



Liquid fuel from waste polyolefins Part II. Thermal and pressure degradation of waste polyolefins in the presence of methyl alcohol

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ABSTRACT

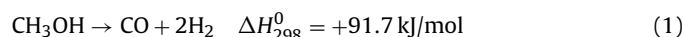
In the paper, the study on co-decomposition of polyolefins and thermally unstable methyl alcohol is presented. The process temperature was maintained above 400 °C. The pressure at the end of process, depending on the feed composition, was 3–25 MPa. In the first variant, the raw material was polyolefin product, in the form of solidifying liquid, previously partially decomposed. Basing on the satisfactory results regarding the methanol influence on the quality of obtained liquid fractions, extended technological concepts were proposed, in which also solid waste polyolefins can be used without the phase of previous thermocatalytic decomposition. Dissolution of raw polymer is facilitated by paraffin oil addition. The only disadvantage is a large fraction of sulphur, purposely introduced in case of methods that use technological oil. In the last case, waste polyolefins were used, but without oil type additions. Although the efficiency of the liquid product is not as high as in oil technologies, the fractions with satisfactory results are obtained. The results show decomposition of polymer bonds with a simultaneous hydroconversion of unsaturated structures.

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1. Introduction

A different solution to hydrotreating of thermal/thermocatalytic polyolefin degradation products is using hydrogen donor liquids under thermal and pressure conditions. Presented in paper [1], the method of co-decomposition of polyolefins in the presence of a model reagent – tetralin – shows a real potential for using hydrogen transfer as a way of enriching polymer materials that are meant to be fuel components. Liquid fractions – a mixture of low molecular weight hydrocarbons – contain reduced amounts of unsaturated structures, sulphur and chlorine compounds. A significant disadvantage of the solution that uses highly reactive organic solvents from the hydronaphthalene group is the fact that many parallel or successive reactions cannot be avoided at the elevated temperature. Therefore, the application of such reagents for technological purposes is not possible for several reasons, including a necessary purification of the final fraction from the products of hydrogen donor transformation as well as its biologic activity and high price. An important issue is the lowest possible cost of the polymer destruction process that can be applied in order to obtain highly valuable liquid components with the use of cheap and eas-

ily available reagents. During a selection of appropriate material for the technological process, many aspects are considered, e.g. a group of decomposition products, reforming temperature or the cost of the whole process. These considerations lead to methanol as, according to reactions (1) and (2), it appears a valuable material for hydrogen – desired in hydroconversion processes – production [2–4]:



Contrary to typical hydrogen donors, the reagent is decomposed, resulting in a rapid growth in the pressure of reaction mixture. 1 kg of methanol can yield even 1.5 m³ of hydrogen (99.9999% purity) [4]. The reaction of methanol reforming is currently used in Japan, and obtained hydrogen is applied in hydrogen powered motor vehicles.

In the paper, the results of laboratory tests regarding thermal and pressure degradation of various waste polyolefin materials in the presence of methanol are presented. The authors focus on the transformation potential of multiple carbon–carbon bonds and reduction of sulphur and chlorine compounds. The tests comprise 3 series of experiments with the use of various waste polyolefins. The preliminary experiments were performed for highly unsaturated systems—crude fractions obtained from industrial installations of waste polyolefin thermocatalytic decomposition. In the second

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Table 1
Process conditions in the preliminary studies.

Experiment		1	2	3	4	5	6
Feed composition	Raw material	CP	CP	CP	CP	CP	CP
	Solvent	Methanol	Methanol	Methanol	Methanol	Methanol	Methanol
Mass ratio		1:8	1:3	2:1	1:1	2:1	2:1
Autoclave filling degree, V_0 (%)		41	3	9.7	12	10	10
Final reactor temperature, RT (°C)		260	260	403	409	402	404
Final pressure, P (MPa)		12.0	2.2	7.3	7.0	10.0	11.5
Cracking time, t (h)		0	0	3	6	3	6

stage, the range of applied materials was expanded with waste polyolefins without previous thermocatalytic decomposition. In this version, a paraffin oil additive was used as it facilitates dissolution of solid polymer. The third series of experiments regarded attempts to perform a polymer degradation process directly in the system: waste polyolefin–methanol, without factors facilitating dissolution of crude materials. This solution is the main aim of the present study because it would allow for complete polymer degradation. Thus, it would create a real potential for the whole process of engine fuel production from waste to be performed within one plant.

2. Experimental

2.1. Polyolefin material

A crude product CP obtained from the initial thermal destruction of polyolefins was used as the analysis material in the preliminary study. The sample was collected from an industrial installation of waste polyolefin thermocatalytic decomposition (mainly polyethylene and polypropylene) on an industrial scale. Selected properties of the material are as follows: average molecular mass = 197.5 g/mol, iodine number = 63.2 g $I_2/100$ g, 500 mg sulphur/kg waste, 200 mg of chlorine/kg of waste, density = 0.8089 g/cm³. A detailed characteristic of the material was presented in the previous paper (point 2.1. in [1]).

In the next variant, waste polyolefins WP without previous thermocatalytic decomposition were directly used. The material for the analysis contained mainly polyethylene waste (90%) and less amount of polypropylene (10%). The material, as waste, contained also small amounts of heteroatoms: 400 mg sulphur/kg waste and 500 mg chlorine/kg waste. This experiment was performed as a co-decomposition with a paraffin oil PO additive. A detailed characteristic of the oil is as follows: average molecular mass = 308.6 g/mol, boiling range: 61–360 °C, iodine number = 4.8 g $I_2/100$ g, 3500 mg of sulphur/kg of waste, chlorine content = abs.

In the last case, waste polyolefins WP without previous thermocatalytic decomposition were used, but without oil type additions.

2.2. Solvent

Methanol was used as a solvent.

2.3. Catalyst

Several types of catalysts were applied in these experiments: the G3 catalyst (CoMo/Al₂O₃) or base metal oxides, such as MgO, and other metal oxides, e.g. ZnO, CuO—which also can be applied as a good catalysts for polymer cracking.

2.4. Reaction equipment

The co-decomposition of waste material and methanol or paraffin oil additive was performed in a closed pressure autoclave

(1 dm³) provided with a mechanical stirring system as well as the electronics and software intended for data collection and analysis, for controlling and monitoring the basic parameters, including: requested power (%), reactor temperature RT (°C), zone temperature ZT (°C), pressure P (MPa) and time t (min). A detailed characteristic of the experimental setup was presented in the previous paper (Fig. 2 in [1]).

2.5. Experimental procedure

The reactions were conducted with different plastic:solvent, plastic:oil:solvent, plastic:oil, oil:solvent mass ratios. A blank reaction of solvent (methanol in absence of polymer material) was also carried out. The waste material (crude product CP or waste polyolefins WP), paraffin oil PO and methanol were weighed and placed in the autoclave. All the experiments (Nos. 1–12) were carried out with addition of the G3 catalyst (5 wt% in relation to the weight of plastic). A part of the experiments (Nos. 1–4) were carried out with addition of the CuO–ZnO catalyst, while Nos. 5–12 with addition of the MgO catalyst (both 3 wt% in relation to the weight of plastic). In Tables 1, 4 and 7, detailed data of the performed experiments (feed composition, mass ratio, autoclave filling degree V_0 , final reactor temperature RT, final pressure P and reaction time t) are presented. For the mixture of organic liquid, paraffin oil and polyolefin material, argon blow was applied and subsequently the autoclave was closed, maintaining atmospheric pressure. The initial experiments (Nos. 1 and 2) were performed at a lower temperature: 260 °C. The other tests were carried out at 400 °C. Reaching that temperature, the reaction was conducted for 180 min (processes Nos. 3 and 5), 360 min (processes Nos. 4 and 6) and 30 min (processes Nos. 7–12) before cooling down to the room temperature. The heating rate of the autoclave was approximately 4 K/min. The pressure obtained during the process depended on the mixture composition and volume, and it was the result of vapour pressures of the mixture reagents in phase and chemical reactions. On completion of the process, the autoclave was left until it completely cooled down to the room temperature. The gas products were then collected in order to measure the volume and determine the chemical composition. After the autoclave lid was opened, the obtained liquid mixture was weighed and distilled in order to remove residual methanol. The obtained hydrocarbon fractions were analysed for physicochemical properties and chemical composition.

2.6. Product analysis

The gas products were analysed for their chemical compositions with the use of the gas chromatography method: an HP 5890 gas chromatograph equipped with FID and TCD. The Carbo-sphere column (1.8 m × 3 mm) and TCD were used for separation and detection of H₂, whereas the Alumina column (1.8 m × 3 mm) and FID were used for separation and detection of C₁–C₄ (C₅, C₆) hydrocarbons.

The liquid product analyses were performed by means of the Saturn 2100T GC–MS analytical system developed by Varian which

consisted of a capillary gas chromatograph GC coupled on-line with an ion trap mass spectrometer MS—with electron ionization at 70 eV. The chromatograph was equipped with a Varian chromatographic VF–5 ms capillary column, 30 m × 0.25 mm, stationary phase of 0.25 μm.

The chlorine content in the liquid products was measured by means of a modified method consistent with British standards: Standard methods for testing tar and its products, Second edition 1938, Serial No.: C.T. 5-38.

Other measurements of liquid fractions were performed according to Polish Standard Methods:

- Normal distillation according to PN-81/C-04012 (ISO 3405).
- Average molecular mass (g/mol) according to PN-64/0530-02 (ASTM D2224-78).
- Iodine number (g I₂/100 g) according to PN-67/C-04068 (ISO 3961).
- Content of sulphur (mg/kg) using Grote–Krekeler method consistent with PN-80/C-97078 (DIN 51400-2).
- Density (g/cm³) according to PN-90/C-04004 (ISO 3675).

3. Results

3.1. Blank reaction of solvent in absence of polymer material

The blank reaction was carried out with the use of solvent and no polymer material in order to determine the solvent stability under the operating conditions (400 °C). The results of this reaction show that methanol undergoes significant conversion, causing distinct and rapid growth in the reaction mixture pressure. The main product of the solvent decomposition is hydrogen: 69.8%, and then carbon monoxide: 6.6%, carbon dioxide: 22.6% as well as methane: 1.1%.

3.2. Degradation of waste material CP in the presence of a methanol

The preliminary tests with the use of methyl alcohol were meant to determine the potential for crude hydrocarbon mixture enriching—regarding reduction of both unsaturated bonds and sulphur and chlorine compounds. 6 Experiments of the waste material CP cracking in the presence of a solvent were carried out. They were performed with the use of various process parameters which strongly influence the outcomes of cracking tests. In Table 1, detailed data of the performed experiments are presented. Exploratory experiments Nos. 1 and 2 were performed at a lower temperature: 260 °C, while Nos. 3–6 in the temperature above 400 °C. Changes in pressure result from vapour pressures of the mix-

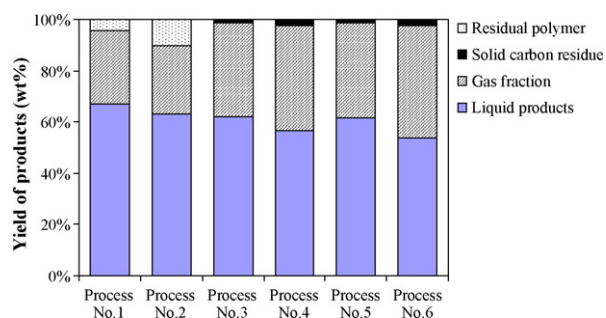


Fig. 1. Distribution of cracking products, gases, liquid and solid carbon residue in the preliminary studies.

ture reagents during phase transitions and chemical reactions (2.2–12.0 MPa).

The results of experiments, in the form of material balance, are presented in Fig. 1. Despite the elevated pressure in the autoclave (up to even 12 MPa), but at a lower process temperature (260 °C), evident depolymerization of the material, in order to obtain volatile products, does not occur. The residue was solid polymer. The temperature elevation up to 400 °C results in rapid decrease in thermal stability of polyolefin chains. In these cases (tests Nos. 3–6), gas, liquid hydrocarbon fraction and solid carbon residue were obtained. The yields of gas products in all the experiments are significant due to the low thermal stability of methyl alcohol. In the autoclave, primarily solvent degradation occurs, causing distinct and rapid growth in the reaction mixture pressure.

The compositions of obtained gas products are presented in Table 2. The GC analysis indicates the presence of typical methanol decomposition components (mainly H₂, CO, CO₂). At 400 °C, a scission of bond at the ends of chains occurs, generating volatile products such as methane as well as ethane, propane and butane. Smaller amounts of olefins and C₅–C₆ hydrocarbons were also found.

The liquid mixture obtained in the experiments was mainly composed of methanol residues and depolymerization products. The methanol residue was removed through distillation. Two fractions: methanol residue and a fraction with the boiling point above 65 °C were obtained. Based on the amount of residual methanol after the reaction and the amount of methanol in the reaction, a conversion degree of solvent was determined: 34.1% (in test No. 1), 33.5% (in test No. 2), 59.5% (in test No. 3), 76.7% (in test No. 4), 61.2% (in test No. 5) and 78.9% (in test No. 6). This value depends on the feed composition and process parameters which strongly influence the outcomes of tests. The results show that methanol has a low stability in high temperatures.

Table 2
Compositions of hydrocarbons and other components in gas products in the preliminary studies.

Experiment	1	2	3	4	5	6
Composition of products (%)						
Hydrogen	54.8	63.5	33.2	31.8	27.5	31.0
Carbon monoxide	3.4	3.1	11.4	13.6	13.4	12.5
Carbon dioxide	41.0	30.7	12.4	12.8	15.0	13.2
Methane	0.7	2.8	22.8	20.6	25.5	25.1
Ethane	0.0	0.0	9.5	11.3	9.8	10.2
Propane	0.0	0.0	6.3	5.8	5.0	4.3
Butane	0.0	0.0	1.1	1.2	1.3	1.2
C ₅	0.0	0.0	0.5	0.4	0.3	0.3
C ₆	0.0	0.0	0.1	0.1	0.1	0.1
Ethylene	0.0	0.0	0.5	0.4	0.3	0.3
Propylene	0.0	0.0	1.4	1.3	1.2	1.3
Butylene	0.0	0.0	0.7	0.6	0.6	0.5
Butadiene	0.0	0.0	0.1	0.1	0.0	0.0

Table 3
Selected properties of liquid hydrocarbon products in the preliminary studies.

Experiment	1	2	3	4	5	6
Liquid product density (g/cm ³)	0.778	0.779	0.783	0.779	0.782	0.778
Average molecular mass (g/mol)	102.1	102.4	103.1	101.5	102.2	101.2
Iodine number (g I ₂ /100 g)	27.1	17.6	36.8	35.9	37.2	36.4
Sulphur content (mg/kg)	200	300	100	50	200	100
Chlorine content (mg/kg)	100	100	20	0	20	0

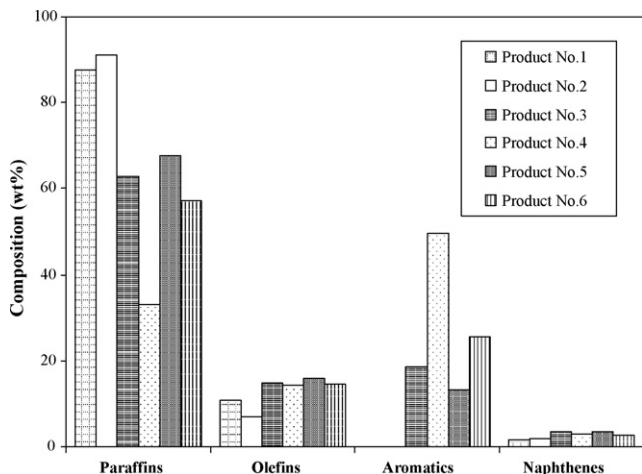


Fig. 2. Effect of the reaction in the presence of solvent on the paraffin, olefin, aromatic and naphthene yields for the hydrocarbon fraction (crude polymer product/methanol; final temperature: 260–409 °C; final pressure: 2.2–12.0 MPa).

The obtained liquid mixture of hydrocarbons – after removal of methanol – was characterized by the density, average molecular mass, iodine number, heteroatoms: chlorine and sulphur (Table 3).

Random scission of bonds in a polymer molecule takes place and results in volatile systems of a molecular mass reduced to approximately 100 g/mol. Despite the progressive material degradation, the iodine number in the obtained fractions decreased from 63.2 g I₂/100 g (in the crude polyolefin product) to 17.6–37.2 g I₂/100 g, and the contents of sulphur and chlorine were considerably reduced. The effect of the process time prolongation from 3 h (test Nos. 3 and 5) to 6 h (test Nos. 4 and 6) is a more effective elimination of heteroatoms from liquid products.

The compositions of liquid fractions are presented in Fig. 2. They contained both paraffins (ranged 33.2–91.1%), naphthenes (ranged 1.5–3.5%) and smaller amounts of olefins (ranged 7.1–15.8%) as well as a certain amount of aromatic hydrocarbons (ranged 0–49.5%). In the test No. 4 (6-h cracking processes), the amount of aromatic compounds in the degraded fraction can be even 49.5%, which is unacceptable for products that constitute a fuel component. The effect of the process time prolongation from 3 (test Nos. 3 and 5) to

6 h (test Nos. 4 and 6) is a more effective aromatization of the system. For minimum aromatization during the polymer destruction process, the presence of a basic medium, such as MgO, is necessary. This modification allows for production of a final fraction with a content of such structures reduced even by 24%, comparing to the analogical process with CuO–ZnO. Almost all aromatic compounds are included in the fractions within the gasoline boiling range. The GC analysis mainly shows benzene and benzene derivatives, such as toluene, xylenes, small amounts of other benzene derivatives. A concern is the presence of benzene in the fraction No. 4 (4.4%) because this level is several times as high as the acceptable standard for fuel substitutes (<1% of benzene) (Fig. 3). On one hand, this particularly toxic compound has a high octane number (97), but on the other hand, it shows highly toxic, carcinogenic, mutagenic, teratogenic and embryotoxic properties. Another disadvantage of this compound is its tendency to emerge during combustion of excessive amounts of coke or soot. The current use of benzene is limited or completely eliminated whenever possible.

3.3. Degradation of waste polyolefins WP in the presence of a methanol and with addition of technological oil

In the next series of experiments, the range of crude materials was expanded to waste polyolefins without previous thermocatalytic decomposition, but with a technological oil additive which is an agent supporting solid polymer destruction. 3 Experiments of waste polyolefin WP cracking in the presence of a solvent and with addition of a paraffin oil PO were carried out. In Table 4, detailed data of the performed experiments are presented. The pressure, obtained during the process, depended on the mixture composition and its volume, ranging from 3.0–25.0 MPa. Due to the tendency towards aromatization of this type of systems, the cracking time was reduced to 0.5 h. Process No. 7 is decomposition of waste polymers WP with paraffin oil PO and methyl alcohol. Process No. 8 was performed in order to determine the effect of methanol on the quality and physicochemical properties of products obtained with the use of this method. Process No. 9 will allow for determination of the potential for refining of sulphur containing technological oil with the use of the applied reagent.

The results of experiments, in the form of material balance, are presented in Fig. 4. As a result of waste polyolefin thermal destruc-

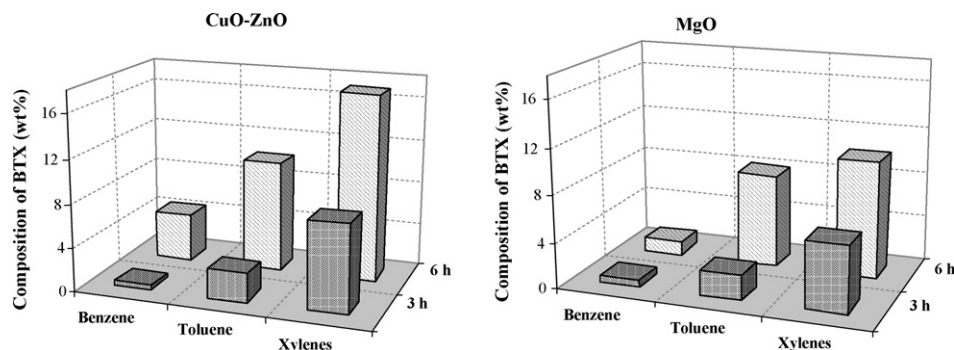
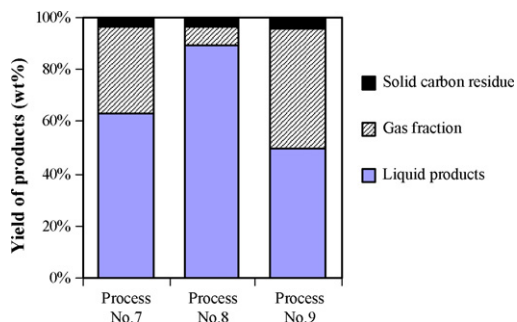


Fig. 3. The contents of benzene, toluene and xylenes in the obtained liquid fractions after 3 and 6-h cracking processes, depending on a catalyst type.

Table 4
Process conditions in the second stage of experiments.

Experiment		7	8	9
Feed composition	Raw material	WP	WP	–
	Solvent	Methanol	–	Methanol
	Technological oil	PO	PO	PO
Mass ratio		1:1:1	1:1	1:1
Autoclave filling degree, V_0 (%)		45	30	30
Final reactor temperature, RT (°C)		401	411	400
Final pressure, P (MPa)		25.0	3.0	24.0
Cracking time, t (h)		0.5	0.5	0.5

**Fig. 4.** Distribution of cracking products, gases, liquid and solid carbon residue in the second stage of experiments.

tion at the elevated pressure, in the presence of paraffin oil and methanol, gas, liquid fractions as well as a small amount of solid coke residue were obtained. The highest yield of liquid hydrocarbon products was obtained in the test No. 8 with a paraffin oil additive. On the contrary, the highest yield of gas product was received in the test Nos. 7 and 9. In these processes, methanol, which quickly decomposes to gaseous products, was present.

The compositions of volatile products are presented in Table 5. The gas compositions are similar to the previous results. The GC analysis indicates the presence of typical methanol decomposition components (mainly H_2 , CO, CO_2). Moreover, mainly methane and smaller amounts of ethane, propane and butane were obtained. Light olefins were also identified. The highest volume content of unsaturated hydrocarbons was found in the gas mixture after test No. 8—performed without methyl alcohol.

The liquid mixtures were composed of methanol residues, depolymerization products and paraffin oil (test No. 7) or methanol residues and paraffin oil (test No. 9). The methanol residue was

Table 5
Compositions of hydrocarbons and other components in gas products in the second stage of experiments.

Experiment	7	8	9
Composition of products (%)			
Hydrogen	34.1	8.6	34.9
Carbon monoxide	11.6	3.8	11.2
Carbon dioxide	10.2	2.5	9.2
Methane	43.0	43.2	36.1
Ethane	5.6	24.9	4.7
Propane	2.1	10.5	2.0
Butane	1.0	2.2	0.8
C_5	0.1	0.3	0.1
C_6	0.0	0.0	0.1
Ethylene	0.2	0.8	0.2
Propylene	0.4	2.1	0.3
Butylene	0.3	0.9	0.3
Butadiene	0.1	0.3	0.1

Table 6
Selected properties of liquid hydrocarbon products in the second stage of experiments.

Experiment	7	8	9
Liquid product density (g/cm^3)	0.794	0.812	0.820
Average molecular mass (g/mol)	146.6	239.5	249.2
Iodine number ($g I_2/100 g$)	27.2	39.2	14.5
Sulphur content (mg/kg)	1200	2500	2000
Chlorine content (mg/kg)	60	140	0

removed through distillation. Two fractions: methanol residue and a fraction with the boiling point above $65^\circ C$ were obtained. Based on the amount of residual methanol after the reaction and the amount of methanol in the reaction, the conversion degree of solvent was determined: 49.5% (in test No. 7) and 52.7% (in test No. 9). The fraction No. 8 did not contain methanol, so it was directly analysed.

The obtained liquid mixture of hydrocarbons was characterized by the density, average molecular mass, iodine number, heteroatoms: chlorine and sulphur (Table 6).

Paraffin oil facilitates crude polymer dissolution which is defined as transformation of solid material into liquid phase with its strong destruction. This can be achieved due to very good solubility of the material in oil, based on a general principle that 'a similar dissolves in a similar'. It is the most efficient variant and the content of liquid fractions reaches 89.7%. Another beneficial aspect is a low level of iodine number or reduced content of chlorine. The only disadvantage of this application is a large amount of sulphur introduced with technological oil, which disqualifies the product from a group of engine fuel components. The method needs modification or replacing sulphur-containing technological oils with substitutes on previous hydrocracking. Introduction of such changes should provide a highly efficient process and allow fuel fractions of sufficient parameters to be obtained.

In the test No. 8 – without methyl alcohol – only a slight increase in pressure is obtained (3 MPa). The elevation of this parameter is known to favour a stability loss of polymer C–C bonds, leading to their scission and molecular mass reduction of the obtained product. Partial material destruction yielded a hydrocarbon fraction which, due to a high molecular mass, solidifies at the ambient temperature. The value of iodine number as well as the amounts of sulphur and chlorine compounds in the product are far higher than those obtained in an analogical process in the presence of methanol (test No. 7). This experiment shows the validity of using alcohol in material destruction processes as it is a valuable source of hydrogen and enables hydrorefining of crude degraded polymer fraction in one reaction system.

Also, within the autoclave, partial destruction of hydrocarbon mixture (contained in paraffin oil) occurs. Comparing the fraction obtained in test No. 9 to crude paraffin oil, a reduction in average molecular mass of the product and partial elimination of sulphur compounds are observed. Under these conditions, hydrocracking with methanol does not allow unfavourable sulphur compounds to be completely eliminated from technological oil, which is necessary when the material is used in the technology of high quality engine fuel production.

The compositions of liquid fractions are presented in Fig. 5. For the test in the presence of methanol and paraffin oil (No. 7), they contained both paraffins: 71.1%, naphthenes: 4.3% and smaller amounts of olefins: 15.7% as well as a certain amount of aromatic hydrocarbons: 8.9%. On the contrary, the fraction No. 8 (without methanol) contains smaller paraffin amounts: 56.8%, naphthenes: 2.4% and aromatics: 3.9%, as well as a higher amount of olefins: 36.9%.

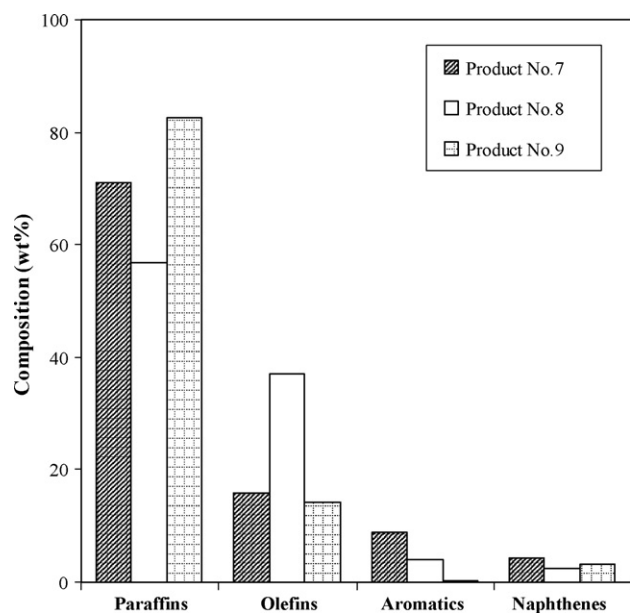


Fig. 5. Effect of the reaction in the presence of solvent on the paraffin, olefin, aromatic and naphthene yields for the hydrocarbon fraction (waste polyolefins/oil/methanol; final temperature: 400–411 °C; final pressure: 3.0–25.0 MPa).

3.4. Degradation of waste polyolefins WP in the presence of a methanol without addition of technological oil

In the third series of experiments, a decomposition of waste polyolefins in the presence of alcohol is proposed, but without oil additives that facilitate crude polymer dissolution. 3 Experiments of waste polyolefin WP cracking in the presence of methanol were carried out. In Table 7, detailed data of the performed experiments are presented. The pressure, obtained during the process, depended on the mixture composition and its volume, ranging from 18.5 to 24.0 MPa.

The results of experiments, in the form of material balance, are presented in Fig. 6. As a result of the polyolefin thermal destruction at elevated pressure, in the presence of methanol, gas and liquid fractions as well as a small amount of solid coke residue were obtained. The yields of the liquid product and solid coke residue increase with the increasing amount of polyolefins in the reaction mixture. In all the tests (Nos. 10–12), the yield of gas product is significant. Methanol quickly decomposes to gaseous products.

The chromatographic analysis showed, in the post-reaction gases, the presence of typical methanol decomposition components (mainly H₂, CO, CO₂) and light products of polymer chain

Table 7
Process conditions in the third stage of experiments.

Experiment	10	11	12
Feed composition	Raw material WP	WP	WP
	Solvent Methanol	Methanol	Methanol
Mass ratio	1:3	1:2	1:1
Autoclave filling degree, V ₀ (%)	40	45	60
Final reactor temperature, RT (°C)	411	402	400
Final pressure, P (MPa)	18.5	21.1	24.0
Cracking time, t (h)	0.5	0.5	0.5

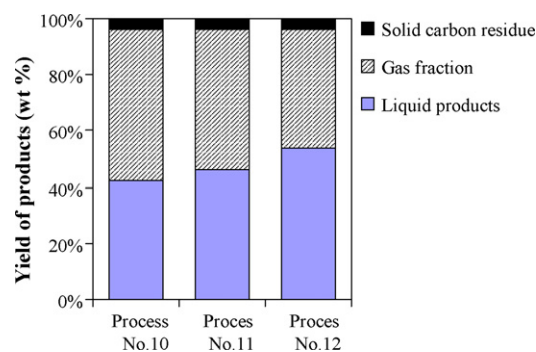


Fig. 6. Distribution of cracking products, gases, liquid and solid carbon residue in the third stage of experiments.

Table 8
Compositions of hydrocarbons and other components in gas products in the third stage of experiments.

Experiment	10	11	12
Composition of products (%)			
Hydrogen	29.4	33.1	35.2
Carbon monoxide	14.9	14.2	13.8
Carbon dioxide	9.4	10.4	11.5
Methane	39.9	34.1	28.6
Ethane	2.8	4.1	5.9
Propane	1.6	2.2	2.8
Butane	0.6	0.8	0.9
C ₅	0.2	0.1	0.1
C ₆	0.0	0.0	0.0
Ethylene	0.2	0.2	0.1
Propylene	0.7	0.6	0.6
Butylene	0.4	0.3	0.3
Butadiene	0.0	0.1	0.2

degradation C₁–C₅ (Table 8). The highest volume content of C₂–C₄ hydrocarbons, both saturated and unsaturated, was observed in the gases after the process No. 12 with the highest content of polymer in the reaction mixture.

The liquid mixtures were composed of methanol residues and depolymerization products. The methanol residue was removed through distillation. Two fractions: methanol residue and a fraction with the boiling point above 65 °C were obtained. Based on the amount of residual methanol after the reaction and the amount of methanol in the reaction, the conversion degree of solvent was determined: 39.7% (in test No. 10), 43.6% (in test No. 11) and 48.2% (in test No. 12).

The obtained liquid mixture of hydrocarbons was characterized by the density, average molecular mass, iodine number, heteroatoms: chlorine and sulphur (Table 9).

Despite the liquid product efficiency being not as high as in the method using a technological oil additive, polymer destruction leads to production of a degraded fraction that is a mixture of hydrocarbons with the molecular mass of approximately 140 g/mol. Depending on the mass ratio of polymer and methanol, the iodine numbers were determined and it ranged 28.1–31.2 g I₂/100 g. Also, a reduction in the content of sulphur compounds and maximally reduced chlorine content are observed.

Table 9
Selected properties of liquid hydrocarbon products in the third stage of experiments.

Experiment	10	11	12
Liquid product density (g/cm ³)	0.789	0.790	0.794
Average molecular mass (g/mol)	138.1	140.2	145.6
Iodine number (g I ₂ /100 g)	28.1	30.1	31.2
Sulphur content (mg/kg)	100	100	200
Chlorine content (mg/kg)	0	0	50

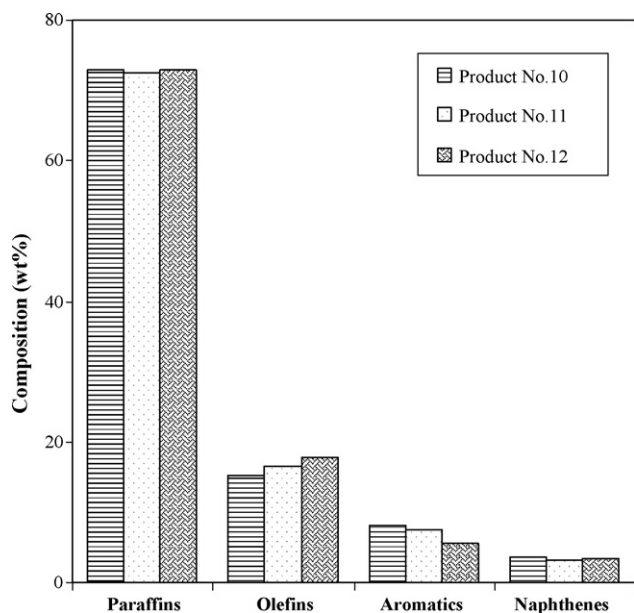


Fig. 7. Effect of the reaction in the presence of solvent on the paraffin, olefin, aromatic and naphthene yields for the hydrocarbon fraction (waste polyolefins/methanol; final temperature: 400–411 °C; final pressure: 18.5–24.0 MPa).

The compositions of liquid fractions are presented in Fig. 7. They contained both paraffins (ranged 72.6–73.0%), naphthenes (ranged 3.2–3.6%) and smaller amount of olefins (ranged 15.3–17.9%) as well as a certain amount of aromatic hydrocarbons (ranged 5.6–8.2%). All these arguments indicate the relationship between several separate reactions in the reaction system. The first reaction is random scission of polymer bonds, resulting in low molecular weight hydrocarbons. At the same time, methanol decomposition occurs with hydrogen as the main product, which enables hydroconversion of both unsaturated and sulphur systems. Moreover, aromatization is observed. Maintaining the system at 400 °C provides maximum 8.2% of aromatic compounds. As in the previous experiments, almost all the structures of this group are included in the fractions within gasoline boiling ranges. The GC analysis showed mainly toluene and xylenes, small amounts of other benzene derivatives Benzene alone was not identified.

4. Conclusions

In the paper, a study on co-decomposition of polyolefins and thermally unstable methyl alcohol is presented. Under the process conditions, the reagent is mainly decomposed into hydrogen (desired for transformation of multiple carbon–carbon bonds and reduction of sulphur compounds) in order to obtain highly valuable saturated systems that can be used as engine fuel components.

The priority of the first, exploratory series of experiments was only to determine of the potential for hydrotreating of highly unsaturated products—crude product of polyolefin thermal destruction. The method enables further thermal decomposition of the material in order to obtain liquid mixture of low molecular weight hydrocarbons. The presence of hydrogen within the autoclave allows for the system hydroconversion which results in reduced amounts of

unsaturated sulphur and chlorine compounds in the obtained fraction. The effect of cracking prolongation is aromatization growth and, also, elimination of sulphur and chlorine compounds. The presence of a basic medium, such as MgO, in the reaction system does not favour generation of aromatic structures. Technologically, the presented variant is unprofitable due to its two-stage character: initial pyrolysis and consequent, in a separate cycle, further polymer degradation in conjunction with the crude product hydroconversion.

A direct use of solid waste polyolefins – without previous thermocatalytic decomposition – allows for the whole process of obtaining engine fuels within one reaction system where both degradation and hydrotreating of polymer products occur. The use of technological oils supports dissolution of crude polyolefins and provide the highest efficiency of the desired liquid fraction. A negative effect of this version is the risk of introducing, together with oil, undesired compounds into the system, e.g. sulphur compounds (ranged 1200–2500 mg/kg). A modification of the method, i.e. replacing sulphur-containing technological oils with substitutes on previous hydrocracking, should provide a high efficiency of the process and allow for production of fuel fractions with satisfactory parameters.

The disadvantages of the obtained study results are eliminated by the third, also one-stage, series of experiments with decomposition of waste polyolefins directly in the presence of methyl alcohol, but without oil additives. Thermal destruction of the polyolefins at the elevated pressure mainly generates a desired liquid hydrocarbon fraction. The mixture characteristic demonstrates a low level of olefins, reduced content of sulphur compounds and even elimination of chlorine content.

For typical hydrogen donor liquids, e.g. tetralin, one problem that limits their technological use in plastics processing was a necessary purification of the final fraction from the decomposition products that are undesired for fuel technology. A marked advantage of the methyl alcohol use as a valuable hydrogen source is the fact that, in this case, a liquid hydrocarbon product does not require additional purification from the products of the reagent decomposition, which is necessary for hydronaphthalenes.

The presented solutions have been applied for a patent [5].

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