HYDROTHERMAL LIQUEFACTION OF THREE TYPES OF POLYURETHANE WASTES; EFFECT OF ETHANOL ON DECOMPOSITION AND CHEMICAL RECOVERY

Sogand Musivand, Department of Chemical Engineering, Sapienza University of Rome, Italy
sogand.musivand@uniroma1.it
Paolo De Filippis, Department of Chemical Engineering, Sapienza University of Rome, Italy
Martina Damizia, Department of Chemical Engineering, Sapienza University of Rome, Italy
Maria Paola Bracciale, Department of Chemical Engineering, Sapienza University of Rome, Italy
Benedetta De Caprariis, Department of Chemical Engineering, Sapienza University of Rome, Italy

Key Words: Polyurethane, HTL, Polyols, Decomposition, Recycling.

Introduction: To construct a sustainable society, the chemical recycling of polymeric materials remains a crucial issue which still need a deep R&D activity. Polyurethanes (PU) are industrially important polymeric materials which have a variety of applications. Degradation reactions (e.g., hydrolysis, aminolysis, alcoholysis, and glycolysis) have been used for the chemical recycling of PUs. However, the urethane linkages are relatively stable; therefore, their hydrolysis process needs harsh reaction conditions.

Aim: The aim of the study is to chemically recycle the PUs in mild conditions by means of hydrothermal liquefaction (HTL) using ethanol and water as solvents. In particular the effect of the ratio between water and ethanol in chemical recycling of three different kind of polyurethane was investigated.

Methods: The HTL experiments were conducted in batch microreactor in the subcritical water using a PU to solvent ratio of 1:10. The effect of the ratio between ethanol and water and of the reaction temperature on PU degradation was investigated. The range of ethanol percentage used was 0%,10%, 30% and 50% and temperature range was 200-300˚C. The reaction time was kept constant to 10 min for all the tests and after the reaction the reactors were immediately quenched. The liquid and solid residue were separated by filtration. The produced oil was separated by washing the solid with acetone which was then evaporated by rotary evaporator. The water phase and the oil phase were analyzed by GC-MS. Three PUs feedstocks were used: the foam (PU-foam), quinoline based PU (q-PU) and high resistance PU (high-PU).

Results: The decomposition of PU-foam at 200°C revealed that the degradation rate in the situation of 0% ethanol (only water) was only 20% while this parameter increased to 90% in the presence of 30% ethanol. The product distribution shows that the highest peaks are 4,4-methylenedianiline (MDA) and 1,4-Butane diol (BD) in the oil and water phase and morpholine as a chain extender. The highest oil recovery was 85% at 250 with10% ethanol.

The behavior of q-PU decomposition was similar to that of PU-foam, the presence of ethanol increased the degradation rate at 200 °C from 45 % to 95% when 30 % of ethanol was used with 57% oil recovery. The GC-MS analyses showed a great variety of organic compounds in the oily and water phase due to the verity of the constructive raw material; esters, amins and polyols were present.

High-PU was relatively more resistant to temperature with merely 4% of decomposition rate at 200c in presence of 50% ethanol it raised to only 14%. The maximum oil production from this sample was 60% and the effect of ethanol on the decomposition of this sample was negligible. The GC data showed higher purity of polyols and MDA production.

Conclusions: The results demonstrated that the decomposition of PU is feasible in mild condition by increasing the ethanol percentage for all three kinds of the polyurethane. However, by increasing the ethanol percentage the yield of the oily phase decreased and most of the organic compounds were transferred into the water phase. The main compound revealed by GC-MS was MDA (50% of the relative peak area) in all the PU types of decomposition. In conclusion it can be demonstrate that HTL is an effective alternative to recycle the PU as one of the most consumed polymers moreover adding ethanol can accelerate the decomposition of this polymer; the optimum concentration of ethanol in term of oil production and decomposition rate is 10 and 30%w/w.