

Study on Pyrolysis of the Waste from the Paper Industry

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ABSTRACT

The object of this study is to investigate the kinetics and products properties for the pyrolysis of wastes from the paper industry in nitrogen environment. The pyrolysis experiments of wastes (plastic, paper, and cloth) from the paper industry were performed in nitrogen environment, and at the heating rates of 2, 5, and 10 K/min, respectively, aims to establish the model of pyrolysis reaction. The pyrolysis products at the temperatures the maximum instantaneous rate (plastic), the ends of the first and second stage reactions (paper and cloth) were collected and analyzed to investigate the pyrolysis mechanism. The results indicated that the pyrolysis behaviors of plastic and paper/cloth can be observed as one- and two-stage mass change reactions, respectively. The total reaction rates can be expressed as follows. Waste plastic $dX/dt = 4.8 \times 10^{12} \exp(-44.85/(RT))(1-X)^{1.6}$ Waste paper $dX/dt = 0.78dX_1/dt + 0.22dX_2/dt$ $dX_1/dt = 9.61 \times 10^{10} \exp(-33.43/(RT))(1-X)^{1.63}$ $dX_2/dt = 32.79 \exp(-9.47/(RT))(1-X)^{0.91}$ Waste cloth $dX/dt = 0.8dX_1/dt + 0.2dX_2/dt$ $dX_1/dt = 3.24 \times 10^9 \exp(-29.23/(RT))(1-X)^{1.41}$ $dX_2/dt = 26.58 \exp(-10.34/(RT))(1-X)^{0.37}$ For the analyses of pyrolysis products, the solid residues have the highest calorific value of 7033 kcal/kg when the cloth pyrolysed to 370 °C. The main gaseous products were H₂, CO, CO₂, H₂O, and hydrocarbons (HCS). The HCS consisted of low molecular mass paraffin and olefin. All kinds sample, the gaseous product had the highest calorific value of 5152.71 kcal/m³ when the plastic pyrolysed to 620 °C in nitrogen environment. The liquid products of the plastic were mainly H₂O, hydrochloric acid, acetic acid and 1-butanol. The liquid main products of the paper/cloth were H₂O and acetic acid.

Keywords : pyrolysis ; paper industry ; plastic ; paper ; cloth

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REFERENCES

1. www.paper.org.tw (台灣造紙產業資訊網 , 2007) 。 2. 孫逸民 , 陳玉舜 , 趙敏勳 , 謝明學 , 劉興鑑 , “ 儀器分析 ” , 全威圖書有限公司 (2000) 。 3. 黃昶潤 , 稻草熱裂解技術之探討 , 大葉大學環境工程學研究所碩士論文 (2005) 。 4. 陳杞文 , 再生紙廠廢棄物資源化可行性之研究 , 元智大學機械工程學研究所碩士論文 (2006) 。 5. 曾昭衡 , 紙類在氮氣中熱裂解產物分析:氣體產物 , 國立台灣大學碩士論文 (1994) 。 6. 謝錦松 , 黃正義 , 固體廢棄物處理 , 高立圖書 (2001) 。 7. David M. Himmelblau 著 , 何宗漢 , 翁文爐 , 郭勝隆 , 鄭進山譯著 , “ 化工基本原理與計算 ” , 高立圖書有限公司 (1998) 。 8. Agrawal, R. K., “ Kinetics of Reactions Involved in Pyrolysis of Cellulose . II. The Modified Kilzer-Broido Model, ” Canadian Journal of Chemical Engineering, Vol. 66, PP. 413-418 (1988) . 9. Ashrae Handbook Fundamentals (AHF), I-P ed. American Society of Heating Refrigerating and Air-Conditioning Engineers, Inc., Atlanta, GA (1993) . 10. Demirbas, A., “ Pyrolysis of Municipal Plastic Waste for Recovery of Gasoline-range Hydrocarbons, ” Journal of Analytical and Applied Pyrolysis, Vol. 72, PP. 97-102 (2004) . 11. Friedman, H. L., “ Kinetics of Thermal Degradation of Char-Form- ing Plastics from Thermogravimetry. Application to a Phenolic, ” Journal of Polymer Science: Part C, Vol. 6, PP. 183-195 (1965) . 12. Gersten, J., Fainberg, V., Garbar A., Hetsroni, G. and Shindler, Y., “ Utilization of Wates Polymers throuth One-stage Low Temperature Pyrolysis with Oil Shale, ” Fuel, Vol. 78, PP. 987-990 (1999) . 13. Grassie, N., “ Thermal Degradation, ” in “ Encyclopedia of Polymer Science and Technology, ” ed. H. F. Mark et. al., Vol. 14, PP. 651 (1971) . 14. Hajaligol, M., Waymack, B. and Kellogg, D., “ Low Temperature Formation of Aromatic Hydrocarbon from Pyrolysis of Cellulosic Materials, ” Fuel, Vol. 80, PP. 1799-1807 (2001) . 15. Kaminsky, W. and Rossler, H., “ Oleffins from Wasre, ” Chemtech, Vol. 22, PP. 108 (1992) . 16. Kaminsky, W., Schlesselmann, B., and Simon C. M., “ Thermal Degradation of Mixed Plastic Wastes to Aromatics and Gas, ” Polymer Degradation and Stability, Vol. 53, PP. 189-197 (1996) . 17. Kaminsky, W. and Kim, J. S., “ Pyrolysis of Mixed Plastics into Aromatics, ” Journal of Analytical and Applied Pyrolysis, Vol. 51, PP. 127-134 (1998) . 18. Katsuhide, M., Hirano, Y., Sakata, Y. and Uddin, M. A., “ Basic Study on a Continuous Flow Reactor for Thermal Degradation of Polymers, ” Journal of Analytical and Applied Pyrolysis, Vol. 65, PP. 71-90 (2002) . 19. Kiran, N., Ekinci, E. and Snape, C. E., “ Recycling of Plastic Waste via Pyrolysis, ” Resources Conservation and Recycling, Vol. 29, PP. 273-283 (2000) . 20. Koo, J. K., Kim, S. W. and Seo, Y. H., “ Characterization of Aroma- tic Hydrocarbon Formation from Pyrolysis of Polyethylene-Polyst- yene Mixtures, ” Resources, Conserv. And Rec., Vol. 5, PP. 365-382 (1991) . 21. Mastral, F. J., Esperanza, E., Garcia, P. and Juste, M., “ Pyrolysis of High-density Polyethylene in a Fluidized Bed Reactor. Influence of the Temperature and Residence Time, ” Journal of Analytical and Applied Pyrolysis, Vol. 63, PP. 1-15 (2002) . 22. McNeill, I. C., “ Thermal Degradation, ” in “ Comprehensive Polymer Sciencs, ” ed. G. C. Eastmond et al., Pergaman Press, Oxford, Vol. 6, PP. 451-500 (1989) . 23. Schnabel, W., “ Polymer Degradation: Principles and Practical Applications, ” Hanser, Wien, Germany (1981) . 24. Sorum, L., Gronli, M. G. and Husted, J. E., “ Pyrolysis Characteris- tics and Kinetics of Municipal Solid Waste, ” Fuel, Vol. 80, PP. 1217-1227 (2001) . 25. Wu, C. H., Chang, C. Y., Hwang, J. Y., Shih, S. J., Chen, L. W., Chang, F. W. and Yang, W. F., “ Pyrolysis Kinetics of Tissue Paper of MSW, ” Journal of the Chinese Institute of Engineers, Vol. 17 (5), PP. 659-669 (1994) . 26. Wu, C. H., Chang, C. Y., Tseng, C. H. and Lin, J. P., “ Pyrolysis product distribution of waste newspaper in MSW, ” Jounal of Analyticaland pyrolysis, Vol. 67, PP. 41.43 (2003) .