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Study of catalytic post-treatment of the vapours from sewage sludge pyrolysis by means of γ-Al_2O_3

M. Azuara [a,*], I. Fonts [a,b], P. Barcelona [a], M.B. Murillo [a], G. Gea [a]

[a] *Thermochemical Processes Research Group (GPT), Aragón Institute for Engineering Research (I3A), Universidad de Zaragoza, Mariano Esquillor s/n, E-50018 Zaragoza, Spain*
[b] *Centro Universitario de la Defensa de Zaragoza, Ctra. Huesca s/n, 50090 Zaragoza, Spain*

HIGHLIGHTS

- ▶ γ-Al_2O_3 is useful for obtaining a better pyrolysis liquid from the point of view of its phase separation.
- ▶ γ-Al_2O_3 application makes it possible to lower the pyrolysis temperature.
- ▶ A general improvement in the higher heating value of the organic phases has been achieved.
- ▶ Energy content of the organic phase is comparable to a conventional fuel.

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ABSTRACT

The present work describes an experimental study on sewage sludge pyrolysis in a Fluidised Bed Reactor (FluBR) and the effect on the pyrolysis liquid product of passing the hot exhaust (pyrolysis) vapours through a Fixed Bed Reactor (FixBR) filled with gamma-alumina (γ-Al_2O_3). Experiments have been done at temperatures of 450 and 550 °C (FluBR) and 400 and 500 °C (FixBR). In the FixBR experiments, the bed was filled with inert sand and two different bed quantities of γ-Al_2O_3 (97.3 g, 194.6 g) giving a weight hour space velocity (WHSV) of between 0.6 and 1.8 h^{-1}. By means of this treatment, the pyrolysis liquid phase separation was improved, obtaining a liquid with two phases (organic and aqueous) instead of the three (two organic and an aqueous phase) usually obtained in sewage sludge pyrolysis without applying γ-Al_2O_3. This organic phase is quite interesting from the point of view of a possible application as bio-oil. Although the product distribution results using γ-Al_2O_3 show a slight liquid yield decrease for both temperatures (compared to sewage sludge pyrolysis without applying γ-Al_2O_3), there is a clear increase in the organic phase yield at 450 °C. Therefore, γ-Al_2O_3 application makes it possible to lower the pyrolysis temperature in order to maximise the organic phase in the sewage sludge pyrolysis liquid. Furthermore, a general improvement in the higher heating value of the organic phases has been achieved.

1. Introduction

Sewage sludge is the main waste produced during the purification of urban wastewater. Nowadays, due to the restrictive European legislation and to the increase in the standard of living, the production of sewage sludge has augmented significantly during recent years. Specifically, in the EU more than 10 million metric tons (dry solids) of sewage sludge are produced annually [1,2]. Application on agricultural land and incineration are two of the most common processes to manage this waste; however, these practices are becoming increasingly difficult due to health, environmental and social concerns. Consequently, alternative thermochemical processes such as gasification or pyrolysis are gaining recognition as promising alternatives for the valorisation and reduction of this waste [3–5]. Nowadays, much attention in sewage sludge research focuses on pyrolysis liquid as a possible solution in the search for new renewable alternatives for fossil fuel [6–9].

Pyrolysis can be used as a sewage sludge management process in which three products are obtained: char, a gas mixture and a liquid product with several phases. According to previous studies by the Thermochemical Processes Research Group (GPT), pyrolysis liquid from sewage sludge obtained in a fluidised bed consists of two organic phases (a light one and a heavy viscous one) and an aqueous phase [10,11]. The organic phases have relatively high heating values and could be applied as sources of chemicals or as fuels [12].

The aqueous phase has a high ammonia content suggesting its application as a fertiliser [13,14]. The organic phases, and especially the heavy phase, contain a significant amount of triglycerides and fatty acids [7,15,16]. Furthermore, in the light organic phase

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[*] Corresponding author. Tel.: +34 976762961.
E-mail address: mazuara@unizar.es (M. Azuara).

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there is a significant amount of aliphatic hydrocarbons. Triglycerides and fatty acids have an important presence in sewage sludge [17] and contribute substantially to the heating value of these phases, but they also increase their viscosity and their oxygen content. These two properties limit their use as fuel due to the difficulties of injection and atomisation [18] and to reduced storage and thermal stability, respectively [19].

The application of a catalyst in order to increase the pyrolysis liquid yield [20,21] and to improve its quality as fuel or chemicals is a common practice. Research in catalytic pyrolysis of wood is mostly focused on removing the oxygen content by using different catalysts such as Zeolites [20,22,23] or Al-MCM-41 (Mesoporous aluminosilicate molecular sieves) [24].

Research in catalytic pyrolysis of sewage sludge is quite limited, usually being based on previous works using lignocellulosic biomass. These studies also focus on the reduction of the oxygen content of the pyrolysis liquids for improving the hydrogen to carbon ratio [25,26]. Owing to the fatty acids content in sewage sludge, other authors have pointed out the good performance of activated gamma-alumina catalysts (γ-Al_2O_3) in the decomposition of these fatty acids and triglycerides. The aim is to produce aliphatic hydrocarbons such as alkanes and alkenes from lipids extracted from the sewage sludge [27–29].

Catalytic treatment with γ-Al_2O_3 may cause the transformation of the triglycerides and fatty acids into aliphatic hydrocarbons with the consequent improvements in the fuel quality of the sewage sludge pyrolysis liquid (homogeneity, heating value or viscosity, among others).

The main goal of this study is to know the effect of a γ-Al_2O_3 catalytic treatment on sewage sludge pyrolysis distribution products. Special attention is focused on the appearance of the liquid phase and on the higher heating value of the organic phase in lab-scale experiments. Furthermore, other characteristics of sewage sludge pyrolysis products have been analysed including the higher heating value (HHV) of the char, the gas composition and its lower heating value (LHV).

2. Materials and methods

2.1. Materials

2.1.1. Raw material

Anaerobically digested and thermally dried sewage sludge provided by a Spanish wastewater treatment plant was used as raw material. Sewage sludge (SS) samples were ground and sieved between 250 and 500 μm prior to each experiment. The proximate, elemental and heating value analyses of the sewage sludge are shown in Table 1.

Table 1
Raw material analyses (as received).

Proximate analysis[a]	Analytical method	wt.%
Total moisture	ISO-589-1981	7.1
Ash	ISO-1171-1976	41.0
Volatile matter	ISO-5623-1974	46.6
Fixed carbon	By difference	5.3
Elemental analysis (organic fraction)[a]		wt.% (dry basis)
C (wt.%)	ASTM D 5373	29.8
H (wt.%)	ASTM D 5373	3.9
N (wt.%)	ASTM D 5373	4.2
S (wt.%)	ASTM D 5373	0.9
O (wt.%)	By difference	13.1
Heating value		
HHV (MJ/kg)	ASTM D-3286-96	11.9

[a] Analyses performed by the *Instituto de Carboquímica* (CSIC, Zaragoza, Spain).

2.1.2. γ-Al_2O_3

The chemical composition of γ-Al_2O_3 is shown in Table 2. The main physical properties are: 142 m^2/g surface area (BET), 10.5 nm average pore size, 150–350 μm particle size and 0.4 cm^3/g mesopore volume (BJH).

For its activation, the γ-Al_2O_3 was calcined at 600 °C for 3 h and kept in a desiccator prior to the experiment.

2.1.3. Inert sand

Inert sand, provided by Panreac, was mostly composed of SiO_2 with a particle size between 0.25 and 0.30 mm. This material was used to compare the possible influence of the FixBR temperature on gas and liquid yield without using the γ-Al_2O_3.

2.2. Experimental system

The sewage sludge pyrolysis runs were carried out in a laboratory scale (<1 kg/h) Fluidised Bed Reactor (FluBR) operating at atmospheric pressure with a continuous feed and ash removal system and heated by means of an electrical furnace. Further information about the FluBR lab-scale plant can be found elsewhere [16,30–32].

Experiments with catalytic treatment were performed using a tubular Fixed Bed Reactor (FixBR) made of AISI 310 steel (length = 25 cm, inner diameter = 5.4 cm) (see Fig. 1). The FixBR was connected by means of a hot filter to the FluBR and placed next to the FluBR. Pyrolysis vapours flowed from the top of the FixBR to the bottom section. The available length of catalyst bed (L) in the FixBR, taking into account the distributor plate (placed 6 cm from the gas output), was between 0 and 15 cm. The FixBR was heated with electrical resistances and its temperature controlled using appropriately placed thermocouples and a PDI controller.

A liquid condensation system placed next to the FixBR ensured the collection of the pyrolysis liquids. This system was composed of two condensers cooled with ice and an electrostatic precipitator (ESP). The composition of the non-condensable gases produced during the pyrolysis was determined on-line using a micro gas chromatograph (Agilent 3000A) connected down flow below the pyrolysis liquid condensation system. A schematic diagram of the whole experimental set-up is shown in Fig. 2 where the spatial distribution of the equipment can be seen.

2.3. Experimental procedure

First, the FluBR and FixBR temperatures and the solid feed rate (g/min) were adjusted. The pyrolysis experiments were carried out during 2 h using nitrogen as fluidisation agent. Char obtained in a previous experiment at the same pyrolysis temperature was used as the initial bed material inside the FluBR in order to minimise the effect of the non-steady state [33,34]. The mass balance was done for each pyrolysis experiment taking into account the yield obtained for each product: gas, liquid and char, as well as coke deposition on the γ-Al_2O_3.

Table 2
γ-Al_2O_3 chemical composition.[a]

Compounds	wt.%
Al_2O_3	95.0 min
C	0.05 max
SiO_2	0.035 max
Fe_2O_3	0.025 max
Na_2O	0.005 max
TiO_2	0.27 max

[a] Data provided by Sasol Germany GmbH.