

Molten Salt Oxidation of Chlorobenzene

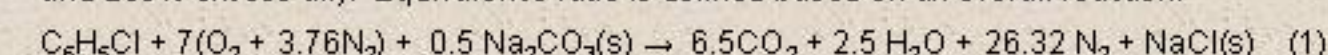
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Abstract

This investigation focuses on the oxidation of chlorobenzene in a laboratory scale molten salt reactor. A Fourier Transform Infrared (FTIR) spectrometer with a long-path cell is used to monitor the organic waste oxidation process, including the formation of byproducts as a function of temperature. The measured oxidation byproducts are compared with results reported in the literature, obtained in a flow reactor at similar oxidation temperatures, and the results are modeled using detailed chemical kinetics. The results outlined in this work provide a direct comparison of the effectiveness of molten salt oxidation compared with conventional combustion oxidation, and highlight the advantages and disadvantages associated with the molten salt oxidation process.

Overview and Discussion:

Experiments were performed for salt bed heights of 11 cm, 16 cm, and 21 cm (corresponding to 1 kg, 1.5 kg, and 2 kg of Na_2CO_3 salt and overall equivalence ratios of $\Phi = 1, 2$, and 3 (0, 100%, and 200% excess air). Equivalence ratio is defined based on an overall reaction:



A relatively low flow rate of chlorobenzene (2 ml / min.) was used for all experiments to avoid rapid saturation of the salt with NaCl product. The air flows required for the defined equivalence ratios were 15, 30, and 45 liters/minute. The reactor was allowed to come to steady state for approximately 10 minutes under a particular condition before measurements were made. Each data point is the average of 3 different samples. Measurements reported as zero should be interpreted as being below the detection limits, which were between 50 and 100 ppm for CO , CH_4 , C_2H_4 , and approximately 400 ppm for C_6H_6 . CO_2 was not measured due to saturation of the signal and interferences from CO_2 evolved from the salt. Under these conditions, chlorobenzene emission was not observed under any conditions; the detection limit for chlorobenzene should be similar to that of benzene.

Products of incomplete reaction benzene, ethylene, and methane were observed to follow similar trends throughout the temperature range studied for $\Phi = 1$, as well as at the lower temperatures for $\Phi = 2$ and $\Phi = 3$ (Fig 2-4). The final intermediate before CO_2 formation, CO followed a trend opposite the earlier intermediates; at all temperatures, CO conversion is higher, and intermediate byproducts (C_6H_6 , C_2H_4 , and CH_4) are lower, under lean conditions. This indicates that oxygen concentrations are important, and likely either mass transfer limitations, i.e. to a reaction occurring on a surface, or kinetics involving oxygen are playing a significant role in determining the overall oxidation rate.

The sum of the measured carbon emissions is shown in Figure 6. As the temperature increases, the total carbon measured as ($6\text{C}_6\text{H}_6 + 2\text{C}_2\text{H}_4 + \text{CH}_4 + \text{CO}$) decreases. It is likely that the majority of the difference between the total carbon injected and the sum of the measured carbon is CO_2 . The striking thing about Figure 6 is that the values of total measured carbon at a particular temperature are seemingly independent of equivalence ratio. Figures 7 and 8 illustrate the importance of residence time under the conditions tested, all byproducts decrease with increasing salt height / residence time.

Perhaps most significantly, no chlorinated byproducts or chlorinated end product of oxidation, HCl, is observed, indicating complete chlorine trapping in the molten salt. Higgins et al. [5], in a lean oxidative combustion study, observed $\text{C}_6\text{H}_5\text{OH}$, o-, m- and p- $\text{C}_6\text{H}_4\text{ClOH}$, CH_2O , $\text{C}_2\text{H}_3\text{Cl}$, C_2H_2 , CO and HCl in the products of lean combustion oxidation of chlorobenzene. Their study was at a slightly lower peak temperature (roughly 425 – 925 °C) than the present study. They reported that most of the chlorine appeared to have been converted to HCl, and that C-Cl scission was not found to dominate chlorobenzene destruction, as had been observed in earlier pyrolytic studies. Rather, a significant fraction of the chlorine remained bound in breakdown products of chlorobenzene, such as vinyl chloride and ethyl chloride, before conversion to HCl.

In contrast, we did not find any vinyl chloride ($\text{C}_2\text{H}_3\text{Cl}$), ethyl chloride ($\text{C}_2\text{H}_5\text{Cl}$), or hydrogen chloride (HCl) but we found benzene in the products during molten salt oxidation of chlorobenzene. This suggests a different reaction pathway from that observed in the lean oxidation of chlorobenzene in a flow reactor. Given the relatively higher (900 – 1000 °C) temperatures compared with the combustion study, it would be more likely in the combustion case that the Cl abstraction reactions would predominate over H abstraction, given the 15% lower bond energy of the C-Cl bond on chlorobenzene compared with the C-H bond. Cl abstraction would leave C_6H_5 , which might reasonably be expected to break down in a similar manner to benzene, with an O addition and CO expulsion, leading to a C5 ring [6].

Instead, C_6H_6 is observed, and no chlorinated species at all are observed in the emission. The latter result would strongly suggest that the chlorine is being absorbed by the sodium carbonate in a surface reaction. A model was set up to test the surface reactions. The detailed chemical kinetic mechanism of Higgins et al. [5] was obtained to model the chlorobenzene destruction. This mechanism includes a complete benzene mechanism as well as a submodel specific to chlorobenzene. Based on the results shown in Figure 9, it appears that direct abstraction of Cl by the salt, i.e. $\text{Na}(\text{s}) + \text{C}_6\text{H}_5\text{Cl} \rightarrow \text{C}_6\text{H}_5 + \text{NaCl}(\text{s})$ predominates, as this is the only reaction that does not result in measurable HCl emissions.

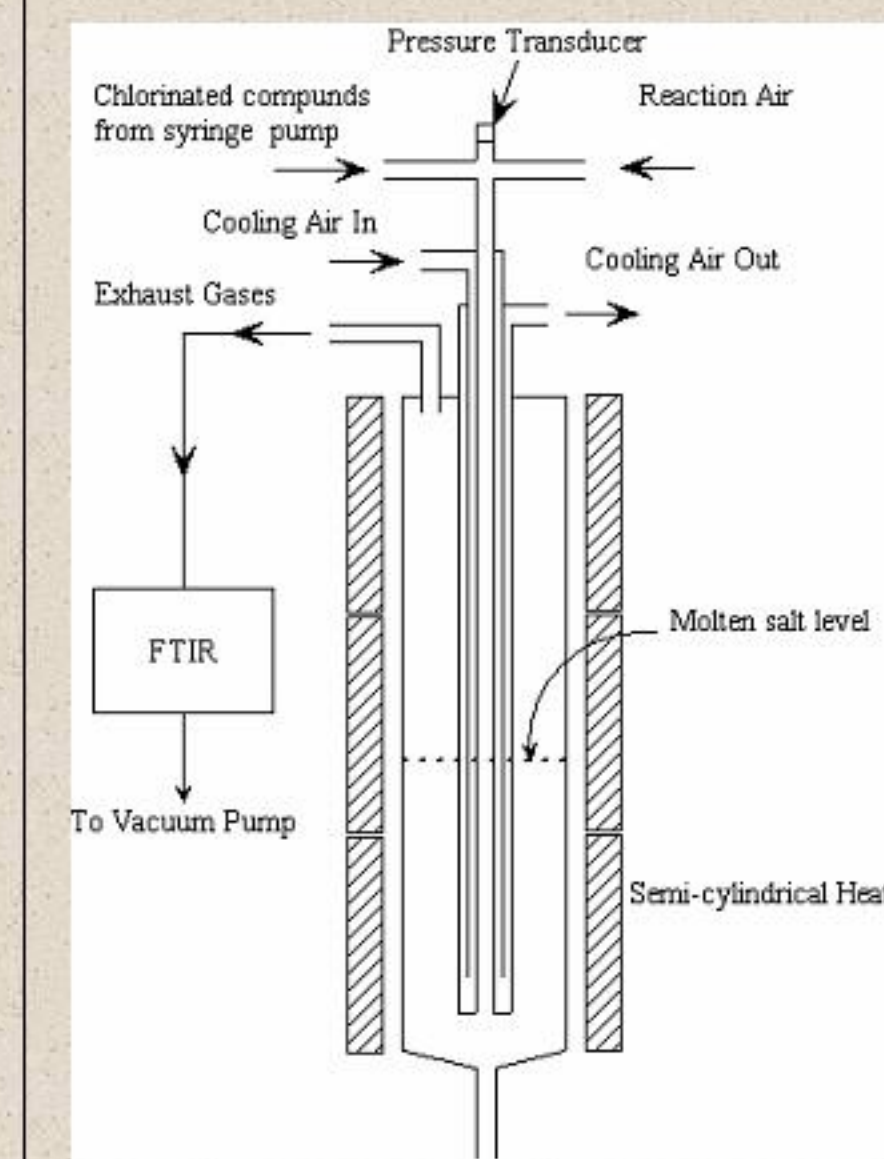


Figure 1: Schematic of the MSO reactor experiment.

Experimental Setup:

The MSO reactor vessel is a 3.5 inch OD, 3 inch ID and 3 foot long circular cylinder, with a tapered base plate welded on the bottom. This base plate has a 1/2-inch NPT port, to which is affixed a 6-inch long drain tube. The top of the vessel is an approximately 15-lb detachable plate with a sealing groove but no hard seal, designed to prevent overpressure of the reactor by simply lifting up freely. In the center of this plate is a 0.75 inch through hole for the air-cooled injector. Additional ports on the center plate are used for a pressure transducer, a 1/4-inch type-K shielded thermocouple for measurement of the molten salt bath temperature, and a gas sample port. The entire reactor is supported on a Unistrut frame, enclosed by steel doors, and has secondary containment to protect the laboratory and the operator(s) from any potential spill of molten salt.

The entire reactor is constructed of Inconel 600, a chromium-nickel alloy, to withstand both high temperatures (900 - 1100 °C) and chlorine attack. The high nickel content of the alloy provides considerable resistance under reducing conditions and makes it resistant to corrosion by a number of organic and inorganic compounds.

Sierra Instruments Mass-Trak™ flow controllers are used to control the reactor air flow and the cooling air to the injector. Liquid solutions were fed using a calibrated syringe pump, and metal solutions may also be introduced using a standard medical nebulizer to create an aerosol. The reactor operation is entirely controlled using an in-house program written in National Instruments' LABVIEW™ software. A schematic of the reactor is shown in Figure 1.

Analysis of gas-phase products was performed with a Bio-Rad Excalibur Fourier Transform Infra-Red (FTIR) spectrometer at 0.1 cm^{-1} resolution. This was coupled to a 1/2-liter long path gas cell (Infrared Analysis) configured for 1.2-meter (4-pass) operation. Samples were transferred from the MSO reactor to the cell in a heated line.

Intermediate Byproducts of Chlorobenzene Destruction Decrease with Increasing Oxygen and Temperature

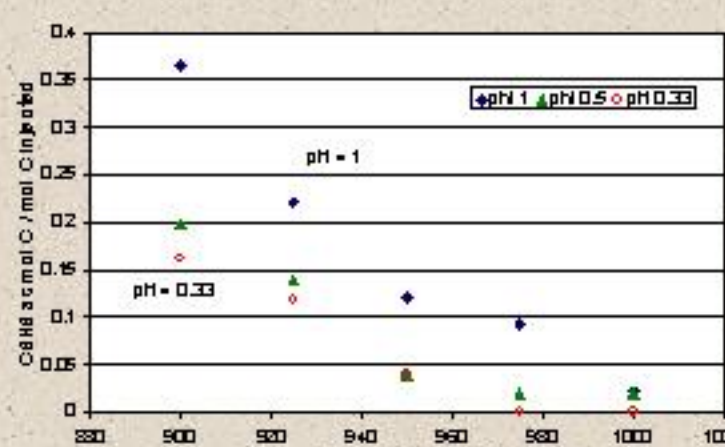


Figure 2: Benzene emissions for 11 cm bed height, as a function of equivalence ratio and temperature.

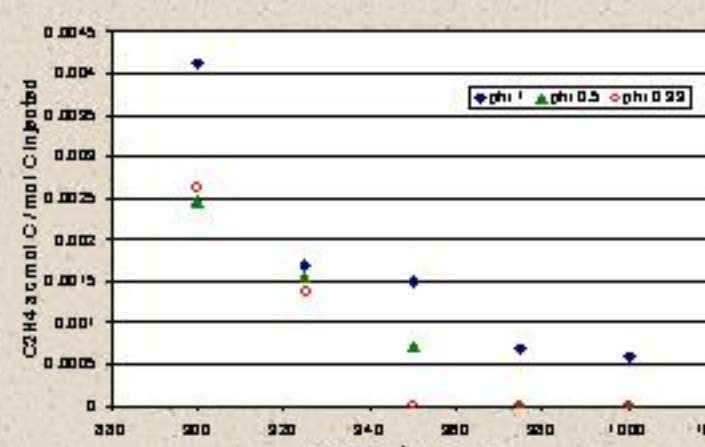


Figure 3: Ethylene emissions for 11 cm bed height, as a function of equivalence ratio and temperature.

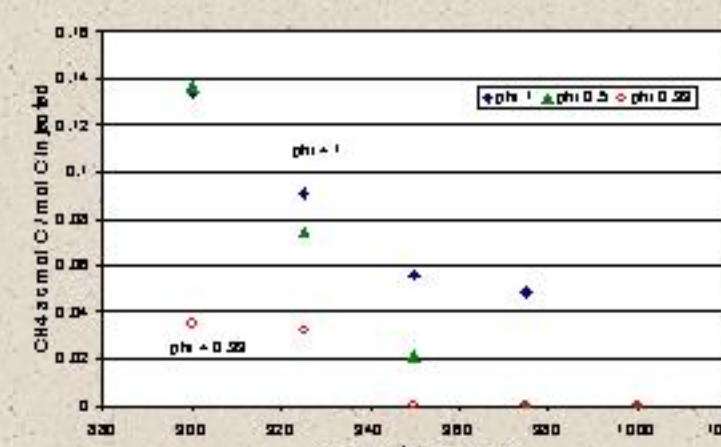


Figure 4: Methane emissions for 11 cm bed height, as a function of equivalence ratio and temperature.

Conversion to CO and CO2 Increases with Temperature for all Equivalence Ratios

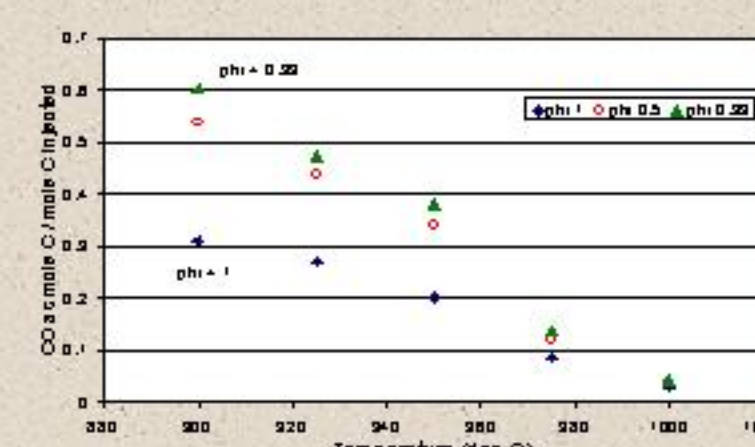


Figure 5: Carbon monoxide emissions for 11 cm bed height, as a function of equivalence ratio and temperature.

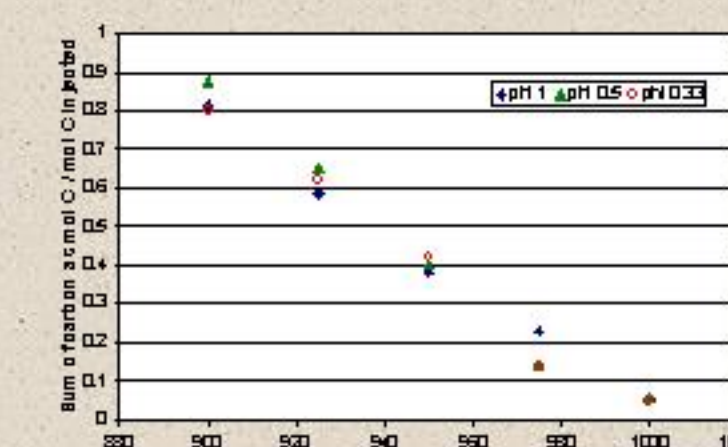


Figure 6: Sum of measured carbon emissions for 11 cm bed height, as a function of equivalence ratio and temperature. CO_2 is not measured, the decline is attributed to CO_2 conversion.

Surface Reaction Modeling

Detailed model used to include each of the following reactions individually:

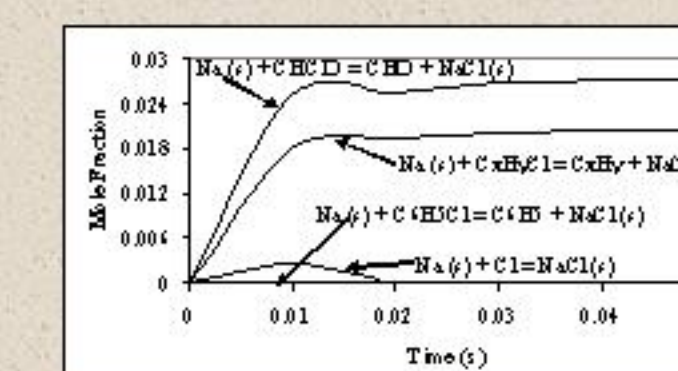
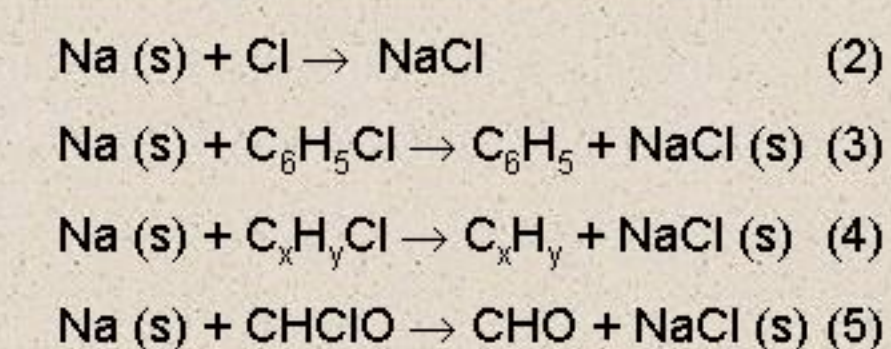


Figure 9: Concentration of HCl predicted by CHEMKIN for various surface reactions

Only inclusion of (3) avoids HCl production – HCl, the expected gas-phase product, was never observed in experiments.

What is Molten Salt Oxidation?

Molten salt oxidation (MSO) is a thermal destruction process in which a waste material is passed along with air through a molten salt, typically sodium carbonate. The molten salts may be mixtures of alkali or alkaline earth carbonates and halides. The salts provide excellent heat transfer and reaction media, catalyze oxidation of organics,[1] and neutralize acid gases such as hydrogen chloride by forming stable salts such as sodium chloride [2]. The relatively high thermal inertia of the melt resists changes in temperature resulting from sudden changes in the feed to heat transfer [3]. The literature suggests that it is a stable and controllable technology that provides in situ scrubbing of acid gases and particulates [4].

Given the promise of MSO technology and its potential for wide application to hazardous waste, mixed waste, and energetic materials disposal, additional details regarding the chemistry and operation of MSO reactors is needed. Previous approaches have essentially ignored the physics of the fuel and air bubbles as they rise through the salt, and do not treat the chemistry occurring in the salt in any detail. Information about the intermediate breakdown products of organic species and of the time/temperature history of waste in these reactors is required for optimal design of MSO systems. In addition, an improved understanding of the trapping of ash and inorganic materials is required for many hazardous and/or mixed waste streams.

Emissions as a Function of Bed Height Illustrate Importance of Residence Time

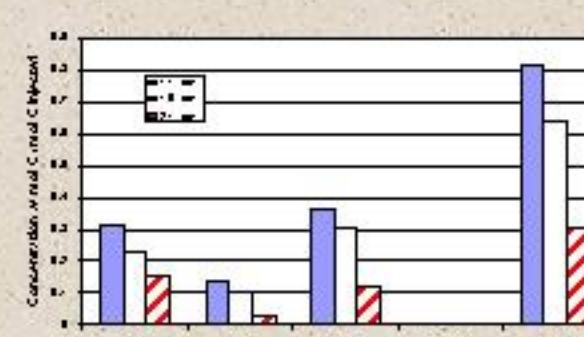


Figure 7: Measured emissions as a function of bed height at 900 °C.

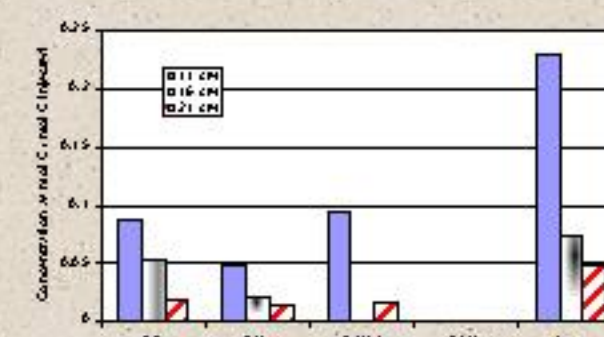


Figure 8: Measured emissions as a function of bed height at 975 °C.

Selected References

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5. B. Higgins, M. Thomson, D. Lucas, C. Koshland and R. Sawyer, *Chemosphere* 42 (2000) 703-717.
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Conclusions

Intermediate byproducts benzene, ethylene, methane, and CO are observed in the molten salt oxidation of $\text{C}_6\text{H}_5\text{Cl}$

→ C_6H_6 , C_2H_4 , and CH_4 decrease with increasing temperature and residence time.

→ CO increases with temperature as a proportion of the byproducts, indicating more complete oxidation at higher temperatures.

→ Total measured carbon (excludes CO_2) decreases with increasing temperature, suggesting more complete oxidation at higher temperatures.

No chlorinated products or byproducts are observed

Modeling suggests that chlorine is abstracted from $\text{C}_6\text{H}_5\text{Cl}$ directly by the salt