Fuel 221 (2018) 346–360

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

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

Stanislav Honus[a,b,*], Shogo Kumagai[c,*], Gabriel Fedorko[d], Vieroslav Molnár[d], Toshiaki Yoshioka[c]

[a] *VŠB – Technical University of Ostrava, Centre ENET, 17. listopadu 15, 708 33 Ostrava – Poruba, Czech Republic*
[b] *VŠB – Technical University of Ostrava, Faculty of Mechanical Engineering, Department of Energy Engineering, 17. listopadu 15, 708 33 Ostrava – Poruba, Czech Republic*
[c] *Tohoku University, Graduate School of Environmental Studies, 6-6-07 Aoba, Aramaki-aza, Aoba-ku, Sendai, Miyagi 980-8579, Japan*
[d] *Technical University of Košice, Letná 9, 042 00 Košice, Slovak Republic*

ARTICLE INFO

Keywords:
Natural gas
Physical properties
Polymers
Pyrolysis
Waste plastic

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_N^{-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_N^{-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 [1]; it produces materials that are useful in the power [2], chemical [3], and building industries [4], and agriculture [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 [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 [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 [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 [12], starting-material grain size [13], process temperature and pressure [14], heating rate [15], and the catalytic properties of the substances present [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_xH_y (maximum C_6) and hydrogen (H_2); in some cases, they also contains carbon dioxide (CO_2) and carbon monoxide (CO), and potentially hydrogen chloride (HCl) [17–23]. Owing to the above-mentioned

---

* Corresponding authors at: VŠB – Technical University of Ostrava, Centre ENET, 17. listopadu 15, 708 33 Ostrava – Poruba, Czech Republic. Tel.: +420 597 323 270 (S. Honus). Tohoku University, 6-6-07 Aoba, Aramaki-aza, Aoba-ku, Sendai, Miyagi 980-8579, Japan. Tel.: +81 22 795 7212 (S. Kumagai).
E-mail addresses: stanislav.honus@vsb.cz (S. Honus), kumagai@env.che.tohoku.ac.jp (S. Kumagai).

https://doi.org/10.1016/j.fuel.2018.02.074
Received 4 September 2017; Received in revised form 26 January 2018; Accepted 8 February 2018
0016-2361/

Nomenclature

a	thermal diffusivity $[m^2\ s^{-1}]$
c_p	Specific heat capacity $[kJ\ kg^{-1}\ K^{-1}]$
d	relative density $[-]$
$E_{\hat{H}_S}$	yield of total energy contained in a pyrolysis gas $[J]$
$\hat{H}_I$	lower calorific value $[kJ\ m_N^{-3}]$
$\hat{H}_S$	gross calorific value $[kJ\ m_N^{-3}]$
M	molar mass $[g\ mol^{-1}]$
N	specific number of carbon atoms in a pyrolysis gas $[-]$
n	number of carbon atoms in a molecule $[-]$
Re	Reynolds number $[-]$
TDT	thermal decomposition temperature $[°C]$
V	yield of a pyrolysis gas $[l,g]$
X	amount of individual flammable component $[kg]$
z	compressibility factor $[-]$
$\sqrt{b_i}$	sum factor $[-]$

Greek symbols

Ω	volumetric fraction of the i-th component in a pyrolysis gas [%]
η	dynamic viscosity $[Pa\ s]$
λ	thermal conductivity $[W\ m^{-1}\ K^{-1}]$
ν	kinematic viscosity $[m^2\ s^{-1}]$
ρ	density$[kg\ m_N^{-3}]$

Subscripts

G	pyrolysis gas
i	i-th component
N	normal cubic meter (e.g.: m_N^{-3})

Abbreviations

EU m.	European mix
HDPE	high-density polyethylene
JP m.	Japanese mix
LDPE	low-density polyethylene
NG	natural gas
PE	polyethylene
PET	poly(ethylene terephthalate)
PP	polypropylene
PS	polystyrene
PVC	poly(vinyl chloride)
TG-FTIR	thermogravimetry coupled with Fourier transform infrared spectroscopy
US m.	USA mix

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-cm^3 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., H_2, methane (CH_4), CO, CO_2, and C_2H_y) 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 H_2 and CO over time; temperatures in the 600–1000 °C range were considered (in increments of 100 °C). Bičáková 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.