Oil Shale, 2008, Vol. 25, No. 2, pp. 203–208
doi: 10.3176/oil.2008.2.02 ISSN 0208-189X

THERMAL PROCESSING OF POLYVINYLCHLORIDE WASTE WITH OIL SHALE ASH TO CAPTURE CHLORIDE

V. OJA[*], A. ELENURM, I. ROHTLA, E. TEARO, E. TALI

Department of Chemical Engineering
Tallinn University of Technology
5 Ehitajate Rd., 19086 Tallinn, Estonia

This study is concerned with thermal processing of polyvinylchloride (PVC) in the presence of alkaline oil shale ash. Solid heat carrier (Galoter process)-type oil shale retorting units, where the feedstock is heated by mixing with ash from retorted feed-stock combustion, are potentially an alternative for polyvinylchloride waste recycling. A bench-scale experimental study was performed to investigate the fate of chlorine in co-pyrolysis of kukersite oil shale ash and PVC waste. Experiments were conducted by applying two sequential laboratory-scale batch processes: pyrolysis of PVC waste (70% PVC) with oil shale ash in a Fischer retort (standard method) followed by solid residue combustion in a muffle furnace.

Introduction

Improving recycling and disposal methods of polyvinylchloride (PVC) waste to produce energy, fuel or raw material for petrochemical industry is of increasing interest as the PVC waste stream is expected to grow considerably in the foreseeable future [1]. High chlorine content of this comparatively widespread plastic is a potential environmental problem, and its environmental impact should be minimized in the recycling process. Thermochemical conversion by pyrolysis, for example *via* stepwise pyrolysis, catalytic pyrolysis or co-pyrolysis including fuels such as coal, wood, petroleum residue or oil shale [2–8] is one class of possible recycling alternatives to recover the potential energy present in PVC waste streams. The distribution and fate of chlorine in the thermal processing of the PVC can be altered to more favorable endpoints with the additional presence of different catalytic and chemisorbing substances such as metal oxides or carbonate-rich materials [9–11]. The interest of this work is utilization of

[*] Corresponding author: e-mail *vahur.oja@ttu.ee*

alkaline oil shale ash in the PVC pyrolysis process, as the presence of alkaline agents in the reaction mixture can facilitate the transfer of chlorine from the decomposing feedstock to the solid residue [12, 13]. This phenomenon in principle should favor PVC waste recycling *via* co-pyrolysis with carbonate-rich oil shales in solid heat carrier type industrial retorting units, where the feedstock is heated by mixing with ash from retorted feedstock combustion. There are many carbonate-rich oil shale deposits in the world resulting ash with considerable alkaline content, for example kukersite oil shale from Estonia [14, 15], El-Lajjun oil shale from Jordan [16] and Green River oil shale from USA [17].

This study was designed to investigate the potential for alkaline oil shale ash to capture chloride from PVC waste and oil shale co-pyrolysis as it can occur in the Galoter type retorting process. To simplify the study, the process was distributed into two sequential bench-scale steps: pyrolysis of PVC waste (70% PVC and 30% plasticizer) with oil shale ash in a Fischer retort followed by solid residue combustion in a muffle furnace. The effect of oil shale and therefore oil shale based carbonates on chloride emission is out of scope of this preliminary study.

Apparatus and materials

The plasticized PVC waste sample under study consisted of 70% PVC by weight and had chlorine content of 39.78% and ash residue 0.35%. Chlorine in this study is determined by standard methods [18].

The kukersite oil shale ash was produced by incinerating the oil shale with air for one hour in a muffle furnace at 900 °C. Ash characteristics were as follows: chlorine content 0.16% and oxide content 99.67% (silicon dioxide, SiO_2 23.68%; aluminium oxide, Al_2O_3 5.79%; ferric oxide, Fe_2O_3 3.75%; calcium oxide, CaO 49.25%; magnesium oxide, MgO 8.43%; sodium oxide, Na_2O 0.87%; titanium oxide, TiO_2 0.28%; potassium oxide, K_2O 3.27%; sulphur trioxide, SO_3 4.35%).

PVC waste and kukersite oil shale ash co-pyrolysis experiments were carried out using a standard Fischer retort-based method [19]. The solid residues of the co-pyrolysis were divided into three parts and combusted in a muffle furnace for one hour at different temperatures: 800, 830 and 860 °C.

Experimental

In the first step, the effect of alkaline ash on PVC pyrolysis was investigated by comparing retorting products and yields from PVC waste and PVC waste / ash mixture (29.9% PVC waste and 70.1% ash by weight) pyrolysis using the standard Fischer retort method. Tables 1 to 3 summarize the results.

Table 1. **Mass distribution of pyrolysis products, wt %**

Pyrolysis product	PVC waste	Mixture of PVC waste and oil shale ash	
		total mixture basis	PVC waste basis
Pyrolysis oil	37.64	8.34	27.86
Solid residue	8.69	82.93	42.99
Pyrogenous water	2.09	4.31	14.40
Gas (by difference)	51.58	4.42	14.75

Table 2. **Characterization of pyrolysis oils and residues**

Characteristic	PVC waste	Mixture of PVC waste and oil shale ash
Cl content of residue, wt % *	2.35	13.33
Cl content of oil, wt %	4.93	2.80
Density of oil, g/cm3	1.0050	0.9220
Iodine number of oil, g I_2 per 100 g oil	19.3	46.3

* note that co-pyrolysis with ash produces 5 times more solid residue per PVC waste mass unit.

Table 3. **Distribution of chlorine in the pyrolysis products**

Pyrolysis product	Weight percent of chlorine in:	
	PVC waste	Mixture of PVC waste and oil shale ash
Pyrolysis oil	4.66	1.81
Solid residue	0.51	85.58
Gas and pyrolysis water (by difference)	94.83	12.61

Table 1 shows that the alkaline ash affects PVC waste pyrolysis by reducing the amount of oil produced (by 9.8% relative to the PVC waste or about 1.4 times), increasing the solid residue (by 34.3% or about 5 times), increasing the amount of pyrogenous water (by 12.3% or about 6.9 times) and decreasing the amount of gas produced (by 36.8% or about 3.5 times).

Table 2 presents comparative chlorine content of solid residues and oils. In addition oil densities and iodine numbers are shown as a rough measure of quality of oils.

The oil produced in the presence of ash is less dense, has higher iodine number, and contains less chlorine than the oil produced from PVC waste sample alone. The chlorine content of the solid residue is increased significantly. The effect of oil shale ash on decreasing the chlorine content of the oil could be limited based on the PVC/ash ratio shown above. The chlorine in oil was reduced only from 4.93% to 2.80%.

Using the above results one can track the fate of chlorine during PVC pyrolysis and co-pyrolysis with ash. Table 3 summarizes the chlorine distribution among the pyrolysis products for both PVC waste and mixture pyrolysis.

In the industrial Galoter process [20], the retorting or the thermal low–temperature decomposition of the feed-stock is performed *via* continuous mixing of feed-stock and solid heat carrier (combusted retorting solid residue) in the rotary drum reactor. The solid heat carrier is produced continuously by regenerating the solid residue of thermal processing (semicoke together with oil shale ash) *via* combustion in a heat regeneration furnace. Therefore, as a second step, the final fate of the chlorine from the co-pyrolysis of PVC with ash was tested by incineration of the co-pyrolysis residue in a muffle furnace at 800, 830 and 860 °C. Table 4 presents the mass of solid residue remaining after incineration together with its chlorine content. Note that the solid residue from co-pyrolysis contains 13.33% chlorine (Table 2) which corresponds to 85.58% of total chlorine from the feedstock (Table 3).

Table 4. **Influence of temperature on the incineration of pyrolysis residue from the 29.9% PVC / 70.1% ash mixture**

Temperature of incineration, °C	Weight percent of:		Percent of chlorine retained
	Ash retained	Chlorine in the ash	
800	92.80	14.22	99.00
830	92.21	13.55	93.73
860	91.85	13.00	89.58

These data indicate that 76.6–84.6% of the total amount of chlorine from the original PVC waste sample becomes bound in the incineration ash as $CaCl_2$ when co-pyrolysed with kukersite ash at about 30/70 PVC waste/ash ratio in a laboratory batch process. The fate of $CaCl_2$ in the combusted solid residue, that is to be removed from the Galoter process and deposited in an ash storage facility, depends on construction of latter and is out of scope of this study. It is only to bring out that the aqueous solubility of $CaCl_2$ is 42–43% at 20 °C [21].

Conclusions

Thermal processing of PVC waste (containing 70% PVC) with oil shale ash (29.9% PVC waste and 70.1% ash) in a laboratory retort followed by the incineration of the solid retorting residue shows that from 76.6–84.6% of the total chlorine in PVC can be trapped through chemisorption by alkaline oil shale ash as inorganic compound $CaCl_2$. As for the decreasing of the chlorine content in the retorting oil of PVC, the oil shale ash as a chemisorbent shows limited effect indicating that chlorine could be reduced only to a certain extent.

Acknowledgements

The financial support to this research was provided by the Estonian Science Foundation (Grants No. 4667 and 7222). The authors are very grateful to Dr D. S. Kellogg from PMUSA for her helpful advice and editorial comments. Authors also appreciate the contribution of Mr. David Schryer in preparation the manuscript.

REFERENCES

1. *Baitz, M., Byrne, E., Makishi, C., Kupfer, T., Frees, N., Bey, N., Hansen, M. S. A., Bosch, T.,Borghi, V., Watson, J., Miranda, M.* Life cycle assessment of PVC and of principal competing materials // Commissioned report, European Commission DG Environment. 2004.
2. *Miranda, R., Yang, J., Roy, C., Vasile, C.* Vacuum pyroysis of commingled plastics containing PVC // Polym. Degrad. Stab. 2001. Vol. 72, No. 3. P. 469–491.
3. *Kim, S.* Pyrolysis kinetics of waste PVC pipe // Waste Manage. 2001. Vol. 21, No. 7. P. 609–616.
4. *Bockhorn, H., Hentschel, J., Hornung, A., Hornung, U.* Environmental engineering: stepwise pyrolysis of plastic waste // Chem. Eng. Sci. 1999. Vol. 54, No. 15–16. P. 3043-3051.
5. *Ali, M. F., Siddiqui, M. N.* Thermal and catalytic decomposition behavior of PVC mixed plastic waste with petroleum residue // J. Anal. Appl. Pyrol. 2005. Vol. 74, No. 1-2. P. 282–289.
6. *Staka, P., Kovareva, J.* Co-pyrolysis of waste PVC with coal // Acta Mont. 1998. Vol. 8. Ser. B. P. 45–50.
7. *Saeed, L., Tohka, A., Haapala, M., Zevenhoven, R.*, Pyrolysis and combustion of PVC, PVC-wood and PVC-coal mixtures in a two-stage fluidized bed process // Fuel Process. Technol. 2004. Vol. 85, No. 14. P. 1565–1583.
8. *Sun, Q.-L., Shi, X.-G., Lin, Y.-L., Zhu, H., Wang, X., Cheng, C.-G., Liu, J.-H.* Thermogravimetric-mass spectrometric study of the pyrolysis behaviour of PVC // J. China Univ. Mining Technol. 2007. Vol. 17, No. 2. P. 242-245.
9. *Zhu, S., Zhang, Y., Zhang, Y., Zhang, C.* Effect of $CaCO_3$/$LiCO_3$ on the HCl generation of PVC during combustion // Polymer Testing. 2003. Vol. 22, No. 5. P. 539–543.
10. *Masuda, Y., Uda, T., Terakado, O., Hirasawa, M.* Pyrolysis study of poly(vinyl chloride)-metal oxide mixtures: Quantitative product analysis and the chlorine fixing ability of metal oxides // J. Anal. Appl. Pyrol. 2006. Vol. 77, No. 2. P. 159–168.
11. *Karayildirim, T., Yanik, J., Yuksel, M., Saglam, M., Vasile, C., Bockhorn, H.* The effect of some fillers on PVC degradation // J. Anal. Appl. Pyrol. 2006. Vol. 75, No. 2. P. 112–119.

12. *Elenurm, A., Rohtla, I.* Reutilization of plastic wastes. – Tallinn: Final report of Estonian Science Foundation Grant 4667, 2004 [in Estonian].
13. *Tiikma, L., Johannes, I., Luik, H.* Fixation of chlorine evolved in pyrolysis of PVC waste by Estonian oil shales // J. Anal. Appl. Pyrol. 2006. Vol. 75, No. 2. P. 205–210.
14. *Kogerman, P. N.* On the Chemistry of the Estonian Oil Shale "Kukersite". – Tallinn, 1931. 40 pp.
15. *Luts, K.* Der estländische Brennschiefer-Kukersit, seine Chemie, Technologie und Analyse. – Reval, 1944. 356 S [in German].
16. *Hamarneh, Y.* Oil Shale Resources Development in Jordan. – Amman, 1998. P. 12–30.
17. *Dinneen, G. U., Smith, J. W., Tisot, P. R., Robinson, W. E.* Constitution of Green River Oil Shale // United Nations Symposium on the Development and Utilization of Oil Shale Resources, Tallinn, 1968 / Tallinn: Valgus, 1970. P. 172–183 [in Russian].
18. ISO 587. Solid Mineral Fuels. Determination of chlorine using Eschka mixture.
19. ISO 647-74. Solid Mineral Fuels. Method for determination of the yield of products by low temperature distillation.
20. *Kann, J., Elenurm, A., Rohtla, I., Golubev, N., Kaidalov, A., Kindorkin, B.* About thermal low-temperature processing of oil shale by solid heat carrier method // Oil Shale. 2004. Vol. 21, No. 3. P. 195–203.
21. *Lide, D. R.* CRC Handbook of Chemistry and Physics. – London: CRC Press, 2003.

Received February 22, 2008