Molten salt oxidation: A reassessment of its supposed catalytic mechanism and hence its development for the disposal of waste automotive tires

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Molten Salt Oxidation, MSO, is a thermal, non-flame process that destroys completely many organic compounds and simultaneously retains non-oxidisable and non-volatile inorganic species in the molten salt. When treated by this process hydrocarbons are converted to carbon dioxide and water.

MSO is not a new concept, having been examined as a possible method for processing nuclear fuels by the Atomic Energy Commission in the USA in the 1950’s. Other applications of MSO were soon envisioned and tested, including the destruction of hazardous waste, of propellants and explosives, and for metal recovery and volume reduction of radioactive waste. Although successful, these processes were not taken beyond pilot plant scale, as established methods then available were acceptable.

In recent years emissions levels and the old disposal methods are now of international concern. Combustion produces ash and unacceptable emissions and the combustion of organic wastes containing chlorinated plastics is seen as source of dioxins. Burial of waste can give concern for the possible future contamination of ground water. The disposal of the large tonnage of tire waste generated worldwide is becoming an increasing environmental and economic problem. In the EU the burial of old tires will soon be prohibited. New methods are therefore now needed.

MOLTEN SALT OXIDATION RE-EXAMINED

Molten Salt Oxidation (MSO) uses a salt at between 400 and 1200ºC with air constantly bubbling through it and into which the candidate for oxidation is added below the melt surface. The enthalpy of oxidation will generally maintain the melt temperature. Sodium carbonate, mp 851ºC, has generally been the melt of choice but, when a lower melt temperature is desired, a binary or ternary eutectic mixture of alkali carbonates can be employed. The literature on the oxidation of various wastes, if it attempts to explain the mechanism of oxidation, refers to the catalytic role of carbonate, justified on the basis that oxidation occurs at a lower temperature than combustion. To improve reaction rates experiments were consequently proposed and undertaken with traditional catalyst promoters, transition metal oxides, added as potential catalysts (1). The amounts needed to produce a slight improvement were around 40% but then the systems were more viscous. However, the role of carbonate is *not* as a catalyst. The action of the molten carbonate is to dissolve *chemically* some of the oxygen bubbling through the melt. We have shown that the active species formed are peroxide and superoxide (2).

IMPROVING MOLTEN SALT OXIDATION

We have also determined that if nitrate is added to the melt it acts as a catalyst, increasing the concentration of the more active species, superoxide, the nitrite formed being readily converted to nitrate (3). Previously, for example, the complete oxidation of paper by MSO has been slow and incomplete, a carbon residue being formed. The addition of a few percent of KNO_3 to molten carbonate was sufficient to achieve rapid and complete oxidation (4). We therefore considered its application to used automotive tires. Scrap tires are non-fusible and insoluble substances that contain carbon black and vulcanising agents for converting the natural or synthetic rubber into an elastomer: flame incineration and pyrolysis can generate toxic off-gases, soot and the ash contains lead and cadmium salts (stabilisers in tire production).

EXPERIMENTAL AND RESULTS

Using just the ternary eutectic $(Li,Na,K)_2CO_3$ at the relatively low temperature of 550ºC, tire samples yielded much unreacted carbon, an oily distillate (pyrolytic oil), and a variety of organic species in the off-gas, as well as CO_2, CO and H_2O. Adding 3% KNO_3 gave a marked improvement: the reaction was faster and the pyrolytic oil was largely absent but there was still a significant amount of unreacted carbon black.

Controlled partial pyrolysis of scrap tires has involved some depolymerisation (5). Devulcanisation, breaking the disulfide bonds in the rubber, can be achieved at room temperature by reaction with various organic materials. We used tributyl phosphate, TBP, a solvent not previously employed, soaking the rubber for 48 h and filtering off the now yellow-brown liquid (4). The rubber appeared unchanged but was now more flexible and when treated by MSO, was almost completely oxidised. No pyrolytic oil was obtained, very little carbon remained in the melt, and the off-gases were mainly CO_2 and H_2O, with traces of CO. When the TBP is exhausted it can be oxidised completely by MSO, the phosphorus remaining in the melt (6).

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