

# COKE FORMATION DURING COPYROLYSIS OF POLYALKENES WITH NAPHTHA

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## Abstract

Copyrolysis of naphtha solutions of oils/waxes, prepared by thermal cracking of individual and mixed polyalkenes, was investigated as a recycling route for waste polyalkenes. Coking of mixtures of oils/waxes with naphtha was studied at 820°C in steel flow reactor in dependence on reaction time. Comparison with coke formation from individual naphtha is given. Different systems of individual or mixed polyalkenes were studied and compared.

Key words: *Coke formation; Copyrolysis; Plastics, Recycling; Polyalkene polymers; HDPE; LDPE; LLDPE; PP*

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## 1. Introduction

Several large-scale processes, e.g. liquid or vapour phase pyrolysis or combustion, involve hydrocarbon feedstock. They are characterized by complex radical reaction systems, involving unsaturated molecules and radicals, universally recognised as precursors in fouling and soot formation <sup>[1]</sup>.

In the case of liquid and gas phase pyrolysis, radiating furnaces are commonly used to transfer the necessary reaction heat to the process fluid. These tubes simultaneously act as heat exchangers and chemical reactors. Due to the presence of unsaturated species and depending on the operating conditions a progressive fouling of the internal walls take place during the running time. This carbonaceous deposit is a severe problem and is an important limiting factor <sup>[1]</sup>. Coke formation not only affects heat transfer, but also results in an increase in the drop of fluid pressure, shortening of the operating cycle, and a decrease in the capacity of the plant and the yield of the desired products. Collectively, these problems make it necessary to periodically shut down the plant <sup>[2]</sup>. That is why formation of coke on the inner surfaces of steam cracking tubes and in transfer line exchangers (TLE) during steam cracking is a negative phenomenon that influences the economy of steam cracking units.

The coke formation during steam cracking is influenced by several factors. The most important of them is feedstock composition. When using different atypical feedstock in steam cracking process it is important to know the coke-forming tendency of a particular feedstock. In our research we focused on possibility of recycling of plastic waste in existing refinery facilities together with conventional feedstock, which would avoid the need to invest and build new processing plants. We prepare 10 mass % solutions of oils/waxes obtained by thermal cracking of individual or mixed polyalkenes in liquid petroleum fraction – naphtha. This solution served as a feedstock for steam cracking experiments. Verification of suitability of the feedstock in term of coke deposition during steam cracking was done in this study.

## 2. Experimental

### 2.1 Solutions of oils/waxes from polyalkenes in naphtha

The oil/wax products were prepared by thermal cracking of individual (HDPE, LLDPE) and mixed polyalkenes: three-component mixture HDPE/LDPE/PP and four-component mixture HDPE/LDPE/LLDPE/PP (1:1:1:1 mass). The thermal decomposition of plastics was carried out in

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a batch reactor at temperatures up to 450°C in nitrogen atmosphere. The prepared oils/waxes are predominantly composed of linear or branched alkenes and alkanes. Contrary to the virgin plastics, the oils/waxes are well soluble in naphtha. Four 10 mass % solutions of oils/waxes in naphtha were prepared and consequently used in copyrolysis experiments. A detailed description of the cracking apparatus and of the procedure was made in [3].

## 2.2 Apparatus for the determination of coke formation

Coke formation in pure naphtha and at copyrolysis was studied without presence of steam in the U-shaped stainless steel flow reactor. The internal diameter of the reactor was 6 mm. A thermocouple was placed in the thermo tube between the arms of the reactor. The S/V ratio was 66.7 mm<sup>-1</sup>. We chose severe conditions, with no steam supporting the course of secondary reactions during the experiments, which is not typical for industrial steam cracking. Experiments were carried at temperature of 820°C and feedstock flow rate 20 g.h<sup>-1</sup>.

We designed the following duration of the individual experiments: 15 min, 15 min, 30 min, 60 min, and 60 min (which summarily represents 15, 30, 60, 120, 180 min of experimental time) to be able to satisfactorily describe the dependence of the amounts of formed coke on experimental times. After each experiment we cooled down the reactor in nitrogen atmosphere and we determined the increase in its mass. After finishing a series of five experiments we removed the coke by burning with air and reduced metal oxides by the solution of acids. Thus we were able to determine the amount of coke on the clean surface in the first stage of coking and after the coke layer formation on the reactor walls. In order to establish a mutual influence of the components during copyrolysis, we made experiments with individual straight-run naphtha at corresponding temperature and flow rates.

## 3. Results and discussion

The aim of our experiments was to study the coke formation and the product distribution during copyrolysis of oils/waxes from waste polyalkenes with naphtha. Residence times lay in the interval 0.15 – 0.17 s at feedstock flow rate 20 g/h and reaction temperature 820°C.

The values of the total mass of coke deposited in the reactor (m) for particular raw materials depending on the time of the experiment show how the amount of coke in the reactor gradually rose up (Fig.1). For the sake of comparison we also plotted the mass increments of coke in single experiments ( $\Delta m$ ) in Fig. 2. These increments allow us to find out if a certain raw material yields a larger amount of coke in the first minutes of the experiment only or during the entire series of five measurements.

Fig.1 shows the total masses of the coke produced in particular solutions of polyalkene raw materials and they are compared to the coke formed from pure naphtha. In all feedstocks the amount of formed coke increased with the time of the experiment in a non-linear way. The highest amount of coke was formed during the first 15-minute experiment in all feedstocks. In our view this is caused by the catalytic effect of the metal surface in the reactor during the reactions leading to coke formation. Also rate of coke formation, expressed in mg of coke deposited on 1 cm<sup>2</sup> of a reactor surface during 1 hour, decreased with prolongation of experimental time (Fig. 3). As can be understood from Fig.1 and Fig.2 the highest amount of coke on the clean surface of reactor was formed from naphtha. The amount of coke from four-component mixture follows. Other solutions of oils/waxes in naphtha showed approximately the same amount of coke formed during the first 15 minutes of experiment. With prolongation of experimental time, the increments in deposited coke were during copyrolysis very close to that from naphtha (Fig.2). approaching to the end of experimental time, amount of coke from LLDPE and HDPE was higher in comparison to the coke from naphtha.

Apart from coke formation we monitored composition and yields of individual gaseous and liquid products. Ethene, propene, methane, 1,3-butadiene were prevailing components in pyrolysis gases (Figs. 4, 5 and 6). The ethene yields varied between 23 and 32.3 %. The lowest ethene yields were produced during copyrolysis of HDPE. Yields of propene varied from 9.8 to 14 % and those of 1,3-butadiene from 2.2 to 4.1 %.

The comparison between the yields of aromates from the copyrolysis of different polyalkenes with yields from naphtha shows that the amount of benzene from individual naphtha was higher than from other feedstocks. But in the case of naphthalene and higher aromates (anthracene, phenantrene, acenaphthene, and fluorene) the tendencies changed. More condensed aromates was formed during copyrolysis of oils/waxes in comparison with naphtha.

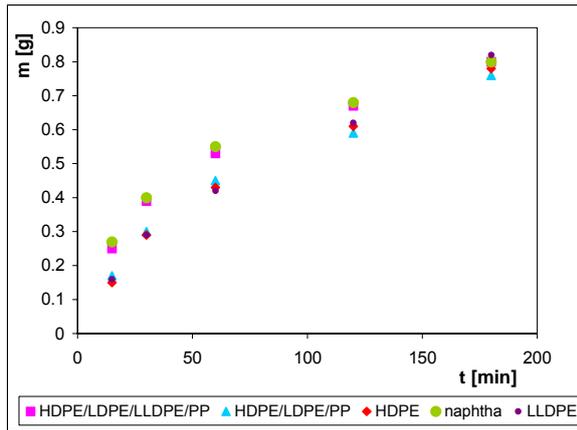


Fig.1 The weight of formed coke (m) in dependence on experimental time (t) for different feedstocks at 820°C

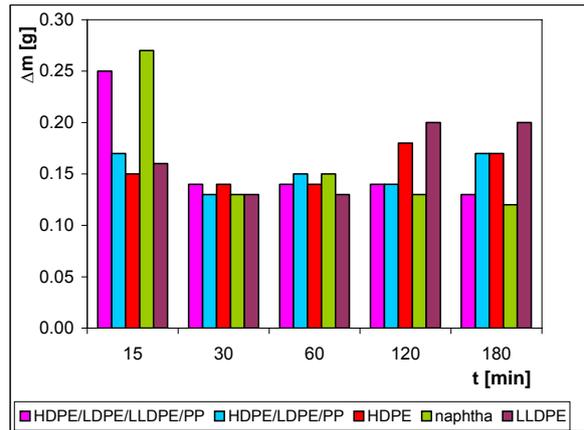


Fig.2 The mass increments (Δm) of coke for different feedstocks at 820°C

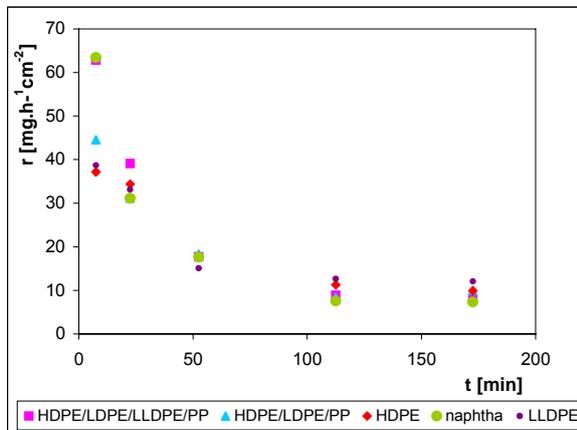


Fig.3 The rate of coke formation (r) in dependence on experimental time for different feedstocks at 820°C

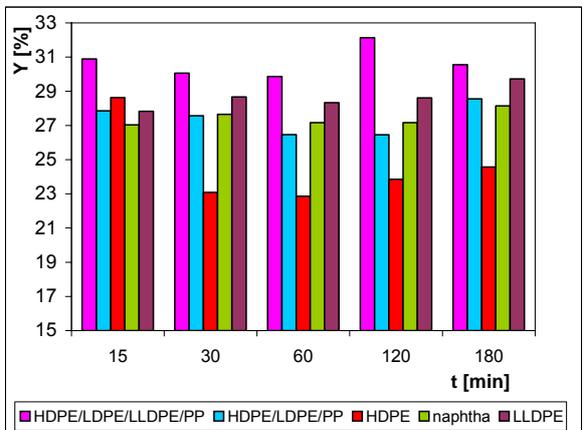


Fig.4 Ethene yields (Y) for different feedstocks and experimental times at 820°C

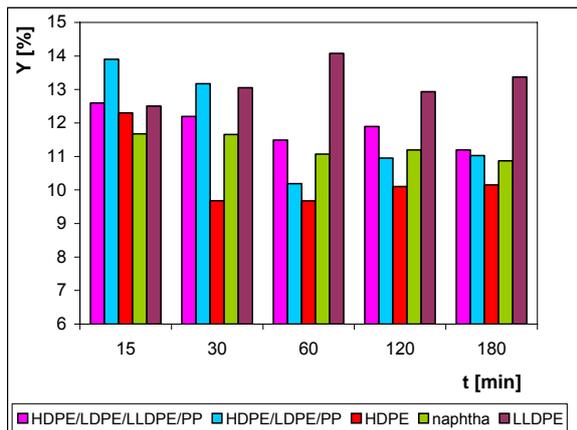


Fig.5 Propene yields (Y) for different feedstocks and experimental times at 820°C

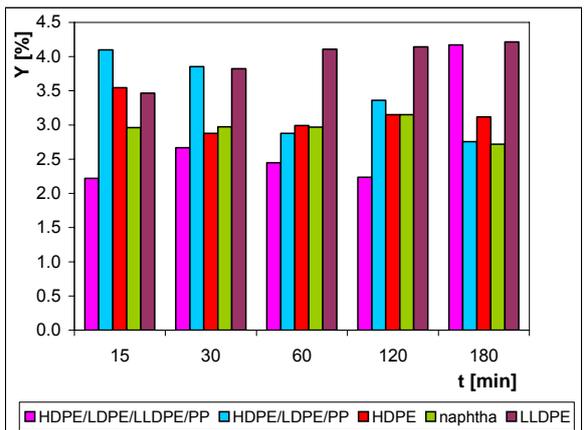


Fig.6 1,3-Butadiene yields (Y) for different feedstocks and experimental times at 820°C

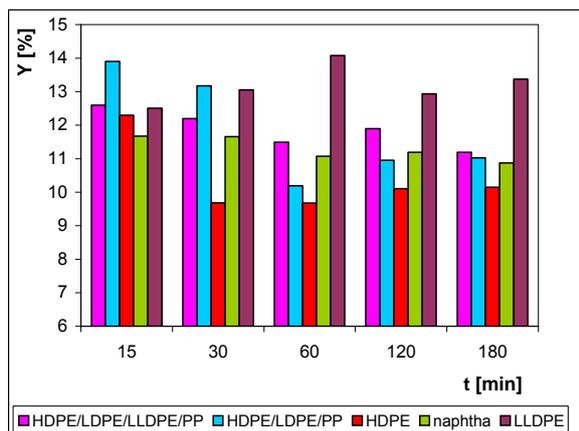


Fig.7 Benzene yields (Y) for different feedstocks at 820°C

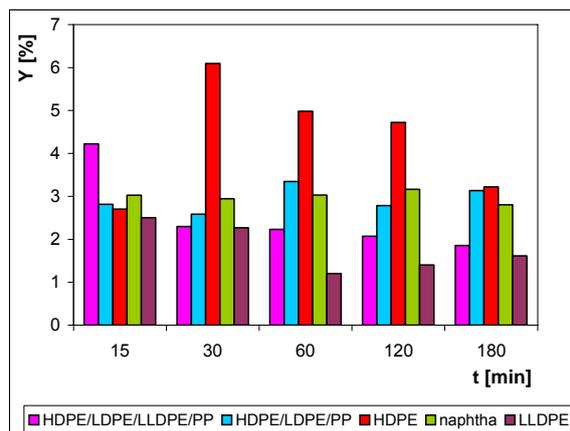


Fig.8 Naphthalene yields (Y) for different feedstocks at 820°C

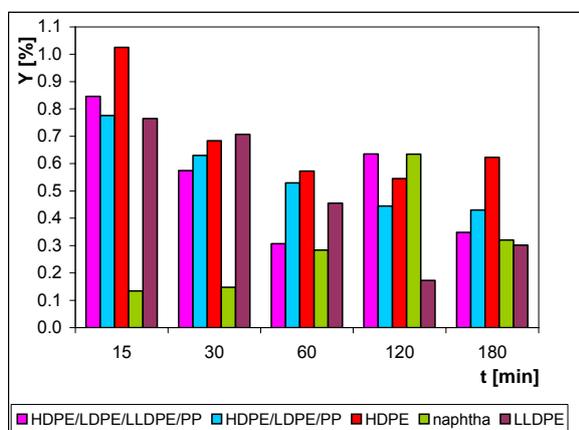


Fig.9 Summation of the yields of higher aromates (anthracene, phenantrene, acenaphthene, fluorene) for different feedstocks at 820°C

#### 4. Conclusions

The results from coke production on copyrolysis show that the secondary reactions leading to coke formation run at minimum levels. The formation of coke during copyrolysis has been comparable or less to the coking of naphtha on the clean surface of reactor. Approaching to the end of experimental time (after the walls are covered by a thin layer of coke) the production of coke from both polyethylenes was slightly higher in comparison to the coke from naphtha. Our observations confirm the possibility of the recycling of individual or mixed polyalkenes via the copyrolysis of oils and waxes with conventional liquid steam cracking feedstock.

#### Acknowledgement

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