OIL PRODUCTION BY FAST PYROLYSIS OF CELLULOSE/POLYETHYLENE MIXTURES IN METAL CHLORIDE PRESENCE

A. Solak, P. Rutkowski*

Wroclaw University of Technology, Faculty of Chemistry, Departament of Polymer and Carbonaceous Materials, Gdanska 7/9, 50-344 Wroclaw, Poland
e-mail: piotr.rutkowski@pwr.wroc.pl

Abstract

Cellulose/polyethylene mixture (3:1 w/w) and Tetra Pak waste with and without metal chloride ($ZnCl_2$, $AlCl_3$, $FeCl_3$) addition were subjected to a fast pyrolysis process at 500°C and heating rate 100°C/s to evaluate the possibility of liquid product formation with high yield. The addition of zinc, aluminum and iron chlorides has influenced the range of samples decomposition as well as the chemical composition of resulted pyrolytic oils. It was found that a formation of levoglucosan, main product of cellulose thermal decomposition, and phenol and its derivatives decreased in a presence of metal chlorides. Contrarily, levoglucosenone was produced with higher yield. Fast pyrolysis of polyethylene leads to the formation of solid long chain hydrocarbons, whereas the addition of metal chlorides promotes the formation of smaller molecules. More hydrocarbon liquid product can be ontained.

Keywords: *pyrolytic oil, GC-MS, cellulose, polyethylene, Tetra Pak waste*

1. Introduction

In view of co-existence of cellulose and polyolefins in packages and other organic solid wastes, their thermochemical co-conversion seems to be an attractive way of use and utilization.

As it has been described in some papers, the co-pyrolysis process could have a potential for the environmentally friendly transformation of lignocellulosic materials and plastic waste to valuable products [1-7].

Waste plastics can be converted to the fuel oil by non-catalytic or catalytic thermal processes. There were many reports on the hydrocarbon polymers degradation processes that led to the formation of liquid fraction [7-9].

The aim of this preliminary study was to evaluate the possibility of catalytic fast pyrolysis application as a method of thermochemical recycling of organic solid wastes.

2. Materials and Methods

Waste Tetra Pak (TP), commercial cellulose (Cellulose powder, Aldrich) and powdered polyethylene (PE) were selected for this study. Cellulose/polyethylene (CPE) mixture in a 75:25 (w/w) ratio was prepared in a blender from powdered samples. Both samples (TP and CPE) were also mixed with 10 wt% metal chloride ($ZnCl_2$, $AlCl_3$, $FeCl_3$) before pyrolysis.

Tetra Pak or CPE mixture were heated up to 500 °C with heating rate of 100°C/s under nitrogen atmosphere. The processes were repeated under the same conditions for all samples mixed with 10 wt% of anhydrous zinc chloride (p.a.), 10 wt% of aluminum chloride (p.a.) and10 wt% of iron(III) chloride (p.a.).

Pyrolytic oils were analyzed by GC-MS with a HP-1701 capillary column. Mass spectrometer was set at an ionizing voltage of 70 eV with mass range m/z 15-450.

3. Results and Discussion

Fast pyrolysis process of cellulose/polyethylene mixture leads to the liquids formation with high yield. A char and gaseous products are formed with a minor contribution.

Pyrolytic oils obtained from CPE mixture and Tetra Pak are composed of three well separated phases, i.e. water, brown organic liquid and yellow wax. The metal chloride additives, i.e. $ZnCl_2$, $AlCl_3$, $FeCl_3$ lead to the increased formation of organic liquids instead of waxy product.

The chemical composition of resultant pyrolytic oils clearly depends on the starting material composition and on the presence of metal chloride during the fast pyrolysis process as can be seen in Figure 1 and in Table 1. Different compounds, i.e. levoglucosan (LG), levoglucosenone (LGon) a highly dehydrated sugar, dianhydro-α-gluco-pyranose (αGP), phenol, phenol derivatives and hydrocarbons (alkanes, alkenes, alkynes) were identified in analyzed oils. Hydrocarbons were divided into two groups, i.e. liquid (HC_{liq}) and solid (HC_{solid}). It was found that the addition of metal chlorides significantly decreases the formation of levoglucosan.

Contrarily, the increased formation of levoglucosenone and dianhydro-α-gluco-pyranose was observed when catalytic pyrolysis was conducted. The addition of metal chlorides enhanced the degradation of polyethylene into a liquid product.

There are clear differences in the pyrolytic degradation of both materials, i.e. CPE mixture and Tetra Pak, which must be related to the differences in their composition. Lower proportion of levoglucosan and higher proportion of phenols were observed for Tetra Pak.

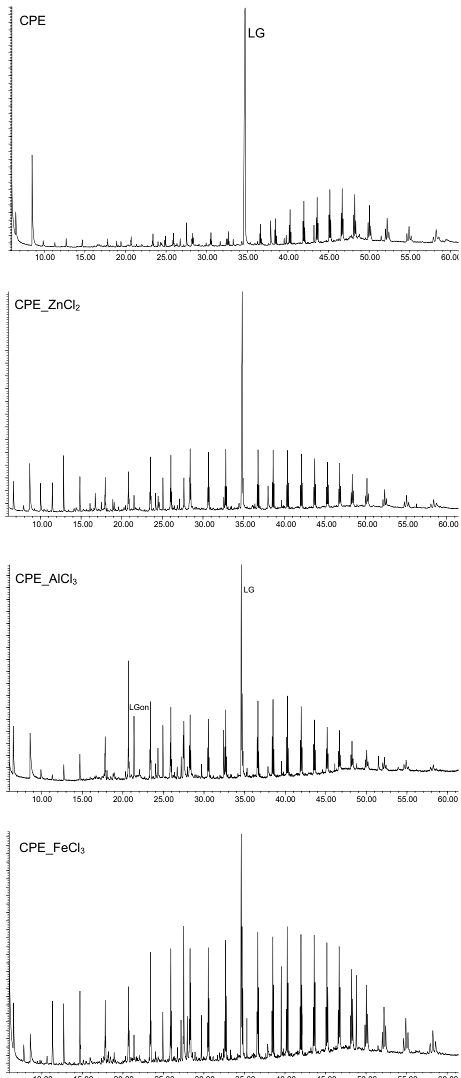

Fig. 1. GC-MS analyses of pyrolytic oils.

4. Conclusions

Fast pyrolysis of cellulose/polyethylene mixture and Tetra Pak with and without catalyst was performed to determine the influence of metal chloride on the chemical composition of liquid products. The use of $ZnCl_2$, $AlCl_3$ or $FeCl_3$ caused a significant decrease of levoglucosan formation and an increased degradation of polyethylene to liquid hydrocarbons.

These preliminary results showed that Tetra Pak or organic wastes containing cellulose and polyolefins can be a useful recycling resources. The fast pyrolysis of beverage package waste seems to be an alternative route of such material recycling.

Table 1. Distribution of different classes of compounds in pyrolytic oils obtained from CPE mixture and Tetra Pak (abbreviations are given in text)

sample	LG	LGon	αGP	HC_{liq}	HC_{solid}
CPE	31.7	0.1	0.5	7.8	49.7
CPE_$ZnCl_2$	16.2	0.2	1.3	26.2	47.8
CPE_$AlCl_3$	10.2	3.1	2.4	28.2	45.1
CPE_$FeCl_3$	5.5	0.7	1.2	24.2	58.2
TP	13.7	1.3	0.5	14.0	65.2
TP_$ZnCl_2$	1.0	1.0	-	28.6	59.0
TP_$AlCl_3$	1.4	0.6	-	27.1	59.8
TP_$FeCl_3$	1.0	0.4	-	34.3	55.4

References

[1] E. Jakab, G. Varhegyi, O. Faix, O. Thermal decomposition of polypropylene in the presence of wood-derived materials. J. Anal. Appl. Pyrol. 56 (2000) 273–285.

[2] E. Jakab, M. Blazso, O. Faix. Thermal decomposition of mixtures of vinyl polymers and lignocellulosic materials. *J. Anal. Appl. Pyrol.* 58-59 (2001) 49–62.

[3] V.I. Sharypov, N. Marin, N.G. Beregovtsova, S.V. Baryshnikov, N. Kuznetsov, V.L. Cebolla, J.V. Weber, Co-pyrolysis of wood biomass and synthetic polymer mixtures. Part I influence of experimental conditions on the evolution of solids; liquids and gases. *J. Anal. Appl. Pyrol.* 64 (2002) 15–28.

[4] N. Marin, S. Collura, V.I. Sharypov, N.G. Beregovtsova, S.V. Baryshnikov, B.N. Kuznetsov, J.V. Weber. Copyrolysis of wood biomass and synthetic polymer mixtures. Part II characterization of liquid phases. *J. Anal. Appl. Pyrol.* 65 (2002) 41–55.

[5] A. Aboulkas, K. El Harfi, A. El Bouadili. Non-isothermal kinetic studies on co-processing of olive residue and polypropylene. *Energ. Convers. Manage.* 49 (2008) 3666–3671.

[6] P. Rutkowski, P and A. Kubacki. Influence of polystyrene addition to cellulose on chemical structure and properties of bio-oil obtained during pyrolysis. *Energ. Convers. Manage.* 47 (2006) 716–731.

[7] A. Demirbas. Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons. *J. Anal. Appl. Pyrol*. 72 (2004) 97–102.

[8] N. Kiran, E. Ekinci, C.E. Snape. Recycling of plastic wastes via pyrolysis. *Resour. Conserv. Recy.* 29 (2000) 273-283

[9] F. Pinto, P. Costa, I. Gulzurtlu, I. Cabrita. Pyrolysis of plastic wastes. 1. Effect of plastic waste composition on product yield. *J. Anal. Appl. Pyrol*. 51 (1999) 39-55.

Acknowledgement

The State Committee for Scientific Research in Poland supported this work. Project No. N209146036.