

報告番号	甲 第 12804 号
------	-------------

主 論 文 の 要 旨

論文題目 **Study on behaviors and reaction mechanisms of steam gasification for wasted plastics**
(廃プラスチックの水蒸気ガス化挙動と反応機構解明に関する研究)

氏 名 **NEDJALKOV Ivan Jordanov**

論 文 内 容 の 要 旨

Plastic waste is problem that both developing and developed countries are facing where Incineration and landfill are still widely used. Gasification of plastic waste for energy recovery is a sustainable alternative. Previous studies have concentrated on mixed streams and mostly on the gaseous products of gasification.

The purpose of this study is to investigate the products of steam gasification, namely gas, tar and soot, as well as to identify the underlying reaction mechanisms for each of the investigated polymers. Ideally the results of this study can be applied in the industry to design and manufacture equipment that can recover energy from wasted polymers, replacing incineration and landfill, and leading to an increase of energy efficiency and reduction of GHG.

Three different polymers have been investigated in this study: Acrylonitrile Butadiene Styrene (ABS), Polyethylene (PE) and Polycarbonate (PC)

Various safety equipment (helmets, goggles, etc.) are made from ABS and PC. Manufacturing losses as well as discarded products can constitute a significant amount of those polymers. Unfortunately the addition of coloring and performance enhancing additives renders many polymers unsuitable for material recycling. This is why energy recovery is the most viable option. However there has been very little in the literature concerning steam gasification of either ABS or PC. For that reason those two materials

are of a special interest to this study. PE on the other hand, is one of the most common polymers with the second highest concentration among plastic wastes. It is also the topic of many scientific studies on various types of gasification and pyrolysis. By comparing the results for PE from this study with those from other researchers, the validity and accuracy of the other results (ABS & PC) can also be quantified.

First a non-isothermal thermogravimetric analysis (TGA) of ABS, PC and PE was performed. The respective moisture, volatile matter (VM), fixed carbon (FC) and ash contents were estimated. The polymers were found to contain no detectable moisture. In addition, utilizing the same data and the Coats-Redfern method, the kinetic parameters of each polymer were also approximated. PE had the fastest decomposition rate (38.45 %/min). ABS became volatalized at lowest temperature (310 °C). ABS and PC consisted of more than 99% volatile matter, and PC contained 23% fixed carbon and 1.5% ash. PE has the highest activation energy (176 kJ/mol) and frequency factor ($4.83 \times 10^{16} \text{s}^{-1}$).

A batch furnace has been used for investigating the gas, tar and soot production as a function of temperature, steam concentration and residence time (Fig.1). The effect of several parameters were investigated: temperature: 600 - 1000 °C, steam concentration and residence time: (25 and 15 seconds)

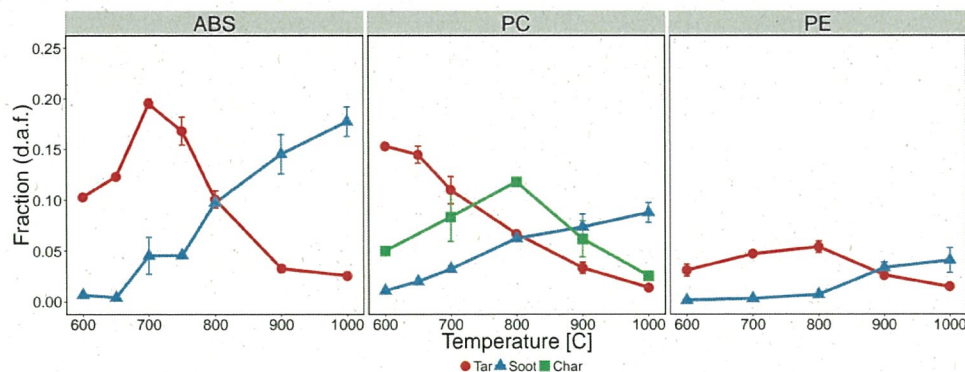


Figure 1: Tar, soot and char production of ABS, PC and PE during batch furnace pyrolysis

Gas chromatography was utilized during gasification and pyrolysis at residence time (RT) of 15s. The main gaseous species that were identified were H_2 , CH_4 , CO , CO_2 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 and C_4H_{10} (Fig.2). With the exception of methane, all other hydrocarbons were grouped based on their carbon number (C_2 , C_3 and C_4). In addition to the volumetric concentration of gaseous species, the result were used in determining the LHV and carbon balance for each experiment condition. In was concluded that the

increase of temperature leads to higher hydrogen yield and lower hydrocarbon yield, due to thermal cracking and carbon formation reactions. Steam addition and temperature increase decrease the total carbon content in the gas phase, leading to lower LHV values, despite the increase of hydrogen content. The addition of steam, increases hydrogen production via the water-gas shift, steam reforming and reverse methanation reactions.

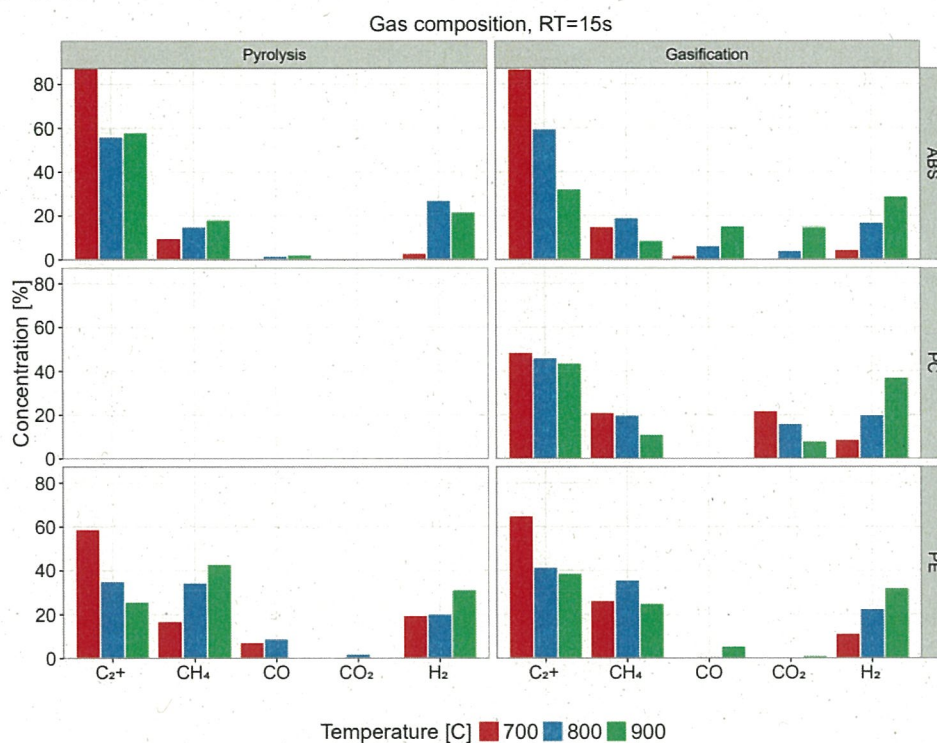


Figure 2: Gas composition of ABS, PC and PE during pyrolysis and gasification

APCI-TOF-MS analysis was performed on ABS, PC and PE tars, collected during batch experiments. The resulting data was used to show the relationship between reaction temperature,

residence time, pyrolysis/gasification and the chemical composition of tar. Combined with the tar and soot yield data, the governing chemical kinetics were identified.

For ABS it was found out that: higher temperature increases the concentration of heavy PAHs, leading to higher soot concentration; Steam addition counteracts that, by the steam reforming and water-gas reactions, lowering soot precursors and subsequently soot; Longer residence time favors soot reforming over soot generation; Longer residence time does not change the tar species during gasification.

For PE it was found out that higher temperature increases the concentration of heavy PAHs; Steam addition reduces the amount of heavy PAHs and soot precursors; PE tar

on average has heavier PAHs than ABS and PC, but the overall yield is lower. Lighter PAHs are converted to gaseous species.

For PC it was found out that: nitrogen and oxygen increase the total amount of tar species;

Higher temperature significantly favors a few species; Steam addition has a limited effect for decreasing heavy PAHs

A series of kinetic simulations were performed on modeled polymers. The models for ABS and PE were based on existing data from the literature, and that of PC designed on the basis of a depolymerization model. The depolymerization model was based on random scission into predetermined species. The calculation was performed using a Monte Carlo simulation.

The polymer models were then used as initial conditions for the kinetic simulations. The results of those simulations were analyzed based and compared with the experimental data from the gas chromatography analysis.

The kinetic models were limited only to light hydrocarbons and some heavier PAHs, providing valuable insight into the mechanisms of syngas and tar generation. The conclusions made in the previous experiments were combined with those from the simulation, to produce a detailed decomposition mechanism for steam gasification for each of the three polymers - ABS, PC and PE. (Fig.3)

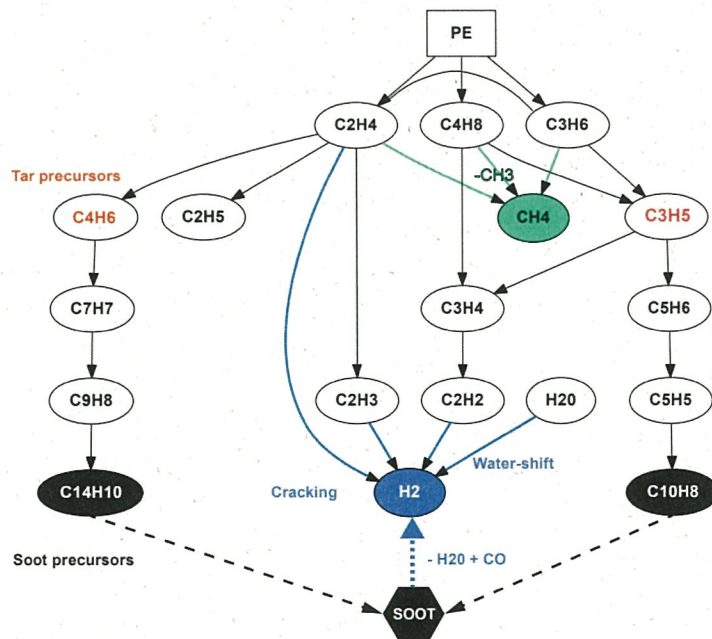


Figure 3: General kinetic model for PE steam gasification

For ABS it was concluded that: Styrene is the major source of tar and soot; Benzene and phenyl are the two major tar precursors; Hydrogen is produced from benzene and soot cracking; At higher temperatures a significant amount of hydrogen is contributed by the oxidizer (steam); Higher temperatures favor soot formation, but the effect is countered to some extent by steam.

For PE it was concluded that: Methane is produced rapidly at the beginning of the reaction, mostly from the polymer and to much lesser extent via the methanation reaction; Butadiene (C_4H_6) and allyl (C_3H_5) are the two most common tar precursors; Hydrogen is produced from exclusively from C_2H_m and soot cracking; At higher temperatures a significant amount of hydrogen is contributed by the oxidizer (steam); Higher temperatures favor soot formation, but the effect is countered to some extent by steam.

For PC it was concluded that: Benzyl (C_7H_7) and cyclopentadienyl (C_5H_5) are the two most common tar precursors; Methanation reaction and methyl radicals are the most common source of methane; Hydrogen is produced from toluene, acetylene (C_2H_2) and ethylene (C_2H_4), as well as tar cracking; Higher temperatures favor soot formation, but the effect is countered to some extent by steam.