

# Kinetic Modeling of Sewage Sludge Combustion and Gasification for Energy Generation

Francesco Negri<sup>a,b</sup>, Francesco Gallo<sup>a</sup>, Flavio Manenti<sup>b,\*</sup>

<sup>a</sup>Itelyum Regeneration SpA, Via Tavernelle 19, Pieve Fissiraga 26854, Lodi, Italy

<sup>b</sup>Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Milan 20133, Italy  
[flavio.manenti@polimi.it](mailto:flavio.manenti@polimi.it)

Sewage sludge is a waste that is difficult to valorize due to its high ash content and presence of pollutants. Thermal conversion of sewage sludge in waste-to-energy systems allows to add value to this waste by exploiting its energy content and significantly reducing the amount of final waste to be disposed in landfill, but these processes must be modeled in detail to obtain reliable results. The GasDS simulation suite can be used for such purpose since it is an advanced tool for the detailed simulation of complex kinetic, mass, and energy transfer phenomena happening inside of gas-solid reacting systems. The peculiar characteristics of sewage sludge both in terms of chemical-physical properties and thermal decomposition behavior make it necessary to add new information in the GasDS database. A simplified kinetic model based on lumps (sludge, gas, tar, char, H<sub>2</sub>O) and two consecutive pyrolysis reactions is proposed and fitted on experimental data, leading to a reaction scheme that can be implemented in the modeling suite. Simulations of air-based sewage sludge thermal conversion systems working at different degrees of oxidation severity are performed, and results regarding flowrate, temperature, and composition of gaseous effluent are shown. Aspen HYSYS simulation software is used to model waste-to-energy systems for the production of electric power. Key performance indicators such as the specific net power output, energy yield, and CO<sub>2</sub> emissions are shown. Gasification-based combined cycles perform better with increasing ER and perform worse than combustion-based Rankine cycles at low ER values.

## 1. Introduction

Sewage sludge is a waste produced by wastewater treatment plants. This substance is difficult to valorize since it typically shows a high content in ash compared with other bio-based feedstock, reaching approximately 50% of inorganic content, and it contains a large number of contaminants such as persistent pollutants and heavy metals (Mateo-Sagasta et al., 2015). For this reason, the main route for sewage sludge disposal starts with a suitable stabilization that may be performed via anaerobic digestion, aerobic digestion, chemical treatment, followed by mechanical and/or thermal dewatering, ending with permanent disposal via landfilling (Kelessidis and Stasinakis, 2012). A possible way to valorize sewage sludge while also significantly limiting the possible drawbacks coming from its pollutants is represented by thermal processes (Werther and Ogada, 1999). Stabilized and dewatered sewage sludge is a suitable feedstock for waste-to-energy plants, where it can be used to generate electrical and/or thermal energy through complete thermal oxidation (Stehlík, 2009). There is also the possibility to stabilize the sludge by treating it at high temperature and pressure through the hydrothermal carbonization process, leading to the production of a type of bio-char called hydrochar (Kambo and Dutta, 2015). Hydrochar can then be valorized through energy generation (Prifti et al., 2021) or even production of high-value chemicals (Negri et al., 2022). It is important to have a detailed description of the complex kinetic, mass and energy transfer mechanisms that take place in sewage sludge thermal conversion processes in order to obtain a precise and reliable estimate of the performances for such systems. The GasDS suite is a powerful tool that can be used to achieve this objective since it is capable of describing in great detail chemical kinetics and transport phenomena happening in thermal conversion processes both for biomass (Ranzi et al., 2014) and coal (Corbetta et al., 2015). It has been shown that the suite can be successfully used when sewage sludge is pretreated via hydrothermal carbonization since the resulting hydrochar has a composition resembling that of coal, making it possible to model its thermal decomposition with suitable species contained

in the software database (Negri et al., 2022). However, this is not true anymore when considering sewage sludge stabilized through aerobic or anaerobic digestion, since its composition and pyrolysis behavior are quite peculiar and do not fall within the data domain already contained in the suite. Thermal conversion processes for such a complex substance can still be successfully modeled with the GasDS suite, but it is first necessary to add information to the database. Specifically, it is required to characterize the sewage sludge in terms of chemical-physical properties and thermal degradation kinetics. The software can then integrate this information with kinetic schemes for the description of secondary gas-phase reactions and it is also capable to analyze the mass and energy transfer phenomena for intra- and inter- particle sections (Ranzi et al., 2016). This paper illustrates a detailed evaluation of sewage sludge valorization through thermal oxidation for waste-to-energy purposes. The evaluation is carried out by including a dedicated species in the GasDS suite along with a thermal decomposition kinetic model developed starting from literature data (Stammach et al., 1989). Simulation results are shown and then used to model different systems for the production of electrical energy from thermal conversion of sewage sludge at different degrees of oxidation severity by using the simulation software Aspen HYSYS. The first system is a combustion based Rankine-cycle, the second one is a gasification-based combined cycle. Key performance indicators such as net power output, energy yield, CO<sub>2</sub> emissions are shown.

## 2. Materials and methods

Chemical-physical properties for sewage sludge stabilized via aerobic digestion are included in the GasDS suite database. A dedicated and simplified thermal degradation kinetic model is then proposed and obtained starting from literature data. The electrically heated experimental system is composed of a fluidized bed with a diameter of 0.14 m and a height of 0.8 m fed continuously by screw conveyors. The char is continuously discharged and the pyrolysis gas first goes through a cyclone, then enters another fluidized bed for possible further conversion, then enters a second cyclone, and finally it is cooled using three coolers to separate condensable fractions. Temperatures between 450-650°C and residence times between 25-260 min have been investigated (Stammach et al., 1989). Air-based processes at different oxidation severities are analyzed with the suite, and the results are used to model waste-to-energy systems in Aspen HYSYS software.

### 2.1 Kinetic model for sewage sludge thermal degradation

Sewage sludge stabilized via aerobic digestion (SS) is added to the GasDS suite database as a new reacting solid species by including literature data regarding density, specific heat, thermal conductivity, darcy coefficient (Drechsel et al., 2015), CHNSO composition, ash, moisture (Stammach et al., 1989), and LHV (Font et al., 2005). Chemical-physical data are shown in Table 1.

*Table 1: Chemical-physical properties for aerobically stabilized sewage sludge*

Properties	Values	Units of measure
Density at 25°C	1250	kg/m <sup>3</sup>
Specific heat at 25°C	1390	J/kg/K
Thermal conductivity at 25°C	0.048	W/m/K
Darcy coefficient	0.03	-
C	27.5	wt.% (dry basis)
H	3.8	wt.% (dry basis)
N	3.3	wt.% (dry basis)
S	0.5	wt.% (dry basis)
O	19.0	wt.% (dry basis)
Ash	45.9	wt.% (dry basis)
Moisture	5.1	wt.% (total)
LHV	12.6	MJ/kg (dry basis)

It has been observed that the combustion of aerobically stabilized sewage sludge proceeds at first with a simple pyrolytic decomposition that starts around 170-200°C, leading to the production of gas, tar, and water that are further decomposed in secondary gas-phase reactions. Then, at 450-500°C char is formed in a consecutive reaction, and it starts to oxidize between 450-550°C (Font et al., 2005). The simplified kinetic scheme that is proposed in this paper for sludge pyrolysis is based on a lumped approach including gas, tar, char, and moisture already used in scientific literature (Stolarek and Ledakowicz, 2001), and it is shown in Figure 1. The scheme includes a first, direct pyrolysis of sewage sludge leading to the production of gas, tar, and water, which is representative of the low-temperature pyrolysis observed in scientific literature. Then, the scheme also considers the decomposition of the most unstable fraction of the tar lump (the one containing more oxygen),

leading to the production of secondary pyrolysis products such as gas, char, and a more stable tar fraction having no oxygen content. When looking at experimental data, almost every fraction either monotonically decreases (sludge) or increases (gas, water, char) with the exception of tar, which is the only lump showing a maximum yield around 500°C (Stammach et al., 1989). The proposed kinetic scheme mimics this behavior by considering tar as the only fraction that is unstable enough to further decompose at higher temperature.

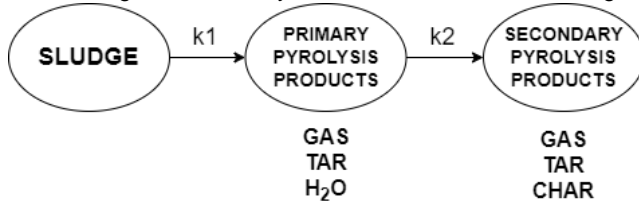


Figure 1: Lumped kinetic scheme proposed for aerobically stabilized sewage sludge thermal decomposition

The numerical procedure used to fit the kinetic model with experimental data starts with the definition of the mass balance that characterizes the system, which is shown in Eq(1).

$$\left\{ \begin{array}{l} \frac{d\omega_{SS}}{dt} = -k1 \cdot \omega_{SS} \\ \frac{d\omega_{GAS}}{dt} = k1 \cdot \omega_{SS} + k2 \cdot \omega_{TAR3} \\ \frac{d\omega_{TAR1}}{dt} = k1 \cdot \omega_{SS} + k2 \cdot \omega_{TAR3} \\ \frac{d\omega_{TAR3}}{dt} = k1 \cdot \omega_{SS} - k2 \cdot \omega_{TAR3} \\ \frac{d\omega_{CHAR}}{dt} = k2 \cdot \omega_{TAR3} \\ \frac{d\omega_{H_2O}}{dt} = k1 \cdot \omega_{SS} \end{array} \right. \quad (1)$$

Where  $\omega_i$  is the mass fraction of the  $i$ -th species. Several approximations have been introduced in the mass balance. First, it is assumed that each decomposition reaction is irreversible and follows a simple first order kinetics. Tar is decomposed in two fractions, both present in the GasDS database and respectively representing a stable, oxygen-free fraction (TAR1) and a reactive, oxygen-rich fraction (TAR3). The kinetic constants follow a simple Arrhenius law. The fitting between the proposed kinetic model and experimental data is performed by applying the least squares method, with pre-exponential factors and activation energies for  $k1$  and  $k2$  as variable parameters. The composition of the gas phase is obtained from literature data (Stammach et al., 1989). The stoichiometry of the reaction considers an equivalent formula for sewage sludge obtained from its elemental composition ( $C_6H_{10.2}O_{3.1}$ ) and it is calculated so that atomic balances are respected and experimental yields are coherent with the literature (Stammach et al., 1989). The results from the fitting procedure are shown in Table 2, including pre-exponential factors (A) and activation energies (E). Sulfur and nitrogen kinetics are not considered since their evolution can be reliably predicted by a simple thermodynamic analysis, which is outside the scope of this work (Ranzi et al., 2014). Given that the equivalent formula for SS is  $C_6H_{10.2}O_{3.1}$ , and that TAR1, TAR3, and CHAR respectively have the formulae  $C_{12}H_{11}$ ,  $C_{11}H_{10}O_2$ , and C, the stoichiometry of the proposed reactions does not violate the principle of mass conservation on an atomic level since the balances on carbon, hydrogen, and oxygen sum to zero with an error smaller than  $1E-3$ , which is considered acceptable.

Table 2: Stoichiometry and kinetic data for the proposed reaction scheme

Reaction stoichiometry	A [ $s^{-1}$ ]	E [J/mol]
SS $\rightarrow$ 0.35 CH <sub>4</sub> + 0.34 CO + 0.28 CO <sub>2</sub> + 0.16 H <sub>2</sub> + 0.07 C <sub>2</sub> H <sub>4</sub> + 0.05 C <sub>2</sub> H <sub>6</sub> + 0.02 C <sub>3</sub> H <sub>6</sub> + 0.17 TAR1 + 0.24 TAR3 + 1.73 H <sub>2</sub> O	6.90E-03	15561
TAR3 $\rightarrow$ 0.79 CH <sub>4</sub> + 0.76 CO + 0.62 CO <sub>2</sub> + 0.36 H <sub>2</sub> + 0.16 C <sub>2</sub> H <sub>4</sub> + 0.11 C <sub>2</sub> H <sub>6</sub> + 0.05 C <sub>3</sub> H <sub>6</sub> + 0.41 TAR1 + 3.20 CHAR	2.98E+00	65231

The results obtained from the fitting procedure show good agreement with experimental data despite the approximations introduced in the analysis. First, activation energies show rather low values which are coherent

with those reported in previous scientific literature, ranging from 18 to 124 kJ/mol for stabilized sludge (Stolarek and Ledakowicz, 2001). Moreover, sewage sludge profile as a function of temperature at 1h reaction time is shown as an example in Figure 2, where it is possible to observe good accordance between the proposed model and experimental data, with a value for  $R^2$  coefficient equal to 0.924.

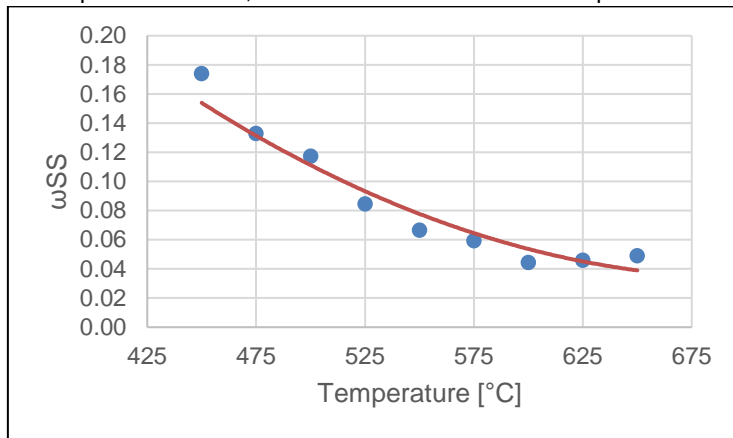


Figure 2: Comparison between experimental data (dots) and model (line) for sewage sludge mass fraction

## 2.2 Design of waste-to-energy systems based on combustion and gasification

The kinetic scheme proposed in this work is used to model a series of air-based fluidized bed reactors that must treat 1000 kg/h of sewage sludge having an average particle size of 1 mm, with an average gas velocity inside the reactor equal to 1 m/s and with different oxidation severity. Combustion is modeled by considering a 5% excess of air. Gasification is modeled by considering values of Equivalence Ratio (ER) of 20%, 30%, 40%. ER is defined as the ratio between the oxygen present in the system and the oxygen necessary to achieve stoichiometric combustion of the feedstock (Basu, 2006). Two different waste-to-energy systems are designed here: one based on combustion and the other using gasification. The fluidized-bed combustion leads to the production of high-temperature flue gas that is used to generate steam. This system works by transforming pressurized water at 60 bar into superheated steam at 300°C, to be expanded in a steam turbine where it exits at 60 mmHg for electric power generation. The effluent from the turbine is condensed by using cooling water, and the cycle repeats. Caustic wash is applied as an emission-control system at the end of the energy generation section, once the flue gas has reached a temperature of 150°C. The fluidized-bed gasification is performed at different values of ER, each one leading to a different yield and composition of crude syngas. Raw syngas must be rapidly quenched to stop any recombination reactions that may lead to soot and tar production, this is done while simultaneously producing steam at 60 bar, 300°C. Syngas is then cleaned with a caustic wash to eliminate sulfur compounds generated in the unit, and it is then compressed to 30 bar and fed to a burner together with combustion air. The effluent exiting from the burner is fed to a gas turbine where it exits at 1 bar, generating electric power. The hot effluent is then used to further increase electric power production by generating steam at 60 bar, 300°C to be used in a Rankine cycle working at the same conditions as the one modeled for sewage sludge combustion. The two streams of superheated steam are expanded in a steam turbine down to 60 mmHg and the effluent is condensed with cooling water, closing the water cycle. A process flow diagram showing the two process configurations is shown in Figure 3.

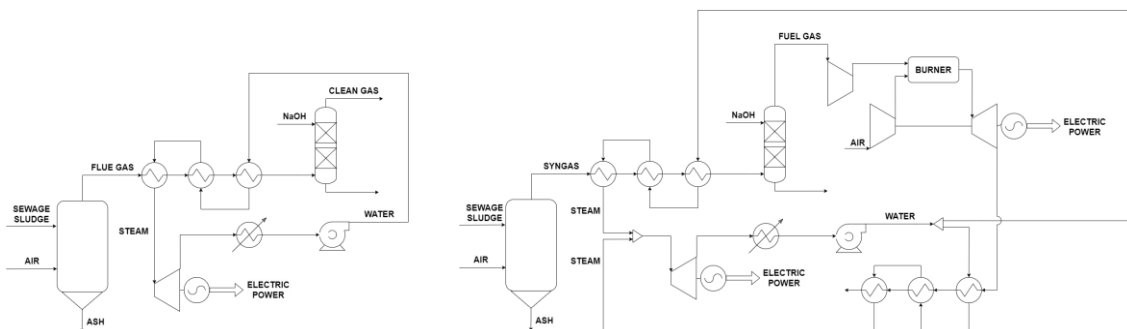


Figure 3: Process flow diagrams for sludge combustion on the left, and sludge gasification on the right

### 3. Results and discussion

The results from the simulations performed in the GasDS suite for the thermal conversion of 1000 kg/h of sewage sludge at different oxidation severities are reported in Table 3. Gasification is studied at three different values of ER (30%, 40%, 50%), while combustion is represented by the case at 105% ER, meaning that a 5 % excess of combustion air is used. It is possible to notice that the gas product flowrate, temperature, and concentration of oxidized species monotonically increases with ER, whereas LHV decreases. Combustion leads to the production of a large amount of high-temperature flue gas that only contains thermal energy, and the best way to exploit this energy is to generate steam to be used in a Rankine cycle for electric power generation. Gasification, being a partial oxidation, leads to the production of raw syngas that has both thermal and chemical energy. Chemical energy content is indicated by the LHV, and can be extracted by performing combustion of the syngas, followed by expansion in a gas turbine. In this case, thermal energy can be recovered in two steps: first, it is possible to generate steam while quenching the syngas exiting the reactor, and then it is also possible to generate more steam by using the hot effluent from the gas turbine, similarly to what was done in the combustion plant. The result is a combined cycle that produces electric power both by gas turbine and steam turbine (Ibrahim et al., 2011).

Table 3: Flowrate, temperature, and composition of gas product from sewage sludge air oxidation

Value	UoM	ER 20%	ER 30%	ER 40%	ER 105%
Flowrate	kg/h	1457	1779	2107	4279
Temperature	°C	934	1084	1211	1820
N <sub>2</sub>	mol %	48.5	50.5	53.0	69.9
O <sub>2</sub>	mol %	0.0	0.0	0.0	1.8
CO <sub>2</sub>	mol %	11.0	9.5	8.3	14.3
H <sub>2</sub> O	mol %	17.4	13.3	13.1	13.9
CO	mol %	11.7	14.2	15.0	0.0
H <sub>2</sub>	mol %	6.2	9.4	9.3	0.0
CH <sub>4</sub>	mol %	4.9	2.9	1.1	0.0
H <sub>2</sub> S	mol%	0.3	0.2	0.2	0.0
SO <sub>2</sub>	mol%	0.0	0.0	0.0	0.1
LHV	kJ/kg	3391	3373	2893	0.0

The results from the simulations performed in Aspen HYSYS for the utilization of sewage-sludge-derived flue gas and syngas for energy generation are reported in Table 4. Net electric power output and energy yield are key performance indicators that refer to the unit of dry sewage sludge. The higher complexity of the process layout for the gasification-based combined cycle is not enough to guarantee better performances compared with the simpler combustion-based Rankine cycle. In fact, the choice of optimal operating conditions also plays a significant role in determining which technology is the best. Looking at Table 4, it is possible to notice that gasification-based systems show better performances as the value of ER increases. When comparing the gasification results to those of combustion, the cases at 30% and 40% ER show better performances, while the case at 20% is worse. It is interesting to notice that the value of energy yield around 20% is typical for such waste-to-energy plants, confirming the validity of the proposed approach (Pavlas et al., 2011).

Table 4: Specific key performance indicators for sewage sludge oxidation processes

Value	UoM	ER 20%	ER 30%	ER 40%	ER 105%
Net electric power output	kWhe/kgSSdry	0.638	0.798	0.838	0.734
Energy yield	kWe/kWSSdry	18.2 %	22.8 %	23.9 %	21.0 %
CO <sub>2</sub> emissions	kgCO <sub>2</sub> /kWhe	1.549	1.239	1.179	1.346

### 4. Conclusions

The modeling of waste-to-energy process solutions based on sewage sludge air oxidation were analyzed by using the GasDS simulation suite. The procedure for adding new species to the database was explained in detail, starting from gathering chemical-physical data for the new feedstock, and then proceeding with the development of a dedicated kinetic model for the description of its thermal decomposition. A simplified kinetic model for aerobically stabilized sewage sludge was proposed by considering lumped reacting species (sludge, gas, tar, char, H<sub>2</sub>O) and two consecutive reactions, one for the primary pyrolysis reaction describing the direct thermal decomposition of sludge, and another one for the secondary pyrolysis reactions referring to the high-

temperature decomposition of the unstable tar fraction leading to the production of char. Least squares method was applied to find the optimal values for kinetic parameters in order to fit experimental data. The GasDS suite updated with the new information regarding sewage sludge decomposition was then used to perform simulation of air-based oxidation processes at different oxidation severities. The results from the simulation allowed to obtain a detailed description of the gaseous effluent exiting from the thermal conversion step in terms of flowrate, temperature, and composition. Such data can be used in the development of waste-to-energy systems based on Rankine and combined cycles for the production of electric power. Aspen HYSYS simulation software was used to model such systems and specific key performance indicators such as net power output, energy yield, CO<sub>2</sub> emissions could be obtained. The more complex gasification-based combined cycle shows better performances as the value of ER increases, and it performs better than the combustion-based Rankine cycle for ER values of 30% and 40%, whereas it performs worse in the case of 20% ER. The methodology described in this paper can be used for other types of sewage sludge that may show different chemical-physical properties and pyrolysis behavior, such as anaerobically or chemically stabilized sludge or even raw sewage sludge.

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