



Liquid fuel from waste polyolefins part I: Thermal and pressure degradation of waste polyolefins in tetralin as H-donor model system

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ABSTRACT

In the paper, the results of the study on a laboratory process of thermal and pressure destruction of waste polyolefins in the presence of tetralin as a model hydrogen donor are presented.

Waste polyolefins were thermally cracked in the presence of a catalyst and hydrogen donor (tetralin) in a closed autoclave (volume: 1 dm³) in the anaerobic atmosphere. The process temperature was maintained 400–500 °C. The pressure at the end of process, depending on the feed composition, was 10–15 MPa. As a result, a desirable liquid fraction was obtained. A product of waste polyolefin decomposition in the presence of tetralin is a complex mixture of hydrocarbons. The analysis of products has shown satisfactory decomposition of polymer chains as well as hydrogenation of unsaturated structures. Low sulphur and chlorine contents in the obtained fractions constitute a highly positive effect, especially in a fuel aspect. A significant disadvantage here is a considerable number of tetralin conversion reactions. The use of this hydrogen donor for technological purposes is not possible as the final fraction must be cleared from disproportionation products or hydrogen donor decomposition products.

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1. Introduction

Polyolefins constitute a group of commonly applied polymers that are used in almost all fields of both economy and daily life. Every year their worldwide production grows together with the increase in their consumption and the amount of waste. Therefore, the use of recycled polyolefins and the focus on utilization of used packages should constitute a priority.






The most effective recycling process should be an area of interest for both manufacturers and the recipients of polymers – not only for purely ecologic, but also economic reasons. The method and kind of recovery are usually determined by the quality of processed waste. Thermal or catalytic cracking of waste polyolefins is an accepted and best described method of their processing. Scission of polymer chains at elevated temperature of 400–430 °C results in a mixture of low molecular weight hydrocarbons. Liquid fractions are the main product of this process which can be further directed to either catalytic cracking or olefin pyrolysis with other petroleum fractions or hydrotreating. The basic aim of the presented conception is to obtain, with maximum efficiency, either recycled materials of polymer synthesis or products which could be used as components of gasolines and diesel oils or at least heating oil [1–12].

Obtaining highly valuable fuel components from waste by means of simple technologies is extremely difficult due to strict quality criteria for fuel substitutes regarding the presence of unsaturated and aromatic compounds as well as chlorine and sulphur compounds. Fuel properties depend on base material for its production. Fuel fractions, resulting from the pyrolysis of plastics, show low stability. It is a random process of a polymer chain decomposition into shorter segments which may lead to liquid fraction generation.

A typical process of thermal destruction of polyolefins proceeds according to the mechanism proposed by Lattimer and leads not only to production of alkenes, but also alkadienes [13]. Generally, three main groups of components are produced in this process: *n*-paraffin, α -olefin and α,ω -diene. The relative proportion of these components depends on the thermal degradation operating conditions. The presence of such unstable systems (about 50%) [6] in a degraded mixture of low molecular weight hydrocarbons is a crucial and still unsolved problem for this technology. Due to generating such excessive amounts of olefins in destruction processes, the application of obtained fractions directly in fuels is impossible. Olefin hydrocarbons demonstrate low stability and, therefore, they tend to undergo various chemical reactions as polymerization or oxidation. A result of their contact with atmospheric oxygen would be dark-brown resins in the mixture which could precipitate from fuels. The presence of these in the engine inlet system has a negative effect on its performance and exhaust gas purity. On the other hand, in slower olefin polymerization reactions, polymer formation

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Table 1
Donor indexes of model hydrogen donor solvents [21].

Structure of the model compounds	Name of the model compounds	Donor index
	Tert-butylbenzene	0.09
	1-methylnaphthalene	0.13
	1,2,3,4-tetrahydronaphthalene	0.27
	9,10-dihydrophenanthrene	0.31
	Indane	0.35

is possible – enhanced by prolongation of fraction storage. Unsaturated structures also has a higher combustion temperature than that of saturated hydrocarbons and intensify NO_x formation in the combustion process. Emission of olefins alone from the supply system is also dangerous due to their high reactivity that contributes to tropospheric ozone generation and, as a result, photochemical smog formation. Therefore, unsaturated hydrocarbons are undesired as gasoline components. The products of polyolefin pyrolysis could be their components, but only after hydrogen processes that lead to total elimination of unsaturated components.

There are many methods of polyolefin cracking, but the priority of our work is selecting the methods leading to a mixture of saturated hydrocarbons with a greater chemical stability. An effective way of eliminating undesired unsaturated systems from crude products of polymer degradation and concurrent enriching hydrocarbon fractions is hydrocracking – cracking of polymers in the presence of a catalyst and at hydrogen pressure [1,2]. The process enables saturation of multiple bonds and obtaining saturated, more chemically stable hydrocarbons. Hydrogenation can also be conducted with liquid cracking products requiring enrichment that are obtained with the use of another method. This version is a separate and last stage of fraction refinement [4,5]. The process is conducted catalytically in the presence of $\text{Pt}/\text{Al}_2\text{O}_3$ or $\text{Pd}/\text{Al}_2\text{O}_3$, and elevated pressure (at least 2 MPa) as well as the temperature of approximately 230–340 °C are required. Under these conditions, up to 90% of sulphur can be removed and the content of components that are sulphonated – both unsaturated and aromatic – does not exceed several percent.

Widely known and described methods for obtaining liquid hydrocarbon fractions in the process of thermal degradation of polyolefins allow for rational management of waste plastics, especially polyethylene and polypropylene which constitute over 70% of municipal wastes. Many reports concerning the subject matter refer to a series of possible applications of plastics pyrolysis products as crude components of liquid fuels. There are several methods that describe the direct procedure of obtaining high-value fuels from waste. An example is Alka Zadgaonkar's process in which fuel is obtained directly from waste plastics. The process was invented and patented by Alka Zadgaonkar [14]. It is carried out in a specially designed reactor in the absence of oxygen and with Zadgaonkar's special catalytic additive. The reaction temperature is up to 600 °C. Zadgaonkar uses almost all kinds of plastic, e.g. polypropylene, low density polyethylene, high density polyethylene, polyvinyl chloride or any other plastics or plastic combination and plastic products – bags, old raincoats and broken buckets. These products can be converted into fuel-range liquids: gasoline, kerosene and diesel fractions – with a higher yield and high quality as well as coke and LPG range gases. These distillates contain no sulphur or lead.

An interesting solution is co-decomposition of polyolefins and organic liquids, hydrocarbon mixtures or petrochemical materials such as gasolines, petro- and other oils [15]. The process runs at the

elevated temperature (up to 400 °C) and increased pressure. The obtained liquid products can be used either for further petroleum processing or olefin pyrolysis – in the case of naphthas, but not as fuel components. A negative aspect of the method is the risk of introducing undesired compounds into the hydrocarbon mixture, e.g. sulphur compounds (even 0.5–1.0%).

An important element of proecological policy and an attractive method of waste management is production of fuels with the use of components obtained from plastics recycling. In Poland, this solution was even more attractive because, according to the Excise Tax Act of 23 January 2004, diesel oils and gasolines produced with the use of established amounts of these components were exempt from the excise duty. The relief of excise duty was valid until 31 December 2006. In that period, thermocatalytic decomposition of polymers was performed on an industrial scale. For the presented conceptions, several patents were also developed [16–18]. In Poland, in 2005, at least 30 thousand tons of liquid or solidifying crude fuel fractions were produced which, after separation, were further processed into gasoline, diesel oil and heating oil fractions with emphasis on the maximum efficiency of diesel oil fraction (approximately 50%). Further possibilities of obtained gasoline fraction refining are zeoforming or olefin pyrolysis, but they were never put into practice. The products were used for raw material recycling in fuel (gasoline) economy. In the case of diesel oils, hydrogenation with the use of gaseous hydrogen was applied in typical catalytic processes at elevated pressure. That way, a high quality diesel oil component was obtained. A significant problem for this technology was hydrogen availability for hydrotreating processes.

It is advantageous if co-decomposition of polyolefins is conducted with organic liquids that are hydrogen donors. The hydrogen transfer reaction has been known since the turn of the XIX and XX centuries when Knoevenagel first observed that dimethyl 1,4-dihydroterephthalate disproportionated into dimethyl terephthalate and cis-hexahydroterephthalate [19,20]. The effect of hydrogen donor solvents has been extensively investigated for coal liquefaction. Considering the issue of material conversion, the most common organic compounds with a high hydrogen donor activity are as follows: dihydrophenanthrene, dihydroanthracene, dihydropropylene, tetrahydronaphthalene, methylnaphthalene, indane and others. In Table 1, several model hydrogen donor solvents applied in these processes are presented. Many studies focus on the mechanism of hydrogen transfer from hydroaromatic hydrocarbons to coals, which so far has not been fully clarified. One reason of different results is the heterogeneity of structures and compositions of coals used in the studies [21–24]. A generally accepted pathway for hydrogen transfer from a donor solvent was summarized by Chawla et al. [25].

Hydrogen transfer reactions are also applied in selective reduction of various organic compounds with characteristic functional groups (such as carbonyl, epoxy or nitro groups) where

aliphatic alcohols or *n*-alkanes are used as hydrogen donors [26–29].

In the literature, there is also some information about the effect of hydrogen donors on thermal degradation of various polymers. First of all, polymers show high viscosity, which complicates the process due to impediment of the heat and mass transfer. To solve this problem, solvent additions are used. A hydrogen donor ability is the second important property of this liquid. The use of solvents has many other advantages, e.g. it may decrease the required temperature and increase the yield of liquid fraction, facilitate obtaining more specific products; certain solvents can modify the plastic degradation mechanism and can be easily separated after the reaction [30–32].

The thermal decomposition of polymers is influenced by the presence of hydrogen donors. Depending on the particular polymer: LDPE, HDPE, PP, PS, PVC, hydrogen donors may increase or decrease the degradation rate.

Most of works have been focused on the thermal degradation of polystyrene. Sato studied the thermal degradation of polystyrene at 300–450 °C with the use of following solvents: tetralin and 9,10-dihydroanthracene, which are hydrogen donors, phenol, 2-naphthol and diphenylamine. A lower styrene yield was obtained in the presence of typical hydrogen donors [31].

Other papers describe the thermal degradation of polystyrene waste at 400 °C in a pressure autoclave with various groups of solvents: aliphatic, cyclic and aromatic, using their most simple representatives: *n*-pentane, cyclohexane and toluene [32]. Cyclohexane caused the highest conversion of polystyrene into liquid and gas, and the lowest yield of solid residue. The use of solvents almost doubled the liquid yield and reduced the solid residue to less than 5%.

The thermal degradation of polystyrene and poly(α -methylstyrene) was studied in several solvents: 1-methylnaphthalene, tetralin and phenol, in the temperature range of 250–450 °C [33,34]. The conversion of these polymers into low molecular weight products depended on the type of solvents. This is explained by a mechanism that includes hydrogen transfer from the solvents to intermediate polymer radicals.

Madras et al. investigated the effect of hydrogen donors on polymer degradation [35]. The authors proposed a model for chain scission degradation reactions according to radical mechanisms of initiation–termination, H-abstraction, degradation and repolymerization reactions. The objective of other papers was to investigate the effect of hydrogen donor solvents on the degradation of poly(styrene-allyl alcohol) in a solution [36]. The degradation experiments were carried out at high pressure and in the presence of tetralin. All the degradation products are dissolved in solution and no repolymerization reactions occur. Tetralin is essential for polymer degradation. The specific rate coefficients are higher by nearly an order of magnitude than the rate coefficients obtained without tetralin.

The degradation of polyvinyl chloride with solvent has been widely studied [37,38]. Kamo and Sato were interested in the role of solvent in the PVC decomposition and removal of chlorine [37,38]. A significantly high yield of oil was observed in the PVC degradation process at 440 °C with the use of a hydrogen donor solvent, such as tetralin [37]. Tetralin was effective for the increase in the oil yield as well as reduction in the total chlorine content in the oil. The presence of appropriate hydrogen donors (e.g. tetralin) prevents condensation reactions and promotes the PVC degradation. The physical properties of decalin that facilitate dissolution and dispersion of polymer are the most important factors in case of this solvent [38].

In the literature, there are also several examples regarding the thermal degradation of polyolefins in the presence of various solvents. Karaduman et al. studied the thermal degradation of low

Table 2
Selected properties of the material.

Selected properties	
Density (g/cm ³)	0.8089
Average molecular mass (g/mol)	197.5
Iodine number (g I ₂ /100 g)	63.2
Sulphur content (mg/kg)	500
Chlorine content (mg/kg)	200

density polyethylene LDPE waste, using cyclohexane in the temperature range of 375–450 °C [39]. The solid residue decreased whereas the liquid yield and the total conversion increased. In other similar papers, Karaduman and Şimşek studied the mechanism of thermal degradation of low density polyethylene LDPE plastic wastes in cyclohexane at 400 and 425 °C [40]. Four reaction mechanisms have been proposed and tested. The best model suggests that gas and liquid are formed directly from the solid.

Aguado et al. studied the effects of hydrogen-donating solvents on the thermal degradation of HDPE at 400 °C [30,41]. The presence of poor hydrogen-donating solvents, e.g. decalin or 1-methylnaphthalene, results in gaseous hydrocarbons (C₁–C₄) and linear hydrocarbons, mainly α -olefins (C₅–C₂₀). The presence of these solvents improves heat and mass transfer rates during the thermal degradation and plastic conversions as well as the yields of hydrocarbon products. When the reaction was carried out with good hydrogen-donating solvents, e.g. 9,10-dihydroanthracene or tetralin, the selectivity to *n*-paraffins was very high (even 97.5%). In this case, the degradation mechanism includes hydrogen transfer reactions from the solvents to HDPE radicals which prevent production of α -olefins.

Hydrogen donor ability will be an important factor in the selection of a practical solvent for an industrial scale waste plastics recycling.

Regarding the pyrolysis of plastics in the presence of some solvents, a lot of papers are available [30–41]. In the present work, we have investigated the thermal and pressure degradation of waste polyolefins with the use of tetralin in order to determine the effect of this solvent. The priority of work was to determine a possible use of the hydrogenation method for highly unsaturated products that are crude fractions of polyolefin thermal destruction – obtained from an industrial installation. Tetralin is a classic organic solvent from the hydronaphthalene group with hydrogen donors of high activity (donor index: 0.27). Tetralin donates the hydrogen atoms from its C₁–H, C₂–H, C₃–H and C₄–H bonds. This model reagent distinguishes from other hydrogen donors with its reactivity and high, advantageous in the case of polymer dissolution processes, boiling temperature (207.5 °C; ~0.1 MPa).

2. Experimental

2.1. Polyolefin material

In order to examine the validity of the method of C=C bond reduction in the presence of a model hydrogen donor (in order to obtain highly valuable saturated systems from waste plastics), 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. In Table 2, selected properties of the material are presented. The complex chemical structure of raw material was determined with the use of the ¹H-NMR (Fig. 1). This technique enabled determination of complex chemical structure of the material through identification of protons in the methyl (0.8–1.0 ppm), and methylene groups (1.2–1.4 ppm)

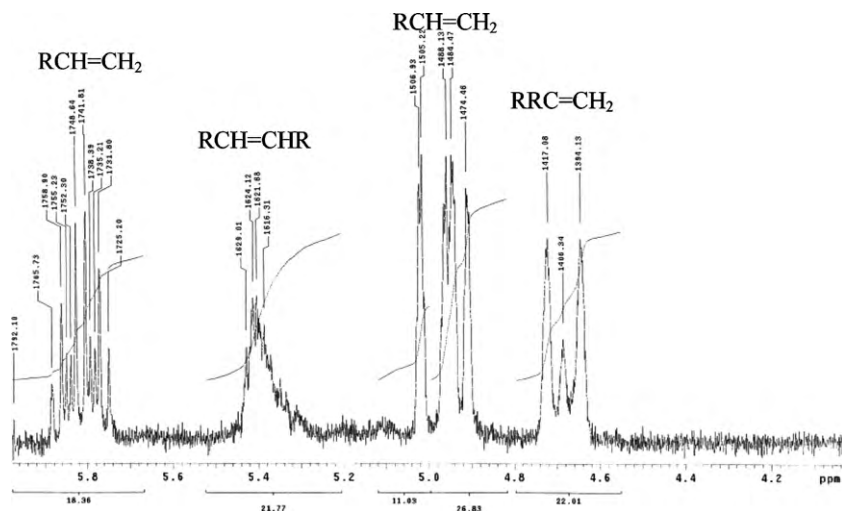


Fig. 1. ^1H -NMR spectra for the product of waste polyolefin degradation. Olefinic region: α -olefin 5.0 and 5.8 ppm; internal olefin 5.4 ppm; 1,1-disubstituted olefin 4.7 ppm.

as well as naphthene and methyne groups (1.4–2.2 ppm). The representative region for olefin compounds is also seen (4.7, 5.0, 5.4 and 5.8 ppm). The analysis shows three possible types of unsaturated systems that are typical products of polyolefin degradation: α -olefin ($\text{RCH}=\text{CH}_2$), internal olefin ($\text{RCH}=\text{CHR}$) and 1,1-disubstituted olefin ($\text{RRC}=\text{CH}_2$). There are slight peaks in the areas typical of aromatic compounds (6.8–7.2 ppm). This may occur due to the fact that the waste plastic mixture may also contain polystyrene, which mainly affects the yield of aromatic hydrocarbons in the pyrolysis.

The chemical composition of raw material was determined with the use of the GC–MS method. The product is a complex mixture of hydrocarbons. It contains both saturated and unsaturated hydrocarbons (both linear and branched) as well as a certain amount of aromatic compounds. The average composition of the group is as follows:

- *n*-paraffins: 11%,
- iso-paraffins: 38%,
- unsaturated hydrocarbons: 49%,
- aromatic hydrocarbons: 2%.

Another specific issue for waste material is the presence of small amounts of heteroatoms (approximately 500 mg of sulphur/kg of waste and 200 mg of chlorine/kg of waste). A source of sulphur compounds in the waste stream is probably pollution or some additives used in the polymer production. A rapid reduction in permissible levels of sulphur compounds in gasolines and diesel oils, minimized to the sulphur-free fuel limits of <10 mg/kg according to valid standards (since 1 January 2009) must be considered [42]. Reduction in contents of sulphur and its compounds in fuel is supported by the argument that they have a negative effect on catalytic exhaust gas purifying systems and corrosive engine wear as well as emissions of SO_x compounds into the atmosphere. Waste polyolefins, as mixtures of waste, normally contain trace amounts of this element, which results in chlorine content of approximately 200 mg/kg in degradation products even despite prior segregation. This level is unacceptable for gasolines as specified by quality standards for liquid fuels (<100 mg/kg). During fuel combustion in the engine, chlorine releases and reacts with water vapor. As a result, hydrochloric acid is produced, causing corrosion of the engine and other elements of the combustion system. This fact confirms the requirement of hydrotreating of polyolefin products for their use as fuel components – due to the negative aspect of unsaturated

compounds and also in regard to reduction in sulphur and chlorine content in gasolines and diesel oils as required.

2.2. Solvent

Tetralin was used as a solvent.

2.3. Catalyst

One type of catalyst was applied in these experiments: $\text{CoMo}/\text{Al}_2\text{O}_3$, containing 16% MoO_3 , 3.6% $\text{CoO}/\text{Al}_2\text{O}_3$, 0.1% SiO_2 . It is a commercial and industrial catalyst (G3 symbol). The cobalt–molybdenum catalyst G3 was developed and produced in the Synthos Dwory Sp. z o.o. in Oświęcim (Poland). The catalyst G3 was introduced in refinery and petrochemical plants. It is used in hydrotreating and hydrodesulfurization of gasoline and petroleum distillates.

2.4. Reaction equipment

Co-decomposition of waste material and tetralin 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 and 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). Fig. 2 presents the experimental set-up, composed of a

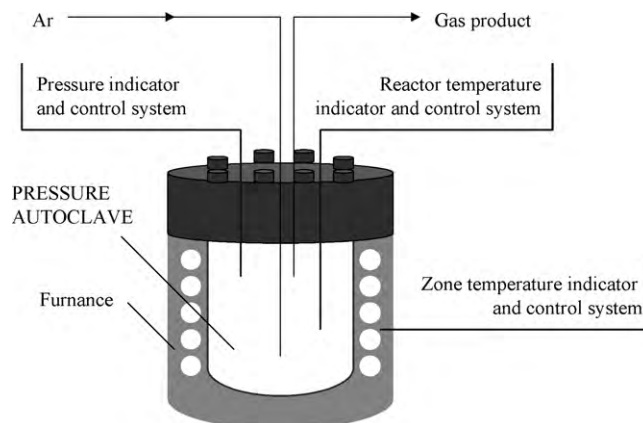


Fig. 2. The experimental set-up.

stainless steel autoclave surrounded by a furnace with an electrical heater and a temperature and pressure control unit. The reactor lid is fitted with a pressure indicator to follow the reaction progress and to maintain the pressure below 35 MPa.

2.5. Experimental procedure

The reactions were conducted with different plastic:solvent mass ratios. A blank reaction of solvent (tetralin in the absence of polyolefin material) was also carried out. The waste material and tetralin were weighed and placed in the autoclave. A part of the experiments (No. 3 and the blank reaction) were carried out with addition of the G3 catalyst (5 wt.% in relation to the weight of the plastic). In Table 3, detailed data of the performed experiments (feed composition, mass ratio, autoclave filling degree V_0 , final reaction temperature RT, final pressure P and reaction time t) are presented. For the mixture of organic liquid and polyolefin material, argon blow was applied and subsequently the autoclave was closed, maintaining atmospheric pressure. The degradation experiments were carried out at 400–500 °C for 180 min before cooling down to the room temperature. The heating rate of the autoclave was approximately 2 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 tetralin. The obtained crude 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 carbosphere 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 ¹H-NMR spectroscopy (300 MHz, DMSO, CDCl₃) was used for further determination of the complex chemical structure of the material.

Table 3
Process conditions in the preliminary studies.

Experiment	1	2	3	4
Feed composition				
Raw material	CP	CP	CP	CP
Solvent	Tetralin	Tetralin	Tetralin	Tetralin
Mass ratio	1:30	1:30	1:8	1:1
Autoclave filling degree V_0 (%)	62	62	45	12
Final reactor temperature RT (°C)	418	447	450	477
Final pressure P (MPa)	13	13	15	10
Cracking time t (h)	3	3	3	3

The chlorine content in 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. The correlation between reaction temperature, pressure and process time

The curves presented in Fig. 3a and b show in detail the reactor temperature RT and pressure P distributions over process duration times t.

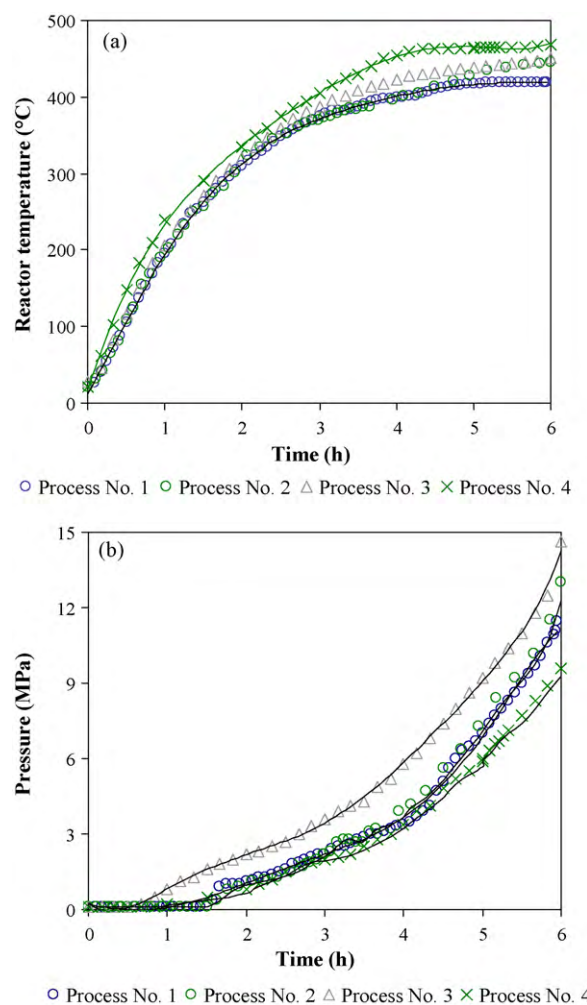


Fig. 3. Relationships between: (a) reactor temperature and (b) pressure versus reaction time for the preliminary studies. Autoclave filling degree: 62% (processes No. 1 and 2), 45% (process No. 3) and 12% (process No. 4).

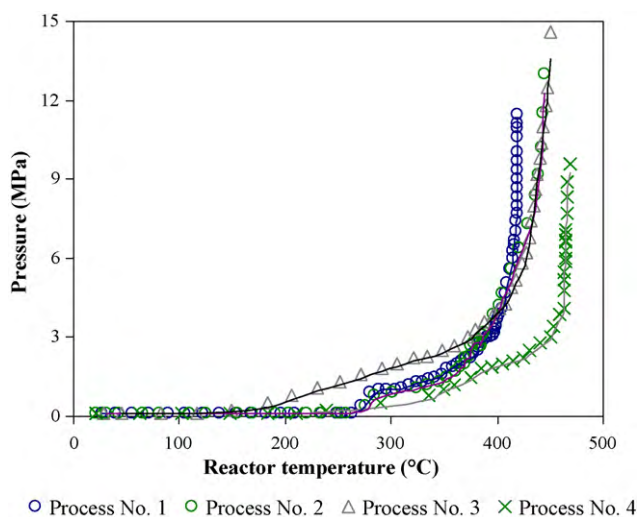


Fig. 4. Relationship between reaction pressure and reactor temperature for the preliminary studies. Autoclave filling degree: 62% (processes No. 1 and 2), 45% (process No. 3) and 12% (process No. 4).

In the initial phase of experiments, the autoclave was heated up to obtain the temperature 400–500 °C. Reaching that temperature, those reaction conditions were maintained for 3 h. Fig. 4 presents the relationship between the process pressure and temperature. For non-catalytic reactions, at up to 200 °C, the pressure remained at a relatively steady level. When the temperature exceeded 250 °C, a slow increase in the pressure was observed, resulting from the vapour pressures of the mixture reagents (at that temperature mainly from tetralin partial pressure).

The analysis of the basic thermodynamic parameters, such as RT and P, is extremely important from a scientific point of view. For the initial conditions of experiments (20 °C; ~0.1 MPa), which are a kind of baseline, an additional parameter was assumed: a degree of the autoclave filling with the reagents V_0 .

There are close relationships between the autoclave filling degree V_0 , reactor temperature RT and autoclave inner pressure P. The system behaviour is well worth a detailed consideration. After loading and closing the autoclave, it starts heating up. The greater amounts of reagents, the slower reactor temperature growth is observed (Fig. 3a).

With the reactor temperature raise, the autoclave inner pressure also increases (Fig. 4). The pressure mainly depends on the boiling temperature of applied solvent, its vapour pressures, critical temperature and critical pressure. The higher reactor inner temperature, the higher inner pressure is demonstrated.

Furthermore, the pressure is determined by the amounts of reagents (Fig. 3b). The higher autoclave filling degree V_0 , the greater changes in the discussed parameter are noticed, resulting from the vapour pressures of the mixture reagents in phase transitions and chemical reactions. For the least amount of reagents (12%), the slowest pressure growth is observed. For a process with an intermediate autoclave filling (45%), but due to a significant role of the catalyst, degradation of the reagents is the fastest.

Having reached the determined optimal process temperature, it is maintained for a specific period of time necessary for obtaining the highest efficiency, and subsequently the reaction products are left to cool down.

3.2. Material balance

Four experiments of waste material 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

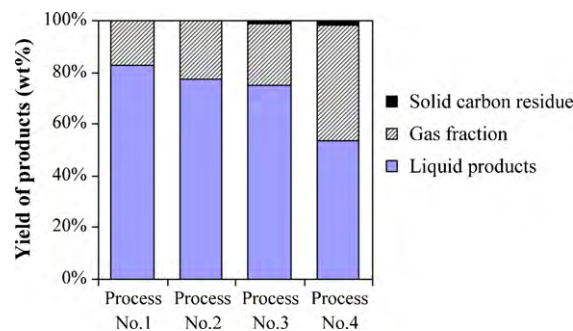


Fig. 5. Distribution of cracking products, gases, liquid and solid carbon residue for applied reactor system for the preliminary studies.

of cracking tests. The results of experiments, in the form of material balance, are presented in Fig. 5. The highest yield of liquid products was obtained in the tests No. 1–3 with a significant excess of tetralin in the reaction mixture. On the contrary – in example No. 4 – the lowest yield of liquid fraction was received, while the highest yield – of the gas product. In this experiment, the reaction mixture was composed of tetralin and the waste material with the mass ratio of 1:1.

3.3. 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 (450 °C). The results of this reaction show that tetralin undergoes significant conversion. The main component of gas mixture from blank reaction is hydrogen. Additionally, a slight degradation of the tetralin ring occurs, identified by the presence of C_1 – C_3 hydrocarbons in the mixture obtained as a result of the experiment performed for a pure solvent without polyolefin material. Detailed contents of products are as follows: hydrogen: 99.28%, and then methane: 0.23%, ethane: 0.36% as well as propane: 0.13%.

It was demonstrated that at elevated temperature, many parallel or successive conversion reactions of hydrogen donor cannot be avoided. This fact was confirmed by the presence of various hydrocarbons in the liquid fraction following the process in the autoclave. The main compounds, identified in the liquid products under argone with the G3 catalyst at 450 °C, are shown in Fig. 6. The product comprises not only naphthalene as a product of tetralin dehydrogenation, but also at least 20 other structures.

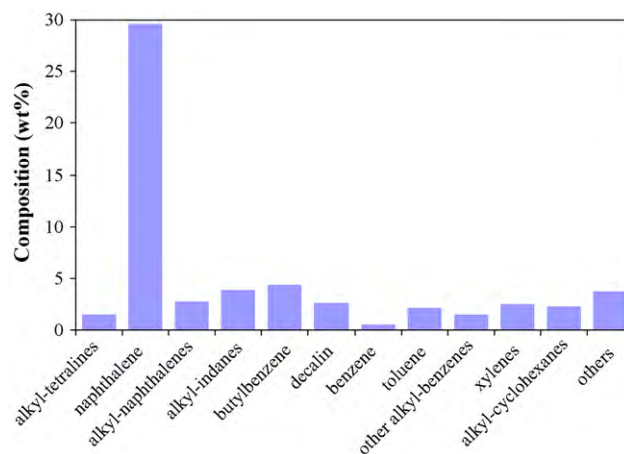


Fig. 6. Yields of the main identified compounds in the liquid product after blank reaction.

Table 4
Compositions of hydrocarbons and other components in gas products.

Experiment	1	2	3	4
Composition of gas products (%)				
Hydrogen	94.66	89.22	92.80	69.92
Methane	3.57	7.46	3.23	17.25
Ethane	1.23	2.51	2.65	7.04
Propane	0.35	0.60	0.99	3.89
Butane	0.09	0.11	0.28	1.81
Ethylene	0.03	0.01	0.01	0.03
Propylene	0.09	0.04	0.01	0.02
Butylene	0.00	0.06	0.02	0.02
Butadiene	0.00	0.00	0.02	0.02

Naphthalene, 1- and 2-methylindane, butylbenzene and decalin were formed from tetralin by dehydrogenation, isomerisation, hydrocracking and hydrogenation, respectively (Fig. 7). Decalin was produced also by disproportionation of tetralin.

3.4. Degradation of waste material in the presence of a solvent

The main component of gas mixture from polyolefin decomposition in the presence of tetralin is hydrogen (Table 4). Such a great amount of the component (up to 94.7% in test No. 1) is mainly explained by dehydrogenation of tetralin to naphthalene which occurs at elevated temperature and pressure.

A scission of bond at the ends of polymer chains generates production of light hydrocarbons such as methane and ethane as well as, to a smaller extent, propane and butane. The thermal stability of polymer bonds decreases with the temperature growth. As expected, the increase in the cracking temperature from 418 °C (process No. 1) to 447 °C (process No. 2) generates a higher amount of volatile hydrocarbons – mainly C₁–C₃.

In the case of cracking, in the absence of hydrogen in the mixture, a certain amount of olefins was found, mainly ethylene. A small

Table 5
Selected properties of liquid hydrocarbon products.

Experiment	1	2	3	4
Liquid product density (g/cm ³)	0.799	0.794	0.792	0.787
Average molecular mass (g/mol)	191.2	147.2	139.6	121.7
Iodine number (g I ₂ /100 g)	9.0	3.7	5.6	3.1
Sulphur content (mg/kg)	50	<50	<50	0
Chlorine content (mg/kg)	20	0	0	0

amount of light olefins (C₂–C₄ alkenes and alkadiene – butadiene) in our experiments may occur due to the presence of hydrogen in a gas product. As a result, primarily light saturated hydrocarbons (C₁–C₄) were identified.

The liquid mixture obtained in the experiments was mainly composed of tetralin residues and depolymerization products. The tetralin residue was removed through distillation. Three fractions: a fraction with the boiling point below 207 °C, tetralin residue and a fraction with the boiling point above 207 °C were obtained. Based on the amounts of residual tetralin after the reaction and the amount of tetralin in the reaction, a conversion degree of solvent was determined: 39.6% (in test No. 1), 43.5% (in test No. 2), 49.2% (in test No. 3) and 77.6% (in test No. 4). This value depends on the process parameters which strongly influence the outcomes of tests. The results show that tetralin undergoes significant conversion and, therefore, this solvent has a low stability in high temperatures.

The obtained liquid mixtures of hydrocarbons – after removal of tetralin – was characterized by the density, average molecular mass, iodine number, heteroatoms: chlorine and sulphur (Table 5).

The priority of the study system using a model reagent was the determine a possible enrichment of the unsaturated hydrocarbon mixture – concerning reduction of both unsaturated bonds, sulphur and chlorine compounds. Co-decomposition of polyolefins at elevated pressure in the presence of tetralin results in a hydrocarbon product of desired liquid character. The degradation of polyolefins

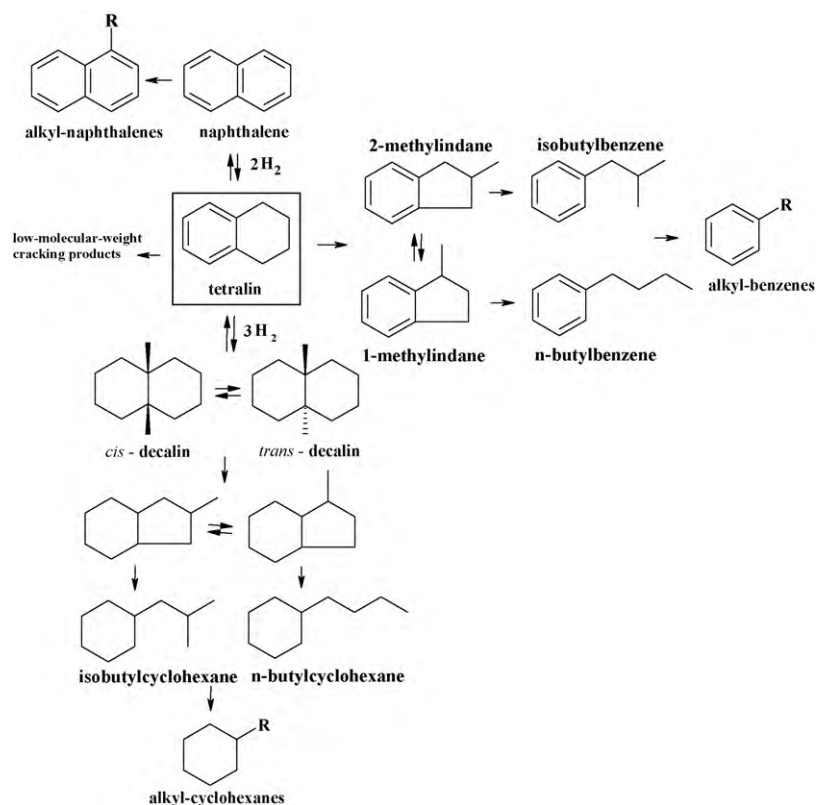


Fig. 7. Main paths of tetralin conversion.

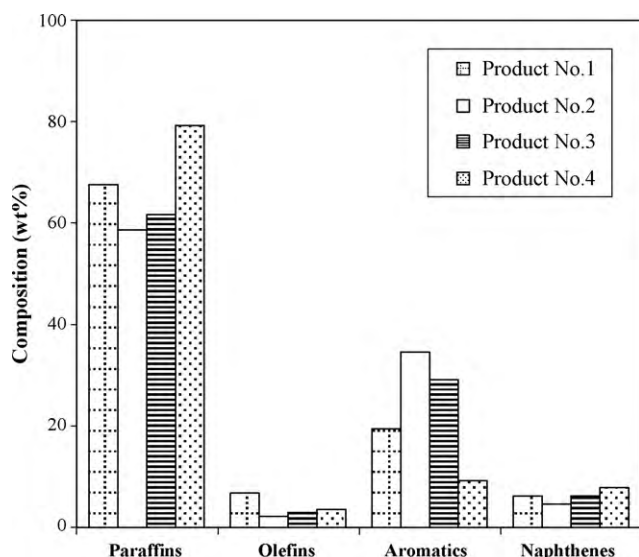


Fig. 8. Effect of the reaction in the presence of solvent on the paraffin, olefin, aromatic and naphthene yields for the hydrocarbon fraction (crude polymer product/solvent; temperature: 418–477 °C; final pressure: 10–15 MPa).

resulted not only in higher liquid product yields, but also in lower olefin contents. The iodine number – as an indicator of olefin contents – decreased from 63.2 g I₂/100 g (in a crude polyolefin product) to 9.0–3.1 g I₂/100 g, depending on the process parameters. Sulphur and chlorine contents are significantly reduced and, in many cases, even eliminated.

The compositions of the liquid fractions are presented in Fig. 8. They contained both paraffins (ranged 58.7–79.3%), naphthenes (ranged 4.5–7.8%) and smaller content of olefins (ranged 2.2–6.8%) as well as some quantity of aromatic hydrocarbons (ranged 9.3–34.6%). Such a system results from many complex, parallel and successive reactions during thermal degradation of

hydrocarbon material as well as reactions in the presence of a hydrogen donor. It is suggested that in this method, two main but separate reactions occur simultaneously within the autoclave. The first reaction is a random scission of polymer bonds which results in low molecular weight hydrocarbons whereas the other reaction is hydrogenation of emerging unsaturated structures. This is explained by the mechanism of hydrogen transfer from solvents to intermediate polymer radicals. The obtained substitutes meet the quality standards specified for liquid fuels in regard to the content of unsaturated compounds.

It was found that main aromatic products were BTX (benzene, toluene and xylenes) hydrocarbons as well as polyaromatic hydrocarbons – mainly naphthalene and its derivatives. A large amount of aromatic hydrocarbons in liquid mixtures is found mainly due to the conversion of hydrogen donor. The analysis of the experiment conducted under comparable conditions for a pure solvent without polymer explained the main source of aromatic hydrocarbons and depicted the disadvantages of the conception of using tetralin in polyolefin processing (Fig. 6). The increase in temperature from 418 to 447 °C during comparable processes (nos. 1 and 2) generates a higher aromatics content in liquid products.

For the discussed liquid fractions, control ¹H-NMR spectra were performed. The results for all samples are comparable. Fig. 9 presents selected ¹H-NMR spectra of the final product after and before hydrogenation, for comparison. It is consistent with the GC analysis results and the low iodine number and means that almost no olefins are contained in the liquid fractions. Within the ranges typical of olefin compounds (δ : 4.7, 5.0, 5.4, 5.8 ppm), only slight signals occur. The representative regions for the protons of methyl (0.8–1.0 ppm), methylene (1.2–1.4 ppm), methyne and naphthene groups (1.4–2.2 ppm) are seen. There are clear proton signals, however, within the ranges of 1.7–3.4, 6.8–7.2 and 7.2–8.0 ppm that are attributed to, respectively: the protons of methyl groups, the protons of methylene groups in the α position to the aromatic ring, the protons linked to carbon in the aromatic ring and the protons in condensed aromatic structures.

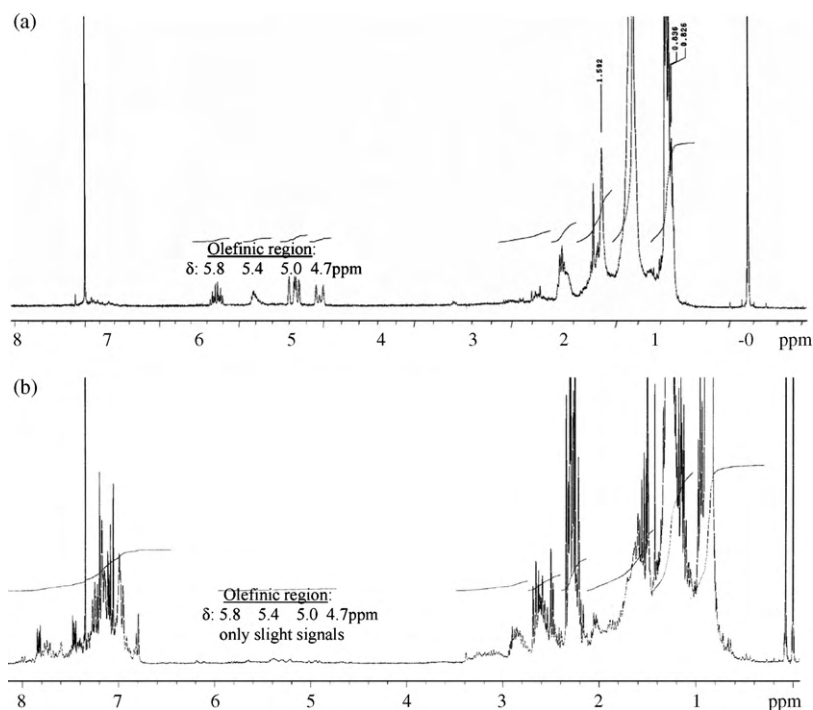


Fig. 9. ¹H-NMR spectra of the crude product before hydrogenation (a) and final product after hydrogenation (b).

4. Conclusions

In the paper, a potential for tetralin adoption as a model organic solvent with a hydrogen donor ability for both transformation of multiple carbon–carbon bonds and reduction of sulphur and chlorine compounds in order to obtain highly valuable saturated systems to be applied as liquid fuel components (including engine fuels) were considered.

A thorough study on the products of waste polyolefin thermo-catalytic degradation obtained under industrial conditions showed a possible use of hydrocarbon hydrogen donors for dissolution and hydroconversion of polymer materials requiring enrichment.

Liquid fractions, obtained with the method of co-decomposition of polymers and tetralin, contain reduced amounts of unsaturated compounds. Also, a positive aspect is a complete elimination of chlorine and sulphur in most cases.

A significant disadvantage of the presented conception is the fact that, at elevated temperature and pressure, many parallel or successive tetralin conversion reactions cannot be avoided. The result is a wide range of by-products belonging to various groups of chemical compounds and demonstrating different properties. Furthermore, naphthalene readily form permanent adducts.

Therefore, the application of hydrogen donors from the hydronaphthalene group for obtaining fuel components from waste polyolefins is not possible. The main problem necessary purification of the final fraction from the products of hydrogen donor conversion. Another disadvantage is a high price of the model reagent.

Studies on the system of hydrogen donor and crude unsaturated polymer products will be continued. The preliminary results, with the use of a model reagent, show a real potential to apply this conception, which is a different solution to hydrotreating of products meant to be fuel components. Through selection of a proper hydrogen donor solvent, it is possible to eliminate the disadvantages of the presented experiments as well as expand the possible applications of organic liquids using cheap and easily available reagents.

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