FORMATION OF POLLUTANTS AT INTERMEDIATE OXYGEN LEVEL IN SEWAGE SLUDGE COMBUSTION

Conesa JA, Galvez A, Font R, Fullana A
Department of Chemical Engineering, UNIVERSITY OF ALICANTE, Ap. 99, E-03080 Alicante, Spain

Abstract
Emissions evolved from the combustion of sewage sludges were studied at different oxygen concentration in order to evaluate the effect of the oxygen present, at a temperature of 850 ºC in a laboratory scale reactor. The reactor is specially designed to optimize the control of the ratio between the stoichiometric required and the actual level of oxygen.. More than 160 compounds, including carbon oxides, light hydrocarbons, PAHs and dioxins, have been identified and quantified. Dioxins and furans present a differentiate behavior.

Introduction

At present, the daily production of dried sewage sludge in Spain is 60-70 g per capita, and the annual production in 2005 was estimated at 1.5 Mt [1]. This massive quantity is a problem because of its enormous volume and its waste condition. There are several ways to treat the sewage sludge: landfilling, composting, energetic valorisation by combustion (thermal recycling) and ash dumping [2].

The energetic use of sewage sludge consists in its thermal recycling through the combustion of the sludge in controlled conditions, using the heat generated to produce thermal, mechanical or electrical energy. This is the case of using sewage sludge as a secondary fuel in industrial processes, which require a huge amount of energy. An example is the cement industry, which requires a lot of fuel to heat the cement kiln. As a consequence, it is common nowadays for the cement industry to regularly use sewage sludge as a secondary fuel in clinker kilns.

Materials and Methods

The material employed was dried sewage sludge (from Tarragona, Spain). An exhaustive analysis of the material used was made, and the results are shown in Table 1.

In order to avoid an instantaneous reduction of the partial pressure of oxygen in the proximity of the sample, as described by other authors[3], the experimental equipment used in the runs is able to maintain the oxygen ratio in the system at least for the necessary period of time. For this purpose, the experimental system consists in a quartz tube, 10 mm wide, where the residue to be studied is introduced uniformly occupying an appreciable length of the tube (approx. 35-40 cm.). A horizontal actuator introduces with a constant linear velocity the tube with the residue inside a furnace maintained at the desired temperature. A scheme of the system is shown:

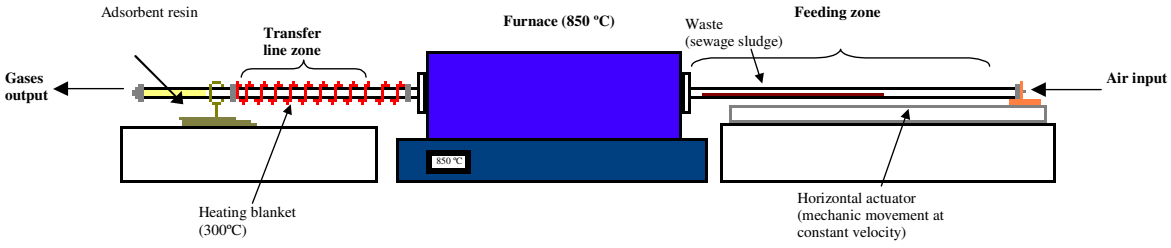

Figure 1. Experimental system

At the exit of the system a module for pollutant retention in a XAD-2 resin is disposed.

Runs have been performed with sewage sludge introduced to the furnace at five linear velocities, then producing five ratios of oxygen calculated using the following relationship:

$$\lambda = \frac{(m_{O_2})_{actual}}{(m_{O_2})_{stoic}} = \frac{m_{air} \cdot 23}{\frac{m_{sample}\nu}{L}\left(\frac{\%C}{12} + \frac{\%H}{4} + \frac{\%S}{32} - \frac{\%O}{32}\right)\cdot 32}$$

where:

%O, %H, %S, %C = weight percentage of oxygen, hydrogen, sulphur and carbon in the sludge
m_{air}= air flow rate (kg/s)
m_{sample}= weight of the residue (kg)
L= leght of tube occupied by the residue (m)
ν= linear velocity of introduction of the tube (m/s)

The specific conditions of the runs were: 1,5 g of sludge, air flow rate 100 ml/min, temperature 850 ºC. Velocities and subsequent oxygen ratios: 0.2 mm/s (λ = 1.25), 0.3 mm/s (λ = 0.83), 0.4 mm/s (λ = 0.63), 0.6 mm/s (λ = 0.42), 1 mm/s (λ = 0.25).

In each run gases (CO, CO_2, O_2 and light hydrocarbons) and condensable (PAHs and PCDD/Fs) were determined.

Sewage Sludge							
Humidity		10 % weight					
Ash content		26,2 % weight				**Cl^-**	1804 mg/kg
Low calorific value		4059,3 kcal/kg				**SO_4^{-2}**	**12408,5 mg/kg**
METALS (mg/kg)							
Cd	3,1	**Mn**	474,3	**Co**	35,5	**Sb**	23,8
Cr	47,7	**Ni**	55,4	**Tl**	8,4	**Sn**	11,7
Cu	318,2	**Pb**	316,3	**V**	85,7	**Hg**	<0,5
PAHs(mg/kg)							
Naphthalene	0,12			**Benzo(a)anthracene**		0,14	
Acenaphthylene	<0,01			**Chrysene**		0,06	
Acenaphthene	0,25			**Benzo(b)fluoranthene**		0,1	
Fluorene	0,21			**Benzo(k)fluoranthene**		0,08	
Phenanthrene	0,27			**Benzo(a)pyrene**		0,05	
Anthracene	0,19			**Indeno(1,2,3-cd)pyrene**		0,28	
Fluoranthene	0,21			**Dibenz(a,h)anthracene**		0,09	
Phenanthrene	**0,31**			**Benzo(g,h,i)perylene**		0,25	
PCDDs/Fs (pg/g)							
2,3,7,8-TCDF	2,76			**2,3,7,8-TCDD**		nd	
1,2,3,7,8-PeCDF	1,25			**1,2,3,7,8-PeCDD**		1,84	
2,3,4,7,8-PeCDF	1,91			**1,2,3,4,7,8-HxCDD**		0,62	
1,2,3,4,7,8-HxCDF	2,12			**1,2,3,6,7,8-HxCDD**		4,21	
1,2,3,6,7,8-HxCDF	1,33			**1,2,3,7,8,9-HxCDD**		2,09	
2,3,4,6,7,8-HxCDF	1,42			**1,2,3,4,6,7,8-HpCDD**		71,86	
1,2,3,7,8,9-HxCDF	0,46			**OCDD**		673,25	
1,2,3,4,6,7,8-HpCDF	23,56						
1,2,3,4,7,8,9-HpCDF	1,25						
OCDF	**104,42**			**TOTAL pg i-TEQ/g**		5,15	

Table 1: Characteristics of the sewage sludge used

Results and Discussion

The analysis of CO, CO_2 and O_2 give us an idea of the conditions of the combustion that actually were presented. Figure 2 shows the results.

The evolution of CO is the expected one, i.e., for a higher ratio of oxygen the level of CO produced is lower, indicating a good combustion. The oxygen and CO_2 evolutions are also logical, except in the last point probably due to dilution of the gas sample with air during sampling.

Respect to the evolution of light hydrocarbons, Figure 3 shows the results of the analysis of major gas hydrocarbons. The figure shows how the production of such compounds is reduced in an air-rich atmosphere. Major PAHs present a similar behaviour. Table 2 shows the results.

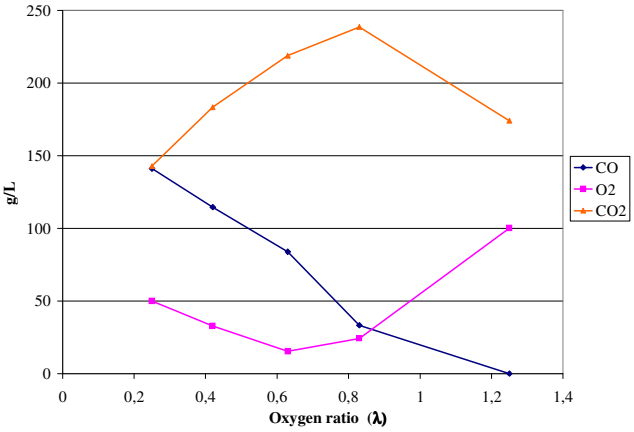

Figure 2. CO, CO_2 and O_2 evolution at different λ

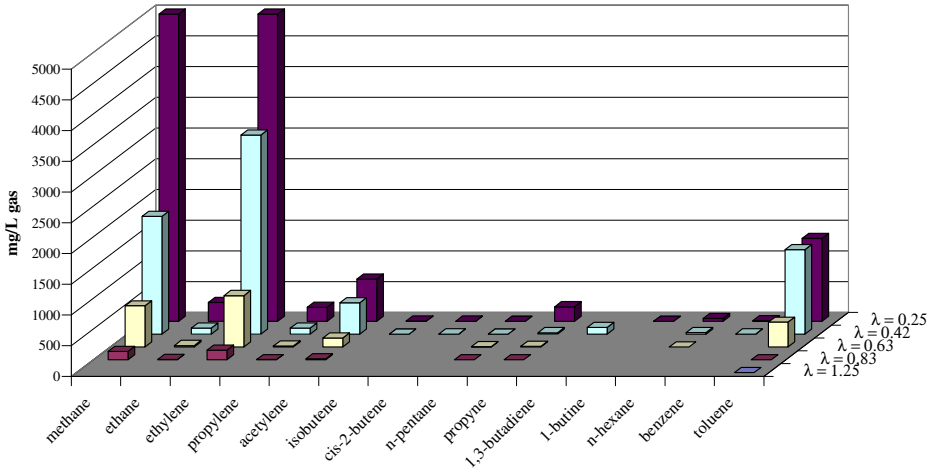

Figure 3. Emission of gas hydrocarbons in all the λ conditions studied

Dioxin and furan analysis evolved were also analysed. Figure 3 shows the results at the five conditions studied.

From this figure is clear that dioxin formation presents a maximum at intermediate oxygen levels, i.e., the presence of oxygen is necessary for dioxin formation, but an excess of oxygen will destroy conveniently these compounds. PCDF.

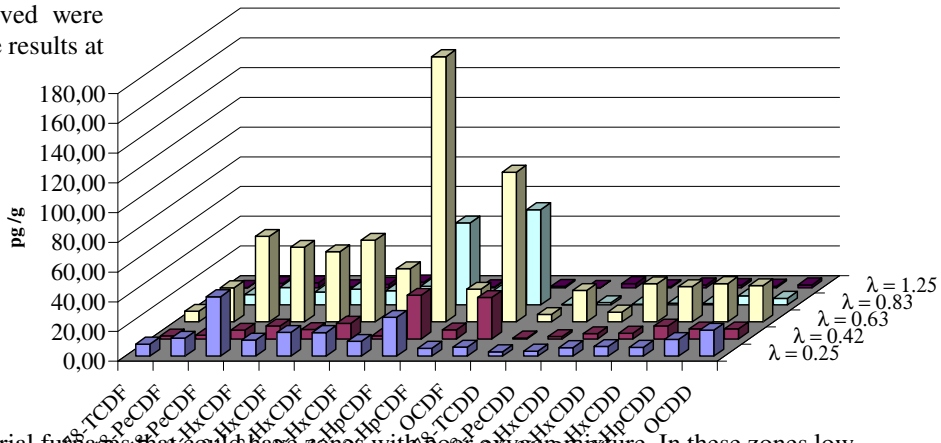

Figure 4. Emission of PCDDs/F in all the λ conditions studied

This result is important for industrial furnaces that could have zones with poor oxygen mixture. In these zones low oxygen ratios are present and the production of dioxins could occur. A system with the appropriate design,

temperature and oxygen level would reduce the emissions. Respect to dioxin and furan congener distribution, it is notorious that oxygen promotes the formation of the most toxic congeners, predominantly.

mg/kg (ppm)	λ = 1.25	λ = 0.83	λ = 0.63	λ = 0.42	λ = 0.25
Naphthalene	0,00	61,50	184,10	546,79	802,86
Acenaphthylene	0,11	3,88	38,35	188,27	267,88
Acenaphthene	0,01	0,10	0,61	4,28	12,67
Fluorene	0,06	2,84	10,09	28,32	57,96
Phenanthrene	0,07	5,72	20,01	61,89	80,83
Anthracene	0,01	0,46	3,77	14,20	18,98
Fluoranthene	0,01	0,88	5,10	14,40	17,01
Phenanthrene	0,01	1,29	4,15	12,29	11,57
Benzo(a)anthracene	0,00	0,14	0,87	2,41	2,56
Chrysene	0,00	0,24	1,02	3,55	3,15
Benzo(b)fluoranthene	0,00	0,29	0,48	1,21	2,27
Benzo(k)fluoranthene	0,00	0,07	0,16	0,58	0,61
Benzo(a)pyrene	0,00	0,11	1,00	1,63	1,28
Indeno(1,2,3-cd)pyrene	0,00	0,18	0,22	0,43	0,41
Dibenz(a,h)anthracene	0,00	0,00	0,03	0,15	0,10
Benzo(g,h,i)perylene	0,00	0,09	0,17	0,16	0,15
TOTAL	0,28	77,80	270,14	880,55	1280,28
Phenol	0,00	4,65	24,85	38,63	99,40
Diphenyl	0,00	16,16	16,59	17,84	63,22
Dibenzofurane	0,30	7,66	5,62	60,33	294,21

Table 2. PAHs emissions in all the λ conditions studied

Acknowledgements

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