ON CATALYTIC PROPERTIES OF IRON ORE AND SINTER AND ITS ROLE IN DIOXIN FORMATION AND DESTRUCTION IN IRON METALLURGY

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Introduction

It has been reported that fly-ash from municipal solid waste incinerators contains considerable amounts of iron, within a range of 10-30 g/kg^[1]. This relatively high content as compared for example to copper (around 1 g/kg) can be responsible for at least part of the catalytic properties of this material as was proven by Halonen et al.^[2]. In said study iron (III) nitrate and chloride (hydrates) were co-fed with aliphatic fuel or injected directly into the flame. A whole array of chloroaromatics was found in the effluent gasses as well as on the fly-dust particles resulting from the combustion.

In another work focused mainly on Deacon-type reactions of several metal oxides^[3], it was observed that iron exhibits properties similar to copper, but much less pronounced. It was concluded though that it could also be an efficient oxychlorination catalyst.

Oxidative properties of iron (III) oxide as well as its ability to catalyze condensation reactions of chloroaromatics have been reported in the investigation performed by Zhicheng et al.^[4]. It was observed that this material promotes formation of PCDD/F's only until a certain concentration, beyond which its oxidative properties take over leading to destruction of chloroaromatics.

Our present work is focused on catalytic properties of much poorer defined material: iron sinter. This mixture of iron ore, coke (fuel) and lime (flux-agent) is a starting material in the pyrrometallurgy of iron. It has been found that in the process of sinter production significant proportions of PCDD/F's^[5] are released.

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Sintering

This slag-like, very porous material is formed in a continuous process in the sinter plant (see Figure 1). Upon ignition by gas-fueled burners (nr. 2 in the Figure) situated at the beginning of the belt, air is sucked through the sinter layer by means of wind legs (4). This moves the burning front down the layer while advancing towards the quench zone. At the end of the belt the sinter is quenched and collected (7). Material falling over from the belt is collected at the bottom of the wind-legs and reprocessed together with fresh mix. Resulting gas effluents upon dedusting (6) are led into a stalk.

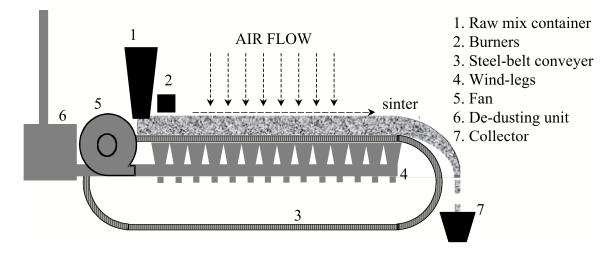


Figure 1: Schematic representation of a sinter-plant.

Results and discussion

Experiments with a fixed bed of sieved sinter (ca. 6 g, fraction with a grain size of 2-4 mm) have been conducted in a plug-flow reactor (details on the setup will be given in the presentation). Air was used as the carrier gas. A void residence time of ca. 4 s was maintained throughout all experiments. As an introductory example, a mixture of benzene and phenol (9:1 mol/mol) has been fed with a rate of ca. 1.9 g/h. The bed was kept at 450-500°C. Benzene reacted for ca. 25% and phenol for ca. 50%. In the outflow CO and CO₂ were detected as predominant products. In the liquid catch oxygenated phenol derivatives (i.e. p-

ORGANOHALOGEN COMPOUNDS 142 Vol. 41(1999) benzoquinone) and condensation products (diphenyl ether, benzofuran, and dibenzofuran) were present. As compared to non-catalytic runs with phenol in the feed^[6] the overall conversion is much higher (one half vs. 15% at 500°C), but the yields of oxidation and condensation products were also increased. Interestingly in the run with benzene only as a feed, no such products were found.

As the used sinter was found to be almost chlorine-free (mg/kg range), in the following series, HCl was co-fed together with the substrates. Substantial amounts of chloroaromatics were found in the products, for example dichlorophenol.

Results on experiments with different feed composition and varying T, so as to get a better insight into the potentials of sinter to form and to destroy pertinent organics, are also under way and will be discussed in more detail.

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