

Destruction of Chlorobenzen and Carbon Tetra Chloride in a Two-Stage Molten Salt Oxidation Reactor System

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INTRODUCTION

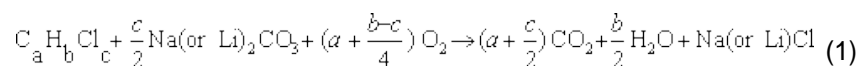
Chlorinated organic solvents are widely used in the chemical industry. Wastes generated from their use include a significant quantity of chlorines. While an incineration is considered as an effective tool for the treatment of those chlorinated organic wastes, the environmental acceptability of the emissions of dioxins is a major criterion for the application of the incineration process.¹ There is therefore the developing need for an alternative oxidation process that can effectively destroy chlorinated organics without an emission of chlorinated organics. One of the promising alternatives is a molten salt oxidation. In a hot molten alkali carbonated salt, hydrogen chloride or chlorine first released at the stage of a dehydrochlorination of chlorinated organics is trapped in the form of alkali chloride. The recombination of toxic chlorinated organics is prevented. Therefore, molten salt oxidation (MSO) has been regarded as one of the emerging technologies that could treat PCBs, various dioxins, pesticides and herbicides, chemical warfare agents, explosives and propellants.²⁻⁴ This study investigated the destruction of chlorinated organic solvents in a two-stage MSO reactor system. The purpose of this study is to investigate the influence of reactor operating temperature on the chlorine retention as well as the organic destruction performance.

MATERIALS AND METHODS

The schematic diagram of a lab-scale MSO system with a designed capacity of 0.5 kg PVC plastics/h is shown in Figure 1. The detailed description of the MSO system and the operating procedure are described in the previous works.^{5,6} Two chlorinated organic solvent tested in this study were C₆H₅Cl and CCl₄. The feed rates of C₆H₅Cl and CCl₄ were fixed to be 1.2 vol.% and 5.4 vol.% in air, respectively. Four investigated molten salt temperatures of primary reactor were 750, 850, 900 and 950°C. The temperature of secondary MSO reactor was fixed to be 900°C through all test runs. During the test runs, the concentrations of O₂, CO and NO_x were measured using a combustion efficiency analyzer (TESTO-300). The emissions of hydrocarbons, HCl and Cl₂ were measured by Levitt Gastec tubes. The speciation of the products of an incomplete combustion (PICs) was performed by the GC(HP5890)-MSD (HP5972) system.

RESULTS AND DISCUSSION

The overall chemical reaction of chlorinated organics by Li₂CO₃-Na₂CO₃ eutectic salt is given by the following equation.



As the products of an incomplete reaction, some hydrocarbons, carbon monoxide and hydrogen chlorides can be emitted from the MSO reactor. The emissions of these incomplete reaction products indicate the MSO reactor performance. The emission of carbon-containing species was measured to be about 5 ppm during the course of the T1-1 test run. Most of carbon containing species was found to be soot, which was efficiently collected in the HEPA filter, together with entrained salt particles. GC-MSD analysis of the off-gas samples indicated that the decomposition products of C₆H₅Cl include a trace amount of C₂H₂ and C₂H₄. But their emissions were in the range

smaller than 100 ppb during the lowest temperature test (T1-1). During the other tests (T1-2, T1-3, T2-1, T2-2 and T2-3), no gaseous organic species were detected in the off-gas sample. This indicates that the further destruction of trace amount of hydrocarbons in the secondary reactor appeared to be substantial. In addition, carbon-containing organic species were not found in the spent salt. This indicates that the MSO reactors have an excellent mixing capacity. During the course of each test run, the operating temperatures were not deviated over 1°C from the set temperatures. This suggests that the temperatures and the heat transfer are completely uniform within the molten salt bed. It can therefore be positively said that the undestroyed organic species as the incomplete reaction products of above reaction (1) are continually mixed with the oxidizing air in the hot molten salt until their complete oxidation is obtained.

Carbon monoxide (CO) emissions from the primary and secondary MSO reactors are plotted in Figure 2. For C_6H_5Cl destruction, the CO emissions of the primary reactor were greatly influenced by the reactor temperature. The averaged CO emissions in 750°C and 850 °C test runs (T1-1 and T1-2) were 1219 ppm and 513 ppm, respectively. During the tests (T1-1 and T1-2), the further oxidation of CO in the secondary reactor was not substantial and their final emissions slightly exceeded 300 ppm and 120 ppm, respectively. The averaged CO emissions from the primary reactor at higher temperature test runs (T1-3 and T1-4) were about 330 ppm and 159 ppm, respectively. It showed the strong dependency of CO emissions on the MSO reactor temperature. During these high temperature test conditions (T1-3 and T1-4), the further oxidation in the secondary reactor was substantial and the final CO emission was averaged to be about 60 ppm and 25 ppm, respectively. As shown in Figure 2, the CO emissions from the primary reactor during CCl_4 destruction was also greatly influenced by the temperature but the emission concentrations were relatively small, compared to that during C_6H_5Cl destruction. This suggests that the destruction of CCl_4 is faster than that of C_6H_5Cl in the MSO reactor. This might result in the longer residence time of CO in the hot molten salt, and therefore the substantial oxidation of CO could be obtained during CCl_4 destruction.

Regardless of tested condition, hydrogen chloride was found to be the only chlorine-containing species in the all flue gas streams. The emissions of HCl from each MSO reactor were plotted in the Figure 3 and the overall chlorine collection efficiencies are listed in Table 2. HCl emissions from the primary reactor were not much varied with the reactor temperature. The averaged HCl emissions from the primary reactor were about 50 ppm during C_6H_5Cl destruction and about 100 ppm for CCl_4 . The final HCl emissions were maintained to be less than 10 ppm. This indicates the significant performance of the molten salt oxidation reactor system. The overall chlorine retention efficiencies were in the range between 99.954 and 99.970% for C_6H_5Cl destruction and in the range between 99.997% and 99.999% for CCl_4 destruction, respectively. This also suggests that the destruction of CCl_4 is faster than that of C_6H_5Cl . This resulted in the longer residence time of chlorine gases in the hot molten salt, and therefore the more substantial collection of HCl could be obtained. The collection of chlorine appears to be a function of residence time and it is not affected by the temperature.

The results of this study indicated that chlorinated organic solvents can be effectively treated by the molten salt oxidation. No hazardous organics were emitted and the acid gas emissions are very limited. The collection of chlorine in the hot molten salt appeared to be really substantial. The emissions of CO were greatly influenced by the MSO reactor temperature. It is therefore recommended that the MSO reactor temperatures should be maintained to be over 900°C in order to prevent the significant emissions of CO during the molten salt oxidation of organic materials.

References

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Table 1. Summary of primary MSO reactor test conditions.

Test run No.	T1-1	T1-2	T1-3	T1-4	T2-1	T2-2	T2-3	T2-4
Temperature, °C	750	850	900	950	750	850	900	950
Solvent feed rate	0.15 kg C ₆ H ₅ Cl/h (1.2 vol.% in air)				1.2 kg CCl ₄ /h (5.4 vol.% in air)			

Table 2. Chlorine retention efficiencies in the two stage MSO reactor system.

Primary reactor temperature, °C	750	850	900	950
C ₆ H ₅ Cl	99.956	99.954	99.958	99.970
CCl ₄	99.997	99.998	99.998	99.999

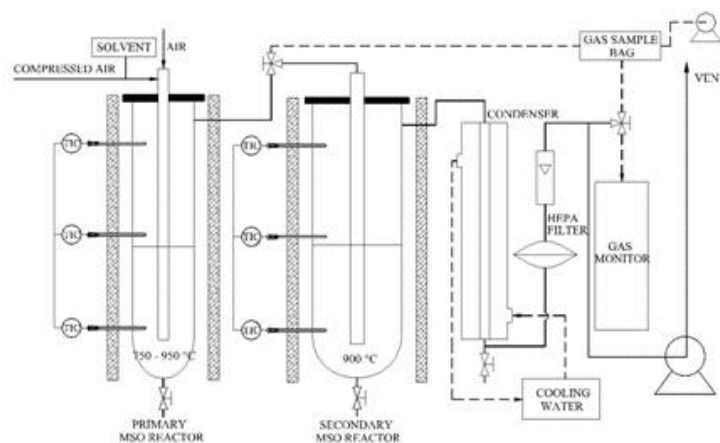


Figure 1. A schematic diagram of lab-scale molten salt oxidation system

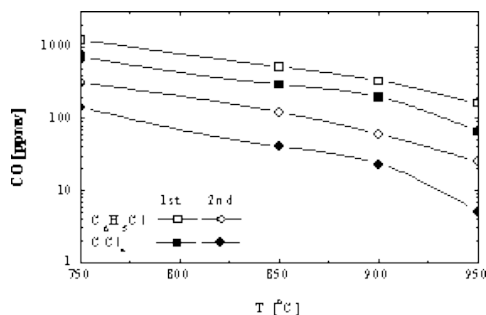


Figure 2. The emissions of carbon monoxide from each MSO reactor

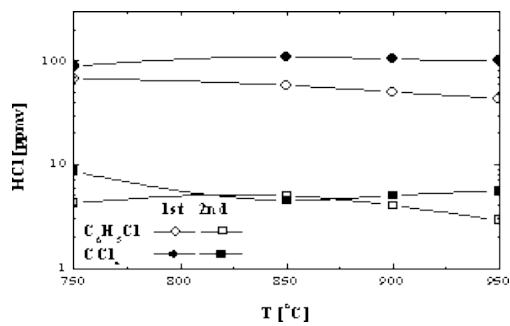


Figure 3. The emissions of hydrogen chloride from each MSO reactor