

## THERMAL AND THERMO-CATALYTIC CONVERSION OF WASTE POLYOLEFINS TO FUEL-LIKE MIXTURE OF HYDROCARBONS

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Results of the investigation of thermal degradation of polyolefins in the laboratory-scale set-up reactors are presented in the paper. Melting and cracking processes were carried out in two different types of reactors at the temperature of 390–420°C. This article presents the results obtained for conversion of polyolefin waste in a reactor with a stirrer. Next, they were compared with the results obtained for the process carried out in a reactor with a molten metal bed, which was described in a previous publication. For both processes, the final product consisted of a gaseous (2–16 % mass) and a liquid (84–98 % mass) part. No solid product was produced. The light, “gasoline” fraction of the liquid hydrocarbons mixture (C<sub>4</sub>–C<sub>10</sub>) made up over 50% of the liquid product. The overall (vapor) product may be used for electricity generation and the liquid product for fuel production.

**Keywords:** waste polyolefins, waste to fuels, energy and raw materials recycling, thermal degradation of waste.

### 1. INTRODUCTION

A depletion of non-renewable natural resources would be very dangerous for the future existence of human civilization. Protection of the natural environment, a decrease of CO<sub>2</sub> emissions and mitigation of climate change is feasible only by reducing consumption of natural resources. Therefore, a search for options to increase energy efficiency, an increase in the use of renewable energy sources and reuse of different types of waste seems to be the obvious direction of scientific activity. Feedstock recycling of waste raw materials (biomass, waste plastics, waste tires) is the best way to reuse primary energy and raw materials. Figure 1 shows a relationship between energy production from fossil fuels and their recovery from waste and technological similarities between these processes. This indicates also the need to develop and improve technologies of waste conversion into raw materials and/or energy.

Thermodynamic analysis based on exergy approach indicates that the best technologies to utilise waste plastics and used tires are gasification and thermal degradation (cracking and pyrolysis) (Fratzcher and Stephan, 2001; Stelmachowski, 2010a). These technologies ensure the highest rate of recovery of primary energy.

Waste plastics contribute to many environmental and social problems due to the loss of natural resources, environmental pollution, depletion of landfill space and demands of an environmentally oriented society. The advantages of plastics (such as lightness, sturdiness, chemical resistance, and low cost) that make them suitable for an enormous number of practical uses simultaneously are their disadvantages due to their impact on the environment. Chemical resistance and sturdiness result in long time of natural decomposition, low price brings out low profitability of recycling and low weight contributes to the fact that scrap plastics take up a large volume. The consumption of plastics per capita

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differs very much in the world even in developed countries. In Europe, the consumption of plastics was about 24-150 kg/person in 2003-2005, while 10 years earlier the average consumption in the EU had been about 20-60 kg/person (Aguado et al., 2008; Spokas, 2008; Stelmachowski, 2010a). The amount of waste polymers increases by 6.6 to 12% each year, depending on the country. Waste plastics represent only 7 to 9% of total waste in terms of mass but about 30% in terms of volume. About 70% of waste are polyolefins, including polyethylene (PE), polypropylene (PP) and polystyrene (PS). The majority of these waste are disposed in landfills or incinerated (20–25%), with no attempt to recycle using of chemical recycling or thermal degradation processes (Scheirs and Kaminsky, 2006; Williams and Slaney, 2007).

In the near future, a disposal of organic waste and plastics in landfills will be almost impossible due to the law, high costs and growing ecological social awareness. However, there are also some technological and economic constraints that limit full and efficient recycling of waste plastics into useful products.

Mechanical recycling, which is probably the best way of reclaiming plastics, refers to the processes that involve sorting, shredding or melting and re-granulation. It may be applied only for clean plastics and plastics of the same type.

Energy recovery by incineration can be considered the second most attractive option for waste plastic utilisation. This process can reduce the amount of waste by over 90%. But sometimes it is strongly criticised because of the lack of recovery of raw materials, low energy efficiency and high costs of gas treatment.

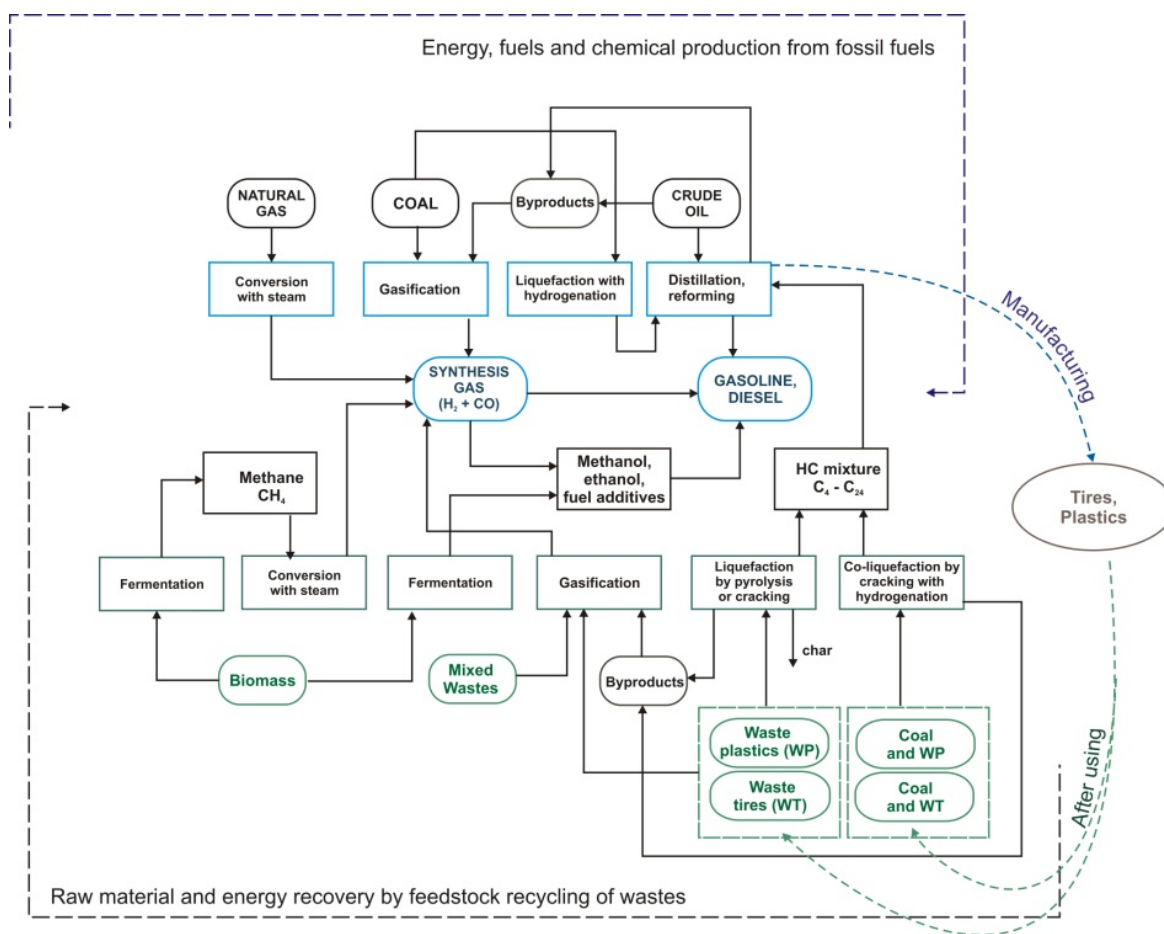


Fig. 1. Connections between energy production and raw materials and energy recovery

Feedstock recycling by thermal and chemical methods of conversion of scrap polymers, such as gasification, liquefaction, liquefaction with hydrogenation, hydrolysis, pyrolysis, and thermo-catalytic degradation, are well known and environmentally accepted. They reduce the environmental impact of plastic waste and may be a cheap source of energy and useful raw materials. These methods have come a long way from a scientific idea to industrial technologies.

Generally, conversion technologies use thermal or catalytic cracking in batch, semi-batch or flow, vessel or tubular reactors, fluidised-bed reactors, furnaces, microwave ovens and other types of reactors. The investigated catalysts are based mainly on silica-alumina, zeolites or other chemical compounds (Scheirs and Kaminsky, 2006; Siddique et al., 2008; Stelmachowski, 2010a; 2010b).

Various types of unconventional technologies have also been investigated and developed. KDV-process have been proposed by Dr. Ch. Koch in the beginning of the 21<sup>st</sup> century. Hydromax® Technology, proposed by Alchemix Corporation (Kinding et al., 2003), is based on the conversion process of organic waste to hydrogen on the surface of molten metal - iron with the addition of tin. Molten salt oxidation - thermal treatment to destroy organic waste is performed by injection of waste beneath the surface of a bed of molten carbonate salts at 900 to 950°C. The catalytic oxidation leads to inorganic products (CO<sub>2</sub>, H<sub>2</sub>O, NO<sub>x</sub>, SO<sub>2</sub>, etc.) with no recycled organic or inorganic products (hydrocarbons, hydrogen, CO) and with no recycled energy (Hsu et al., 2000). The technology of waste polymers conversion (into a mixture of hydrocarbons) based on their thermal degradation beneath or on the surface of the alloy of molten metals (tin, lead and bismuth; Newborough et al., 2002), called sometimes "*Clementi Process*", is carried out below 600°C (often between 350 and 550°C).

However, so far industrial plants using thermal cracking, catalytic cracking or pyrolysis have been rare or were in operation for only a very short time although over 60 technologies have been developed and several plants in a pilot or even industrial scale have been constructed and run. The reason for their closure was that the proposed systems were technologically imperfect and that their profitability was poor. The new technology (and the reactor) should have the following features:

- low costs (operating and investment) due to the fact that plastics (waste plastics) as well as products of degradation are inexpensive; the conversion process must be profitable,
- the process should be carried out without catalysts due to difficulties and cost of their recovery,
- the yield of the liquid product should be high; it is usually the most valuable one,
- the frequency of reactor cleaning should be low,
- industrial plants should have modular construction to make raw streams more flexible.

These results indicate that thermal decomposition of a mixture of hydrocarbons can be just as beneficial as the process of catalytic cracking. The reactor's construction is crucial as well as proper stirring of the reaction mixture and the way of heat transfer to the reaction mixture from a heating medium. In this article, we present a comparison of two conversion technologies of polyolefin waste products based on experiments conducted on a laboratory scale.

## 2. EXPERIMENTAL

### 2.1. Materials

#### *Raw materials*

Commercial polymers, PE and PP were used in the laboratory-scale experiments:

- polyethylene, HDPE, (CAS 9002-88-4), diameter of pellets 3÷4 mm, melting temperature 50÷140°C, manufacturer Slovnaft, trade name Tipelin,
- polypropylene, PP, (CAS 9010-79-1), diameter of pellets 3÷5 mm, melting temperature 116-165°C, manufacturer Slovnaft, trade name Tatren,

### Catalysts:

- aluminum oxide  $\gamma\text{-Al}_2\text{O}_3$  with particle size below 0.1 mm, (Merck),
- aluminum hydroxide  $\text{Al}(\text{OH})_3$  particle size below 0.1 mm (Merck),
- tungsten trioxide supported on silica dioxide, the catalyst contains 8% of  $\text{WO}_3$  by mass; the particle size is 0.1 - 0.3 mm (Merck, obtained from SASOL, RSA),
- natural bauxites that contained alumina hydroxide, hydrated alumina oxides, silica dioxide and iron hydroxides. The particle size is between 0.01 and 0.1 mm (Eastern Industries And Trading Co., Ltd, China).

## 2.2. Experimental set-up

Laboratory investigation was conducted for two types of technologies. The first part of the experiments was performed by thermal degradation of waste PE and PP in molten metal. The conversion of polyolefins was carried out in a new type of a vertical tubular reactor (Stelmachowski, 2008), with molten metal called “the tube in the tube”. The construction of the reactor differs from the known basin reactors that had been patented until now (Domingo and Cabanero, 1949; Mausre et al., 1989). A description of the laboratory set-up and results of the laboratory thermal degradation of waste polyethylene and polypropylene in the molten metal using this type of the reactor can be found in a previous study (Stelmachowski, 2010b).

The experimental set-up for second part is shown in Figure 2. The main part of the set-up was a semi-batch vessel reactor with stirring. The conversion of PE or PP was performed by thermal or catalytic cracking.

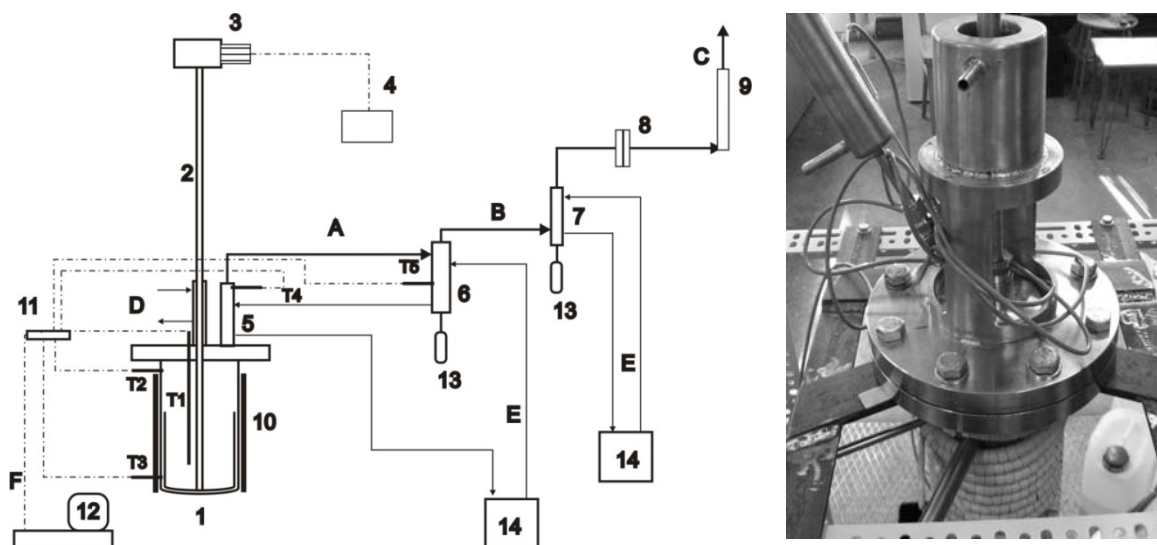


Fig. 2. The scheme and photograph of the experimental set-up with a semi-batch reactor; (1) reactor, (2) horseshoe stirrer, (3) stirrer drive (electric motor with gear), (4) inverter for the gear, (5) reflux condenser, (6) (7) condensers (coolers), (8) gas sample port, (9) bubble flow meter, (10) electric heating mantle, (11) (12) data acquisition system and computer, (13) receivers for liquid product, (14) thermostats, (streams: A – total vapor products stream, waste polymers, B – vapor product after first condenser, C – non-condensable gases, D, E – cooling water; F – temperature signal to the data acquisition system

## 2.3. Measurements and analytical procedures

The liquid and gas product samples were analysed by gas chromatography. The GC (gas chromatography) analytical conditions are presented in Table 1. The internal normalisation method was

applied to calculate concentrations of all the components. Equation (1) was used to determine the molar fraction of component “i”:

$$x_i = \frac{\frac{A_i}{nC_i} \cdot f_i}{\sum_{j=1}^N \left( \frac{A_j}{nC_j} \cdot f_j \right)} \quad (1)$$

$$f_i = \frac{\frac{A_i}{nC_i} \cdot x_i}{\frac{A_R}{nC_R} \cdot x_R} \quad (2)$$

where:  $A_j$  – peak area,  $x_j$  – molar fraction,  $nC_j$  – carbon number, and  $f_j$  – relative response factor (RRF) of component  $j$ . Subscript  $R$  represents the reference component (heptane) in the mixture.

Table 1. Gas chromatography analytical conditions

	Liquid samples	Gas samples
Gas Chromatograph	GC Autosystem XL Perkin – Elmer	
Column	PE – Volatile N931-6393 (Length) L = 75 m (Inner Diameter) ID = 0.52 mm Film 2.55 μm	Supelco SPB-1 25349 L = 60 m ID = 0.53 μm Film 5 μm
Detector	FID (Flame Ionization Detector)	FID
Injector	For capillary column; split 1:50	
Temperature program	60°C, 3 min 20°C/min 100°C, 5 min 40 to 240°C/min 240°C, 120 min	35°C, 5 min 23°C/min 150°C, 12 min 30 to 210°C/min 210°C, 15 min
Detector temperature	260°C	240°C
Injector temperature	260°C	210°C
Gases	Helium 2 ml/min Hydrogen 45 ml/min Air 450 ml/min	Helium 2 ml/min Hydrogen 45 ml/min Air 450 ml/min
Syringe	10 μL	100 μL
Sample	5 μL	50 μL

The relative response factors were calculated from Equation (2) based on the analysis of the reference mixtures (of 11 components) that were composed of pure hydrocarbons (olefins and paraffins) GC standards (Fluka). Each mixture was analysed three times. The estimated error of factors  $f_i$  (RRF) determination was below 0.1%. Nevertheless, the error of gas sample analysis was estimated to be 0.5 to 2% depending on the component; the error of liquid sample analysis for hydrocarbons  $C_5 \div C_{10}$  was below 0.5%, for  $C_{11} \div C_{16}$  1.5% and for higher hydrocarbons below 3.0%. The factors for isomers were nearly the same. Factors  $f_i$  (RRF) for other components, not included in the reference mixtures, were extrapolated because it was impossible to determine experimentally the factors for all components (over 200) present in genuine liquid mixtures derived in the runs.

Gas flow was measured by a bubble flowmeter that was calibrated for air at 20°C. The error of calibration was 0.05%. However, the measurement error of gas flow was greater because of difficulties

in measuring the temperature and flow in the reaction conditions which were quickly changing. It was estimated to be 1.5%. The liquid product flow was measured on-line by taking small weighted samples of the mixture of condensed hydrocarbons. The error of measurement of liquid product mass was 0.05-0.1%. A detailed specification of all measurement accuracies is given in Table 2.

Table 2. A detailed specification of the accuracy of all measurements

Measurement parameter	Device	Measurement accuracy
Gas flow	Bubble flowmeter	< 1.5%
Liquid samples weight	Balance (Metler)	< 0.05%
Temperature	K-type thermocouple	±1°C
Gas sample analysis	GC Autosystem XL PE	0.5÷2.0%
Liquid sample analysis C <sub>5</sub> ÷C <sub>10</sub>	GC Autosystem XL PE	< 0.5%
Liquid sample analysis C <sub>11</sub> ÷C <sub>16</sub>	GC Autosystem XL PE	< 1.5%
Liquid sample analysis C <sub>17</sub> ÷C <sub>24</sub>	GC Autosystem XL PE	< 3.0%

#### 2.4. Run description

The reactor was heated electrically. The installed electric power reached 4.5 kW but only about a half of it was exploited. The heat stream to the reactor was 2.2-2.3 kW. Particles of PE or PP were put through the loading port into the reactor and next the reactor was purged with nitrogen to check leak-tightness of the reactor as well as to create inert atmosphere prior to an experiment and at its first stage. Then electric heaters were turned on and voltage was increasing until the desired temperature of the reaction mixture was reached. Meanwhile, polymers were melted. After reaching a proper temperature, polymers were decomposed. Hydrocarbon vapors and partially non-degraded polyolefins flowed out to the reflux cooler. The heavy hydrocarbons, waxes and non-degraded polymers have been recycled to the reactor. Other vapor products flowed out from the reactor, were condensed in coolers and collected in small receivers which enabled on-line measurement of the liquid stream. The stream of gaseous hydrocarbons flowed through the bubble flowmeter and sampling port to the ventilation system. Temperatures of the liquid reaction mixture gas phase in the reactors and in the coolers were measured and recorded by the acquisition data system. Selected samples of the liquid product and 2-4 samples of gas product were analysed using a gas chromatograph during all the experiments. For some runs, a certain amount of wax (derived in previous experiments) was added to the polymer in order to create better conditions for heat transfer during the melting of the charge.

#### 2.5. Results

The process was carried out in a semi-batch reactor. The profile, yields and basic mass balances for PE and PP decomposition are given in Table 3. The course of experiments was described and illustrated in graphic diagrams in a previous publication (Stelmachowski, 2010a). Selected liquid samples from each run were analysed by gas chromatography. Three/four samples of the gaseous stream were also analysed by GC. All liquid samples received during the degradation process of PE and PP were fluid in ambient conditions, although the products of PE cracking were more dense (like “diesel” fraction or heavy oil fraction mixed with light waxes) than those for PP. The composition of all of them was almost stable in the time of the run.

Only the first taken sample usually contains more light products. The carbon number liquid product distributions for thermal degradation of PE and PP are presented in Figure 3 for the representative runs. They present the composition of samples taken and analysed for these

experiments. The distributions are different for PE and PP degradation. It means that the mechanisms of cracking of PP and PE were different as it was earlier mentioned in many published papers (e.g. Scheirs and Kaminsky, 2006) describing laboratory experiments of degradation (thermal and catalysed) processes of these plastics.

The last two experiments (presented in Table 3) carried out with bauxites as catalysts lasted for several minutes and only 7-16% of the charge was degraded to the final product. It was the initial stage of the process at which the gaseous product dominated. Results of these experiments are only presented but not discussed as being not representative. These results are given only to indicate the differences (shown in Figures 4a and c) in the content of light and heavy hydrocarbons in the liquid product (in the initial phase of the process). In this stage, light hydrocarbons dominated in the liquid product. Then, when the reaction takes place in the whole volume of the reaction mixture, the content of heavier hydrocarbons will be increasing.

Table 3. The profile, yields and basic mass balances of performed experiments

Symbol of the run		PELU 27	PEMA 21	PEKW 11	PEKW 21	PEMJ 9	PEMJ 18	PPWR 24	PPPZ 02	PPPZ 08	PPPZ 15	PPPZ 25	PELI 05	PELI 19
Polymer		PE	PE	PE	PE	PE	PE	PP	PP	PP	PP	PP	PE	PE
Temperature of the reaction mixture		378-438	382-435	378-431	381-427	379-430	381-418	358+368	360+388	359+368	354-364	356-368	354-365	344-390
Mass of stock	g	600.0	800.0	873.4	699.2	700.0	700.0	600.0	652.0	637.0	600	600	600	600
Mass of wax added to the polymer	g	123.0	0.0	0.0	142.0	154.8	160.5	0	0	0	0	0	0	0
Mass of the catalyst	g	0.0	0.0	0.00	10.5	14.5	15.2	0	0	0	80.2	60	60	60
Catalyst	-	-	-	-	Al <sub>2</sub> O <sub>3</sub>	Al(OH) <sub>3</sub>	WO <sub>3</sub>	-	-	-	bauxi-tes	bauxi-tes	bauxi-tes	bauxi-tes
Mass of the total liquid product	g	518.0	525.0	574.5	493.2	417.4	399.7	354.1	338.7	300.9	206.9	321.4	17.7	48.7
Volume of the gas product	Ndm <sub>3</sub>	14.5	18.0	23.9	19.1	16.1	31.6	9.1	10.1	9.1	6.4	8.8	4.6	6.4
Mass of the decomposed charge	g	593.0	591.0	641.4	550.3	483.3	475.9	409.8	397.7	347.2	235.0	345.5	39.3	86.9
Yield of the liquid product	% mass	87.4	88.4	89.6	89.6	86.4	84.0	86.4	85.2	86.7	88.0	93.0	45.1	56.0
Degree of conversion	% mass	82.0	73.9	73.4	65.4	56.5	55.3	68.3	61.0	54.5	39.2	57.6	6.6	14.5

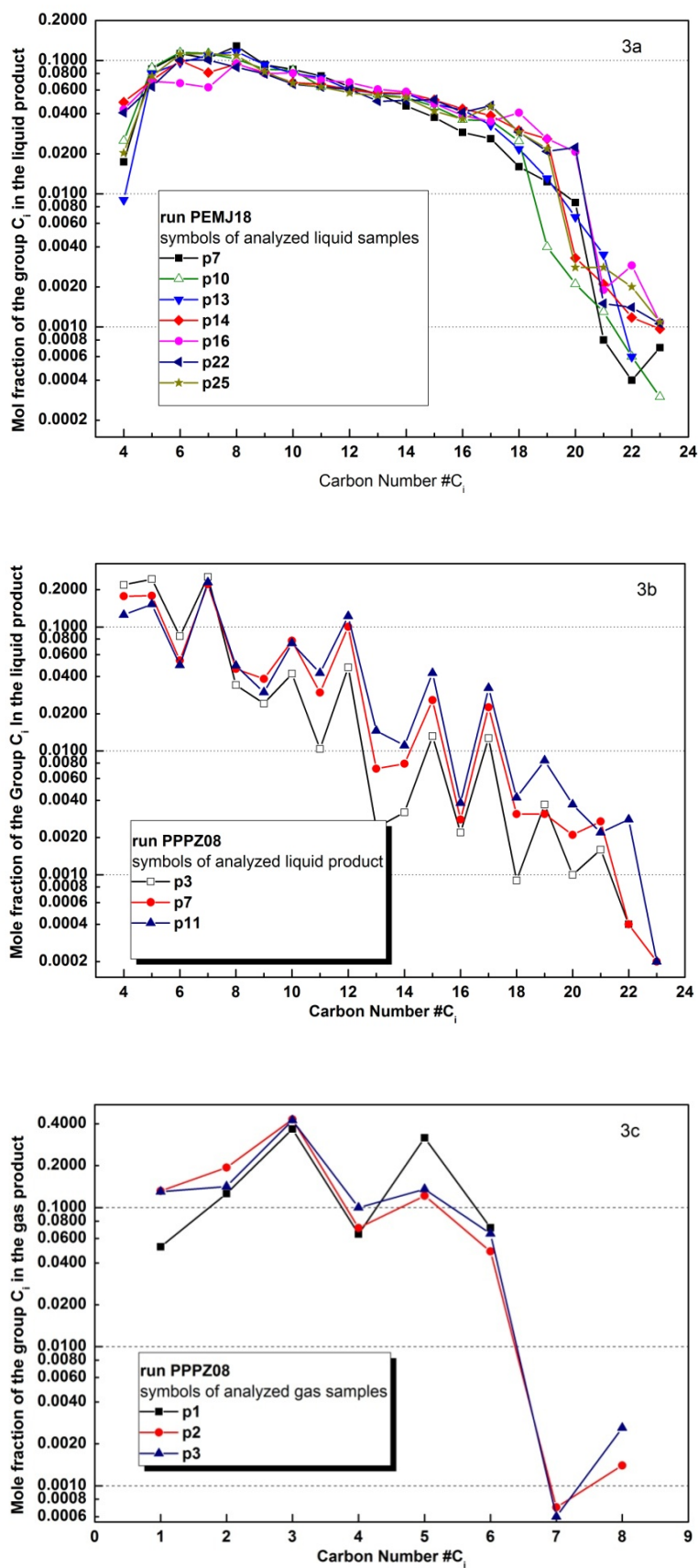


Fig. 3. The carbon number distributions of the liquid (3a,b) and gas (3c) products for PP and PE decomposition in the runs PEMJ18, PPPZ08 (p1,p2...pi...p14 - symbols of received and analysed samples during the run)



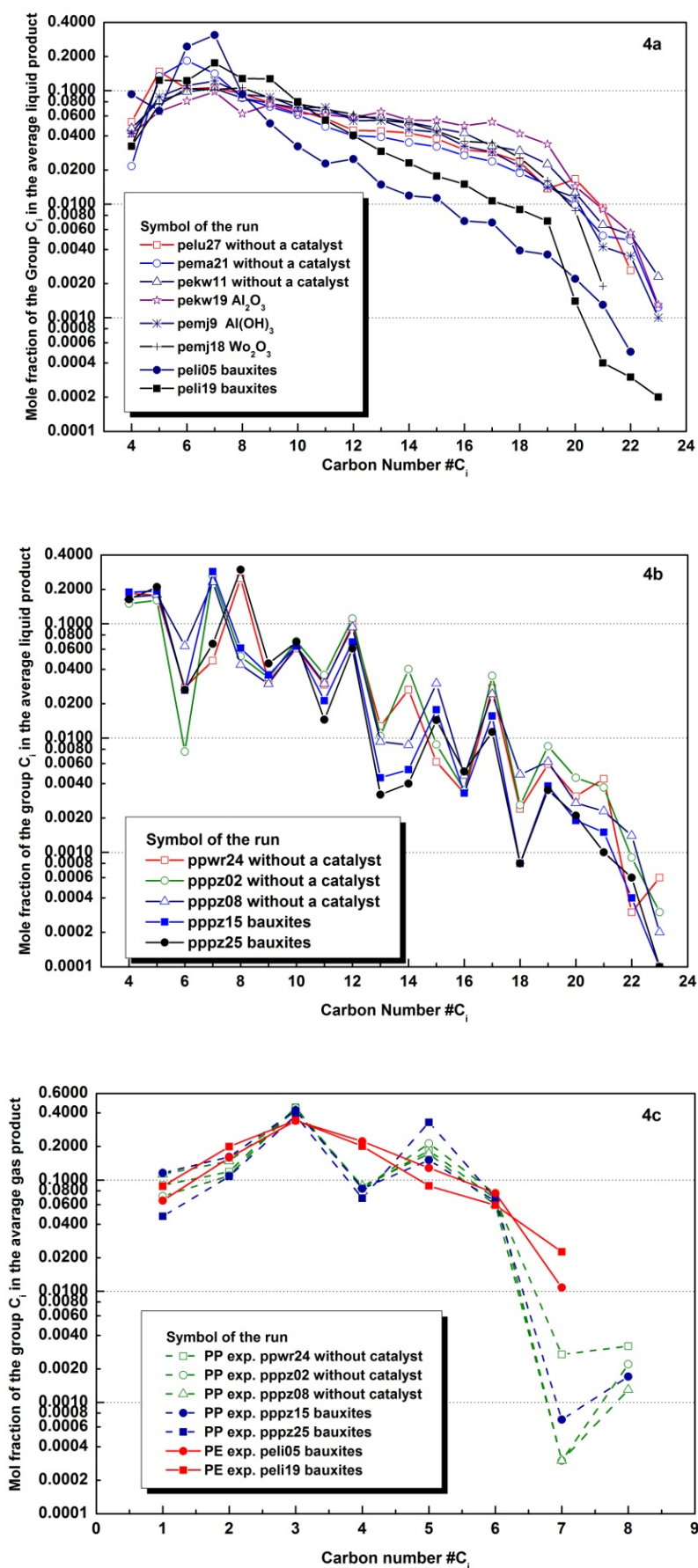


Fig. 4. The carbon number distributions of the average liquid (4a,b) and gas products (4c) for PP and PE decomposition in different runs

The compositions of total (average) liquid products and gaseous products were similar in all the experiments for the same polymer regardless of the experimental conditions. Figure 4 shows it as the carbon number average liquid and gas product distributions. It means that the process was very stable, repeatable and the quality and product composition might change in a very narrow range. The influence of used catalysts was irrelevant. Only the composition of the liquid product obtained for PE degradation with bauxites was different, but as it was mentioned, these runs were performed only for the first period of the decomposition process.

Three basic fractions in the liquid product are usually distinguished for polymer degradation by pyrolysis or cracking: light (“gasoline”; C<sub>4</sub>÷C<sub>10</sub>), medium (“diesel” C<sub>11</sub>÷C<sub>16</sub>); and heavy (“light waxes” C<sub>17</sub>÷C<sub>24</sub>). Table 4 gives the content of these fractions in the liquid hydrocarbon mixtures obtained in the experiments. Similar experimental results obtained for thermal degradation in molten metal bed (Stelmachowski, 2010a) are added for a comparison of both technologies.

Table 4. The mean (average) composition of the products in all runs and yield of the liquid product

Type of the reactor	Semi-batch tank reactor				Semi-batch “tube in tube” reactor with molten metal	
	Thermal cracking		Catalytic cracking		Thermal cracking	
Polymer	PE	PP	PE*	PP**	PE	PP
Fractions	% mol					
C <sub>4</sub> -C <sub>10</sub>	64.9–70.0	73.5–78.2	88.9–58.4	85.5–87.9	48.8–52.1	67.4–70.2
C <sub>11</sub> -C <sub>16</sub>	25.7–22.2	20.9–17.6	34.4–9.3	12.1–10.2	30.9–33.6	20.7–23.4
C <sub>17</sub> -C <sub>24</sub>	9.5–7.9	4.6–4.2	16.9–1.8	2.4–1.9	16.9–17.9	9.1–9.3
Fractions	% mol					
Paraffins	54.4–55.2	42.8–45.0	58.7–51.5	44.6–44.7	46.7–54.8	33.5–46.1
Olefins	45.6–44.8	57.2–55.0	41.3–48.5	55.4–55.3	45.2–53.3	53.9–66.5
Fractions	% mol					
n-paraffins	43.4–46.5	34.0–34.9	36.2–48.6	28.7–29.8	36.1–41.6	32.8–44.8
1-olefins	33.0–31.5	45.8–40.1	31.0–24.6	33.0–34.1	36.3–34.4	62.4–50.0
Iso-parafins	23.9–11.0	10.2–8.8	15.3–9.9	15.9–14.9	13.2–10.8	2.3–0.7
Iso-olefins	23.0–14.1	15.4–11.4	21.6–12.2	22.3–21.1	18.3–14.4	10.6–1.2
	% mass					
Yield of the liquid product	87.4–89.6	84.0–86.7	85.2–86.7 (45.1–56.0)***	88.0–93.0	83.1–90.1	90.9–91.9

\* the highest values of “light fraction” of the liquid product were obtained for bauxites as catalysts,

\*\* only bauxites were used as catalyst,

\*\*\* with bauxites as a catalyst – in the first period of degradation.

The products contain also a very small amount of aromatic hydrocarbons amounting to below 0.5 % mol for the processes carried out without catalysts and below 2 % mol with a catalyst. Their content was estimated approximately using an FTIR spectrophotometer. Aromatic hydrocarbons were included in the mixture of aliphatic hydrocarbons in the presented balances.

Table 5. Comparison of the results for different feedstock recycling of waste polyolefins (PE and PP)

Type of the process and reactor	Type of the catalyst	Type of the polymer	Temperature	Products			In the liquid product		
				Gas	Liquid and waxes	Residue and coke	“Gasoline fraction”	Aromatics	
			[°C]	% mas					
General estimation									
Fluidized bed reactor	Thermal and catalytic	Zeolites		500÷760	1÷72	31÷92	0÷6		
Batch and semi-batch, tube reactors, □ or stirred tank	Catalytic (fix bed)	Zeolites	PE, PP, PS and their mixtures	380÷700	6÷55	31÷71	0÷21		
	Thermal	-		350÷700	4÷75	15÷90	1÷10		
Vacuum pyrolysis	Thermal	-		500	0-3	5	2		
Ultrafast pyrolysis	Thermal	-		700-800	93	5	2		
Examples, 1996-2008					% mas				
Semi-batch steel, lab, mini-reactor; Zhibo et al (1996)	Thermal	-	PE	400	20	57	17	20	3
	Catalytic	HZSM5	PE	400	50	46	1	45	35
Semi-batch glass, lab mini-reactor, Kim, et al (2002)	Thermal		PP	400-420	14	75	11		11
	Catalytic	HSC LZ4	PP	400	15-46	53-75	0-9		15-18
Extruder with tube reactor; Demonstration scale, Walendziewski (2005)	Catalytic	Zeolites	PE/PP/PS	300-420	5-10	82-85	4-8	29-42	-
Commercial scale (extruder, pyrolysis reactor, catalytic reactor (fixed bed), Nishino et al. (2008)	Thermal & Catalytic	Ga-ZSM5	PE+PP	270-550	34-44	36-60	2-18		25-55
Fluidized bed reactor (different scales of the set-up); Predel and Kaminski (2000)	Catalytic	Zeolites	PE/PP/PS	510	2-7	41-55		~50%	
our works					% mol				
Reactor with molten metal, Stelmachowski (2010 a, b)	Thermal	-	PE	408-428	6-17	83-94	0	49-52	< 0.5
			PP	362-430	2-9	91-98	0	67-70	
Semi-batch tank reactor with stirrer, this work	Thermal	-	PE	378-435	10-13	87-90	0	65-70	< 0.5
			PP	358-388	14-15	85-86	0	74-78	
	catalytic	Al <sub>2</sub> O <sub>3</sub> W <sub>2</sub> O <sub>3</sub> Al(OH) <sub>3</sub>	PE	379-430	10-14	86-90	0	58-89	< 2.0
			PP	354-368	7-12	88-93	0	86-88	

### 3. DISCUSSION

The yield of the liquid product and its composition is crucial for its applicability. The results of the presented work indicate that degradation of waste polyolefins by thermal cracking is a very good way to obtain valuable products that can be used in different ways. The yield of more valuable liquid product is high and it is equal to 83-93 % mass. The content of the gasoline fraction is equal to

67-88 % mol and wax fraction to 2-17 % mol of the liquid. No solid product was obtained in the experiments carried out in the laboratory scale set-up. However, for the degradation of genuine waste polyolefins a small amount of solid waste consisting of mineral compounds and coke may occur. The results indicate also that the use of catalysts is not crucial to recover raw materials and/or energy.

The utilisation of waste polyolefins may be performed efficiently without catalysts in typical vessel reactors as well using unconventional technology based on thermal degradation in molten metal bed (an alloy of tin, lead and bismuth) at 400-420°C. A detailed description of this type of a reactor and experiments performed in it may be found in the previous works (Stelmachowski, 2010a). The summary results are also presented in Table 4.

A comparison of the obtained results with other published results for pyrolysis of disintegrated PE and PP in tubular or fluidised bed reactors is difficult due to different conditions of the considered processes. Nevertheless, the compositions of liquid products obtained in different processes and yields of the gas and liquid products can be compared. The comparison was presented in Table 5. The basic difference between the liquid products lies in the fact that the content of aromatic hydrocarbons in the liquid is definitely lower for the process carried out in the molten metal than for processes performed in other types of reactors. Many researchers (Aguado et al., 2008; Nishino et al., 2008; Scheirs and Kaminsky, 2006; Siddique et al., 2008; Walendziewski, 2005) reported that the content of aromatic hydrocarbons may be small or even very small for non-catalysed pyrolysis but in the presence of catalysts (particularly zeolites) they observed an increase in the amount of aromatic hydrocarbons in the liquid. The yields of the gas and liquid products for different thermal processes performed at similar temperatures were almost the same. Catalysts (zeolites) and/or higher temperature cause an increase of gas product yield. If the goal is to produce electric power using vapor product the application of catalysts is favorable. In other cases thermal degradation seems to be a better solution.

#### 4. CONCLUSIONS

The consumption of plastics has been continuously increasing and will be increasing in the future due to great differences in their consumption between developed and developing countries. Therefore, the amount of this type of waste will also be increasing. Growing environmental consciousness of people and law will make it impossible to dispose of such waste in landfills.

Feedstock recycling is the best way to recycle waste and to recover raw materials and primary energy. The presented results indicate that thermal degradation of polyolefin wastes is a good method to utilise them and it meets all the demands of environmentally friendly method of waste recycling as well as energy recovery. The conversion degree, yield of the most valuable liquid product (approximately 80-90%) and its composition indicate that the use of catalysts is not necessary. The process will be more profitable and easier to carry out without them.

The process is usually carried out in typical reactors (tube, tank, extruder or a combination of these reactors). The process in a laboratory-scale facility is easy to run and products are very useful. The presented results proved this statement. However, thermal degradation of plastic waste in industrial plants has been very rare up to now. It means that this type of technology is still imperfect in operation and/or its profitability is low. The main reasons are coke formation during the process, the necessity of frequent cleaning of the reactors, using of catalysts and unfavorable economic climate for this branch of industry.

These problems may be reduced or eliminated due to the process of waste degradation in molten metal. In this case heat transfer between the reaction mixture and heating medium is more efficient. The yield of the solid product (coke) may be very small which enables the process to be performed for a long time without the necessity of cleaning the reactor. The products are not worse than those obtained in a

typical process as it can be seen in Table 5. The thermodynamic calculations based on exergy approach indicated that energy efficiency was high (Stelmachowski, 2010a) which meant that recovery of primary energy from polyolefins wastes was also high.

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