Pyrolysis gases produced from individual and mixed PE, PP, PS, PVC, and PET—Part I: Production and physical properties

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ABSTRACT

This article describes the production and properties of gases produced by the pyrolyses of poly(ethylene terephthalate) (PET), polypropylene (PP), polyethylene (PE), poly(vinyl chloride) (PVC), and polystyrene (PS), and three of their mixtures at process temperatures of 500, 700, and 900 °C. The overall aim was to characterize all 24 gases in terms of their production and physical properties, and compare the data obtained to those of traditional fuels, namely natural gas (NG) and propane. In addition to experimental and analytical approaches for determining quantities and compositions of the pyrolysis products, various mathematical methods and their combinations were also used to determine product properties. The highest conversion of material into gas occurred during the pyrolysis of PP at 900 °C (66.88 wt% conversion into gaseous products). The pyrolyses of PE and PP at 500 °C were found to generate pyrolysis gases with the highest energy, with gross calorific values of 86.58 and 81.09 MJ m\(^{-3}\), respectively. The highest chemical energy yield was obtained by the pyrolysis of PP at 900 °C. Gases produced from PVC had a high thermal conductivity of about 104.83 mW m\(^{-1}\) K\(^{-1}\). The gas generated from PP at 500 °C exhibited a high specific heat of 2.94 kJ m\(^{-3}\) K\(^{-1}\), and that obtained from PS at 500 °C had a very low kinematic viscosity (5.28 \(10^{-6}\) m\(^{2}\) s\(^{-1}\)) and thermal diffusivity (7.90 \(10^{-6}\) m\(^{2}\) s\(^{-1}\)).

Even though numerous reports have dealt with pyrolysis gases, there is still not sufficient information about the specific physical properties of these gases. This article attempts to fill this gap and induce scientific interest in this field.

1. Introduction

Pyrolysis process is described as the thermal transformation of organic materials into valuable products in all three states of matter and is in widespread use \cite{1}; it produces materials that are useful in the power \cite{2}, chemical \cite{3}, and building industries \cite{4}, and agriculture \cite{5}. The process is suitable for the thermal processing of various materials, including waste, and is considered to be ecologically and economically acceptable because it ultimately contributes to reducing the volume of waste material and fossil fuel consumption \cite{6–8}. The main principle of pyrolysis involves heating a material in the absence of oxygen above its chemical stability, due to which high-molecular-weight substances are broken down into low-molecular-weight substances \cite{9,10}. The literature provides a variety of information regarding the range of temperatures to which substrates are generally subjected to; for example, temperatures of 300–1000 °C have been reported for the pyrolysis of waste tires \cite{11}. The reaction products of the pyrolysis process are liquids, solids, and gases usually referred to as “pyrolysis oils,” “pyrolysis coke,” and “pyrolysis gases,” respectively. In addition to chemical composition, the quantity and quality of the products are also affected by humidity \cite{12}, starting-material grain size \cite{13}, process temperature and pressure \cite{14}, heating rate \cite{15}, and the catalytic properties of the substances present \cite{16}.

This article focuses on the production and properties of the gaseous products of the pyrolyses and co-pyrolyses of the most commonly used plastics; i.e., poly(ethylene terephthalate) (PET), polypropylene (PP), polyethylene (PE), poly(vinyl chloride) (PVC), and polystyrene (PS), and the impact of the process temperature. The gaseous products of polymer pyrolysis generally consist of mixtures of hydrocarbons C\(_n\)H\(_n\) (maximum C\(_6\) and hydrogen (H\(_2\))), in some cases, they also contains carbon dioxide (CO\(_2\)) and carbon monoxide (CO), and potentially hydrochloric acid (HCl) \cite{17–23}. Owing to the above-mentioned
compositions, pyrolysis gas generally has a high net calorific value and therefore has great potential for use in the power industry [24,25]. Several authors have published studies into the gaseous products from the pyrolyses of various materials. Examples include the 2009 investigation of Siddiqui and Redhwi [26] into the pyrolyses of mixtures of LDPE, HDPE, PP, and PET with PS (e.g., PP + PS) in ratios of 1:1, 1:2, and 1:3 (w/w), in which they report the effects of the plastics on the production of pyrolysis gases at process temperatures of 430–440 °C. In these experiments, a 25-cm³ stainless-steel tubular micro autoclave reactor was used. Zhao et al. [27] studied the effect of CaO on the net calorific value of the pyrolysis gas obtained from sawdust in a moving bed pyrolyzer at a process temperature of 700 °C. Zhong et al. [28] investigated the proportional dependences of the individual components of the pyrolysis gas (i.e., H₂, methane (CH₄), CO, CO₂, and C₂H₄) obtained from coal on the process temperature over the 750–980 °C range; a fluidized bed pyrolysis reactor was used in these experiments. Duan et al. [29] researched the effect of the rate of heating (at 2 and/or 20 °C⋅h⁻¹) on the composition of the gas produced at temperatures ranging from 337 to 600 °C when peat and two types of coal were pyrolyzed in a set of gold tubes. In 2015, Chen et al. [30] reported the effect of process temperature, in the 300–700 °C range, on the net calorific value of the pyrolysis gas produced from bamboo, utilizing TG-FTIR and a laboratory fixed-bed pyrolysis reactor. Ahmed and Gupta [31] compared the pyrolysis and gasification of food waste at temperatures of 800 and 900 °C in terms of the mass yield of the gas product and the chemical energy accumulated. Lou and Wu [32] examined how the composition of the gaseous product from the pyrolysis of lignin in a tube reactor depended on the process temperature (400, 500, 600, 700, 800, and 900 °C). The article by Ahmed and Gupta (2009) [33] featured a comparison of the pyrolysis and steam gasification of paper in terms of the generation of H₂ and CO over time; temperatures in the 600–1000 °C range were considered (in increments of 100 °C). Bíčáková and Straka [34] studied the compositions, net calorific values, and specific densities of pyrolysis gases produced from mixtures of tires and coal in various ratios.

Although pyrolysis gases have been discussed from a variety of perspectives in the literature, the majority of these reports discuss the factors mentioned above, while important information regarding specific physical and fuel properties has not been presented. To the best of our knowledge, no detailed studies into the evaluation of pyrolysis gases from widely used plastics and their mixtures, as fuels, have been reported. The aim of this work is to present a detailed evaluation of these alternative fuels and, at the same time, arouse interest in related research concerning the physical aspects of their combustions in thermal-power facilities. Herein, the properties of the evaluated gases are compared to those of natural gas (NG) and propane, which are used here as the “main representatives” of current conventional gas fuels. The area of pyrolysis gases from plastics is very broad; hence, our results are divided into two articles. Part I deals with the production, composition, energy quality, and physical properties of the pyrolysis gases from different plastics, while Part II focuses solely on the fuel characteristics of the different gases. These two articles build on our previous research dealing with the interchangeability of plastic pyrolysis gases [35,36], which investigated whether or not these gases can be combusted in conventional burners without any requirement for changes in burner construction. This article and Part II deal with concrete physical (e.g., viscosity, gross calorific value, and thermal conductivity) and fuel (e.g., flammability limits, methane number, and autoignition temperature) properties of pyrolysis gases, respectively.

2. Experimental

2.1. Materials

For broadness, five frequently used plastics were selected for pyrolysis, namely PET, PP, PE, PVC, and PS, as well as three of their mixtures for co-pyrolysis. The ratios of the plastics in the mixtures correspond to their current ratios in waste plastics in Japan (JP m.) [37], Europe (EU m.) [38], and the USA (US m.) [39]; see Table A.1 (Appendix A). These mixtures were chosen because waste plastics are processed as mixtures in high-performance pyrolysis units, as their separation is problematic. At the same time, we aimed to obtain results for representative plastic mixtures for the above-mentioned regions of the world. Basic analyses of the samples were undertaken using the combustion method with a Micro Corder JM10 analyzer provided by J-Science Lab Co., Ltd. (Kyoto, Japan). The results are presented in Table A.2.
2.2. Experimental unit and experiments

A total of 24 pyrolysis experiments were performed (8 input samples × 3 process temperatures) in a laboratory vertical dual-chamber reactor. Thermal input was provided by an electrical heating spiral. A 500 mg sample was placed into a perforated holder attached to the top of the reactor (furnace exterior, where samples are not melted or decomposed). The holder with the sample was placed into the reactor when it reached the required process temperature. Each sample was pyrolyzed in the top reactor section for 60 min at a process temperature of 500, 700, or 900 °C, whereas the bottom section of the reactor was maintained at a constant temperature of 300 °C for each experiment to prevent condensation of specific components of the generated pyrolysis gas. Air was removed using helium at a flow rate of 200 mL min⁻¹. The produced gas was vented from the bottom section of the reactor into a condenser cooled with dry ice, and then into a condenser cooled with liquid nitrogen. Condensed compounds (oil, terephthalic acid, and wax) were collected in the condensers. When the input sample contained PVC, the produced hydrogen chloride was absorbed by 0.1 M sodium hydroxide (NaOH). The cooled gas was then pumped into a gas bag. All pyrolysis experiments were once repeated to ensure reliability. A schematic diagram of the experimental setup is provided in Fig. B.1 (Appendix B). The experimental equipment has been described in detail in our previous publications [35,36].

In this work, individual pyrolysis gases are referred to by the same abbreviation as the input material, with a subsequent numerical value that represents the process temperature. For example, the pyrolysis gas produced from PVC at a process temperature of 700 °C is referred to as "PVC (7 0 0)."

2.3. Analytical methods

The analytical methods used are listed in Table 1. In the present work, all gaseous components which were collected in the gas bag and detected by GC analysis are defined as "pyrolysis gas."

2.4. Mathematical methods

This section describes the mathematical methods used for determining the selected pyrolysis-gas parameters discussed in Section 3.

2.4.1. Density, molar mass, specific heat, and gross calorific value

The density, ρ, molar mass, M, specific heat, c, and gross calorific value, Hₘ, of a pyrolysis gas can be derived from Dalton’s law, which states that the pressure of a mixed gas is equal to the sum of the respective partial pressures [30,40]:

\[ \rho = \sum_{i=1}^{n} \frac{M_i}{\Omega} [\text{kg m}^{-3}] \]  

(1)

\[ M = \sum_{i=1}^{n} M_i [\text{g mol}^{-1}] \]  

(2)

\[ c_p, \theta = \frac{1}{\rho} \sum_{i=1}^{n} \frac{c_p, \theta}{\Omega} [\text{kJ kg}^{-1} K^{-1}] \]  

(3)

\[ H = \frac{1}{\rho} \sum_{i=1}^{n} \frac{H_i}{\Omega} [\text{MJ m}^{-3}] \]  

(4)

where \( \rho, M, c_p, \theta, \) and \( H \) are the density, molar mass, specific heat, and heat of combustion of the i-th component of a pyrolysis gas whose volume content is given by \( \Omega, [\text{vol} \%] \). The values of density, molar mass, and specific heat for the components were obtained from the National Institute of Standards and Technology (NIST) database [41] and standard ISO 6976 heats of combustion were used [42]. Parameter \( z_G \) refers to the compressibility factor in the equation, which corrects for the behavior of real gases, specifically for the deviation in the volume of a real gas from that of an ideal gas [43]. No pyrolysis gas behaves as an ideal gas; therefore, this factor was included in these equations for improved accuracy; \( z_G \) can be determined using the following equation:

\[ z_G = 1 + \left( \frac{\Omega}{100} \right) \sqrt{\phi_i} \]  

(5)

where \( \phi_i \) is the “sum factor” whose value for component \( i \) is available in, for example, standard ISO 6976 [42]. The resultant \( z_G \) values for the pyrolysis gases are shown in Table C.1, Appendix C.

Based on data reported elsewhere [44], the relative density can be expressed by the following equation:

\[ d_G = z_G \frac{\rho_G}{\rho_{\text{air}}} [-] \]  

(6)

where \( \rho_{\text{air}} \) is the density of air.

2.4.2. Dynamic viscosity, kinematic viscosity, thermal conductivity, and Prandtl number

According to the literature [45,46], the dynamic viscosity \( \eta \) of a mixed gas can be determined by several methods such as those proposed by (i) Wilke, (ii) Graham, and (iii) Herning-Zipperer.

(i) Wilke’s method expresses dynamic viscosity using the following equation:

\[ \eta = \frac{\eta_{\text{Wilke}}}{\sum_{j=1}^{n} \frac{\eta_i / 100}{\sum_{j=1}^{n} \eta_j \phi_j}} \]  

(7)

where

\[ \phi_j = \frac{1 + (\eta / \eta_j)^{1/2}(M / M_j)^{1/4}}{8(1 + (M / M_j))^{3/2}} [-] \]  

(8)

If the component indices are exchanged:

\[ \phi_j = \frac{M_j}{M} \frac{\phi_j}{\phi_j} \]  

(9)

where indices “i” and “j” represent gas components.

Therefore, if the gaseous mixture in question has two components, the final expression involving components 1 and 2 would be:

Table 1
Summary of analytical methods used and apparatus.

<table>
<thead>
<tr>
<th>Objective</th>
<th>Method of analysis</th>
<th>Apparatus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification of gases</td>
<td>Gas chromatography–mass spectrometry (GC-MS)</td>
<td>Hewlett Packard system (GC: HP6890; CP-PoraBOND Q)</td>
</tr>
<tr>
<td>Quantification of products</td>
<td>GC-flame ionization detection (GF-FID)</td>
<td>GC-FID: GL Science, GC4000; column for gas: CP-PoraBOND Q</td>
</tr>
<tr>
<td></td>
<td>GC-thermal conductivity detection (GC-TCD)</td>
<td>GC-TCD: GL Science, GC323; column: molecular sieve, 30-60 mesh</td>
</tr>
<tr>
<td>Quantification of HCl</td>
<td>Ion chromatography (IC)</td>
<td>Quantified by peak area method using standard gas with known gas concentration. IC: Metrohm, 883 Basic IC plus; column: Metrosep A Supp4-250/4.0</td>
</tr>
</tbody>
</table>
\[ \eta_{(Wilk)} = \frac{\eta_1 \Omega_1}{100 + \varphi_{12} \Omega_2 / 100} + \frac{\eta_2 \Omega_2}{100 + \varphi_{21} \Omega_1 / 100} [\text{Pa s}], \]  
(10)

where

\[ \varphi_{12} = \frac{[1 + (\eta_1 / \eta_2)^{1/4} (M_2 / M_1)^{1/4}]^2}{8(1 + M_1 / M_2)^{1/2}} [-]. \]  
(11)

\[ \varphi_{21} = \frac{M_2 M_1}{M_1 M_2} \varphi_{12} [-]. \]  
(12)

As stated in the literature \[45\], the very high accuracy of this equation has been verified through experiments undertaken by several researchers.

(ii) Graham proposed a simple equation for dynamic viscosity:

\[ \eta_{(Graham)} = \frac{\sum_{i=1}^{n} \eta_i \Omega_i}{100} [\text{Pa s}], \]  
(13)

(iii) Herning-Zipperer’s equation for viscosity \( \eta_{(HZ)} \) is similar to Wilke’s equation, but \( \varphi_{ij} \) (Eq. (9)) in this case is approximated by the following equation:

\[ \varphi_{ij} = (M_j / M_i)^{1/2} = \varphi_{ji}^{-1} [-]. \]  
(14)

In our case, the results using these three methods were slightly different; therefore, the final viscosity of a pyrolysis gas was determined as the arithmetic mean of the above-mentioned three methods; i.e.,

\[ \eta_0 = \frac{\eta_{(Wilk)} + \eta_{(Graham)} + \eta_{(HZ)}}{3} [\text{Pa s}]. \]  
(15)

Kinematic viscosity is simply derived from the dynamic viscosity and the density of the gas:

\[ \nu = \frac{\eta_0}{\rho_0} [\text{m}^2 \text{s}^{-1}]. \]  
(16)

The thermal conductivity of a pyrolysis gas, \( \lambda_0 \), was determined based on the equation recommended by Brocaw \[47\]:

\[ \lambda_0 = \sum_{i=1}^{n} \lambda_i \Omega_i / 100 [\text{mW} \text{m}^{-1} \text{K}^{-1}]. \]  
(17)

The viscosities and thermal conductivities, \( \eta_i \) and \( \lambda_i \), of the \( i \)-th component of a pyrolysis gas, were adopted from well-known databases, namely InfoTherm (Wiley) \[48\], Air Liquide Gas Encyclopedia \[49\], and Dortmund Data Bank (DDB) \[50\].

Based on the above equations, expressions for thermal diffusivity, \( a_0 \), and the Prandtl number, \( Pe \), are easily derived:

\[ a_0 = \frac{\lambda_0}{\rho_0 \sqrt{\eta_0}} [\text{m}^2 \text{s}^{-1}], \]  
(18)

\[ Pe = \frac{\eta_0}{\lambda_0} [\text{].} \]  
(19)

3. Results and discussion

3.1. Volume and mass of the gas produced

During experiments, feed samples underwent thermal decomposition as the process temperature (500 °C) was higher than the thermal decomposition temperature (TDT) of the polymers studied; the average TDT values for PET, PP, PE, PS and PVC are 385, 361, 423, 257, and 349 °C, respectively \[51–53\]. The conversions of the input materials into gases strongly depend on the pyrolysis temperature; increases in the pyrolysis temperature always lead to greater volumetric gas yields \( (V_G) \), as observed in many studies \[54,55\]. The \( V_G \) (900 °C)/\( V_G \) (500 °C) ratio was 3.84 for PET, 11.95 for PP, 1.41 for PVC, 436.60 for PS, 9.23 for JP m., 5.43 for EU m., and 8.11 for US m. It is clear from these ratios that temperatures of 500 °C and 700 °C are insufficient for the pyrolysis of PS, which is ascribable to the presence of very stable benzene rings in the PS polymer matrix that are not easily decomposed into gases. Pyrolysis gases were only produced above 900 °C, although only in small volumes (Fig. 1(a)).

The biggest conversion was observed for the pyrolysis of PVC from which the volume of gas produced was, on average, 1.56 times greater than that of the remaining polymers (PS is not included in this comparison due to the negligible amounts of gas produced, as mentioned above). When compared to the other polymers, significant amounts of gas were produced from PVC, even at a process temperature of 500 °C; on average, PVC produced 6.27 times more gas than that produced from other materials/samples. With the exception of PVC and PS, the volumes of gas produced from the remaining samples were roughly the same at the same temperature.

Even the mass yield of the produced gas increased with increasing process temperature. The highest average mass yield was observed during the pyrolysis of PVC, for which an average of 285.98 mg of input mass (from an initial 500 mg sample) was transformed to gas, which is about 1.68 times more than that achieved for the other samples. The mass yields of gas produced from mixtures of plastics were very similar...
at the same temperatures. If we include the input materials into the comparison, as well as the process temperature, the most suitable combinations of materials and temperature for pyrolysis-gas production were PP, PE, and PVC, at a process temperature of 900 °C; 334.53, 325.10, and 303.94 mg of these samples were converted into gases, respectively.

Mass balance sheets, including gases, liquids, and solids, are summarized in Fig. C.1 (Appendix C). In this work, we focused on the gaseous fractions; therefore, liquid and solid fractions are not discussed. In addition, the effect of temperature on the distributions of pyrolysis products and the mechanisms of their formation are outside of the main purpose of this work, which aims to reveal the physical and fuel properties of the obtained gases.

### 3.2. Chemical energy accumulated in the pyrolysis gas

The total energy yield ($E_{Hi}$) of a pyrolysis gas can be expressed in terms of the amounts of the individual flammable components, $X_i$ (e.g., methane) and their gross calorific values, $f_i$; $E_{Hi} = \sum_{i=1}^{n} f_i \times X_i$ [kJ].

The most energy-yielding materials were PP and PE, for which the chemically accumulated energies for the gaseous products were, on average, 9.45 and 8.90 kJ, respectively (the average mass yields of these gases were 188 and 176 mg, respectively). If we compare these values with the energies obtained from the remaining materials, they are 5.7 and 5.4 times higher than those of the others. The specific heat, $c_p$, of PP is 1.92 kJ kg$^{-1}$ K$^{-1}$ (average of values given in literature [56–60]); if we simply assume that the thermal energy necessary to heat a material during pyrolysis is equal to $c_p$, this is a relatively undemanding amount of energy when compared to that required for other materials frequently subjected to pyrolysis (e.g., specific heat of biomass (pine) is 2.50 kJ kg$^{-1}$ K$^{-1}$ [61]). In this sense, PE is a less suitable material because its average $c_p$ is 2.22 kJ kg$^{-1}$ K$^{-1}$. The high $E_{Hi}$ values of the gases from PP and PE (when compared with the other gases) are ascribed to a combination of higher levels of hydrocarbons in the gases produced from these polymers, and the absence of incombustible components (e.g., CO$_2$); gas compositions are discussed in Section 3.3.

PP (900) and PE (900) were followed by US m. (900), JP m. (900), and EU m. (900) in terms of $E_{Hi}$ values (Fig. 2). Due to the negligible amount of gas generated from PS at 500 and 700 °C, this material was deemed to be least suitable in terms of chemical energy produced (average yield of 0.62 kJ). The $E_{Hi}$ yielded by PVC was also very low (average 1.12 kJ), which is due to high levels of incombustible HCl; during the pyrolysis of PVC, an average of 267.89 mg of the mass of this polymer is converted into HCl, which is found in the gas due to the presence of chlorine in the molecular structure of PVC ((C$_2$H$_3$Cl)$_n$; the Cl content in PVC is 57 wt%). HCl is a toxic substance that causes high-temperature corrosion in combustion equipment [62,63]; for this reason, all of the following “PVC” results are related to HCl-scrubbed gas.

Increasing the process temperature was shown to have a significant and positive impact on the amount of energy obtained, because the energy yielded at a process temperature of 900 °C was on average 9.95 times higher than that obtained at 500 °C (these averages do not include PS, as previously discussed).

### 3.3. Volumetric compositions of the pyrolysis gases

#### 3.3.1. Carbon monoxide (CO) content

CO is present only in gases generated from input materials that contain PET because its molecular structure contains oxygen. In the case of PET, the average CO content was 37.84% (v/v), and temperature had no significant impact on its concentration (Fig. 3). CO was also present in gases from mixed plastics and the impact of temperature was more significant in these cases: an increase in the temperature (500 → 700 → 900 °C) led to a decrease in the CO content: 36.44 → 16.00 → 11.74% because volume of gaseous $\Sigma$CO$H_Y$ and $H_2$ derived from PE and PP is increased with increasing temperature.

#### 3.3.2. $H_2$ content

The $H_2$ content varied greatly and in 75% of cases it increased with increasing temperature because pyrolysis at higher temperature promotes further splitting of hydrocarbons present in the gas. In the case of JP m. (500), EU m. (500), and US m. (500), the $H_2$ content was zero, as was observed for PS (500, 700). The gas with the highest $H_2$ content was produced by the pyrolysis of PVC, in which its average volume content was 53.59% across all temperatures, and rose to 67.87% at a process temperature of 900 °C. Similarly, PS (900) contained a large amount of $H_2$ (45.36%). The results are presented in Fig. 4.
3.3.3. Hydrocarbon (C$_x$H$_y$) content

Hydrocarbons (ΣC$_x$H$_y$) constitute the majority of most pyrolysis gases. The gases from both PP and PE had average hydrocarbon contents of about 87% (Fig. 5). In contrast, PET has a low ΣC$_x$H$_y$ content (an average value of 10.03%). For JP m., EU m., and US m., the average ΣC$_x$H$_y$ contents are 59.24%, 51.50%, and 62.20%, respectively. With respect to the impact of temperature on ΣC$_x$H$_y$, no direct dependence was observed across the entire temperature range. Except for PVC and EU m., the highest hydrocarbon contents were observed at 700 °C for the remaining samples; this observation requires further analysis. However, at higher temperatures, ΣC$_x$H$_y$ decreased, which is attributable to the promotion of further decomposition due to the increase in supplied thermal energy.

Furthermore, the fractions of alkanes and alkenes in the gases were also of interest. Except for PET (700, 900) and PVC (500, 700, 900), the remaining samples exhibited mainly alkenes + C$_5$H$_8$ (which are also included in the comparison for completeness). The highest ratios of (alkenes + C$_6$H$_{12}$):alkanes were obtained for PP (500) and PP (700), with values of 5.5 and 2.8, respectively (see Fig. 6). This is attributed to the high proportion of propylene (C$_3$H$_6$) and butylene (C$_4$H$_8$) in these gases (see Fig. 7). PVC produced gases with high levels of alkanes, with an average volumetric concentration of 34.99%. The highest alkane content (49.87%) was found in PVC (500), followed by PE (500) (36.07%), and PP (900) (33.78%). The impact of temperature on this trend was interesting. For about two-thirds of the tested materials (PET, PP, JP m., EU m., and US m.), the production of alkanes increased with increasing temperature. As for alkenes, their proportions from all materials decreased with increasing temperature to 700 °C, a result of their splitting into lower-density products (H$_2$).

Methane (CH$_4$) was the most prevalent hydrocarbon. In most cases (PET, PP, PE, JP m., EU m., and US m.), the production of CH$_4$ increased with rising process temperature. The highest volumetric content of CH$_4$ was observed in gases produced from PVC and PS, with average values of 25.86% and 31.50%, respectively. The contents of CH$_4$ in JP m., EU m., and US m. were almost identical at the same temperatures. The materials that produced the least amounts of CH$_4$ were PET, followed by EU m. In general, propane (C$_3$H$_8$) was found in small quantities, mostly in the gas from PE (500), at a concentration of 9.91%. The production of C$_3$H$_8$ decreased with increasing temperature.

In addition to CH$_4$, other relatively abundant hydrocarbons include ethylene (C$_2$H$_4$) and propylene (C$_3$H$_6$), whose average concentrations were 15.17% and 11.17%, respectively. The contents of C$_3$H$_6$ in PP (500) and PP (700) were almost identical with values of over 36% (v/v).
Fig. 7. Volumetric proportions of individual hydrocarbons in individual gases.
Butylene (C₄H₈) was mostly found in PS (500) (25.11%) and was also relatively abundant in PP (700) and PE (700), with contents of 16.44% and 10.76%, respectively. The concentration of butane (C₄H₁₀) in almost all cases was low or zero (at 900 °C). The exception was PE (500), which contained 8.90% C₄H₁₀. The pyrolysis of PP at 500 °C was exceptional in terms of C₅H₈ production, which was present in the gas produced at a concentration of 22.0%. Its levels in JP m. (500), EU m. (500), and US m. (500) are also worth noting; concentrations of 8.18%, 4.20%, and 6.49% were found, respectively, owing to the high PP content of these mixtures. C₅H₁₀ was most abundant in gases produced from PE, at an average content of 4.01%. C₅H₁₂ was generally always contained in small quantities that never exceeded 1% by volume (except for PE (700)). The highest hydrocarbon, C₆H₁₂, had the highest concentrations in PE (500) and PP (500), at 8.08% and 6.47%, respectively. It was also present in small volumes in gases produced from mixtures of plastics, with a total average value of approximately 1.3% (Fig. 7).

3.3.4. Carbon dioxide (CO₂) content
CO₂ was present only in gases obtained from PET (due to the oxygen present in its molecular structure (C₁₀H₈O₄)n) at an average concentration of 38.79%; the highest content of 49.79% was found in PET (500) (Fig. 8). As PET is a component of the mixtures investigated, CO₂ was also present in the gases produced from the mixtures; the highest values for these mixtures recorded at 500 °C were 25.60%, 30.89%, and 25.48% for JP m., EU m., and US m., respectively. At higher temperatures, the CO₂ content was substantially lower because volume of gaseous ΣCXHY and H₂ derived from PE and PP is increased with increasing temperature. In addition, well known Boudouard equilibrium (2CO ⇄ CO₂ + C) for producing CO is favorable at higher temperatures. The high concentration of CO₂ observed in the gas generated from EU m. can be explained by the fact that EU m. contains the highest amount of PET. CO₂ is an inert component and therefore reduces the energy quality of the gas. On the contrary, it increases the methane number, which is desirable.

3.4. Physical properties of the pyrolysis gases
This section focuses on the physical properties of the gases with respect to the input material and process temperature. All results are compared to those obtained for natural gas (NG (□)) and propane (○) denoted in Figs. 9–12. The composition of NG is shown in Table 2. All volume data were converted to their respective values at a temperature of 0 °C and a pressure of 101.325 kPa.
3.4.2. Specific heat and thermal conductivity

The specific heat \( (c_{p,c}) \) during the pyrolysis of an individual plastic always decreases with increasing temperature, while this dependence does not apply to co-pyrolysates. This is related to the proportion of carbon atoms in the gas, \( N_C \), which can be expressed in term of the volumes of the various carbon-components, \( \Omega_i \), and the number of carbon atoms in the molecular structure of a given component, \( N_i \): \( N_C = \sum_{i=1}^{\Omega_i} \Omega_i \times N_i \). (The final values of \( N_C \) are displayed in Table C.1 in Appendix C). The highest specific heat of 2.94 \( \text{kJ m}^{-3} \text{K}^{-1} \) was observed for PP (500). At the same time, this was the only pyrolysis gas with a specific heat higher than that of propane. High specific heat values were also found for PE (500), PP (700), PE (700), and PS (500), with values of 2.70, 2.48, 2.43, and 2.43 \( \text{kJ m}^{-3} \text{K}^{-1} \), respectively, owing to their high \( \text{C}_4 \text{C}_6 \text{hydrocarbon contents, whose average specific heat is about 2.8 times higher than of CH}_4 \). Except for PET (500, 700, 900), PVC (900), and PS (900), the values of specific heat were lower than that of NG. A graphical representation of these results is provided in Fig. 10(a).

The highest thermal conductivities \( (\lambda_C) \) were demonstrated by the pyrolysis gases produced from PVC, with an average value of 104.83 \( \text{mW m}^{-1} \text{K}^{-1} \), which is approximately 3.6 times higher than that of NG and 6.7 times higher than that of propane. Except for PP and PE, the value of thermal conductivity increased with rising process temperature, which corresponds to increasing levels of \( \text{H}_2 \), whose thermal conductivity is 172.6 \( \text{mW m}^{-1} \text{K}^{-1} \) [49]. The results are presented in Fig. 10(b).

3.4.3. Energy quality

In practice, the most important parameter of a fuel that determines its energy quality is its net calorific value and gross calorific value \( (\hat{H}_c) \), as they are indicators of chemical energy accumulated in a unit of matter or volume of a given fuel, respectively. Generally, pyrolysis gases are very valuable sources of fuel for use in gas-fired combustion equipment because their gross calorific values are often relatively high.

If we focus on the quantity of energy contained in a volume of \( 1 \text{ m}^3 \) (as is illustrated in Fig. 11(a)), PE, PP, and PS can be considered to be significant. For example, PE (500), PP (500), and PS (500) exhibited gross calorific values of 86.58, 81.09, and 78.89 \( \text{MJ m}^{-3} \), respectively, which is attributable to their relatively high contents of energy-rich higher alkanes and alkenes. As inert \( \text{CO}_2 \) is a dominant component of gases generated from PET, gases produced from it had the lowest gross calorific value (average \( 11.50 \text{ MJ m}^{-3} \)) and are referred to as “lean” or “low-heating” gases [66]; in terms of their energy content, they are comparable to generator or furnace gases. The gross calorific value of NG (40.52 \( \text{MJ m}^{-3} \)) was closest to that of PVC (500), US m. (500), and JP m. (500), which had values of 40.68, 40.23, and 38.70 \( \text{MJ m}^{-3} \), respectively. Therefore, these gases are considered to be substitutes for NG with regard to the thermal input for combustion equipment. Except for PET, the gross calorific value decreased with decreasing process temperature during the pyrolysates of individual plastics, while for co-pyrolysates, the order observed was: \( \hat{H}_{\text{PET}2000} < \hat{H}_{\text{PET700}} < \hat{H}_{\text{PET9000}} < \hat{H}_{\text{PET5000}} \).

Gross calorific values per kg are shown in Fig. 11(b). Some results are very satisfactory when compared to the data from NG and propane, particularly those obtained for PP, PE, PVC, and PS. The highest gross calorific values of 54.45, 58.01, and 66.55 \( \text{MJ kg}^{-1} \), which exceeded those of propane and NG, were observed for PVC (500, 700, 900), respectively. PET is a less-suitable material for conversion to gas because the produced gas had an average gross calorific value of only 8.57 \( \text{MJ kg}^{-1} \) (i.e., ~5.7 times less than that of NG or propane). The gross calorific value always increased with rising process temperature, corresponding to an increase in hydrogen content, which is energetically a very high quality gas per unit mass (e.g., \( \hat{H}_{\text{PET2000}} = 141.8 \text{ MJ kg}^{-1} \) according to the literature [41].)
Pursuant to the standards detailed in the literature [66], Table 3 summarizes the classifications of individual gases according to their gross calorific values. According to this standard, PET (500, 700, 900) are classified in the group of gases with “low gross calorific value,” while PP (500) and PE (500) are classified in the group of gases with “high gross calorific value.” The remainder of the gases correspond to the group with “very high gross calorific value.” For completeness, the same table also shows gases classified according to their flammabilities, including the signal word pursuant to the standards mentioned in the literature [67].

3.4.4. Viscosity, thermal diffusivity and Prandtl number

All gases had dynamic viscosities ($\eta$) higher than that of propane. In particular, PP (500) showed a dynamic viscosity of $5.47 \times 10^{-5}$ Pa s, ascribable to high concentrations of C$_6$H$_8$ and C$_6$H$_{10}$ (see above), which have dynamic viscosities of $2.95 \times 10^{-4}$ and $2.05 \times 10^{-4}$ Pa s, respectively [48]. High dynamic viscosities were also demonstrated by JP m. (500), US m. (500), PE (500), and EU m (500). If high dynamic viscosity is undesirable for some reason, a higher pyrolysis process temperature is recommended in order to produce gases that generally have lower dynamic viscosity values (lower C$_x$H$_y$ concentration). The highest kinematic viscosities ($\nu$) of $2.90 \times 10^{-3}$ m$^2$ s$^{-1}$ and $2.71 \times 10^{-5}$ were exhibited by PVC (900), due to its very low gas density (0.38 kg m$^{-3}$), and PP (500), due to its high dynamic viscosity, respectively. Compared to other gases, PVC (900) and PP (500) have the lowest Reynolds numbers ($Re_d$) at the burner mouth outlet (of specific diameter $d$), since $Re_d = (w_d d) / \eta$ (assuming that the gas outlet rate, $w_d$, is identical for all gases under examination). Increasing the process temperature led to a decline in the kinematic viscosities of all mixtures and PE; however, they increased for PET and PS. The viscosities of the gases produced from PP and PVC did not show a direct relationship with process temperature (Fig. 12(b)).

PVC gases reached the top value of thermal diffusivity ($6.71 \times 10^{-5}$ m$^2$ s$^{-1}$ on average), which may be explained by their high thermal conductivity (104.83 mW m$^{-1}$ K$^{-1}$ on average) and low density (0.580 kg m$^{-3}$ on average). The value of thermal diffusivity is inversely proportional to the Prandtl number ($Pr$) which is used to calculate convection heat transfer. Except for PE and PS gases, it held true that higher $Pr$ values were reached by gases produced at 500 °C. Among such gases, the highest $Pr$ was obtained in PP (500) (1.117) and JP m. (500) (1.086) as a partial consequence of their rather high kinematic viscosity. The values of natural gas, the $Pr$ of which is 0.700, were most closely approximated by PS (700), PE (700), and JP m. (700) with Pr 0.696, 0.717, and 0.724 respectively.

4. Conclusion

This article focuses on the thermal conversion of the most common waste plastics by pyrolysis and co-pyrolysis. The subjects of interest included the quantities of gases produced during these processes and their physical properties. The most significant conclusions are summarized as follows:

(i) The production of all pyrolysis gases were observed to increase rapidly with increasing temperature, as has been proposed in numerous publications. The highest conversion of input material to gas occurred during the pyrolysis of PVC (average gas yield of 57.10%). In contrast, the pyrolysis of PS provided a very low yield (2.14% on average). The production of pyrolysis gases from the

![Fig. 11. Gross calorific values of gases: (a) in m$^{-3}$ and (b) in kg.](image-url)
three evaluated plastic mixtures did not differ much at the same temperature.

(ii) Increases in the energy yield of the pyrolysis gases were observed with increasing temperature. The highest energy yield was obtained from the pyrolysis of PP.

(iii) With regards to safety, all gases produced at 500 and 700 °C were heavier than air, except for those produced from PVC and PS. If the required density of the gas is lower than that of air, we recommend the use of higher process temperatures, because gas density decreases with increasing temperature.

(iv) Energetically, the highest quality gases were obtained from the pyrolysis of PE and PP, for which the average gross calorific values were 75.43 and 74.45 MJ m$^{-3}$, respectively. Moreover, gases produced by the co-pyrolysis of plastic mixtures at 700 °C had a relatively high average gross calorific value of 58.75 MJ m$^{-3}$. The highest average gross calorific value per unit mass (59.54 MJ kg$^{-1}$) was observed for gases obtained from PVC. With respect to gas energy yields, the most suitable materials for pyrolysis were PP and PE when processed at 900 °C. Usually, the chemical energy in a pyrolysis gas increases substantially with increasing process temperature.

(v) Pyrolysis gases from PVC showed high thermal conductivities (104.83 mW m$^{-1}$ K$^{-1}$ on average) and low Prandtl numbers (0.331 on average), a consequence of the high proportion of hydrogen in these gases.

(vi) The gas produced from PET (500) is classified as an “extremely flammable gas.” All other gases fall into the “flammable gas” class.

Acknowledgement

This study was conducted within the framework of projects LO1404: Sustainable Development of the ENET Centre, and CZ.01.1.02/0.0/0.0/15_019/0004681 Pyrolysis Unit with Induction Heating.
Appendix A. Input materials

Table A.1
Contents of individual plastics in plastic mixtures.

<table>
<thead>
<tr>
<th>Component</th>
<th>Plastic Mixture [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>JP m.</td>
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<tr>
<td>PET</td>
<td>16.90</td>
</tr>
<tr>
<td>PP</td>
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</tr>
<tr>
<td>PE</td>
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</tr>
<tr>
<td>PVC</td>
<td>6.13</td>
</tr>
<tr>
<td>PS</td>
<td>21.56</td>
</tr>
</tbody>
</table>

Table A.2
Compositions of tested materials (our results) \[35\].

<table>
<thead>
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<th>Component</th>
<th>Input Material [wt%]</th>
</tr>
</thead>
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<td></td>
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</tr>
<tr>
<td>C</td>
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</tr>
<tr>
<td>H</td>
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<tr>
<td>O</td>
<td>33.69</td>
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<tr>
<td>Cl</td>
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</tbody>
</table>

\(^a\) Japanese mix.
\(^b\) European mix.
\(^c\) USA mix.

Appendix B. Experimental system

![Fig. B.1. Schematic diagram of the experimental system.](image-url)
Appendix C. Complementary results

![Mass fractions of gaseous, liquid, and solid (balance) products from pyrolysis of plastics](image)

<table>
<thead>
<tr>
<th>Input Material (Process Temperature °C)</th>
<th>Gas [%]</th>
<th>Liquid [%]</th>
<th>Solid (balance) [%]</th>
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<td>PET (500)</td>
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Fig. C.1. Mass fractions of gaseous, liquid, and solid (balance) products from pyrolysis of plastics.
Fig. C.2. Molar masses of individual gases.

<table>
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<tr>
<th>Input Material</th>
<th>Process Temperature [°C]</th>
<th>Compressibility Factor $z_0$ [-]</th>
<th>Specific Gas Constant $r_0$ [kJ kg$^{-1}$ K$^{-1}$]</th>
<th>Number of Carbon Atoms $N_C$ [-]</th>
<th>Net Calorific Value $\hat{N}_l$ [MJ m$^3$]</th>
<th>Net Calorific Value $\hat{N}_l$ [MJ kg$^{-1}$]</th>
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References


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