

RECYCLING OF WASTE FLEXIBLE POLYURETHANE FOAM

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ABSTRACT

THE TREATMENT OF WASTE POLYURETHANES (PU) IS MORE AND MORE IMPORTANT, AS THE APPLICATION OF PU IS STEADILY ON THE INCREASE. THE MAJOR METHODS FOR TREATING WASTE PU INCLUDE LANDFILL, ENERGY RECOVERY, MATERIAL RECYCLING, AND CHEMICALS RECYCLING ETC. THE CHEMICALS RECYCLING IS THE CHEMICAL CONVERSION OF WASTE PU INTO THE RAW MATERIALS OF PU OR PRIMARY PETROCHEMICALS BY THE ADEQUATE CHOICE OF REAGENTS AND CATALYSTS IN THE CHEMICAL GLYCOLYSIS CONDITIONS. GLYCOLYSIS IS ONE OF THE PRINCIPAL METHODS IN CHEMICALS RECYCLING. THE FACTORS THAT AFFECT THE GLYCOLYSIS OF PU INCLUDE THE TYPES OF SOLVENT AND CATALYST, THE CONCENTRATIONS OF SOLVENT AND CATALYST AND THE REACTION TIME. IN THIS STUDY, THE GLYCOLYSIS OF PU IS INVESTIGATED TO PROVIDE THE USEFUL DATA FOR THE DESIGN OF A PILOT SCALE PLANT. THE STUDY FOR THE GLYCOLYSIS OF FLEXIBLE PU FOAM ARE CARRIED OUT AT VARIOUS FORMULAS CONSISTED OF REAGENT AND CATALYST. THE EXPERIMENTS ARE PERFORMED UNDER THE ATMOSPHERIC PRESSURE AND ISOTHERMAL CONDITION (220 °C). DIETHYLENE GLYCOL (DEG), POTASSIUM ACETATE (CH₃COOK) ARE USED AS THE SOLVENT AND CATALYST, RESPECTIVELY. THE PROPERTIES OF GLYCOLYSIS PRODUCTS SUCH AS HYDROXYL VALUE, MASS MEAN MOLECULAR WEIGHT, VISCOSITY AND THE CONVERSION OF THE -NCOO- FUNCTIONAL GROUP IN PU ARE ANALYZED WITH DIFFERENT EXPERIMENTAL CONDITIONS. THE RESULTS INDICATE THAT THE CONCENTRATIONS WITH DEG/PU = 150%, KAC/PU = 1%, AND THE REACTION TIME = 90 MIN ARE THE BEST RATIO OF SOLVENT AND POLYURETHANE, THE CONCENTRATION OF CATALYST, AND THE REACTION TIME, RESPECTIVELY. THE AMOUNTS OF THE DISTILLATE IN THE SECOND STAGE DISTILLATION (GAS-PHASE TEMPERATURE 245 ~ 260 °C) ARE ABOUT 13.4 ~ 43.78% UNDER THE EXPERIMENTAL CONDITIONS. SINCE THE HYDROXYL VALUE OF THE DISTILLATE OBTAINED FROM THE SECOND STAGE DISTILLATION IS CLOSED TO THAT OF THE DEG. THE RECYCLING OF PU BY THE GLYCOLYSIS WILL BE ATTRACTIVE. THE CONVERSION OF -NCOO- FUNCTIONAL GROUP IN PU AT THE OPTIMUM FORMULA (DEG/PU = 150% AND KAC/PU = 1%) CAN BE EXPRESSED BY THE TOTAL RATE EQUATION, $DX/DT = 0.014 \times (1-X) \times 3.71 \times (KAC) \times 0.6 \times (DEG) \times 1.12$. THE PROPOSED KINETIC MODEL CAN BE ACCEPTED WITH THE COEFFICIENTS OF DETERMINATION 0.8202.

Keywords : POLYURETHANE (PU) 、 GLYCOLYSIS、 PRODUCTS ANALYSIS、 KINETIC、 PURIFYING

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REFERENCES

1. ATANASOV, VI., TROEV, K., TSEVI, R., GRANCHAROV, G., AND TSEKOVA, A., "CHEMICAL DEGRADATION OF POLYURETHANES. DEGRADATION OF MICROPOROUS POLYURETHANE ELASTOMER BY DIMETHYL PHOSPHONATE," POLYMER DEGRADATION AND STABILITY, 67, 159-165 (2000). 2. BORDA, J., PASZTOR, G., AND ZSUGA, M., "GLYCOLYSIS OF POLYURETHANE FOAMS AND ELASTOMER -S," POLYMER DEGRADATION AND STABILITY, 68, 419- 422 (2000). 3. FRULLA, F. F., ODINAK, A., AND SAYIRY, A. A. R., "CONVERSION OF SCRAP POLYURETHANE FOAM TO POLYOL," U. S. PATENT NUMBER 3,738,946 (1973). 4. GASSAN, M., NABER, B., AND NEISS, V., "PREPARATION OF RECYCLATE POLYOLS, AND THE USE THEREOF IN THE PREPARATION OF PUS," U. S. PATENT NUMBER 5,357,006 (1994). 5. GERLOCK, J. L., MAHONEY, J., MAHONEY, L. R., AND FERRIS, F. O., "REACTION OF POLYURET -HANE FOAM WITH DRY STEAM: KINETICS AND MECHANISM OF REACTIONS," JOURNAL OF POLYMER SCIENCE, 18, 541-57 (1980). 6. HOPPER, F. G., PARRINELLO, G., PARFONDY, A., AND KROESEN, D. I. K. W., "RECENT DEVEL -OPMENTS IN THE CHEMICAL RECYCLING OF FLEXIBLE POLYURETHANES," CELLULAR POLYMERS, 11 (5), 388-396 (1992). 7. KERSCHER, J., SCHWAGER, H., RABHOFER, W., AND PFEFFERKORN, R., "CHEMICAL RECYCLING OF AN ALL-PU INSTRUMENT PANEL-INDUSTRIAL REALISATION," UTECH, 1-10 (1996). 8. KINOSHITA, O., "PROCESS FOR DECOMPOSITION OF A POLYURETHANE RESIN," U. S. PATENT NUM -BER 3,632,530 (1972). 9. KONDO, O., HASHIMOTO T., AND HASEGAWA, H., "PROCESS FOR OBTAINING A POLYOL-CONTAINING HOMOGENEOUS LIQUID COMPOSITION USEFUL FOR THE PRODUCTION OF RIGID PU FOAM FROM A RIG -ID PU FOAM," U. S. PATENT NUMBER 4,014,809 (1977). 10. MACHADO, R. M., MITCHELL, J. W., BULLOCK, J. P., AND FARRELL, B. E., "KINETICS OF THE -REACTION OF 4, 4'-METHYLENEDIANILINE WITH PROPYLENE OXIDE IN ETHYLENE GLYCOL," THERMO -CHIMICA ACTA, 177-187 (1996). 11. MAHONEY, L. R., WEINER, S. A., AND FERRIS, F. C., "HYDROLYSIS OF POLYURETHANE FOAM WAS -TE," ENVIRONMENTAL SCIENCE AND TECHNOLOGY, 8 (2), 135-139 (1974). 12. MODESTI, M., SIMIONI, F., MUNARI, R., AND BALDOIN, N., "RECYCLING OF FLEXIBLE POLYURET -HANE FOAMS WITH A LOW AROMATIC AMINE CONTENT," REACTIVE AND FUNCTIONAL POLYMERS, 26, 157-165 (1995). 13. NIEDERDELLMANN, G., ROEMER, N., SCHENK, J., HETZEL, H., AND GRIGAT, E., "PROCESS FOR SEPARATING POLYURETHANE HYDROLYZATES INTO POLYETHER AND DIAMINE," U. S. PATENT NUMBER 4,399,236 (1983). 14. PARRINELLO, G., COLLINS F., THORPE D., AND VERHELST, G., "RECYCLING OF FLEXIBLE FOAM," U. S. PATENT NUMBER 5,691,389 (1997). 15. RICARDO, J. C., SALVADOR, G., RICARDO, E. S., AND MIGUEL, G., "SPECTROPHOTOMETRIC DET -ERMINATION OF CARBARYL BY ON-LION ELUTION AFTER ITS PRECONCENTRATION ONTO POLYURETHA -NE FOAM," TALANTA, 52, 717-725(2000). 16. ROBERT, E., ERIC, B., SHI, C. M., AND KARMANA, E., "FORMATION OF FLUOROETHER POLYURET -HANE IN CO₂," JOURNAL OF SUPERCRITICAL FLUIDS, 127-134 (1998). 17. SAUNDERS, J. H. AND FRISCH, K. C., "POLYURETHANES CHEMISTRY AND TECHNOLOGY, PART I. CHEMISTRY," IN HIGH POLYMERS, ED. H. MARK, P. J. FLORY, C. S. MARVEL AND H. W. MELVILLE, 文京圖書, (1977A)。 18. SAUNDERS, J. H. AND FRISCH, K. C., "POLYURETHANES CHEMISTRY AND TECHNOLOGY, PART II. TECHNOLOGY," IN HIGH POLYMERS, ED. H. MARK, P. J. FLORY, C. S. MARVEL AND H. W. MELV -ILLE, 文京圖書, (1977B)。 19. SCHEIRS, J., "RECYCLING OF POLYURETHANES," IN POLYMER RECYCLING, JOHN WILEY AND SONS, UK., 355-359 (1998) . 20. SHERATTE, M. B., "PROCESS FOR CONVERTING THE DECOMPOSITION PRODUCTS OF PU AND NOVEL COMPOSITIONS THEREBY OBTAINED," U. S. PATENT NUMBER 4,110,266 (1978). 21. SIMIONI, F. AND BISELLO, S., "POLYOL RECOVERY FROM RIGID PU WASTE," CELLULAR POLYMERS, 2, 281-293 (1983). 22. TROEV, K., GRANCHAROV, G., AND TSEVI, R., "CHEMICAL DEGRADATION OF POLYURETHANES. DEG -RADATION OF MICROPOROUS POLYURETHANE ELASTOMER BY DIETHYL PHOSPHONATE AND TRIS(1-MET -HYL-2-HLOROETHYL) PHOSPHATE," POLYMER DEGRADATION AND STABILITY, 70, 43-48(2000A). 23. TROEV, K., GRANCHAROV, G., TSEVI, R., AND TSEKOVA, A., "A NOVEL APPROACH TO RECYCLING OF POLYURETHANES: CHEMICAL DEGRADATION OF FLEXIBLE POLYURETHANE FOAMS BY TRITHYL PHOS -PHATE," POLYMER, 41, 7017-7022 (2000B). 24. TUCKER, B. AND ULRICH, H., "NOVEL PROCESS OF RECLAIMING POLYURETHANE FOAM," U. S. PATE -NT NUMBER 3,983,087 (1976). 25. ULRICH, H., TUCKER, B., ODINAK, A., AND GAMACHE, A. R., "RECYCLING OF THERMOSET POLYUR -ETHANE ELASTOMER," JOURNAL OF ELASTOMERS AND PLASTICS, 11, 208-212 (1979). 26. VAN DER WAL, H. R., "NEW CHEMICAL RECYCLING PROCESS," JOURNAL OF REINFORCED PLASTICS AND COMPOSITES, 13, 87-96 (1994). 27. VAN SCHAİK A., FRANUNHOLCZ, N., AND DALMIJN, W. L., "CONFLICTING DEVELOPMENTS IN TODAY' S RECYCLING OF END-OF-LIFE VEHICLES," RECYCLING INTERNATIONAL, SEPTEMBER, NO.8 (1999). 28. 李俊坤, "聚氨基甲酸乙酯泡綿化學裂解技術基礎研究", 碩士論文, 台灣大學環境工程研究所 (1997)。 29. 吳照雄、鄭建民、黃宏章、張慶源, "軟質廢PU泡綿化學裂解研究()", 第十五屆廢棄物處理技 術研討會論文集, 第1-199~1-205 (2000) 。 30. 薛敬和, "高分子化學", 高立圖書有限公司, 台北市 (1992)。 31. 賴耿陽, "PU原理與實用", 復漢出版社, 台南市 (1997)。 32. 蘇銘千、蔣本基、李公哲、李清華, "廢機動車輛拆解及資源回收技術", 土木技術, 第1卷, 第10期, 第64~74 頁 (1998)。 33. [HTTP://WWW.BAYER.COM.TW/BUSINESS_0.HTM](http://www.bayer.com.tw/business_0.htm)