PYROLYSIS OF TETRA PACK PACKAGING

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(1) Introduction

Aseptic packages along with milk and juice cartons are recycled through hydropulping process that separates the thin layers of plastic and Al from cellulose fibers. However humidity and impurities affect products' quality. Wu and Chang studied the kinetic of thermal decomposition of Tetra Pack by using TGA and found that the total reaction rate was a summation of individual behavior of LDPE and Kraft paper.[1] In this work the pyrolysis of Tetra Pack packaging in various conditions has been investigated as an alternative treatment.

(2) Experimental and analytical sections

Tetra Pack samples were collected from waste. The composition was of 63 wt% paper cardboard (Kraft cellulose), 30 wt% PE and 7 wt% Al. TG/DTA analysis of different layers separated from Tetra Pack was performed in N_2 atmosphere and heating rate of 10 °C/min to find decomposition temperatures and possible interactions between components. Pyrolysis was carried out by semi-batch operation in N_2 atmosphere.The reactor was heated with 5 ºC/min up to the desired temperature of 400, 500 or 600 °C at which it was held for 1 hour. Stepwise pyrolysis was performed by maintaining the reactor at 350 °C for one hour then heating it up to 500 °C for another one hour. The volatile products were swept from the reactor by N_2 gas to collection traps cooled in water-ice bath. The condensed aqueous and organic phase (wax + tarry compounds) were separated by centrifugation. Solid residue consisted of coke and aluminum that were separated by sinking in water. Pyrolysis products were characterized by chromatographic and spectroscopic methods described elsewhere.[2]

(3) Results and Discussion

TG showed that cardboard layers have a main degradation step at 200 – 400 °C, at lower temperature than PE layer that degrades at 380 – 515 °C; however there is a small overlapping region (380 – 400 °C) of the two temperature ranges. DTG curve of cardboard shows a long tail in the temperature range of PE degradation. Therefore some interactions could occur between PE and cardboard (especially its residue from the main degradation step). Above 105 °C the DTG curve of Tetra Pack shows two degradation steps at 200 - 500 °C, the first one for decomposition of cardboard layers and the second one for decomposition of polyethylene. It seems that aluminum had no effect on decomposition of these components.

Wax yield in semi-batch pyrolysis of Tetra Pack sharply increased and the amount of char decreased with increasing temperature up to 500 °C but no considerable change in product yield was observed with further increase of temperature at 600 °C (Table 1). Stepwise pyrolysis showed clear separation of aqueous phase, tar and most part of gases resulted from degradation of cardboard in the first pyrolysis step (at 350 °C) while PE wax was collected from the second pyrolysis step. The total yield of products from stepwise pyrolysis was close to that from semi-batch pyrolysis at 500 °C but both were slightly different from the theoretical one calculated based on product yield from degradation of Tetra Pack components. Therefore small interactions occur mainly during degradation of PE layer and the second step of cardboard degradation leading to less wax, char and tar and more aqueous phase.

Table 1. Influence of process parameters on the pyrolysis yields (wt%) of Tetra Pack waste

	cardboard	PE	Th. mix.*	Tetra Pack semi-batch			Tetra Pack stepwise		
	500 °C	500 °C	500 °C	400 °C	500 °C	600 °C	step I 350°C	step II 500°C	total
Gas	29.9	18.4	24.4	23.9	23.3	23.9	19.9	2.3	22.2
Aqueous phase	39.4	-	24.8	32.6	31.8	29.6	32.8	-	32.8
Tar	3.1	-	1.9	2.0	1.5	0.7	1.1	-	1.1
Wax	-	73.1	21.9	4.8	17.9	20.4	-	18.7	18.7
Char	27.6	8.5	20.2	29.7	18.6	18.4	46.2**	18.4	18.4
Al foil				7.0	6.9	7.0		6.8	6.8

* Theoretical mixture as in Tetra Pack: cardboard 63%, PE 30%; ** decomposed in step II of pyrolysis

The gas composition from the stepwise pyrolysis of Tetra Pack is given in Table 2. The gas products from the first pyrolysis step at low temperature of 350 °C consisted largely of CO_x compounds, main gaseous products from degradation of cellulose. In the second step at 500 °C, which corresponds to PE degradation, the major gaseous products were H_2, C_1, C_2 and C_3 hydrocarbons. However the presence of CO and CO_2 gases in this step is a proof of degradation of cardboard residue resulted in the first pyrolysis step. As most part of gaseous products was formed in the first pyrolysis step and contains a high content of

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carbon oxides, it can be said that the obtained gases from Tetra Pack pyrolysis did not have a high calorific value. However they could provide some part of the energy requirements for a pyrolysis plant.

Table 2. Composition of the gas products (mol %) from the stepwise pyrolysis of Tetra Pack

Pyrolysis step	CO	CO_2	H_2	C_1	C_2	C_3	C_4	C_5	C_6
Step I – 350 °C	34.79	52.70	5.86	2.60	1.60	1.16	0.78	0.27	0.24
Step II – 500 °C	4.87	2.12	32.08	28.02	15.00	9.45	5.62	2.86	0.01

Wax quality depends on pyrolysis conditions and purity. Its average molecular weight and molecular weight distribution increases with pyrolysis temperature and after purification – Table 3. The most polydisperse waxes were obtained at 600^{o}C and by stepwise procedure.

Table 3. Average molecular weight and polydispersity index of the pyrolysis waxes

	Mw	Mn	Polydispersity index
Semi-batch, 400 °C	403	356	1.134
Semi-batch, 500 °C	443	378	1.172
Semi-batch, 500 °C (washed with acetone)	520	436	1.193
Semi-batch, 600 °C	844	663	1.273
Stepwise	847	676	1.253
Polyethylene, semi-batch, 500 °C	531	458	1.159

(4) Conclusions

Pyrolysis of Tetra Pack wastes was performed studying the effect of pyrolysis temperature and procedure on the yields of products. Gas and liquid products (aqueous phase and tar) from degradation of cellulose as well as polyethylene wax were obtained. The aluminum was quantitatively recovered by separation from carbon residue in char.

(5) References

1. C.H. Wu, H.S. Chang, “Pyrolysis of tetra pack in municipal solid waste”, J. Chem. Technol. Biotechnol. 76 (2001) 779-792.
2. C. Vasile, M. A. Brebu, M. Totolin, J. Yanik, T. Karayildirim, H. Darie, “Feedstock Recycling from the Printed Circuit Boards of Used Computers”, *Energy & Fuels 22 (2008)* 1658–1665.

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