hexene	0.2	0.1	0.1	0.2
Benzene	0.2	0.1	0.1	0.1
C6+ unknown	0.6	0.7	0.7	0.7

The volume-flow rate of pyrogas decreased during the experiment. It was very low in comparison with the flow obtained form other feedstocks. Relatively low temperature was probably not sufficient for deep scission of cyclohexane molecules. During the first experiment the molar content of hydrogen in pyrogas was more than 65%. Hydrogen yields decreased with experiment prolongation (1.5-0.3 %wt). Ethylene, 1,3-butadiene, methane, propene, and butenes were prevailing products in pyrogas, just after hydrogen (Table. 4). From the listed observations we can state that, especially during first experiments, there occurred dehydrogenation of cyclohexane ring catalysed by reactor walls. Splitting of the ring increased with experiment duration.

Table 3. Comparison for yields of profiling gaseous products from pyrolysis of hexadecane, isooctane, and their mixture at 740°C

Component/ feedstock	Hexadecane	Isooctane	Mixture I
Ethene	14.5 - 21.1	4.1 - 4.4	12.8 - 15.4
Propene	9.1 - 14.6	17.8 - 19.3	13.2 - 16.8
Methylpropene	0.1 - 0.2	31.1 - 36.2	12.1 - 14.1
Mehane	4.8 - 6.2	11.5 - 12.6	7.1 - 8.0
Ethane	3.9 - 4.7	0.7 - 0.8	2.7 - 3.5
1-Butene	2.3 - 3.5	1.1 - 1.2	2.0 - 2.9
1,3-Butadiene	1.6 - 3.0	0.7 - 0.8	1.5 - 2.2
Pyrogas	*44.0 - 61.3*	*75.9 - 85.5*	*61.0 - 69.7*

Pyrolysis of Hexadecane at 710°C

To be able to estimate mutual influence of cyclohexane and hexadecane during their copyrolysis we made experiments with hexadecane at 710°C. During the first 15-minute experiment approximately 1.5 fold more coke was formed in comparison with cyclohexane pyrolysis. During the following experiments 1.2- till 1.3-fold more coke was formed considering cyclohexane. A high beginning rate of coking (286.3 mg.cm^{-2}.h^{-1}) decreases with duration of experiment. It is around 3.5 – times lower at the end of experiments

(71.8 mg.cm^{-2}.h^{-1}) in comparison with the start value. The produced amount of coke was lower by 15% in comparison with the amount of coke in pyrolysis of hexadecane at 740°C.

Pyrolysis of Mixture II at 710°C

Experiments were carried out at the same conditions as pyrolysis of individual pure components – 710°C, 30 g.h^{-1}. During the first 15 minutes the amount of formed coke was lower only by 5% in comparison with pure cyclohexane. During the following three experiments increments in coke mass as well as mass yields of coke were lower than those obtained during pyrolysis of each pure component. The overall amount of coke formed after 120 minutes of pyrolysis was equal to the amount formed during pyrolysis of pure cyclohexane (Tab.3).

The volume flow rate of pyrogas decreased during the whole experiment. Ethylene (14.2 – 17.2 % wt) and propene (7.9 – 11.4 % wt) were dominant components of pyrolysis gas. Yields of methane, ethane, 2-butenes and 1,3-butadiene were also fairly high (Table. 3). The obtained yields of pyrogas were higher by about 40% in comparison with the yields calculated on the basis of additivity. The mass yields of profiling components also increased proportionally. 1,3-Butadiene showed markedly higher yields (up to 120% during the first 15-minute experiment). Hexadecane strongly accelerated splitting of the cyclohexane ring. Cyclohexane only slightly influenced pyrolysis of hexadecane.

Table 4. Comparison for yields of profiling gaseous products from pyrolysis of hexadecane, cyclohexane, and their mixture at 710°C

Component/ feedstock	Hexadecane	Cyclohexane	Mixture II
Ethene	14.5-18.2	4.6-6.5	14.2-17.2
Propene	9.8-13.2	1.9-3.3	9.4-11.4
Methane	4.6-5.6	0.5-1.4	3.8-4.5
Ethane	4.5-5.0	1.5-2.2	4.3-5.2
Butenes	4.0-5.0	1.5-3.0	3.9-4.8
1,3-Butadiene	1.6-2.8	2.2-4.2	4.2-5.1
Pyrogas	*47.0-55.5*	*14.9-22.2*	*44.3-53.1*

Conclusion

The mechanism of coke formation is very complicated, as well as is the mutual influence of feedstock components during copyrolysis. However we can state that from the dependences of coke mass on experiment duration established for the investigated mixtures it is evident that there exists mutual influence of the components during experiments. In the previous experiments we found out that isooctane accelerates hexadecane decomposition in the presence of steam. By this acceleration we can partly explain a considerable similarity of coke creating in pyrolysis of mixture I with coke creating from hexadecane. The acceleration of cyclohexane decomposition by hexadecane (observed also during copyrolysis in the presence of steam) is evident from the shape of the dependence curve for coke formation and occurs from the 15th minute of the experiment.

Symbols

m_C	mass of coke, g
t	experiment time, min
r_C	coking rate, mg/cm^2.h
V_F	volume flow of pyrogas, l/h
Y_G	mass yield of pyrogas, %wt
τ	residence time, s

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