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Characterisation of tar from sewage sludge gasification. Influence of gasifying conditions: Temperature, throughput, steam and use of primary catalysts

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HIGHLIGHTS

- Tar removal efficiencies of olivine, alumina and dolomite are compared.
- Higher throughputs decreased the H_2 content of the syngas and increased tar production.
- The use of steam improved by 20% catalysts performance in gravimetric tar removal.
- Only dolomite performance remained fairly constant over the range of studied throughputs.
- Under the tested experimental conditions, syngas dew point never dropped below 108 °C.

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ABSTRACT

This work shows the influence of parameters such as temperature, throughput (TR), the gasifying agent and the use of catalysts (olivine, alumina and dolomite) on the products resulting from the gasification of sewage sludge on a fluidised bed. An increase in temperature of between 750 and 850 °C rises the production of combustible gas and reduces the production of gravimetric tar (by 65%, at TR = 110 kg/h m^2, and 49% at TR = 322 kg/h m^2), while the increase in TR at a given temperature produces the contrary effects. An analysis of the composition of the tar detected by gas chromatography (GC), shows that higher temperatures increase the concentration of polycyclic aromatic hydrocarbons (PAH). In spite of all the catalysts being active in tar removal, dolomite showed the most marked results in the air tests, with a reduction in the production of gravimetric tar of 40–50% and a conversion of the heavy PAHs (4–7 aromatic rings) of up to 90%. The combined use of a catalyst and air + steam increases the H_2 and CO_2 content in the synthesis gas and reduces the CO, CH_4 and C_nH_m production, in addition to improving by 20% the catalysts performance in gravimetric tar removal compared to the tests with catalyst and air. Under the evaluated gasification conditions, the dew point of the gas was never below 108 °C, which means that technical problems could be expected due to tar condensation if the synthesis gas were to be used in combustion engines without applying additional tar removal measures.

1. Introduction

Gasification is the thermal process by which the carbonaceous content of a material is converted to combustible gas and ash in a reducing atmosphere. The most used gasifying agents are air, oxygen, steam or mixes of them [1,2].

Gasifying sewage sludge from wastewater treatment plants may be an alternative management option to conventional disposal routes for this waste (agricultural use, landfilling or incineration, among others). This technology recovers energy from the sewage sludge by producing a synthesis gas (syngas, mainly a mix of H_2, CO, CO_2, CH_4 and gaseous hydrocarbons) that can be burnt to produce energy in gas engines, gas turbines, and can be used as raw material in the production of Fisher–Tropsch fuels, dymethyl ether (DME) and synthetic natural gas (SNG) [3].

Although the main product in gasification is the syngas, depending on the characteristics of the sludge and the gasification conditions, variable quantities of a solid waste (char) and a condensable product (tar) are also obtained. The presence of tar is a large drawback for using the syngas in most of its potential applications as it causes problems of corrosion and obstruction in

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equipments and pipes due to its viscous nature and its propensity to condense, even at high temperatures [4].

Gasification tar is the heterogeneous fraction of organic compounds with a molecular weight higher than benzene that are produced by the thermochemical reactions that occur during gasification [5–7].

The application of measures to reduce the tar produced in gasification has been studied by many authors [8,9]. These measures are usually grouped into primary measures (applied in the gasifier) and secondary measures (physical–chemical treatments applied downstream the gasifier).

Primary measures include design criteria for the gasifier, modifying the gasification conditions and using catalysts inside the reactor. They are more economical than the secondary measures since they avoid or reduce investment in additional equipment such as gas scrubbers and secondary reactors [10].

For each specific gasifier design, two essential parameters for achieving an acceptable syngas quality are the temperature and the equivalent ratio (ER) [11], this latter defined as the ratio between the flow rate of air introduced into the gasifier and the stoichiometric flow rate of air required for complete combustion of the sludge. Both factors influence the composition of the syngas and the carbon conversion by means of oxidation and gasification reactions [12–14].

Tar decomposition reactions (cracking and reforming) are endothermic and, therefore, favoured by increasing the temperature. However, the temperature affects the molecular structure of the compounds making up the tar fraction. During the volatilisation of the organic matter (300–500 °C), the so-called "primary tar" is produced, made up of a complex mix of hydrocarbons containing heteroatoms (alcohols, acids, ketones and esters). At temperatures >600 °C this primary tar rapidly decomposes into light gases, low molecular weight hydrocarbons and substitution aromatic compounds that are more stable at the temperature than aliphatic chains. This secondary tar is made up of aromatic hydrocarbons that contain from mono-aromatic to poly-aromatic compounds. At temperatures >900 °C these aromatic compounds are converted into soot through polymerisation reactions [15].

As previously stated, the ER is related to the amount of oxygen used in the gasification process and usually varies between 0.2 and 0.4. A high ER means adding more oxygen to the gasifier, which increases the CO_2 content and reduces the calorific value of the gas produced. A low ER means a reduction in the gasification temperature (the oxidation and partial oxidation reactions are exothermic) and an increase in tar production [13,16,17]. Regarding the composition of the tar, the increase in ER leads to a drop in the fractions made up of heterocyclic, mono-aromatic hydrocarbon and polycyclic aromatic hydrocarbon compounds [18].

The gasification atmosphere also influences the amount and the composition of the tar formed. Using steam as gasifying agent favours the tar reforming reactions, carbon conversion through the water–gas reaction and increases the production of hydrogen by the water–gas shift reaction [19].

Of the primary measures for reducing tar formation, the presence of certain catalysts in the gasifier increases the speed of the hydrocarbon reforming reactions [20]. Among the different options available, it has been shown that dolomite, olivine and alumina are effective for producing hydrogen and eliminating tars under fluidisation conditions [21]. Dolomite and olivine are natural minerals whose catalytic activity is mainly due to the presence of magnesium and iron oxides [22]. Although dolomite is more effective at removing tar than olivine, the latter has greater mechanical strength [23], which makes it an interesting option in fluidised bed gasification processes. Alumina is considered as an acid catalyst and contains hydroxylated alumina oxides. The catalytic activity of the alumina is comparable to that of dolomite. However, one of its drawbacks is its deactivation through the appearance of coke on its surface [9,24].

Regarding the use of catalysts, it should be mentioned that their effectiveness in eliminating tars can be highly influenced by the throughput (henceforth TR), which is defined as the kilograms of sewage sludge "as received" fed to the gasifier per hour and per square metre of cross sectional area of the gasifier. According to [25], some studies carried out at small scale use very low TRs (close to 100–150 kg/h m^2), which means that the tar removal efficiencies found may differ greatly from what would be obtained on a commercial scale under TRs close to 750 kg/h m^2. Bearing this in mind, it is necessary further develop the analysis regarding how the TR influences the tar removal efficiencies of the different catalysts.

In [26], the influence of TR, the gasifying agent (air and air + steam) and the use of dolomite in the gasification products in a fluidised bed reactor at 800 °C was studied. This study goes deeper into the results obtained then. To do this, tests at different temperatures were conducted (750, 800 and 850 °C), with different throughputs, using not only dolomite but also olivine and alumina as primary catalysts. The tests with catalyst were conducted in the presence of air and an air + steam mix. In this way, additional information was obtained on the influence of the different parameters in gasification products. The following results analysis is mainly focused on the composition of the syngas, the gravimetric tar production and the conversion of different tar classes that are

Table 1
Elemental analysis of sewage sludge (dry basis) from a sewage sludge drying plant.

Parameter		Value[a]	Analytical method
Moisture (%)		8.7 ± 2.1	UNE-EN 12880-2001
Organic Mat. (%)		58.3 ± 3.2	UNE-EN 12879-2001
Ash (%)		41.7 ± 3.2	UNE-EN 12879-2001
Carbon (%)		29.5 ± 1.2	Elementary micro analyser LECO CHNS-932
Hydrogen (%)		4.8 ± 0.2	
Nitrogen (%)		4.1 ± 0.2	
Sulphur (%)		1.6 ± 0.1	
Oxygen (%)	By difference	18.3 ± 4.5	
Heavy metals (mg/kg)	Cu	382.2 ± 4.1	UNE-EN 13346-2001
	Ni	70.0 ± 0.4	
	Pb	109.6 ± 0.6	
	Zn	1926.2 ± 44.4	
	Cd	3.1 ± 0.1	
	Cr	117.3 ± 8.8	

[a] Mean value of three analytical assays.