

Advancement in the Catalytic Combustion of Tannery Sewage Sludge by Studies in a Fixed Bed Reactor

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Abstract

Nowadays the processes used for the treatment of tannery wastewater produce sludge containing the pollutants removed from water. To minimize the needs of their final disposal an interesting alternative is the thermal treatment of the sludge. In the present study the combustion of tannery sewage sludge was evaluated in the absence and in the presence of cerium oxide or perovskites in a stainless steel fixed bed reactor.

A microreactor was employed in order to evaluate the reactivity of the mixture sludge-catalyst. Constant temperature oxidation tests were carried out in air flow. Exhaust gas composition was measured by on-line continuous analyzers for CO₂, CO, O₂ and SO₂ concentration. The test started raising the temperature to the desired value (T= 350°C) in static air. Then the air stream was fed to the reactor starting the oxidation. The feeding air flow rate was 30 L/h (STP). Operating pressure was 1 atm. The oxidation profiles evidence two main stages. The first occurring in the five minutes of reaction due to the combustion of volatiles and the second associated to the char combustion. The presence of catalysts determined an increase of the reactivity with respect to the sludge alone. CeO₂ catalyst enhanced mainly the reaction rate associated to the combustion of volatiles while it is not active in the combustion of the char. On the contrary, both LaFeO₃ and LnFeO₃ perovskites accelerated the latter step.

Key words: Catalytic combustion tannery sewage sludge, fixed bed reactor.

1 Introduction

Tannery wastewater treatment produces polluting sludge, containing both organic and inorganic substances. To minimize both requirements and costs for final disposal in landfills, a promising process is the thermal treatment of the sludge (Werther and Ogada, 1999). The most used thermal processes are carried out without the presence of catalytic materials that can realize an improvement of the incineration systems. In general, there are very few papers about the catalytic combustion of wastes, such as sludge. With reference to municipal solid waste (MSW), the existence of catalysts in the first step enhances the emission of volatiles from the MSW. When the concentration of volatiles around the MSW is high enough, the MSW ignites. Several catalysts were tested such as TiO₂, Al₂O₃, Fe₂O₃,

MnO₂/CuO/CaO demonstrating that with the addition of catalysts, the ignition of MSW is enhanced and in particular the most promising was MnO₂/KOH (Shen and Qinlei, 2006). The influence of catalysts was also investigated in the thermal incineration of industrial sludge. In this case K₂CO₃, NaCl and Al₂O₃ were used. The catalytic performance of K₂CO₃ was better than NaCl and Al₂O₃ (Jingyong et al., 2009).

Very recently, we studied the combustion behavior of dried tannery sewage sludge in the absence and in the presence of CeO₂ as catalyst, investigating the influence of catalyst loading. The presence of catalyst improved the selectivity of the sludge combustion process, reducing the emission of cyclic and aromatic substances, (Sannino et al., 2010b). Moreover by adding the catalysts in the step of sludge formation, i.e. immediately after the addition of flocculant into the coagulation-flocculation step of tannery wastewater, the combustion peak of the sludge organic fraction occurred at about 300 °C lower than in the absence of catalyst (about 525 °C), pointing out to a significant improvement of the oxidation process due to the catalytic material (Sannino et al., 2010a).

One of toxic heavy metals largely abundant in tannery sewage sludge is chromium. Chromium is usually present as oxide of trivalent chromium Cr(III), natural compound of low toxicity. On the other hand, hexavalent chromium Cr(VI) is a highly-toxic product. Consequently, a crucial point in the catalytic combustion of tannery sewage sludge is also to avoid the oxidation of Cr(III) to Cr(VI) (Chen et al., 1998).

This work is focused on the catalytic combustion of tannery sludge by using ferrites and CeO₂ in a fixed bed reactor.

2 Experimental

2.1 Materials and methods

Tannery sewage sludge samples were supplied by an Italian tannery wastewater treatment plant. Sludge conditioning was accomplished by preliminary sample milling. In particular sludge was dried in a stove at 80°C for 8 hours and then pounded in an electric mortar to a size between 180-250 µm.

CeO₂, LaFeO₃ and LnFeO₃ (Ln = Ce, La, Nd, Pr, Sm) as catalysts were mixed with sludge by gently grinding in an agate mortar to obtain a contact between the two solid phases. The obtained samples are named Cex, Lay and Lnz, where x, y and z represent the weight percentage of CeO₂, LaFeO₃ and LnFeO₃ in the mixture catalyst-sludge, respectively. The catalyst loading was in the range 3-6 wt%.

A microreactor was employed in order to evaluate the reactivity of the mixture sludge-catalyst. The microreactor comprises a 500 mm length, 17 mm I. D. stainless steel tubular flow reactor, heated by an electrical furnace. Constant temperature oxidation tests were carried out in air flow. ABB continuous analyzers determined exhaust gas concentrations: URAS 14 (for CO, CO₂ and SO₂ concentrations) and MAGNOS 106 (for oxygen). Signals from the analyzers were sent to a personal computer for data processing. Samples to be tested were diluted with quartz particles to avoid local raise of temperature during the tests. The diluted mixture was loaded to the reactor filling about 3 cm in length of its central zone. The test started raising the temperature to the desired value (T= 350°C) in static air. Then the air stream was fed to the reactor starting the oxidation. The feeding air flow rate was 30 L/h

(STP). Operating pressure was 1 atm. The initial mass of the sample was about 70 mg. The dispersion of catalysts before and after the combustion process was analyzed by SEM-EDAX technique.

3 Results and discussion

For all the samples, during the combustion test in the microreactor, there was the emission of CO₂, CO and SO₂. The behaviour of CO₂ produced from the oxidation of sludge in the absence of catalyst is depicted in Fig.1.

Two main stages can be distinguished. The first occurring in the five minutes of reaction is due to the combustion of volatiles and the second, with a maximum in CO₂ of about 0.14 vol. %, is associated to the char combustion. From these data it is possible to observe that gas-phase combustion of volatiles is the dominant reaction in sludge combustion (Cui et al., 2006) while char combustion is the slowest reaction step (Cui et al., 2006). Because the surface flux of water and volatiles probably prevents O₂ from reaching the pellet (Atimtay, 1987) char combustion follows after gas-phase combustion. A similar behavior was obtained for all the samples.

Table 1 summarizes the results obtained as a function of type and catalyst loading in terms of percentage of carbon burned (%C) evaluated with respect to the total sludge weight loaded in the microreactor.

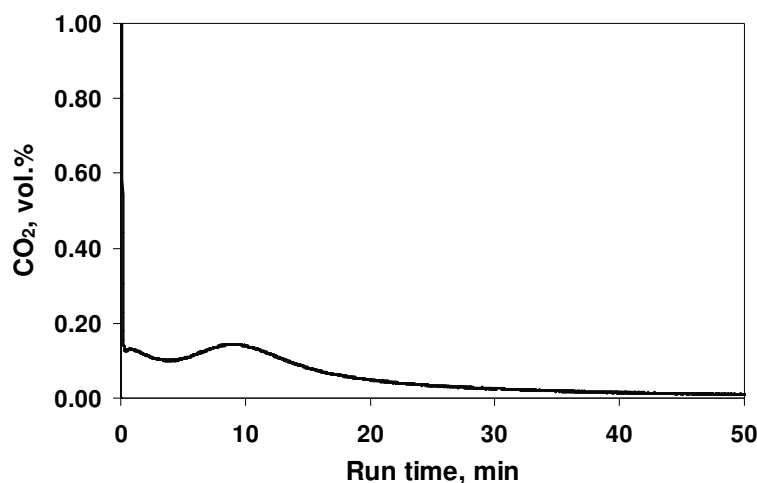


Fig. 1 Behavior of CO₂ produced during the oxidation of sludge in the absence of catalyst

The mass of carbon burned was calculated by the integral of the signal associated to the CO and CO₂ produced as a function of run time.

The amount of carbon burned increased from 18 to 25.6 wt % by increasing CeO₂ loading.

The highest value of %C was obtained in presence of LaFeO₃ and LnFeO₃ catalysts. In particular it was equal to about 32 wt % with respect to 18 wt % for the sludge alone.

These results clearly indicate that at fixed temperature, the presence of catalyst enhanced the combustion process allowing to burn a higher amount of organic substances contained in the sludge.

Tab. 1 Percentage of carbon burned evaluated with respect to the total sludge weight loaded in the microreactor

Catalyst	Percentage of carbon burned wt %
Sludge	18.0
Ce3	18.3
Ce4	18.9
Ce6	25.6
La3	30.4
La4	32.0
La6	29.1
Ln3	31.9
Ln4	30.4
Ln6	30.5

The results are also analyzed considering the reactivity defined as the rate of change of the carbon conversion degree dX/dt (where $X=(m_0-m)/m_0$, m and m_0 being the current and the total mass of carbon that can be burn, respectively) as a function of X (Ciambelli et al., 2007).

The comparison between sludge, La3, La4 and La6 is reported in Fig 2.

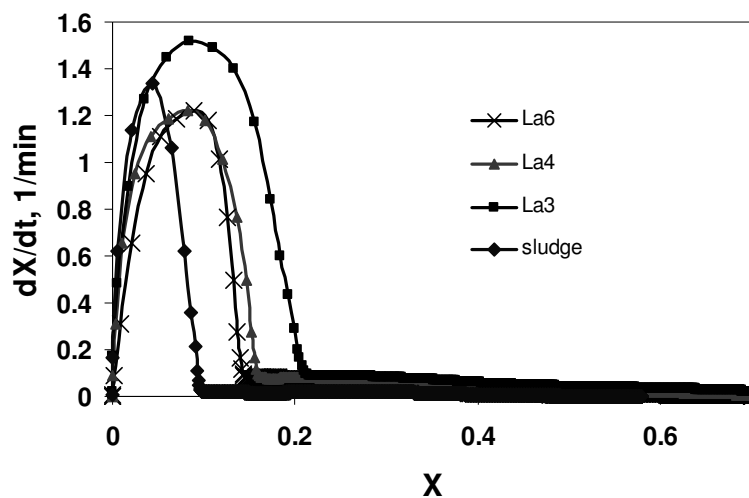


Fig. 2 Behavior of dX/dt as function of X for sludge, La3, La4 and La6

For all the samples, the reactivity initially increased by increasing X , reached a maximum and then decreased to about zero. The maximum reactivity value of the sludge was about 1.33 min⁻¹ and was reached at $X=0.043$. With the addition of catalyst, dX/dt reached the maximum value at $X=0.08$. The highest reactivity was obtained with La3 and its value was 1.5 min⁻¹, higher than sludge alone.

The behaviour of dX/dt for sludge, Ce3, La3 and Ln3 is shown in Fig.3.

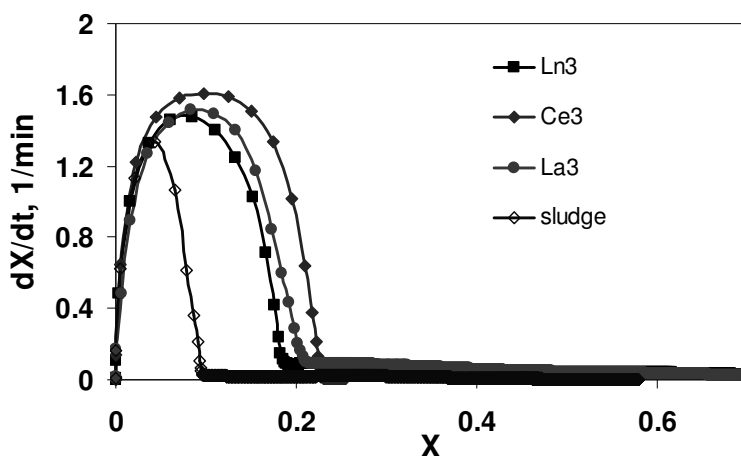


Fig. 3 Behavior of dX/dt as function of X for sludge, Ln3, La3 and Ce3

In all cases, the presence of catalysts determined an increase of the reactivity with respect to the sludge. Ce3 sample presented the highest dX/dt up to $X=0.24$ in which there was the combustion of volatiles.

Fig. 4 shows the profiles of dX/dt as a function of X in the range 0.2-1 for the same samples.

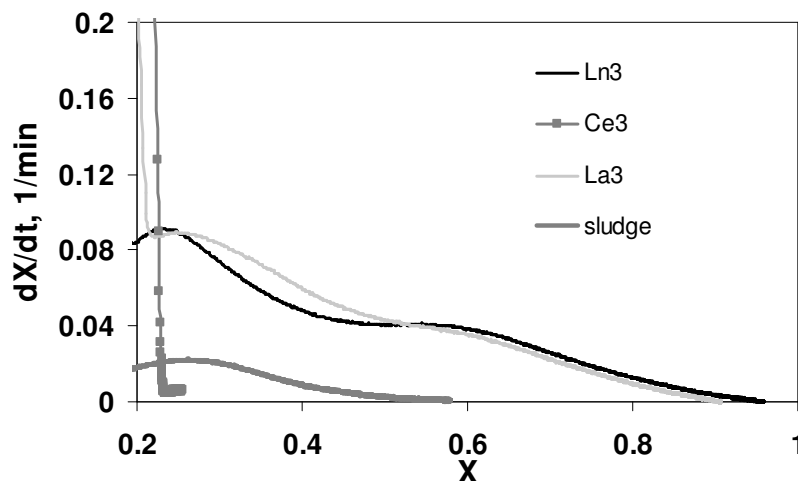


Fig. 4 Behavior of dX/dt as function of X in the range 0.2-1 for sludge, Ln3, La3 and Ce3

For X higher than 0.24, the reactivity of Ce3 sample is equal to zero underlining that CeO_2 catalyst enhanced mainly the reaction rate associated to the combustion of volatiles while it is not active in the combustion of the char. On the contrary, both $LaFeO_3$ and $LnFeO_3$ accelerated the latter step. In fact the two perovskites showed reactivity higher than sludge alone and allowed to burn all the organic fraction of the sludge.

The dispersion of catalyst inside the sludge matrix is analyzed using SEM-EDAX technique. Fig.5 shows La and Fe maps of mixture sludge- $LaFeO_3$ before (a) and after the reaction (b).

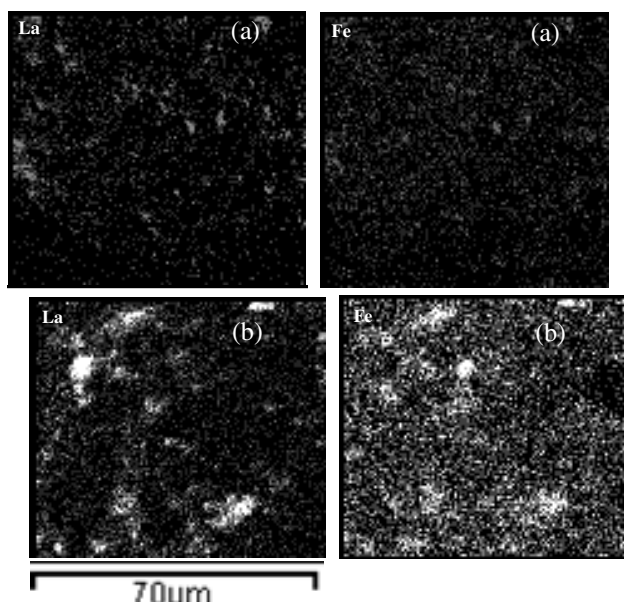


Fig. 5 Mapping of La and Fe before and after the combustion

Lanthanum was clearly correlated with a fraction of the iron contained in the sample and its presence is due to LaFeO_3 catalyst. Before the combustion, the catalyst particles are smaller and have a higher dispersion in the sludge matrix if compared with their distribution in the sample recovered after the combustion. This result indicates that agglomeration phenomena could be verified during the oxidation process.

4 Conclusions

In the present study a stainless steel fixed bed reactor was used for studying the combustion of tannery sewage sludge in the absence and in the presence of cerium oxide or perovskites as catalysts. The oxidation profiles evidence two main stages. The first occurring in the five minutes of reaction due to the combustion of volatiles and the second associated to the char combustion. The presence of catalysts determined an increase of the reactivity with respect to the sludge alone. CeO_2 catalyst enhanced mainly the reaction rate associated to the combustion of volatiles while it is not active in the combustion of the char. On the contrary, both LaFeO_3 and LnFeO_3 perovskites accelerated the latter step.

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