

ANDRZEJ MIANOWSKI, IZABELA BARANIEC*

TECHNOLOGICAL POSSIBILITY OF THERMAL
AND PRESSURE DEGRADATION OF WASTE
POLYOLEFINS IN THE PRESENCE OF LIQUID REAGENTS

WARIANTY TECHNOLOGICZNE TERMICZNO-
-CIŚNIENIOWEJ DEGRADACJI ODPADOWYCH
POLIOLEFIN W OBECNOŚCI CIEKŁYCH REAGENTÓW

Abstract

Recycling of waste polyolefins is important as a hydrocarbon source for fuel production and for environmental protection as well. The technological possibility of thermal and pressure degradation of waste polyolefins in the presence of liquid reagents, was proposed. Basic physicochemical properties of products obtained in presented methods of polyolefins processing were characterized and discussed.

Keywords: waste polyolefins, dissolution, compaction, hydrogen donor, hydrogenation

Streszczenie

W artykule przedstawiono warianty technologiczne utylizacji odpadowych poliolefin, wykorzystując najprostsze metody termicznego rozkładu pod zwiększonym ciśnieniem, w kierunku pozyskiwania wysokowartościowych frakcji węglowodorowych. Scharakteryzowano podstawowe właściwości fizykochemiczne otrzymanych produktów.

Słowa kluczowe: odpadowe poliolefiny, roztworzenie, zagęszczanie, donor wodoru, uwodornienie

* Prof. dr hab. inż. Andrzej Mianowski, mgr Izabela Baraniec, Katedra Chemii i Technologii Nieorganicznej, Wydział Chemiczny, Politechnika Śląska.

1. Introduction

Utilization of plastics can be carried out in many ways, such as thermal pyrolysis and cracking, catalytic cracking and hydrocracking in the presence of hydrogen. These processes enable transformation of waste plastics into valuable petrochemicals or fuels [1–3].

In case of cracking processes, their main products are gaseous hydrocarbons and liquid fractions of hydrocarbons as well as solid carbon residue. Liquid products obtained in this process are very valuable chemicals, but there are too many unsaturated compounds which require further hydrogen refinement. Unsaturated fractions show chemical instability and readily undergo various reactions, such as polymerization or oxidation. These reactions are intensified when the amount of unsaturated hydrocarbons is bigger and the storage time longer. Cracking of polymers connected with the hydrogenation step gives mainly paraffin fractions. Unfortunately, the classical methods of hydrorefining are too expensive to be used for economic entities.

Thermal decomposition of selected polymers towards synthesis of liquid fuel components is an objective in many of our investigations [4–6]. We study decomposition of various polymers: not only PE and PP, but also PS, PVC and many others [4, 6]. It is an important issue because the stream of waste polyolefins can also contain other polymers, influencing the quality of fuel components. In case of PS, for example, aromatic hydrocarbons cause problems, and especially benzene, whose volume content in the fuel fraction should not exceed 1% v/v. PVC should always be avoided because of chlorine content and a solid residue after HCl release which is difficult to be thermally decomposed and shows coking tendency. The course of thermal processes is more difficult when waste polyolefins contain PETs. In decomposition process, sublimate compounds (terephthalic acid) are formed, clogging the installation, while liquid products contain oxygen compounds which deteriorate the quality of fuel fractions. Small amounts of condensation materials, polyesters or polyamides, reduce the efficiency of a desired product and enhance the efficiency of coke and gas. In the analysis of raw materials, the problems of sulphur compounds are very important. Typical plastics are free of sulphur, however it may come from incidental or uncontrolled sources. This issue is extremely important because since January 1st, 2009, the production of nearly sulphur-free (below 10 ppm) engine fuels is intended. According to the European Union standards, the following criteria are in force: maximum content of olefinic hydrocarbons: in the gasoline fraction at the level of 18% v/v and 35% v/v of aromatic type (benzene < 1% v/v), however for diesel fuel fractions it is 11.0% m/m (polyaromatic hydrocarbons) [7]. Generally, in the processes of thermal polyolefin degradation aromatic hydrocarbons are not created. However, they have been reported in case of certain catalysts and process conditions [2, 3]. Tightened quality criteria, both for sulphur and unsaturated and aromatic compounds, will complicate the realization of these objectives and make them hardly available in simple technologies.

In the present work, several technological variants for waste polyolefins utilization by means of basic thermal and pressure methods (caused by vapour pressures of the mixture reagents) in order to obtain high-value hydrocarbon fractions were proposed (Fig. 1).

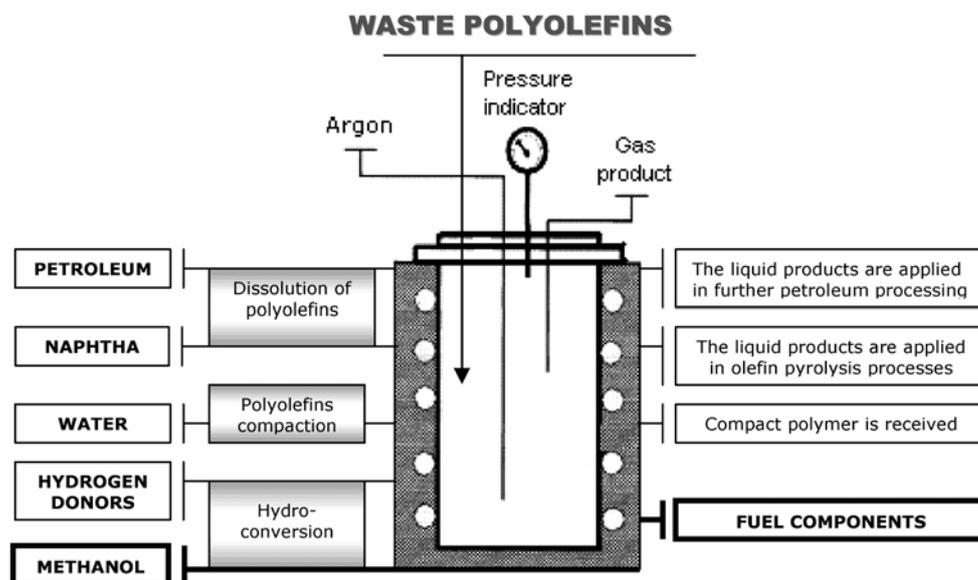


Fig. 1. Several technological variants for waste polyolefins utilization by means of basic thermal and pressure methods

Rys. 1. Warianty technologiczne utylizacji odpadowych poliolefin metodami termiczno-ciśnieniowymi

2. Study – technological variants

2.1. Dissolution of waste plastics

The first suggestion is dissolution of waste polyolefins [8]. This alternative is based on the similarity of the composition of plastics and petroleum fractions.

The process is carried out in the autoclave at higher temperature (400°C) in the presence of petroleum or naphtha. The pressure, obtained during the process, depends on the mixture composition, its volume as well as the end temperature and equals 2–23 MPa. In Table 1, two examples of the method are illustrated.

In the process, dissolution and degradation of plastics occur. This method allows liquid fractions with different properties, which are very valuable chemicals, to be obtained. The method allows reduction of unsaturated compounds by 10–20%, soothing the process conditions and enhancement of its efficiency, but it does not solve the problem in case of the fuel variant. The unsaturated content, depending on the solvent type and the conditions of process conducting, falls within 30–50% m/m. It means that the obtained products will require further refinement processes. Nevertheless, the presented method can be successfully used in typical petroleum processing, allowing utilization of the afteruse parts of polyolefins and retrieval of valuable chemical materials.

Table 1

Characteristics of dissolution of waste polyolefins

No.	Reagents	Mass ratio	Temperature at the end of process [°C]	Pressure at the end of process [MPa]	Characteristic of product
I	waste polyolefins <i>petroleum</i>	3:10	400	11	liquid
II	waste polyolefins <i>naphtha</i>	1:1	411	19	liquid

In case of naphtha, the obtained liquid products undergo olefin pyrolysis, becoming a source for the production of olefins which are the most important petrochemical resources.

Thermal decomposition of polyolefins, based on copyrolysis with the use of technological oils (e.g. paraffin oil), gives products which must undergo further refinement. In view of the future production of sulphur-free fuels, the methods using sulphurised technological oils will have to be modified or replaced by methods using sulphur-free substitutes.

2.2. Waste polyolefins compaction

Waste plastic packages slowly become a real problem and a hazard, not only for the environment, but also for our life space. The alternative version of polyolefins utilization is the process of compacting waste (e.g. waste plastic packages). In this method, the mixture of water and waste polyolefins (at least 10% m/m) is heated (< 420°) in the autoclave, which is accompanied by pressure increase resulting from water pressure. After cooling, solid and compact product separates from water [8] (Tab. 2).

Table 2

Characteristics of waste polyolefins compaction

No.	Reagents	Mass ratio	Temperature at the end of process [°C]	Pressure at the end of process [MPa]	Characteristic of product
I	waste polyolefins <i>water</i>	2:10	375.4	23	compact polymer

This variant can be a proposition for a solution to a problem of fast dump volume (surface) filling.

2.3. Degradation of polyolefins in the presence of hydrogen donors

Decomposition of selected polymers together with organic solvents (which are also hydrogen donors) is a different and extremely interesting way of utilization. It is an alternative for expensive and necessary hydrorefining methods (in which gaseous hydrogen is used), resulting in obtaining highly valuable fuel components.

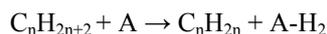
In this method, a combination of two separate reactions which simultaneously occur in the reactor is used. One reaction is random scission of bonds, causing molecular mass reduction, while the other is hydrogenation of created unsaturated structures.

Saturation of C = C bonds with a hydrogen donor as a mediator was first observed by Knoevenagel in 1904 [9, 10]. Since then these reactions have been used many times, among others in studies on reduction of unsaturated functional groups by means of aliphatic alcohols or *n*-alkanes, naphthenes and cycloparaffin-aromatic hydrocarbons or their nitric derivatives [11, 12].

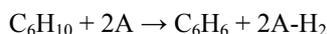
The basis for investigations with the use of hydrogen donors was the group of studies on hydrogen transfer from the model reagent – tetralin – to hydrogen acceptor structures in carbons and their macerals which are a laboratory stage of processes resulting in liquid fuels obtained from carbons [13, 14].

Detailed studies conducted by our research team showed a possibility of using liquid hydrogen donors (e.g. tetralin, decalin, *n*-hexane, cyclohexene) in dissolution and hydrorefining processes regarding waste polyolefin decomposition products [15, 16].

n-Alkanes used as hydrogen donors in the presence of catalyst and hydrogen acceptor (multiple carbon-carbon bonds) transform mainly into alkenes, according to the equation



During the reaction, cyclohexene dehydrogenates to a benzene molecule, the most stable product due to its aromatic nature



The basic quality criteria concerning liquid fuels indicate the content minimization of unsaturated and aromatic compounds (including benzene). Because of the character of dehydrogenation products, their use in polyolefin utilization technologies in order to obtain liquid fuels or their components is irrelevant.

2.3.1. Results and discussion of study in the presence of model reagent – tetralin

The studies using the model factor, i.e. tetralin, appeared to be the most promising (Table 3). Hydrogen transfer from the solvent to the acceptor is usually determined by measuring naphthalene content being the only product of the compound dehydrogenation, mentioned by many authors [14, 17].

In order to study the relevance of this method, a polyolefin product (previously partially thermally decomposed) in the form of solidifying liquid was used, requiring further refinement because of high contents of unsaturated compounds (49.1%) and sulphur (0.05%). All processes were carried out in an autoclave (volume: 1 dm³) in anaerobic atmosphere. The temperature of processes was kept above 400°C (with the aim of degradation of solid stage long polymer chains). The pressure at the end of process, depending on the composition, was 10–15 MPa.

The products of decomposition of waste polyolefins in the presence of tetralin are a complex mixture of hydrocarbons. Results show a lower average molecular mass as well as a lower unsaturated content of liquid hydrocarbon products in comparison with the raw material (Tab. 4). Decomposition of polymer chains with simultaneous hydrogenation of

created unsaturated structures is suggested. Moreover, a low sulphur content in the obtained fractions is a very positive fact (< 0.01% S).

Table 3

Characteristics of processes in the presence of tetralin

No.	Reagents	Mass ratio	Temperature at the end of process [°C]	Pressure at the end of process [MPa]
I	polyolefin product <i>tetralin</i>	1:30	418	13
II	polyolefin product <i>tetralin</i>	1:30	447	13
III	polyolefin product <i>tetralin</i>	1:8	450	15
IV	polyolefin product <i>tetralin</i>	1:1	477	10

Table 4

Raw material and selected properties of liquid products

Raw material	I	II	III	IV	V
Average molecular mass, g/mol	197.5	191.2	147.2	139.6	121.7
Iodine number, g I ₂ /100 g	63.2	9.0	3.7	5.6	7.6
Unsaturated content, %	49.1	6.8	2.2	3.1	3.6
Sulphur content, %	0.05	< 0.01	< 0.01	< 0.01	0

A significant disadvantage here is a considerable number of tetralin conversion reactions. Additional studies showed that at temperatures higher than 400°C this reagent undergoes not only beneficial dehydrogenation to naphthalene, but also many other parallel reactions: hydrogenation, disproportionation, isomerisation and degradation with ring opening. The result of these changes is the presence of indane, methyl-indane, *cis*- and *trans*-decalin and a large group of benzene derivatives in liquid products. These compounds belong to different groups, have different properties and can easily form adducts. Isolation of all products of tetralin conversion is difficult.

These facts mean that the use of this hydrogen donor for technological purposes is not possible as there is a necessity of purifying the final fraction from disproportionation products or hydrogen donor decomposition products as well as because of its biological activity and high price.

2.4. Degradation of polyolefins in the presence of lower alcohols

As a result of the conducted experiments, a variant eliminating the disadvantages of using hydrogen donors from the series of naphthene-aromatic hydrocarbons was proposed.

It is reasonable to suggest lower alcohols as a potential source of inexpensive hydrogen. Selection of the primary fuel for hydrogen generation is a compromise that takes into account the energy value of the fuel, the temperature conditions of the refinement process, the spectrum of gases formed during reforming, and costs. Methanol is a highly adaptive raw material suitable for the production of hydrogen [18]:



The most thermodynamically probable products of methanol reforming are hydrogen, carbon monoxide, and carbon dioxide as well as methane. Purification of the obtained gas is simple and requires only removing created carbon monoxide (II) or dioxide – in case of methanol steam reforming.

2.4.1. Results and discussion of study in the presence of methanol

The technological process should be realized with cheap and easily available reagents. The newest stage of investigations on thermal degradation of polymers under high pressure in the presence of methanol, are discussed. The characteristics of selected processes are presented in Table 5.

Table 5

Characteristics of processes in the presence of methanol

No.	Reagents	Mass ratio	Temperature at the end of process [°C]	Pressure at the end of process [MPa]
I*	polyolefin product <i>methanol</i>	1:1	412	10.3
II*	polyolefin product	–	440	4.8
III**	crude waste polyolefins paraffin oil <i>methanol</i>	1:1:1	401	25.0
IV**	crude waste polyolefins paraffin oil	1:1	411	3.0
V***	crude waste polyolefins <i>methanol</i>	1:3	411	18.5
VI***	crude waste polyolefins <i>methanol</i>	1:1	400	24.0

* variant I – in the presence of partially degraded waste polyolefins

** variant II – in the presence of crude waste polyolefins and paraffin oil

*** variant III – in the presence of crude waste polyolefins

In the first variant, the raw material was polyolefin product, in the form of solidifying liquid, that had been previously partially decomposed (average molecular mass = 235.5 g/mol, iodine number = 66.5 g I₂/100 g), containing about 62% unsaturated compounds and about 0,05% sulphur compounds.

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. Therefore, additional raw materials in the experiments were solid polyolefin agglomerates (0.03% S). The aim of the experiments was creating a real possibility of comprising the whole process of engine fuel production in one stage, including both decomposition and enrichment of polymer products.

The selected studies were conducted in the presence of paraffin oil (average molecular mass = 308.6 g/mol, iodine number = 4.8 g I₂/100 g, unsaturated content = 5.8%, sulphur content = 0.35%) which was used in order to facilitate dissolution of solid polymers.

In exploratory studies, the process of methanol decomposition was confirmed. Using chromatographic analysis, in post-reactive gases the following compounds were identified: hydrogen (69.8% v/v), carbon monoxide (6.6% v/v), carbon dioxide (22.6% v/v) and methane (1.0% v/v).

Degradation of polyolefins at the reaction temperature of ~400°C, under increased pressure (3-25 MPa) and in the presence of methanol results mainly in a hydrocarbon product of a desired liquid character (Tab. 6).

Table 6

Selected properties of liquid products

Raw material	I	II	III	IV	V	VI
The yield of liquid product	86.1	80.0	91.5	*89.7	79.0	77.7
Average molecular mass, g/mol	123.4	128.6	146.6	239.5	138.1	145.6
Iodine number, gI ₂ /100g	33.6	64.7	27.2	39.2	28.1	31.2
Unsaturated content, %	16.3	32.8	15.7	36.9	15.3	17.9
Sulphur content, %	0.01	0.04	0.12	0.25	0.01	0.02

* in the form of solidifying liquid

In the first variant (processes I and II), the polyolefin product (previously partially thermally decomposed) was used as the raw material. Further degradation in the presence of methanol leads to the fraction with a reduced average molecular mass, reduced unsaturated content and reduced sulphur content (I) in comparison with the initial product. For the comparative variant (II), conducted without methanol (so without hydrogen in the reaction zone), the contents of both unsaturated structures and sulphur compounds are far greater.

In the next variant (processes III and IV), dissolution of raw polymer is facilitated by paraffin oil addition. The only disadvantage here is the great fraction of sulphur, purposely introduced in case of methods using technological oil. In the comparative process (IV), conducted without alcohol, the analogical (typical of these cases) result is observed: greater contents of unsaturated compounds and sulphur in obtained fractions.

In the last case, waste polyolefins were used (also in the solid state), but without oil type additions (processes V and VI). 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 (average molecular mass = 140 g/mol) with a simultaneous hydroconversion of created unsaturated structures because the olefins content in the obtained fractions equals about 16% m/m. For comparison, I would like to remark that in

typical polyolefins thermodestruction the contents of these types of compounds fall within 40–60% m/m.

3. Conclusions

Several technological variants of waste polyolefins utilization were proposed, among which the following most basic methods of thermal decomposition under increased pressure caused by vapour pressure of reagent mixture were used in order to obtain highly valuable hydrocarbon fractions:

- The method of waste polyolefins dissolution in organic liquids (petroleum, naphtha) at increased temperature and under increased pressure, leading to creation of liquid materials as a result of strong destruction of polymers. The obtained products are used for further petroleum processing or olefin pyrolysis – in case of naphtha.
- The physical method of waste polyolefins compaction (e.g. waste plastic packages), consisting in a waste polyolefins mixture heating, also under increased pressure, which results in obtaining a compact polymer. This variant can be a proposition for a solution of a problem related to fast dump volume (surface) filling.
- Presented in the paper, the studies on the possibility of combining the process of polyolefin decomposition with simultaneous hydrogenation of created unsaturated structures in the presence of liquid of hydrogen donor character give promising effects. The realization of this assumption is related to simultaneous utilization of waste materials and allows liquid fuel fractions or their components to be obtained. Using the method of thermal degradation of waste polyolefins (~400°C) under increased pressure and in the presence of reagents, liquid hydrocarbon fractions are obtained, containing small amounts of both unsaturated compounds and sulphur.
- Decomposition of polyolefin products in the presence of methanol allows realization of several processes simultaneously: degradation of polymers, their dissolution and refining expressed by hydrorefining of sulphur compounds and saturation of binary bonds. Expanding the technological concepts with the use of solid waste polyolefins without previous thermocatalytic decomposition is an extremely interesting issue, allowing realization of the whole process of obtaining engine fuel within one stage which integrates both decomposition and enrichment of polymer products. The studies on the possibility of combining waste polyolefins decomposition with hydroconversion in the presence of methanol give promising results. Despite short times of process conducting at increased temperature and under increased pressure, satisfactory effects of a desired liquid hydrocarbon fraction with both low olefin contents (about 16% m/m) and low sulphur content (0,01%) were obtained.

The studies on the possibility of realization of processes in a thermal-pressure version, directly in the solid waste polyolefins – refining liquids system, without the initial pyrolysis of polymers, will be continued. The preliminary experiments with a longer process conducting time result in more effective hydroconversion of both unsaturated compounds and sulphur.

The additional advantage of the methanol use is the fact that the final product does not require additional purification from reagent decomposition products which takes place in

case of e.g. naphthen-aromatic hydrogen donors. The method using technological oils will have to be modified or replaced by the method using sulphur-free substitutes.

This study was financed by the Ministry of Education and Science (Poland) under Grant No. PBZ-MNiSW-5/3/2006.

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