

CO-PYROLYSIS OF ESTONIAN SHALES WITH LOW-DENSITY POLYETHYLENE

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The effect of co-pyrolysis of low-density polyethylene with Estonian kukersite oil shale, its semicoke and Dictyonema shale on the yield and composition of the pyrolysis oil was investigated. The oil obtained in autoclaves was analyzed by thin-layer chromatography, and the composition of hydrocarbon fractions by capillary gas chromatography. The effect of co-pyrolysis was evaluated by comparison the quantity of destruction products obtained in co-pyrolysis experiments with the hypothetical mean of the destruction product quantity from single objects pyrolysis. The yield and chemical group composition of co-pyrolysis oil depends to a certain degree on the shale type used. The yields of co-pyrolysis products (gas, oil, solid residue) practically coincide with those calculated. Dictyonema shale has the strongest effect on the yield and composition of co-pyrolysis products, it increases polyethylene conversion which results in increasing the quantity of gas and decreasing that of oil because of the degradation of hydrocarbons to shorter and more volatile ones. High content of aliphatic hydrocarbons and low content of aromatic ones in the oil obtained from polyethylene changes the composition of co-processing oil resulting in low content of aromatic hydrocarbons, especially polycyclic ones.

Introduction

The disposal of waste plastics (WP) has been recognized as a major environmental problem. WP are undesirable components for landfilling, since they are not biodegradable. Household municipal waste is one of the main sources of WP. For example, in the US, waste plastics currently amount to around 20% by volume and 8% by weight of all municipal solid waste [1]. Treatment of WP by direct incineration is not very desirable due to increased emission of greenhouse gas, primarily CO₂ and other toxic pollutants.

Many recycling plants have already practiced chemical modification technologies (hydrolysis, methanolysis and ammonolysis) for

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polycondensation polymers such as PET and polyurethane; pyrolysis, gasification, catalytic cracking, hydrogenation, coking and visbreaking for polyolefins, PS and PVC [1].

Thermal degradation of waste plastics to liquid fuel is one of the most promising methods among various waste plastics treatment and recycling methods. For the hard coal, the atomic H/C ratio is roughly 0.6 and hence, hydrogenation of coal is necessary to realize its liquefaction to the liquid fuel. For alkanes characterized by carbon atoms number n , the atomic H/C ratio is approaching 2.0 for long-chain molecules. The H/C ratio of some plastics is similar to that of alkanes. Thus, liquefaction of waste plastics should produce liquid fuels with high H/C ratios by very little H addition [2, 4–7].

Thermal degradation of plastic wastes has been studied by thermogravimetry [6], by batch operation in a glass reactor [7], in autoclaves [5, 11], in retorts [12], in temperature-programmed reactors [13] or in fluidized-bed reactors [8].

There is a considerable interest in the efficient conversion of waste plastics mixed with coal into clean hydrocarbon fuel or other valuable products such as lubricants [11]. It has been suggested that the addition of plastic to the coal during liquefaction may result in enhanced coal conversion and oil production compared with the yields obtained when coal alone is treated. This unilateral synergistic effect is believed to base on the fact that the high hydrogen content of plastics serves as an inexpensive hydrogen source contributing the dissolution of coal during the liquefaction.

Although co-processing of coal with waste plastics has been extensively studied and promising results have been obtained by processing rubber and tires with oil shale [9, 10], only few works have been focused on co-liquefaction of oil shales with plastics.

Some reports have been published on catalytic degradation of polyethylene (PE) where the thermally degraded hydrocarbon vapors were brought into contact with solid acid catalysts to obtain secondary cracking products. Various types of zeolite, silica-alumina, platinum-sulphated zirconia catalysts were used [7]. When these PE samples were degraded in the presence of silica-alumina catalyst, no wax-like compounds were obtained, and the yield of both liquid and gaseous products increased. The initial rate of degradation of all types of PE over the silica-alumina catalyst was about 3–4 times faster than that of thermal degradation without catalysts. These results suggest that the acid sites of silica-alumina in contact with the melted PE accelerated its degradation significantly [7].

Spent shale (the residue after retorting Israeli oil shale at 500–550 °C) was used as a solid fuel constituent in mixture with waste rubber and plastics [12]. The spent shale played the role of a heat-transfer medium, and of a mechanical carrier of the processed polymers.

Temperature-programmed co-pyrolysis of two Turkish oil shales (shale oil content by Fisher assay 31.8 and 6.4 wt%) with low-density PE (LDPE)

was investigated [13]. The kerogen type was found not to have a great effect on hydrocarbon distribution, but the experimental results indicated that the conversion of LDPE can be increased by catalytic effect of mineral materials.

The aim of the current study was to determine the effect of co-processing of LDPE with Estonian kukersite oil shale, its semicoke and Dictyonema shale on the yield and composition of pyrolysis oil. LDPE was chosen for experiments as the main component of plastic waste from domestic refuse.

Experimental

LDPE ESCORENE LD650 in bead form was obtained from EXXON Chemical, Belgium.

To study the influence of organic and mineral part of shales on the oil yield and composition, kukersite, its semicoke and Dictyonema shale samples (Table 1), crushed and ground to the particle size 40 μm , were co-processed with LDPE.

Pyrolysis was carried out in 20-ml autoclaves in a preheated oven. To study the co-pyrolysis effect on the yield of pyrolysis products, equal quantities of pyrolysis objects (LDPE, oil shale, and LDPE : oil shale 1 : 1 wt.) were processed. The quantity of the initial material in every pyrolysis test was about 4 g.

Table 1. Characteristic Components of Shales, %

| Indices | Kukersite [3, 14] | | Dictyonema shale [3] |
|-----------------------------------|-------------------|-----------|----------------------|
| | shale | semicoke | |
| Moisture | 0.5 | – | 1.0 |
| Content of organic part | 50.2 | 22.8 | 16.0 |
| Ultimate analysis of organic part | | | |
| C | 77.3 | 92.0–93.0 | 70.5 |
| H | 9.8 | 3.3–3.5 | 7.4 |
| S | 1.7 | 0.4–0.5 | 4.2 |
| N | 0.4 | 3.2–4.0 | 2.5 |
| O | 10.8 | – | 15.4 |
| H/C ratio | 1.52 | 0.44 | 1.26 |
| Composition of ash | | | |
| SiO ₂ | | 31.0 | 61.1 |
| Al ₂ O ₃ | | 8.2 | 15.4 |
| Fe ₂ O ₃ | | 5.9 | 0.6 |
| TiO ₂ | | 0.5 | 0.7 |
| CaO | | 39.5 | 0.9 |
| MgO | | 4.8 | 1.6 |
| SO ₃ | | 5.0 | 1.1 |
| K ₂ O | | 4.2 | 8.8 |
| Na ₂ O | | 0.3 | 0.7 |
| P ₂ O ₅ | | 0.1 | 0.2 |

The pyrolysis temperature and time were varied within 420–540 °C and 20–120 min. At the end of reaction the autoclave was cooled down to room temperature. The mass of gas formed was determined by discharging the gas. The slurry was solvent-extracted with hexane [5] to remove the oil and a small quantity of water which was not separated. The hexane-insolubles were extracted from dried and weighed solid residue with tetrahydrofuran to remove asphaltenes and preasphaltenes. The solid residue on the glass filter was dried and weighed. The amount of oil was determined by subtracting the weight of gas, asphaltenes and residue from the sample weight.

Preparative thin-layer chromatography (TLC), using (24 × 24)-cm plates coated with a 2-mm layer of silica gel (40 μm) and hexane as eluent, was applied for estimation of the group composition of oils. Five groups of compounds were separated and extracted from silica gel with ethyl ether:

- Aliphatic hydrocarbons (AHC)
- Monocyclic hydrocarbons (MCHC)
- Polycyclic hydrocarbons (PCHC)
- Neutral heteroatomic compounds (NHet)
- Polar heteroatomic compounds (PHet)

Gas chromatograph Chrom 5 (equipped with integrator CI 100A and FID-detector) with temperature programming on OV-101 capillary column was used for determination of the individual composition of aliphatic hydrocarbons present in AHC fraction.

Results and Discussion

Yield of Products

Pyrolysis results (Table 2) evidence that co-processing with Dictyonema shale has a negative hysteresis in the oil yield and positive ones in the gas and coke yields.

The effect of LDPE co-pyrolysis with kukersite is evaluated in detail by comparison the experimental conversion values of the mixes and the hypothetical mean of the component conversion values (Tables 3 and 4). When the difference between the experimental and hypothetical mean is positive, then co-processing of the two materials enhances oil yield.

Table 2. Yield of Pyrolysis (500 °C, 40 min) Products, %

| Pyrolysis products | Single objects | | | Co-pyrolysis with LDPE (1 : 1 wt.) | | |
|--------------------|----------------|-----------|------------|------------------------------------|----------|------------|
| | LDPE | Kukersite | Dictyonema | Kukersite | Semicoke | Dictyonema |
| Gas | 12.59 | 11.40 | 3.24 | 9.77 | 7.00 | 20.44 |
| Oil | 86.03 | 15.53 | 6.73 | 55.23 | 43.88 | 29.82 |
| Asphaltenes | 0.85 | 0.92 | 1.56 | 2.10 | 1.37 | 1.45 |
| Solid residue | 0.53 | 72.15 | 88.47 | 32.90 | 47.75 | 48.29 |

Table 3. Differences between the Experimental and Calculated Yields of Pyrolysis Products at LDPE Co-Processing with Kukersite

| Pyrolysis conditions | | Differences in product yields, g/g of initial object | | | |
|----------------------|-----------|--|--------|-------------|---------------|
| Temperature, °C | Time, min | Oil | Gas | Asphaltenes | Solid residue |
| 420 | 120 | -0.009 | -0.015 | +0.022 | +0.001 |
| 450 | 60 | +0.015 | -0.015 | | +0.007 |
| 450 | 90 | -0.042 | +0.055 | -0.006 | -0.008 |
| 450 | 120 | +0.044 | -0.045 | | -0.001 |
| 490 | 120 | +0.031 | -0.027 | -0.000 | -0.002 |
| 500 | 20 | -0.012 | +0.025 | | -0.022 |
| 500 | 30 | -0.012 | +0.052 | -0.019 | -0.022 |
| 500 | 40 | +0.064 | -0.020 | +0.012 | -0.035 |
| 500 | 60 | +0.005 | 0.000 | -0.004 | 0.000 |
| 540 | 50 | +0.095 | -0.078 | -0.018 | -0.010 |

Table 4. Differences between the Experimental and Calculated Yields of Pyrolysis Products at Co-Processing of LDPE with Semicoke

| Pyrolysis conditions | | Differences in product yields, g/g of initial object | | | |
|----------------------|-----------|--|--------|-------------|---------------|
| Temperature, °C | Time, min | Oil | Gas | Asphaltenes | Solid residue |
| 420 | 120 | -0.045 | -0.005 | +0.017 | +0.033 |
| 450 | 90 | -0.001 | -0.010 | +0.002 | -0.012 |
| 450 | 120 | -0.045 | +0.028 | | +0.017 |
| 490 | 120 | +0.008 | -0.020 | +0.004 | +0.007 |
| 500 | 20 | -0.008 | -0.003 | | +0.010 |
| 500 | 30 | +0.001 | +0.033 | -0.002 | -0.031 |
| 500 | 40 | +0.028 | +0.010 | +0.010 | -0.025 |
| 500 | 60 | -0.006 | -0.003 | +0.004 | +0.005 |
| 540 | 50 | +0.024 | -0.025 | +0.007 | -0.005 |

The results obtained evidence that the differences in most experiments with kukersite 4-g samples are rather irregular and do not exceed the accuracy of the experiments.

The amount of both asphaltenes and solid residue increases with increasing pyrolysis time. Hence, LDPE co-pyrolysis with kukersite at shorter time (up to 2 h) is promoted compared to that of single objects. Therefore synergistic effect of co-processing on the yield of destruction products is not discussed in more detail.

Mostly positive differences in the asphaltene fraction in the case of co-pyrolysis of LDPE and semicoke can be resulted from the hydrogenisation of the semicoke. The mineral part of spent kukersite has no positive effect on the gas and oil yield from LDPE.

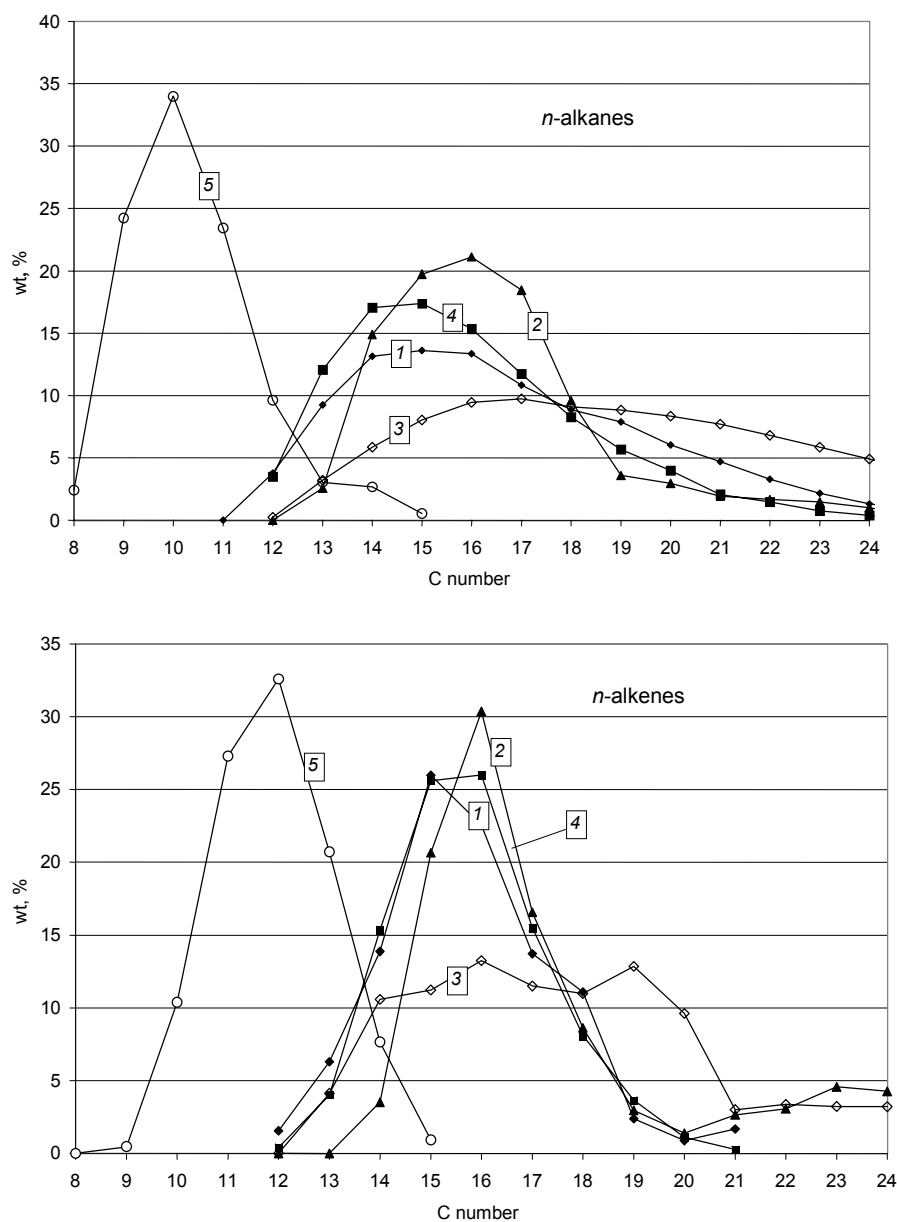


Fig. 1. Distribution of carbon number (NP-gram) of hydrocarbons (*n*-alkanes and *n*-alkenes) of AHC fraction obtained by pyrolysis of single LDPE (1) and kukersite (2), and by co-pyrolysis of LDPE with kukersite oil shale (1 : 1 wt.) (3), its semicoke (4) and Dictyonema shale (5) at 500 °C during 40 min

Oil Composition

The effect of co-processing on LDPE degradation and composition of pyrolysis oil was studied comparing the quantity of chemical groups obtained by TLC (Table 5) and the composition of AHC (Fig. 1).

Table 5. Chemical Group Composition of Pyrolysis Oil, %

| Compounds | Single objects | | Co-pyrolysis with LDPE (1 : 1 wt.) | | |
|----------------------------|----------------|-----------|------------------------------------|----------|------------|
| | LDPE | Kukersite | Kukersite | Semicoke | Dictyonema |
| Aliphatic HC | 78.8 | 14.4 | 65.7 | 61.8 | 27.2 |
| Aromatic HC | 19.1 | 32.6 | 16.6 | 36.1 | 42.5 |
| Among them: | | | | | |
| Monocyclic HC | 4.7 | 2.1 | 4.4 | 11.5 | 22.8 |
| Polycyclic HC | 14.4 | 30.5 | 12.2 | 24.6 | 19.7 |
| Neutral heterocompounds | 1.4 | 12.6 | 4.3 | 1.6 | 22.8 |
| High-polar heterocompounds | 0.7 | 40.4 | 13.4 | 0.5 | 7.5 |

The desired end result of co-processing was to obtain higher conversion to more volatile organic liquid products (C₅–C₁₅ with BP range 36 to 270 °C).

The carbon number distribution of *n*-alkanes and *n*-alkenes in AHC fraction obtained proves that co-pyrolysis of LDPE with kukersite is depressed – the alkane chains are longer. A substantial decrease in C numbers in the case of Dictyonema shale agrees with the increase in the gas yield given above (see Table 2).

The results of experiments (see Fig. 1) demonstrate that Dictyonema shale affects the destruction of LDPE stronger than kukersite. Therefore the co-processing of LDPE was carried out varying the share of Dictyonema shale from 5 to 50 wt% at the same conditions (Table 6).

The results obtained evidence that the chemical group composition of oil depends considerably on the quantity of Dictyonema. Only 5% of it increases both the total oil quantity and the content of AHC fraction. Any further increase in the Dictyonema shale in the mixture decreases the quantity of the most valuable AHC fraction.

Moreover, any percentage of tested Dictyonema shale added to LDPE narrows the HC number range (Fig. 2). For example, with 25 wt% of Dictyonema, AHC fraction consists mainly of hydrocarbons *n*-C₅ to *n*-C₁₂ (BP range 36 to 216 °C). Therefore, addition of Dictyonema shale degraded the LDPE sample to more volatile hydrocarbon fuel oil than kukersite and its semicoke.

The composition of pyrolysis oil depends also on the type of pyrolysis reactor. If the pyrolysis is carried out in a reactor at atmospheric pressure, the relation of alkenes to alkanes is about 1 : 1 [13]. The oil obtained by pyrolysis in a fluidized-bed reactor had the alkane/alkene/diene ratio 1 : 2.2 : 0.25 [8]. The composition of oil obtained from PE in an autoclave was about 70% alkanes, 22% alkenes and 8% aromatics [2].

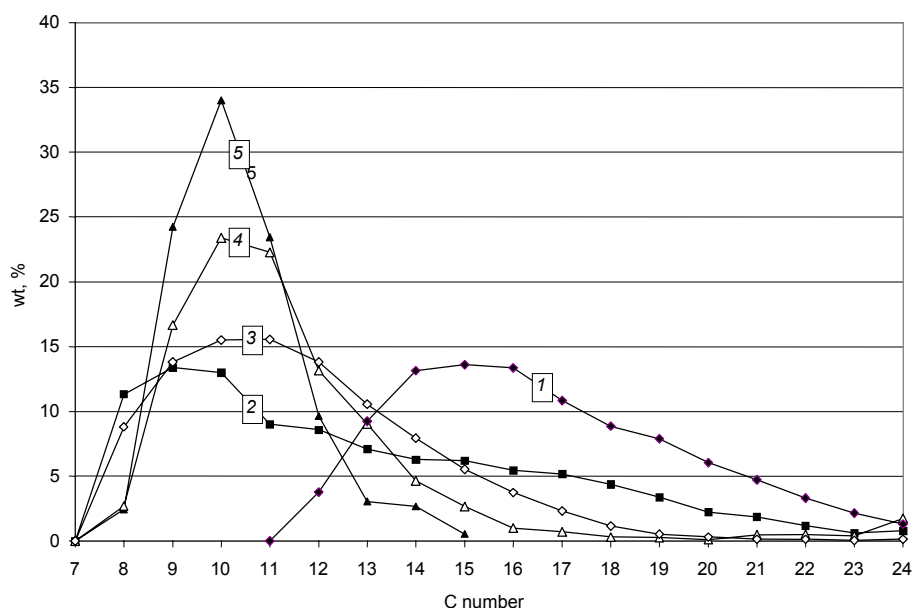


Fig. 2. The effect of Dictyonema percentage (5 (2), 10 (3), 25 (4) and 50 wt% (5)) in the mix with LDPE (single LDPE (1)), on the distribution of carbon number of *n*-alkanes in AHC fraction of co-pyrolysis oil

Table 6. Characteristics of LDPE and Dictyonema Shale Co-Pyrolysis Products (500 °C, 40 min) at Their Different Ratios

| Products | LDPE and Dictyonema ratio, wt% | | | | | |
|---|--------------------------------|--------|---------|---------|---------|---------|
| | 100 : 0 | 95 : 5 | 90 : 10 | 75 : 25 | 50 : 50 | 0 : 100 |
| Yield of destruction products, %: | | | | | | |
| Gas | 12.59 | 10.21 | 11.93 | 19.72 | 20.44 | 3.24 |
| Oil | 86.03 | 86.68 | 79.54 | 55.72 | 29.82 | 6.73 |
| Asphaltenes + solid residue | 1.38 | 3.11 | 8.53 | 24.56 | 49.74 | 90.03 |
| Differences in oil yield, % from the pyrolysis of single LDPE | | | | | | |
| | | +5.46 | +2.09 | -17.8 | -55.2 | |
| Chemical group composition of oil, %, determined by TLC: | | | | | | |
| AHC | 78.8 | 80.8 | 56.6 | 57.2 | 27.2 | 35.7 |
| MCHC | 4.7 | 6.2 | 8.6 | 12.3 | 22.8 | 8.1 |
| PCHC | 14.4 | 11.0 | 13.6 | 15.9 | 19.7 | 25.1 |
| NHet | 1.4 | 1.3 | 18.6 | 10.2 | 22.8 | 16.9 |
| PHet | 0.7 | 0.7 | 2.6 | 4.4 | 7.5 | 14.2 |
| Differences in AHC fraction yield, % from the pyrolysis of single LDPE | | | | | | |
| | | +8.0 | -35.7 | -59.9 | -332 | |

The composition of the AHC fractions obtained by LDPE pyrolysis and its co-pyrolysis with Dictyonema presented in chromatograms (Fig. 3) demonstrates that the total unsaturation degree is higher in the co-pyrolysis product. The same effect was observed in catalytic degradation of PE with silica-alumina catalyst [7].

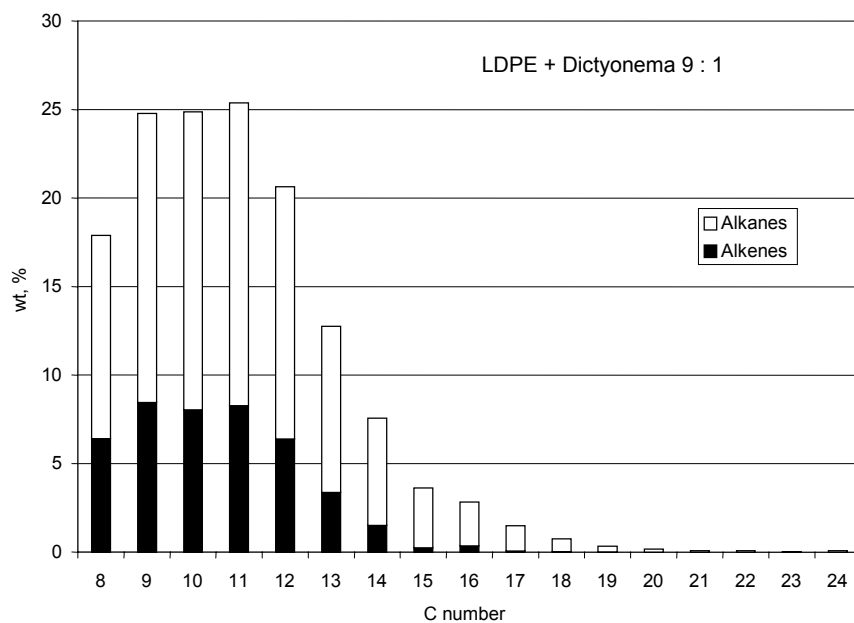
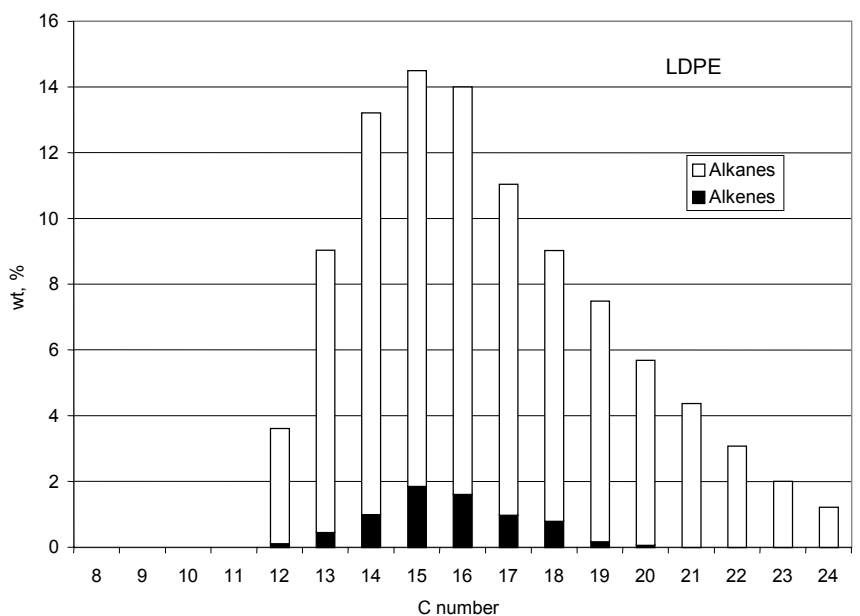


Fig. 3. Composition of AHC fraction of oil from single LDPE pyrolysis and its co-pyrolysis with Dictyonema shale (10 wt%).

Conclusions

Co-pyrolysis of LDPE as the main component of plastic wastes with Estonian kukersite oil shale, its semicoke and Dictyonema shale in autoclaves was investigated. The amounts of gas, oil, solid residue formed in the co-pyrolysis process consist of partial contributions of the initial objects. The composition of the co-process oil differs from that of LDPE alone. Dictyonema shale has a most marked effect on the LDPE destruction rate. It narrows the HC number range of *n*-alkanes and *n*-alkenes and increases the unsaturation degree of the aliphatic HC fraction. The chemical group composition of oil depends considerably on the quantity of Dictyonema shale. When used in quantity up to 5% of the mixture, it increases both the total oil quantity and the content of AHC fraction. At higher percentages Dictyonema shale decreases the oil yield on account of gas formation.

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