

Development of kinetic model for mono-combustion of sewage sludge

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Extended abstract: The chemical kinetics of individual decomposition stages were integrated into an overall process model, where oxygen content terms were coupled with volatilized sludge compounds to render the kinetics independent on the gaseous phase composition. Additionally, conductive heat transfer was appended in order to account for the influence of these physical mechanisms. In this manner, the model can be veritably applied to sludge valorisation optimisation, intensification and scale-up, upon coupling it with relevant reactor characteristics, packed-bed gas fluid flow dynamics and mass transfer resistances.

Keywords: pelletized sewage sludge; mono-combustion fingerprint; kinetic model

Introduction

Incineration is still one of the most common forms of energy utilization of different types of biomass. Excess sludge from municipal wastewater treatment plants is due to its increasing quantity and content of organic matter therefore a perspective form of alternative fuel. Dried anaerobically stabilized sludge sewage is suitable for energy utilization and thus an appropriate substitute for fossil fuels[1]. In the search of possibilities for energy self-sufficient operation of wastewater treatment plants, mono-combustion of sewage sludge on site or at a central location is a promising approach for increasing the energy efficiency of wastewater treatment process.

For the purpose of achieving the desired energy efficiency in the energy utilization of waste [2], the stakeholder should be familiar with the characteristics of alternative solid fuel used at the existing incineration devices. In addition, the design of new incinerators for the energy recovery of sewage sludge is much easier and more successful when the kinetic properties of this kind of alternative fuel are known[3].

The aim of the development of kinetic model was the ultimate prediction of the most appropriate mono-combustion procedure (or more thereof) with optimal energy extraction from sewage sludge, given the compounds being produced herewith.

Material and Methods

As the material for the research, the dried sewage sludge was used (further referred to as pellets). Characterization was carried out on a representative, mass-proportional

composite annual sample of pellets for the year 2012. Representative sample was collected and prepared in accordance with the instructions of the Technical Standards: i) EN ISO 5667-13:2011, Water Quality - Sampling - Part 13.: Guidance on the sampling of sludges from wastewater treatment plants, water treatment plants and industrial processes and ii) EN 14899:2005, Characterization of waste. Sampling of waste materials. Framework for the preparation and application of a sampling plan. The composite sample was then ground to <1 mm by a hammer mill.

Pellets are stable, hygienic and non-hazardous bio-waste. They are in the shape of granules with size distribution $d_{50} < 3$ mm and $d_{90} < 4$ mm. The pellets have a substantial calorific value which matches the quality criteria for alternative solid fuels, SRF. Yearly-average data on pellets calorific value is rather stable at 13.3 MJ/kg, with mean fluctuation of 3.9 %. Classification of pellets as an alternative solid fuel has been determined as "NCV 4; Cl 1; Hg 4-5" according to technical standard CSN EN 15359:2011[4]. Portion, which can be burned in the presence of oxygen at 450 °C and which can be assumed as organic, is 66.9% DS, a further portion of which can be combusted in the presence of oxygen at 550 °C, is 0.7% DS [4].

Physico-chemical analysis of pellets were made according to Standard methods prepared by Technical Committee CEN/TC 343 'Solid Recovered Fuels'. It is necessary to conduct extensive characterization of pellets by advanced thermal analysis to determine the combustion behaviour and mass loss of pellets: i) thermogravimetry (TG), differential thermogravimetry (DTG), differential thermal analysis (DTA) and evolved gas analysis (EGA).

Test for thermal decomposition of sewage sludge in a laboratory heating furnace using a combustion atmosphere Ar:O₂ = 80 Vol% : 20 Vol% was made to determine its combustion fingerprint. To determine the kinetic model, we evaluated the combustion at the dynamic thermal regime with the different heating rates in two different atmospheres: i) Ar:O₂ = 80 Vol% : 20 Vol% and ii) Ar:O₂ = 90 Vol% : 10 Vol%.

To determine kinetic parameters, parallel n^{th} order reaction kinetics, using multi-heating rate data, were adopted. The latter method took into account the change in the reaction rates at the various stages of mass conversion (α) and temperatures. Using the proposed approach, a series of non-isothermal measurements of the sample weight loss at the selected different heating rates (2–20 K min⁻¹) was carried out. A , E_a and n (the apparent pre-exponential factor, activation energy and order of reaction) for each reaction were calculated through non-linear regression; several regression strategies were undertaken to determine the optimal parameters.

Mechanistic kinetic models, while having more integrational capacity (*i.e.* with pertinent fluid mechanics and transport phenomena), are often subjected to a not appropriate model application (kinetics being dependent on external heating rate) [5], or the combustion process itself may be treated in an over-simplified description manner, complex volatilization mechanisms (realistic sludge composition) being considered as single [6] or two-staged [7–8]. Some combustion studies, nonetheless,

acknowledge the reactions, proceeding in series and in parallel, even though still taking into account only limited conversion stages that is, either for sludge-derived char materials [9] or the sewage sludge itself [10–12]. The latter are quite comprehensive in terms of pertinent mechanism examination, still in a lumped kinetic manner, while they mostly disregard heat transfer resistances due to finite sludge particle size.

The aim of the study at hand was thus to veritably describe the chemical reaction kinetics of a multi-stage combustion process, taking heat transfer phenomena into account as well, owing to a varying thermal diffusivity of the sewage sludge feedstock during incineration.

Modelling

The sludge combustion model, acknowledging internal heat transfer and chemical reaction kinetics, was formulated for seven ($i = 7$) sludge components (Table 1). The latter were ascribed to the distinct sludge mass loss regions within the thermograms at different process conditions applied.

The model introduces sludge component and total conversion, X_i and X , respectively, time, t , reaction rate constants, k_i , the orders of reaction, x_i and y_i , gas phase oxygen mole fraction, y , decomposable weight fractions of components, w_i , pre-exponential (frequency) factors, A_i , reactions' activation energies, E_{ai} , the universal gas constant, R , sample and sample/furnace interface temperatures, T and T_s , respectively, material thermal diffusivity, α , sludge sample thickness, L , and furnace heating rate, β . The model differential equations were solved by the Runge–Kutta method, while the parameters were obtained by applying the Levenberg–Marquardt algorithm. In order to attain the most meaningful parameters, the regression was performed in several consequent stages.

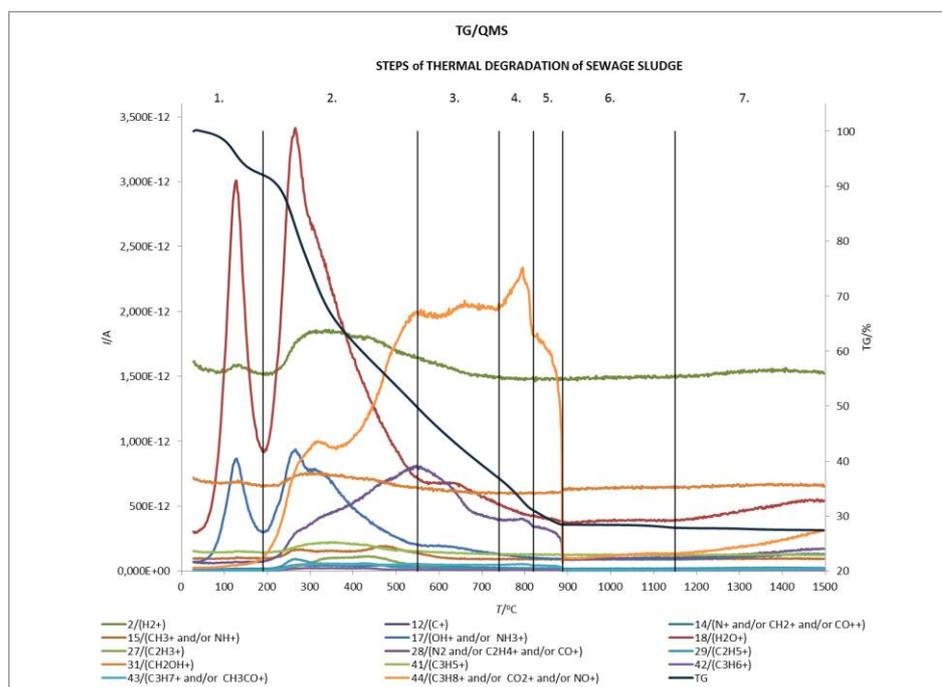
Results and Conclusions

Weight loss of a sample during the thermo-chemical process is dependent of time and temperature of the combustion. Optimal energy recovery maximizes the mass conversion of selected alternative fuels in the shortest possible time and at the optimal combustion temperature. To achieve the optimum, we need a good knowledge of selected material's properties.

Test for thermal decomposition of sewage sludge in a laboratory heating furnace using a combustion atmosphere Ar:O₂ = 80 Vol% : 20 Vol% was made to determine its combustion fingerprint and the main thermal degradation steps (Graph 1, Table 1). To determine the kinetic model, we evaluated the combustion at the dynamic thermal regime with the different heating rates in two different atmospheres: i) Ar:O₂ = 80 Vol% : 20 Vol% and ii) Ar:O₂ = 90 Vol% : 10 Vol% (Graph 2).

We evaluated the most intense part of the combustion process and determined the behavior of sludge thermo-chemical conversion (Graph 1): i) the loss of moisture and

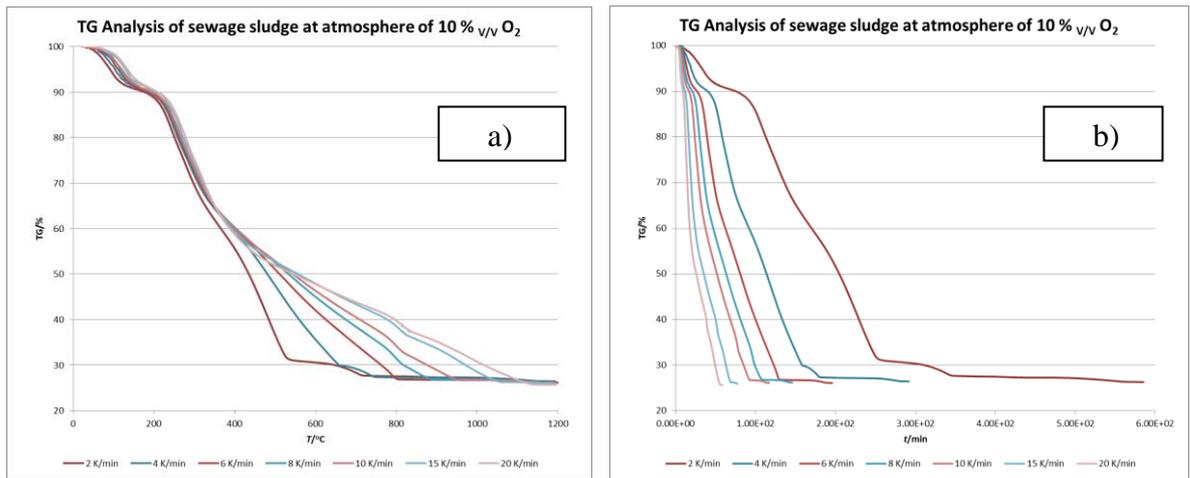
chemically bound water, ii) reaction water production, iii) volatility of organic and inorganic compounds, iv) organic compounds depolymerization and oxidation.



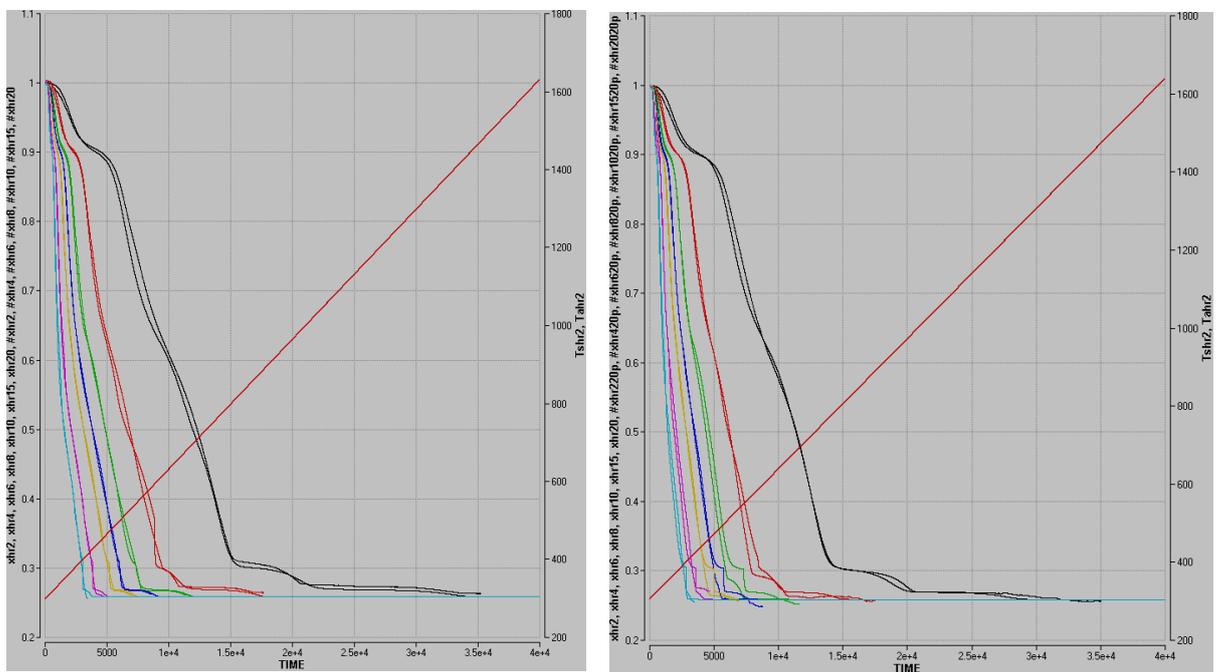
Graph 1: Combustion fingerprint of sewage sludge at oxidative atmosphere in temperature range from 28 °C to 1500 °C.

Table 1: Overview of mass loss at the different temperature range.

Step of degradation	Temperature range, °C	Intermediate mass loss, %	Cumulative mass loss, %	DTG/(%min ⁻¹)	Mass loss, mg	Cumulative mass conversion α	Intermediate mass conversion α
I	Troom - 190	7.94	7.94	-0.54	7.96	0.11	0.11
II	190 - 350	25.48	33.43	-1.59	33.50	0.46	0.35
II	350 - 550	42.32	50.26	-0.84	50.37	0.69	0.23
III	550 - 740	12.90	63.16	-0.68	63.30	0.87	0.18
IV	740 - 820	5.81	68.97	-0.72	69.12	0.95	0.08
V	820 - 888	2.58	71.54	-0.37	71.70	0.99	0.04
VI	888 - 1150	0.59	72.13	-0.02	72.29	0.99	0.01
VII	1150 - 1500	0.45	72.57	-0.01	72.73	1.00	0.01



Graph 2: a) The dependance of mass loss according to the temperature and b) according to the time of combustion process.



Graph 3: Measured and predicted weight loss using 10% (left) and 20% (right) oxygen in carrier gas phase.

The study at hand presents the process model development for the combustion and incineration of waste sewage sludge (Graph 3). The advantage of the addressed modelling work lies in proposing seven-stage reaction kinetics (Graph 1, Table 1), independent of the heat transfer flows to material, as well as gaseous phase composition. In this manner, the model may be utilized in a more extrapolative fashion upon tackling incineration process scale-up; nonetheless, with fluid mechanics/transport phenomena consideration. The final process description thus allows the prediction of the weight loss during combustion (Graph 3), not just for an arbitrary gas composition, heating rate of the sample, and the final temperature of the process, but also for different temperature regimes (where optimization yields maximal applicability), the transfer of the process to a larger scale of incineration, and to some extent, a variable composition of the sludge.

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